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FORMATIONS AND REACTIONS

OF

ALLENES

THESIS

PRESENTED FOR THE

DEGREE

OF

DOCTOR OF PHILOSOPHY

IN THE

UNIVERSITY OF DURHAM

BY

PETER MICHAEL GREAVES

JULY 1967

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ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Prof. S. R. Landor for introducing him to the basic concepts of modern organic chemistry, and for his subsequent supervision throughout the course of this work. To the North Atlantic Treaty Organisation who, through the Science Research Council, made available the studentship enabling this work to be undertaken, and to Dr. E. Mooney of Birmingham University for some of the n.m.r. spectra.

ABSTRACT

Aryl and alkyl 1-bromoallenes, 1-iodoallenes, 1,1-dibromoallenes and 1-halo-1-deuteroallenes have been prepared; the mechanism of their formation and their spectroscopic properties are discussed.

Conversion of propargylic alcohols to 1-cyanoallenes either directly or via the corresponding allenic bromides is described. The mechanism of formation of cyanoallenes and their spectral properties are discussed. 1-Cyanoallenes have been converted to enamines, to allenic amides and to allenic acids. Evidence for the structures of dimerisation products of 1-cyanoallenes is presented.

1,4-Elimination reactions of 1-bromoallenes are shown to give alkenynes in good yield. 1-Bromoallenes form Grignard compounds and these are reacted with carbon dioxide, water, oxygen and acetone to give mixtures of acetylene and allenic products.

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PART I

INTRODUCTION

HALO-ALLENES

Many attempts in the past to prepare and identify allenic compounds failed for lack of adequate methods to detect and unequivocally prove the presence of cumulative double bonds. Twenty years ago infra-red spectroscopy provided such a method when it was found that non-symmetrical allenes absorbed strongly in the 1920 - 1980 cm^{-1} region; this absorption is readily distinguishable in the presence of most other absorbing frequencies.

It is probable that prior to 1930 allenic halides were present in products obtained by many workers[1-6] but were not identified as such, e.g. in 1929 Krestinski and Kostovskaia[3] tried to rearrange 2,5-dimethylhex-3-yn-2, 5-diol using phosphorus tribromide and claimed to obtain mixtures of three compounds, two of which were identified as 2,5-dibromo-2,5-dimethylhex-3-yne and 3,4-dibromo-2, 5-dimethylhexa-2,4-diene. The third component was tentatively assigned the allenic structure, 2,3-dibromo-2,5-dimethylhexa-3,4-diene on the basis of degradative oxidation.

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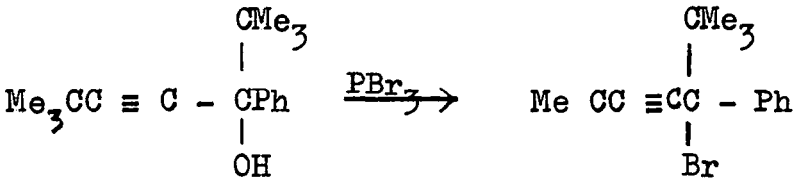
$$Me_2C(OH)C \equiv CC(OH)Me_2 \xrightarrow{PBr_3} Me_2C(Br)C \equiv CC(Br)Me_2$$

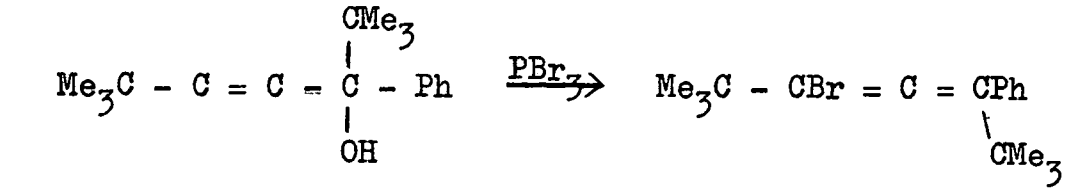
$$+ \quad Me_2C = C(Br)C(Br) = CMe_2$$

$$+ \quad Me_2C = C = C(Br)C(Br)Me_2$$

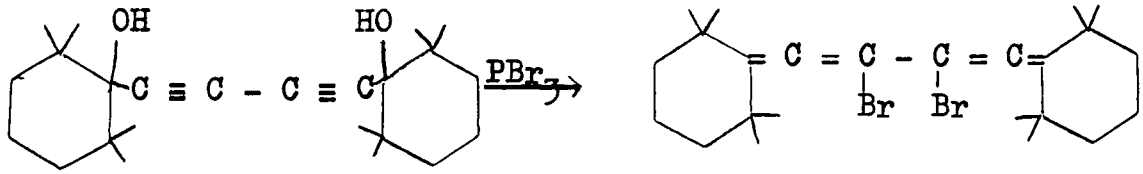
In 1935 Ford, Thompson and Marvel [7] carried out a similar reaction using 2,2,6,6-tetramethyl-3-phenylhept-4-yn-3-ol. They obtained a product, which had a high molecular refraction, and which was slow to react with silver nitrate; this data would fit the allenic compound, 5-bromo-2,2,6,6-tetramethyl-3-phenylhepta-3,4-diene, but hydrolysis using moist silver oxide regenerated the starting alcohol which led these authors to the conclusion that the product was the acetylenic bromide 3-bromo-2,2,6,6-tetramethyl-3-phenylhept-4-yne.



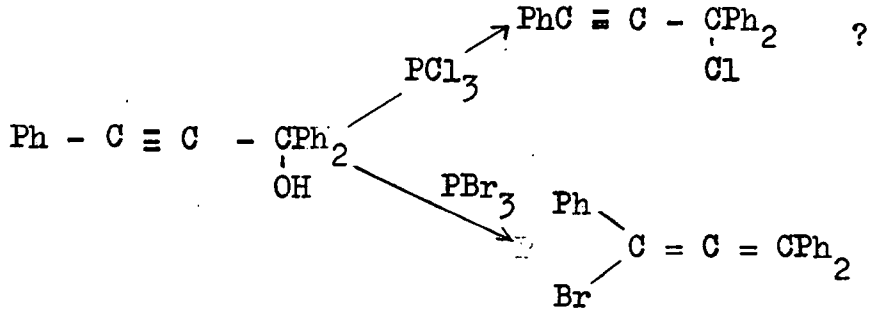
As the hydrolysis of 1-bromoallenes by means of silver oxide has now been shown to yield acetylenic carbinols [8,9] it is probable that Ford, Thompson and Marvel [7] had obtained the allenic bromide; infra-red spectroscopy would have proved this point beyond doubt.



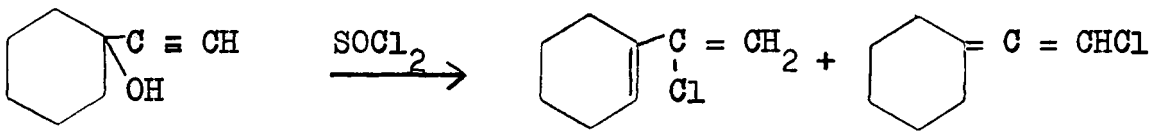
Nearly thirty years later Bohlmann and Kieslich[10] reacted phosphorus tribromide and 1,4-bis-(2,2,6,6-tetramethylcyclohexyl)-buta-1,3-diene and obtained the diallenic dibromide 1,4-bis-(2,2,6,6-tetramethylcyclohexylidene)-2,3-dibromobuta-1,3-diene, the compound having the expected ultra-violet spectrum for the dibromoallenes but not the dibromodiacetylene.



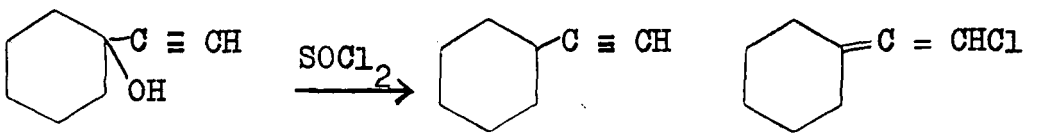
An attempt was made to prepare an arylallenic chloride by reacting phosphorus trichloride and 1,3,3-triphenylprop-1-yn-3-ol in 1923 by Mourreu, Dufraisse and Machall[11]; they obtained a solid product which was said to be 3-chloro-1,3,3-triphenylprop-1-yne, however a similar reaction using phosphorus tribromide gave a product which Jacobs and Petty[16] later considered to be 1-bromo-1,3,3-triphenylpropa-1, 2-diene.



The first reports of the formation of some allenic chlorides by the action of phosphorus trichloride on propargylic alcohols appeared in 1934, when Hurd and Jones [12] treated 1-ethynylcyclohexanol with thionyl chloride and pyridine at 50 - 60° and reported the presence of small quantities of cyclohexylidenevinylchloride in the main product, α-chlorovinylcyclohexene.

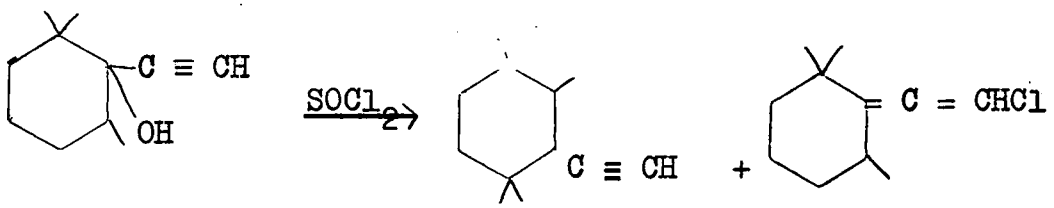


This reaction was repeated by Bhatia, Landor and Landor [8,13] at different temperatures (between 0 and 80°) and they obtained up to 25% of the allenic chloride, the major product being ethynylcyclohexene.

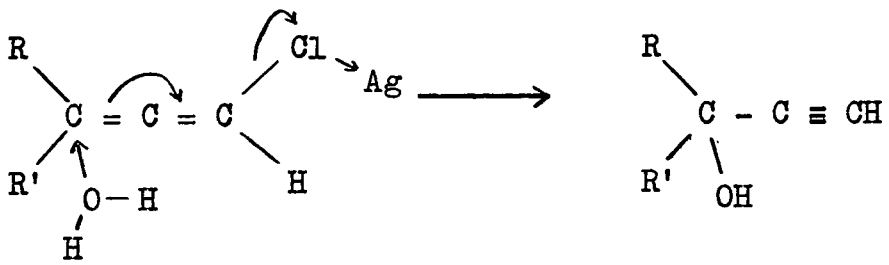


A fairly pure sample of the allenic chloride was obtained by removing terminal acetylenes as their insoluble silver salts. Hennion and Lynch [14] in 1960 found that, on varying the conditions, the optimum yield of chloroallene was obtained when an ether-pyridine solution was used at 3°. They obtained a product by fractionation followed by chromatography on alumina, which was 86% pure by g.l.c.

Sobotka and Chanley [15] reacted the stearically blocked molecule 1-ethynyl-2,6,6-trimethylcyclohexanol with thionyl chloride in presence of pyridine to obtain 54% of an unidentified product which on hydrolysis with silver oxide gave the starting material; a modification of their method by Bhatia, Landor and Landor [8] gave 60% of a product with similar physical properties, this was shown to be 2,2,6-trimethylcylohexylidenevinyl chloride by means of infra-red spectrophotometry.



The same authors [8] obtained 91% yield of silver chloride and the starting carbinol when the chloride was refluxed with alcohol/silver nitrate. They suggested the rearrangement was due to an S_N2' mechanism in which co-ordination of the chlorine to silver was followed by an attack of a water molecule.



The action of thionyl chloride on prop-1-yn-3-ols was found to be a general method for the preparation of d-polysubstituted 1-chloroallenes.

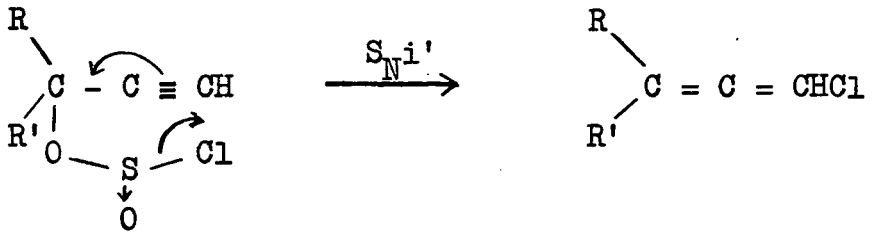
The chloroallenes were identified by infra-red spectroscopy with ν_{max} 1945 (C=C=C) and 735 cm^{-1} (C=C=CHCl); these compounds had shown only end absorption in the ultra-violet region.

In 1955 Jacobs, Teach and Weiss [17] reported the formation of 1-chlorohexa-1,2-diene from reaction of hex-1-yn-3-ol with thionyl chloride in diethyl ether/di-isopropyl ether solvent,

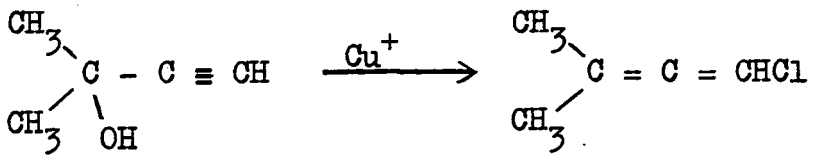
$$CH_3CH_2CH_2-\underset{\underset{OH}{|}}{CH}-C\equiv CH \longrightarrow CH_3CH_2CH_2CH=C=CHCl \quad 40\%$$
$$+\ CH_3CH_2CH_2\underset{\underset{Cl}{|}}{CH}-C\equiv CH$$

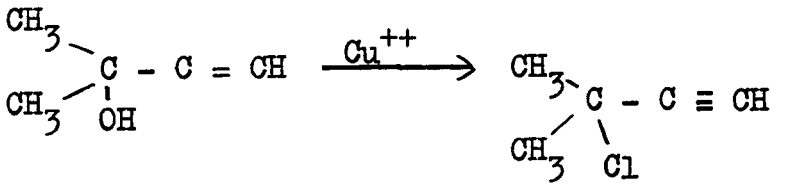
This work was followed in 1960 by a detailed study [18] of reactions of secondary acetylenic carbinols with thionyl chloride, in which solvent and temperature were varied. In this work Jacobs, Petty and Teach found that the ratio of allene to acetylene could be raised as high as 3:1 using diethylcarbitol as solvent. Separations were by gas chromatography.

Bhatia, Landor and Landor [8] proposed a mechanism in which a chlorosulphite intermediate could react by an S_N1, S_N2', or S_Ni' process, then by use of optically active compounds showed an S_Ni' to be the favoured path.

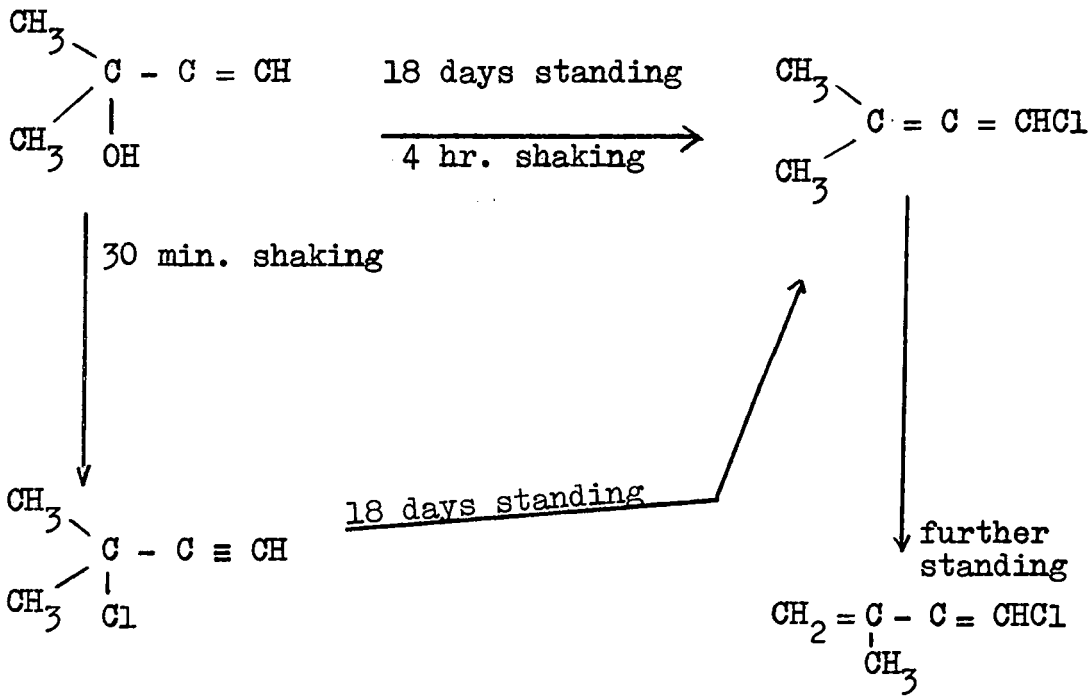


Other workers had been pursuing alternative methods of preparing 1-haloallenes; thus in 1935 Favorskii and Favorskaya [19] reacted 3-methylbut-1-yn-3-ol with concentrated hydrochloric acid, ammonium chloride and different copper catalysts. Using cuprous chloride they obtained some conversion to 1-chloro-3-methylbuta-1,2-diene whilst cupric salts gave 3-chloro-3-methylbut-1-yne.

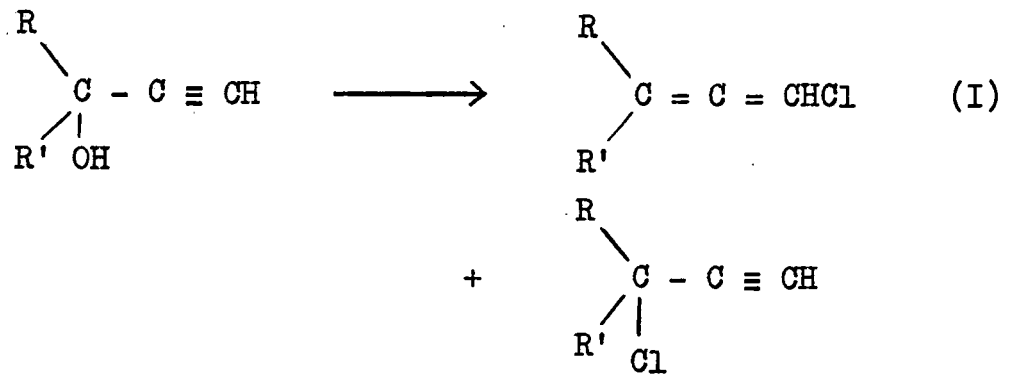




A more detailed account of this reaction was given by Favorskaya [20] in 1939. She reacted 3-methylbut-1-yn-3-ol, concentrated hydrochloric acid, cuprous chloride and ammonium chloride by shaking the mixture for 30 min. when working up showed the product to be mainly 3-chloro-3-methylbut-1-yne in 63% yield, however 4 hr. shaking or 18 days standing gave 1-chloro-3-methylbuta-1,2-diene in yield of up to 65%, further standing led to rearrangement product 1-chloro-3-methylbuta-1,3-diene.



Similar work [21,22] was done using 3-methylpent-1-yn-3-ol and 3-ethylpent-1-yn-3-ol



$R = CH_3$) yield of I = 15%
$R' = C_2H_5$)

$R = R' = C_2H_5$ yield of I = 30%

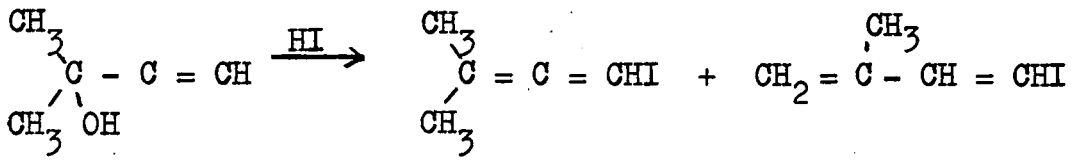
There is no evidence that any of these compounds were obtained pure and it is probable that they were contaminated with acetylenic compounds.

A similar series of reactions was carried out by Favorskaya [23] in 1940 using different haloacids.

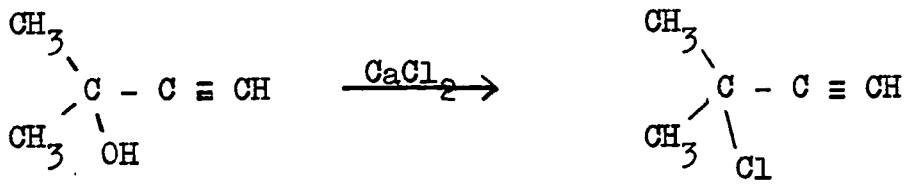
Using concentrated hydrobromic acid she obtained 1-bromo-methylbuta-1,3-diene from 3-methylbut-1-yn-3-ol irrespective of the conditions employed, this does not agree with the present work.

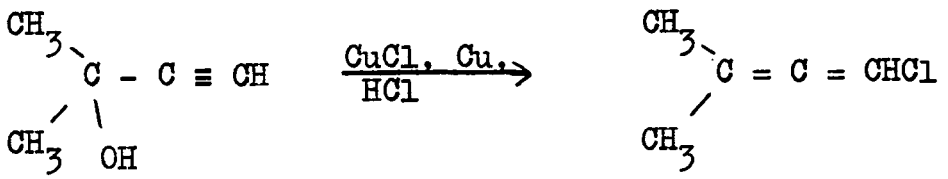
Using hydriodic acid and 3-methylbut-1-yn-3-ol she obtained a dark unstable liquid, the components of which could not be separated by distillation. She suggested that the product was a mixture of 1-iodo-3-methylbuta-1,

2-diene and 1-iodo-3-methylbuta-1,3-diene, however the evidence for this rested only on degradative oxidation.

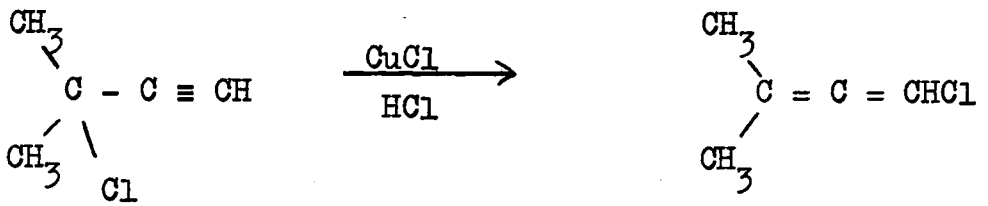


Hennion, Sheehan and Maloney [25] studied the reaction between 3-methylbut-1-yn-3-ol and concentrated hydrochloric acid. They found that using only concentrated hydrochloric acid they obtained 3-chloro-3-methylbut-1-yne in poor yield, however addition of calcium chloride gave high yields of the same chloroacetylene. They repeated Favorskaya's work [20] but used a catalytic amount of copper bronze and obtained 1-chloro-3-methylbuta-1,2-diene and 1-chloro-3-methylbuta-1,3-diene.

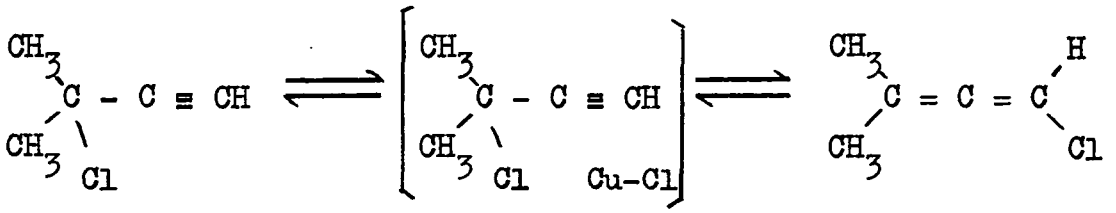




The infra-red spectrum of the purified product showed it to be free from acetylenic or diene impurities. The same authors [25], rearranged the acetylenic chloride by stirring it with concentrated hydrochloric acid, cuprous chloride and ammonium chloride, to give allenic chloride (33%) together with some starting material(8%).



They suggested a chelate type intermediate was responsible for the conversion



These claims were contradicted by Bergmann and Herman [26] who in 1951 repeated the experiment using calcium chloride and claimed to get the isomeric 4-chloro-3-methylbuta-1,2-diene. This is the only report of a 4-chloroallene being obtained from this reaction, no infra-red or other spectral data was given. Results by Hennion and Boisselle [27] in 1961 throw considerable doubt on the work of Bergmann and Herman, since tertiary acetylenic chlorides were obtained in good yields.

Jacobs and Brill [28] gave the first authentic report for the preparation of a 1-bromoallene in 1953. They refluxed propargyl bromide with cuprous bromide and obtained the allenic bromide by careful fractionation.

$$BrCH_2 - C \equiv CH \xrightarrow{CuBr} H_2C = C = CHBr$$

An arylallene bromide was prepared in 1960 by Pansevich-Kolyada [29], he reacted 1,1-diphenylprop-1-ol with bromine in different solvents and was able to prepare 1-bromo-3,3-diphenylpropa-1,2-diene. No yields or spectral data were given and the only evidence of the structure is bromine analysis and the fact that oxidation gives benzophenone. His quoted melting point is some 20° less than that obtained in the present work (61° cf. 81°).

$$Ph_2\underset{OH}{C} - CH_2CH_3 \xrightarrow{Br_2\ 80\%HAc} Ph_2\underset{OH}{C}-CHBrCH_3 \xrightarrow[CHCl_3]{Br_2\ UV} \left[Ph_2\underset{OH}{C}-CHBrCH_2Br\right]$$

$$\longrightarrow \left[Ph_2CBr.CHBrCH_2Br\right] \longrightarrow Ph_2C{+}CBrCH_2Br \xrightarrow{KOH} Ph_2C{=}C{=}CHBr$$

Allenic iodides have received very little attention prior to the work by Baker, Landor, Landor and Patel [30]. In 1884 Henry [31] refluxed propargyl bromide with sodium iodide in acetone and obtained what he thought was propargyl iodide.

In light of later work by Jacobs and Brill [28] it seems likely that Henry had a mixture of allene iodide and propargyl iodide. These latter workers prepared an equilibrium mixture of iodoallene in different ways

i)	$BrCH_2C \equiv CH + NaI$	in anhydrous ethonol, 3 days, room temperature.
2)	$BrCH_2C \equiv CH + NaI$	in acetone below 20°
3)	$BrHC = C = CH_2 + NaI$	in acetone, reflux 20 hrs.

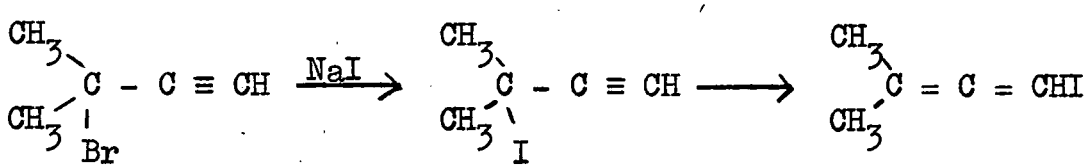
Respective yields were 31,23, and 34% of a mixture which in each case had the same composition, (verified by infra-red spectra). This led the authors to conclude that the reaction was via the acetylenic iodide which then rearranged to give allene-acetylene equilibrium.

$$\begin{array}{ccc} CH \equiv C - CH_2Br & \xrightarrow{NaI} & CH \equiv C - CH_2I \\ & & \Updownarrow \\ CH_2 = C = CHBr & \xrightarrow{NaI} & CH_2 = C = CHI \end{array}$$

In 1955 Hatch and Mangold [32] confirmed the presence of allene in samples of proporgyl iodide prepared in this way. They showed that the allene band was present in the infra-red spectra of the product but absent in the starting material. Jacobs and Petty [16] reacted 3-bromo-3-methylbut-1-yne with sodium iodide in acetone and after 3 days got 68%

of a product which was mainly the 1,3-diene but contained some allene and acetylene, attempts at distillation led to explosions.

The experiment was repeated reducing the time to 4 hr. when 38% of a product believed to be mainly allenic iodide was obtained.



Favorskaya [23] obtained a mixture of 1-iodo-3-methylbuta-1,2-diene and 1-iodo-3-methylbuta-1,3-diene on reacting 3-methylbut-1-yn-3-ol with hydriodic acid.

Baker, Landor, Landor and Patel [30] reacted secondary propargyl alcohols with triphenylphosphite methiodide in dimethylformamide and obtained good yields of pure allenic iodides. Until the present work there has been no method of preparing pure 1-iodo-3,3-dialkylallenes.

A number of authors [33 - 40] have studied the addition of halogens and haloacids to conjugated enynes and have found allenes among the products. None of these methods are of preparative importance.

$$HC \equiv C - CH = CH_2 \xrightarrow{HX} H_2C = C = CH - CH_2X$$

$$HC \equiv C - CH = CH_2 \xrightarrow{X_2} XCH_2 - HC = C = CHX \quad + \text{others}$$

CYANOALLENES AND CYANOACETYLENES.

Cyanoacetylenes were first synthesised in 1915 by Grignard [41] and his co-workers, they reacted cyanogen chloride with acetylenic Grignard compounds,

$$R - C \equiv CMgBr \quad + \quad ClCN \longrightarrow R - C \equiv C - CN$$

This remained for many years the only method of obtaining such compounds. In 1946 Johnson [42] attempted to prepare cyanoacetylenes from the corresponding haloacetylenes, he reacted 1,4-dibromobut-2-yne and 1,4-dichlorobut-2-yne with cuprous or potassium cyanides and found that no acetylenic cyanide was formed although extensive reaction and decomposition took place.

Newman and Wotiz [43] first prepared cyanoacetylenes from the corresponding haloacetylenes in 1949. They found that haloacetylenes with at least three methylene groups between the point of unsaturation and the halogen atom, would undergo exchange when heated in acetone with potassium or sodium iodide, to give the corresponding iodoacetylene.

$$C_2H_5C \equiv C-(CH_2)_3-Cl \xrightarrow{NaI} C_2H_5C \equiv C(CH_2)_3-I$$

This iodide was then refluxed with acetone/water solution of potassium cyanide when the cyanoacetylene resulted.

$$C_2H_5-C \equiv C(CH_2)_3I \xrightarrow{KCN} C_2H_5-C \equiv C-(CH_2)_3CN$$

The same authors [43] also prepared 1-cyanohept-2-yne by refluxing a mixture of cuprous cyanide and 1-bromohept-2-yne in xylene for 1 hr., the same bromide gave no cyanide when treated with aqueous potassium cyanide.

$$C_4H_9-C \equiv C-CH_2Br \xrightarrow{CuCN} C_4H_9C \equiv C-CH_2CN$$

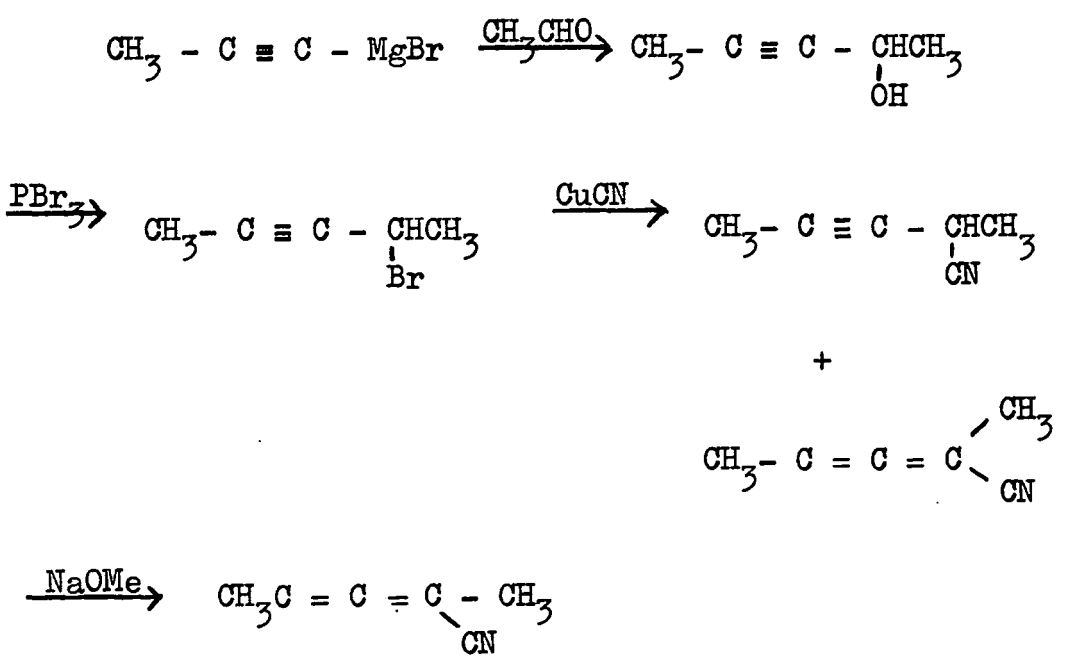
In 1953 Eglington and Whiting [44] obtained 5-cyanopent-1-yne in 75% yield by refluxing an ethanolic solution of potassium cyanide with pent-4-ynyltoluene-p-solphonate

$$CH \equiv C-(CH_2)_3-O-SO_2- \quad CH_3 \xrightarrow{KCN} HC \equiv C-(CH_2)_3CN$$

Wotiz and Hudack [45] obtained a mixture from the reaction of 1-bromo-oct-2-yne and cuprous cyanide in p-cymene which was thought to consist of 1-cyano-oct-2-yne as the main product and some 3-cyano-octa-1,2-diene. The only evidence for the latter was a split band at 1960 cm^{-1} in the infra-red spectrum. Later work [46] has shown that 1-cyanoallenes do not have a split allene band, and it is therefore likely that more than one allene was present.

The work of Wotiz and Hudack [45] was repeated in 1959 by Schlogl and Orgler [47] and they obtained only 32% of 1-cyano-oct-2-yne.

In 1957 Smith and Swenson [48] prepared what was probably the first pure allene cyanide, but obtained only a 4% overall yield. They prepared the acetylenic carbinol pent-2-yn-3-ol from Grignard compound of methylacetylene and acetaldehyde, this was reacted with phosphorus tribromide and gave 3-bromopent-2-yne. The bromide was refluxed with cuprous cyanide in dry benzene giving a mixture of the two cyanides, 2-cyanopent-2-yne and 2-cyanopenta-2,3-diene, they were unable to separate this mixture by physical means but found that on treatment of 3-cyanopent-2-yne with sodium methoxide rearrangement to the allene took place.



Schlogl and Orgler [47] proposed an allene cyanide as an unisolated intermediate in their preparation of octan-1, 2,3-tricarboxylic acid

$$C_5H_{11}C \equiv C - CH_2\overset{+}{N}(CH_3)_3I \xrightarrow{KCN} \begin{array}{c} C_5H_{11}- C \equiv C - CH_2CN \\ \rightleftarrows \\ C_5H_{11}- C = C = CHCN \end{array}$$

$$\xrightarrow[\text{ii } H+]{\text{i } CN} C_5H_{11}- CH = \underset{CN}{C} - CH_2CN \xrightarrow[\text{ii } H+]{\text{i } CN} C_5H_{11}- \underset{CN}{CH} - \underset{CN}{CH} - \underset{CN}{CH_2}$$

$$\xrightarrow{OH -} C_5H_{11}- \underset{COOH}{CH} - \overset{COOH}{CH} - CH_2COOH$$

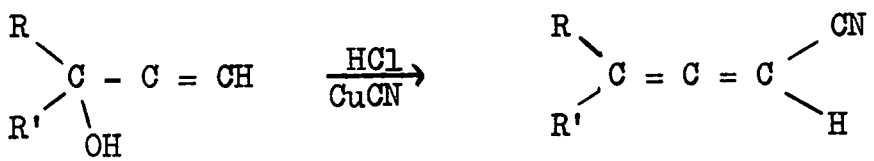
This addition of hydrogen cyanide to the allenic system is rather surprising and in the present work no such addition has been observed.

Kurtz, Gold and Disselnkotter [49] prepared a mixture of 1-cyanoallene and 3-cyanoprop-1-yne by refluxing a mixture of proporgyl chloride, cuprous chloride and hydrogen cyanide.

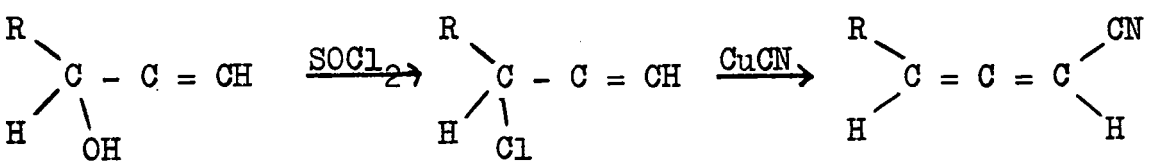
$$CH \equiv C - CH_2Cl \xrightarrow[CuCl]{HCN} \begin{array}{c} CH \equiv C - CH_2CN \\ \rightleftarrows \\ CH_2 = C = CHCN \end{array}$$

A similar reaction using propargyl bromide and cuprous cyanide was carried out in 1961 by Reddy, Mandell and Goldstein [50] who obtained the same mixture, these workers interpreted the N.M.R. spectrum of the mixture as being consistant with the 3-cyano-prop-1-yne but the typical allene band at 1950 cm^{-1} in the infra-red spectrum was not explained. (see discussion p. 97)

Laws [51] prepared a series of 1-cyanoallenes using two methods (a) tertiary acetylenic alcohols with concentrated hydrochloric acid, cuprous cyanide and potassium cyanide gave a mixture of 1-cyanoallene and 1-chloroallene which could be separated by distillation.

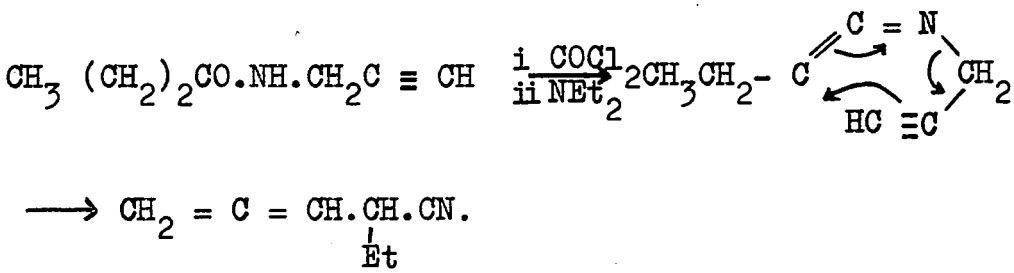


(b) Secondary acetylenic alcohols were converted to the 3-chloroacetylenes which were treated with cuprous cyanide in benzene to give cyanoallenes.



These reactions gave only poor yields of impure allene cyanides and will be discussed in the light of the present work.

In 1965 Brannock and Burpitt [52] made a 3,4-pentadiene-nitrile by a novel type of Claisen rearrangement.



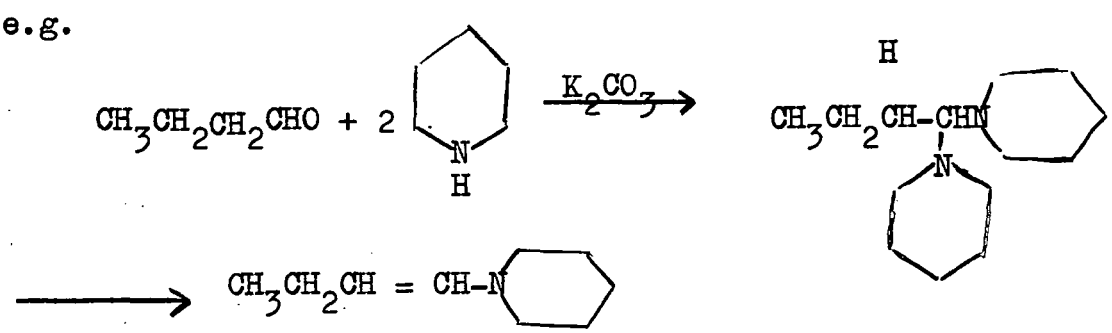
They gave infra-red and N.M.R. data which supported this structure.

ENAMINES FROM ALLENIC AND ACETYLENIC NITRILES.

Enamines [53] have come into prominence in recent years and provide interesting new paths in organic synthesis, particularly since their alkylation reactions developed by Stork [54]. The enamines derived from reaction of simple cyclic ketones with simple amines are well known in the literature, but consist mainly of permutations of only a few ketones with a limited number of amines.

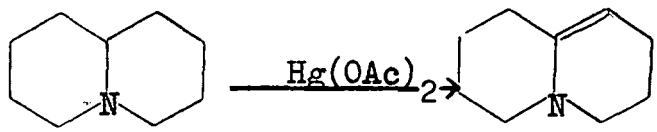
The first general synthesis of enamines ~~was discovered~~ were developed by Mannich and Davidson [55] in 1936, they found that secondary amines and aldehydes reacted in the cold, in presence of potassium carbonate to give a 1,1-diamine, which on distillation yielded an enamine.

e.g.



In case of ketones it was found necessary to use a higher temperature and calcium oxide. This reaction was not found to be successful with many ketones e.g. diethylketone, acetophenone, benzophenone etc. Aliphatic ketones often gave an aldol condensation product.

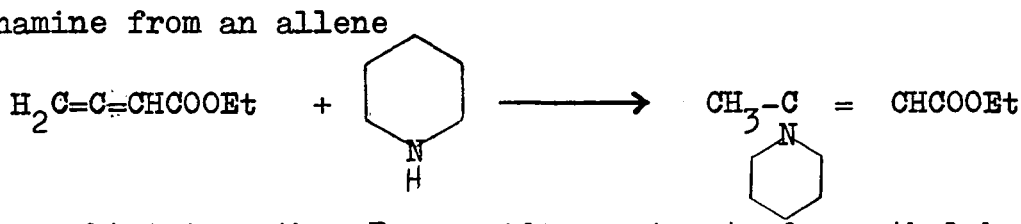
In 1955 Leonard, Hay, Fulmer and Gash [56] developed a method of oxidising cyclic amines by mercuric acetate to give cyclic enamines.



Addition of amines to activated double bonds have been known for a long time e.g. Holley & Holley [57] in 1949 added methylamine to ethyl acrylate and obtained ethyl β-methylaminopropionate

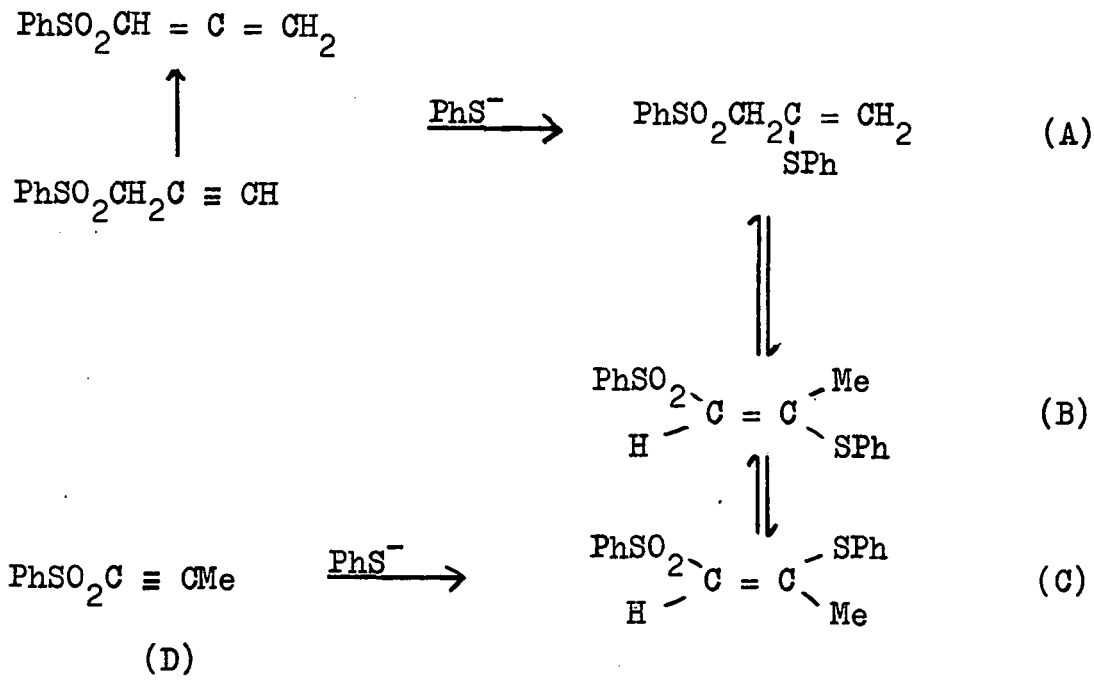
$$H_2C = CHCOOEt + MeNH_2 \longrightarrow MeNH.CH_2\text{-}CH_2COOEt$$

and in 1954 Eglington, Jones, Mansfield and Whiting [58] applied this reaction to an activated allene double bond to obtain an enamine from an allene



thus obtaining ethyl-β-piperidinocrotonate from ethyl-buta-2, 3-dienoate.

In 1964 Stirling [59] investigated the addition of sulphur nucleophiles to allenic and acetylenic sulphones



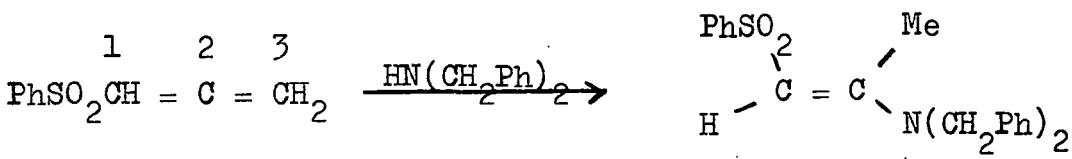
He assigned structure (A) on the basis of n.m.r. spectra and assumed isomerisation of the terminal acetylenic sulphone to the allene before reaction. He states that the position of protonation of the allene (C3) is in accordance with "Ingolds rule"[60] i.e. protonation occurs rapidly to give the isomer of lesser thermodynamic stability; and since the sulphonyl group is a powerful electron acceptor it distorts the electron distribution over carbons 1,2 and 3 so that the electron density is greatest at C3. However it should be noted that Ingolds rule is applied to mesomeric anions and the allene system is not a system of this type.

He found that when the sulphone (D) was treated trans addition to give the cis product was observed and assigned

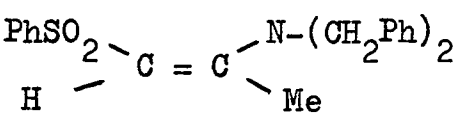
structure (C). In the many examples of addition of thiols to acetylenes [61] which have been studied, addition was always found to be trans, in spite of variation of adduct and substrate. This was accounted for on the basis of maximum separation of the entering nucleophile, and the electron pair displaced from the triple bond,[62] together with the known configurational stability of the vinyl carbanions.

Isomers (A) and (C) were transformed to the trans product (B) by sodium methoxide, thus giving the more thermodynamically stable product.

Continuing his studies Stirling [63] reacted phenylsulphonylpropadiene with dibenzylamine and found that trans-2-dibenzylamino-1-phenyl-sulphonylpropene was the sole product.



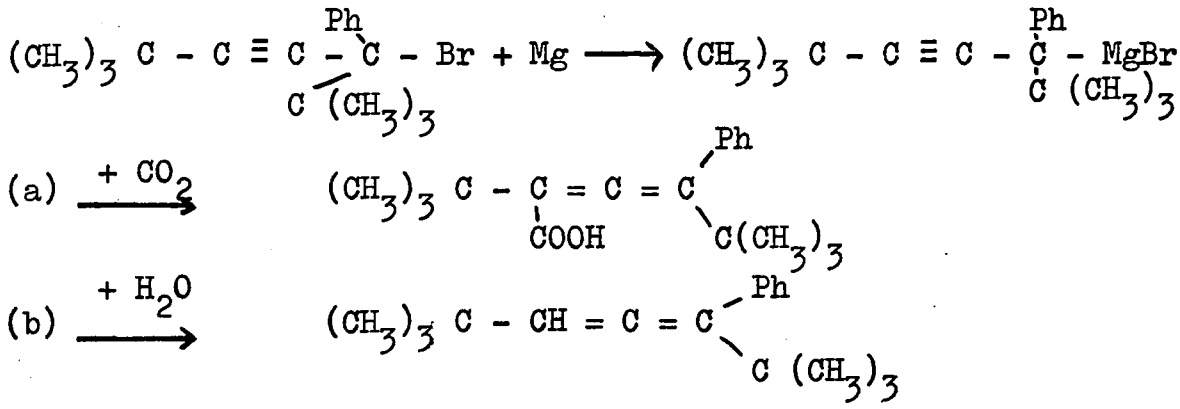
His interpretation of these results was that this could be obtained by addition at C_2 followed by protonation at C_3. This was shown to be unlikely by use of deuterium labled dibenzylamine, n.m.r. analysis of the product showed that "scrambling" had taken place.

If  was reacted with $(PhCH_2)_2ND$ little scrambling occurs showing that no hydrogen-deuterium exchange takes place, hence the deuterium must be introduced during the actual addition mechanism and cannot be introduced by addition to a mesomeric carbanion at a later stage, hence an internal proton transfer mechanism is almost certain. Our results throw a new light on this work and the full implications are discussed later.

GRIGNARD REACTIONS

OF ALLENES AND ACETYLENES

In 1935 it was reported by Ford, Thompson and Marvel[7] that allenic compounds were amongst the products from the Grignard compound of the acetylenic bromide (I) with water or carbon dioxide.



The structures were identified by the analysis of ozonolysis products. It is possible, however, that the allenic products were due to presence of undetected allenic bromide in the starting product (see p.2).

Danehy and Nieuwland [64] reported coupling of acetylenic Grignard compounds, i.e.

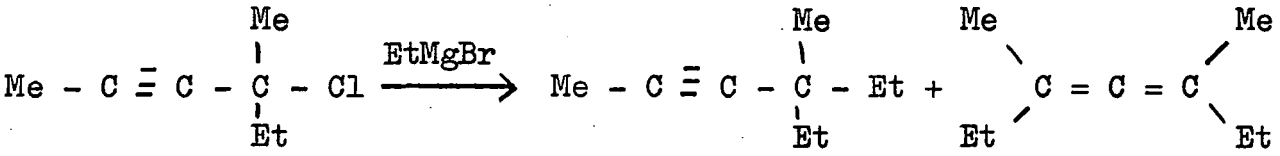
$$R\text{-}C \equiv C - MgBr \xrightarrow{Cu\ +} R - C \equiv C - C \equiv C - R$$

and later work by Campbell and Eby[65] showed that tertiary acetylenic chlorides coupled easily with alkylmagnesium compounds to give acetylenic hydrocarbons

$$R - C \equiv C - CCl\,R_2 + R'MgBr \longrightarrow R - C \equiv C - CR_2R'$$

Structures were proven by physical constants, analysis and hydrogenation; however, since spectroscopic data was not

available the presence of allenes cannot be ruled out. Zakhavova [66] reported the presence of allenic and acetylenic isomers in the product from the reaction of ethyl magnesium bromide with 3-chloro-3-methyl-3-ethyl-hen-4-yne.



Wotz[67] in 1951 showed that a mixture of acetylenic and allenic hydrocarbons was obtained on hydrolysis of the Grignard reagent from bromopropynes.

$$R - C \equiv C - CH_2MgBr \xrightarrow{H_2O} R - CH = C = CH_2 + R - C \equiv C - CH_3$$

$$R - \underset{\underset{MgBr}{|}}{CH} - C \equiv CH \xrightarrow{H_2O} RCH = C = CH_2 + RCH_2 - C \equiv CH$$

He suggested the rearrangements could proceed via the following scheme:

$$R - C \equiv C - CH_2MgBr \longrightarrow \left[\begin{array}{l} R - C \equiv C - \bar{C}H_2 \\ \\ R\bar{C} = C = CH_2 \end{array}\right] + MgBr \xrightarrow{H_2O} \begin{array}{l} R = C \equiv C\text{-}CH_3 \\ \\ RCH = C = CH \end{array}$$

and

$$R - \underset{\underset{MgBr}{|}}{CH} - C \equiv CH \longrightarrow \left[\begin{array}{l} R - \bar{C}H - C \equiv CH \\ \\ RCH = C = \bar{C}H \end{array}\right] \xrightarrow{H_2O} \begin{array}{l} RCH_2C \equiv CH \\ \\ RCH = \overset{+}{C} = CH_2 \end{array}$$

in each case the products were identified by infra-red spectroscopy.

A similar reaction [68-70] of the Grignard compound with carbon dioxide gave rise to mixtures of acetylenic and

allenic acids.

$$R - C \equiv C - CH_2MgBr \xrightarrow{CO_2} R - C \equiv C - CH_2COOH + R\underset{COOH}{C} = C = CH_2$$

R = ^{n}Pr, ^{n}Bu or ^{n}Am.

The acids were separated by fractional crystallization and characterised by physical constants, ozonolysis and infrared spectra. Whereas 2-bromooct-3-yne gave only 9% of the allenic acid, 2-bromo-2-methyloct-3-yne gave only the allenic acid, this was explained on the basis of stearic effects.

$$^{n}C_4H_9 - C \equiv C - \underset{Br}{\overset{CH_3}{C}} - CH_3 \xrightarrow[CO_2]{Mg} {}^{n}C_4H_9 - \underset{COOH}{C} = C = C\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

Propargylic bromides were shown to be coupled with acetylenic Grignard compounds by Gensler and Thomas,[71] they used a cuprous chloride catalyst and prepared pentadeca-6,9-diyne and 1-chlorohexadeca-7,10-diyne from 1-bromooct-2-yne and the corresponding Grignard compound.

$$C_5H_{11}-C{=}CMgBr + BrCH_2-C{\equiv}C-C_5H_{11} \longrightarrow C_5H_{11}-C{\equiv}C-CH_2-C{\equiv}C-C_5H_{11}$$

Gaudemar[71a] in 1956 reacted propargyl bromide with alkyl Grignard compounds at -10 to -15° in etherial solution, he found that mixtures of allenic and acetylenic hydrocarbons were formed in good yield (80%).

$$RMgBr + BrCH_2-C{\equiv}CH \longrightarrow RCH_2C{\equiv}CH = RCH{=}C{=}CH_2$$

Yields of allene were ^{n}Bu 80%, ^{i}Bu 80%, ^{n}Am 75%, Ph 35%.

He reported that propargyl Grignard compounds condensed

with aldehydes or ketones to give alcohols which contained no $CH_3C{\equiv}CC(OH)RR'$ and with carbon dioxide to give two products:- $HC{\equiv}C{-}CH_2COOH$ and a compound which was undoubtedly the allene.

Serratosa [71b] reported that propargyl bromide reacted with alkyl magnesium bromides in ether below 0° to give initially a bromopropargyl magnesium bromide, this subsequently formed an allenic carbene which added to another molecule of the alkyl Grignard to give an allene Grignard which on hydrolysis gave an allene hydrocarbon.

$$RMgBr + BrCH_2C{\equiv}CH \longrightarrow BrCH_2C{\equiv}CMgBr \longrightarrow CH_2{=}C{=}C:$$

$$\xrightarrow{RMgBr} CH_2{=}C{=}C\begin{matrix} R \\ MgBr \end{matrix} \xrightarrow{\text{hydrolysis}} CH_2{=}C{=}CHR.$$

Goodson[72] showed that allenic halides could be made to form Grignard compounds when reacted with magnesium in tetrahydrofuran, he found them reactive to water and solid carbon dioxide but not to alkylhalides.

He used the allenic chloride ,2,2,6-trimethylcyclohexylidenevinyl chloride and, on reacting its Grignard complex with water, obtained a mixture of 1-ethynyl-2,2,6-trimethylcyclohexane and 1-vinylidene-2,2-6-trimethylcyclohexane in about 35% yield.

$$= C = CHMgCl + H_2O \longrightarrow \quad {}^{=}C = CH_2 + \quad C{\equiv}CH$$

Reaction with carbon dioxide led to a mixture of allenic and acetylenic acids.

Patel[9 73] obtained similar results using 2,2,6-trimethylcyclohexylidenevinyl bromide.

PART II

DISCUSSION.

Preparation of Haloallenes.

The reaction of 3,3-dialkylprop-1-yn-3-ols with hydrogen bromide was first carried out by Favorskaya [23] in 1940. She used hydrobromic acid and 3-methylbut-1-yn-3-ol and stated that only 1-bromo-3-methylbuta-1,3-diene was obtained.

$$Me_2C(OH)C \equiv CH \longrightarrow CH_2{=}C(Me){-}CH{=}CHBr$$

Moulin [73] reported that using dry hydrogen bromide the product was a mixture of 1,3-dibromo-3-methylbut-1-ene and 3-methyl-1,2,3-tribromobutane. These results are not consistent with the present work.

Patel and Whiter [24] showed that the reaction of hydrobromic acid with acetylenic carbinols gives impure 1-bromoallenes contaminated by unsaturated carbonyl compounds as shown by an infra-red band at 1685 cm^{-1} and ultra-violet absorption at 224-228 m μ. The reaction did not go to completion even after shaking for 2 weeks. However in the presence of cuprous bromide, ammonium bromide and copper powder as catalysts goods yields of 1-bromoallenes were obtained after 1-6 hr. preferably at a temperature of 40°.

Further work described in this thesis has shown that excellent yields of pure 1-bromoallenes may be obtained at room temperature ($25-27^{o}$) by the following procedure.

1. 3-Methylbut-1-yn-3-ol, 3-methylpent-1-yn-3-ol and 3-ethylpent-1-yn-3-ol best gave 1-bromoallenes as follows:-

The acetylenic alcohol (1 eq.) was added over 5 min. to a stirred mixture of cuprous bromide (0.5 equiv.), ammonium bromide (0.5 equiv.), copper powder (1g.) and 45% or 48% hydrobromic acid (2 eq.)

The mixture was vigorously stirred at room temperature (25 - 27°), but stirring was interrupted from time to time to allow a lighter organic layer to separate. The organic layer was tested by infra-red spectroscopy and this proved to be the most convenient method of following the reaction. The strong 3400 cm^{-1} (OH) band being replaced by a strong 1950 cm^{-1} (C=C=C) absorption band. When the reaction was complete the mixture was decanted through a sintered glass filter funnel into a separating funnel and the lower layer of acid removed. The remaining upper layer of 1-bromoallene was washed several times with 45% hydrobromic acid until the acid washings no longer showed a purple colour, indicating that all the copper salts had been removed. After drying over a mixture of magnesium sulphate and sodium carbonate, filtration gave 85 - 95% of the 1-bromoallene. The products gave only one peak on g.l.c. and the infra-red spectra contained no bands in the 1600 - 1700 cm^{-1} region (C=C).

Reaction times varied between $\frac{1}{2}$ - $2\frac{1}{2}$ hr. depending on (a) the efficiency of the stirring, (b) the scale of the reaction and (c) the substitu~~tion~~ents on the alcohol. The optimum conditions are shown in the table.

	Time (hr)	Yield
1-Bromo-3-methylbuta-1,2-diene	$\frac{1}{2}$	90%
1-Bromo-3-methylpenta-1,2-diene	1	85%
1-Bromo-3-ethylpenta-1,2-diene	$1\frac{1}{2}$	88%

The reaction time was considerably longer if the reagents were not stirred extremely vigorously; stirring normally regarded as efficient was found to be inadequate. This is probably due to the fact that the reaction mixture tends to separate into an aqueous and non aqueous phase, the reaction taking place in the aqueousphase.

It was surprising that shaking did not give good results (except on a small scale); this was probably due to the fact that the shakers employed had only a slow oscillation time. The use of a supersonic dispenser would probably result in even shorter reaction times. Large scale reactions took longer than small scale reactions due to the fact that efficient mixing is more difficult to achieve on a large scale.

Acetylenic alcohols with larger substituents are less soluble in hydrobromic acid and consequently take longer to react under standard conditions. Solutions of hydrobromic

acid in glacial acetic acid resulted in faster reaction times, but the progress of the reaction was difficult to follow, the products were much inferior in purity and separation of the products from acetic acid was sometimes difficult.

2. More vigorous conditions were employed with alcohols with larger substituents, e.g. 3,4,4-trimethylpent-1-yn-3-ol and 3,5-dimethylhex-1-yn-3-ol - cuprous bromide (0.75 equiv.), ammonium bromide (0.5 equiv.) and 55-60% hydrobromic acid (2.5-3 equiv.); with temperatures up to 40° were used. Mono and di-isopropylethynyl carbinols tend to give 1,4-dienes as biproducts and in these cases it is better to keep the temperature below 30° and use slightly longer reaction times.

3. Secondary acetylenic alcohols of higher molecular weight were best converted to 1-bromoallenes by use of 60% hydrobromic acid and shaking for 12 - 24 hr. The resulting monoalkylbromoallenes are contaminated with 5 - 10% of the corresponding acetylenic bromides which are difficult to remove by fractionation but do not usually interfere in subsequent reactions.

Most of the simple 3,3-dialkylbromoallenes were obtained in high yields within two hours of starting the reaction and of such high purity that no further purification was necessary; they can now be considered to be readily available starting materials.

Whiter [74] attempted to prepare arylbromoallenes but met with only moderate success. Although the main products obtained by Whiter were shown to be bromoallenes they contained sufficient impurities so that no reliable analyses or spectral data could be recorded. Attempts at purification of these arylbromoallenes led to fast decay of the allenic band at 1950 cm^{-1} in the infra-red spectra indicating that these compounds were unstable.

In the present work three arylbromoallenes were prepared in excellent yield and high purity and the compounds were found to be far more stable than had previously been believed. (A sample of 1-bromo-3,3-diphenylpropa-1,2-diene has been kept unchanged in the refrigerator for several months.)

It was reasoned that the solution to the problem of preparing these compounds lay in preventing the allenic bromide, once formed, from reacting further with the hydrogen bromide. Removal of the product immediately after its formation was achieved by the presence of an immiscible, non-polar solvent which does not react with hydrogen bromide. Light petroleum ether was chosen as the arylbromoallenes are very soluble in this solvent whereas the acetylinic carbinols used as starting materials are considerably less soluble.

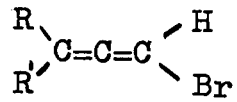
In addition this solvent is easily removed after completion of the reaction. 60% hydrobromic acid was used in order to complete the reaction as quickly as possible, the method being as follows:-

An ice cold mixture of cuprous bromide (1 equiv.), ammonium bromide (1 equiv.), copper powder (1 g., catalytic) and 60% hydrobromic acid (4 equiv.) was stirred and a suspension of the acetylenic carbinol (1 equiv.) in light petroleum ether was added. The reaction was stirred vigorously at 0° and the upper layer was examined by infra-red spectroscopy in the usual manner. Reaction was complete after approximately 1 hr. and the organic layer was separated from the aqueous part and the latter was extracted with light petroleum, the petroleum fractions were combined, dried by shaking with magnesium sulphate and evaporation gave the pure 1-bromoallene.

Infra-red and ultra-violet spectral data are shown in Table I. All the 1-bromoallenes show an absorption maximum at 204-6mμ in the ultra-violet spectrum (Whiter reported 201-2mμ but the present data has been carefully checked and is considered more reliable.)

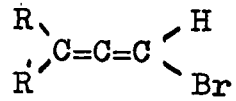
TABLE I

Infra-red and Ultra-violet Absorptions of Arylbromoallenes.



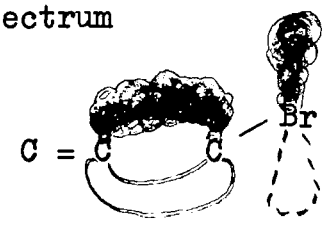
R	R'	Yield	I.R.No.	ν max cm^{-1}	λ max	ε	λ max	ε	λ max	
Ph	H	95%	1	1950, 1500, 1450, 1190, 756, 705, 685.	205	17,730	268	14,210		
Ph	Me	90%	2	1955, 1500, 1450, 1158, 765, 730, 690.	206	16,860	272	11,570		
Ph	Ph	84%	3	1945, 1600, 780, 710, 685.	205	30,340	230 sh	14,200	281	12,040

Infra-red and ultra-violet Absorptions of other 1-Bromoallenes.

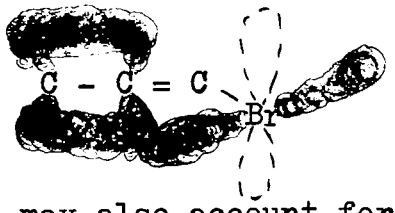


R	R'	Yield	I.R.No.	ν max cm^{-1}	λ max	ε	λ max	ε
H	Me	41%		1950, 1195, 840, 680	204	5,200	215sh	3,500
H	^{n}Pr	67%		1950, 1190, 830, 690	206	7,200	215sh	4,700
Me	Et	90%		1950, 1165, 730	205	9,570	217-23sh	6,150
Me	Bu^{t}	78%		1950, 1155, 728	206	9,000	224	6,600
Bu^{i}	Bu^{i}	52%		1965, 1165, 720	206	9,090	230	9,000

A shoulder at 215 mμ in the ultra-violet spectrum is typical for 3-monoalkyl-1-bromoallenes and this is bathochromically displaced to 217-23 mμ in the ultra violet spectrum of 3,3-dialkyl-1-bromoallenes, 1-bromo-3,4,4-trimethylpenta-1,2-diene shows a clear maximum at 224 mμ. It is surprising that haloallenes show ultra-violet absorption in this region at all as the only conjugation is between the unbonded electrons of the bromine and the 1,2-π electrons as in vinyl bromide which does not show a maximum or shoulder in the ultra-violet spectrum



It is considered that there is a non-bonded interaction between the bromine 3d. electrons and the 2,3-π electron system.



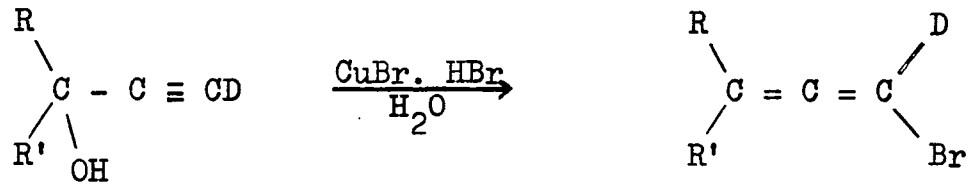
This interaction may also account for the unusual intensity of the 1950-60 cm^{-1} absorption in the infra-red spectrum (page 69).

Mechanism of 1-bromoallene formation.

Evans [75] has shown that the reaction catalysed by cuprous bromide is highly stereospecific and that the configuration of the resulting bromoallene is the same as that of the starting acetylenic carbinol. This was done by reacting the Grignard compound of the bromide with carbon dioxide and comparing the allenic acid produced with the acid from carbonation of an allenic chloride of known configuration.

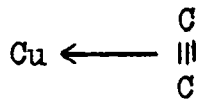
(+)-alcohol --- (-) -allenic bromide ----- (-) allenic acid.
(-)-alcohol --- (+) -allenic bromide ----- (+) allenic acid.
R(-)-alcohol --- (S)-(-)-allenic chloride ----- (+)-allenic acid
therefore (+)-allenic bromide has the S configuration.

Acetylenic carbinols and cuprous salts usually form cuprous acetylides; under strong acid conditions cuprous acetylides are usually decomposed but there was no evidence available which excluded the transient formation of cuprous acetylides during the reaction. To test this 1-deuteroethynyl carbinols were prepared and converted to 1-bromo-1-deuteroallenes in isotopically normal aqueous hydrobromic acid.



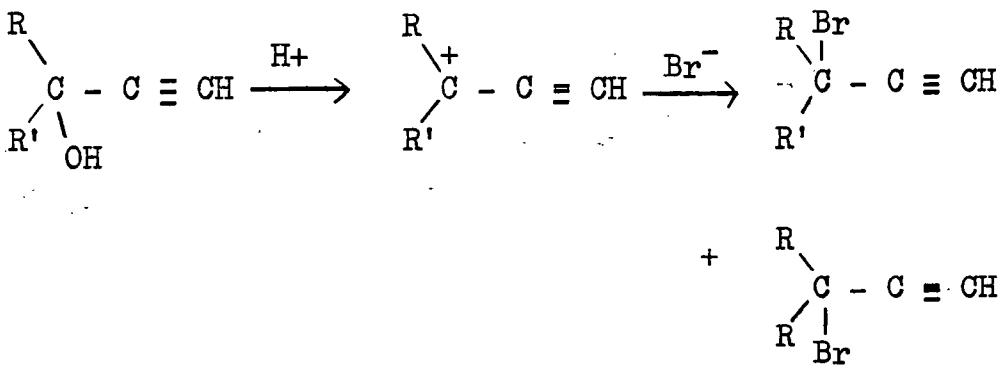
No hydrogen-deuterium exchange took place and this excludes the possibility of transient formation of cuprous acetylides during the reaction.

It has been established that the cuprous bromide plays an essential role in the reaction mechanism and the only alternative to the formation of a cuprous acetylide is the formation of a π - Cu complex.

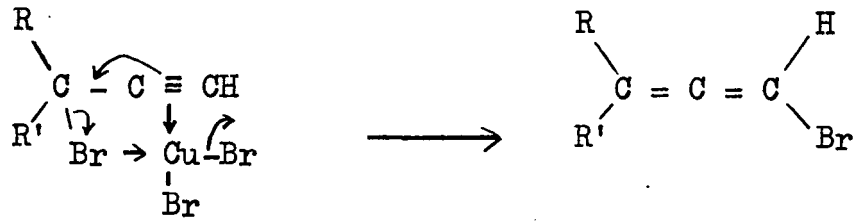


Three possible reaction mechanisms which involve a π -Cu complex may be considered:

(i) Formation of bromoacetylene (S_N1) followed by rearrangement to bromoallene (S_Ni').



The acetylenic bromide could then undergo S_Ni' reaction as follows:



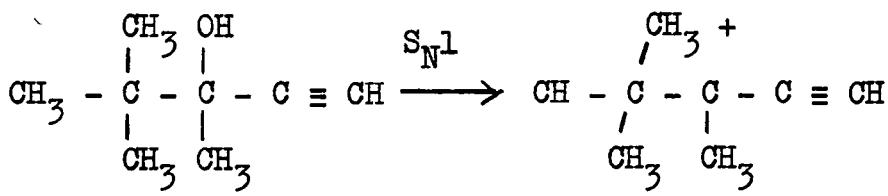
Such a path may be discounted on the following grounds.

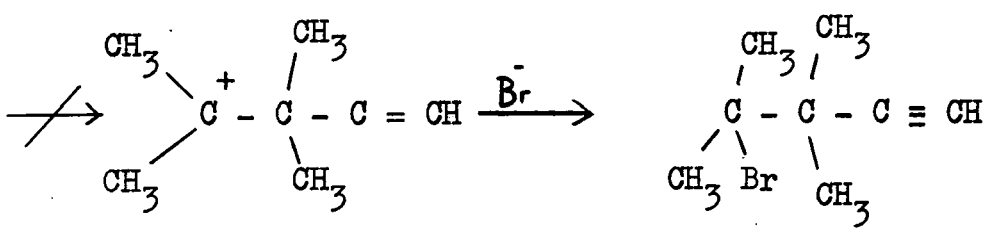
(a) Such a reaction would be expected to give racimisation or invertion, not retention of configuration.

(b) Rearrangements of 3-haloacetylenes to 1-haloallenes have been reported [25, 28], but reactions are slow and do not go to completion. Only traces of 3-bromoacetylenes have been encountered in this work either during or on completion of the reaction (< 1-2%).

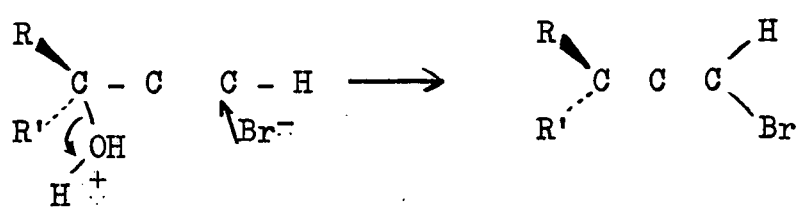
(c) As there is no build up of 3-bromoacetylene during the reaction the first stage must be considerably slower than the second stage and therefore rate determining. In that case addition of cuprous salt should not affect the overall rate of reaction, whereas in fact it is known to produce a 10-100 fold increase in reaction rate.

(d) The neopentylcarbonium ion usually undergoes a Wagner-Meerwein type of rearrangement. In 3-tert-butylethynyl carbinols an S_N1 reaction would lead to a neopentylcarbonium ion, and the expected rearrangement products are never found, indeed compounds of this type usually give the least by-products.





(ii) the S_N2' mechanism



This would lead to retention of configuration, since the two sets of π bonds being at right angles to each other, the

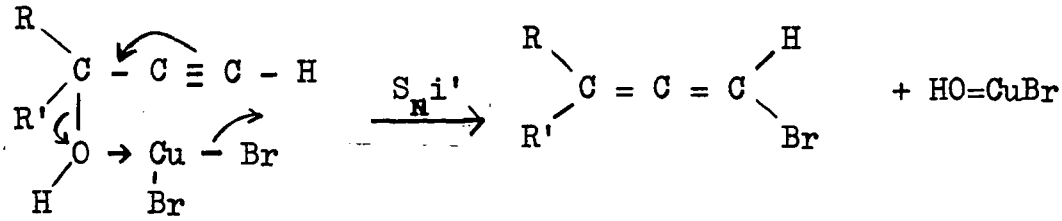
bromine ion would be required to attack from the same side as the protonated hydroxyl group leaves. However this mechanism does not involve cuprous bromide which has been shown to play an important part in the reaction.

(iii) The S_Ni' mechanism.

This mechanism seems to fit the known facts best, and utilize the complex of copper which is known to be formed in strong acid solution.

$$HBr + CuBr \longrightarrow \overset{+}{H}[CuBr_2]^-$$

i.e.

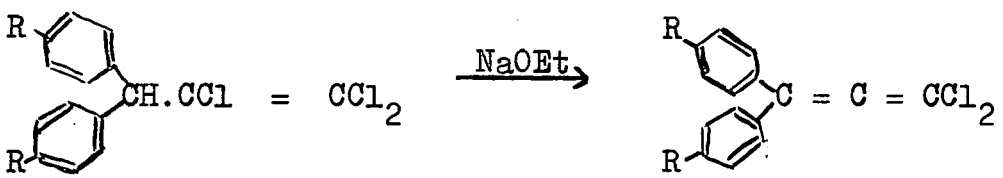


It has been shown by Demetriou [76] that 20% hydrobromic acid gives incomplete reaction even after several days, and also leads to exchange of acetylenic proton with deuterium in D_2O/HBr. Cuprous acetylide formation therefore slows down the reaction, presumably by competing with the π -Cu complex formation. The basic copper bromide formed is probably reconverted to cuprous bromide by excess hydrobromic acid.

$$[HO - Cu - Br]^- + HBr \longrightarrow [CuBr_2]^- + H_2O$$

1,1-Dibromoallenes.

1,1,-Dibromoallenes are reported for the first time in this work. Previously Roedig and Niedenbruck [77] had prepared 1,1-dichloro-3,3-diphenylallenes by elimination of hydrogen chloride from 1,1,2-trichloroprop-2-enes with sodium ethoxide



The starting materials for this reaction are not readily available.

1-Bromopropargylic alcohols were prepared by the action of sodium hypobromite on ethynylcarbinols. Best yields (~ 90%) and purest products were obtained by adding an ice cold solution of sodium hypobromite over 8 hr. to the ice cold acetylenic carbinol, and stirring vigorously all the time.

The 1-bromopropargyl alcohols were shown to be pure by infra-red spectra and gas liquid chromatography.

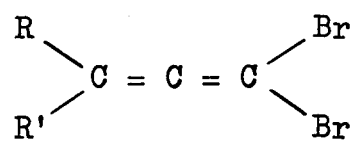
1-Bromo-3,3-dialkylprop-1-yn-3-ols with concentrated hydrobromic acid, cuprous bromide, ammonium bromide and copper gave products which contained the desired 1,1-dibromoallene, but which were not very pure. It was difficult to follow reaction by means of infra-red spectroscopy as the density of the starting material was such that two layers did not form easily. The reaction was therefore carried out in the presence of light petroleum ether which extracted the product as it was formed and prevented it from reacting further with hydrobromic acid.

Furthermore the light petroleum ether layer could easily be removed from the top of the reaction mixture for infra-red examination. 60% hydrobromic acid resulted in complete reaction in the shortest time; however, 1,1-dibromo-3-methylbuta-1,2-diene was best prepared by using 45% hydrobromic acid, as impurities tended to form rather easily with 60% hydrobromic acid.

The ultra-violet spectra of the 1,1-dibromoallenes is very similar to that of the 1-bromoallenes but the extinction coefficients are generally higher. (Table II).

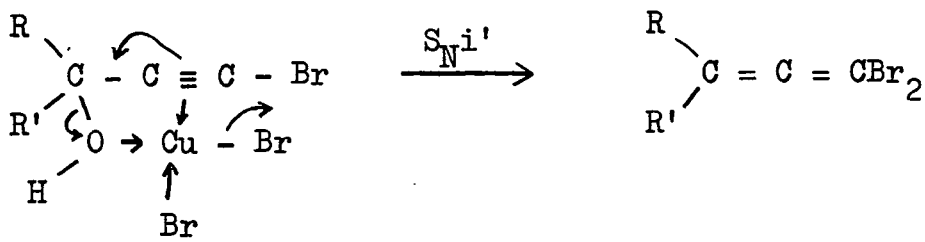
Table II.

Ultra-violet spectra of 1,1-dibromoallenes.



R	R'	I.R.No.	Yield	λmax	ε	λmax	ε
Me	Me	8	62%	206	13,040	215sh	9,990
Me	Et	9	67%	206	13,850	215sh	10,000
Me	Bu^t	10	69%	206	16,290	218sh	10,000
H	Pr^n	11	31%	205	10,000	215sh	7,700
Ph	Ph	12	60%	207	24,000	289	6,000

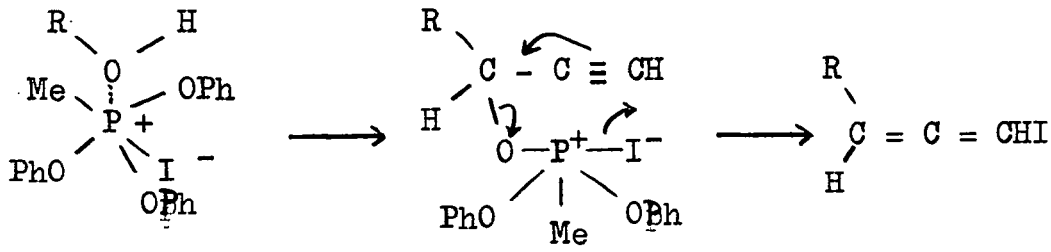
1,1-Dibromoallenes are probably formed by the same mechanism proposed for the formation of 1-bromoallenes.



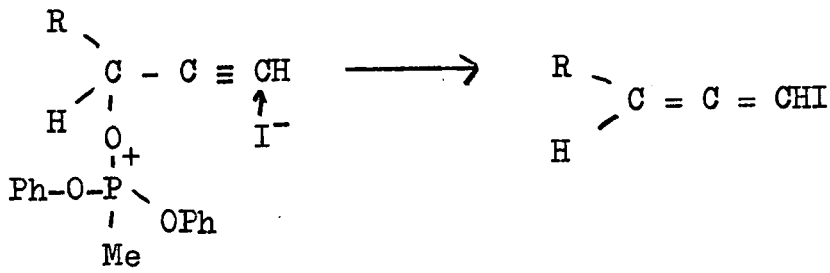
3,3-Dialkyl-1-iodoallenes.

The first general preparative method for 1-iodoallenes was due to Baker, Landor, Landor and Patel [30]. A solution of triphenyl-phosphite methiodide in dimethylformamide with a secondary propargylic alcohol at 80 - 100° gave good yields of 1-iodoallenes. It was thought that the mechanism was S_Ni' or S_N2, both mechanisms requiring the formation of an alkoxyphosphorus intermediate as an essential step in the mechanism of the reaction.

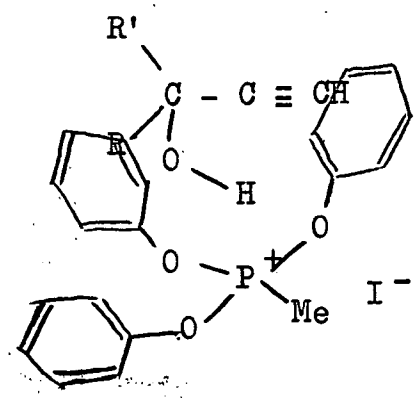
S_Ni'



S_N2'

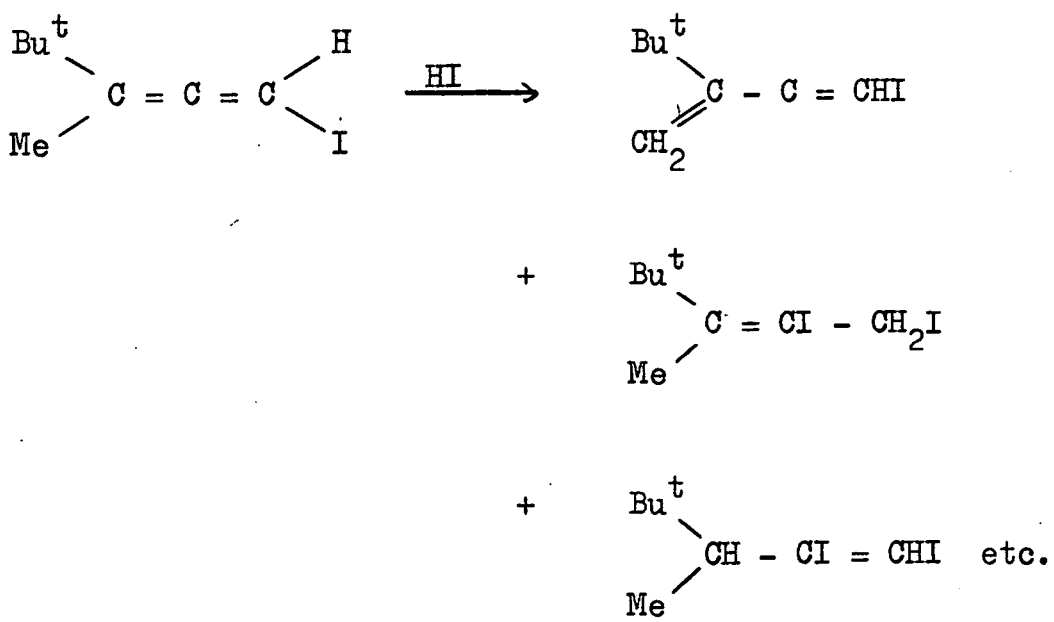


These workers [30] found that 3,3-dialkylprop-1-yn-3-ols did not react with this reagent and this may be due to steric hindrance since the oxygen of the tertiary alcohol cannot approach close enough to the phosphorus of the triphenylphosphite methiodide for co-ordination to take place.



Other workers [28, 31, 32] had tried to prepare allenic iodides by reacting proporgylic bromides with sodium iodide in acetone, but had obtained only poor yields of very impure and unstable products. Favorskaya [23] had obtained mixtures of 1-iodo-3-methylbuta-1,2-diene and 1-iodo-3-methylbuta-1,3-diene on reacting 3-methylbut-1-yn-3-ol with hydriodic acid but she was not able to isolate the allenic iodide.

As a consequence of the work on 1-bromoallenes and 1,1-dibromoallenes it was decided to see if the reaction could be extended to the preparation of 3,3-dialkyl-1-iodoallenes. 3,4,4-Trimethylpent-1-yn-3-ol was reacted with 45% hydriodic acid in presence of cuprous iodide, ammonium iodide and copper powder, some allene formation was found but the product was very dark and highly contaminated with impurities showing bands at 1650 cm^{-1} in the infra-red spectrum. These probably arose from attack of hydriodic acid on the iodoallene or by rearrangement reactions.



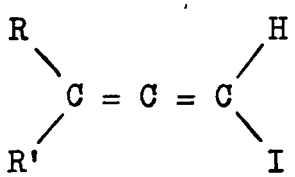
It was therefore decided to use the petroleum ether technique. 3,4,4-Trimethylpent-1-yn-3-ol in petroleum

ether with 45% hydriodic acid for 18 hr. gave 40% of the starting alcohol and 50% of the required allenic iodide. Increasing the strength of the hydriodic acid to 60% reduced the reaction time to 6 hr. and increased the yield of iodoallene to 76%.

Table III summarises the conditions used for these preparations. In all cases elevated temperatures ($> 20^{o}$) lead to formation of by-products which are difficult to remove.

Table III.

Preparation of 1-Iodo-3,3-dialkylallenes.



	R	R'	Moles Carbinol	Moles CuI	Moles HI	Strength HI	Time	Yield	I.R.No.
a	Me	Me	.2	.2	.4	45%	2 hr	Highly impure	
b	Me	Me	.2	.2	.4	45%	2 hr.	61%	4
b	Me	Et	.15	.15	.3	45%	2½hr.	62	5
	Et	Et	.15	.15	.3	45%	3 hr.	65	6
bc	Me	Bu^t	.1	.1	.15	45%	18hr	50	7
b	Me	Bu^t	.1	.1	.2	60%	6 hr.	76	7

a. no solvent used

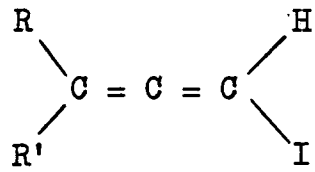
b. solvent partition method

c. 50% recovered alcohol

It has previously been reported [30] that 1-iodoallenes have no absorption in the ultra-violet region, but the present work shows that this report is erroneous and in fact mono-alkylallenes show an absorption at λ max 207mμ and λ max 235-9mμ whilst dialkyliodoallenes have a λmax 206-7mμ and λmax 246-8mμ. Again it is not known what the cause of the absorption is, other than to postulate a similar non-bonded interaction to that of the allenic bromides. (Table IV.)

Table IV.

Ultra-violet Absorption of 1-Iodoallenes.

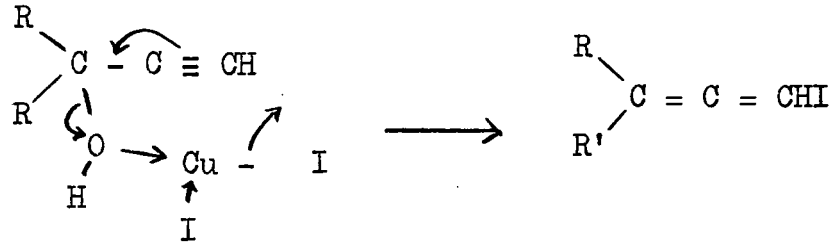


R	R'	λ_{max}	ε	λ_{max}	ε
H	Me	207	14,000	235	5,000
H	Pr^n	207	12,700	239	4,000
Me	Me	206	15,875	246	9,525
Me	Et	206	15,560	247	6,645
Et	Et	207	17,053	248	6,963
Me	Bu^t	207	18,475	247	7,171

Mechanism.

By analogy with the mechanisms proposed for the formation of 1-bromoallenes it seems probable that the mechanism of formation of iodoallenes is as follows:

S_Ni'



Only traces (< 2%) of 3-iodoacetylenes are found in the products and in the reaction mixture.

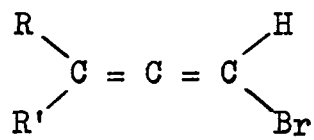
The Infra-red Spectra of 1-Halloallenes.

Characteristic bands in the infra-red spectrum, in order of decreasing wave number, these are 3050w, 1950-1975s, 1130-1190s, and either 720-730 (1-bromo-3,3-dialkylallenes) or 830-855 and 680-700 (1-bromo-3-alkylallenes) or 780-820 and 710-715 (1-iodo-3,3-dialkylallenes) or 870-885 and 830-840 cm^{-1} (1-iodo-3,3-dialkylallenes). This is clearly shown in Tables V and VI. These bands may be assigned with some certainty to the following vibrational modes:

3050 cm^{-1}	= C - H	stretching mode
1940-1965 cm^{-1}	C = C = C	stretching mode
1130-1190 cm^{-1}	= C - H(X)	in plane deformation mode

Table V.

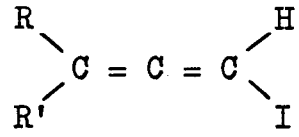
Infra-red Spectra of 1-Bromoallenes.



R	R'	Wave	Numbers	cm^{-1}		
Me	Me	1950	1160	1050	750	730
Me	Et	1950	1165			730
Et	Et	1950				720
Me	Bu^i	1950	1160			730
Me	Bu^t	1950	1155			728
Pr^i	Pr^r	1950	1165			728
Bu^i	Bu^i	1965	1165			720
Bu^t	Bu^t	1940	1135			720
H	Me	1950	1195	890	840	680
H	Et	1950	1190	870	850	690
H	Pr^n	1950	1190	880	830	690
H	Pr^i	1950	1195		855	704
H	Ph	1950	1190			
Me	Ph	1955	1160			
Ph	Ph	1945	1165			

Table VI.

Infra-red Spectra of 1-Iodoallenes.

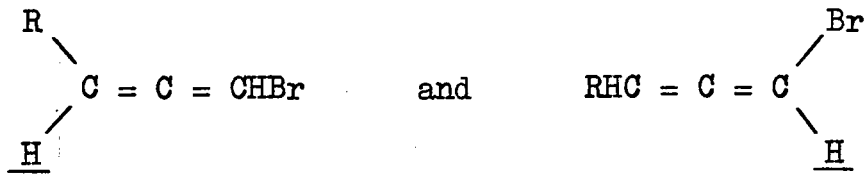


R	R'	Wave Numbers cm^{-1}				
Me	Me	1955		1135	750	710
Me	Et	1955		1130	780	715
Et	Et	1950		1130	800	710
H	Me	1945	1160	1110	885	835
H	Et	1940	1155	1100	870	840
H	Pr^n	1940	1160	1100	870	830

Out of plane = C - H(X) deformation modes are difficult to assign but tentative placings are:

1-bromo-3-alkylallenes	880 and 840 cm^{-1}
1-iodo-3-alkylallenes	880 and 835 cm^{-1}
1-iodo-3,3-dialkylallenes	720 - 800 cm^{-1}

The two inplane and the two out-of-plane vibration modes seen in the monoalkylallenes are due to there being two allenic hydrogens with different surroundings, i.e.



To test these assignments a series of 1-deuteroallenes was prepared and the ratio $\frac{\nu_H}{\nu_D}$ was compared with the theoretical value of 1.36. (Table VII.) The theoretical value was derived as follows:

$$\nu_H = \frac{1}{2\pi c}\left(\frac{f}{\mu_H}\right)^{\frac{1}{2}} \qquad \nu_D = \frac{1}{2\pi c}\left(\frac{f}{\mu_D}\right)^{\frac{1}{2}}$$

c = velocity of light; f = force constant of bond, assume $f_H = f_D$; μ = reduced mass of a system A, B defined

$$\mu = \frac{M_A . M_B}{M_A + M_B}$$

Thus

$$\frac{\nu_H}{\nu_D} = \frac{\mu_D}{\mu_H} = \sqrt{\frac{M_C \cdot M_D}{M_C + M_C} \cdot \frac{M_C + M_H}{M_C \cdot M_H}} = \sqrt{\frac{M_D}{M_C + M_D} \cdot \frac{M_C + M_H}{M_H}}$$

$$\frac{\nu_H}{\nu_D} = \sqrt{\frac{2 \cdot 13}{14 \cdot 1}} = 1.36$$

<u>1-Chloro-3,4,4-trimethylpenta-1,2-diene</u>: The 3070 cm^{-1} = C - H stretching band moves to 2300 cm^{-1} on deuteration, the 1180 cm^{-1} = C - H in place deformation band moves to 890 cm^{-1} on deuteration. The out-of-plane = C - H deformation band moves off scale and its shift therefore cannot be measured. It is thought that the 740 cm^{-1} band which on deuteration appears at 710 cm^{-1} is the = C - Cl stretching mode. (It is known that C - Cl stretching in $CHCl_3$ moves on deuteration.)

<u>1-Bromo-3-methylpenta-1,2-diene</u>: The 3050 cm^{-1} =C-H stretching band moves to 2300 cm^{-1} on deuteration, the 1180 cm^{-1} =C-H in plane deformation band shifts to 870 cm^{-1}. There is no clear band which may be assigned to the out-of-plane deformation. The 720 cm^{-1} band moves only slightly on deuteration and cannot be due to =C-H, it is thought that this band may be a =C-Br stretching mode.

Table VII.

Comparison of 1-Haloallene and 1-Deutero-1-Haloallene Spectra.

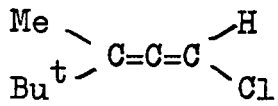
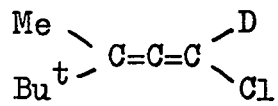
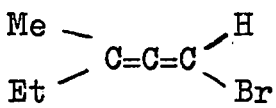
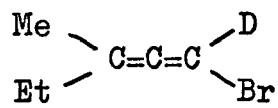
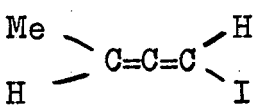
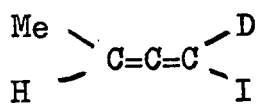
		ν_H/ν_D	ν_H/ν_D (calc.)
			
3070 cm^{-1}.	2300 cm^{-1}.	1.34	1.36
1180 cm^{-1}.	890 cm^{-1}.	1.33	1.36
830 cm^{-1}.	off scale		
			
3050 cm^{-1}.	2300 cm^{-1}.	1.33	1.36
1180 cm^{-1}.	870 cm^{-1}.	1.36	1.36
			
3100 cm^{-1}.	2300 cm^{-1}.	1.34	1.36
1160 cm^{-1}.	900 cm^{-1}.	1.29	1.36
880 cm^{-1}.	off scale		

Table VIII

Infrared Spectra of 1- Halohallenes *

ε^{ν} = apparent extinction coeff at wave number ν in $mole^{-1} cm^{-1}$. $\Delta_{\frac{1}{2}}$ = corresponding half bandwidth in cm^{-1}.

1-Chlorohexa-1,2-diene	a	ε^{1965} = 12.8	$\Delta_{\frac{1}{2}}$ 15,	ε^{840} = 23.2	$\Delta_{\frac{1}{2}}$ 20;	ε^{745} = 111	$\Delta_{\frac{1}{2}}$ 12
1-Bromohexa-1,2-diene		ε^{1970} = 23.2	$\Delta_{\frac{1}{2}}$ 15;	ε^{830} = 30.9	$\Delta_{\frac{1}{2}}$ 15;	ε^{745} = 193	$\Delta_{\frac{1}{2}}$ 12
1-Iodohexa-1,2-diene	b	ε^{1950} = 12.5	$\Delta_{\frac{1}{2}}$ 15;	ε^{830} = 33.9	$\Delta_{\frac{1}{2}}$ 10;		
1-Chloro-3,4,4-trimethylpenta-1,2-diene	c	ε^{1955} = 40.5	$\Delta_{\frac{1}{2}}$ 15;	ε^{830} = 23.5	$\Delta_{\frac{1}{2}}$ 8;	ε^{740} = 152	$\Delta_{\frac{1}{2}}$ 20
1-Bromo-3,4,4-trimethylpenta-1,2-diene		ε^{1955} = 47.5	$\Delta_{\frac{1}{2}}$ 15;	ε^{830} = 24.6	$\Delta_{\frac{1}{2}}$ 8;	ε^{730} = 133	$\Delta_{\frac{1}{2}}$ 12
1-Bromo-3-methylpenta-1,2-diene		ε^{1975} = 57.1	$\Delta_{\frac{1}{2}}$ 15;			ε^{725} = 69.2	$\Delta_{\frac{1}{2}}$ 15
1-Iodobuta-1,2-diene		ε^{1950} = 12.6	$\Delta_{\frac{1}{2}}$ 15;	ε^{830} = 105	$_{\frac{1}{2}}$ 8; †		

* 10 solution in nujol, 0.1mm cell.

† also ε^{880} = 32.4 $\Delta_{\frac{1}{2}}$ 8

a T. L. Jacobs, W. L. Petty and E. G. Teach, J. Amer. Chem Soc., 1960, 82,4090.

b C. S. L. Baker, P. D. Landor and A. N. Patel, J. Chem Soc., 1965, 4348. (and S. R. Landor)

c Y. R. Bhatia, P. D. Landor and S. R. Landor, J. Chem Soc., 1959, 24; R. D. J. Evans and S. R. Landor, ibid, 1965, 2553

1-Iodo-3-methylbuta-1,2-diene: The two =C-H groups may be considered as isolated modes as cis-trans and coupled vibration will be negligible. The two 3100 cm^{-1} =C-H stretching modes are superimposed in the hydrogen form, but on deuteration the $=C\begin{smallmatrix}-I\\-D\end{smallmatrix}$ stretching band moves to 2300 cm^{-1}. The in plane deformations are assigned to 1160 cm^{-1} $(=C\begin{smallmatrix}-I\\-H\end{smallmatrix})$ and 1110 cm^{-1} $(\begin{smallmatrix}R\\H\end{smallmatrix}>C=)$, the former moves to 900 cm^{-1} on deuteration. The out-of-plane vibration modes are assigned to 880 cm^{-1} $(=C\begin{smallmatrix}-I\\-H\end{smallmatrix})$ and 850 cm^{-1} $(\begin{smallmatrix}R\\H\end{smallmatrix}>C=)$, the former moves off-scale on deuteration, the latter is only slightly displaced.

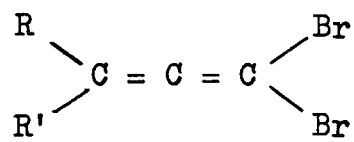
As may be seen from Table VIII the infra-red stretching frequency at 1950 cm^{-1} (C=C=C), is exceptionally intense in the 1-bromoallene, especially when compared with the corresponding chloro or iodoallenes. This is thought to be a consequence of the halogen - π non-bonded interaction already discussed (p.44) which is greatest for bromine as chlorine is too small for adequate overlap and iodine too diffuse.

The 1,1-dibromoallenes show only the characteristic 1950 cm^{-1} absorption in the infra-red region; (Table IX.) the intense absorption shown by these compounds in the 735-

750 cm^{-1} region is stronger than the band as shown by the monobromoallenes (720-730 cm^{-1}) and it is possible therefore to tentatively assign this mode to a =C- Br stretching vibration.

Table IX.

Infra-red Spectra of 1,1-Dibromoallenes.

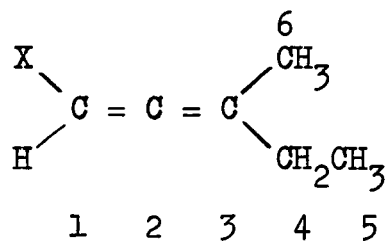


R	R'	Wave Numbers in cm^{-1}			
Me	Me	1960	1013	779	735
Me	Et	1960			740
Me	Bu^t	1950	1120	830	745
H	Pr^i	1955	1200	835	750
Ph [a]	Ph	1950			

a This compound shows absorption at 775; 760; 740 and 694 cm^{-1}.

Nuclear Magnetic Resonance of 1-Haloallenes.

The data from a number of different 1-haloallenes has been collected in Table X and has allowed a number of general conclusions to be formed.



The above compound is taken as a convenient skeleton for reference, all compounds of this type are simple AM_mX_x systems.

Chemical Shifts.

1. The absorption of the ^1C Protons is usually in the region of $\tau = 4.1$ for bromoallenes and $\tau = 4.4$ for iodoallenes, these values are consistent with the differences in electronegativity of bromine and iodine. The exception is in $Ph_2C = C = CHBr$ where the $= {}^1CHBr$ absorption is $\tau = 3.65$, this is probably due to a deshielding effect of the phenyl groups.

2. The ^{4}C protons usually absorb at τ=7.8-8.2, this is in fair agreement of the position calculated using Shoolery's additive constants ($\tau \approx 8.2$).

3. The $^{6}CH_3$ absorption is fairly constant at τ=8.1-8.22, which is about the expected position for a methyl group attached to a double bond.

4. The $^{5}CH_3$ absorption is in the normal position of τ=8.92.

<u>Spin-spin Coupling and Coupling Constants.</u>

The system shows the usual couplings between ^{4}CH, ^{5}CH coupling constants were found to be $J \approx 7.5$ c.p.s., and ^{4}CH, ^{6}CH $J \approx 0.5$ c.p.s. In addition there is a long range coupling between ^{1}CH and ^{4}CH; and ^{1}CH and ^{6}CH coupling constants were found to be $J \approx 2.3$ c.p.s. In all cases where the ^{1}C proton was replaced by ^{1}C deuterium or ^{1}C bromine the long range coupling vanished, thus proving that it was caused by the ^{1}C proton. Couplings constants of the type ^{1}CH, ^{3}CH are usually high with coupling constants in the order of $J \approx 6$ c.p.s.

1-Bromobuta-1,2-diene $CH_3CH = C = CHBr$ has a rather more complex spectrum as it is an ABX_3 system. The corresponding 1-chlorobuta-1,2-diene has been examined in detail by

Manatt and Elleman [80] and Snyder and Roberts [81] and all 20 of the bands have been assigned. The spectra consists of two sets of two superimposed quartets, τ, centred on τ = 4.15 and τ_3 on τ = 4.71. τ_4 the methyl group shows as a doublet of doublets at τ = 8.27 and τ= 8.3. $J_{4,1}$ = 2.5 c.p.s.; $J_{4,3}$ = 7.5 c.p.s.; $J_{1,3}$ = 6 c.p.s.

Table X.

NUCLEAR MAGNETIC RESONANCE DATA OF 1-HALO-ALLENES.

Compound	τ Value	Spin-spin coupling constants in c.p.s	
Br-CH=C=CHMe 1 2 3 4	τ_1=4.09 (doublet of quartets)	$J_{1,3}$	5.8
		$J_{1,4}$	2.6
	τ_3=4.68 (quartet of doublets)	$J_{3,1}$	5.8
		$J_{4,1}$	2.6
	τ_4=8.22 (doublets of doublets)	$J_{4,3}$	6.9
		$J_{4,1}$	2.6
Br-CH=C=C(6Me)-CH_2Me 1 2 3 4 5	τ_1=4.1 (sextet)	$J_{1,4}$	2.3
		$J_{1,6}$	2.3
	τ_4=8.19 (quartet of doublets)	$J_{4,5}$	7.5
		$J_{4,1}$	2.2
	τ_6=7.6-8.4 (doublet of triplets)	$J_{6,1}$	2.0
		$J_{6,4}$	0.5
	τ_5=8.93 (triplet)	$J_{5,4}$	7.5

$BrCD{=}C{=}C(6Me).CH_2Me$ 1 2 3 4 5	τ_4 = 7.87 (quartet)	$J_{4,5}$	7.5
	τ_6 = 8.14 (singlet)		
	τ_5 = 8.94 (triplet)		

$BrCH{=}C{=}C(CH_2Me)_2$ 1 2 3 4 5	τ_1 = 4.0 (pentet)	$J_{1,4}$	2.2
	τ_4 = 7.85 (quartet of doublets)	$J_{4,5}$	7.8
		$J_{4,1}$	2.2
	τ_5 = 8.94 (triplet)	$J_{5,4}$	7.5

$BrCH{=}C{-}C(6Me)(Bu^t)$ 1 2 3 5	τ_1 = 4.17 (quartet)	$J_{1,6}$	2.0
	τ_6 = 8.21 (doublet	$J_{6,1}$	2.0
	τ_5 = 9.15 (singlet)		

$BrCH{=}C{=}C{-}(Bu^t)_2$ 1 2 3 5	τ_1 = 4.16 (singlet)		
	τ_5 = 9.2 (singlet)		

---

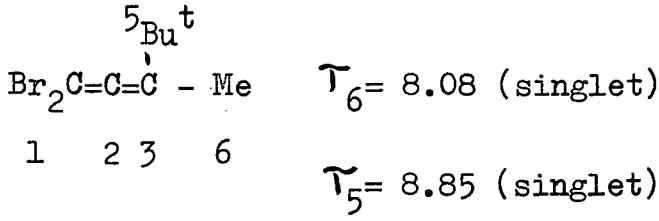
cont'd/...

$BrCH{=}C{=}CPh_2$	$\tau_1 = 3.65$ (singlet)	
1 2 3 4	$\tau_4 = 2.72$ (multiplet)	
$CH_3CH{=}C{=}CHBr$	$\tau_x = 8.24$ (doublet of doublets)	J_{XB} 7.2
X B A		J_{XA} 2.5
	$\tau_B = 4.72$ (two quartets)	J_{BX} 7.2
		J_{AX} 2.5
	$\tau_A = 4.15$ (quartet of doublets)	J_{AX} 2.5
		J_{AB} 6.0
$ICD{=}C{=}CH.CH_3$	$\tau_3 = 6.99$ (quartet)	$J_{3,4}$ 4.2
1 2 3 4	$\tau_4 = 8.93$ (doublet)	$J_{4,3}$ 4.2
$ICH{=}C{=}C\ Me_3$	$\tau_1 = 4.5$ (septet)	$J_{1,4}$ 2.3
	$\tau_4 = 8.2$ (doublet)	$J_{4,1}$ 2.3

cont'd/...

$ICH{=}C{=}C(^{6}Me).CH_2Me$ (1 2 3 4 5)	τ_1 = 4.38 (sextet)	$J_{1,4}$	2.3
		$J_{1,6}$	2.3
	τ_4 = 7.9 (quartet of doublet of quartets)	$J_{4,5}$	8.9
		$J_{4,1}$	2.3
		$J_{4,6}$	0.5
	τ_6 = 8.22 (doublet of triplets)	$J_{6,1}$	2.3
		$J_{6,4}$	0.5
	τ_5 = 8.93 (triplet)	$J_{5,4}$	8.9
$ICH{=}C{=}C(^{5}Bu^{t})-Me$ (1 2 3 4)	τ_1 = 4.43 (quartet)	$J_{1,4}$	2.2
	τ_4 = 8.23 (doublet)	$J_{4,1}$	2.2
	τ_5 = 8.9 (singlet)		
$ClCD{=}C{=}C(^{5}Bu^{t})-Me$ (1 2 3 4)	τ_4 = 8.93 (singlet)		
	τ_5 = 9.36 (singlet)		
$Br_2C{=}C{=}C(^{6}Me)CH_2Me$ (1 2 3 4 5)	τ_4 = 7.7 (quartet)	$J_{4,5}$	7.3
	τ_6 = 8.0 (triplet)	$J_{6,4}$	0.5
	τ_5 = 8.89 (triplet)	$J_{5,4}$	7.3

cont'd/...



1-CYANOALLENES.

Preparation of 1-Cyanoallenes from Acetylenic Alcohols.

A preliminary investigation by Laws [51] showed that a number of 1-cyanoallenes could be prepared by two methods, one of which was applicable only to 3-alkylcyanoallenes, the other only to 3,3-dialkylcyanoallenes.

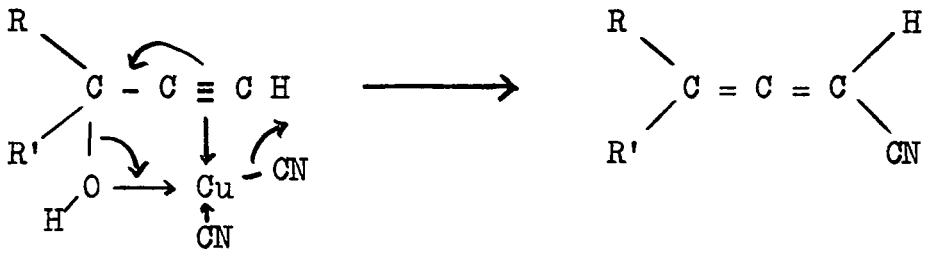
Laws found that poor yields of 1-cyanoallenes together with the corresponding 1-chloroallenes could be obtained by reacting 3,3-dialkylpropyn-3-ols with hydrochloric acid, cuprous cyanide and potassium cyanide. It was found necessary to use a large excess of hydrochloric acid at elevated temperatures. Sulphuric acid, formic acid and acetic acid in place of hydrochloric acid did not give cyanoallenes, but hydrobromic acid yielded some cyanoallenes together with 1-bromoallene, from which it could not be separated readily.

In the present work the tertiary acetylenic alcohol was reacted with cuprous cyanide (1.5 eq.), potassium cyanide (1.o eq.), copper (catalytic) and concentrated hydrobromic acid (2.5 sq. 48%w/w) for 3 days. It was found that good yields of pure 1-cyanoallenes could be

obtained. Unchanged starting material could be recovered in a pure state, and except in one case 1-bromoallene was not formed, Table XI shows the yields of allenic cyanide by this method.

Mechanism.

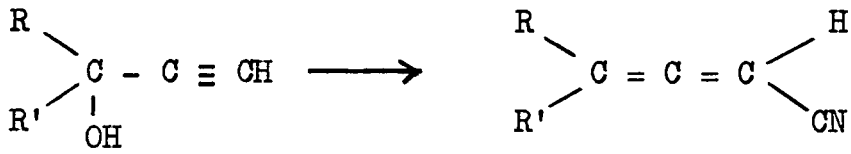
The mechanism favoured here is on S_Ni' type, similar to the one proposed for the 1-bromoallene formation



This type of mechanism would account for the fact that only the hydrogen halides give allene formation, since sulphuric acid and other acids would not allow formation of cyanocuprite or bromocyanocuprite complex ions.

Table XI.

1-CYANOALLENES FORMED BY REACTION OF ACETYLENIC CARBINOL WITH HBr.



R	R'	Yield %	Reaction Time
Me	Me	30	76 hr
Me	Et	51	67 hr
Et	Et	75	76 hr
Me	Bu^i	40	72 hr
Me	Bu^t	25	90 hr

The following equilibria are probably established as a slight excess of hydrobromic acid is added to the rest of the reagents

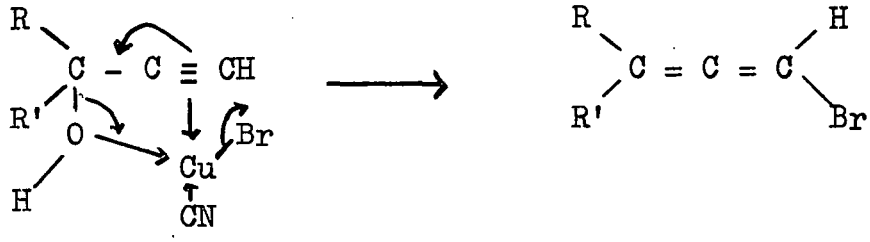
(i) $KCN + HBr \rightleftharpoons KBr + HCN$

(ii) $CuCN + HBr \rightleftharpoons H^+ (CuCNBr)^-$

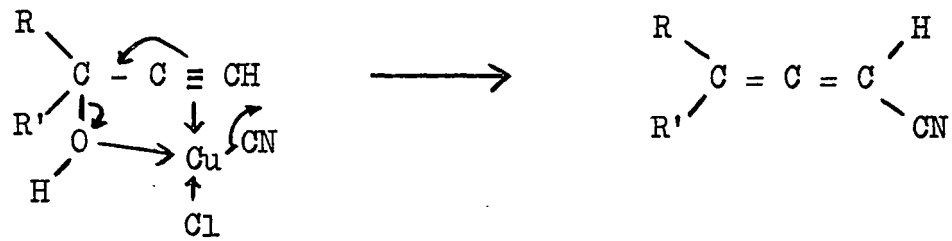
(iii) $H^+ (CuCNBr)^- + CN^- \rightleftharpoons Br^- + H^+ [Cu(CN)_2]^-$

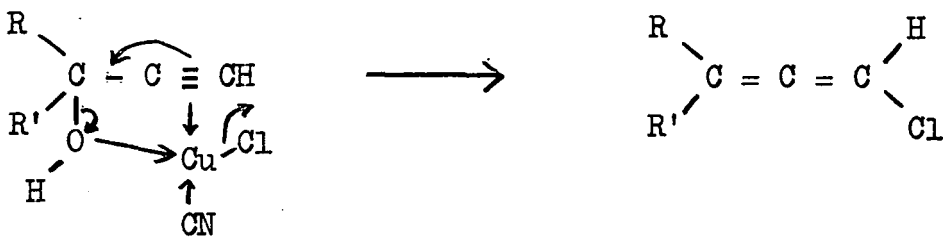
The cyanocuprite ion then reacts with the acetylenic carbinol to give the 1-cyanoallene.

A large excess of hydrobromic acid forces the equilibrium of (ii) to the left and leads to increasing quantities of 1-bromoallene in the product

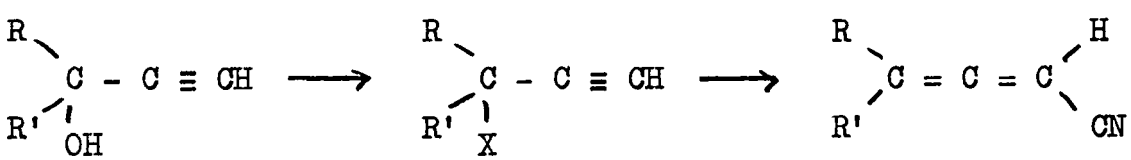


Similarly a large excess (5 fold) of hydrochloric acid gives equal quantities of 1-chloroallene and 1-cyanoallene as would be expected from a similar mechanism:-





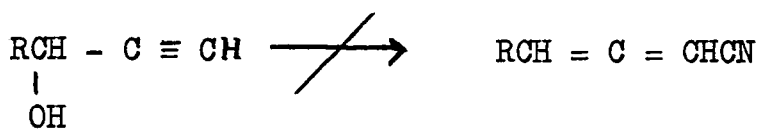
Laws [51] showed that 3-chloroacetylenes reacted with cuprous cyanide under the reaction conditions used here to give 1-cyanoallenes and suggested that the reaction of the alcohol with cuprous cyanide would proceed by initial formation of the 3-haloacetylene



However 3-chloroacetylenes are never completely converted to 1-cyanoallenes - some 3-haloacetylene is always recovered; since little or no 3-haloacetylene was found in the product this mechanism seems unlikely. Also it would require a slow

initial formation of a 3-bromo-propyne followed by a fast conversion to 1-cyanoallene, this is unlikely as under parallel conditions 1-bromoallenes are formed up to 70 times faster using hydrobromic acid and cuprous bromide.

Secondary acetylenic alcohols did not give 1-cyanoallenes by this method



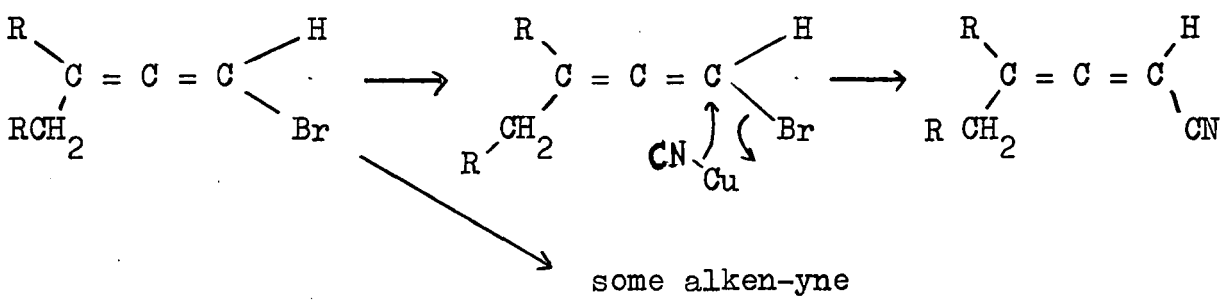
This is probably due to the hydroxyl group being more firmly bound in the secondary alcohols; in the case of the preparation of 1-bromoallenes this was overcome by using 60% hydrobromic and excess CuBr but a similar increase in concentration of cyanocuprite was ineffective in the preparation of 3-monoalkyl-1-cyanoallenes.

Preparation of 1-Cyanoallenes from 1-Bromoallenes and Cuprous Cyanide.

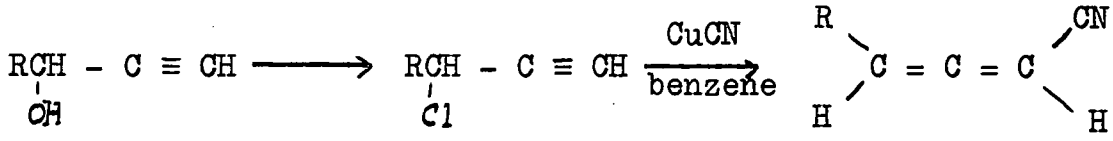
A general method for the preparation of cyanides is the treatment of a bromide with cuprous cyanide in benzene. Several attempts were made to prepare 1-cyanoallenes by heating 1-bromoallenes with cuprous cyanide in various solvents (benzene, acetone, alcohol silicone fluid, etc.) but in all cases 1-cyanoallene formation was negligible.

When 1-bromoallenes were heated with dry cuprous cyanide a vigorous reaction occurred at elevated temperature (110°) which resulted in the elimination of hydrogen cyanide to give alken-ynes; this reaction will be fully discussed in section IV of this thesis. However, highly stearically crowded molecules such as 1-bromo-3,4,4-trimethylpenta-1,2-diene and 1-bromo-3-tert-butyl-4,4-dimethylpenta-1,2-diene did give the corresponding 1-cyanoallenes in 60% and 90% yield respectively.

A simple four centre transition state best accounts for the formation of cyanoallene under these conditions



Laws [51] prepared some 3-momoalkyl-1-cyanoallenes by converting monoalkylprop-1-yn-3-ols to the corresponding 3-chloroalk-1-yne and by heating the chloroacetylene with cuprous cyanide in benzene



This method gave only poor yields of impure 1-cyanoallenes.

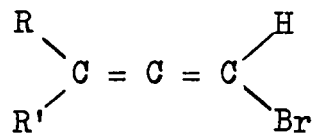
It was felt that a better method for the preparation of 3-monoalkyl-1-cyanoallene could be found and it was reasoned that an inert solvent of high dielectric constant was needed to dissolve both cuprous cyanide and 1-bromoallene. Such a solvent would have to be easily removable from the product and N,N-dimethylformamide was found to be suitable. The following procedure gave excellent yields of 1-cyanoallenes:-

Pure, dry dimethylformamide and dry cuprous cyanide are stirred until a partial solution is effected. 1-Bromoallene was added to this solution and the solution rapidly became dark. Excess cuprous cyanide dissolved quickly and heat was evolved. The contents of the flask were not allowed to rise above 50° during this initial exothermic reaction, then when the initial

evolution of heat stopped, the flask and contents were maintained at 50-60° for 1-2 hr. The solution was cooled and ether added until the turbidity produced by this addition was only just permanent (the addition of too much ether led to the formation of two layers which made working up difficult). The ether/dimethylformamide solution was then slowly added to a large volume of rapidly stirred water when copper salts were precipitated and an ether layer separated. The ether layer was removed and the aqueous suspension was filtered then extracted several times with ether, ether solutions were combined and washed 10-15 times with cold water to remove any residual dimethylformamide; efficient washing at this stage leads to a considerably improved product. The ether solution was then dried ($MgSo_4$) and distilled to give excellent yields of pure 1-cyanoallenes; Table XII contains a list of cyano-allenes prepared by this method.

Table XII.

1-CYANO-ALLENES FROM 1-BROMOALLENES.



	R	R'	Method	Yield	n_D^{25}
	Me	Me	a	40	1.4840
	Me	Et	a	51	1.4800
	Et	Et	a	60	1.4718
	Me	Bu^i	a	50	1.4685
	Me	Bu^t	a,b	65	1.4725
	Pr^i	Pr^i	a	61	1.4650
	Bu^i	Bu^i	a	60	1.4
	Bu^t	Bu^t	b	90	1.4745
*	H	H	a		
	H	Me	a	55	
	H	Et	a	55	
	H	Pr^i	a	55	
	H	Pr^n	a	60	1.4750
	H	Ph	a	70	

Method a Allene bromide + cuprous cyanide in D.M.F.
Method b Allene bromide + cuprous cyanide, no solvent
* see text.

An attempt was made to prepare allene cyanide (1-cyanopropa-1,2-diene) by reacting the dimethylformamide azeotrope of 1-iodopropa-1,2-diene with cuprous cyanide in the usual manner. Elemental analysis and infra-red spectra showed a mixture of 1-cyanopropa-1,2-diene and 3-cyanoprop-1-yne in the ratio 7:3 resulted (estimated by n.m.r.) This could be due to the initial iodoallene containing some 3-iodoprop-1-yne. Work by Baker, Landor, Landor and Patel [30] has shown that the iodopropadiene always contains at least 20% of 3-iodoprop-1-yne.

Attempts to separate pure 1-cyanopropa-1,2-diene by removing the 3-cyanoprop-1-yne as its insoluble silver salt were unsuccessful. After three washings with ammoniacal silver nitrate the ratio of the allene to acetylene remained unchanged even though large quantities of silver acetylide were precipitated. This suggests an equilibrium of the type

$$CH_2 = C = CHCN \xrightleftharpoons{NH_3} CN - CH_2 - C \equiv CH$$

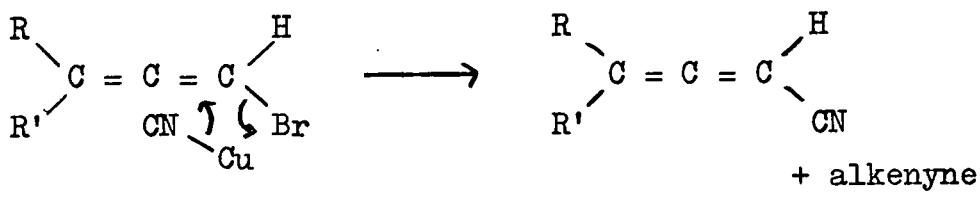
which is re-established after the removal of some of the acetylene by the precipitation of its silver salt.

Mechanism of Reaction.

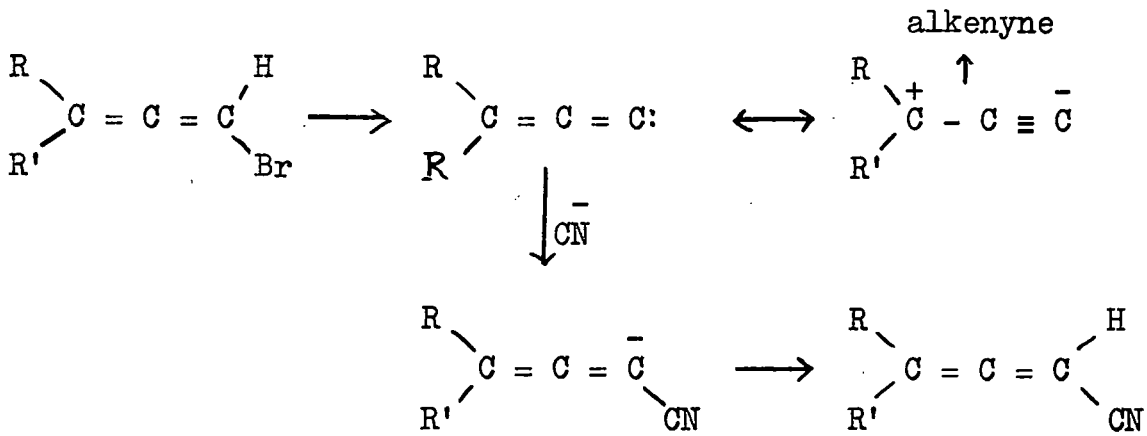
It has been discovered as a direct consequence of this work that a solution of cuprous cyanide in N,N-dimethylformamide yields several crystalline complexes; S.R. Landor and V.C. Patel [82] are at present working in these laboratories to try and elucidate the structure of these compounds. When 1-bromoallenes are added to a solution of cuprous cyanide in dimethylformamide an exothermic reaction immediately results and quickly proceeds to completion. 1-Bromoallenes of higher molecular weight require heating at 50-60° for about 2 hr. to ensure maximum conversion to 1-cyanoallene.

The choice of reaction mechanisms seems to lie between simple substitution of cyanide for bromide (or other halide) and an elimination reaction giving a carbene which then attacks cyanide. It was found that some alkenyne (10-15%) was formed at the same time as 1-cyanoallene, but since the latter is shown by separate experiments to be stable to heat in the presence of cuprous cyanide, the alkenyne must be formed from the 1-bromoallene.

(a) Four-Centre Reaction.



(b) Carbene Formation.



However when a 1-bromo-1-deuteroallene was reacted with cuprous cyanide and worked up in aqueous solution only 1-cyano-1-deuteroallene was formed, no exchange between deuterium and hydrogen occurred, this therefore precludes a carbene mechanism.

Cuprous cyanide dissolves readily in dimethylformamide to form a complex and it would be difficult for the large complex molecule to lie flat across the 1-bromoallene, thus the normal elimination mechanism (see p.150) is prevented and a substitution reaction occurs. Under similar conditions cuprous iodide and cuprous bromide which are not soluble in dimethylformamide ~~and~~ yield en-ynes (see page 154) due to the fact that they do not form complexes with dimethylformamide hence can lie flat across the bromoallene molecule.

Infra-red and Ultra-violet Absorption of 1-Cyanoallenes.

1-Cyanoallenes have very intense absorption bands in the infra-red spectrum at 2230-50 and 1955-80 cm^{-1}. The former is due to stretching mode of the conjugated cyanide and the latter to the allene group. In addition to these very strong bands weaker absorption occurs at 790 and 760-770 cm^{-1} (3,3-dialkylallenes) and 865-870 and 725-40 cm^{-1} (3-alkylallenes).

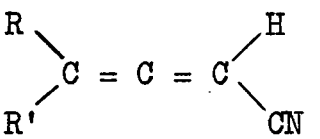
That the lower of each of these pairs of bands is due to a hydrogen deformation mode is fairly certain, since on conversion of 1-cyano-3-methylpenta-1,2-diene to 1-cyano-1-deutero-3-methylpenta-1,2-diene the 760 cm^{-1} band moves off scale.

All the 1-cyanoallenes show a maximum in the ultra-violet region at 207-9 mμ extinction coefficients being in the region of 10,000. This may be compared with α-β unsaturated cyanides which absorb at 215-17 mμ [84]

Table XIII shows these spectral characteristics.

Table XIII.

Infra-red and Ultra-violet Spectra of 1-Cyanoallenes.



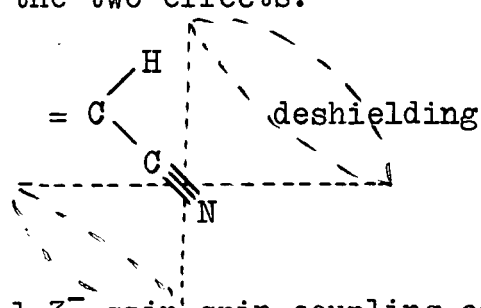
R	R'	ν_{max} cm^{-1}				λ_{max}. ε	
Me	Me	2245	1950	790		207	10,000
*Me	Et	2245	1955	790	760	207	10,000
Et	Et	2240	1955	790		207	10,140
Me	Bu^i	2245	1960		765	207	10,150
Me	Bu^t	2250	1960		765	207	10,000
Pr^i	Pr^i	2250	1955		770	207	10,880
Bu^i	Bu^i	2250	1980		760	207	11,010
Bu^t	Bu^t	2235	1970		760	207	11,050
H	Me	2225	1965	860	730	207	9,730
H	Et	2235	1950	865	725	207	11,100
H	Pr^n	2255	1970		730	207	9,000
H	Pr^i	2250	1965	870	740	208	8,600
+H	Ph	2250	1155			209	14,800

* in the 1-deutero form the 760 cm^{-1} is absent.

\+ i.r. lower bands obscured by phenyl absorption, u.v. also has bands λ_{max} 244 mμ, (ε, 7,860); 272mμ, (ε, 5,170); 283mμ, (ε, 5,180)

Nuclear Magnetic Resonance Spectra of 1-Cyanoallenes.

Table XIV shows the n.m.r. spectra of several 1-cyanoallenes. It is worth noting that the hydrogen on C_1 of the allene which also bears the cyanide is at a much higher field than the corresponding allenic hydrogen in the 1-haloallenes. Obviously this cannot be explained on the basis of electronegativities as the cyanide group has a much greater electronegativity than the halides, and the signal should therefore be below $\tau = 4$. This high value is probably due to the hydrogen lying in the shielding cone of the cyanide, and the result is a balance between the two effects.



The $1,4^-$ and $1,3^-$ spin-spin coupling constants of protons in the 1-cyanoallenes are 3-3.5 c/sec. and 6 c/sec. respectively, the $1,4^-$ coupling constants being considerably higher than the 2-2.4 c/sec. of the corresponding 1-bromoallene. 4,6-spin-spin coupling was not observed with the resolution of the 60 M. C instrument. This is in contrast to the 1-bromoallenes which gave 4,6-coupling constants of o.5 c/sec. It

is interesting also to note that the methyl protons in the t-butyl group (τ = 8.75-8.8) were deshielded relative to the methyl protons in the t-butyl group of 1-bromoallenes (τ = 9.15-9.2).

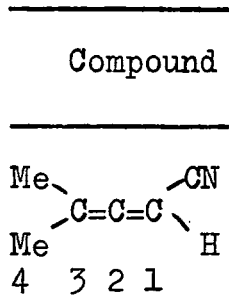
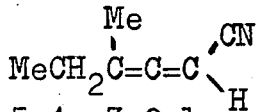
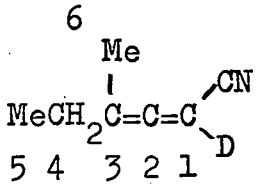
The n.m.r. spectrum of a mixture of 1-cyanopropa-1,2-diene and 3-cyanoprop-1-yne showed the ratio of the compounds to be 7:3. A low field triplet τ = 4.3 was obviously the C_1 allenic proton coupled with the two C_3 allenic protons J = 6 c/sec. The other two C_3 allenic protons showed at τ = 5.4 and are split into a doublet by the C_1 proton.

1-Cyanobuta-1,2-diene has a similar spectrum to the other 1-substituted buta-1,2-dienes; it is an ABX_3 system showing a multiplet at τ = 5.0 ($=C\langle^{CH_3}_{\underline{H}}$) two quartets, a multiplet at τ = 4.37 ($=C\langle^{CN}_{\underline{H}}$), two quartets and a pair of doublets τ = 8.17, 8.30 ($=C-\underline{C}H_3$). The coupling constants are $J_{4,1}$ = 3 c/sec.; $J_{4,3}$ = 7.5 c/sec.; $J_{1,3}$ = 6 c/sec.

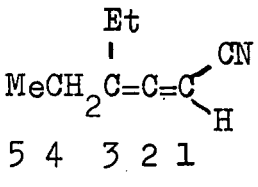
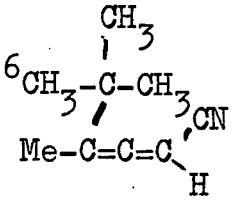
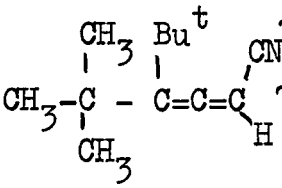
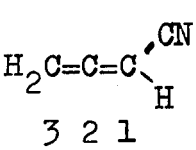
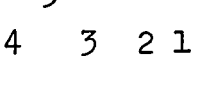
Pasternak and Pfeiffer [86] claimed to have prepared 1-cyano-3-methylbuta-1,2-diene, 1-cyano-3-methylpenta-1,2-diene and 1-cyano-propa-1,2-diene. These authors reacted 3-bromoacetylenes with hydrogen cyanide in the presence of cuprous bromide and obtained 1-cyanoallenes. Yields were not stated and they described the mechanisms as being complex and varied. They isolated a dimer of 1-cyano-3-methylbuta-

Table XIV.

N.m.r. of 1-Cyanoallenes.

Compound	Value	spin-spin constant in c/sec.
	τ_4 = 8.2 (doublet)	$J_{4,1}$ 3
	τ_1 = 5.1 (heptet)	$J_{1,4}$ 3
	τ_5 = 8.92 (triplet)	$J_{5,4}$ 7
	τ_6 = 8.18 (doublet)	$J_{6,1}$ 3
	τ_4 = 7.88 (quartet of doublets)	$J_{4,5}$ 7
		$J_{4,1}$ 3
	τ_1 = 4.9 (sextet)	$J_{1,4}$ 3
		$J_{1,6}$ 3
	τ_5 = 8.93 (triplet)	$J_{5,4}$ 7
	τ_6 = 8.15 (singlet)	
	τ_4 = 7.92 (quartet)	$J_{4,5}$ 7

cont'd...

	τ_5 = 8.9	(triplet)	$J_{5,4}$	7
	τ_4 = 7.9	(quartet of doublets)	$J_{4,5}$	7
			$J_{4,1}$	3.5
	τ_1 = 4.75	(pentet)	$J_{1,4}$	3.5
	τ_6 = 8.8	(singlet)		
	τ_4 = 8.25	(doublet)	$J_{4,1}$	3
	τ_1 = 4.83	(quartet)	$J_{1,4}$	3
	τ_5 = 8.75	(singlet)		
	τ_1 = 4.83	(singlet)		
	τ_3 = 5.4	(doublet)	$J_{3,1}$	6
	τ_1 = 4.3	(triplet)	$J_{1,3}$	6
	τ_4 = 8.23	(pair of doublets)	$J_{4,1}$	3
			$J_{4,3}$	7.5
	τ_3 = 5.0	(two quartets)	$J_{3,4}$	7.5
			$J_{3,1}$	6
	τ_1 = 4.37	(two quartets)	$J_{1,3}$	6
			$J_{1,4}$	3

1,2-diene which was claimed to be 1,2-di-(cyanomethylene)-3,3,4,4-tetramethylcyclobutane, but the present work shows this to be erroneous.

Preparation of 1-Cyanoacetylenes.

A literature survey [82a] shows that few methods for the preparation of 1-cyanoacetylenes are available at the present time. It was therefore decided to try to extend the methods used for the preparation of 1-cyanoallenes to the preparation of cyanoacetylenes. 1-Bromoacetylenes may conveniently be prepared by the action of sodium hypobromite on the alkyne, or by decomposing the acetylenic Grignard compound with bromine.

$$R - C \equiv CH \xrightarrow[\text{(b) Grignard + } Br_2]{\text{(a) NaOBr}} RC \equiv C - Br$$

The bromoacetylene was then heated with cuprous cyanide in dimethylformamide and worked up in the same manner as for the 1-cyanoallenes.

β-Bromophenylacetylene was converted to β-cyanophenylacetylene in 70% yield; a higher boiling fraction which later solidified was shown to be 1,4-diphenylbuta-1,3-diyne by analysis and ultra-violet spectrum.

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u.v. of product of		u.v. of 1,4-diphenylbuta-1,3-diyne	
λ max	ε	λ max	ε
204 m μ	42,830		
218 m μ	32,320		
228 m μ	28,700	227 m μ	30,200
248 m μ	27,480	248 m μ	29,510
260 m μ	27,070	260 m μ	29,510
288 m μ	21,010	287 m μ	22,390
297 m μ	17,170	296 m μ	19,050
306 m μ	31,520	306 m μ	33,880
317 m μ	13,330	316 m μ	14,450
327 m μ	29,490	327 m μ	31,620

Thus it can be seen that a coupling reaction has taken place.

$$C \equiv C - Br \xrightarrow[\text{D.F.M.}]{CuCN} - C \equiv C - C \equiv C + C \equiv CCN$$

Use of nitrogen or other inert gas would probably prevent this coupling as it is almost certainly due to an oxidative mechanism requiring oxygen.[82b]

After the present work had been completed a preliminary report by the Russian worker Sladkov and Ukhim[85] described

B-bromophenylacetylene, obtained by the action of bromine on the cuprous salt of phenylacetylene.

$$PhC \equiv C - Cu + Br \longrightarrow PhC \equiv CBr$$

They reacted this with cuprous cyanide in dimethylformamide and obtained β-cyanophenylacetylene, however no details were given.

$$PhC \equiv C - Br \xrightarrow{CuCN,\ D.M.F.} PhC \equiv CCN$$

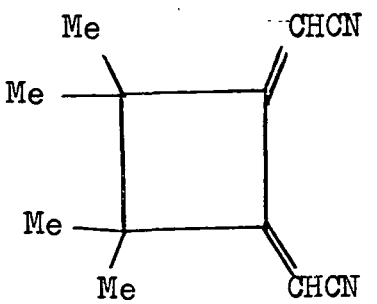
This reaction is of interest since during the present work similar conditions were used.

DIMERS OF ALLENIC CYANIDES.

It was found during the course of the present work on allenic cyanides, that 1-cyano-3-methylbuta-1,2-diene deposited crystals after standing for 3-4 weeks. These crystals showed the following physical constants: ν_{max} 2252 and 2235 (-CN); 1680 and 1650 (C=C); λ_{max} 281 mμ (ε, 11,420) and melting point 81°.

In 1964 a preliminary communication by Pasternak and Pfeiffer [86] reported the isolation of a dimer of 1-cyano-3-methylbuta-1,2-diene.

They claimed that by analogy to compounds prepared by Bertrand, their compound was 1,2-di-(cyanomethylene)-3,3,4,4-tetramethylcyclobutane.



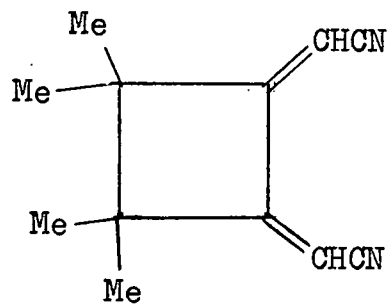
Pasternak and Pfeiffer claimed that the spectral data obtained for this compound supported the above structure; ultra-violet

absorption λ_{max} 285 m μ (no extinction coefficient given); infra-red absorption, doublets at ν_{max} 2230 (-CN) and 1650 cm^{-1} (C=C), and n.m.r. absorption at 5.0 p.p.m. (ethylenic) and 3.35 p.p.m. (non-ethylenic), the melting point was given as 73.5°. We thus concluded that our compound was the same as the one obtained by the French workers [86]; the difference in melting points could be due to impurities in their compound. (The elemental analysis for our compound fitted the theoretical value more closely than the one obtained by the French workers.)

The n.m.r. spectrum showed six peaks, four of which at τ = 8.7, 8.6, 8.02 and 7.75 were clearly three proton signals (as shown by the integram), and corresponded to four magnetically different methyl groups; the other two peaks at τ= 6.6 and 5.04 were single proton signals. This spectrum is not of the pattern expected for a compound whose structure is as proposed by the French workers.

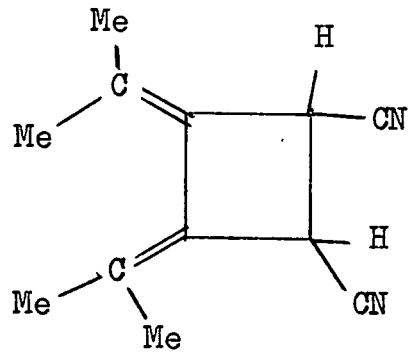
All the possible dimer structures are discussed here, rearrangements of initially formed dimers to other structures might occur but such structures will be ignored as they would not possess the extensive conjugated systems which

would give absorption at λ_{max} 281 mμ in the U.V. The following structure would more or less fit the infra-red and ultra-violet spectral data, but can be eliminated on the basis of n.m.r. spectral data.



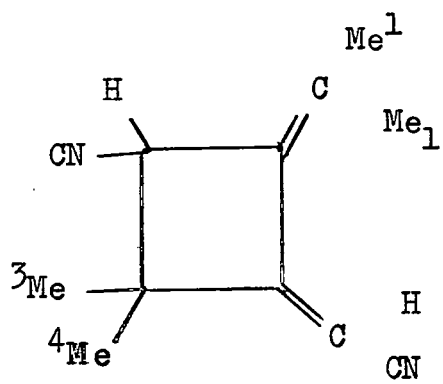
(I)

There are three possible stereoisomers, depending on the orientation of the cyano-methylene groups, i.e. cis-cis, trans-trans or cis-trans. In the cis-cis and trans-trans forms all the methyl groups are magnetically equivalent hence would give one signal in the n.m.r., not four; these forms can be ruled out. The cis-trans form should give signals for two non-equivalent methyl groups but not four, and should also give two signals for ethylenic protons. This stereoisomer cannot therefore be the correct formulation.



(II)

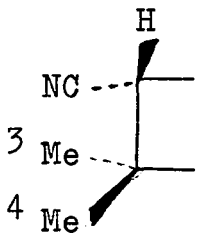
This isomer should give one C ≡ N stretching band in the infra-red absorption spectra and an absorption maximum in the ultra-violet spectrum at λ_{max} 240 mμ. Both the cis and trans forms of (II) would give rise to only two magnetically different methyl groups, and only one single proton signal. Hence this type of structure can also be ruled out.



(III)

On initial examination of this structure it appears that there are only two different kinds of methyl group, however closer examination shows that all four methyl groups are magnetically non-equivalent. Methyl group ^{2}Me will be different surroundings to ^{1}Me due to proximity of a hydrogen or cyano group. Either ^{3}Me or ^{4}Me will be cis to the ring cyano group whilst the other one is trans.

i.e.



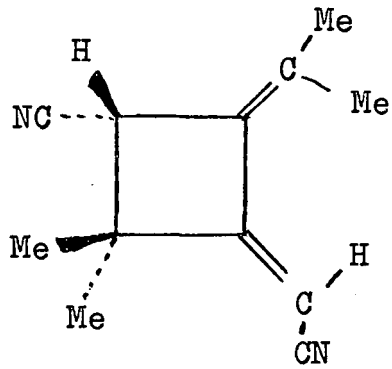
^{3}Me is cis to cyano group.

^{4}Me is trans to cyano group.

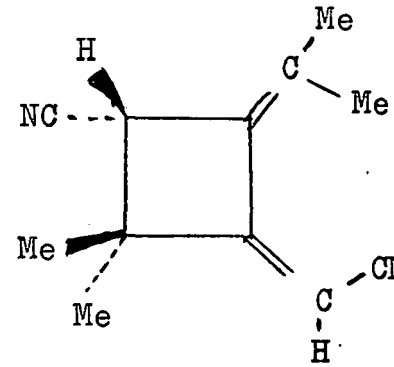
Thus the methyl groups ^{3}Me and ^{4}Me lie in different parts of the cyanide deshielding zone (see later).

In structure (III) there are two magnetically different single protons, i.e. a ring proton of higher field and an ethylenic proton of lower field.

So far this type of structure agrees well with the known data; however, two sterioisomeric forms, III A and III B are possible.



(III A)

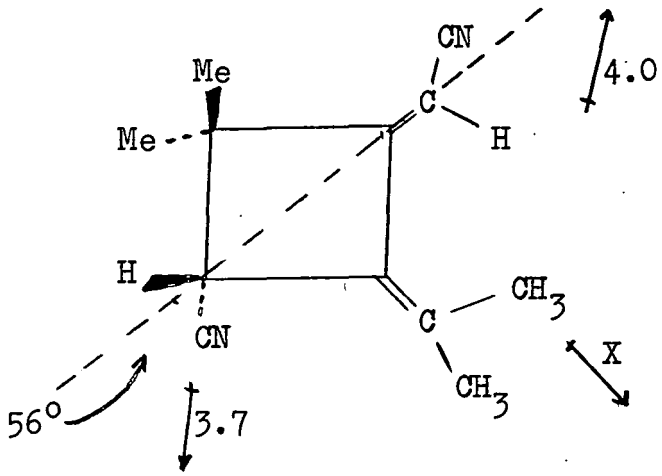


(III B)

The dipole moment of the dimer was determined experimentally and found to be 3.2D [87]. A calculation of dipole moments expected for structures III A and III B was carried out on the following basis:- literature values for the group moments of cyanide are rather perplexing, aliphatic cyanide is given as 4.0D (vapour) or 3.7D (solution); $CH_3CH = CHCN$ is given as 4.5D (vapour) and $CH_2= CH - CH = CHCN$ is given as 3.9D (vapour). It is not stated whether or not these cyano compounds are pure cis or pure trans or mixtures of cis and trans, quite apart from possible contributions of S-cis and S-trans conformations. It was decided to use a value of 4.0D for the group moment of =CHCN and 3.7D for CHCN. No figures were available for the group moment of the isopropylidene group in conjugation

with a nitrile - and this moment was designated as X. Its approximate magnitude may be deduced from the following considerations which also permit differentiation between sterioisomers III A and III B. As this is an induced dipole it must be in the same sense as the cyanide dipole.

Thus for III A



The expected dipole moment μ is given by

$$\mu^2 = (4\cos 60 - 3.7\cos 56)^2 + (4.0\sin 60 + X)^2 + (3.7\sin 56)^2 = 3.2^2$$

$$0 \qquad + (3.46 + X)^2 \quad + \quad 9.4 \quad = 10.24$$

$$(3.46 + X)^2 = 10.24 - 9.4$$

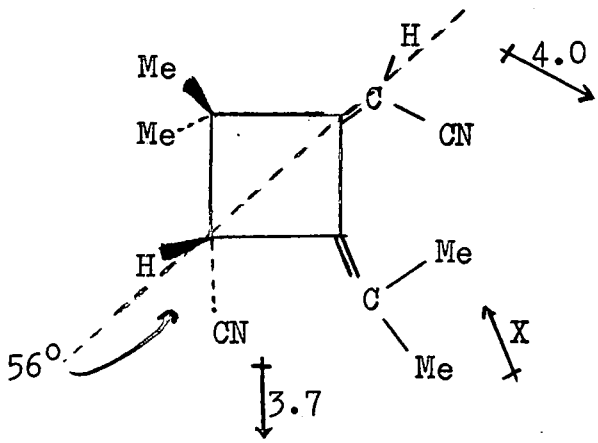
$$(3.46 + X)^2 = .84$$

$$3.46 + X = \pm .86$$

$$X = -2.60$$

$$\text{or} \quad X = -4.32$$

for isomer III B



$$\mu^2 = (4 \cos 60 - 3.7 \cos 56)^2 + (4.0 \sin 60 - x)^2 + (3.7 \sin 56)^2 = 3.2^2$$

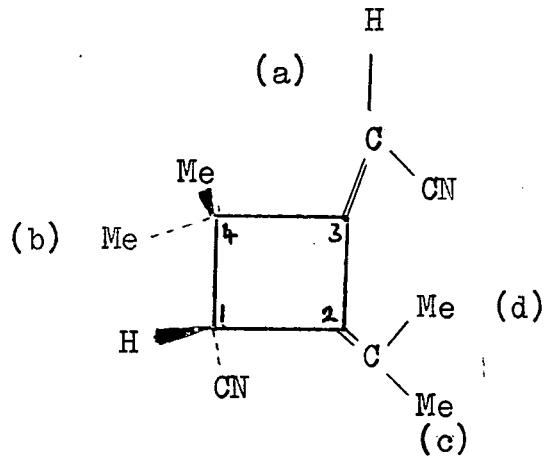
$$+ (3.46 - x)^2 + 9.4 = 10.24$$

$$3.46 - x = \pm .86$$

$$x = + 2.6$$

$$\text{or} \quad x = + 4.32$$

As already stated the direction of the isopropylidene moment must be in the same sense as that of the cyanide, it follows therefore that structure III B is correct and the dimer is

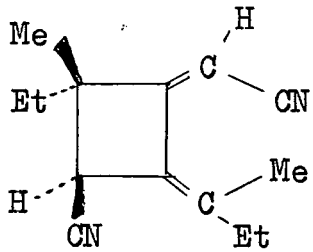


An interpretation of the n.m.r. spectrum satisfactorily accounts for structure III B (but not III A). The signal at τ = 8.7 is due to Me protons (a) which are trans to the cyanide group on C_3, the signal slightly downfield from this at τ = 8.6 is due to Me protons and cis to the cyanide group on C_3 and lies in the deshielding zone of this cyanide. The signal at τ = 8.02 is due to Me protons (c) and is in the normal position for a methyl group on a conjugated system, the other "ethylenic" methyl, Me (d) is directly in the deshielding cone of the cyanomethylene cyanide group and it is found downfield at τ = 7.75.

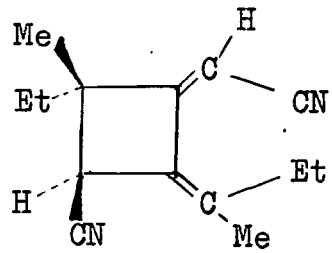
The proton at τ = 6.6 is the ring-proton on C_1 and is somewhat deshielded due to the proximity of the cyano group also on C_1, the low field proton at τ = 5.04 is due to the cyanomethylene proton, which is deshielded by the double bond and by the cyanomethylene cyano group.

Structure III B also explains the infra-red spectra and the following assignments may be made. The doublet in the region of 2240 cm^{-1} is due to absorption by the saturated ring cyanide on C_3 at 2252 cm^{-1} and the unsaturated cyanide of cyanomethylene at 2235 cm^{-1}. Similarly the doublet in the double bond region is due to the isopropylidene double bond at 1680 cm^{-1} and the cyanomethylene double bond at 1650 cm^{-1}.

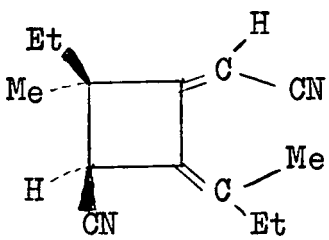
The corresponding dimer of 1-cyano-3-methylpenta-1,2-diene shows similar infra-red and ultra-violet absorption i.e. ν_{max} 2245 s (cyanide); 2220s (conjugated cyanide); 1665s (isobutylidene double bond); 1630s cm^{-1}. (cyanomethylene double bond); λ_{max} 283 M μ (ε, 18,300) and is considered to be 2-(2-butylidene)-1-cyano-3-cyano-methylene-4-ethyl-4-methylcyclobutane. However since the alkyl groups are different and racemic cyanoallene was used a mixture of sterioisomers must be present, i.e. IV a, b, c and d.



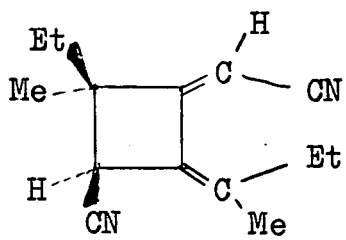
(a)



(b)



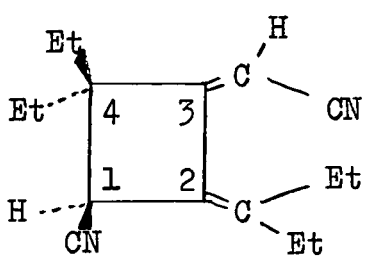
(c)



(d)

IV

The dimer of 1-cyano-3-ethylpenta-1,2-diene may be considered to have the structure 1-cyano-3-cyanomethylene - 4,4-diethyl-2-(3-pentylidene)-cyclobutane (V) since it has similar infra-red and ultra-violet spectra to the previous dimers (III B) and (IV).

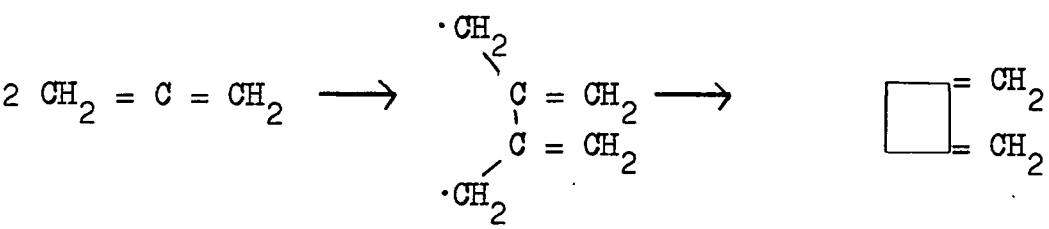


(V)

i.e. ν_{max} 2240s (cyanide); 2215s (cyanomethylene cyanide); 1650s (isopentylidene double bond); 1625s cm^{-1}. (cyanomethylene double bond); λ_{max} 283 mμ (ε, 17,000). The n.m.r. spectrum is reasonably consistant with the above structure and shows τ = 8.7-9.3 a multiplet from protons of four methyl groups split into triplets, τ = 7.2-8.55 a multiplet from protons of four methyl groups split into quartets, an unexplained doublet τ = 6.65 from the proton on ring carbon C_1, and two unexplained peaks making one proton τ = 5.14 and τ = 4.75 assigned to the cyanomethylene proton.

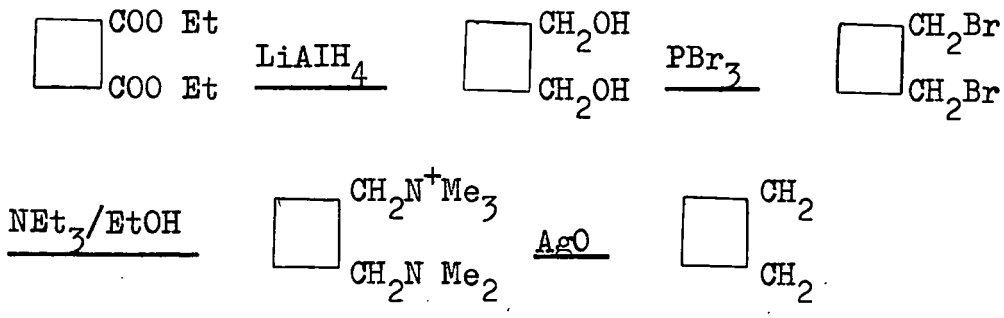
The structure of this compound is based mainly on analogy to the original structure (III B), the n.m.r. pattern being too complex for definite assignments.

In 1913 Lebedev [88, 89] prepared the first cyclobutane by dimerisation of an allene and started a controversy which lasted for over 50 years as many workers in this field were not convinced that the structure of his product was a cyclobutane. From allene Lebedev isolated what he considered to be 1,2-dimethylenecyclobutane (as expected from a diradical mechanism).



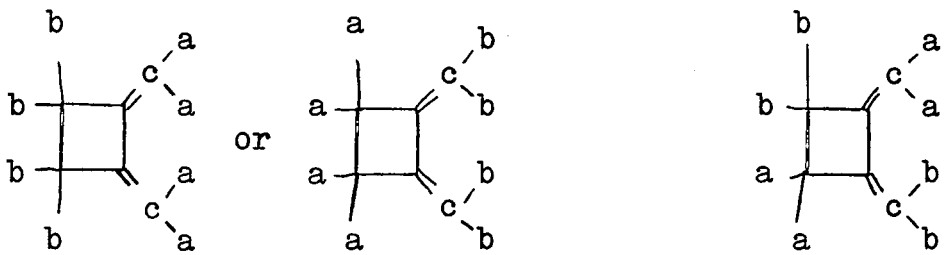
Although the oxidative and reductive methods which he used to prove this structure were not absolutely conclusive, later work has completely validated his results.

E. Vogel [90] in 1955 still contested the cyclobutane structure but in 1956 Blomquist [91] synthesised 1,2-dimethylenecyclobutane by an unambiguous route, thus ending the controversy:



Dimerisation of 1,1-dimethylallene gave at least two of three possible head to head isomers

Head to head is defined as head to tail is defined as

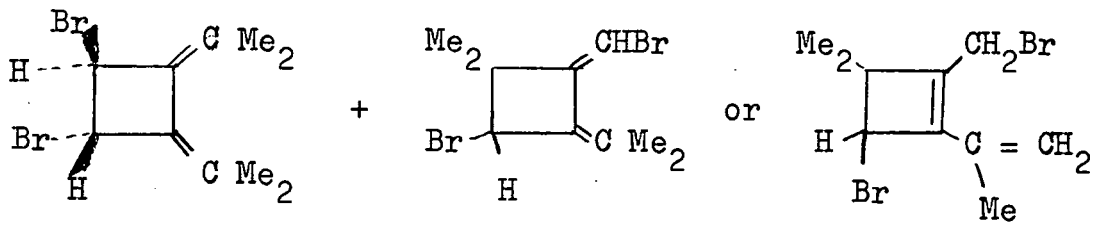


(see Fig. I), but it is possible that smaller amounts of the third dimer was present.

Williams and Sharkey [92] working with allene in the vapour phase obtained an 85:15 ratio of the 1,2- and 1,3-dimethylenecyclobutanes, which indicates that at higher temperatures the dimerisation is less stereo-selective.

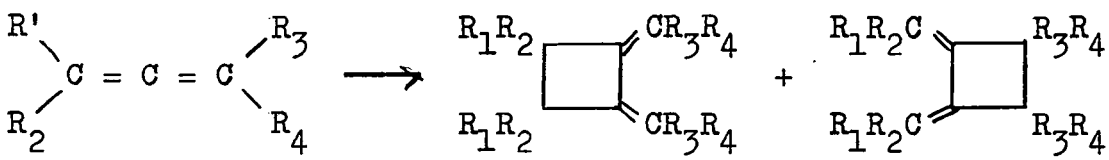
Jacobs and Petty [93] showed that the major dimer from 1-bromo-3,3-dimethylallene was the di-isopropylidene form

in which the ring bromines were trans to each other (ozonolysis gave (±)-dibromosuccinic acid) and that a second dimer had two possible structures



however McClennon [94] has since shown that both of these alternatives are present.

It has been noted that the major products of dimerisation of allenes are head to head products (see Fig. I),



the only exception being the dimer from 1,2-difluoroallene, which gives the head to tail isomer as the major product. This structure has been clearly shown by infra-red and nuclear magnetic resonance spectroscopy.

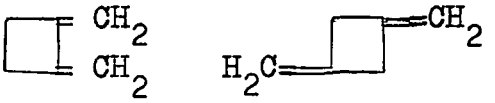
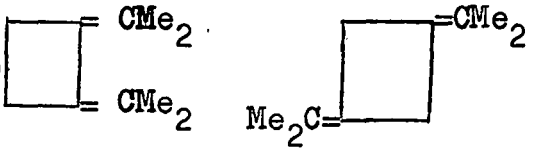
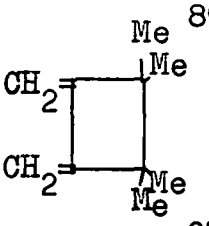
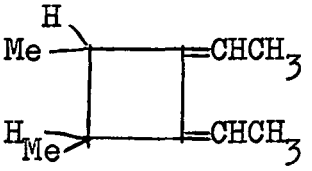
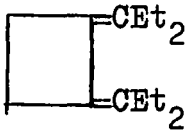
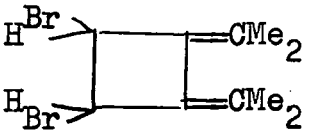
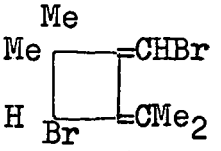
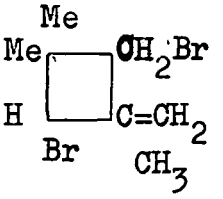
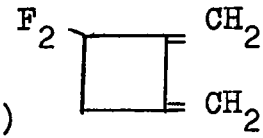
ALLENE	TYPES OF DIMER FORMED	REF.
$CH_2=C=CH_2$	(a) 	89-92.
$Me_2C=C=CH_2$	(a)  	97,98.
$MeCH=C=CHMe$	(a) 	89.
$Et_2C=C=CH_2$	(a) 	99.
$Me_2C=C=CHBr$	(a)   	93.

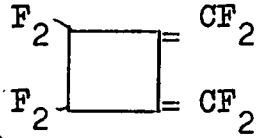
Fig. 1

$F_2C{=}C{=}CH_2$



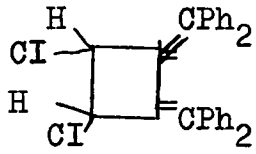
(b) 100.

$F_2C{=}C{=}CF_2$



(a) 101.

$Ph_2C{=}C{=}CHCl$



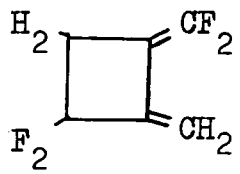
(a) 102-105.

(a) defined as head to head

(b) defined as head to tail

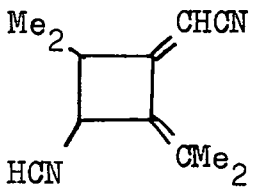
Fig. 1

$F_2C = C = CH_2 \longrightarrow$

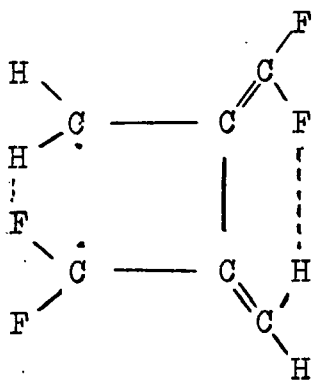


The present work has shown that 1-cyano-3,3-dimethylallene also gives the head to tail dimer as the major product.

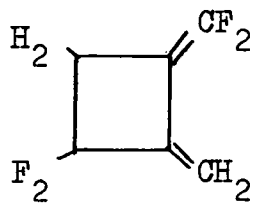
$Me_2C = C = CHCN \longrightarrow$

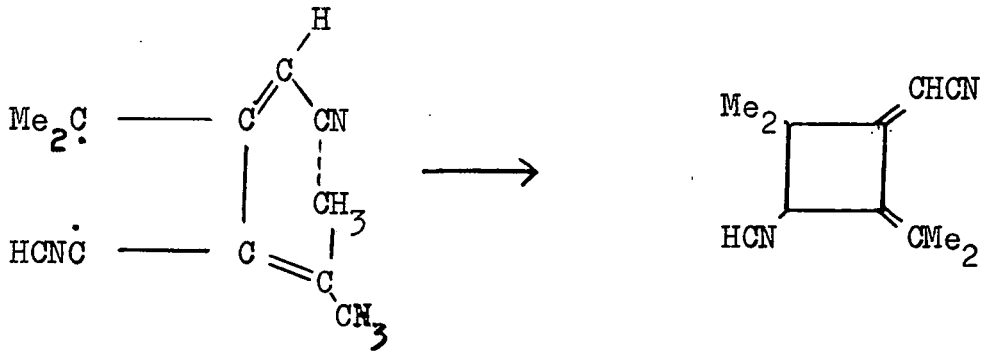


As yet there has been no explanation of this anomaly, but it is possible that if the diradical is formed and has a fairly long lifetime then a weak bonding or attraction between the hydrogen and fluorine atoms (or the hydrogen and the cyano group) would tend to stabilise the conformation in the head to tail form.

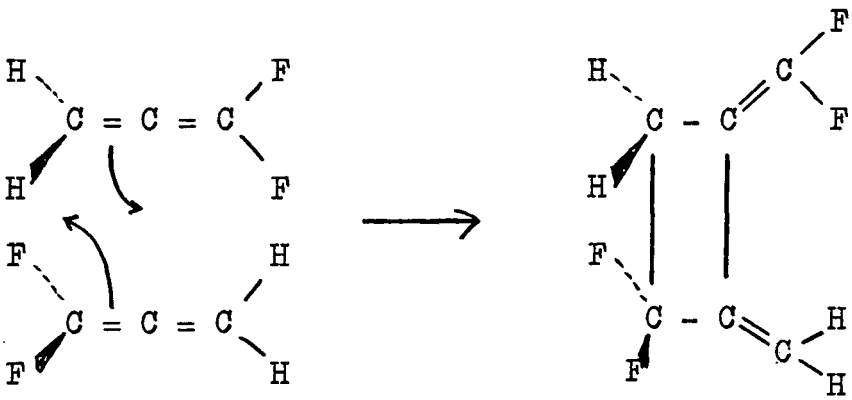


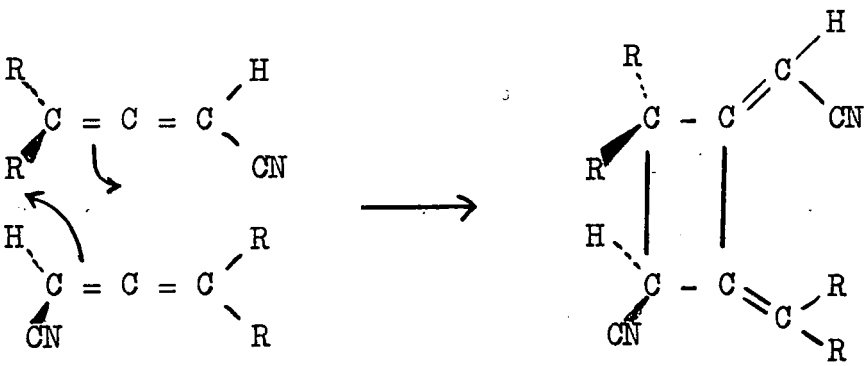
$\longrightarrow$





However since this free radical mechanism is most favourable with ~~low polar~~ structures of low polarity an ionic mechanism is more likely with such strongly polarised molecules



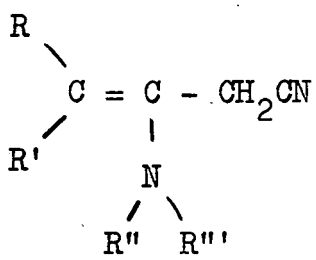


ENAMINES FROM ALLENES.

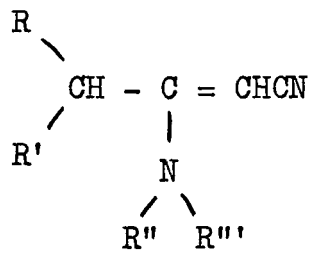
In the present work a number of 1-cyanoallenes were reacted with different amines. The reaction was carried out by adding amines to the stirred 1-cyanoallene and moderating the reaction by cooling in a water-bath to keep the temperature below about 60° (some of the ensuing reactions were highly exothermic). If the reaction was not moderated the same products resulted but were much darker in colour and contained high molecular weight impurities. The same products in the same ratios were obtained if the reaction was carried out under reflux in etherial solution.

The reaction with ammonia was best carried out by heating the 1-cyano-3-ethylpenta-1,2-diene to about 60° and passing dry ammonia gas continuously (ammonia was obtained from a reservoir of slowly evaporating anhydrous liquid ammonia). With lower members of the cyano-allenes, e.g. 1-cyano-3-methylbuta-1,2-diene dimerisation of the allene competed with the reaction with ammonia. At room temperature the addition of ammonia was very slow (1-2% after 6 hr.) The addition of amines to 1-cyanoallenes gave two products which could easily be separated by fractionation, these

resulted from the addition of nitrogen to C_2 and protonation at either C_1 (type A) or C_3 (type B), the product of type B being invariably the higher boiling compound. (See Table XIV)



Type A.

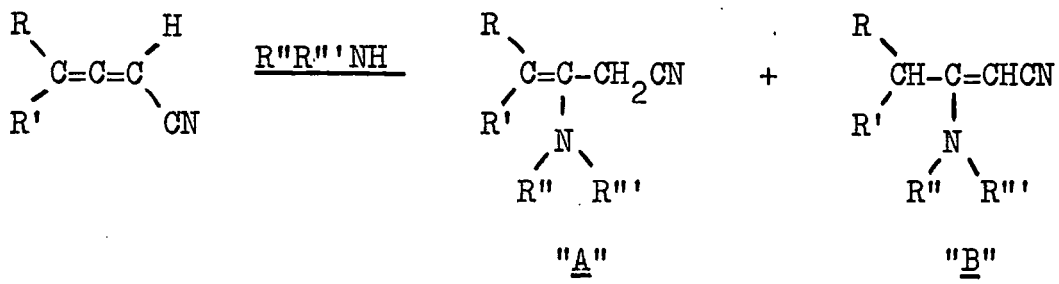


Type B.

Both types of enamines are stable under the reaction conditions used and do not isomerise (as shown by separate experiments); they are therefore probably formed by different mechanistic pathways.

Table XIV.

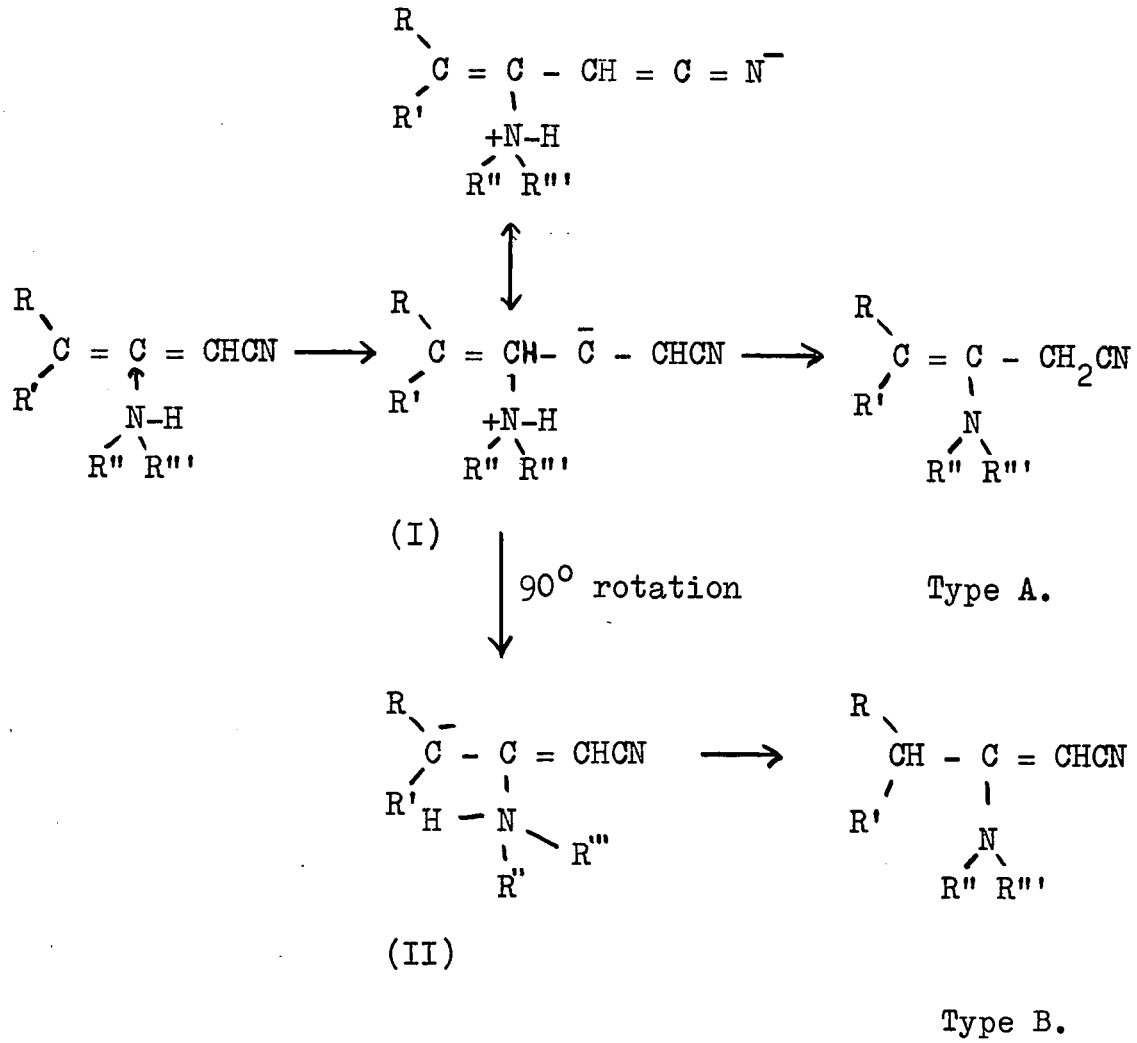
COMPARATIVE YIELDS OF ENAMINES ISOMERS FROM CYANOALLENES.



Cyanide R	Cyanide R'	Amine R"	Amine R"	Yield Type A	Yield Type B
H	Pr^i	Et	Et	-	90%
Me	Me	Et	Et	74%	-
Me	Me	$(CH_2)_5$	NH	8%	78%
Me	Et	Bu^n	H	-	80%
Me	Et	Et	Et	72%	17%
Me	Et	$(CH_2)_5$	NH	-	75%
Me	Et	$(CH_2)_5$	NH	8%	81%
Et	Et	H	H	-	60%
Et	Et	Et	Et	70%	*
Et	Et	$(CH_2)_5$	NH	*	66%
Et	Et	iso C_9H_{10}	NH	a	b
Et	Et	C_9H_{10}	NH	0%	0%
Me	Bu^t	Et	Et	-	43%
Me	Bu^t	$(CH_2)_4$	NH	-	83%
Me	Bu^t	$(CH_2)_5$	NH	58%	23%
Pr^i	Pr^i	Et	Et	16%	54%

* not isolated pure.

a, b yields not accurate.



Addition of the nitrogen to C_2 initially gives an anion best represented as (I); the charge is delocalised through molecular orbitals embracing C_1, C_2 and the cyano nitrogen atom, but there will be no delocalisation to C_3 since the C_2-C_3 π-orbital is at right angles to this delocalised orbital.

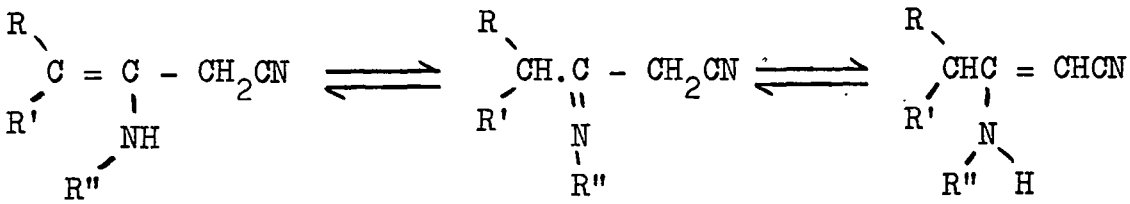
Thus only after a 90° rotation about the C_1-C_2 bond can delocalisation occur to give carbanion II.

It seems probable that an intra-molecular proton transfer from the nitrogen to the either C_1 or C_3 then takes place to form enamine type A or B respectively. The different ratios of types A and B in the product are explained in the following manner:- After the initial opening of the α-β bond to give the carbanion I the quaternary nitrogen is in a state of sp^3 hybridisation and rotation about the C_2-N bond can occur, if this rotation is fast the hydrogen will be conformationally favourably placed for transfer to the negatively charged C_1 thus giving a type A enamine. However if the rotation about the C_2-N bond is slow then the proton transfer will be slow since only when the hydrogen is opposite to the electron pair of the C_1 sp^3 orbital will transfer occur. This allows rotation round the C_1-C_2 bond and after a 90° rotation maximum overlap of π-orbitals gives a distribution of negative charge, part of which will reside on C_3. Internal proton transfer to C_3 then gives the thermodynamically ~~more~~ stable type B compound.

The factors which affect the rotation about the C_2-N bond are (a) The inertia of the group about its axis of

rotation i.e. smaller more symmetrical groups will rotate quickly - this explains the preponderance of type A enamines with diethylamine; unsymmetrical, larger groups have a higher moment of inertia and hence rotate more slowly thus giving more time for the other (C_1-C_2) bond to rotate, thus tending to give a mixture of types A and B. (b) Stearic interaction between R' and R" and R"' would tend to hinder rotation thus again a mixture results.

These observations are apparently contradicted by the results obtained when either R" or R"' or both are hydrogen i.e. in the case of the amines being n-butylamine and ammonia, when fast rotation would be expected to lead to formation of type A enamine, in fact type B is formed exclusively. This is best explained by prototropic rearrangement to the imine which allows the more thermodynamically more stable type B to form from the type A enamine.

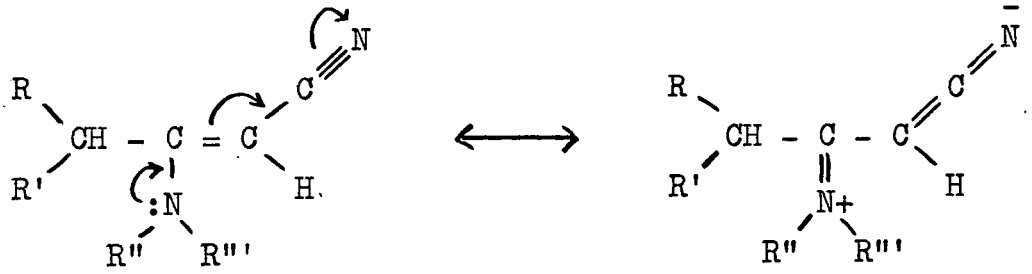


Type A Type B.

The imine structure has actually been detected by nuclear magnetic resonance in the case of 2-amino-1-cyano-3-ethylpent-1-ene (see later).

The two cases of 2-amino-1-cyano-3-ethylpent-1-ene, and 2-(n-butylamino)-1-cyano-3-methylpent-1-ene clearly show that extended conjugation stabilises the amino forms relative to the imino form of these type B enamines, since very little of the imino form is detected in the former (1 part in 8) and none in the latter at all. This is clearly shown by infra-red, ultra-violet and n.m.r. spectra. This is paralleled by the stabilisation of enols by conjugation (e.g. acetyl-acetone or ethylacetoacetate).

The high wavelength absorption of type B enamines in the ultra-violet region (260-284m) is due to the presence of an extended conjugated system due to resonance forms of the type

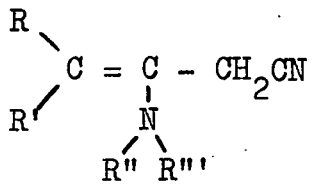


since α-β unsaturated cyanides would be expected to absorb about 215-17 mμ [84].

The two different types of enamine can be readily distinguished by means of their infra-red and ultra-violet spectra (Table XV and Table XVI). Type A enamines show an absorption at 2250-2290 cm^{-1} (unconjugated cyanide) and a weak absorption at 1625-1675 cm^{-1} (unconjugated double bond), they have a weak ultra-violet absorption at 203-7 mμ (ε, 5,000), and in some cases a weaker secondary absorption at 233-46 mμ (ε, 2,000). In contrast the type B enamines show an exceptionally intense infra-red absorption at 2200-2210 cm^{-1} (conjugated cyanide) and another exceptionally intense band at 1560-1595 cm^{-1} (double bond conjugated to cyanide); their ultra-violet spectra show a strong absorption in the 261 mμ region (secondary nitrogen) or 273-84 mμ region (tertiory nitrogen).

Table XV.

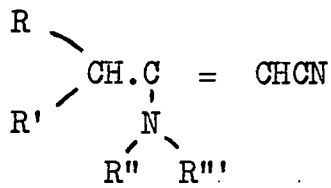
INFRA-RED AND ULTRA VIOLET SPECTRA OF TYPE A ENAMINES.



Cyanide		Amine		ν max cm^{-1}	λmax	ε	λmax	ε
R	R'	R"	R"'					
Me	Me	Et	Et	2280, 1675, 740	203	4,820	235	1,160
Me	Me	$(CH_2)_5NH$		2250, 1660, 740	203	5,235	236	3,140
Me	Et	Et	Et	2250, 1650, 735	204	5,040		
Me	Et	$(CH_2)_5NH$		2260, 1675, 740	205	4,000	233	2,300
Et	Et	Et	Et	2250, 1650, 730	204	6,640		
Et	Et	iso $C_9H_{10}NH$		2290, 1650, 750	207	14,530		
Me	Bu^t	$(CH_2)_5NH$		2270, 1625, 760	203	5,130	246	2,880
Pr^i	Pr^i	Et	Et	2280, 1645, 775	203	6,860		

Table XVI.

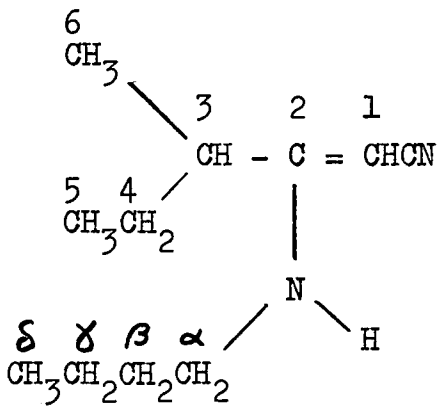
INFRA-RED AND ULTRA-VIOLET SPECTRA OF TYPE B ENAMINES.



Cyanide		Amine		ν max	cm^{-1}	λ max	ε
R	R'	R"	R"'				
H	Pr^i	Et	Et	2210s, 1580vs,	1097	720	273	24,300
Me	Me	$(CH_2)_5NH$		2205s, 1580vs,	860	750	276	19,750
Me	Et	Bu^n	H	2205s, 1595vs,		737	261	19,500
Me	Et	Et	Et	2197 , 1570		730	276	19,700
Me	Et	$(CH_2)_4NH$		2210 , 1575		720	274	22,500
Me	Et	$(CH_2)_5NH$		2210 , 1580			277	18,700
Et	Et	H	H	2200 , 1585		760	261	18,300
Et	Et	$(CH_2)_5NH$		2210 , 1575		740	276	23,700
Et	Et	$isoC_9H_{10}NH$		2210 , 1580		750	274	16,000
Me	Bu^t	Et	Et	2210 , 1580		750	282	18,260
Me	Bu^t	$(CH_2)_4NH$		2200 , 1570		720	279	21,000
Me	Bu^t	$(CH_2)_5NH$		2210 , 1580			284	16,000
Pr^i	Pr^i	Et	Et	2200 , 1560		725	277	22,500

Nuclear Magnetic Resonance Spectra of Enamines.

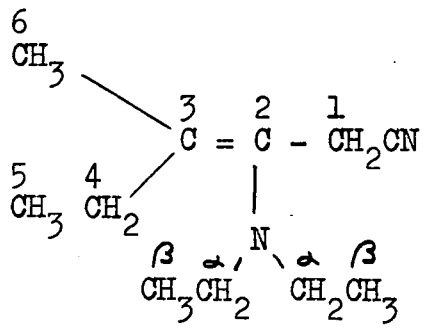
1. 2-(n-Butylamino)-1-cyano-3-methylpent-1-ene.



n.m.r. 21.

The methyl groups $^{5}CH_3$ and $^{4}CH_3$ show up as overlapping triplets $\tau = 9.1$, $J_{CH_3CH_2} = 6$ c.p.s., methyl group $^{6}CH_3$ shows as a doublet at $\tau = 8.85$, $J_{CH_3,H} = 8$ c.p.s. An overlapping quartet and triplet $\tau = 8.3 - 8.75$ are the β and γ methylenes of the n-butylamino, a pentet at $\tau = 6.9 - 7.4$ consists of the α-methylenes of the butylamino and the methine. A singlet at $\tau = 6.26$ is due to the ethylenic hydrogen shielded by cyanide, and a broad peak $\tau = 5.2 - 5.6$ is the proton on nitrogen, probably coupled to the α-methylene of the n-butylamino group.

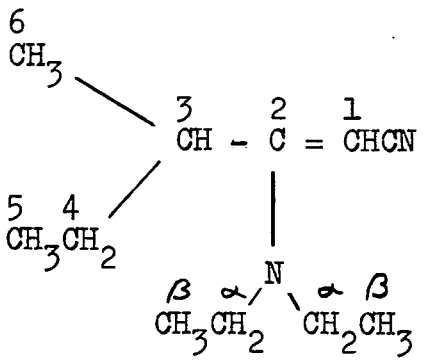
2. <u>1-Cyano-2-(diethylamino)-3-methylpent-2-ene.</u>



n.m.r. 22.

Two triplets at τ = 8.8 - 9.2 indicate $^{5}CH_3$ and $^{\beta}CH_3$, $^{J}CH_3$, CH_2 = 7 c.p.s., a singlet or possibly a very closely split triplet at τ = 8.2 is given by $^{6}CH_3$, a very small coupling across the double bond to $^{4}CH_2$ could account for the triplet $J < 0.5$ c.p.s. A quartet centred on τ = 7.75 is $^{4}CH_2$ split by $^{5}CH_3$, $J_{4,5}$ = 7 c.p.s., a quartet of doublets τ = 7.37 is due to the methylene groups of the diethylamine, where it is proposed that a partial double bond character of the ^{2}C - N bond is enough to hold the methylene groups next to the nitrogen, in different surroundings, and lead to their non-equivalence. A singlet at τ = 7.04 is $^{1}CH_2CN$.

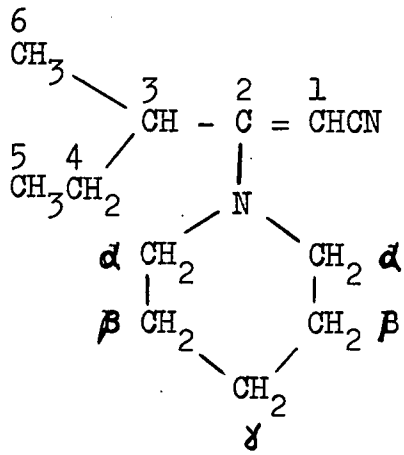
3. <u>1-Cyano-2-(diethylamino)-3-methylpent-1-ene.</u>



n.m.r. 23

Showed a triplet centred on $\tau = 8.95$, $^{5}CH_3$ split by $^{4}CH_2$ $J_{5,4} = 7$ c.p.s.; a triplet centred on $\tau = 8.86$, $^{\beta}CH_3$ split by $^{\alpha}CH_2$ $J_{\beta,\alpha} = 7$ c.p.s. A doublet $\tau = 8.64$ due to $^{6}CH_3$ split by the methine $J_{6,3} = 8$ c.p.s. and a doublet of quartets $\tau = 8.2$ due to the $^{4}CH_2$ split by $^{5}CH_3$ $J_{4,5} = 7$ c.p.s. further split by the methine $J_{4,3} = 8$ c.p.s.; a sextet of doublets centred on $\tau = 7.3$ due to splitting of the methine by the $^{6}CH_3$ and $^{4}CH_2$ $J_{3,6} = 8$ c.p.s. $J_{3,4} = 8$ c.p.s. further split by long range coupling to ^{1}CH $J_{3,1} = 2.5$ c.p.s.; a quartet centred on $\tau = 6.75$ due to the methylenes of the ethylamino group split by the $^{\beta}CH_3$, $J_{\alpha,\beta} = 7$ c.p.s., and finally a doublet $\tau = 6.23$ due to $^{1}CHCN$ split by long range coupling to ^{3}CH $J_{1,3} = 2.5$ c.p.s.

4. <u>1-Cyano-3-methyl-2-piperidino-pent-1-ene.</u>

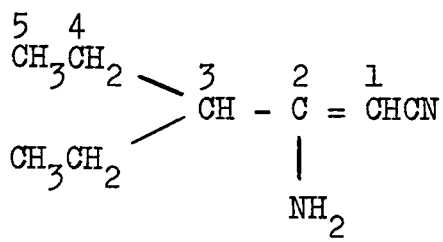


n.m.r. 24.

A triplet $\tau = 9.05$ $^{5}CH_3$ split by $^{4}CH_2$ $J_{5,4} = 7$ c.p.s. is mixed with a low intensity triplet which may be caused by non-equivalence due to restricted rotation, a doublet $\tau = 8.7$ due to $^{6}CH_3$ split by methine $J_{6,3} = 7$ c.p.s., a quartet $\tau = 8.5$ due to $^{4}CH_2$ split by $^{5}CH_3$ is hidden under the broad envelope of the β and γ methylene groups of the piperidine but the intergram clearly shows 8 protons, similarly the sextet of doublets $\tau = 7.1$ is partially hidden by the broad envelope of the d methylenes of the piperendene ring ($\tau = 6.7 - 6.95$) but it can clearly be seen $J_{3,6} = J_{3,4} = 7$ c.p.s. and $J_{3,1} = 1.8$ c.p.s. the latter being due to long range coupling of the methine with the ethylenic proton. A doublet $\tau = 6.03$ is due to long

range coupling of the ethylenic proton $^{1}CHCN$ with the methine $J_{1,3}$ = 1.8 c.p.s.

5. <u>1-Amino-3-ethylpent-1-ene.</u>



n.m.r.25

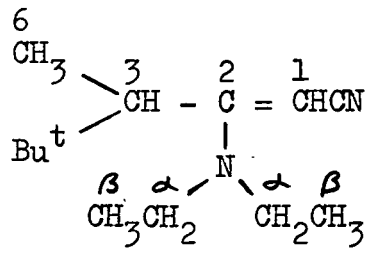
A multiplet τ = 9.1 is the $^{5}CH_3$ split by $^{4}CH_2$ with some contribution from other methyl groups, possibly from other tautomer (i.e. imine form) $J_{5,4}$ = 7 c.p.s. A multiplet at τ = 8.5 indicates quartet of doublets of $^{4}CH_2$ split by $^{5}CH_3$, $J_{4,5}$ = 7 c.p.s. and further split by the methine $J_{4,3}$ = 2 c.p.s. The expected pentet of doublets due to the methine split by $(^{4}CH_2)_2$ and long range coupling to the ethylenic proton cannot be seen, it is probably so broadened by interaction with the nitrogen protons as to be smoothed out completely. A triplet τ = 6.2 is due to the ethylenic proton $^{1}CHCN$ being split by the nitrogen protons

J_{H,NH_2} = 1 c.p.s., a doublet at τ = 5.83 is due to a contribution from the imino form $-\underset{\underset{NH}{\|}}{C} - CH_2CN$ $J_{H_2.NH_2}$ = 0.5 c.p.s. Two broad humps at τ = 5 - 5.8 are due to NH_2 and NH. A total integram of the region τ = 6.2 - 5 gives three protons as would be expected from a tautomeric system

$$-\underset{\underset{NH}{\|}}{C} - CH_2CN \rightleftharpoons -\underset{\underset{NH_2}{|}}{C} = CHCN$$

The integram also shows that the ratio of the amino to imino forms is about 7:1. (This is in carbon tetrachloride, infra-red in liquid phase shows no imino form.)

6. <u>1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene.</u>

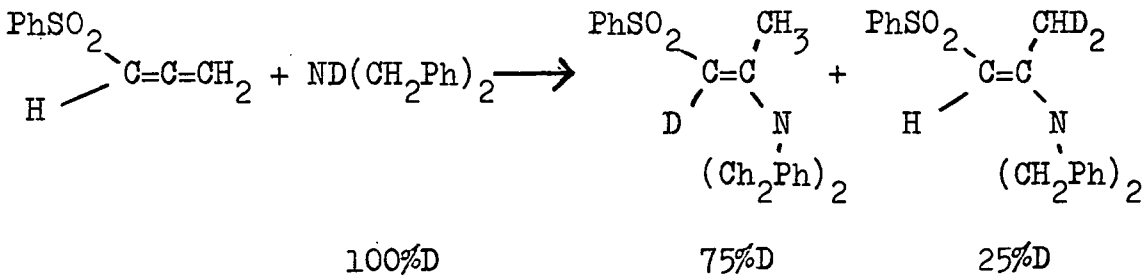


n.m.r.26.

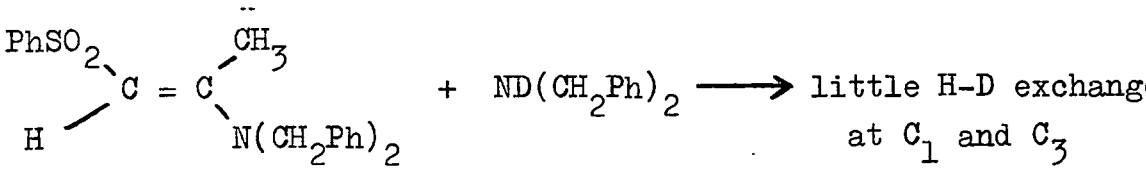
Showed a singlet τ = 9.03, Bu^t, a multiplet τ = 8.85 for the diethylamino methyl groups (possibly non-equivalent due to restricted rotation), a doublet τ = 8.5 $^6CH_3$ split

by methine $J_{6,3}$ = 7.2 c.p.s. a quartet τ = 7.55 due to the methine ^{3}CH split by $^{6}CH_3$. The diethylamino methylenes τ = 6.6 show a multiplet again probably a result of restricted rotation, and a singlet τ = 6.3 due to ethylenic = C<u>H</u>CN.

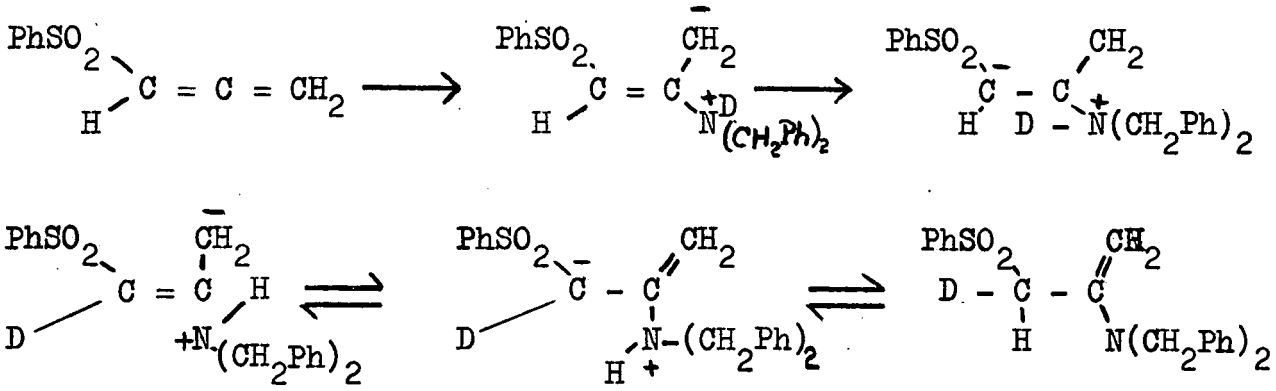
Stirling [63] reacted phenylsulphonylpropadiene with N-deutero-dibenzylamine and obtained an addition product which contained 25% of the deuterium in the 1 position and 75% of the deuterium in the 3 position



Reaction of the isotopically normal product with N-deutero-dibenzylamine gave a product which showed little exchange to have taken place

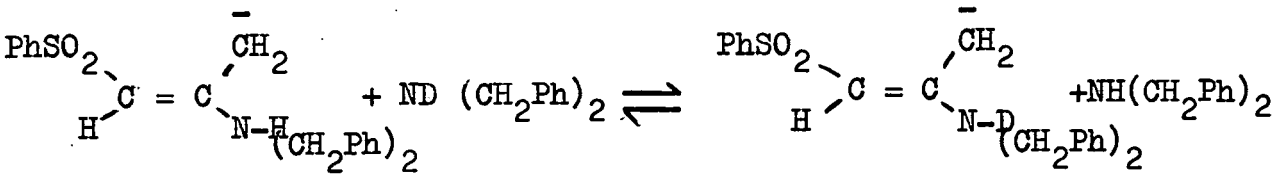


He interpreted these results ~~to show~~ indicating that proton transfer occurs after the addition of the nucleophile by means of an internal proton transfer in the adduct i.e.



Only if such equilibria are present can the statistical distribution of deuterium occur i.e. 75% on C_1 and 25%D on C_2, and the fact that the isotopically normal adduct shows little exchange was interpreted by Stirling to show that the exchange must be by multiple internal proton transfer otherwise a much greater proportion of deuterium would be introduced into the adduct.

The small amount of deuterium which is introduced in the case of the isotopically normal adduct may be explained by an exchange of the type



These interpretations are not in accordance with our work, if such equilibria are established then the thermodynamically more stable compound (type B) should be exclusively formed. Our experiments have shown that pure adducts of type A or type B in contact with excess amine do not isomerise, again if such equilibria were established isomerisation would be expected.

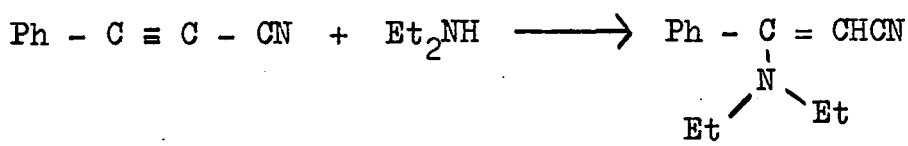
The enamine nitrogen is considerably less basic than the nitrogen of the nucleophile (amine), therefore proton abstraction by the amine would be expected and not an internal proton transfer from the carbon to the nitrogen of the enamine. Thus a larger proportion of deuterium (than explained on statistical addition grounds) would be expected to enter the molecule via such a mechanism.

It is possible that the 75:25 distribution of the deuterium is entirely coincidental, due to formation of a mixture of type A and type B adduct. In the series of cyano enamines which have been prepared in this work, identification of types A and B is easily carried out by spectroscopic examination and it is possible that Stirling's compounds have no intense bands which could be used for identification. (No infra-red or ultra-violet spectral data is given in any of Stirling's papers).

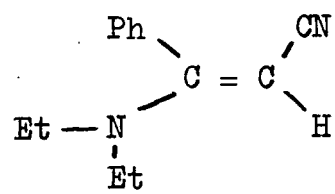
When Stirling [63] reacted his allenic sulphone with dibenzylamine he obtained a product m.p.104° which was sometimes obtained in a form m.p.111°, this is the product which when recrystallised was identified as trans-2-dibenzylamino-1-phenylsulphonyl propene by means of n.m.r. spectra. It is possible that on reacting the sulphone with deuterobenzylamine the n.m.r. was carried out on the crude material and unknown to Stirling this was a mixture of types A and B adducts.

Enamine derived from β-cyanophenylacetylene.

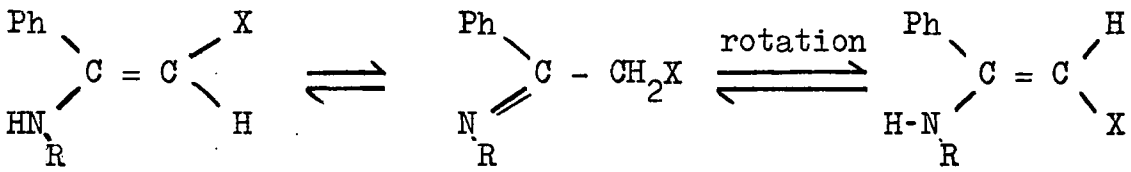
The addition of diethylamine to β-cyanophenylacetylene gave the enamine under similar conditions to those used for 1-cyanoallenes.



The proposed internal proton addition mechanism would lead to cis addition to give



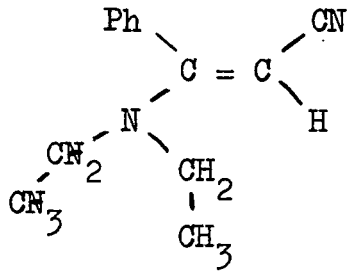
Spectral evidence can be used to prove this structure Stirling [106] and Huisgen [107] have shown that cis addition products are formed from the nucleophilic addition of secondary amines to acetylenes and that the trans product (activating group and nucleophile are trans) is always obtained. Only in the case of primary amines does a cis-trans equilibrium result, this presumably being due to the initial trans product forming an imine-type intermediate



<u>Enamine Derived from β- Cyanophenylacetylene.</u>

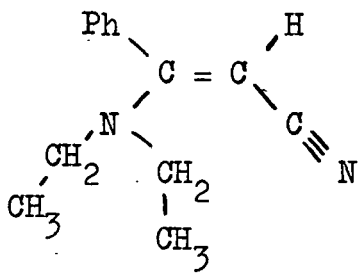
The methods applied by Stirling [106] and Huisgen [107] for determining configuration are peculiar to the type of molecules used by these workers and cannot be applied in the present case, however a novel method for finding the configuration has been worked out for 1-cyano-2-amino-alk-1-enes.

The cis and trans forms can be written



trans

and



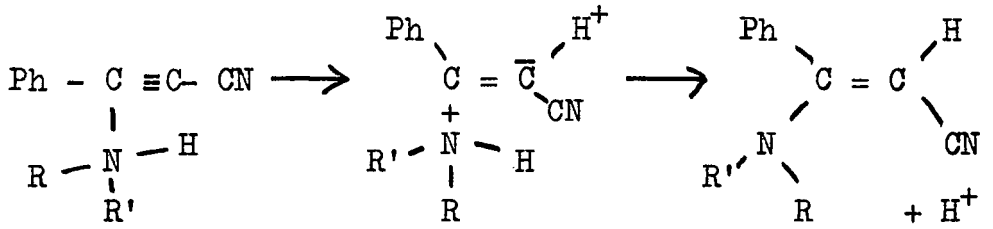
cis

Models show that the methylene of the amino group falls directly in the deshielding zone of the cyano group in the cis addition product thus the proton resonance signal of the - methylenes would be shifted downfield relative to the corresponding signal in the trans form.

Reaction under aprotic conditions yields a product which has a sharp n.m.r. spectra.

A triplet $\tau = 8.89$ ($N-CH_2\underline{CH_3}$) $J_{CH_3,CH_2} = 7$ c/sec., a quartet $\tau = 6.92$ ($N-\underline{CH_2}-CH_3$) $J_{CH_2,CH_3} = 7$ c/sec., a singlet $\tau = 6.0$ ($C{=}C\begin{smallmatrix}\underline{H}\\CN\end{smallmatrix}$), and a multiplet $\tau = 2.57$ ($\underline{Ph}$). This was believed to be the trans product.

If the reaction is carried out under conditions where protons are available (e.g. in methanol) then external proton transfer can give the cis product.



The n.m.r. of the product obtained using such conditions (reaction carried out in methanol) was similar to that obtained from the product under aprotic conditions except that two quartets were shown for the α-methene protons, the new quartet appearing 13 c/sec. downfield from the original one.

The ratio of cis to trans isomers was shown by planimetric measurements to be 1:4.

Preparation of β-Ketonitriles from Cyano-enamines.

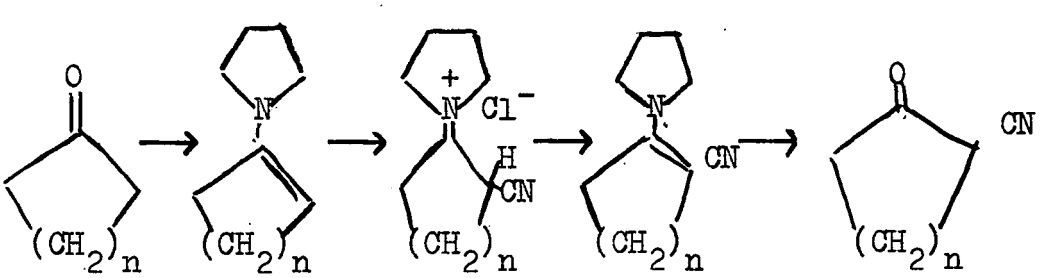
Aliphatic and aromatic β-Ketonitriles have previously been prepared by Claisen ester type condensations of nitriles having active α-methylene groups and either esters (J.B.Dorsel and S.M.McElvain [108]) or nitriles (A. Dornow, I. Kulilche and F. Boxmann [109]), but these methods are of limited synthetic value,

e.g.

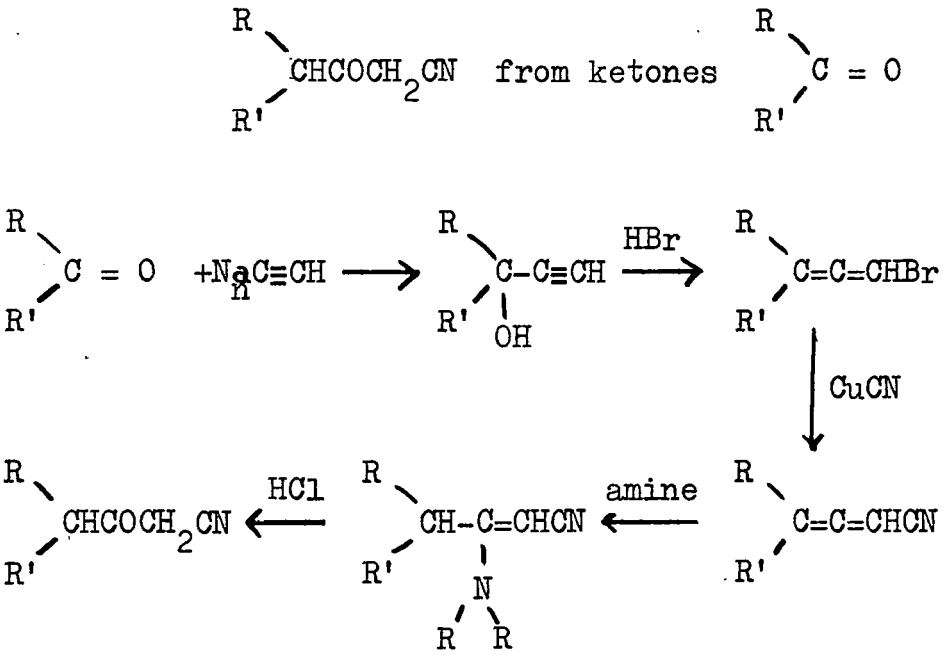
$$C_6H_5COOC_2H_5 + RCH_2CN \xrightarrow{NaOEt} C_6H_5COCHRCN \qquad 50\text{-}60\%$$

$$C_6H_4CN + CH_3CN \xrightarrow{NaNH_2} C_6H_4C{=}NHCH_2CN \longrightarrow C_6H_4COCH_2CN$$

In 1959 M. E. Kuehne [110] prepared a limited number of cyclic β-Ketocyanides from the corresponding cyclic ketone. A ketone is reacted with a secondary amine, e.g. pyrrolidine, and the resulting enamine treated with cyanogen chloride and hydrolysed with dilute mineral acid to give the cyano ketone.



The preparation of cyano enamines from allenic cyanides followed by hydrolysis provides the first convenient general synthesis for cyanomethylene ketones of the type

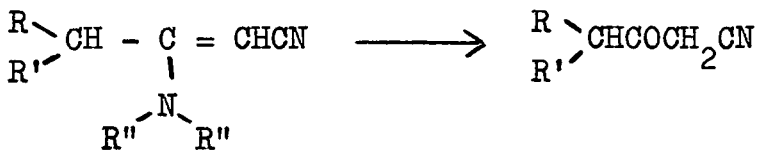


ca 30% overall yield.

The type A and type B enamines lead to the same cyano ketone on refluxing with dilute hydrochloric acid for 1 hr.

TABLE XVII

YIELDS OF CYANOKETONES FROM DIFFERENT ENAMINES

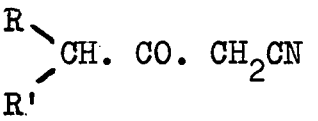


Type	R	R'	R"	R"'	time	Yield
A	Me	Et	Et	Et	2.5hr	55
B	Me	Et	Et	Et	2.5hr	60
B	Me	Et	(C_5H_{10})		1 hr	-
A	Me	Et	(C_5H_{10})		1 hr	84
A	Et	Et	Et	Et	1 hr	78
B	Et	Et	H	H	1 hr	-
B	Me	Bu^t	Et	Et	2 hr	25
B	Me	Bu^t	(C_5H_{10})		2 hr	49
A	Me	Bu^t	(C_5H_{10})		2 hr	-
B	Me	Bu^t	(C_5H_{10})		2 hr	52

- yield not determined accurately

TABLE XVIII

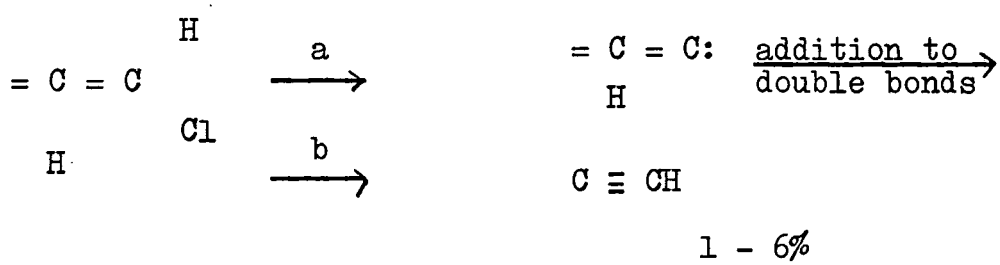
INFRA-RED AND ULTRA-VIOLET SPECTRA OF β-KETOCYANIDES



R	R'	ν max	λ max	ε
Et	Me	2260,1730,780	232mu	2,880
Et	Et	2280,1730,785	232mu	4,415
Me	Bu^t	2280,1730 710	234mu	3,225
$Ph.CO.CH_2CN$		2280,1700,755	204mu	15,820
			245mu	11,600
			282mu	2,636

1,4-Eliminations of 1-haloallenes.

S.R. Landor and P.F. Whiter [111] have recently shown that under basic conditions 1-haloallenes give 1,1-elimination of the hydrogen halide to form allenic carbenes, which can then add on electrophilically to any electron source i.e. double bonds etc. Some of Whiters products were found to contain from 1 - 6% of hydrocarbon ey-yne, presumably originating from a 1,4-elimination.

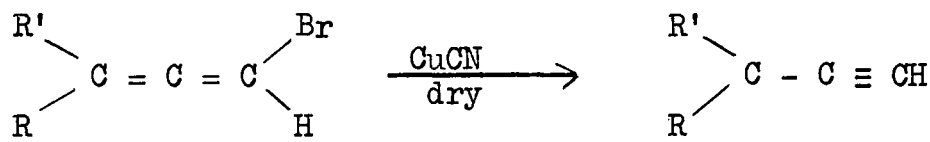


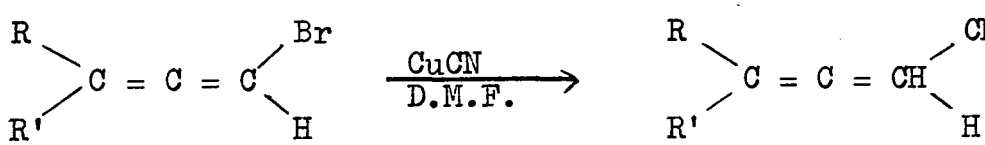
Thus under strong basic conditions the 1,1-elimination is a more highly favoured process than the 1,4-elimination.

During the present work on 1-cyanoallenes attempts were made to prepare 1-cyanoallenes from 1-bromoallenes by heating, either alone or in a solvent, with cuprous cyanide. It was found that very little allenic cyanide resulted, but a low boiling compound was often formed, sometimes with explosive force.

If the apparatus was modified and a slow continuous distillation occurred then the low boiling product could often be collected, and was shown to be the hydrocarbon en-yne mixed with hydrogen cyanide. The en-yne could be obtained in a pure form by redistillation of this mixture. (Table XIX.)

If the 1-bromoallene is heated with cuprous cyanide in N,N-dimethylformamide then the main product is the corresponding 1-cyanoallene and only about 15% of the en-yne is formed. If however the 1-bromoallene is heated in N,N-dimethylformamide with other cuprous salts (e.g. cuprous halides) then the main product is the en-yne.





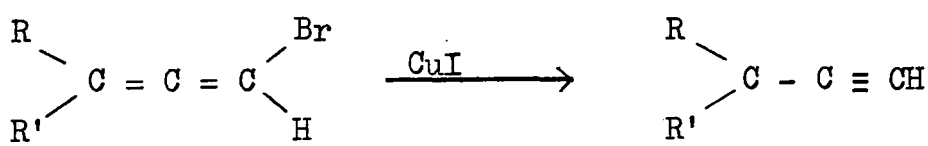


TABLE XIX.

ENYNES FROM 1-HALOALLENES AND CUPROUS SALTS.

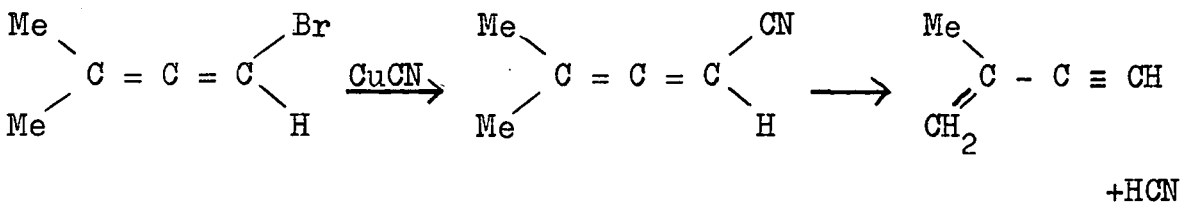
Allenic	Bromide	Cuprous Salt	Solvent	Yield
R	R'			
Pr^n	H	CuCN	-	50%
Me	Me	Cu CN	-	22%
Me	Me	Cu I	D.M.F.	57%
Me	Et	Cu CN	-	57%
Me	Et	Cu I	D.M.F.	50%
Me	Et	Ag CN	-	21%
Me	Et	Cu Br	D.M.F.	60%
Me	Et	Cu Cl	D.M.F.	40%
Et	Et	Cu CN	-	44%
Et	Et	Cu I	D.M.F.	61%
Me	Bu^t	Cu CN	-	*
Me	Bu^t	Cu I	D.M.F.	63%

* Gave 60% 1-cyano-3,4,4-trimethylpenta-1,2-diene.

Heating the 1-bromoallene with cuprous iodide with no solvent gives only a small amount of en-yne, possibly because the hydrogen iodide liberated attacks any en-yne to give unsaturated iodo compounds, (in D.M.F. the hydrogen iodide seems to form a solvated complex which does not attack en-ynes.)

Mechanism.

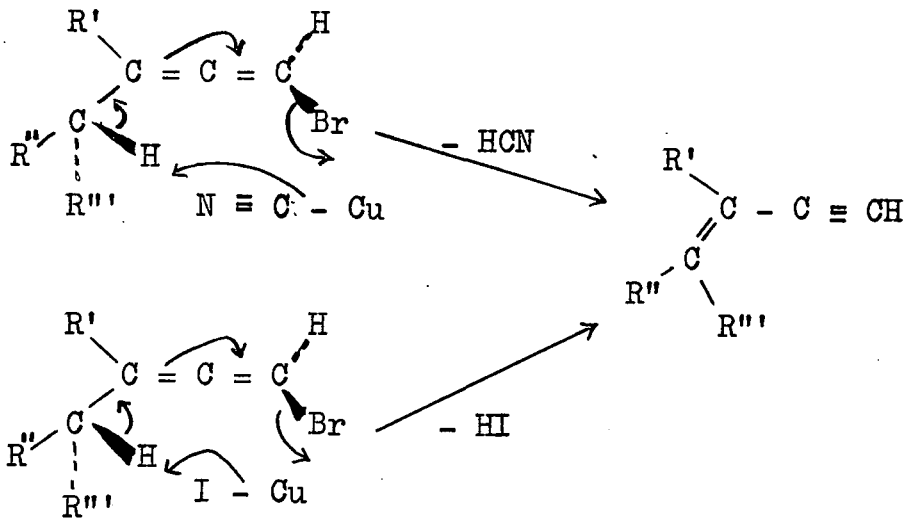
It was first thought that when heated with cuprous cyanide, 1-bromoallenes would form 1-cyanoallenes which then underwent elimination of hydrogen cyanide, thus accounting for the formation of the latter compound.



however heating 1-cyanoallenes alone and with cuprous salts showed that only polymerisation occurred, thus proving that the allenic cyanide was not an intermediate in the elimination.

A cyclic mechanism best explains this 1,4-elimination. The bromine atom co-ordinates with the copper of the cuprous salt, then if a suitable hydrogen atom is available on C_4 an

eight or nine membered cyclic transition state can occur, when elimination at the 1 and 4 protons leads to the separation of hydrogen cyanide or hydrogen halide and production of the en-yne.



The different course of the reaction of 1-bromo-allenes with cuprous cyanide and cuprous iodide in dimethylformamide solvent is best explained by the fact that cuprous cyanide complexes strongly with dimethylformamide thereby being prevented from lying flat across the bromoallene, where as the cuprous iodide complex with dimethylformamide appears to be weak, thus allowing preferential complexing with the 1-bromoallene. Cuprous cyanide is very soluble in N,N-dimethylformamide and on standing precipitates a number of solid complexes which are now being examined by Landor

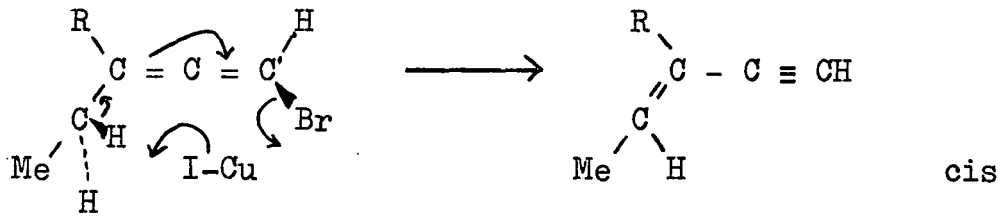
and Patel. Cuprous iodide is almost insoluble in dimethylformamide, but dissolves when 1-bromoallene is added.

When 1-bromo-3-methylpenta-1,2-diene is reacted with cuprous iodide in N,N-dimethylformamide at 80° an en-yne mixture consisting of two products in the ratio 12:88 is formed. Preparative g.l.c. separation followed by spectroscopic examination showed these to be 2-ethylbut-1-en-3-yne (910 cm^{-1}, $C = CH_2$) and trans-3-methylpent-3-en-1-yne (820 cm^{-1}, $C = CH$).

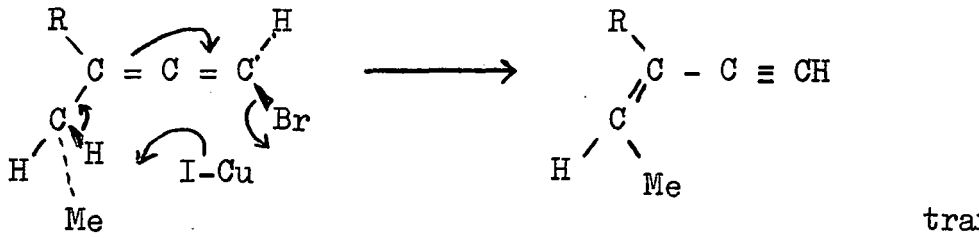
With cuprous cyanide alone, the temperature necessary for reaction is 115° and at this or higher temperatures three products in the ratio 6:74:20 were formed. These were separated by preparative g.l.c. and shown to be 2-ethylbut-1-en-3-yne, trans-3-methylpent-3-en-1-yne and cis-3-methylpent-3-en-1-yne respectively.

This could be explained by a kinetically controlled reaction at the lower temperature, with the methyl groups on C_3 and C_4 trans i.e. in the lowest energy state and a thermodynamically controlled reaction at the higher temperature giving an equilibrium mixture of cis- and trans-methyl groups on C_3 and C_4.

Similarly 1-bromo-3-ethylpenta-1,2-diene with cuprous iodide at 80° gave one product only which was considered to be trans-3-ethylpent-3-en-1-yne having the ethyl group on C_3 and the methyl group on C_4 in the trans positions



cis



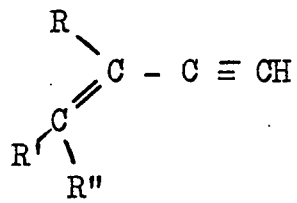
trans

R = Me or Et

All the en-ynes showed strong terminal acetylenic bands 3300 vs (C ≡ CH) and 2100m (C ≡ C) cm^{-1}. The double bond showed only a weak band in the region of 1630 cm^{-1}. Terminal methylene groups were detected or proven absent by the very strong 900 cm^{-1} ($=CH_2$) absorption assignation of cis or trans structure was based on 845 (cis) and 820 (trans) cm^{-1} bands. (Table XX.)

Table XX.

INFRA-RED AND ULTRA-VIOLET SPECTRA OF EN-YNES.



R	R'	R"	ν_{max} cm^{-1}	λ_{max}	ε	λ_{max}	ε
H	H	Et	3300, 2090, 1635, 740	223	12,900		
H	Et	H	3300, 2090, 1635, 955	223	12,900		
Me	H	H	3300, 2100, 1625, 900	222	11,000	236	9,700
Me	H	Me	3310, 2100, 1620, 820				
Me	Me	H	3310, 2100, 1640, 845	222	8,900		
Et	H	H	3310, 2100, 1620, 909				
Et	H	Me	3300, 2100, 1630, 840	222	13,800		
Bu^t	H	H	3300, 2100, 1630, 910	210	7,200	218	10,000
				226	7,400		

Hydrolysis of 1-Cyanoallenes.

At the present time the only method for the preparation of allenic acids is due to Jones, Witham and Whiting [112].

They reacted acetylenes with nickel carbonyl

$$\text{eg}\quad Me_2CClC{\equiv}CH \xrightarrow{Ni(CO)_4} Me_2C{=}C{=}CH_2$$

It was thought that hydrolysis of 1-cyanoallenes would provide a convenient route for the synthesis of allene-1-carboxylic acids.

$$RR'C = C = CHCN \longrightarrow RR'C = C = CHCOOH$$

However attempts at hydrolysis using mineral acids, alkalis and bases did not prove satisfactory. The products in most cases being mixtures of unchanged allene cyanide and dark high molecular compounds containing no carbonyl band. Dimers of the allene cyanides were recovered from the high molecular weight material in the cases of 1-cyano-3-methylbuta-1,2-diene, 1-cyano-3-methylpenta-1,2-diene, and 1-cyano-3-ethylpenta-1,2-diene.

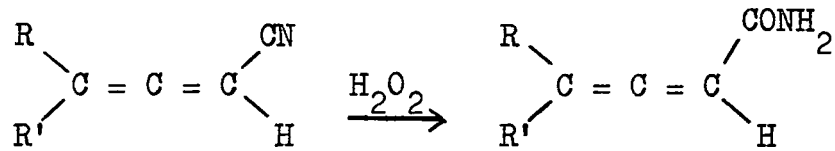
1-Cyano-3,4,4-trimethylpenta-1,2-diene gave an allenic acid, on heating the cyanide at 90° for 48 hr. in 30% sodium hydroxide.

It is possible that less stearically blocked molecules dimerise and polymerise faster under hydrolysis conditions than hydrolysis, and more stearically blocked molecules, e.g. 1-cyano-3-t-butyl-4,4-dimethylpenta-1,2-diene show low solubility and hence react slowly.

An oxidative hydrolysis using alkaline hydrogen peroxide gave good yields of allenic-1-amides in all cases except the monoalkylallene cyanides and the 3,3-dimethyl- and 3-ethyl-3-methyl-allene cyanide, it is suspected but not proven that in these cases some addition to the unsaturated centre is taking place.

Table XXI.

YIELDS OF ALLENIC AMIDE FROM ALLENIC CYANIDE

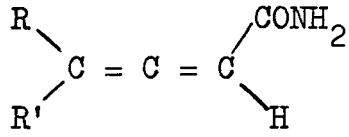


R	Et	Me	Pr^i	Bu^i	Bu^t
R'	Et	Bu^t	Pr^i	Bu^i	Bu^t
% Yield		70	70	41	70

The allenic amides were all stable crystalline white solids and had characteristic spectral bands, ν_{max} 3200-3410s a doublet (two N-H stretching bands), 1950-1980s (allene), 1650-1675s (the Amide I band, C=O), 1600-1630s (Amide II band, N-H bonding). λ_{max} 208-211mμ. (Table XXII.)

Table XXII.

INFRA-RED AND ULTRA-VIOLET SPECTRA OF ALLENIC AMIDES



R	R'	ν_{max} in cm^{-1} -N-H stretch		Amide I	Amide II	λ_{max}	ε
Et	Et	3400	3200,	,1670,	1625		
Me	Bu^t	3400	3200,	,1670,	1625	209	13,000
Pr^i	Pr^i	3400	3210,	,1655,	1630	210	15,000
Bu^i	Bu^i	3410	3210,	,1655,	1625	211	10,140
Bu^t	Bu^t	3410	3200,	,1675,	1600	208	8,150

Grignard Reactions of 1-Bromoallenes.

Wotiz, Matthews and Leib [113] proposed that propargyl magnesium bromide existed in two resonance forms, i.e.

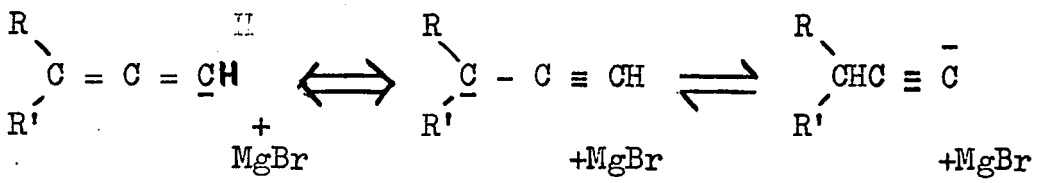
$$\left[\begin{array}{c} H - C \equiv C - \overset{-}{C}H_2 \\ \updownarrow \\ H - \overset{-}{C} = C = CH_2 \end{array}\right] \overset{+}{MgBr}$$

The corresponding allene magnesium bromide would also be expected in this form. Support for the above was obtained when in 1951 Wotiz and Palchak [114] found that treatment of the Grignard compound of 2-bromo-2-methyloct-3-yne with carbon dioxide gave the allenic acid 2-methylocta-2,3-dien-4-carboxylic acid,

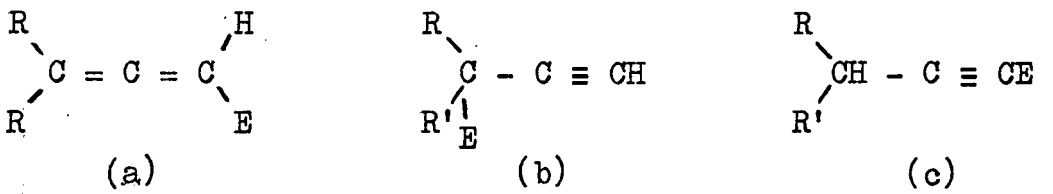
$$C_4H_9 - C \equiv C - CBrMe_2 \xrightarrow[CO_2]{Mg} C_4H_9 - \underset{\underset{COOH}{|}}{C} = C = CMe_2$$

the authors thought that the acetylenic acid was not formed due to steric factors.

In considering an allenic Grignard compound three forms must be taken into account.



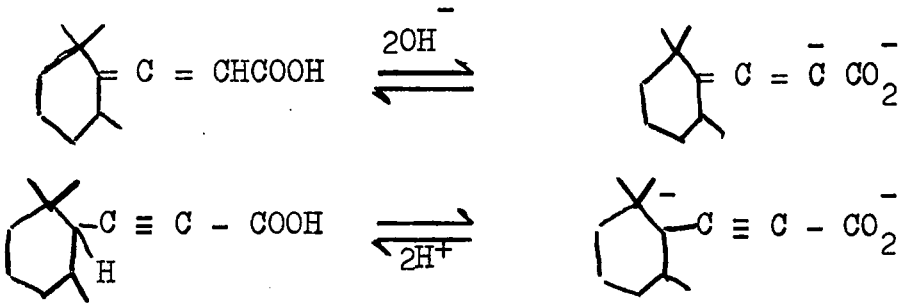
Thus if an electrophile E attacks the Grignard three products may result.



In practice usually one or two of these products predominate depending on the electrophile used, i.e. in addition of carbon dioxide products (a) and (c) result; treatment with oxygen gives mainly product (b), treatment with acetone gives mainly product (c). The reasons for these differences are as yet unknown.

When Goodson [115] treated 2,2,6-trimethylcyclohexylidene-vinyl magnesium chloride with carbon dioxide he obtained by extraction with sodium hydroxide, a neutral fraction and an acid fraction. The acid fraction consisted of a mixture of allenic and acetylenic acids which Goodson proposed to

have been formed by prototropic rearrangement during the alkaline extraction.



This being based on the prototropic rearrangement of buta-2,3-dienoic acid reported by Eglington, Jones and Mansfield ~~116~~ and Whiting.[58]

$$CH \equiv C\text{-}CH_2CO_2H \xrightarrow{K_2CO_3} CH_2 = C = CHCO_2H \underset{90^\circ}{\overset{K_2CO_3}{\rightleftharpoons}} CH_3 - C \equiv CCO_2H$$

In later experiments Goodson extracted the mixture with aqueous sodium carbonate and found that although the extracted portion had a band at 2200 cm^{-1} (-C≡C-) the acid remaining in the neutral portion did not, this he believed confirmed his view that the acetylenic acid was formed by prototropic rearrangement during extraction.

During the present work it has been conclusively shown that the mixture of acetylenic and allenic acids results

from a rearranged Grignard compound and the "rearrangement" during extraction is the result of a separation due to differences in acidities.

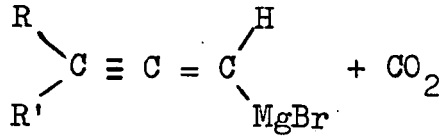
Allenic bromides react smoothly with magnesium, both in tetrahydrofuran and ether, to give the corresponding Grignard products, the magnesium is never completely used up even if a slight molar deficiency is used.

After formation the Grignard compound was cooled and a steady stream of dry carbon dioxide gas was passed through the suspension. When reaction was complete dilute hydrochloric acid was added, the etherial solution separated and dried. The infra-red spectra of this mixture was compared with that of the same mixture which had been shaken with sodium hydroxide and reacidified without separating, no change was observed thus prototropic rearrangement does not occur.

With the lower members of the series only a mixture of allenic and acetylenic acids can be isolated, no effective means of separation has yet been found. (Preparative thin layer chromotography holds out the best chance but has not yet been tried.)

Table XXIII.

ALLENIC GRIGNARDS + CARBON DIOXIDE

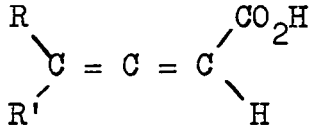


R	R'	Yield of mixed acid	Allenic acid obtained pure
Me	Me	28%	No
Me	Et	13-60%	No
Et	Et	49%	No
Me	Bu^t	45%	Yes
Pr^i	Pr^i	40%	Yes
Me	Ph	18%	Yes

Table XXIV.

INFRA-RED AND ULTRA-VIOLET SPECTRA

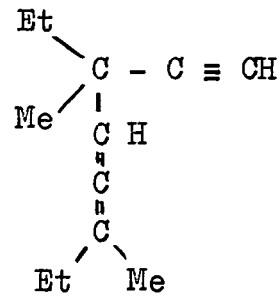
OF ALLENIC ACIDS



R	R'	ν_{max} Cm^{-1}	λ_{max}	ε	λ_{max}	ε
Me	Bu^t	3400-2500, 1960, 1700, 835	212	11,550		
Pr^i	Pr^i	3400-2600, 1975, 1700, 850	213	9,850		
Me	Ph	3400-2500, 1950, 1695,	207	32,000	248	15,470

The more sterically hindered compounds may be separated by extraction with sodium bicarbonate the acetylenic compound being preferentially extracted, however as yet only the allenic acid has been obtained pure, and this in only three cases. (Table XXIII.)

The high boiling hydrocarbon mixture obtained when the same Grignard compound was reacted with different electrophiles was thought to be due to the coupling of the bromide with previously formed Grignard compound. In several reactions the high boiling hydrocarbon mixture has been isolated, in one case the mixture was separated by preparative g.l.c. and one component was found to have ν_{max} 3300ms(C ≡ CH), 3110w(C ≡ C) and 1960w cm^{-1} (C = C = C), it is possible that this is a hydrocarbon of the type

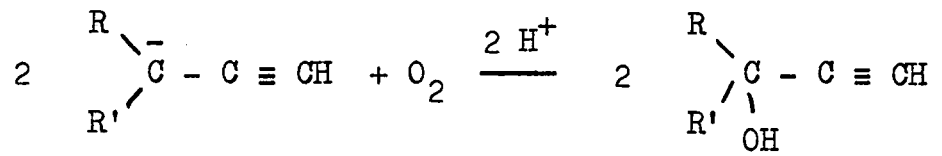


Allenic acids arefound to have ν_{max} 3300-2500us (hydrogen bonded OH), 1950s(C = C = C) and 1700s (C = O)cm^{-1}.

λ_{max} 212-3m μ for alkyl substituted compounds, and λ_{max} 207m μ and λ_{max} 248m μ for the phenyl substituted compound. (Table XXIV.)

Reaction with Oxygen.

Reaction of the oxygen nucleophile with allenic Grignard compounds leads to formation of the corresponding acetylenic alcohol in about 48% yield.



the main by-product is the previously mentioned hydrocarbon mixture. In some reactions unexplained carbonyl bonds appeared in infra-red spectra of products but no carbonyl compound was obtained pure. The acetylenic alcohols were identified by comparing infra-red and g.l.c. spectra with those of authentic compounds.

Reaction with Acetone.

3-methylpenta-1,2-diene-1-magnesium bromide was reacted with acetone at 5°, working up after decomposing the magnesium complex with dilute hydrochloric

acid gave a main fraction of 3-methylhept-3-yn-2-ol along with other volatile products, no allenic compound was obtained ν_{max} (I.R.77.) 3400(s) (-OH).

PART III.

EXPERIMENTAL.

EXPERIMENTAL

Infra-red spectra were determined with a Perkin-Elmer Infracord spectrometer. The abbreviations vs, s, m, w and vw are used to indicate the strength of the infra-red absorption bonds, i.e. very strong, strong, medium, weak and very weak respectively. Ultra-violet spectra were determined on absolute alcohol solutions with a Bausch and Lombe Spectronic 505 recording spectrometer. Nuclear magnetic resonance spectra were determined in carbon tetrachloride or deuterochloroform solution using either a Varian A40 or a Perkin-Elmer R10 spectrophotometer. A Griffin and George Mk. II chromatographic apparatus was used to determine gas liquid chromatograms (g.l.c.), glass columns (6' x 0.25") being employed, the nitrogen flow rate was 2 l./hr. unless otherwise stated. Melting points were determined on a Reichert-micro-Kofler block and are uncorrected.

Solvents designated as dry had been dried with sodium wire, N,N-dimethylformamide being dried by ayeotropic distillation from benzene.

Preparation of 3,3-dialkylprop-1-yn-3-ols.

1) 3-Ethylpent-1-yn-3-ol.

Anhydrous liquid ammonia (3.5 l.) was added to a 5l flask contained in a well lagged box. The flask was fitted with an acetylene gas inlet which dipped below the surface of the ammonia, a mechanical stirrer, a dropping funnel, and a calcium oxide guard tube. Ferric nitrate (0.3 g) was added to the stirred ammonia followed, after a few minutes, by the addition of sodium (55.2 g., 2.4 mole) in small pieces. When about half the sodium had been added the passage of acetylene gas was started, (the cylinder gas being purified by passing through two traps cooled to -40°, then through two wash bottles containing concentrated sulphuric acid and finally through a calcium oxide U tube.)

The mixture was stirred, and acetylene was passed until the original deep blue solution had changed, first to a white suspension (sodamide), then to a dark grey suspension of sodium acetylide, (approx. 4-6 hr.)

Diethyl ketone (172 g., 2.0 mole) was then added dropwise over 2 hr. and the mixture stirred a further 3 hr.

while continuing to pass acetylene. After addition of ammonium chloride (134 g., 2.5 mole) over 30 min. the flask was removed from its lagging and stood outside in a water bath until the ammonia had evaporated, ether (300 ml.) was then added and the contents of the flask filtered, the solid residue of sodium chloride was washed several times with ether and the combined etherial solutions dried ($MgSO_4$).

Distillation, after first removing the ether, gave a small forerun of diethyl ketone followed by 3-ethylpent-1-yn-3-ol (102 g., 72%), b.p. 61.5-62.5°/40mm., ν_{max} 3400vs (-OH), 3300s(C≡CH), and 2100w(C≡C) cm^{-1}; g.l.c. (silicone oil 100°) showed only one peak, t, 5.5 min.

2. <u>Pent-1-yn-3-ol.</u>

Sodium acetylide (from sodium 56 g., 2.2 mole, in liquid ammonia 3.3 l) and propionaldehyde (116 g., 2.0 mole) after working up in the usual manner gave pent-1-yn-3-ol (63 g., 38%), b.p. 121°/760 mm., ν_{max} 3400vs(-OH), 3300s(C≡CH), and 2100w(C≡C) cm^{-1}; g.l.c. (silicone oil: 100°) showed only one peak, t, 3 min.

3. 3,4,4-Trimethylpent-1-yn-3-ol.

Sodium acetylide (from sodium 58 g., 2.5 mole, in liquid ammonia 3 l.) and tert-butyl methyl ketone (200 g., 2.0 mole) after working up in the usual manner gave 3,4,4-trimethylpent-1-yn-3-ol (210 g., 83%), b.p. $62^{o}/36$ mm., ν_{max} 3400vs(-OH), 3300s(C≡CH), and 2100w(C≡C) cm^{-1}; g.l.c. (silicone oil,100°) showed only one peak, t, 6.3 min.

4. 3,5-Dimethylhex-1-yn-3-ol.

Sodium acetylide (from sodium 29 g., 1.25 mole, in liquid ammonia 2 l.) and 4-methylpentan-2-one (100g., 1 mole) after working up gave 3,5-dimethylhex-1-yn-3-ol (77 g., 61%) b.p. $56^{o}/20$ mm., ν_{max} 3400s(-OH), 3300s(C≡CH) and 2100w(C≡C) cm^{-1}; g.l.c. (silicone oil, 100°) showed only one peak, t, 6.25 min.

5. 3-Isopropyl-4-methylpent-1-yn-3-ol.

Sodium acetylide (from sodium 25.3 g., 1.1 mole, in liquid ammonia 2 l.) and di-isopropylketone (114 g., 1 mole) after working up gave 3-isopropyl-4-methylpent-1-yn-3-ol (101 g., 72%), b.p. $67/69^{o}$/

22 mm., ν_{max} 3400s(-OH), 3300s(C≡CH) and 2100w(C≡C) cm^{-1} g.l.c. (silicone oil, 120°) showed one peak, t, 6.5 min.

6. <u>3-Isobutyl-5-methylhex-1-yn-3-ol.</u>

Sodium acetylide (from sodium 58 g., 2.5 mole in liquid ammonia 3.5 l) and di-isobutyl ketone (288 g., 2 mole) after working up gave 3-isobutyl-5-methyl-hex-1-yn-3-ol (103 g., 32%), b.p. 74-75°/9 mm.; ν_{max} 3400s(-OH), 3300s(C≡CH) and 2100w (C≡C) cm^{-1}; g.l.c. (silicone oil, 120°) gave only one peak, t, 15 min.

Preparation of 3-alkyl and 3,3-dialkyl-1-bromoallenes.

1. 1-Bromo-3-methylbuta-1,2-diene.

(a) 3-Methylbut-1-yn-3-ol (67.2 g., 0.8 mole) was added to a mixture of powdered cuprous bromide (40 g., 0.28 mole), powdered ammonium bromide (32 g.), copper powder (2 g.) and concentrated hydrobromic acid (48% w/w, S.G. = 1.5, 192 ml., 1.7 mole). The stirred mixture was warmed to 30° for 1 hr. The upper layer then showed no ν_{max} 3400 cm^{-1}. (OH). The mixture was cooled, filtered, the residue washed with petroleum ether, the filtrate separated, and washed with 48% hydrobromic acid until the lower acid layer shows no violet colouration. The upper layer was dried ($NaHCO_3$, $MgSO_4$), and fractionated giving 1-bromo-3-methylbuta-1,2-diene b.p. 53-54°/60 mm. (90 g., 77%) (Found: C, 41.0; H, 4.9; Br, 54.0 C_5H_7Br requires C, 40.8; H, 4.8; Br, 54.4%). ν_{max} 1950vs (C=C=C), 1160vs, 1050vs, 750vs and 730 cm^{-1}; λ_{max} 205m μ (9,570), $\lambda_{shoulder}$ 214-6m μ (ε,10,050).

(b) 3-Methylbut-1-yn-3-ol (21 g., 0.25 mole) was added to a mixture of powdered cuprous bromide (14.3 g., 0.1 mole),

powdered ammonium bromide (9.8 g., 0.1 mole) copper powder (5 g.) and concentrated hydrobromic acid (4.5% w/w 62 ml. 0.5 mole). The mixture was stirred vigorously for 1 hr. at room temperature when the upper layer was found to contain no ν_{max} 3400 cm^{-1} (-OH) on I.R. examination. The mixture was filtered, separated, the upper organic layer washed several times with concentrated hydrobromic acid, and dried ($MgSO_4$, Na_2CO_3). The product was found to be pure 1-bromo-3-methylbuta-1,2-diene (33 g., 90%) and had identical spectra with that of the pure distilled product from (a) g.l.c. (silicone oil, 80°) showed only one peak, t, 8 min.

2. <u>1-Bromo-3-methylpenta-1,2-diene.</u>

(a) 3-Methylpent-1-yn-3-ol (14.7 g., 0.15 mole) was added over 6 min. to a vigorously stirred mixture of cuprous bromide (7.5 g., 0.052 mole), ammonium bromide (6 g.) copper powder (0.3 g.) and concentrated hydrobromic acid (48% w/w, 36 ml. 0.32 mole) at 30°. When the addition was complete the stirring was continued for ¾ hr. Working up gave 1-bromo-3-methylpenta-1,2-diene

(17 g., 73%) b.p. 51-52.5°/24 mm. (Found: C, 44.4; H, 5.6; Br 49.6. C_6H_9Br requires C, 44.8; H, 5.6; Br, 49.7%). ν_{max} (I.R. 19)., 1950vs (C=C=C), 1165vs and 730vs cm^{-1}, λ_{max} 205m μ (ε, 7,100), $\lambda_{shoulder}$ 217-223m μ, (ε, 6,150), g.l.c. (dinonyl phthalate, 82°) showed only one peak t, 12.5 min.; n.m.r. (n.m.r. 1)., showed a triplet τ = 8.93 ($\underline{CH_3}$ CH_2 C=C=CH), J_{CH_3,CH_2} 7.5 c.p.s., a doublet of triplets τ = 7.6 - 8.4 ($\underline{CH_3}$ =C=C=CH), $J_{CH_3,H}$ 2 c.p.s., J_{CH_3,CH_2} 0.5 c.p.s.; a quartet of doublets τ = 8.19 ($CH_3\underline{CH_2}$ C=C=CH) J_{CH_2,CH_3} 7.5 c.p.s., $J_{CH_2,H}$ 2.2 c.p.s., and a 1:5:10:10:5:1 sextet τ = 4.1 ($CH_3CH_2(CH_3)C=C=\underline{CH}$), J_{H,CH_3} 2.3 c.p.s. J_{H,CH_2} 2.3 c.p.s. Double resonance of the $\underline{CH_3}$ -C=C group causes collapse of the sextet to a triplet.

(b) 3-Methylpent-1-yn-3-ol (49 g., 0.5 mole), was added to a mixture of powdered cuprous bromide (36 g., 0.25 mole), powdered ammonium bromide (20 g., 0.22 mole), copper powder (1 g) and concentrated hydrobromic acid (45% w/w., 124 ml., 1 mole) and the mixture stirred vigorously for 1 hr. at room temperature. Working up in the usual manner gave pure 1-bromo-3-methylpenta-1,2-diene (68 g., 85%) which had identical spectra to the pure distilled product from (a) g.l.c. (dinonylphthalate, 82%) gave only one peak to 12.5 min.

3. <u>1-Bromo-3-ethylpenta-1,2-diene</u>.

3-Ethylpent-1-yn-3-ol (56 g., 0.5 mole), cuprous bromide (28.9 g., 0.2 mole) ammonium bromide (20.0 g., 0.2 mole) copper powder (2.8 g) and concentrated hydrobromic acid (45% w/w. 124 ml., 1.0 mole) at 40° for 1½ hr. gave 1-bromo-3-ethylpenta-1,2-diene, (56.9 g., 65%) b.p. 74°/30mm. (Found: C, 47.8; H, 6.2; Br, 45.9 $C_7H_{11}Br$. requires C, 48.0; H, 6.3; Br, 45.7% n_D^{24} 1.5015. ν_{max} 1950vs (C=C=C); 720 cm^{-1} λ_{max} 206.mμ. (ε, 7,800) $\lambda_{shoulder}$ 220mμ (ε, 7,100); g.l.c. (silicone oil: 151°) gave only one peak, t, 9½ min., n.m.r. (n.m.r.2) showed a triplet τ = 8.94 ($\underline{CH_3}CH_2$-C=C=C), J_{CH_3,CH_2} 7.5 c.p.s.; a quartet of doublets τ = 7.85 ($CH_3\underline{CH_2}$ -C=C=CH), $J_{CH_2,H}$ 2.2 c.p.s., J_{CH_2,CH_3} 7.8 c.p.s.; and a 1:4:6:4:1 pentet, τ = 4.0 (CH_3CH_2 C=C=$\underline{CH}$) J_{H,CH_2} 2.2 c.p.s.

(b) 3-Ethylpent-1-yn-3-ol (11.2 g., 0.1 mole) was added to a mixture of cuprous bromide (7.2 g., 0.05 mole), ammonium bromide (4 g., 0.044 mole) copper powder (0.2 g) and concentrated hydrobromic acid, (45% w/w., 16.2 ml., 0.2 mole) and the mixture stirred vigorously for 1.5 hr. at room temperature. Working up in the usual manner gave pure 1-bromo-3-

ethylpenta-1,2-diene (15.4 g., 88%), which had identical spectra to the pure distilled product from (a) g.l.c. (silicone oil, 150°) gave only one peak, t, 9.6 min.

4. <u>1-Bromo-3,4,4-trimethylpenta-1,2-diene.</u>

3,4,4-Trimethylpent-1-yn-3-ol (63 g., 0.5 mole), cuprous bromide (85 g., 0.59 mole), ammonium bromide (42 g.) copper powder (6 g) and concentrated hydrobromic acid (48% w/w. 180 ml. 1.6 mole) warmed to 40° and stirred for 2 hr. gave 1-bromo-3-4,4-trimethylpenta-1,2-diene (73.2 g., 78%), b.p. 45-47°/5 mm. (Found: C, 50.5; H, 7.1; Br, 42.3. $C_8H_{13}Br$ requires C, 50.8: H, 6.9: Br, 42.3%) ν_{max} 1950vs (C=C=C), 1155vs and 728vs cm^{-1}; λ_{max} 206 mμ (ε, 9,000), λ_{max} 224 mμ (ε, 6,600); n.m.r. showed a singlet τ = 9.15 (Bu^t), a doublet, τ = 8.21 (CH C=C<u>M</u>e Bu^t), and a quartet τ = 4.17 (<u>C</u>H=C=CMe), $J_{H,Me}$ 2.0 c.p.s. g.l.c. (dinonylphthalate; 100°) showed only one peak, t, 20 min.

5. <u>1-Bromo-3,5-dimethylhexa-1,2-diene.</u>

3,5-Dimethylhex-1-yn-3-ol (31.5 g., 0.25 mole), cuprous bromide (8.425 g., 0.3 mole), ammonium bromide (21 g.), copper powder (3 g) and concentrated hydrobromic acid (48% w/w., 90 ml., 0.8 mole) warmed to 40° and

stirred for 2 hr., gave 1-bromo-3-5-dimethylhexa-1,2-diene (32 g., 60%) b.p. 50-51°/7 mm. (Found: C, 50.8; H, 7.12; Br 42.41. $C_8H_{13}Br$ required C, 50.8; H, 6.9; Br, 42.3%) ν_{max} 1950s (C=C=C); 1160s and 730s cm^{-1}. λ_{max} 204m μ (ε, 8,900), $\lambda_{shoulder}$ 225m μ (ε, 5,850). g.l.c. (silicone oil: 80°) showed one main peak, t, 28 min.

6. <u>1-Bromo-3-isopropyl-4-methylpenta-1,2-diene.</u>

4-Methyl-3-isopropylpent-1-yn-3-ol (56 g., 0.5 mole), cuprous bromide (68 g., 0.47 mole) ammonium bromide (36 g.), copper powder (6 g.) and concentrated hydrobromic acid (48% w/w, 144 ml., 1.27 mole) at 40° for 3 hr. gave 1-bromo-3-isopropyl-4-methylpenta-1,2-diene, (66.2 g., 82%) b.p. 49-50°/6mm. (Found: C, 53.6; H, 8.1; Br, 39.7. C_9H_{15} Br requires C, 53.2; H, 7.5; Br 39.3%) ν_{max} 1950s (C=C=C) 1660vw (C=C), 1165s and 895 cm^{-1} w ($CR_1R_2{=}CH_2$) λ_{max} 204m μ (ε, 9,750) $\lambda_{shoulder}$ 219-233m μ (ε, 6,850); g.l.c. (dinonylphthalate; 100°) showed only one peak, t, 20 min.

7. <u>1-Bromo-3-isobutyl-5-methylhexa-1,2-diene.</u>

3-Isobutyl-5-methylhex-1-yn-3-ol (51.0 g. 0.3 mole), cuprous bromide

(20.0 g., 0.14 mole), ammonium bromide (12.0 g., 0.12 mole) copper powder (2.0 g) and concentrated hydrobromic acid (45% w/w., 72 ml., 0.6 mole) at 40° for 20 hr. gave 1-bromo-3-isobutyl-5-methylhexa-1,2-diene (36.1 g., 52%) b.p. 66°/1.7 mm (Found: C, 57; 57.2; H, 8.2; Br, 34.6. $C_{10}H_{19}$ Br requires C, 57.1; H, 8.2; Br, 34.6%), ν_{max} 1965s (C=C=C); 1390m, 1370m, 1165m, 720s cm^{-1} λ_{max} 206m μ (ε, 9,090), 230m μ (ε, 9,000); g.l.c. (G.E.O. 100; 120°) t, 18 min.

8. <u>1-Bromo-3-t-butyl-4,4-dimethylpenta-1,2-diene.</u>

3-t-butyl-4,4-dimethylpent-1-yn-3-ol (25.2 g., 0.15 mole), cuprous bromide (25.5 g., 0.178 mole), ammonium bromide (13.5 g), copper powder (2 g.) and concentrated hydrobromic acid (48% w/w, 54 ml., 0.48 mole) 17 hr. at 40° gave 1-bromo-3-t-butyl-4,4-dimethylpenta-1,2-diene (7.2 g., 21%) b.p. 70-74°/5 mm. (Found: C, 57.2; H, 8.2; Br, 35.2. $C_{11}H_{19}Br$ requires C, 57.1; H, 8.3; Br, 34.6%), ν_{max} 1940ms (C=C=C), 1135s and 720s cm^{-1} λ_{max} 205m μ (ε, 12,100), λ_{max} 227m μ (ε, 7,400); n.m.r. showed a singlet τ= 9.2 ($\underline{Bu}^t_2$C=C=CH Br) and a singlet τ = 4.16 (Bu^t_2C=C=$\underline{CH}$ Br).

9. <u>1-Bromobuta-1,2-diene.</u>

A mixture of but-1-yn-3-ol (35 g., 0.5 mole) cuprous bromide (72 g., 0.5 mole) ammonium bromide (45 g.), copper powder (5 g.) and concentrated hydrobromic acid (48% w/w, 180 ml., 1.6 mole), shaken for 4 hr. at room temperature, left overnight, and then shaken for a further 2 hr. concentrated hydrobromic acid (60% w/w. 60 ml., 0.75 mole) was added and the mixture shaken for 4 hr. Working up gave 1-bromobuta-1,2-diene, b.p. 62.5-63°/168 mm. (27.1. g., 41%). (Found: C, 36.4; H, 4.0. C_4H_5Br requires C, 36.1; H, 3.8%), ν_{max} 3200w (C≡CH), 1950s (C=C=C), 1195vs, 840vs and 680vs cm^{-1}; g.l.c. (silicone oil; 90°) gave one main peak t, 9 min. and one other peak for 3-bromobutyne (1-2%) t, 5.5 min. λ_{max} 201m μ (ε, 5,200), $\lambda_{infl.}$ 215m μ (ε, 3,500) n.m.r. a doublet of doublets at τ = 8.22 (<u>Me</u> CH=C=CH) $J_{4,1}$ 2.6 c.p.s. a doublet of quartets at τ = 4.09 (MeCH=C=<u>CH</u>) $J_{3,1}$ 5.8 c.p.s. and a doublet of quartets at τ = 4.68 (Me <u>CH</u> =C=CH) $J_{4,1}$ 6.9 c.p.s.

10. <u>1-Bromopenta-1,2-diene.</u>

Pent-1-yn-3-ol (21g., 0.25 mole) cuprous bromide (36g., 0.25 mole) ammonium bromide (24.5 g.

0.25 mole) copper powder (4 g.) and concentrated hydrobromic acid (60% w/w 96 ml., 1.24 mole) at room temperature for 9 hr. gave 1-bromopenta-1,2-diene b.p. $62^{o}/66$ mm. (20.5g. 56%), (Found: C, 41.0; H, 5.1; Br, 53.1. C_5H_7Br requires C, 40.9; H, 4.8; Br, 54.4%) ν_{max} 1950s (C=C=C), 1190vs, 850vs and 690vs cm^{-1} λ_{max} 205mμ (ε, 7,000) $\lambda_{infl.}$ 215mμ (ε, 5,500); g.l.c. (silicone oil, 104°) showed one main peak (99%) t, 5 min. and a small peak at t, $2\frac{1}{2}$ min. ($<1\%$, 3-bromopentyne).

11. <u>1-Bromohexa-1,2-diene.</u>

Hex-1-yn-3-ol (49 g., 0.5 mole), cuprous bromide (67 g., 0.47 mole), ammonium bromide (45 g.) copper powder (5 g.) and concentrated hydrobromic acid (60% w/w, 180 ml., 2.3 mole) shaken at room temperature for 10 hr. left overnight and then shaken for a further 3 hr. gave 1-bromohexa-1,2-diene b.p. $51-52.5^{o}/22$ mm. (53.5 g., 67%) (Found: C 45.5; H, 5.9; Br, 49.1. C_6H_9Br requires C, 44.8; H, 5.6; Br 49.6%), ν_{max} 1950s (C=C=C), 1190vs, 830 and 690 cm^{-1} λ_{max} 206mμ. (ε, 7,200). $\lambda_{infl.}$ 215mμ. (ε, 4,700).

12. <u>1-Bromo-4-methylpenta-1,2-diene.</u>

4-Methylpent-1-yn-3-ol (39.2g. 0.4 mole) cuprous bromide (58 g., 0.4 mole) ammonium bromide (40 g., 0.4 mole) copper powder (4 g) and concentrated hydrobromic acid (45% w/w, 248 ml; 2 mole) shaken at room temperature for 42 hr. then hydrobromic acid (60% w/w, 25 ml. 0.35 mole) was added and the mixture shaken for a further 4 hr. gave 1-bromo-4-methylpenta-1,2-diene (23 g., 35%); b.p. 60-62°/35 mm. ν_{max} 1950s (C=C=C); 1195s, 855s, 704s cm^{-1} no band at 3300 cm^{-1} (C≡CH); g.l.c. (dinonyl phthalate, 120°) showed only one peak, t, 5½ min.

13. <u>1-Bromo-3-phenylpropa-1,2-diene.</u>

3-Phenylprop-1-yn-3-ol (19.8 g., 0.15 mole) was added to an ice cold mixture of cuprous bromide (20 g., 0.14 mole), ammonium bromide (13.5 g.), copper powder (2 g.), and concentrated hydrobromic acid (60% w/w, 56 ml., 0.7 mole) over 10 minutes with hand shaking and cooling in ice. The mixture was kept in an ice bath an extra 40 min. with occasional shaking by hand. The mixture was filtered, the solid washed with a little light petroleum spirit and the filtrate extracted with light petroleum spirit

(4 x 10 ml.). The organic layer was separated and washed with 45% hydrobromic acid until the acid layer was no longer coloured violet, then dried over a mixture of magnesium sulphate and anhydrous sodium carbonate.

Removal of the petroleum spirit under reduced pressure gave pure 1-bromo-3-phenylpropa-1,2-diene (28 g., 95%), (Found: Br, 40.7; C_9H_7Br requires Br, 41.0%) ν_{max} (I.R.l.), 1950vs (C=C=C), 1500s, 1450s, 1190vs, 756vs, 705vs, 685vs, cm^{-1}. λ_{max} 205m μ, (ε, 17,730); λ_{max} 268m μ, (ε, 14,210).

14. <u>1-Bromo-3-phenylbuta-1,2-diene.</u>

3-Phenylbut-1-yn-3-ol (29.2 g., 0.2 mole), was added to an ice cold mixture of cuprous bromide (36 g., 0.25 mole) ammonium bromide (15 g.), copper powder (2 g.) and concentrated hydrobromic acid (60% w/w, 56 ml., 0.7 mole) over 10 min. with stirring, then light petroleum spirit (20 ml.) was added and stirring continued in an ice bath for 35 min. The mixture was filtered, the solid washed with a little petroleum spirit and the filtrate extracted with light petroleum spirit (4 x 15 ml.). The organic layer was separated and washed with 40% hydrobromic acid until the acid layer was no longer coloured violet, then

dried ($MgSO_4/Na_2CO_3$). Removal of the petroleum spirit under reduced pressure gave pure 1-bromo-3-phenylbuta-1,2-diene (37.7 g. 90%), (Found: Br, 37.8; $C_{10}H_9Br$ requires Br, 38.2%). ν_{max} (I.R.2)., 1955s (C=C=C), 1500s, 1445s, 1158s, 765vs, 730vs, 690vs cm^{-1} λ_{max} 206m μ, (ε, 16,860); λ_{max} 272m μ (ε, 11,570.)

15. <u>1-Bromo-3,3-diphenylpropa-1,2-diene.</u>

3,3-diphenylprop-1-yn-3-ol (10.4 g., 0.05 mole) in 50 ml. light petroleum spirit was added to an ice cold mixture of cuprous bromide (10.7 g., 0.075 mole), ammonium bromide (4.9 g.), copper powder (1 g.) and concentrated hydrobromic acid (60% w/w., 20 ml., 0.25 mole) over 5 min. with constant stirring, then stirring continued at 0° for $2\frac{1}{2}$ hr. The mixture was filtered, the solid washed with a little petroleum spirit, the organic layer was decanted and the aqueous layer extracted with petroleum spirit (3 x 10 ml.), the petrol solutions were combined and washed with 45% hydrobromic acid until the acid layer was no longer coloured violet, then dried ($MgSO_4$, Na_2CO_3 and active Al_2O_3). Slow evaporation of the petrol under reduced pressure gave white crystals of 1-bromo-3,3-diphenylpropa-

1,2-diene (11 g., 84%) m.p. 81.5-82°. (Found: C, 66.0; H, 4.3; Br, 29.7. $C_{15}H_{11}Br$ requires C, 66.5; H, 4.1; Br, 29.5).

ν_{max} (I.R.3), 1945ms (C=C=C); 1600m (aromatic); 780s; 710s; and 685 cm^{-1}. λ_{max} 205m μ (ε, 30,340), $\lambda_{shoulder}$ 230mμ (ε, 14,200), λ_{max} 281m μ (ε, 12,040). n.m.r. (n.m.r.3), showed a singlet τ = 3.65 (C=C-H) and a multiplet of 10 protons τ = 2.72 (Ph_2 C=C).

Preparation of 3,3-dialkyl-1-iodoallenes

1) 1-Iodo-3-methylbuta-1,2-diene.

(a) Cuprous iodide (16.8 g., 0.2 mole), ammonium iodide (29.0 g., 0.2 mole), copper powder (1 g.) and concentrated hydriodic acid (45% w/w., 76 ml., 0.4 mole) were stirred together at room temperature and 3-methylbut-1-yn-3-ol (16.8 g., 0.2 mole) was added over 5 min., after stirring for 2 hr. light petroleum ether (50 ml.) was added and the mixture filtered. Extraction of the organic layer with light petroleum (2 x 20 ml) followed by drying ($MgSO_4$) and evaporation yielded a product which contained 1-iodo-3-methylbuta-1,2-diene as shown by ν_{max} 1950s. cm^{-1}, but was highly contaminated with double bond products as shown by ν_{max} 1650s 1600s cm^{-1}. These impurities could not be removed by careful fractionation.

(b) Cuprous iodide (16.8 g., 0.2 mole), ammonium iodide (29.0 g., 0.2 mole), copper powder (1 g) and concentrated hydriodic acid (45% w/w., 76 ml., 0.4 mole) were stirred at room temperature and a solution of 3-methylbut-1-yn-3-ol (16.8 g., 0.2 mole) in light petroleum ether (30 ml) was added in one portion. Stirring was continued and at

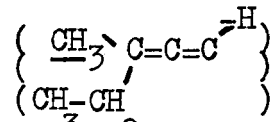
intervals of ½, 1, 1½, and 2 hr. small portions of the organic upper layer were examined by I.R. spectroscopy. The I.R. spectra showed decreasing intensity of the 3400 (OH) band and increasing intensity of the 1950cm (C=C=C) band until at 2 hr. reaction was considered complete.

The suspension was filtered and the filtrate extracted with light petroleum ether (3 x 20 ml). The organic extracts were combined and dried ($MgSO_4$). Distillation after first removing the petroleum ether gave a small fore-run of 3-methylbut-1-yn-3-ol $_{max}$ 3400s (-OH), 3300s (C=CH), and 2100w (C≡C) cm^{-1} followed by pure 1-iodo-3-methylbuta-1,2-diene (23.7 g., 61%) bp. 56°/20 mm, (Found: C, 30.8; H, 3.6; I, 65.7. C_5H_7I requires C, 30.9; H, 3.6; I, 65.4%) ν_{max} (I.R.4) 1955s (C=C=C), λ_{max} 246m μ (ε, 9,595). g.l.c. (silicone oil, 100°) gave only one peak, t, 9.5 min. n.m.r. (n.m.r.4), showed a doublet centred on τ = 8.23 ($(C\underline{H}_3)_2$ C=C=CH) $J_{CH_3,H}$ = 2.3 c.p.s. and a heptet centred on τ = 4.5 ($(CH_3)_2C=C=C\underline{H}$) J_{H,CH_3} = 2.3 c.p.s.

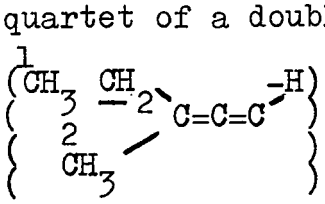
2. <u>1-Iodo-3-methylpenta-1,2-diene.</u>

Cuprous iodide (28.5 g., 0.15 mole), ammonium iodide (28.5 g., 0.15 mole), copper powder (1 g.) and concentrated hydriodic acid (45% w/w, 57 ml., 0.3 mole) were stirred at room temperature and a solution of

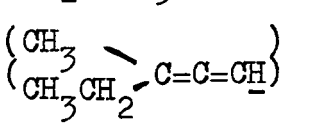
3-methylpent-1-yn-3-ol (14.7 g., 0.15 mole) in light petroleum ether (30 ml) was added in one portion. After stirring for 6 hr. I.R. examination of the upper layer showed no band at 3400 cm^{-1} (-OH). The suspension was filtered and the filtrate extracted with light petroleum ether (2 x 30 ml) the organic extracts were combined and dried ($MgSO_4$). Distillation after first removing the light petroleum gave a small fore-run followed by 1-iodo-3-methylpenta-1,2-diene (19.1 g., 62%) b.p. 55°/6 mm, (Found: C, 34.4; H, 4.5; I, 61.1. C_6H_9I required C, 34.6; H, 4.4; I, 61.0%) ν_{max} (I.R.5) 1950s (C=C=C), 1130vs, 780m, and 709(vs cm^{-1}, λ_{max} 206m μ, (ε, 15,560), λ_{max} 247m μ, (ε, 6,645). g.l.c. (silicone oil, 100°) gave only one peak, t, 17 min. n.m.r. (n.m.r.5) showed a triplet centred on τ = 8.93 ($\underline{CH_3}CH_2CCH_3$=C=CH) J_{CH_3,CH_2} = 8.9 c.p.s.; a triplet of doublets centred on τ = 8.22



J_{CH_3,CH_2} = 0.7 c.p.s; $J_{CH_2,H}$ = 2.3 c.p.s., a quartet of a doublet of quartets, centred on τ = 7.9



$J_{CH_2,{}^1CH_3}$ = 8.9 c.p.s., $J_{CH_2,H}$ - 2.3 c.p.s. $J_{CH_2,{}^2CH_3}$ = 0.7 c.p.s., and a sextet centred on τ = 4.38



J_{H,CH_3} = 2.3 c.p.s.
H,CH_2

3. <u>1-Iodo-3-ethylpenta-1,2-diene.</u>

Cuprous iodide (2.85 g., 0.15 mole), ammonium iodide (21.7 g., 0.15 mole), copper powder (1 g) and concentrated hydriodic acid (45% w/w., 57 ml., 0.3 mole) were stirred at room temperature and a solution of 3-ethylpent-1-yn-3-ol (16.8 g., 0.15 mole) in light petroleum ether (30 ml.) was added in one portion. After stirring for 3 hr. I.R. examination of the organic layer showed no band at 3400 cm^{-1} (-OH). The suspension was filtered, and the filtrate extracted with light petroleum ether (2 x 30 ml) the organic extracts were combined and dried ($MgSO_4$). Distillation after first removing the light petroleum gave a small forerun followed by 1-iodo-3-ethyl-penta-1,2-diene (21.6 g., 65%) b.p. $60^{o}/5.5$ mm. (Found: C, 37.8; H, 5.0; I. 57.2. $C_7H_{11}I$ requires C, 37.9; H, 5.0; I, 57.1%) ν_{max} (I.R.6)., 1945s (C=C=C) 1125s, 710vs cu^{-1} λ_{max} 207m μ, (ε, 17,053), λ_{max} 248m μ, (ε, 6,963). g.l.c. (silicone oil, 100°) gave only one peak, t, 28.5 min.

4. <u>1-Iodo-3-4,4-trimethylpenta-1,2-diene.</u>

(a) Cuprous iodide (190 g., 0.1 mole), ammonium iodide (14.5 g., 0.1 mole), copper powder (1 g) and concentrated hydriodic acid (45% w/w.,

28.5 ml., 0.15 mole) were stirred at room temperature and a solution of 3,4,4-trimethylpent-1-yn-3-ol (12.6 g., 0.1 mole) in light petroleum ether (30 ml) was added in one portion. After stirring for 18 hr. I.R. examination of the organic layer still showed a band at 3400 cm^{-1} (OH). The suspension was filtered and the filtrate extracted with light petroleum ether (2 x 30 ml). The organic extracts were combined and dried ($MgSO_4$). Distillation after first removing the light petroleum gave a forerun of the starting product (5.0 g., 40%) followed by 1-iodo-3,4,4-trimethylpenta-1,2-diene (12 g.,51%) b.p. 62°/5mm. (Found: C, 40.7; H, 5.7; I, 54.1; $C_8H_{13}I$ requires C, 40.7; H, 5.6; I, 53.8%) ν_{max} (I.R.7), 1948m (C=C=C), 1120vs, 825m, 711s cm^{-1}, λ_{max} 207m μ (ε, 18,475), λ_{max} 247m μ (ε, 7171). g.l.c. (silicone oil, 100°) showed only one peak, t, 32.5 min. n.m.r. (n.m.r.6) showed a singlet τ = 8.9, ($\underline{Bu}^{t}C(CH_3)$=C=CH), a doublet centred on τ = 8.23. ($\underline{CH_3}C(Bu^{t})$ = C=CH) J_{CH_3H} = 2.2 c.p.s., and a quartet centred on τ = 4.43 ($CH_3C(Bu^{t})$ =C=C=$\underline{CH}$) J_{H,CH_3} = 2.2 c.p.s.

(b) A similar experiment using concentrated hydriodic acid (60% w/w./ml., 0.2 mole) showed removal of the 3400 cm^{-1} (OH) after only 6 hr. and working up gave an identical product (18g., 76%).

C. Preparation of 1-Bromo alk-1-yn-3-ols.

1. 1-Bromo-3-methylbut-1-yn-3-ol.

An ice cold solution of sodium hypobromite, (made from addition of bromine 84 g., 0.503 mole, to an ice cold solution of sodium hydroxide 63g., 1.5 mole in water 100 ml, and ice 150 g.) was added to 3-methylbut-1-yn-3-ol (42 g., 0.5 mole) stirred at $5^{o}C$, over 4 hr. The mixture was stirred a further 1 hr. whilst being allowed to reach room temperature.

The heavy organic layer was separated, dissolved in ether, washed with water (3 x 50 ml) then dried ($MgSO_4$). Removal of ether under vacuum gave 1-bromo-3-methylbut-1-yn-3-ol (62 g., 76%) ν_{max} 3400vs (-OH), 2220s (-C≡C-) cm^{-1}; g.l.c. (silicone oil, 120°) gave only one peak, t, 3.5 min.

2. 1-Bromo-3-methylpent-1-yn-3-ol.

Sodium hypobromite (from bromine 84 g., 0.503 mole, sodium hydroxide 63 g., 1.5 mole water, 100 ml., and ice 150g) was added to 3-methylpent-1-yn-3-ol (49 g., 0.5 mole) at 5°, over 4 hr., working up in the usual manner gave 1-bromo-3-methylpent-1-yn-3-ol (87 g.,

95%), ν_{max} 3400vs (-OH), 2220s (-C≡C) cm^{-1} g.l.c. (silicone oil, 150°) gave only one peak, t, 3.5 min.

3. <u>1-Bromo-3,4,4-trimethylpent-1-yn-3-ol.</u>

Sodium hypobromite (from bromine 42 g., 0.252 mole, sodium hydroxide 31.5 g., 0.76 mole water 60 ml and ice 130 g) was added to 3,4,4-trimethylpent-1-yn-3-ol (31.25 g., 0.25 mole) at 0° over 4 hr. working up gave 1-bromo-3,4,4-trimethylpent-1-yn-3-ol (37 g., 72%) ν_{max} 3450vs (-OH), 2215s (C≡C) cm^{-1} g.l.c. (silicone oil, 120°), gave only one peak, t, 15.5 min.

4. <u>1-Bromohex-1-yn-3-ol.</u>

Sodium hypobromite (from bromine 25.2 g., 0.15 mole; sodium hydroxide 18.9 g., 0.24 mole; water 20 ml., and ice 50 g.) was added to hex-1-yn-3-ol (14.7 g., 0.15 mole) at 5° over 3 hr., working up gave 1-bromohex-1-yn-3-ol (21.2 g., 80%) ν_{max} 3370s (-OH), 2210s (C≡C) cm^{-1}; g.l.c. (silicone oil, 100°) gave only one peak, t, 4 min.

5. <u>1-Bromo-3-3-diphenylprop-1-yn-3-ol.</u>

Sodium hypobromite (from bromine 16.1 g., 0.1 mole) sodium hydroxide 12.1 g., 0.34 mole,

water, 30 ml., and ice 70 g. was added to 3,3-diphenylprop-1-yn-3-ol over 10 min. at 5°.

After stirring for 5 hr. a semi solid organic layer resulted, on testing this was found to be a mixture of the expected product and starting material. The organic layer was ether extracted (50 ml) and the ether solution recycled with sodium hypobromite (0.1 mole) at $5^{o}C$ stirring being continued over night. Working up in the usual manner gave 1-Bromo-3,3-diphenylprop-1-yn-3-ol (25 g., 86%). ν_{max} 3400s (-OH); 2210m (C≡C); 1640m and 1600m (aromatic C=C) and 1175m, 1000m, 732s, and 700s, (mono substituted benzene) cm^{-1}.

D. Preparation of 1,1-dibromo-alk-1,2-dienes.

1. 1,1-dibromo-3-methylbuta-1,2-diene.

1-Bromo-3-methylbut-1-yn-3-ol (8.15 g., 0.05 mole) in light petroleum ether (20 ml), was added to a stirred suspension of cuprous bromide (3.6 g., 0.025 mole), ammonium bromide (2.0 g., 0.025 mole), copper powder (.2 g) and concentrated hydrobromic acid (45% w/w., 12.4 ml., 0.1 mole) at 5°.

The mixture was stirred at room temperature for 1.5 hr., filtered, and the filtrate extracted with light petroleum ether (2 x 20 ml), evaporation of the solution after drying ($MgSO_4Na_2CO_3$) followed by distillation gave, 1,1-dibromo-3-methylbuta-1,2-diene (7.2 g., 62%) b.p. $34-38^{o}$/.3mm (Found: C, 26.4; H, 2.7; Br, 71.2. $C_5H_6Br_2$ requires C, 26.6; H, 2.7; Br, 70.8%) distillation at higher temperatures leads to some rearrangement.) ν_{max} (I.R.S.), 1960vs (C=C=C), 1013s, 779s, 735vs cm^{-1}; λ_{max} 206m μ, (ε, 13,040); $\lambda_{inf.}$ 215m μ, (ε, 9,990); g.l.c. (silicone oil, 120°) gave only one peak t, 11.3 min.

2. 1,1-dibromo-3-methylpenta-1,2-diene.

1-Bromo-3-methylpent-1-yn-3-ol (8.9 g., 0.05 mole) in light petroleum ether (20 ml)

was added to a stirred suspension of cuprous bromide (3.6 g., 0.025 mole), ammonium bromide (2 g., 0.025 mole) copper powder (0.2 g.) and concentrated hydrobromic acid (60% w/w., 10 ml., 0.125 mole at 5° and stirred for 15 min. at 5° followed by stirring for 45 min. at room temperature.

The mixture was filtered, the filtrate extracted with light petroleum ether (3 x 20 ml) and the organic layer dried ($MgSO_4/Na_2CO_3$). Distillation after first removing the petroleum ether gave 1,1-dibromo-3-methylpenta-1,2-diene (9.5 g., 79%) b.p. $64^{o}/2$ mm (Found: C, 29.7; H, 3.5; Br, 66.8. $C_6H_8Br_2$ requires C, 30.0; H, 3.3; Br, 66.7%) ν_{max} (I.R.9), 1960vs (C=C=C), 740vs cm^{-1}; λ_{max} 206m μ (ε, 13,850); $\lambda_{infl.}$ 215m μ (ε, 10,000); g.l.c. (silicone oil, 120°), gave only one peak, t, 18 min. n.m.r. (n.m.r.7), showed a triplet centred on τ = 8.89 ($^{5}\underline{CH_3}\,^{4}CH_2C(^{6}CH_3)=C=CBr_2$) $J_{5,4}$ 7.3. c.p.s., a triplet centred on τ = 8.0 ($^{6}\underline{CH_3}C(Et)C=C=CBr_2$) $J_{6,4}$ 0.5 c.p.s. and a quartet centred on τ = 7.7 ($^{5}CH_3\,^{4}\underline{CH_2}C(CH_3)C=C=CBr_2$) $J_{4,5}$ 7.3 c.p.s. (should be quartet of quartets but is not resolved).

3. <u>1,1-dibromo-3,4,4-trimethylpenta-1,2-diene.</u>

1-Bromo-3,4,4-trimethylpent-1-yn-3-ol (15.3 g., 0.075 mole) in light

petroleum ether (20 ml) was added to a stirred suspension of cuprous bromide (7.2 g., 0.05 mole), ammonium bromide (4 g., 0.05 mole), copper powder (.5 g) and concentrated hydrobromic acid (60% w/w., 16 ml., 0.2 mole) and the mixture stirred at room temperature for 1 hr. Working up in the usual manner gave 1,1-dibromo-3,4,4-trimethylpenta-1,2-diene (13.9 g., 69%) b.p. 42-44°/0.45 mm. (Found: C, 35.8; H, 4.4; Br, 59.6. $C_8H_{12}Br_2$ requires C, 35.8; H, 4.8; Br, 59.5%) ν_{max} (I.R.10), 1950vs (C=C=C), 1120s, 829s, and 745vs cm^{-1} λ_{max} 206mμ (ε, 16,290) $\lambda_{shoulder}$ 218mμ (ε, 10,000) g.l.c. (silicone oil 120°) gave one main peak, t, 28 min., with a small peak on the trailing edge (less 5%) which may by 1,3-dibromo-3,4,4-trimethylpent-1-yn. n.m.r. (n.m.r.2) showed two peaks τ = 8.85 ($\underline{Bu}^t$ C(CH_3)C=C=CBr_2) and τ = 8.08 ($\underline{CH}_3$C (Bu^t)C C Br_2).

4. <u>1,1-dibromohexa-1,2-diene.</u>

1-Bromohex-1-yn-3-ol (17.7 g., 0.1 mole) in light petroleum ether (20 ml) cuprous bromide (14.4 g., 0.1 mole), ammonium bromide (10 g., 0.125 mole), copper powder (0.5 g.) and concentrated hydrobromic acid

(60% w/w., 40 mls., 0.5 mole) were shaken in an oscillating shaker for 48 hr. then the product worked up in the usual manner giving 1,1-dibromohexa-1,2-diene (7.6 g., 31%) b.p. $35^{o}/2$ mm. (Found: C, 29.5; H, 3.3; Br, 66.6 $C_6H_8Br_2$ requires C, 30.0; H, 3.3; Br, 66.7%) ν_{max} (I.R.11), 1955s (C=C=C), 1199vs, and 835s cm^{-1}; λ_{max} 205m μ (ε, 10,000) $\lambda_{shoulder}$ 215m μ (ε, 7,700) g.l.c. (silicone oil 120°), gave only one peak, t, 6.5 min.

5. <u>1,1-Dibromo-3,3-diphenylprop-1,2-diene.</u>

1-Bromo-3,3-diphenyl prop-1-yn-3-ol (14.35 g., 0.5 mole), in light petroleum (50 ml) was added to an ice cold mixture of cuprous bromide (10.7 g., 0.075 mole), ammonium bromide (4.9 g., 0.05 mole) copper powder (1 g.) and concentrated hydrobromic acid (60% w/w., 20 ml., 0.25 mole) and stirred for 3 hr. Evaporation after first extracting with petroleum ether (3 x 25 ml) and drying ($MgSO_4/Na_2CO_3$) yielded yellow crystals (10.4 g., 60%) which on recrystallisation from light petroleum gave white needles m.p. $91-2^{o}$. (Found: C, 51.2; H, 2.9; Br, 45.6. $C_{15}H_{10}Br_2$ requires C, 51.4; H, 2.9; Br, 45.7%) ν_{max} (I.R.12) 3050vw (aromatic C-H), 1945s (C=C=C), 777s, 740s and 694s cm^{-1} λ_{max} 207m μ (ε, 24,000), λ_{max} 289m μ (ε, 6,000).

Preparation of Deuterated acetylenic alcohols and haloallenes.

1. 1-Deuterobut-1-yn-3-ol.

But-1-yn-3-ol (105 g., 0.15 mole) in dry ether (30 ml) was added over 30 min. to a stirred solution of ethyl magnesium bromide (0.4 mole), made from ethyl bromide (43.6 g., 0.4 mole), magnesium (9.6 g., 0.4 mole) and ether (300 ml.). When addition of the carbinol was complete the suspension was stirred at reflux temperature for 1 hr. before being cooled to 20° when deuterium oxide (18 ml., 0.9 mole) was added over 30 min.

The suspension was again heated to reflux and vigorously stirred for 3 hr. then cooled and decomposed with hydrochloric acid (10 ml., 1;1).

The mixture was filtered, ether extracted (3 x 50 ml), dried ($MgSO_4$) and distilled after first removing ether, giving 1-deuterobut-1-yn-3-ol (8 g., 75%) b.p. $108^{o}/750$ mm.

This was found to be completely deuterated in the 1 position and also had some -OD content which could be removed by treating with dilute acid. ν_{max} (I.R.14), 3400s (-OH), 2610s (-C≡C-D), 2510m (-OD), 1995s (-C≡C-D), cm^{-1} g.l.c. (silicone oil 60°) gave only one peak, t, 6 min. n.m.r.

(n.m.r. 9), showed on a doublet centred on τ = 9.14 ($^4\underline{CH}_3$-^{3}CH.(OH)C≡CD), $J_{3,4}$ c.p.s., a singlet τ = 7.75 (-C-$\underline{OH}$), and a quartet centred on τ = 7.34 ($^4CH_3$ $^3\underline{CH}$(OH)C≡CD), $J_{4,3}$ 3.6 c.p.s.

n.m.r. after shaking with D_2O showed an identical spectrum except for complete removal of the τ = 7.75 (-C-$\underline{OH}$) band.

2. <u>1-Deutero-3-methylpent-1-yn-3-ol.</u>

3-Methylpent-1-yn-3-ol (15 g., 0.15 mole) in dry ether (30 ml) was added over 30 min. to a stirred solution of ethyl magnesium bromide (0.4 mole) (made from ethyl bromide (43.6 g., 0.4 mole). When addition of the carbinol was complete the suspension was stirred at the reflux for 30 min. before being cooled to 20° when deuterium oxide (20 ml., 1 mole) was added over 15 min. The suspension was then vigorously stirred for 3 hr. before being decomposed with hydrochloric acid, (10 ml., 1:1), filtered, ether extracted (3 x 50 ml), and dried ($MgSO_4$).

Distillation after first removing the ether gave 1-deutero-3-methylpent-1-yn-3-ol. (14 g., 87.5%) b.p. 121°/760 mm. This was shown to be completely deuterated in the 1 position by

ν_{max} (I.R.15), 3400vs (-OH), 2600s (-C≡C-D), 1975s (-C≡C-D) g.l.c. (silicone oil 80°) showed only one peak, t, 3.1 min. n.m.r. (n.m.r.10), showed a triplet centred on τ = 8.95 ($^5\underline{CH_3}^4CH_2{}^3D(CH_3)(OH)C{=}CD$) $J_{4,5}$ 6.5 c.p.s.; a singlet τ = 8.52 ($\underline{CH_3}C(C_2H_5)(OH)C{\equiv}CD$); a quartet centred on τ = 8.27 ($^5CH_3{}^4\underline{CH_2}C(CH_3)(OH)C{\equiv}CD$), $J_{5,4}$ 6.5 c.p.s.; and a singlet τ = 7.39 (C-$\underline{OH}$).

3. <u>1-Deutero-3,4,4-trimethylpent-1-yn-3-ol.</u>

3,4,4-Trimethylpent-1-yn-3-ol (20 g., 0.15 mole) was added over 30 min. to a stirred solution of ethyl magnesium bromide (0.4 mole) and after refluxing for 30 min. then cooling deuterium oxide (20 ml., 1 mole) was added. Working up after stirring for 3 hr. gave 1-deutero-3,4,4-trimethylpent-1-yn-3-ol (18 g., 85.7%) b.p. 142°/760 mm. This was shown to be completely deuterated in the 1 position by ν_{max} (I.R.16) 3450m (-OH); 2600s (C≡C-D); 1960m (-C≡C-D) cm^{-1} g.l.c. (silicone oil 100°) showed only one peak, t, 6.3 min.; n.m.r. (n.m.r.11) showed a singlet τ = 9.38 ($\underline{Bu^t}C(CH_3)(OH)C{\equiv}CD$), a singlet τ = 9.15 ($\underline{CH_3}C(Bu^t)(OH)C{\equiv}CD$); and a singlet τ = 8.81 (C-$\underline{OH}$).

4. <u>1-Deutero-1-iodobuta-1,2-diene.</u>

Triphenylphosphite methiodide (60 g., 0.14 mole) was dissolved in dry N,N-dimethyl formamide (66 ml.) and stirred at 80° when 1-deuterobut-1-yn-3-ol (7.1 g., 0.1 mole) was added, the mixture was stirred at 80° for 40 min. and then about 35 ml. liquid was distilled off at reduced pressure (ca.20 mm). This distillate was added to water (100 ml) when a heavy oil separated; the mixture was ether extracted (3 x 25 ml) and the combined ether layers washed with water (12 x 40 ml) to remove any N,N-dimethyl-formamide, the etherial solution was dried ($MgSO_4$) and evaporated giving 98% pure 1-deutero-1-iodbuta-1,2-diene (7.3 g., 40%) ν_{max} (I.R.18), 2,300m (=C<D/I); 1950s (C=C=C); 900m and 820s (C-D inplane deformation); and 790s cm^{-1} g.l.c. (silicone oil 80°) showed only one peak, t, 9 min. n.m.r. (n.m.r.12), showed a doublet centred on τ = 8.93 ($\underline{CH_3}$CH=C=CDI), $J_{CH_3,H}$ 4.2 c.p.s.; and a quartet centred on τ = 6.99 ($CH_3\underline{CH}$=C=CDI), J_{H,CH_3} 4.3 c.p.s.

5. <u>1-Bromo-1-deutero-3-methylpenta-1,2-diene.</u>

1-Deutero-3-methylpent-1-yn-3-ol (4 g., 0.04 mole) was added to a mixture

of cuprous bromide (2.1 g., 0.014 mole), ammonium bromide (1.7 g., 0.017 mole) copper powder (0.2 g.) and concentrated hydrobromic acid (48% w/w., 10.5 ml., 0.088 mole) and stirred vigorously at room temperature for 25 min. when the infra-red spectrum of a small sample showed complete absence of the 3400m (-OH) bond. The mixture was filtered and separated, the aqueous portion being extracted with light petroleum, the organic layers were combined and washed with concentrated hydrobromic acid (45% w/w., 10 ml) and dried ($MgSO_4/Na_2CO_3$). Distillation after first removing the petrol gave 1-bromo-1-deutero-3-methylpenta-1,2-diene (4 g., 62%) b.p. $60^o/30$ mm. ν_{max} (I.R.20), 2300w (≡C-D); 1950s (C=C=C); 955s; 870s (-C=C-D in plane deformation) and 7.5 m cm^{-1} g.l.c. (silicone oil 82°) showed one main peak, t, 15 min, n.m.r. (n.m.r.13) showed a triplet centred on τ=8.94 ($^5\underline{CH_3}^4CH_2C(CH_3)=C=CDBr$) $J_{4,5}$ 7.5 c.p.s.; a singlet τ = 8.14 ($\underline{CH_3}C(C_2H_5)=C=CDBr$; and a quartet centred on τ = 7.87 ($^5CH_3{}^4\underline{CH_2}C(CH_3)=C=CDBr$), $J_{5,4}$ 7.5 c.p.s.

6. <u>1-Chloro-1-deutero-3,4,4-trimethylpenta-1,2-diene.</u>

1-Deutero-3,3,4-trimethylpent-1-yn-3-ol (6.3 g., 0.05/ mole) and thionyl

chloride (8.3 g., 0.07 mole, purified by Cottle's method) were dripped slowly and simultaneously into dry refluxing dioxon (150 ml.) After addition was complete the mixture was stirred for two min. then cooled to room temperature before adding dry pyridine (7.9 ml.). The suspension was stirred for 30 min. then ether (300 ml) was added, the suspension was filtered washed with 2.5 N hydrochloric acid (5 x 100 ml), then 2N sodium bicarbonate solution (2 x 20 ml), finally with water (5 x 100 ml) then dried ($MgSO_4$). Distillation after first removing the ether gave 1-chloro-1-deutero-3,4,4-trimethylpenta-1,2-diene (4.8 g., 31%) b.p. 145.50°/760 mm.

The product was contaminated with the acetylenic impurity 3-chloro-1-deutero-3,4,4-trimethylpent-1-yne, in quantities which grew less as distillation proceeded, the purest cut contained only 2% of this acetylenic impurity. ν_{max} (I.R.22), 2310w (C≡C-D), 1950s (C=C=C); 890vs (-CD in plane deformation); 710vs (C-Cl) cm^{-1}; g.l.c. (silicone oil 120°), showed one main peak, t, 21 min. and another peak (less than 3%) t, 117 min. (the acetylenic impurity). N.m.r. (n.m.r. 14), showed a singlet τ = 9.36 ($\underline{Bu}^tC(CH_3)=C=CDCl$), and a singlet τ = 8.93 ($Bu^tC(\underline{CH_3})=C=CDCl$).

Preparation of 1-cyanoallenes from acetylenic carbinols.

1. 1-Cyano-3-methylbuta-1,2-diene.

Cuprous cyanide (30 g., 0.3 mole), potassium cyanide (13g., 0.2 mole), copper powder (0.5 g.) and 3-methylbut-1-yn-3-ol (17 g., 0.2 mole) were placed in a flask fitted with mechanical stirrer and dropping funnel, and stirred until a cream-like consistency was obtained. The flask was then surrounded by an ice-bath, and concentrated hydrobromic acid (45% w/w., 62 ml., 0.5 mole) was added dropwise over 45 min; the flask was left in the gradually warming bath whilst the contents were stirred for 76 hr., when saturated sodium bicarbonate solution (150 ml.) was added. The mixture was filtered, the solid washed with ether and the filtrate extracted with ether (4 x 30 ml.) the etherial solutions were combined and washed with water (2 x 15 ml.) then dried ($MgSO_4/Na_2CO_3$). Distillation after first removing the ether gave a forerun of 3-methylpent-1-yn-3-ol (2.5 g. 14.7%) b.p. $35^{o}/14$ mm ν_{max} 3400s (-OH); 3300s (-C≡CH); 2100w (-C≡C-) cm^{-1} followed by 1-cyano-3-methyl-penta-1,2-diene (5.5 g., 30%) b.p. $50-55^{o}/10$ mm. (Found:

C, 77.3; H, 7.7; N, 15.1. C_6H_7N requires C, 77.4; H, 7.6; N, 15.0%) ν_{max} (I.R.23) 2245vs (-CN), 1950vs (C=C=C); and 790 cm^{-1} λ_{max} 207m μ (ε, 10,000); g.l.c. (dinonylphthalate, 120°) showed only one peak, t, 10 min. n.m.r. showed a doublet τ = 8.2. $((^4\underline{CH_3})_2\overset{3}{C}=\overset{2}{C}=\overset{1}{C}HCN)$ $J_{4,1}$ 3 c.p.s., and a heptet τ = 5.1. $((CH_3)_2C=C=\underline{C}HCN)$ $J_{1,4}$ 3 c.p.s.

2. <u>1-Cyano-3-methylpenta-1,2-diene.</u>

Cuprous cyanide (30 g., 0.3 mole), potassium cyanide (13 g., 0.2 mole), copper powder (0.5 g.) and 3-methylpent-1-yn-3-ol (20 g., 0.2 mole), were mixed together and cooled as before and concentrated hydrobromic acid (45% w/w., 62 ml., 0.5 mole) added over 45 min. stirring being continued for 67 hr. The reaction mixture was worked up as previously described when distillation gave a forerun of 3-methylpent-1-yn-3-ol (2 g., 10%) b.p. 30°/6 mm ν_{max} 3400s (-OH); 3300s (-C=CH); 2100w (-C=C-) cm^{-1} followed by 1-cyano-3-methylpenta-1,2-diene (11 g., 51%) b.p. 54-55°/6 mm (Found: C, 77.3; H, 8.4; N, 13.1; C_7H_9N required C, 78.5; H, 8.5; N, 13.1%) ν_{max} (I.R.24) 2245s (-CN); 1955s (C=C=C); 760m, and 790m cm^{-1}; λ_{max} 207m μ (ε, 10,100) g.l.c. (dinenylphthalate, 120°) gave only one peak, t, 19 min.

n.m.r. (N.R.M.15), showed a triplet centred on τ = 8.92 ($^{5}\underline{CH_3}^{4}CH_2{}^{3}C(^{6}CH_3)$=C=CHCN), $J_{5,4}$ 7 c.p.s.; a doublet centred on τ = 8.18 ($^{6}\underline{CH_3}C(Et)C$=C=CHCH), $J_{6,1}$ c.p.s. a quartet of doublets centred on τ = 7.88 ($^{5}CH_3{}^{4}\underline{CH_2}C(CH_3)$=C=CHCN), $J_{4,5}$ 7 c.p.s., $J_{4,1}$ 3 c.p.s.; and a sextet centred on τ = 4.9 ($CH_3CH_2C(CH_3)$=C=$\underline{C}$HCN), $J_{1,4}$ = 3 c.p.s. $J_{1,6}$ = 3 c.p.s.

3. <u>1-Cyano-3-ethylpenta-1,2-diene.</u>

Cuprous cyanide (30 g., 0.3 mole) potassium cyanide (13 g., 0.2); copper powder (0.5 g.) and 3-ethylpent-1-yn-ol (22.4 g., 0.2 mole) were mixed together and cooled as before and concentrated hydrobromic acid (45% w/w., 62 ml., 0.5 mole) was added over 45 min., stirring being continued for 76 hrs. The reaction mixture was worked up as previously described when distillation gave a forerun of 3-ethylpent-1-yn-3-ol (2 g., 9.5%) b.p. 30°/5 mm ν_{max} 3400s (-OH), 3300s (-C=CH), 2100w (-C≡C-) cm^{-1}, followed by 1-cyano-3-ethylpenta-1,2-diene (17 g., 75%) b.p. 71°/5mm (Found: C, 79.2; H, 9.2; N, 11.6. $C_8H_{11}N$ requires C, 79.3; H, 9.2; N, 11.6%); ν_{max} (I.R.25), 2240vs

(-CN), 1955vs (C=C=C), and 790s cm^{-1}; λ_{max} 207m μ (ε, 10,140); g.l.c. (dinonylphthalate, 120°) showed only one peak, t, 30 min. n.m.r. (n.m.r.16) showed a triplet centred on τ = 8.9 ($^5\underline{CH}_3{}^4CH_2)_2$ C=C=CHCN), $J_{4,5}$ = 7 c.p.s.; a quartet of doublets centred on τ=7.9 ($^5CH_3{}^4\underline{CH}_2$) C=C=$\overset{1}{C}$HCN), $J_{4,5}$ = 7 c.p.s., $J_{4.1}$ = 3.5 c.p.s. and a pentet centred on τ = 4.75, (Et_2C=C=$\underline{CH}$CN), $J_{1,4}$ = 3.5 c.p.s.

4. <u>1-Cyano-3-4,4-trimethylpenta-1,2-diene.</u>

Cuprous cyanide (30 g., 0.3 mole), potassium cyanide (13 g., 0.2 mole), copper powder (0.5 g) and 3,4,4-trimethylpent-1-yn-3-ol (25.2 g., 0.2 mole) were mixed together and cooled as before and concentrated hydrobromic acid (45% w/w., 62 ml., 0.5 mole) was added over 45 min., stirring being continued for 90 hrs. The reaction mixture was worked up as previously described when distillation gave 3,4,4-trimethylpent-1-yn-3-ol (15 g., 60%) b.p. 60°/28 mm. ν_{max} 3400s (-OH), 3300s (-C≡CH), 2100w (-C≡C-) cm^{-1}. followed by 1-cyano-3,4,4-trimethylpenta-1,2-diene (3.3 g., 25%) b.p. 75°/9 mm (Found: C, 79.8; H, 9.6; N, 10.3. $C_9H_{13}N$ requires C, 79.9; H, 9.7; N, 10.4%); ν_{max} (I.R.27), 2250s (-CH), 1960s (C=C=C), and

765m cm^{-1}; λ_{max} 207m μ (ε, 10,000); g.l.c. (dinonylphthalate 120°) gave only one peak, t, 24 min. n.m.r. (n.m.r. 17) showed a singlet τ = 8.8 ($\underline{Bu}^t$ C(Me)=C=CHCN); a doublet centred on τ = 8.25 (Bu^t C($\underline{Me}$)=C=CHCN) $J_{4,1}$ = 3 c.p.s. and a quartet centred on τ = 4.83 (Bu^tD(Me)=C=$\underline{CH}$CN), $J_{1,4}$ = 3 c.p.s.

5. <u>1-Cyano-3,5-dimethylhexa-1,2-diene.</u>

Cuprous cyanide (30 g., 0.3 mole), potassium cyanide (13 g., 0.2 mole) copper powder (0.5 g.) and 3,5-dimethylhex-1-yn-3-ol (25.2 g., 0.2 mole) were mixed and cooled as before and concentrated hydrobromic acid 45% w/w., 62 ml., 0.5 mole) was added over 45 min. and stirring continued for 72 hrs.

The reaction mixture was worked up as previously described when distillation gave a forerun of 3,5-dimethylhex-1-yn-3-ol (64 g., 25%) b.p. 52°/15 mm. ν_{max} 3400s (-OH), 3300s (-C≡CH) and 2100w (-C≡C-) cm^{-1}; followed by a mixture of 1-bromo-3,5-dimethylhex-1,2-diene and 1-cyano-3,5-dimethylhexa-1,2-diene b.p. 55°/6-7 mm ν_{max} 2245m (-CN), 1960s (C=C=C) cm^{-1} g.l.c. (dinonylphthalate, 120°) gave two peaks in ratio 1:2, t, 20 min. (1-bromo-3,5-dimethylhexa-

1,2-diene) and t, 46 min. (1-cyano-3,5-dimethylhexa-1,2-diene); both compounds were proved by g.l.c. with admixtures of authentic compounds. The third fraction was pure 1-cyano-3,5-dimethylhexa-1,2-diene (10.8 g., 40%) b.p. 60-65°/1mm (Found: C, 79.8; H, 9.5; N, 10.3. $C_9H_{13}N$ requires C, 79.9; H, 9.7; N, 10.4%) ν_{max} (I.R.26), 2245 (=CN), 1960s (C=C=C), and 765m cm^{-1}; λ_{max} 207m μ (ε, 10,150) g.l.c. (dinonylphthalate, 120°) gave only one peak, t, 46 min.

Preparation of 1-cyanoallenes using 1-bromoallenes and cuprous cyanide (no solvent).

1-Cyano-3,4,4-trimethylpenta-1,2-diene.

1-Bromo-3,4,4-trimethylpenta-1,2-diene (37.8 g., 0.2 mole) and anhydrous cuprous cyanide (20 g., 2.2 mole) were stirred together at 115° for 3½ hours. The mixture was allowed to cool, ether (30 ml) added to precipitate any copper salts, and then filtered. Distillation after first removing ether gave 1-cyano-3,4,4-trimethylpenta-1,2-diene (16.5 g., 61%) b.p. 70-4°/7-8mm. (Found: C, 79.8; H, 9.6; N, 10.3. $C_9H_{13}N$ requires C, 79.9; H, 9.6; N, 10.4%) ν_{max} (I.R.27), 2250s (-CN), 1960s (C=C=C) and 765m cm^{-1}; λ_{max} 207m μ (ε, 10,000). g.l.c. (dinonylphthalate 120°) gave only one peak, t, 24 min.

1-Cyano-3-tertbutyl-4,4-dimethylpenta-1,2-diene.

1-Bromo-3-tert-butyl-4,4-dimethylpenta-1,2-diene (9.5 g., .041 mole) and anhydrous cuprous cyanide (5.0 g., 055 mole) were stirred together at 125° for 2 hrs. The mixture was allowed to cool, ether added to precipitate copper salts and filtered. Distillation after first removing the ether gave 1-cyano-3-

terbutyl-4,4-dimethylpenta-1,2-diene (6.2 g., 86%) b.p. 92-4°/0.4mm. (Found: C, 81.8; H, 10.7; N, 7.5; $C_{12}H_{19}N$ requires C, 81.3; H, 10.8; N, 7.9%) ν_{max} (I.R.30), 2235s (-CN), 1970w, 1945s (C=C=C), and 760 cm^{-1}; λ_{max} 207m μ (ε, 11,050), g.l.c. (silicone oil 152°) gave only one peak, t, 40 min. n.m.r. (n.m.r.18), showed two singlets τ = 8.75 ($\underline{Bu}^t{}_2C{=}C{=}CHCN$) and τ = 4.83 ($Bu^t{}_2C{=}C{=}CHCN$).

Preparation of 1-cyanoallenes from 1-bromoallenes using N,N-dimethylformamide solvent

1-Cyano-3-methylbuta-1,2-diene.

Anhydrous cuprous cyanide (45 g., 0.5 mole) was added to dry N,N-dimethylformamide (120 ml) and 1-bromo-3-methylbuta-1,2-diene (49 g., 0.33 mole) was added slowly so the temperature did not rise above 35° and the mixture stirred at 35-40 for 2 hrs. allowed to cool and ether (50 ml) added. The solution was then slowly added to vigorously stirred water (500 ml) the resulting suspension was stirred until the solid was no longer sticky then allowed to settle. After filtration the aqueous solution was extracted with ether (4 x 30 ml), the solid was stirred with ether (3 x 20 ml) and the suspension filtered. Distillation, after drying the combined ethereal solutions and removing ether gave 1-cyano-3-methylbuta-1,2-diene (12.5 g., 40%) b.p. $55^{o}/9$ (Found: C, 77.3; H, 7.7; N, 15.1; C_6H_7N requires C, 77.4; H, 7.6; N, 15.0%) ν_{max} (I.R.23), 2245vs (-CN), 1950s (C=C=C), and 790 cm^{-1} λ_{max} 207m μ (ε, 10,00); g.l.c. (dinonylphthalate 120°) showed only one peak, t, 10 min.

1-Cyano-3-methylpenta-1,2-diene.

Anhydrous cuprous cyanide (45 g., 0.5 mole) was added to dry N,N-dimethylformamide (120 ml.) and the mixture stirred at 55-60° when 1-bromo-3-methylpenta-1,2-diene (54 g., 0.33 mole) was added over 5 min. The mixture was stirred at 53-60° for 2 hrs., allowed to cool and ether (100 ml) added; working up after pouring into vigorously stirred water (1000 ml) gave 1-cyano-3-methylpenta-1,2-diene (18 g., 51%) b.p. 55°/16mm. (Found: C, 77.3; H, 8.4; N, 13.1. C_7H_9N requires C, 78.5; H, 8.5; N, 13.0%) ν_{max} (I.R.24), 2245s (-CN); 1955s (C C C); 760m and 790cm^{-1}; g.l.c. dinonylphthalate, 120°) gave only one peak, t, 19 min. n.m.r. (n.m.r.15).

1-Cyano-3-ethylpenta-1,2-diene.

Anhydrous cuprous cyanide (65 g., 0.7 mole) was added to dry N,N-dimethylformamide (200 ml) and the mixture stirred at 55-60° when 1-bromo-3-methylpenta-1,2-diene (58.2 g 0.33 mole) was added over 5 min.

The mixture was stirred at 55-60° for 2 hrs. cooled and ether (100 ml) added. The solution was then slowly poured into vigorously stirred water (1000 ml), filtered ether

extracted (3 x 100 ml), the ethereal solution washed with water (12 x 100 ml) and dried ($MgSO_4$).

Distillation after first removing the ether gave 1-cyano-3-ethylpenta-1,2-diene (25 g., 60%) b.p. $65^o/7$ mm. (Found C, 79.2; H, 9.2; N, 11.6. $C_8H_{11}N$ requires C, 79.3; H, 9.2; H, 11.6%) ν_{max} (I.R.25) 2240s (-CN); 1955s (C=C=C); and 790 cm^{-1}; g.l.c. (dinonylphthalate 120°) showed only one peak, t, 30 min. n.m.r. (n.m.r.16).

<u>1-Cyano-3,5-dimethylhexa-1,2-diene.</u>

Anhydrous cuprous cyanide (4.50 g., 0.5 mole) was added to dry N,N-dimethylformamide (150 ml) and the mixture stirred at $55-60^o$ when 1-bromo-3,5-dimethylhexa-1,2-diene (25 g., 0.2 mole) was added over 5 min. The mixture was stirred at $55-60^o$ for 2 hrs., cooled, ether added (100 ml), the solution slowly drowned into vigorously stirred water (1000 ml), filtered, ether extracted (3 x 100 ml), the etherial solution was washed with water (10 x 100 ml) then dried ($MgSO_4$), Distillation after first removing the ether gave 1-cyano-3,5-dimethylhexa-1,2-diene (12.8 g., 50%) b.p. $65-70^o/2$ mm. (Found: C, 79.9; H, 9.6; N, 10.3, $C_9H_{13}N$ requires C, 80.0; H, 9.7; N, 10.4%). ν_{max} (I.R.26), 2250s (-CN), (C=C=C), and 760 cm^{-1} g.l.c. (dinonylphthalate, 120°) gave only one peak, t, 45 min.

1-Cyano-3,4,4-trimethylpenta-1,2-diene.

Anhydrous cuprous cyanide (45 g., 0.5 mole) was added to dry N,N-dimethylformamide (150 ml) and the mixture heated to 55-60° when 1-bromo-3,4,4-trimethylpenta-1,2-diene (25 g., 0.2 mole) was added over 5 min. The mixture was stirred at 55-60° for 2 hrs., cooled, ether (100 ml) added, drowned in vigorously stirred water (1000 ml), filtered, ether extracted (3 x 100 ml), the ethereal solution washed with water (10 x 100 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3,4,4-trimethylpenta-1,2-diene (15.5 g 65%), b.p. 80°/mm. (Found: C, 79.8; H, 9.6; N, 10.3. $C_9H_{13}N$ requires C, 79.9; H, 9.7; N, 10.4%) ν_{max} (I.R.27) 2240s (-CN), 1955s (C=C=C), and 770 cm^{-1}, g.l.c. (dinonylphthalate 120°) showed only one peak, t, 34 min.

1-Cyano-4-methyl-3-isopropylpenta-1,2-diene.

Anhydrous cuprous cyanide (12 g., 0.13 mole) was added to dry N,N-dimethylformamide (75 ml) and heated to 50-55° when 1-bromo-4-methyl-4-isopropylpenta-1,2-diene (20.3 g., 0.1 mole) was added over 5 min. The mixture was heated at 50-55° for 3 hrs., cooled, ether (30 ml) added, the solution drowned into

vigorously stirred water (500 ml), filtered, ether extracted (3 x 100 ml.), the etherial solution washed with water (10 x 100 ml) and dried ($MgSO_4$). Distillation after first removing ether gave 1-cyano-4-methyl-3-isopropylpenta-1,2-diene (9.1 g., 61%) b.p. $80^o/5$mm. (Found: C, 80.4; H, 10.0; N, 9.4; $C_{10}H_{15}N$, requires C, 80.5; H, 10.1; N, 9.4%) ν_{max} (I.R.28), 2250s (-CN); 1955s (C=C=C) and 770 cm^{-1}, λ_{max} 208mμ (ε, 10,880) g.l.c. (dinonylphthalate, 120°) gave only one peak, t, 30 min.

<u>1-Cyano-3-isobutyl-5-methylhexa-1,2-diene.</u>

Anhydrous cuprous cyanide (9 g., 0.1 mole) was added to dry N,N-dimethylformamide (30 ml) and heated to $55-60^o$ when 1-bromo-3-isobutyl-5-methylhexa-1,2-diene (11.6 g., 0.05 mole) was added over 5 min. The mixture was stirred at $55-60^o$ for 2 hrs., cooled, ether (10 ml) added and the solution drowned into vigorously stirred water (200 ml), filtered, ether extracted (3 x 50 ml), the etherial layer was washed (6 x 50 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3-isobutyl-5-methylhexa-1,2-diene (5.5 g. 60%) b.p. $80^o/2.6$ mm. (Found: C, 80.8; H, 10.6; N, 8.8; $C_{12}H_{19}N$ requires C, 81.3;

H, 10.8; N, 7.9%) ν_{max} (I.R.29), 2250s (-CN); 1980s (C=C=C) and 760 cm^{-1}; λ_{max} 207m μ (ε, 11,010); g.l.c. (dinonylphthalate 120°) showed only one peak, t, 132 min.

1-Cyanopropa-1,2-diene.

Anhydrous cuprous cyanide (9 g., 0.1 mole) was added to dry N,N-dimethylformamide (50 ml.) and the mixture heated to 40-45° when 1-iodopropa-1,2-diene. 3-iodopropyne (70:30) (16.6 g., 0.1 mole) was added over 2 minutes and the mixture stirred at 40° for 1½ hr., cooled, ether added and the solution drowned into vigorously stirred water (500 ml), filtered ether extracted (4 x 30 ml), the etherial solution washed with water (10 x 100 ml) and dried. Distillation after first removing the ether gave a mixture of 1-cyanopropa-1,2-diene and 3-cyanoprop-1-yne (2.1 g., 30%). (Found: C, 74.0; H, 4.6; N, 21.3. C_4H_3N requires C, 73.9; H, 4.6; N, 21.5%) ν_{max} 3300m (C≡CH), 2225s (CN), 1900m cm^{-1}. N.m.r. showed a doublet τ = 5.4 (=CH_2) $J_{CH_2,H}$ = 6 c/sec., a triplet τ = 4.3 (=CHCN) J_{H,CH_2} = 6 c/sec. A triplet at τ = 5.6 (≡CH) J_{H,CH_2} = 6 c/sec. and a doublet 7.5 ($CNCH_2$) $J_{CH_2,H}$ = 6 c/sec. indicated the presence of propargyl cyanide, planimetric measurements indicates that the ratio of allene to a cetylene was 7:3. Attempts to remove

the acetylene by washing with silver nitrate solution were unsuccessful.

1-Cyanobuta-1,2-diene.

Anhydrous cuprous cyanide (45 g., 0.5 mole) was added to dry N,N-dimethylformamide (200 ml) and the mixture heated to 40-45° when 1-bromobuta-1,2-diene (40 g., 0.3 mole) was added over 5 minutes and the mixture stirred at 40-45° for 2 hr., cooled, ether (70 ml) added, the solution drowned into vigorously stirred water (1000 ml), filtered, ether extracted (3 x 100 ml), the etherial solution washed with water (10 x 100 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyanobuta-1,2-diene (14.7 g., 55%) b.p. 100°/760 mm. (Found: C, 76.2; H, 6.1; N, 17.5; C_6H_7N requires C, 76.0; H, 6.3; N, 17.7%) ν_{max} 2225s (CN); 1965s (C=C=C) 860m and 730cm^{-1}. λ_{max} 207mμ (ε, 9,730). g.l.c. (silicone oil 60°) showed only one peak, t, 4 min.

1-Cyanopenta-1,2-diene.

Anhydrous cuprous cyanide (45 g., 0.5 mole) was added to dry N,N-dimethylformamide (200 ml) and the mixture heated to 45-50° when 1-bromopenta-1,2-diene (44.1 g.,

0.3 mole) was added over 5 min. and the mixture stirred at 45.50° for 2 hr. cooled, ether (70 ml) added, the solution drowned into vigorously stirred water (1000 ml)filtered ether extracted (3 x 100 ml), the etherial solution washed with water (10 x 100 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyanopenta-1,2-diene (15.4 g., 55%), b.p. 40°/5-6mm. (Found: C, 77.2; H, 7.5; N, 14.9. C_6H_7N requires C, 77.4; H, 7.6; N, 15.0%) ν_{max} 2220s (CN) 1950s (C=C=C); 865m and 725m. cm^{-1} λ_{max} 207m μ (ε, 11,100). g.l.c. (silicone oil 120°) showed only one peak, t, 8 min.

<u>1-Cyanohexa-1,2-diene.</u>

Anhydrous cuprous cyanide (8.9 g. 0.1 mole) was added to dry N,N-dimethylformamide (50 ml) and heated to 50-55° when 1-bromohexa-1,2-diene (8 g. 0.05 mole) was added, the mixture was stirred at 50-55° for 3 hrs. cooled, ether (20 ml) added and the solution was drowned into vigorously stirred water (200 ml) filtered, ether extracted (3 x 50 ml) the etherial layer washed with water (10 x 50 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyanohexa-1,2-diene (3 g., 60%) b.p. 80°/15 mm. (Found: C, 78.8; H, 8.6; N, 12.6. C_7H_9N requires C, 78.5; H, 8.5; N, 13.0%) ν_{max} (I.R.31), 2255s (-CN); 1970s (C=C=C),

and 730 cm^{-1} λ_{max} 207mμ (ε, 9,000); g.l.c. (dinonylphthalate, 120°) showed only one peak, t, 16 min.

1-Cyano-4-methylpenta-1,2-diene.

Anhydrous cuprous cyanide (9.8 g., 0.11 mole) was added to dry N,N-dimethylformamide (40 ml) and heated to 60° when 1-bromo-4-methylpenta-1,2-diene (13 g., 0.075 mole) was added. The mixture was stirred at 60° C for 2 hrs. cooled, ether (15 ml) added, filtered, ether extracted (3 x 50 ml), the etherial layer was washed with water (7 x 50 ml) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-4-methylpenta-1,2-diene (4.4 g., 55%) b.p. 75°/20 mm. (Found: C, 78.3; H, 8.4; H, 13.0. C_7H_9N requires C, 78.5; H, 8.5; N, 13.1%) ν_{max} (I.R.32), 2250s (-CN); 1965s (C=C=C); 870s and 740s cm^{-1} λ_{max} 208mμ (ε, 8,600); g.l.c. (dinonylphthalate, 120°) gave only one peak, t, 12 min.

1-Cyano-3-phenylpropa-1,2-diene.

Anhydrous cuprous cyanide (22.5 g., 0.25 mole) was added to dry N,N-dimethylformamide (75 ml) and the mixture stirred at room temperature when 1-bromo-3-phenylpropa-1,2-diene (19.5 g., 0.1 mole) was added over 5 min.

The mixture becomes warm and was cooled to 5°, stood in a cool place for 15 min. ether (20 ml.) added, the solution drowned into vigorously stirred water (500 ml), decanted through a filter, the filtrate ether extracted (3 x 20 ml), the etherial solution washed with water (10 x 100 ml) and dried ($MgSO_4$). Evaporation gave a brown oil which was found to be 1-cyano-3-phenylpropa-1,2-diene (10.5 g., 74%) ν_{max} (I.R.33) 3310 m (aromatic CH), 2250s (CN), 1955m (C=C=C), 1680, (C=C impurity), 1630, 1600m (aromatic C=C), 1500s, 1450s, 695vs cm., λ_{max} 209m μ, (ε, 14,800); 244m μ (ε,7,860); 272m μ, (ε, 5,170), 283m μ, (ε, 5,180).

Cyclobutane Dimers of 1-Cyanoallenes.

1. 1-Cyano-3-cyanomethylene-4,4-dimethyl-2-isopropylidene-cyclobutane.

1-Cyano-3-methylbuta-1,2-diene was allowed to stand for about 6 - 8 weeks in a cool place, after which time crystals formed. The crystals were washed with, then recrystallised from light petroleum ether, giving white needles m.p. 85° (Found: C, 77.5; H, 7.6; N, 14.9. $C_{11}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%); ν_{max} (I.R.34), 2252s (CN): 2235s (conj. CN); 1680vs (conj. C=C); 1650vs (conj. C=C-CN) cm^{-1}; λ_{max} 281m μ, (ε, 11,420); dipole moment in benzene solution 3.20 D. n.m.r. (n.m.r.19) shows four singlets τ = 8.68; τ = 8.6; τ = 8.2; τ = 7.75 representing four methyl groups in different surroundings, a doublet τ = 6.6 (C=CN) and a singlet τ = 5.05 (= CH CN).

2. 2-(2'-butylidene)-1-cyano-3-cyanomethylene-4-ethyl-4-methylcyclobutane.

1-cyano-3-methylpenta-1,2-diene was allowed to stand for about 10 weeks in a cool place, during which time the liquid was seen to become very viscous. This viscous liquid was distilled at low pressure giving 2-(2'-butylidene)-1-cyano-3-cyanomethylene-4-ethyl-4-methyl-

cyclobutane, b.p. 180°/1 mm. (Found: C, 79.16; H, 8.1; N, 13.12. $C_{14}H_{18}N_2$ requires C, 78.55; H, 8.4; N, 13.08%) ν_{max} (I.R.35) 2245s (CN); 2220s (conj. CN); 1665vs (conj. C=C); 1630s (conj. C=C-CN); and 800 cm^{-1}; λ_{max} 282mμ, (ε, 18,300).

1 - <u>Cyano-3-cyonomethylene-4,4-diethyl-2-(3'-pentylidene)-cyclobutane.</u>

1-Cyano-3-ethylpenta-1,2-diene was allowed to stand for about 14 weeks in a cool place, during which time the liquid was seen to become very viscous. This viscous liquid was distilled at low pressure and after a forerun of 1-cyano-3-ethylpenta-1,2-diene, gave 1-cyano-3-cyanomethylene-4,4-diethyl-2-(3'-pentylidene)-cyclobutane b.p. 150°/0.5 mm. (Found: C, 79.4, H, 9.1; N, 11.4. $C_{16}H_{22}N_2$ requires C, 79.3; H, 9.1; N, 11.6.) ν_{max} (I.R.36); 2240s (CN); 2215s (conj. CN); 1650s (conj. C=C); (conj. C=C-CN); and 800m cm^{-1} λ_{max} 283mμ, (ε, 17,000) n.m.r. (n.m.r. 20) showed a multiplet τ = 9.0 (methyl groups), a multiplet τ = 7.2 - 8.55 (methylene groups), a doublet τ = 6.56 (CHCN), a singlet τ = 5.14 (C=C<u>H</u>CN) and a singlet τ = 4.75.

ENAMINES FROM ALLENES

1-Cyano-2-(diethylamine)-4-methylpent-1-ene.

Redistilled diethylamine (1.5 g., 0.02 mole) was added slowly with cooling to 1-cyano-4-methylpenta-1,2-diene (1.6 g., 0.015), the mixture was then refluxed gently for 12 min., cooled and excess diethylamine removed by evaporation under reduced pressure. The product was then distilled giving, after a small forerun, pure 1-cyano-2-(diethylamine)-4-methylpent-1-ene (2.4 g., 89%), b.p. 106°/.45mm. (Found: C, 73.3; H, 11.3; N, 15.4. $C_{11}H_{20}N_2$ requires C, 73.3; H, 11.2; N, 15.68%); ν_{max} (I.R.37). 2210s (conj. -CN), 1580vs (C=C-C-CN) 1097m; 720 cm^{-1} λ_{max} 273mμ (ε, 34,300).

1-Cyano-2-(diethylamino)-3-methylbut-2-ene.

Redistilled diethylamine (2.1 g., 0.03 mole) was added slowly with cooling to 1-cyano-3-methylbuta-1,2-diene (1.86 g., 0.02 mole) the mixture was then refluxed gently for 15 min., cooled and excess diethylamine removed by evaporation under reduced pressure. The product was then distilled giving, after a small forerun, pure 1-cyano-2-(diethylamino)-3-methylbut-2-

diene (2.5 g., 74%), b.p. 46°/0.25mm. (Found: C, 72.2; H, 10.7; N, 17.0. $C_{10}H_{18}N_2$ requires C, 72.2; H, 10.9; N, 16.9%) ν_{max} (I.R.38) 2280s (-CN); 1675w (C=C); 900m; 815m; 790m; 740m cm^{-1} λ_{max} 203m μ (ε, 4,820), $\lambda_{infl.}$ 235m μ (ε, 1,160).

<u>1-Cyano-3-methyl-2-piperidinobut-2-diene and 1-cyano-3-methyl-2-piperidinobut-1-ene.</u>

Redistilled piperidine (2 g., 0.024 mole) was added slowly with cooling to 1-cyano-3-methylbuta-1,2-diene (2 g., 0.021 mole), over 5 min. and the mixture stirred at room temperature for 10 min. Excess piperidine was removed by evaporation under reduced pressure. Distillation under reduced pressure gave three fractions;

(i) was shown to be 1-cyano-3-methyl-2-piperidinobut-2-ene (0.3 g., 8%) b.p. 74°/4mm. (Found: C, 74.1; H, 10.1; N, 15.8; $C_{11}H_{18}N_2$ requires C, 74.2; H, 10.1; N, 15.7%); ν_{max} (I.R.39), 2250m (-CN); 1660w (C=C); 740 cm^{-1} λ_{max} 203m μ (ε, 5235), λ_{max} 236m μ (ε, 3,140).

(ii) was shown to be a mixture of 1-cyano-3-methyl-2-piperidinobut-2-ene and 1-cyano-3-methyl-3-piperidinobut-1-ene (0.9 g., 24%); ν_{max} 2250w (-CN); 2205m (conj. - CN); 1606w (C=C); 1580s (C=C-CN); λ_{max} 203m μ (weak), λ_{max} 276m μ (strong)

(iii) was shown to be 1-cyano-3-methyl-3-piperidinobut-1-ene (2.5 g., 66%) b.p. 86-90°/0.38mm. (Found: C, 74.0; H, 10.1; N, 15.8. $C_{11}H_{18}N_2$ requires C, 74.2; H, 10.1; N, 15.7%) ν_{max} (I.R.40) 2205s (conj. CN); 1580vs (C=C=CN); 860m; 750w cm^{-1} λ_{max} 276m μ (ε, 19,750).

<u>2-(n-Butylamino)-1-cyano-3-methylpent-1-ene.</u>

Redistilled n-butylamine (1.5 g., 0.02 mole) was added slowly with cooling to 1-cyano-3-methylpenta-1,2-diene (1.6 g., 0.015 mole), the mixture was then refluxed gently for 5 min., cooled, and excess n-butylamine removed by evaporation under reduced pressure. Distillation gave 2-(n-butylamino)-1-cyano-3-methylpent-1-ene (2.4 g., 80%) b.p. 110-12°/0.2mm. on standing this solidifies m.p. 51-2° (Found: C, 73.6; H, 11.4; N, 15.4. $C_{11}H_{20}N_2$ requires C, 73.3; H, 11.2; N, 15.5%). ν_{max} (I.R.41), 3350m (NH); 3080w (C=CH); 2205vs (conj. CN); 1650w (NH); 1595vs (C=C-CN); 737w cm^{-1} λ_{max} 261m μ (ε, 19,500). n.m.r. (n.m.r.21), was complex, consisting of triplets centred on τ = 9.1 ($\underline{CH_3}$-CH_2) mixed with (N-$CH_2CH_2CH_2$ $\underline{CH_3}$), $J_{CH_3CH_2}$ = 6/c.p.s.; a doublet centred on τ = 8.85 ($\underline{CH_3}$-CH), J_{CH_3H} = 8/c.p.s., a quartet mixed with a triplet τ = 8.3 - 8.75 ($CH_3\underline{CH_2}$ and the β and γ methylenes of the

n-butylamino), a pentet τ = 6.9 - 7.4 (probably the α- methylene of the n-butylamino and the methine), a singlet τ = 6.26 (=C$\underline{H}$ CN) and a broad peak τ = 5.2 - 5.6 (N$\underline{H}$ coupled with the α-methylenes of the n-butylamino)

<u>1-Cyano-2-(diethylamino)-3-methylpent-2-ene and 1-cyano-2-(diethylamino)-3-methylpent-1-ene.</u>

Redistilled diethylamine (3.4 g., 0.06 mole) was added slowly with cooling to 1-cyano-3-methylpenta-1,2-diene (3.5 g., 0.033 mole), the mixture was then refluxed gently for 1 hr., cooled, and the excess diethylamine removed by evaporation under reduced pressure. Distillation gave three fractions:-

(i) was shown to be 1-cyano-2-(diethylamino)-3-methylpent-2-ene (4.2 g., 72%) b.p. 63°/0.2mm. (Found: C, 73.2; H, 11.3; N, 15.4, $C_{11}H_{20}N_2$ requires C, 73.3; H, 11.2, N, 15.5%) ν_{max} (I.R.42), 2250m (-CN); 1650w (C=C) cm^{-1} λ_{max} 204m μ (ε, 5,040). n.m.r. (n.m.r.22) showed two triplet τ = 8.8 - 9.2 ($\underline{CH_3}CH_2$ - C and CH_3CH_2N), J_{CH_3,CH_2} = 7 c.p.s., a singlet (possibly a closely split group) τ = 8.2 ($\underline{CH_3}$- C=), a quartet centred on τ = 7.75 (CH_3CH_2-C) J_{CH_2,CH_3} = 7.5 c.p.s., a quartet of doublets centred on

τ = 7.37 (N $-CH_2$ CH_3) J_{CH_2,CH_3} = 7 c.p.s. (the further splitting of the quartet may be due to partial double bond character of the $^2C-N^1$ bond thus leading to non equivalence of the methylenes of the diethylamine); and a singlet τ = 7.04 ($- CH_2CH$).

(ii) was shown to be a mixture of 1-cyano-2-(diethylamino)-3-methylbut-2-ene and 1-cyano-2-(diethylamino)-3-methylbut-1-ene. (0.4 g., 7%), ν_{max} 2250w (-CN); 2197m (conj.-CN); 1650w (C=C); 1570s (C=C-CN) cm^{-1}; λ_{max} 203m μ (weak) λ_{max} 276m μ (strong).

(iii) was shown to be 1-cyano-2-(diethylamino)-3-methylbut-1-ene (1.1 g., 17%) b.p. 100°/0.2mm; (Found: C, 73.2; H, 11.1; N, 15.6. $C_{11}H_{20}N_2$ requires C, 73.3; H, 11.2; N, 15.6%); ν_{max} (I.R.43), 2197s (conj. -CN); 1570vs (C=C-CN); 785w; 730 cm^{-1} λ_{max} 276m μ (ε, 19,700). n.m.r. (n.m.r.23), showed a triplet centred on τ = 8.95 ($\underline{CH_3}CH_2$-C) J_{CH_3,CH_2} = 7 c.p.s.; a triplet centred on τ = 8.86 ($\underline{CH_3}CH_2N$), J_{CH_3,CH_2} = 7 c.p.s. a doublet centred on τ = 8.64 ($\underline{CH_3}CH$), $J_{CH_3,H}$ = 8 c.p.s; a quartet of doublets centred on τ = 8.2 ($CH_3\underline{CH_2}CH$-) $J_{CH_2CH_3}$ = 7 c.p.s. J_{CH_2H} 2 c.p.s.; a sextet

of doublets centred on τ 7.3 $\begin{pmatrix} CH_3 & \\ & CH-C=CH \\ CH_3CH_2 & \end{pmatrix}$ $J_{H,CH_3} = J_{H,CH_2} =$ 8 c.p.s., $J_{H,H}$ = 2.5 c.p.s. (long range coupling); a quartet centred on τ = 6.75 ($CH_3\underline{CH_2}N$) J_{CH_2,CH_3} 7 c.p.s. and a doublet centred on τ = 6.23 ($CH-C=\underline{CH}CN$) $J_{H,H}$ 2.5 c.p.s. (long range coupling).

<u>1-Cyano-3-methyl-2-pyrrolidinopent-1-ene.</u>

Redistilled pyrrolidine (2.0 g., 0.025 mole) was added slowly to a solution of 1-cyano-3-methylpenta-1,2-diene (2.1 g., 0.02 mole) in dry ether (10 ml.). After the initial vigorous reaction had subsided the solution was refluxed for 1 hr. before removing pyrrolidine by evaporation under reduced pressure. Distillation gave one product, 1-cyano-3-methyl-2-pyrrolidinopent-1-ene (2.9 g., 75%) b.p. 110°/0.2mm. (Found: C, 74.2; H,9.9; N, 15.7. $C_{11}H_{18}N_2$ requires C, 74.1; H, 10.2; N, 15.7%) ν_{max} (I.R.44), 2210vs (conj. -CN); 1575vs (C=C-CN); and 720s cm^{-1} λ_{max} 274m μ, (ε, 22,500).

<u>1-Cyano-3-methyl-2-piperidinopent-1-ene and 1-cyano-3-methyl-2-piperidinopent-2-ene.</u>

Redistilled piperidine (3.51 g., 0.06 mole) was added slowly with cooling to 1-cyano-3-methyl-

penta-1,2-diene (3.5 g., 0.05 mole) after the initial reaction had subsided the mixture was heated on a boiling water bath for 30 min. then excess piperidine was removed by evaporation under reduced pressure. Distillation gave three fractions:

(i) was shown to be 1-cyano-3-methyl-2-piperidinopent-2-ene (0.5 g., 8%) b.p. $79^{o}/3$mm. (Found: C, 74.2; H, 10.2; N, 14.0. $C_{12}H_{20}N_2$ requires C, 75.0; H, 10.5; N, 14.6%) ν_{max} (I.R.45) 2260m (-CN), 1675m (C=C) $cm.^{-1}$ λ_{max} 205m μ (ε, 4,000) λ_{max} 232-3m μ (ε, 2,300).

(ii) was shown to be a mixture of 1-cyano-3-methyl-2-piperidinopent-2-ene and 1-cyano-3-methyl-2-piperidinopent-1-ene (0.2 g., 3%) b.p. $79\text{-}110^{o}/.3$mm ν_{max} 2260m (-CN); 2210s (-conj -CN); 1675w (C=C); and 1580s (C=C-CN) cm^{-1} λ_{max} 205m μ (weak); λ_{max} 277m μ (strong).

(iii) was shown to be pure 1-cyano-3-methyl-2-piperidinopent-1-ene (5 g., 81%) b.p. $110^{o}/0.3$mm (Found: C, 74.9; H, 10.5; N, 14.6. $C_{12}H_{20}N_2$ requires C, 75.0; H, 10.5; N, 14.6%) ν_{max} (I.R.46), 2210vs (conj. -CN); 1580vs (C=C-CN) cm^{-1}, λ_{max} 277m μ, (ε, 18,700). n.m.r. (n.m.r.24). The expected

triplet at $\tau = 9$ ($\underline{CH}_3$-CH-$_2$) is not clear as other bands are present. A doublet, $\tau = 8.7$ ($\underline{CH}_3$-CH-) $J_{CH_3,H} = 7$ c.p.s confirms the methyl split by methine. The expected quartet $\tau = 8.5$ (CH_3-$\underline{CH}_2$ -) J_{CH_2,CH_3} 7 c.p.s. is hidden by the broad envelope due to the β and γ methylenes of the piperidine ring ($\tau = 8.4$), but the intigram clearly shows 8 protons at this point. The methine shows up as a sextet of doublets $\tau = 7.1$ $\begin{matrix}(CH_3 \\ (CH_3CH_2\end{matrix}$ $\underline{CH}$ - C=CH CN) $J_{H,CH_3} = J_{H,CH_2} = 7$ c.p.s. $J_{H,H} = 1.8$ c.p.s. but is partially hidden by the broad envelope of the α-methylenes of the piperidine ring ($\tau = 6.8$) A doublet $\tau = 6.03$ shows the ethylinic hydrogen (CH-C=$\underline{CH}$ CN), $J_{H,H} = 1.8$ c.p.s. split by long range coupling to the methine proton.

<u>2-Amino-1-cyano-3-ethylpent-1-ene.</u>

Anhydrous ammonia gas (obtained by controlled evaporation of anhydrous liquid ammonia) was passed through 1-cyano-3-ethylpenta-1,2-diene (6.0 g., 0.05 mole) at room temperature, after 10 hr. infra-red examination showed little or no reaction had taken place.

The 1-cyano-3-ethylpenta-1,2-diene was then heated to 60-70° and passage of ammonia continued, examination after a further 4 hr. showed complete absence of the allene bond

(1950 cm^{-1}). The reaction mixture was cooled, and distilled giving 2-amino-1-cyano-3-ethylpent-1-ene (4.1 g., 60%) b.p. $90^{o}/0.2mm$. (Found: C, 69.5; H, 10.4; N, 20.1. $C_8H_{14}N_2$ requires C, 69.5; H, 10.2; N, 20.3%) ν_{max} (I.R.47) 3430m, 3350s, 3220m (N- H stretchings); 2200s (conj. - CN); 1645s (NH deformation) and 1585s (C=C-CN) cm^{-1} λ_{max} 261m μ (ε, 18,300). The n.m.r. (n.m.r.25) indicated that the compound was present in the amino (enamine) and the imide forms in a ratio of about 7:1. A multiplet at τ= 9.1 indicated a methyl group split by methylene ($\underline{CH}_3CH_2$-) J_{CH_3,CH_2} = 7 c.p.s. with smaller contributions from a different methylene group. A multiplet τ= 8.5 indicates a quartet of doublets ($CH_3\underline{CH}_2CH$) J_{CH_2,CH_3} = 7 c.p.s. $J_{CH_2,H}$ = 2 c.p.s., the expected pentet split further by long range coupling with the ethylinic proton at τ = 7.2 - 3 is absent, the intigram shows that this could be mixed with the multiple at τ = 8.3. A triplet at τ = 6.2 (CN $\underline{H}$C =C -NH_2) J_{H,NH_2} = 1 c.p.s., a doublet τ = 5.83 (CN H_2C -C=NH) $J_{H,NH}$ = 0.5 c.p.s. and broad humps τ= 5 - 5.5 (NH_2, =NH) intigrate to give the expected 3 protons for the system $-\underset{\underset{NH}{\|}}{C}-CH_2CN \rightleftharpoons \underset{\underset{NH_2}{|}}{C} = CHCN$

1-Cyano-2-(diethylamino)-3-ethylpent-2-ene.

Redistilled diethylamine (2.85 g., 0.04 mole) was added slowly with cooling to 1-cyano-3-ethylpenta-1,2-diene (4 g., 0.034 mole) after the initial vigorous reaction was completed the mixture was heated on a boiling water bath for 15 min., cooled and excess diethylamine removed by evaporation under reduced pressure. Distillation gave 1-cyano-2-(diethylamino)-3-ethylpent-2-ene (5 g., 70%) b.p. $58^{o}/0.2$mm. (Found: C, 74.2; H, 11.2; N, 14.6. $C_{12}H_{22}N_2$ requires C, 74.2; H, 11.4; N, 14.4%) ν_{max} (I.R.48) 2250m (-CN), 1650w (C=C) cm^{-1} λ_{max} 204mμ, (ε, 6,640). A later fraction indicated that a small quantity of 1-cyano-2-(diethylamino)-3-ethylpent-1-ene had been formed (UV showed a small hump at 274mμ and I.R. indicated conjugated CN (2200 cm^{-1}) but the quantity was too small to isolate pure.

1-Cyano-3-ethyl-2-piperidinopent-1-ene.

Redistilled piperidine (3.4 g., 0.04 mole) was added slowly with cooling to 1-cyano-3-ethylpenta-1,2-diene (4 g., 0.034 mole) after the initial reaction had subsided the mixture was heated on a boiling water bath for 30 min., cooled and the excess piperidine was

removed by evaporation under reduced pressure. Distillation gave 1-cyano-3-ethyl-2-piperidinopent-1-ene (6 g., 81%) b.p. 125°/0.1mm. (Found: C, 74.8; H, 10.7; N, 14.4. $C_{13}H_{22}N_2$ requires C, 75.7; H, 10.8; N, 13.6%) ν_{max} (I.R.49), 2210s (conj. CN), 1575vs (C =C-CN) cm^{-1}. λ_{max} 276m μ, (ε, 23,700).

<u>1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinolino)-pent-1-ene</u>
<u>1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinolino)-pent-2-ene.</u>

Redistilled 1,2,3,4-tetrahydroisoquinoline (2.2 g., 0.015 mole) was added slowly with cooling to 1-cyano-3-ethyl-penta-1,2-diene (2.0 g., 0.016 mole), infra-red examination after 0.5 hr. showed complete removal of the allene band. After several hours in a refrigerator crystals began to form in the liquid. The crystals were removed by filtration, washed with light petroleum ether and recrystallised from aqueous alcohol. The crystals were found to be pure 1-cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinolino)-pent-2-ene ν_{max} (I.R.50), 2290m (CN); 1650m (C=C); 1600w (aromatic C=C); 940s and 750vs cm^{-1} λ_{max} 207m μ (ε, 14,530). The mother liquors consisted of an oil which was only very slightly soluble in light petroleum, this fraction was boiled with light petroleum and the solvent portion decanted away. Removal of the solvent from the oil resulted in nearly pure 1-cyano-3-ethyl-(1,2,3,4-

tetrahydriosoquinolino)-pent-1-ene ν_{max} (I.R.51) 2210 (conj. CN); 1580vs (C=C-CN) and 750vs cm^{-1} λ_{max} 274m μ, (ε, 16,000).

1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroquinolino)-pent-1-ene.

Redistilled 1,2,3,4-tetrahydroquinoline (2.2 g., 0.015 mole) was added to 1-cyano-3-ethylpenta-1,2-diene (2 g., 0.016 mole), the mixture rapidly darkened but after 6 hr. there was no reduction in the intensity of the 1950 cm^{-1} band, (C=C=C) and no indication of enamine formation.

1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene.

Redistilled diethylamine (2.2 g., 0.03 mole) was added to 1-cyano-3,3,4-trimethylpenta-1,2-diene (3.6 g., 0.027 mole) and the mixture heated on a boiling water bath for 2.5 hr. The mixture was cooled and excess diethylamine removed by evaporation under reduced pressure. Distillation gave a forerun of the starting product followed by 1-cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene (2.5 g., 46%), b.p. 110°/0.5mm. (Found: C, 74.9; H, 11.5; N, 13.6. $C_{13}H_{24}N_2$ requires C, 74.9; H, 11.6; N, 13.5%) ν_{max} (I.R.52). 2210s (conj. CN) 1580s (C=C-CN) cm^{-1} λ_{max} 282m μ, (ε, 18,260) n.m.r. (n.m.r.26)

showed a singlet $\tau = 9.03$ ($\underline{Bu}^t$-), but the expected triplet for ($\underline{CH}_3$-CN_2-N) at τ=8.85 showed up as five or more bands this is probably due to magnetic non equivalence of the methyl groups. A doublet $\tau = 8.5$ ($\underline{CH}_3$-CH-C) $J_{CH_3H} = 7.2$. c.p.s. a quartet $\tau = 7.55$ (CH_3-$\underline{CH}$-C) $J_{H,CH_3} = 7.2$ c.p.s. The expected quartet $\tau = 6.6$ ($CH_3\underline{CH}_2$ -N) again shows as a more complex multiplet due to magnetic non equivalence of the methylene groups; a peak $\tau = 6.3$ shows (CH-C=$\underline{CH}$CN).

<u>1-Cyano-2-pyrrolidino-3,4,4-trimethylpent-1-ene.</u>

Redistilled pyrrolidine (1.7 g., 0.025 mole) was added slowly with cooling to 1-cyano-3,4,4-trimethylpenta-1,2-diene (2.7 g., 0.02 mole) and after the initial vigorous reaction was completed the mixture was heated on a boiling water bath for 1 hr., after cooling, the excess pyrrolidine was removed by evaporation under reduced pressure. Distillation gave 1-cyano-2-pyrrolidino-3,4,4-trimethylpent-1-ene (3.5 g., 83%) b.p. $120^o/2 \times 10^{-2}$mm. (Found: C, 75.9; H, 10.9; N, 13.4. $C_{13}H_{22}N_2$ requires C, 75.7; H, 10.8; N, 13.6%) ν_{max} (I.R.53) 2200vs (conj. CN); 1570vs (C=C-CN); 760s; 720s cm^{-1} λ_{max} 279m μ, (ε, 21,000).

1-Cyano-2-piperidino-3,4,4-trimethylpent-1-ene and 1-cyano-2-piperidino-3,4,4-trimethylpent-2-ene.

Redistilled piperidine (2 g., 0.025 mole) was added to 1-cyano-3,4,4-trimethylpenta-1,2-diene (2.7 g., 0.02 mole) and the mixture was heated on a boiling water bath, for 2.5 hr. After cooling, the excess piperidine was removed by evaporation under reduced pressure; the resulting viscous liquid was allowed to stand in a refrigerator, when after some time crystals appeared. The mixture was recrystallised from an ethyl alcohol/water mixture yielding 3 crops of 1-cyano-2-piperidino-3,4,4-trimethylpent-2-ene (2.5 g., 55%) m.p. 45° (Found: C, 75.7; H, 10.9; N, 12.6. $C_{14}H_{24}N_2$ requires C, 76.3; H, 11.0; N, 12.7%) ν_{max} (I.R.54) 2270m (-CN) 1625m (C=C); 760m cm^{-1} λ_{max} 203m μ, (ε, 5,130), λ_{max} 246m μ, (ε, 2,880).

After crystals had ceased to appear from the mother liquor an oil was precipitated by addition of water, the oil was separated, dissolved in ether, washed with water and dried ($MgSO_4$). Removal of the ether gave 1-cyano-2-piperidino-3,4,4-trimethylpent-1-ene (1.0 g., 23%) (Found: C, 76.4; H, 10.8; N, 12.5, $C_{12}H_{24}N_2$ requires C, 76.3; H_2 11.0; N, 12.7%), ν_{max} (I.R.55); 2210vs (conj. CN); 1580vs (C=C-CN) cm^{-1} λ_{max} 284m μ, (ε, 16,000).

1-Cyano-2-(diethylamino)-3-isopropyl-4-methylpent-1-ene and 1-Cyano-2-(diethylamino)-3-isopropyl-4-methylpent-2-ene.

Redistilled diethylamine (2.0 g., 0.028 mole) was added slowly with cooling to 1-cyano-3-isopropyl-4-methylpenta-1,2-diene (3.0 g., 0.015 mole); after the initial reaction was over the mixture was heated on a boiling water bath for 6 hr. the mixture was cooled and excess diethylamine was removed by evaporation under reduced pressure. Distillation gave a smal forerun followed by three fractions:-

(i) was found to be 1-cyano-2-(diethylamine)-3-isopropyl-4-methylpent-2-ene (0.7 g., 16%) b.p. 65-6°/0.1 mm. (Found: C, 74.8; H, 11.7; N, 14.0. $C_{14}H_{26}N_2$ requires C, 75.6; H, 11.8 N, 12.7%) ν_{max} (I.R.56) 2280m (CN); 1645m (C=C) cm^{-1} λ_{max} 203m μ, (ε, 6,860).

(ii) was found to be a mixture of 1-cyano-2-(diethylamino)-3-isopropyl-4-methylpent-2-ene and 1-cyano-2-(diethylamino)-3-isopropyl-4-methylpent-1-ene by ν_{max} 2280w (CN) 2200m (conj. CN), 1645w (C=C), 1560m (C=C-CN) cm^{-1} λ_{max} 203m μ (weak) λ_{max} 277m μ (strong).

(iii) was found to be 1-cyano-2-(diethylamino)-3-isopropyl-4-methylpent-1-ene (2.3 g., 54%) b.p. 115°/0.15mm. (Found: C, 75.1; H, 11.8; N, 13.3. $C_{14}H_{26}N_2$ requires C, 75.6; H, 11.8;

N, 12.6%); ν_{max} (I.R.57) 2000s (conj. CN) 1560s (C=C-CN) cm^{-1} λ_{max} 277m μ, (ε, 22,500).

β- Bromophenylacetylene.

An ice cold solution of sodium hypobromite (prepared by addition of bromine 33.6 g., 0.201 mole, to an ice cold solution of sodium hydroxide 25.2 g., 0.625 mole in water, 50ml. and ice, 100 g.) was added to vigorously stirred, ice cold phenylacetylene (20.4 g., 0.2 mole) over 3 hr. The mixture was stirred a further 1 hr. whilst being allowed to reach room temperature. The heavy organic layer which separated was dissolved in ether, washed with water (3 x 50 ml.) and dried ($MgSO_4$).

Removal of the ether under reduced pressure gave -bromophenylacetylene (34 g., 94%), ν_{max} 3080m (aromatic C-H); 2210m (conj. CN); 1600m (aromatic C=C); 755s and 690s cm^{-1}; g.l.c. (silicone oil, 120°) showed only one peak, t, 27 min.

Cyanophenylacetylene.

Anhydrous cuprous cyanide (10 g., 0.11 mole), was added to dry N,N-dimethylformamide (50 ml.) and bromophenylacetylene (18.1 g., 0.1 mole) was added to the stirred suspension, the temperature not being allowed to

exceed 50°. The resulting solution was stirred at 50° for 1½ hr., cooled and ether added, the solution was then slowly poured into vigorously stirred water (500 ml.) and the resulting suspension was stirred until the solid was granular in form. After filtration and subsequent washing of the solid with ether, the filtrate was extracted with ether (3 x 20 ml.) and the etherial solution washed with water (10 x 100 ml) before being dried ($MgSO_4$). Distillation after first removing the ether gave a small forerun followed by two fractions:-

(i) was found to be cyanophenylacetylene (9.0 g., 70%), b.p. 65°/1mm., the liquid collected solidified m.p. ν_{max} 3050w (aromatic C-H), 2290vs (conj. CN), 2155m (conj. C≡C), 1600m (aromatic C=C), 760s and 688s cm^{-1}, λ_{max} 207m μ, (ε, 22,580); 211m μ, (ε, 22,260); 249m μ, (ε, 13,870); 262m μ, (ε, 21,900) and 275m μ, (ε, 15770).

(ii) was found to be 1,4-diphenylbuta-1,3-diyne (2 g., 16%), b.p. 85-90°/0.3mm., this gave white crystals on recrystallisation from light petroleum-ether m.p. 84-5°. (Found: C, 94.9; H, 4.9. $C_{16}H_{10}$ requires C, 95.0; H, 5.0%); ν_{max} 3090m (aromatic C-H); 2170w (-C≡C-); 1600m (aromatic C=C); 760s

and 690s cm^{-1}. λ_{max} 204m μ, (ε, 42,830); 218m μ, (ε, 32,320); 228m μ, (ε, 28,700); 248m μ, (ε, 27,480); 260m μ, (ε, 27,070); 288m μ, (ε, 21,010); 297m μ, (ε, 17,170); 306m μ (ε, 31,520); 317m μ, (ε, 13,330) and 327m μ, (ε, 29,490). Literature values for 1,4-diphenylbuta-1,3-diyne.

<u>β-(Diethylamino)-β-phenylocrylonitrile.</u>

Redistilled diethylamine (1.6 g., 0.022 mole) was added slowly with cooling to cyanophenylacetylene (2.54 g., 0.02 mole) and after the initial reaction had ceased the solution was heated on a boiling water bath for 0.5 hr. Excess diethylamine was removed by evaporation under reduced pressure and distillation of the residue gave β-(diethylamino)-β-phenylacrylonitrile (2.3 g., 82.5%) b.p. 137°/0.15mm. m.p. 71°. (Found: C, 78.0; H, 7.8; N, 14.2. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.1; N, 14.0%); ν_{max} (I.R.58)., 2210s (conj. CN); 1570vs (C=C-CN) 780m; 726m; and 700 cm^{-1}, λ_{max} 205m μ, (ε, 13,090) λ_{max} 280m μ, (ε.12,180). n.m.r. indicated that the product was pure trans (with respect to nucleophile and activating groups). A triplet τ = 8.89 ($\underline{CH}_3CH_2N$) J_{CH_3,CH_2} = 7 c.p.s., a quartet τ = 6.92 ($CH_3\underline{CH}_2N$) J_{CH_2,CH_3} = 7 c.p.s., a singlet τ = 6.0 (= $C\underline{H}CN$) and an aromatic multiplet τ = 2.57 (Ph-C).

-(diethylamino)- -phenylacrylonitrile.

Redistilled diethylamine (.8 g., 0.011 mole) was added slowly to a solution of cyanophenylacetylene (1.27 g., 0.01 mole) in methanol (5 ml); after refluxing for 10 min. the excess solvent was removed under high vacuum. n.m.r. showed the product to be a mixture of cis and trans (with respect to nucleophile and aclivatery group). β-diethylamino-β-phenylacrylonitrile in a ratio of about 15:85. The quartet of the amino methylenes showed as two distinct quartets, the cis form being 17 c.p.s. downfield due to deshielding by the cyano group when in the cis configuration.

PREPARATION OF CYANOMETHYLENE KETONES FROM CYANO ENAMINES.

1-Cyano-3-methylpenton-2-one.

(a) 1-Cyano-2-(diethylamino)-3-methylpent-2-ene (9.0 g., 0.05 mole) was stirred with 5% hydrochloric acid (50 ml.) at 100° for 2.5 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3-methylpenton-2-one (3.5 g., 55%); b.p. 70°/0.5mm (Found: C, 67.1; H, 8.7; O, 13.0; N, 11.2. $C_7H_{11}ON$ requires C, 67.2; H, 8.9; O, 12.8; N, 11.2%). ν_{max} (I.R.59), 2280m (-CN); 1730vs (C=O) and 780m cm^{-1}. λ_{max} 232mμ (ε, 2,880) g.l.c. (silicone oil 150°) gave only one peak, t, 5 min.

(b) 1-Cyano-2-(diethylamino)-3-methylpent-1-ene (9.0 g., 0.05 mole) was stirred with 5% hydrochloric acid (50 ml.) at 100°C for 2.5 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3-methylpenton-2-one (3.8 g. 60%) which had identical spectra with the product from the first experiment.

(c) 1-Cyano-3-methyl-2-piperidino-pent-1-ene (1.0 g., 0.005 mole) was stirred with 5% hydrochloric acid (10 ml.) at 100° for 1 hr. The mixture was cooled, extracted with ether (3 x 10 ml.) and dried ($MgSO_4$). Removal of the ether gave a pale brown liquid which had identical spectra with the products from the previous experiments.

(d) 1-Cyano-3-methyl-2-piperidino-pent-2-ene (7.0 g., 0.04 mole) was stirred with 5% hydrochloric acid (50 ml.) at 100° for 1 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3-methylpent-2-one (4.2 g., 84%) which had identical spectra with the products from the previous experiments.

<u>1-Cyano-3-ethylpenton-2-one.</u>

(a) 1-Cyano-2-(diethylamino)-3-ethylpent-2-ene (5.0 g., 0.025 mole) was stirred with 5% hydrochloric acid (50 ml.) at 100° for 1 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3-ethylpenton-2-one (2.8 g., 78%) b.p. 65°/0.4 to 0.5mm. (Found: C, 69.0, H, 9.4; O, 11.6; N, 10.0. $C_8H_{13}ON$

requires C, 69.0; H, 9.4; O, 11.5; N, 10.1); ν_{max} (I.R.60), 2275m (CN); 1725s (C=O) and 780 cm^{-1}; λ_{max} 232m μ, (ε, 4,415) g.l.c. (silicone oil, 150°) gave only one peak, t, 6 min.

(b) 2-Amino-1-dyano-3-ethylpent-1-ene (0.7 g., 0.005 mole) was stirred with 5% hydrochloric acid (10 ml.) at 100° for 1 hr. The mixture was cooled, extracted with ether (3 x 10 ml. and dried ($MgSO_4$). Removal of the ether gave a product with identical spectra to the previous product.

(c) 1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinolino)-pent-1-ene (1.0 g., 0.004 mole) was stirred with 5% hydrochloric acid at 100° for 2 hr. The mixture was cooled, extracted with ether (3 x 10 ml.) and dried ($MgSO_4$). Removal of the ether gave a product which was nearly identical to the previous products but showed slight traces of the starting product.

(d) 1-cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinolino)-pent-2-ene (1.0 g., .004 mole) was stirred with 5% hydrochloric acid at 100° for 2 hr. The mixture was cooled, extracted with ether (3 x 10 ml.) and dried ($MgSO_4$), removal of the ether gave a product which was identical with the previous ones.

1-Cyano-3,4,4-trimethylpenton-2-one.

(a) 1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene (6 g., .03 mole) was stirred with 5% hydrochloric acid at 100° for 2 hrs. Examination showed only partial hydrolysis had taken place, the strength of the acid was increased to 10% and the mixture re-heated for a further 2 hrs. after working up in the usual way the product was found to be a mixture of 1-cyano-3,4,4-trimethylpenton-2-one and 1-cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene by ν_{max} (I.R.61), 2270w (CN); 2210s (conj. CN); 1730s (C=O) and 1580s (C=C-CN) cm^{-1}.

(b) 1-Cyano-2-piperidino-3,4,4-trimethylpent-1-ene (4.4 g., 0.02 mole) was stirred with 10% hydrochloric acid (.50 ml.) at 100°C for 2 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after first removing the ether gave 1-cyano-3,4,4-trimethylpenton-2-one (1.5 g., 49%) b.p. 80°/0.15mm. (Found: C, 70.6; H, 9.7; O, 10.4; N, 9.3. $C_9H_{15}ON$ requires C, 70.6; H, 9.8; O, 10.4; N, 9.2%) ν_{max} 2270m (CN) 1730s (C=O) cm^{-1}., λ_{max} 234m μ, (ε, 3,225); g.l.c. (silicone oil 150°) showed only one peak, t, 9 min.

(c) 1-Cyano-2-piperidino-3,4,4-trimethylpent-2-ene (1.1 g., 0.005 mole) was stirred with 10% hydrochloric acid (10 ml.) at 100° for 2 hr. The mixture was cooled, extracted with ether (3 x 10ml.) and dried ($MgSO_4$). Evaporation of the ether gave a product with identical spectra to the previous one.

(d) 1-Cyano-2-pyrrolidino-3,4,4-trimethylpent-1-ene (4.2 g., 0.02 mole) was stirred with 10% hydrochloric acid (50 ml.) at 100° for 2 hr. The mixture was cooled, extracted with ether (3 x 15 ml.) and dried ($MgSO_4$). Distillation after removing the ether gave 1-cyano-3,4,4-trimethylpenton-2-one (1.6 g., 52%), which was identical to the product from experiment b.

Benzoylacetonitrile.

β-(diethylamino)-β-phenylacrylonitrile (2.5 g., 0.0125 mole) was stirred with 10% hydrochloric acid (40 ml.) at 100° for 4 hrs. The mixture was cooled, extracted with ether (3 x 10 ml.) and dried ($MgSO_4$). Evaporation of the ether gave a solid which was recrystallised from aqueous alcohol. The compound was shown to be benzoylacetonitrile (1.8 g., 82%) m.p. 80-1° (Found: C, 74.5; H, 4.7; O, 11.1 N, 9.7. C_9H_7ON requires C, 74.5; H, 4.81; O, 11.0; N, 9.7%) ν_{max} (I.R.62), 2265m (CN); 1730s (C=O) cm^{-1}. λ_{max} 204mμ, (ε, 15,820); λ_{max} 245mμ (ε, 11,600); λ_{max} 282mμ (ε, 2,636).

PREPARATION OF ALLENIC-1-AMIDES FROM 1-CYANOALLENES.

4-Ethylhexa-2,3-dienamide.

1-Cyano-3-ethylpenta-1,2-diene (3.0 g., 0.025 mole) was dissolved in absolute ethanol (i ml.) to which 6N sodium hydroxide (1 ml.) had been added. The solution was stirred and hydrogen peroxide (30% w/v; 100 Volume; 12ml.) added over 4 min. The reaction became very vigorous and caused the solution to boil, when the initial reaction had subsided the solution was stirred at 80° for 1 hr. On slow cooling of the solution white crystals of the amide separated, these were removed by filtration, washed with a little ether, and recrystallised from aqueous alcohol. (Further cooling and evaporation of the mother liquors deposited more crystals which were washed with ether, recrystallised and combined with the first crop.) The combined crop was dried in vacuo at 60° (2 g., 57%) m.p. 138-9°. (Found: C, 68.9; H, 9.4; O, 11.4; N, 10.2. $C_8H_{13}ON$ requires C, 69.0; H, 9.4; O, 11.5; N, 10.1%) ν_{max} (I.R.63) 3410vs, 3210vs (N-H stretch); 1970s (C=C=C); 1660s (C=O, amide I band); 1630s (NH deformation, amide II band); 905m; and 843s cm^{-1}; λ_{max} 208mμ (ε, 14,600).

4,5,5-Trimethylhexa-2,3-dienamide.

1-Cyano-3,4,4-trimethylpenta-1,2-diene (4 g., .03 mole) was dissolved in absolute ethanol (12 ml.) to which 6N sodium hydroxide (1 ml.) had been added. The solution was stirred and hydrogen peroxide (30% w/v., 100 volume; 12 ml.) added in two equal portions. The reactio became very vigorous and caused the solution to boil, when this initial vigorous reaction had subsided the solution was maintained at 80° by external heating and stirred for 1 hr. On slow cooling of the solution white crystals separated, these were removed by filtration, and a further crop obtained by evaporation and cooling of the mother liquors. The two crops were combined, recrystallised from aqueous alcohol and dried in vacuo at 60° (3.2 g., 70%). (Found: C, 70.4; H, 9.7; O, 10.8; N, 9.0. $C_9H_{15}ON$ requires C, 70.5; H, 9.8; O, 10.5; N, 9.1%) ν_{max} (I.R.64), 3400s, 3200s (N-H stretching); 1975m (C=C=C); 1670s (C=O, amide I band); 1625s (N-H deformation, amide II band); 890m; 712s cm^{-1}. λ_{max} 209m μ, (ε, 13,000); n.m.r. (n.m.r.27) showed a singlet τ = 8.85 ($\underline{Bu}^t$), a doublet centred on τ = 8.15 ($Bu^t(\underline{Me})C{=}C{=}CH$), $J_{CH_3,H}$ = 3 c.p.s., a quartet centred on τ = 4.5 ($C{=}C{=}C\underline{H}$), J_{H,CH_3} = 3 c.p.s., and a broad hump τ = 4.0 - 4.6 ($N\underline{H}_2$).

4-Isopropyl-5-methylhexa-2,3-dienamide.

1-Cyano-3-isopropyl-4-methylpenta-1,2-diene (1.5 g., 0.01 mole) was dissolved in absolute ethanol (6 ml.) to which 6N sodium hydroxide (0.6 ml.) had been added. The solution was stirred and hydrogen peroxide (30% w/v.; 100 volume; 5 ml.) was added in one portion. The reaction became very vigorous and caused the solution to boil, when the initial vigorous reaction was over the solution was maintained at 80° by external heating and stirred for 1 hr. On slow cooling of the solution white crystals separated, these were filtered off, washed with a little cold water and dried in vacuo at 60° (1.1 g., 65%) m.p. 112-3°. (Found: C, 71.93; H, 10.42; O, 9.34; N, 8.31. $C_{10}H_{17}ON$ requires C, 71.81; H, 10.25; O, 9.57; N, 8.53%) ν_{max} (I.R.65), 3400s, 3210s (NH stretching); 1955s (C=C=C); 1655s (C=O, amide I band); 1630s (NH deformation, amide II band); 840s; 640s cm^{-1}. λ_{max} 210m μ, (ε, 15,000).

4-Isobutyl-6-methylhepta-2,3-dienamide.

1-Cyano-3-isobutyl-5-methylhexa-1,2-diene (0.9 g., 0.005 mole) was dissolved in absolute ethanol (4 ml.) to which 6N sodium hydroxide (0.5 ml.)

had been added. The solution was stirred and hydrogen peroxide (30% w/v.; 100 volume; 3 ml.) was added in one portion, the reaction became very vigorous and caused the solution to boil, when the initial vigorous reaction had subsided, the solution was maintained at 80° by external heating and stirred for 1 hr. On cooling no crystals were observed, but after standing 5 hr. in a cool place, white crystals were deposited, these were removed by filtration, washed with a little water and dried in vacuo at 60°. (0.6 g., 61%); m.p. 93-4°. (Found: C, 72.4; H, 10.5; O, 8.2; N, 7.0. $C_{12}H_{21}ON$ requires C, 73.9; H, 10.8; O, 8.2; N, 7.1%); ν_{max} (I.R.66), 3410s, 3210s (N-H stretching); 1960s (C=C=C); 1655s (C=O, amide I band); 1625s (N-H deformation, amide II band) cm^{-1}, λ_{max} 211m μ, (ε, 10,140).

<u>4-Tert-Butyl-5,5-dimethylhexa-2,3-dienamide.</u>

3-tert-Butyl-1-cyano-4,4-dimethylpenta-1,2-diene (1.0 g., .006 mole) was dissolved in absolute ethanol (4 ml.) to which 6N sodium hydroxide (5 ml.) had been added. The solution was stirred and hydrogen peroxide (30% w/v.; 100 volume; 3 ml.) was added in one portion, the solution grew only slightly warm so after 15 min. more hydrogen peroxide (3 ml.) was added. The solution

was maintained at 80° and stirred for 45 min., when on cooling only a small quantity of solid was deposited and the solution had a strong smell of organic cyanide. Absolute ethanol (3 ml.), 6N sodium hydroxide (0.5 ml.) and hydrogen peroxide (2 ml.) were then added and the solution stirred at 80° for a further 1 hr. On cooling an oily liquid separated, which after the whole solution had been in a cool place for 8 day changed into white crystals. The crystals were removed by filtration and when water was added to the mother liquor a further crop was obtained. The combined crop of crystals was washed with water and recrystallised from aqueous alcohol. (0.8 g., 70%). m.p. 96°. (Found: C, 72.3; H, 10.7; O, 8.2; N, 6.8. $C_{12}H_{21}ON$ requires C, 73.9; H, 10.8; O, 8.2; N, 7.2%); ν_{max} (I.R.67), 3410s, 3200s (N-H stretching); 1945m (C=C=C); 1675s (C=O, amide I band); 1600s cm^{-1}. (NH deformation, amide II band); λ_{max} 208mμ, (ε, 8,150).

1.4-Elimination reaction of 1-Bromoallenes.

2-Methylbut-1-en-3-yne

(a) 1-Bromo-3-methylbuta-1,2-diene (6.0 g., 0.04 mole) and anhydrous cuprous cyanide (4.5 g., 0.05 mole) were heated very slowly, in an apparatus set for distillation, until a product b.p. 55° distilled. The product after washing with water (2 x 10 ml.), drying ($MgSO_4$) and redistilling was found to be 2-methylbut-1-en-3-yne (0.6 g., 22%). ν_{max} (I.R. 68) 3300vs (C ≡CH); 2100m (C≡C); 1625vs (C=C) and 900vs cm^{-1}. ($C=CH_2$). λ_{max} 222m μ, (ε, 11,000); λ_{max} 236m μ, (ε, 9,700). g.l.c. (silicone oil, 18°) gave only one peak, t, 12 min. One peak was also given on admixture with authentic specimen.

(b) 1-Bromo-3-methylbuta-1,2-diene (6.0 g., 0.04 mole) and cuprous iodide (10.5 g., 0.055 mole) were heated slowly, in an apparatus set for distillation, at a bath temperature of about 100° a very vigorous reaction occurred (some experiments became uncontrollable) and a small quantity of distillate was collected, iodine vapour and a fuming gas were also evolved.

Infra-red examination of the product indicated that no en-yne was present; g.l.c. examination (silicone oil, 80°) showed the product to be a complex mixture of six or more components.

(c) 1-Bromo-3-methylbuta-1,2-diene (15 g., 0.1 mole) and cuprous iodide (19 g., 0.1 mole) in dry N,N-dimethylformamide (50 ml.) were stirred at 80° for 1 hr. The apparatus was then set for vacuum distillation and the product was slowly distilled at about 10-20mm pressure, the portion condensing in a trap cooled to -50° being collected. Redistillation of this trap fraction after drying ($MgSO_4$) gave 2-methylbut-1-en-3-yne (4.0 g., 57%) b.p. 32-33°/750mm. ν_{max} 3300vs (C≡CH); 2100m (C≡C); 1625vs (C=C); and 900vs cm^{-1}. (C=CH_2) λ_{max} 222mμ, (ε, 11,000); λ_{max} 236mμ, (ε, 9,700). g.l.c. (silicon oil, 18°) gave only one peak, t, 12 min., one peak was also given on admixture with authentic sample.

(d) 1-Bromo-3-methylbuta-1,2-diene (49 g., 0.33 mole) was added slowly to a stirred solution of anhydrous cuprous cyanide (45 g., 0.5 mole) in dry N,N-dimethylformamide (120 ml.) and the mixture stirred at 30-45° for 2 hr. The apparatus was then set for vacuum distillation and the product was distilled at about 10-20mm. pressure, the portion condensing in a trap cooled to -50° being collected. Redistillation of this trap fraction after drying ($MgSO_4$) gave 2-methylbut-1-en-3-yne (4.5 g., 12%), the spectra and g.l.c. of which were identical with those previously obtained.

The residue (ca 80 ml.) from the distillation was worked up in the way previously described for the preparation of 1-cyanoallenes and gave 1-cyano-3-methylbuta-1,2-diene (12.9 g. 42%); ν_{max} 2245vs (CN); 1950s (C=C=C); and 790 cm^{-1}.

3-Methylpent-3-en-1-yne.

(a) 1-Bromo-3-methylpenta-1,2-diene (16.1 g., 0.1 mole) and anhydrous cuprous cyanide (10 g., 0.11 mole) were heated at 115° for 10 min. and then the apparatus was set for distillation and a low boiling product was collected. Redistillation of this product gave hydrogen cyanide, (1.3 g., 46%) b.p. 28° and the en-yn product (4.8 g., 58%) b.p. 62-65°/750mm. (Found: C, 90.15; H, 9.9. C_6H_8 requires C, 90.1; H, 9.9%); ν_{max} 3300vs (C≡CH); 2110m (C≡C); 1620m (C=C) 910m ($C=CH_2$); and 825m cm^{-1}. (C=CH-); λ_{max} 222mμ (ε, 8,900); g.l.c. (silicone oil, 18°) gave three peaks, t, 8 min., (6%), 2-ethylbut-1-en-3-yne; t, 10 min., (74%), trans-3-methylpent-3-en-1-yne; t, 13 min., (20%), cis-3-methylpent-3-en-1-yne. These three isomers were separated by preparative g.l.c. (20 ft. x 3/8" column filled with 15% silicone oil on carbowax, 30°); 2-ethylbut-1-en-3-yne $_{max}$ (I.R.69)., 3330vs (C≡CH); 3100w ($C=CH_2$); 2340w (overtone); 2100w (-C≡C); 1800m (overtone of vs.900); 1750w (combustion overtone) 1620 vs

(conj. C=C); 900vs ($C=CH_2$); 800m cm^{-1}. g.l.c. (silicone oil, 18°) gave only one peak, t, 8 min. trans-3-Methylpent-3-en-1-yne ν_{max} (I.R.70), 3300vs (C≡CH); 2340w (overtone); 2100m (-C≡C); 1850w (combination overtone); 1630w (conj. C=C); 1040s; 940m; 820vs cm^{-1}. (no 900 cm^{-1} band $C=CH_2$). g.l.c. (silicone oil, 18°) gave only one peak, t, 10 min. cis-3-Methylpent-3-en-1-yne ν_{max} (I.R.71), 3320vs (-C≡CH); 2340w (overtone); 2105s (C≡C); 1855w (combination overtone); 1675m (overtone of 839vs); 1645m (conj. C=C); 1010s; 839vs; 750m cm^{-1}; g.l.c. (silicone oil, 18°) gave only one peak, t, 13 min.

(b) 1-Bromo-3-methylpenta-1,2-diene (8.05 g., 0.055 mole) and cuprous iodide (10.5 g., 0.055 mole) were heated slowly in an apparatus set for distillation. At a bath temperature of about 140° a vigorous reaction took place, iodine vapour and a fuming gas being liberated, the small quantity of distillate collected showed no trace of en-yne and the g.l.c. showed a complex mixture with at least six components.

(c) 1-Bromo-3-methylpenta-1,2-diene (5 g., 0.03 mole) was heated with silver cyanide (4 g., 0.03 mole) at 130° for 5 hr. The apparatus was then set for distillation and only 0.75 g.

of a product (which was found to be 70% en-yne and 30% starting product) ν_{max} 3300vs (C≡CH); 2100m (C≡C) and 1950m cm^{-1} (C=C=C); λ_{max} 222m μ, (ε, 5,500) was obtained.

(d) 1-Bromo-3-methylpenta-1,2-diene (5 g., 0.03 mole) was heated with cuprous bromide (4.3 g., 0.03 mole) at 100° for 4 hrs. infra-red and g.l.c. examination showed the mixture to be mainly starting product with some rearrangement products but no trace of en-yne was observed.

(e) 1-Bromo-3-methylpenta-1,2-diene (24 g., 0.15 mole) and cuprous iodide (28.5 g., 0.15 mole) were stirred in dry N,N-dimethylformamide (72 ml.) at 80° for 2½ hr. The apparatus was then set for vacuum distillation and the product was slowly distilled at about 10-20mm pressure, the portion condensing in a trap cooled to -50° being collected. Redistillation of the trap fraction after drying ($MgSO_4$) gave the en-yne product (6.1 g., 50%) b.p. 63°/760mm. Infra-red and ultra-violet spectra were similar to the sample obtained from (a), but g.l.c. (silicone oil, 18°) showed only two peaks, t, 8 min., (12%), 2-ethylbut-1-en-3-yne; and t, 10 min., (88%), trans-3-methylpent-3-en-1-yne. Mixed g.l.c. (silicone oil, 18°) of this product in turn with authentic

samples of 2-ethylbut-1-en-3-yne and trans-3-methylpent-3-en-1-yne gave enhancement of the t, 8 min. and t, 10 min. peaks respectively. No trace of the cis-3-methylpent-3-en-1-yne was indicated.

(f) 1-Bromo-3-methylpenta-1,2-diene (20.1 g., 0.125 mole) and cuprous bromide (21.75 g., 0.15 mole) were stirred in dry N,N-dimethylformamide (100 ml.) at 56° for 2 hr. Working up in the usual manner gave a mixture of en-ynes (6 g., 60%), the g.l.c. of which showed (silicone oil, 18°) three peaks, t, 8 min., (15%), 2-ethylbut-1-en-3-yne; t, 10 min. (72%), trans-3-methylpent-3-en-1-yne and t, 13 min. (13%), cis-3-methylpent-3-en-1-yne. Admixture with authentic samples of each en-yne gave enhancement of the expected peak in each case.

(g) Similarly a reaction using cuprous chloride in place of cuprous bromide gave 40% mixture of en-ynes in the same proportions as (f).

(h) 1-Bromo-3-methylpenta-1,2-diene (53.8 g., 0.33 mole) was added slowly to a stirred solution of anhydrous cuprous cyanide (45 g., 0.5 mole) in dry N,N-dimethylformamide (200 ml.) and the mixture stirred at 55° for 1½ hr. The

apparatus was then set for vacuum distillation and the product was distilled at about 10-20mm pressure, the portion condensing in a trap cooled to -50° being collected. Redistillation of this trap fraction after drying ($MgSO_4$) gave the en-yne mixture (4.0 g., 15%) which was shown by spectra and g.l.c. to be 2-ethylbut-1-en-3-yne (6%), trans-3-methylpent-3-en-1-yne (74%) and cis-3-methylpent-3-en-1-yne (20%).

The residue from the distillation (120 ml.) was worked up in the way previously described for preparation of 1-cyanoallenes and gave 1-cyano-3-methylpenta-1,2-diene (18.0 g., 51%); ν_{max} 2245vs (CN); 1955vs cm^{-1}. (C=C=C).

<u>3-Ethylpent-3-en-1-yne.</u>

(a) 1-Bromo-3-ethylpenta-1,2-diene (8.75 g., 0.05 mole) and anhydrous cuprous cyanide (5.0 g., 0.056 mole) were heated at 115° for 15 min. and then the apparatus was set for distillation and the low boiling product was collected. Redistillation of this product gave hydrogen cyanide (0.5 g., 37%) b.p. 28°/750mm and the en-yne product (2.1 g., 45%); b.p. 85°/760mm. (Found: C, 89.0; H, 10.5.

C_7H_{10} requires C, 89.4; H, 10.6%); ν_{max} 3300vs (C≡CH); 2100m (C≡C); 1630w (C=C); and 840 cm^{-1} (C=CH-); λ_{max} 222mμ (ε, 13,800). g.l.c. (silicone oil, 20°) showed two components, t, 25 min. (85%), trans-3-ethylpent-3-en-1-yne and t, 30 min. (15%), cis-3-ethylpent-3-en-1-yne.

(b) 1-Bromo-3-ethylpenta-1,2-diene (8.75 g., 0.05 mole) and cuprous iodide (9.5 g., 0.05 mole) were stirred in dry N,N-dimethylformamide (30 ml.) at 80° for 1½ hr. The apparatus was then set for vacuum distillation and the product was slowly distilled at about 10-20mm pressure, the portion condensing in the trap cooled to -50° being collected. Redistillation of the trap fraction after drying ($MgSO_4$) gave pure trans-3-ethylpent-3-en-1-yne (2.9 g., 61%) b.p. 85°/750mm. ν_{max} (I.R.73) 3300vs (C≡CH); 2100m (-C≡C-); 1630w (C=C); and 840s cm^{-1} (C=CH-). λ_{max} 222mμ, (ε, 13,800); g.l.c. (silicone oil, 20°) gave only one peak, t, 25 min.

(c) 1-Bromo-3-ethylpenta-1,2-diene (58.2 g., 0.33 mole) was slowly added to a stirred solution of anhydrous cuprous cyanide (65 g., 0.7 mole) in dry N,N-dimethylformamide (200 ml. and the mixture stirred at 55-60° for 2 hr. The apparatus was then set for vacuum distillation and the product distilled

at about 15-20mm pressure, the portion condensing in a trap cooled to -50° being collected. Redistillation of this trap fraction gave the en-yne (4.4 g., 14%) which had identical spectra and g.l.c. to the product from (a).

The residue from the distillation (120 ml.) was worked up as previously described for the preparation of 1-cyano-allenes and gave 1-cyano-3-ethylpenta-1,2-diene (25 g., 60%); ν_{max} 2240s (CN); 1955s (C=C=C); and 790m cm^{-1}.

2-t-Butylbut-1-en-3-yne.

(a) 1-Bromo-3,4,4-trimethylpenta-1,2-diene when heated with anhydrous cuprous cyanide gives 1-cyano-3,4,4-trimethylpenta-1,2-diene in about 60% yield. (See section on 1-cyanoallenes p.87).

(b) 1-Bromo-3,4,4-trimethylpenta-1,2-diene (8.75 g., 0.05 mole) and cuprous iodide (9.5 g., 0.05 mole) were stirred in dry N,N-dimethylformamide (30 ml.) at 80° for 1½ hr. The apparatus was then set for vacuum distillation and the product slowly distilled at about 5mm pressure, the portion condensing in a trap cooled to -50° being collected. After drying ($MgSO_4$) redistillation using a spinning band apparatus gave 2-t-butylbut-1-en-3-yne (3.5 g., 63%) b.p. 93-5°/750mm.

(Found: C, 88.4; H, 11.5. C_8H_{22} requires C, 88.1; H, 11.9%) ν_{max} (I.R.72), 3300vs (C≡CH); 2100m (C≡C); 1630s (C=C); and 910vs cm^{-1} ($C=CH_2$). λ_{max} 210m μ, (ε, 7,200) λ_{max} 218m μ (ε, 10,000); λ_{max} 226m μ, (ε, 7,400); g.l.c. (silicone oil 80°) gave only one peak, t, 4 min.

1,4-ELIMINATION REACTION OF 1-IODOALLENES.

2-Methylbut-1-en-3-yne.

(a) 1-Iodo-3-methylbuta-1,2-diene gave a violent reaction on being heated with cuprous cyanide, the small portion of distillate collected showed evidence of en-yne formation ν_{max} 3300 (C≡CH); 2100 (C≡C); and 1630 (C=C).

(b) 1-Iodo-3-methylbuta-1,2-diene (19.4 g., 0.1. mole) and cuprous iodide (19 g., 0.1 mole) in N,N-dimethylformamide (100 ml.) gave 2-methylbut-1-en-3-yne identical in spectra to the sample obtained in the earlier experiments. (3.7 g., 55%).

3-Methylpent-3-en-1-yne.

(a) 1-Iodo-3-methylpenta-1,2-diene gave an almost uncontrollable reaction on being heated with cuprous cyanide. Again the distillate collected showed large en-yne content.

(b) 1-Iodo-3-methylpenta-1,2-diene (20.8 g., 0.1 mole) and cuprous iodide (19 g., 0.1 mole) in N,N-dimethylformamide (100 ml.) gave trans-3-methylpent-3-en-1-yne contaminated with a small amount of 2-ethylbut-1-en-3-yne. (4.2 g., 52%).

2-t-Butylbut-1-en-3-yne.

1-Iodo-3,4,4-trimethylpenta-1,2-diene (12 g., 0.05 mole) and cuprous iodide (10 g., 0.11 mole) in N,N-dimethylformamide (100 ml.) gave 2-t-butylbut-1-en-3-yne. (3 g., 55%).

Action of heat on a mixture of 1-Cyano-3-methylpenta-1,2-diene and cuprous salts.

(a) 1-cyano-3-methylpenta-1,2-diene (2.7 g., 0.025 mole) and cuprous cyanide (2.3 g., 0.025 mole) were heated at 130° for 3 hrs. No low boiling en-yne fraction could be collected. The mixture (a black, sticky gum) was extracted with 40°-60° petroleum ether and yielded a little of the dimer 2-(2'-butylidene)-1-cyano-3-cyanomethylene-4-ethyl-4-methylcyclobutane, characterised by ν_{max} 2260s (CN); 2250s (conj. CN); 1660s (conj. C=C); and 1630s (conj. C=CHCN) cm^{-1} λ_{max} 282mμ, (ε, 11,400).

(b) 1-cyano-3-methylpenta-1,2-diene and cuprous bromide gave the same result as (a).

(c) 1-cyano-3-methylpenta-1,2-diene and silver cyanide gave the same result as (a).

GRIGNARD REACTIONS OF 3-DIALKYLALLENIC 1- MAGNESIUM BROMIDES.

A. Reaction with Carbon Dioxide.

Reaction of 3-Methylpenta-1,2-diene-1-magnesium bromide with carbon dioxide.

(a) Magnesium turnings (1.83g., 0.075 mole), dry tetrahydrofuran (40 ml) and a crystal iodine were placed in a dry flask through which a current of dry, oxygen-free nitrogen was passed. A few millilters of a solution of 1-bromo-3-methyl-penta-1,2-diene (12.0g., 0.075 mole) in dry tetrahydrofuran (20 ml) were added to the flask, then after about 5 min. when formation of the Grignard compound had started, the bromoallene solution diluted with a further amount of tetrahydrofuran (100 ml) was added dropwise at a rate just sufficient to keep the mixture refluxing gently. When addition of the bromoallene solution was complete the mixture was stirred and maintained at a gentle reflux by external heating for 1hr.
The suspension was then cooled to about -5° and a rapid stream of dry carbon dioxide gas was passed for 2-3hr. dilute hydrochloric acid was then added slowly until

complete solution of the inorganic salts was obtained. The mixture was separated, the aqueous portion was extracted with ether (2x20 ml) and this was added to the tetrahydrofuran solution. The organic solution was washed with water then extracted with sodium bicarbonate solution (10x20 ml). The sodium bicarbonate extracts were combined, washed with ether (20 ml) then cooled and acidified with cold dilute hydrochloric acid, the acidified mixture was then extracted with ether (3x20 ml) the ether extract was washed with water and dried ($MgSO_4$).

Evaporation gave a brown viscous liquid (5.9g. 60%) which was found to be a mixture of 4-methylhexa-2,3-dienoic acid and 4-methylhex-2- ynoic acid ν_{max} 3400-2400 vs (hydrogen bonded OH); 2220 m (C=C); 1960s (C=C=C) and 1750-1670 vs (C=O) cm^{-1}. The neutral fraction was examined after distillation and the product was found to be a high boiling hydrocarbon but no pure sample could be isolated.

(b) The above reaction was repeated using ether (200 ml) in place of tetrahdrofuran, working up gave the same acid mixture (4.2g. 43%).

(c) The reaction was repeated, adding solid carbon dioxide instead of passing the dry gas. Working up showed the presence of the low boiling hydrocarbons 3 methylpenta-1,2-diene and 3-methylpent-1-yne and a small amount of acid mixture. (1.5g. 13%).

(d) The reaction was repeated using ether (200 ml) and passing carbon dioxide at 0°, after working up the product was found to be identical with that from experiment (b).

(e) The reaction was repeated using ether (200 ml) and passing carbon dioxide at 10°, after working up the product was found to be identical with that from experiment (b).

Reaction of 3-methylbuta-1,2-diene-1-magnesium bromide With carbon dioxide.

Magnesium turnings (3.7g. 0.15 mole), dry ether (80 ml) and a crystal of iodine were placed in a dry flask through which a slow current of dry, oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-methylbuta-1,2-diene (21g. 0.15 mole) in dry ether (60 ml) were added, then after about 10 mins, after reaction had started, the remaining solution was added dropwise at such a rate to cause the reaction mixture to reflux gently, after the addition was completed the suspension was stirred and refluxed gently for 1hr. The suspension was cooled to 0° and dry cardon dioxide was passed at such a rate to keep the temperature between 0° and 5° , when the mixture showed no further tendency to heat up the gas was passed at a faster rate for 0.5hr. The mixture was then cooled and dilute hydrochloric acid was added until all the inorganic salts had dissolved, the organic layer was separated, washed with water, then extracted with sodium bicarbonate, extracts were combined washed with

ether (20 ml) then cooled and acidified with dilute hydrochloric acid. The acidified mixture was extracted with ether (3x20 ml), the ether extract washed with water then dried ($MgSO_4$). Evaporation gave a brown oil which was found to be a mixture of 4-methylpenta-2,3-dienoic acid and 4-methylpent-2-ynoic acid (4.8g. 28%); ν_{max} 3400-2500vs (hydrogen bonded - OH); 2250s (conj C=C); 1950m (C=C=C); 1800-1650vs (C=O) cm^{-1}.

Reaction of 3-Ethylpenta-1,2-diene-1-magnesium bromide with carbon dioxide

Magnesium turnings (1.83g. 0.075 mole). dry ether (80 ml) and a crystal of iodine were placed in a dry flask through which a slow current of dry oxygen free nitrogen was passed. A few millitiers of a solution of 1-bromo-3-ethylpenta-1,2-diene (13.2g. 0.075 mole) in ether 120 ml were added, then after about 10 mins when formation of the Grignard reagent had started, the rest of the solution was added dropwise at a rate just sufficient to keep the mixture refluxing gently, when addition of the solution was complete the mixture was stirred at a gentle reflux for 1 hr. Afer cooling to 0° dry carbon dioxide gas was passed for 2 hrs. at a rate which did not allow

the temperature to rise above 5°, the mixture was then acidified with dilute hydrochloric acid until the inorganic salts had dissolved and the ether layer separated. The etherical solution was washed with water then extracted with sodium bicarbonate solution (6 x 30 ml). The sodium bicarbonate extracts were combined, washed with ether than acidified with dilute hydrochloric acid. The acidified mixture was extracted with ether (3 x 20 ml), the ether extract washed with water and dried ($MgSO_4$). Evaporation gave a brown oil which was found to be a mixture of 4-ethylhexa-2,3-dienoic acid and 4-methylhexa-2-ynoic acid (5.5g., 49%) ν_{max} 3400-2500 vs (hydrogen bonded OH), 2240 s (C=C); 1960m (C=C=C); and 1790-1650 vs (C=C) cm^{-1}.

Reaction of 3,4,4-trimethylpenta-1,2-diene-1-magnesium bromide with carbon dioxide.

Magnesium turnings (1,83 g. 0.075 mole), dry ether (60 ml) and a crystal of iodine were placed in a dry flask through which a dry current of oxygen free nitrogen was passed. A few milliliters of a solution of 1-bromo-3,4,4-trimethylpenta-1,2-diene (15 g. 0.075 mole) in ether (140 ml) was added and after about 10 mins, when the Grignard reagent had started to form the rest of the solution was added dropwise at a rate just sufficient to keep the mixture refluxing gently, when the addition was complete the suspension was stirred at a gentle reflux of 1 hr. The suspension was cooled to 0° and dry carbon dioxide gas was passed at such a rate as to keep the temperature between 0° and 5°, and then

more quickly for a further 1 hr. The mixture was then acidified with dilute hydrochloric acid until the inorganic salts had dissolved, then the ether layer was separated. The etherical solution was washed with water then extracted with sodium bicarbonate solution (5 x 30 ml), the sodium bicarbonate extracts were combined, washed with ether, acidified with dilute hydrochloric acid and ether extracted (3 x 30 ml). The etherical solution was washed with water and dried ($MgSO_4$). Evaporation gave a brown oil which was found to be a mixture of 4,5,5-trimethylhex-2-ynoic acid (5.7 g., 45%) ν_{Max} 3400-2600vs (hydrogen bonded -OH); 2240m (C=C); 1955m (C=C=C); 1790-1650vs (C=O). The acid mixture was dissolved in ether and extracted with sodium bicarbonate solution (3 x 10 ml). The ether residue was dried ($MgSO_4$) and on evaporation gave the pure 4,5,5-trimethylhexa-2,3-dienoic acid. The sodium bicarbonate extract was acidified, extracted with ether and the process repeated, the cycle was carried out four times. The first three times the residue was pure allenic acid, but the fourth

time a mixture of allenic and acetylenic acids resulted. The allenic acid was recrystallised from pentane m.p. 48-9° (lit. 47-8°) ν_{max}(I.R.74) 3400-2500s (hydrogen bonded OH); 1960s (C=C=C); 1700s (C=O); 1115m; and 835 m cm^{-1}. λ_{max}212mμ, (ε, 11,550).

<u>Reaction of 3-Isopropyl-4-methylpenta-1,2-diene-1-magnesium bromide with carbon dioxide.</u>

Magnesium turnings (1.83 g. 0.075 mole), dry tetrahydrofuran (50 ml) and a crystal of iodine were placed in a dry flask through which a current of dry oxygen free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-isopropyl-4-methylpenta-1,2-diene (15.1 g. 0.075 mole) in dry tetrahydrofuran (20 ml) were added, and after about 10 mins, when formation of the Grignard reagent had started the rest of the solution was added dropwise at such a rate as to maintain the suspension at a gentle reflux. When addition of the solution was complete, more tetrahydrofuran (30 ml) was added and the suspension stirred at reflux temperature for 1 hr. The suspension was cooled to 0°

and a slow stream of dry carbon dioxide gas was passed at such a rate as to maintain the temperature between 0° and 4°, when the temperature of the reaction ceased to rise a rapid stream of carbon dioxide was passed for 2 hrs. The mixture was then acidified at 5° with dilute hydrochloric acid until the inorganic salts had dissolved, then the ether layer was separated. The etherial solution was washed with water then extracted with sodium bicarbonate solution (5 x 30 ml). The sodium bicarbonate extracts were combined, washed with ether, acidified with dilute hydrochloric acid and ether extracted (3 x 30 ml), the etherial solution was washed with water and dried ($MgSO_4$). Evaporation gave a light yellow oil which was found to be a mixture of allenic and acetylenic acids (5.0g. 40%) ν_{max} 3300-2500vs (hydrogen bonded OH); 2260 m and 2220,m (C=C); 1965s (C=C=C) and 1740-1670vs (C=O) cm^{-1}. The acid mixture was dissolved in ether and extracted with sodium bicarbonate solution (3 x 10 ml). The ether solution was dried and on evaporation yielded pure 4-isopropyl-5- methylhexa-2,3-dienoic acid. The sodium bicarbonate extract was acidified, extracted

with ether and the process repeated, the cycle was carried out four times, the fourth time the ether solution yielded a mixture of allenic and acetylenic acids. The total yield of allenic acid was (3.8 g. 30%). The allenic acid was recrystallised from hexane m.p. 53.5^{o} - 54.5^{o} (Found C, 70.6; H, 9.4; O, 19.0. $C_{10}H_{16}O_2$ requires C, 71.4; H,9.5 O, 19.1%) ν_{max} (I.R. 75) 3400-2600vs (hydrogen bonded -OH); 1975s (C=C=C); 1700vs (C=O); 850m; 792m. cm^{-1}. λ_{max} 213 mμ, (ε, 9,850).

<u>Reaction of 3-phenylbuta - 1,2-diene-1-magnesium bromide with carbon dioxide</u>.

Magnesium turnings (3.7g. 0.15 mole), ether (50 ml) and a crystal of iodine were placed in a dry flask through which a slow stream of dry, oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-phenylbuta-1, 2-diene (2.44g. 0.12 mole) in ether (50 ml) were added and after about 10 mins. when formation of the Grignard reagent had started the rest of the solution diluted with ether (100 ml) was added dropwise at such a rate as to maintain

the solution at a gentle reflux. When addition of the solution was complete the solution was allowed to cool, then cooled to 0° and a current of dry carbon dioxide was passed at such a rate as to keep the temperature between 0° and 5°, when the temperature of the reaction ceased to rise carbon dioxide was passed for 2hrs. The solution was then acidified at 5° with dilute hydrochloric acid until the inorganic salts had dissolved then the ether layer was separated. The etherial solution was extracted with sodium bicarbonate solution (5 x 30 ml), the sodium bicarbonate extracts were combined, washed with ether, acidified with dilute hydrochloric acid and ether extracted (3 x 30 ml), the etherial solution was washed with water and dried ($MgSO_4$). Evaporation of the ether left a yellow solid (3.5g. 18%) m.p. 108-10° which on recrystallisation from aqueous alcohol or ether petrolium spirit gave pure 4-phenylbuta-2,3-dienoic acid m.p. 129-30° ν_{max} (I.R.76) 3400-2500s (hydrogen bonded -OH); 1950s (C=C=C); 1695vs (C=O); 1600w (aromatic C=C); 767s and 690s cm^{-1}., λ_{max} 207 mμ, (ε, 32,000); λ_{max} 248 mμ, (ε, 15,470).

B. Reaction with Oxygen.

Reaction of 3-methylpenta-1,2-diene-1-magnesium bromide with oxygen.

(a) Magnesium turnings (4.8g., 0.2 mole), dry ether (30 ml) and a crystal of iodine were placed in a dry flask through which a slow current of dry oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-methylpenta-1,2-diene (32.2g., 0.2 mole) in dry ether (20 ml) were added to the flask, then after about 5 mins. when formation of the Grignard compound had started the bromoallene solution was added dropwise at a rate just sufficient to keep the mixture refluxing gently. When addition of the bromoallene solution was complete the mixture was stirred and maintained at a gentle reflux (by external heating) for 1 hr. The suspension was cooled to -5° and dry oxygen was passed, slowly at first then more rapidly, for 2 hrs., the cooling bath being removed after the first hr. The suspension was again cooled and dilute hydrochloric acid was added until all the inorganic salts had dissolved, the mixture was separated, the aqueous portion was extracted

with ether (2 x 20 ml) the ether solutions were combined and dried ($MgSO_4$). Distillation after first removing the ether gave 3-methylpent-1-yn-3-ol (9.4g., 48%) ν_{max} 3400vs (OH), 3300vs (C=CH), 2110w (C=C); g.l.c. (silicone oil, 80°) gave only one peak, t, 7 min.; g.l.c. of -mixture with authentic 3-methylpent-1-yn-3-ol also gave only one peak, t, 7 min. Careful fractionation of the residue gave a mixture of two compounds b.p. 57°/11 mm which could not be separated ν_{max} (I.R.78) 3330 vs (C=CH), 3120w (C=C), 1965w (C=C=C) cm^{-1}., g.l.c. (dinonyl phtholate, 80°) showed two compounds t, 31 min, t, 43 min in the ratio of about 7:2.

(b) In another similar experiment the Grignard compound was formed over 4 hr. and gave a large proportion of the latter two compounds in the same proportion. (8.4g., 52%).

<u>Reaction of 3-ethylpenta-1, 2-diene-1-magnesium bromide with oxygen</u>.

Magnesium turnings (2.4g., 0.1 mole), dry ether (20 ml) and a crystal of iodine were placed in a dry flask through which a slow current of oxygen-free nitrogen was passed.

A few milliliters of a solution of 1-bromo-3-ethylpents-1, 2-diene (17.5g., 0.1 mole) in dry ether (15 ml) was added, after about 10 mins. when formation of the Grignard compound had started, the rest of the solution, diluted with dry ether (100 ml) was added dropwise at a rate just sufficient to keep the mixture refluxing gently. The mixture was then stirred for 1 hr. cooled and dry oxygen passed for 1.5 hr. at about 5°; after stirring for a further 0.5 hr. the mixture was acidified at $5-10^{o}$ with dilute hydrochloric acid until all the inorganic salts had dissolved. The ether layer was then separated, the aqueous portion was ether extracted (3 x 15 ml), the ether layers combined, washed with a little water and dried ($MgSO_4$) Distillation after first removing the ether gave a first fraction of 3-ethylpent-1-yn-3-ol (5.1g., 45%), ν_{max} 3400vs (-OH), 3300vs (C=CH), 2120w (C=C) cm^{-1}. g.l.c. (silicone oil, 100°) gave only a peak at t, 5.5 min. The second fraction again proved to be on an inseparable mixture of two compounds ν_{max} 3330vs (C=CH), 3120 w(C=C), 1960w (C=C=C) cm^{-1}.

C. Reactions with Active Hydrogen.

Reaction of 3-Methylpenta-1,2-diene-1-magnesium bromide with Water.

(a) Magnesium turnings (1.8g., 0.075 mole), dry ether (20ml) and a crystal of iodine were placed in a dry flask through which a slow current of dry oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-methyl-penta-1,2-diene (12g., 0.075 mole) in dry ether (10 ml) was added, then after about 10 min when formation of the Grignard compound has started, the rest of the solution diluted with dry ether (30 ml) was added dropwise at a rate just sufficient to keep the reaction going, when all the solution had been added the mixture was stirred for 1 hr. at room temperature before cooling to 5° and adding water (20 ml). The suspension was then acidified with dilute hydrochloric acid until the inorganic salts had dissolved, the organic layer was separated, washed with water and dried ($MgSO_4$). Distillation after first removing the ether gave a mixture of 3-methylpenta-1,2-diene and 3-methylpent-1-yne (2.5g., 41%), b.p. 67°/760 mm. g.l.c. showed the ratio of products to be 3:1.

(b) Magnesium turnings (1.8g., 0.075 mole), dry ether (20 ml) and a crystal of iodine were placed in a dry flask, through which a slow stream of oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-methylpenta-1,2-diene (12g., 0.075 mole) in ether (10 ml) was added. After about 10 min when the formation of the Grignard compound had started the rest of the solution was added dropwise, the solution being allowed to reflux vigerously, when addition was complete the suspension was heated under reflux for 1 hr. cooled to 5° and water (20 ml) added. Working up as above gave the same mixture of 3-methylpenta-1,2-diene and 3-methylpent-1-yne.

D <u>Reaction with Ketones</u>.

<u>Reaction of 3-Methylpenta-1,2-diene-1-magnesium bromide with Acetone</u>.

Magnesium turnings (2.4g., 0.1 mole), dry ether (25 ml) and a crystal of iodine were placed in a dry flask through which a slow stream of oxygen-free nitrogen was passed. A few milliliters of a solution of 1-bromo-3-methylpenta-1,2

-diene (16. 1g., 0.1 mole) in ether (50 ml) was added, after about 10 min when formation of the Grignard compound had started, the rest of the solution, diluted with ether (100 ml) was added dropwise at a rate just sufficient to keep the reaction refluxing gently, the mixture was then stirred for 30 mins. cooled and dry redistilled acetone (6.4g., 0.11 mole) was added slowly. The mixture was then refluxed for 1.5hr. cooled to 5° and acidified with dilute hydrochloric acid until all the inorganic salts had dissolved. The ether layer was separated, washed with water and dried ($MgSO_4$).

Distillation after removing the ether gave a low boiling fraction which was shown to be a mixture of four products followed by 2,5-dimethylhept-3-yn-2-ol (4.4g., 31%) b.p. $94-100^{o}$/1.5mm. recrystalised from hexane m.p. 41°

ν_{max} (I.R.77) 3400s (-OH) 2260w (C=C), 940m cm^{-1}.

PART IV

SPECTRA

INFRA-RED SPECTRA

I.R. 1	1-Bromo-3-phenylpropa-1,2-diene
2	1-Bromo-3-phenylbuta-1,2-diene
3	3-3-Diphenylpropa-1,2-diene
4	1-Iodo-3-methylbuta-1,2-diene
5	1-Iodo-3-methylpenta-1,2-diene
6	1-Iodo-3-ethylpenta-1,2-diene
7	1-Iodo-3,4,4-trimethylpenta-1,2-diene
8	1,1-Dibromo-3-methylbuta-1,2-diene
9	1,1-Dibromo-3-methylpenta-1,2-diene
10	1,1-Dibromo-3,4,4-trimethylpenta-1,2-diene
11	1,1-Dibromohexa-1,2-diene
12	1,1-Dibromo-3,3-diphenylpropa-1,2-diene
13	1-Bromo-1-chloro-3-methylpenta-1,2-diene
14	1-Deuterobut-1-yn-3-ol
15	1-Deutero-3-methylpent-1-yn-3-ol
16	1-Deutero-3,4,4-trimethylpent-1-yn-3-ol
17	1-Iodobuta-1,2-diene
18	1-Deutero-1-iodobuta-1,2-diene

I.R. 19 1-Bromo-3-methylpenta-1,2-diene

20 1-Bromo-1-deutero-3-methylpenta-1,2-diene

21 1-Chloro-3,4,4-trimethylpenta-1,2-diene

22 1-Chloro-1-deutero-3,4,4-trimethylpenta-1,2-diene

23 1-Cyano-3-methylbuta-1,2-diene

24 1-Cyano-3-methylpenta-1,2-diene

25 1-Cyano-3-ethylpenta-1,2-diene

26 1-Cyano-3,5-dimethylhexa-1,2-diene

27 1-Cyano-3,4,4-trimethylpenta-1,2-diene

28 1-Cyano-3-isopropyl-4-methylpenta-1,2-diene

29 1-Cyano-3-isobutyl-5-methylhexa-1,2-diene

30 1-Cyano-3-t-butyl-4,4-dimethylpenta-1,2-diene

31 1-Cyanohexa-1,2-diene

32 1-Cyano-4-methylpenta-1,2-diene

33 1-Cyano-3-phenylpropa-1,2-diene

34 1-Cyano-3-(cis-cyanomethylene)-4,4-dimethyl-2-isopropylidenecyclobutane

35 1-Cyano-3-(cis-cyanomethylene)-4-ethyl-4-methyl-2-(2'butylidene)-cyclobutane

I.R. 36 1-Cyano-3-(cis-cyanomethylene)-4,4-diethyl-2-(3'-pentlylidene)- cyclobutane

37 1-Cyano-2-(diethylamino)-4-methylpent-1-ene

38 1-Cyano-2-(diethylamino)-4-methylpent-2-ene

39 1-Cyano-3-methyl-2-piperidinobut-2-ene

40 1-Cyano-3-methyl-2-piperidinobut-1-ene

41 2-(n-Butylamino)-1-cyano-3-methylbut-1-ene

42 1-Cyano-2-(diethylamino)-3-methylpent-2-ene

43 1-Cyano-2-(diethylamino)-3-methylpent-1-ene

44 1-Cyano-3-methyl-2-pyrrolidinopent-1-ene

45 1-Cyano-3-methyl-2-piperidinopent-2-ene

46 1-Cyano-3-methyl-2-piperidinopent-1-ene

47 2-Amino-1-cyano-3-ethylpent-1-ene

48 1-Cyano-2-(diethylamino)-3-ethylpent-2-ene

49 1-Cyano-3-ethyl-2-piperidinopent-1-ene

50 1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinoline)-pent-2-ene

51 1-Cyano-3-ethyl-2-(1,2,3,4-tetrahydroisoquinoline)-pent-1-ene

52 1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene

I.R. 53 1-Cyano-2-pyrrolidino-3,4,4-trimethylpent-1-ene

54 1-Cyano-2-piperidine-3,4,4-trimethylpent-2-ene

55 1-Cyano-2-piperidine-3,4,4-trimethylpent-1-ene

56 1-Cyano-2-(diethylamino)-3-isopropyl-4-methylpent-2-ene

57 1-Cyano-2-(diethylamino)-3-isopropyl-4-methylpent-1-ene

58 β-(Diethylamino)-β-phenylacrylonitrile

59 1-Cyano-3-methylpentan-2-one

60 1-Cyano-3-ethylpentan-2-one

61 1-Cyano-3,4,4-trimethylpentan-2-one

62 Benzoylacetonitrile

63 4-Ethylhexa-2;3-dienamide

64 4,5,5-Trimethylhexa-2,3-diendmide

65 4-Isopropyl-5-methylhexa-2,3-dienamide

66 4-Isobutyl-6-methylhepta-2,3-dienamide

67 4-t-Butyl-5,5-dimethylhexa-2,3-dienamide

68 3-Methylbut-3-en-1-yne

69 3-Ethylbut-3-en-1-yne

70 *trans*-3-Methylpent-3-en-1-yne

71 *cis*-3-Methylpent-3-en-1-yne

72 3-t-Butylbut-3-en-1-yne

73 *trans*-3-Ethylpent-3-en-1-yne

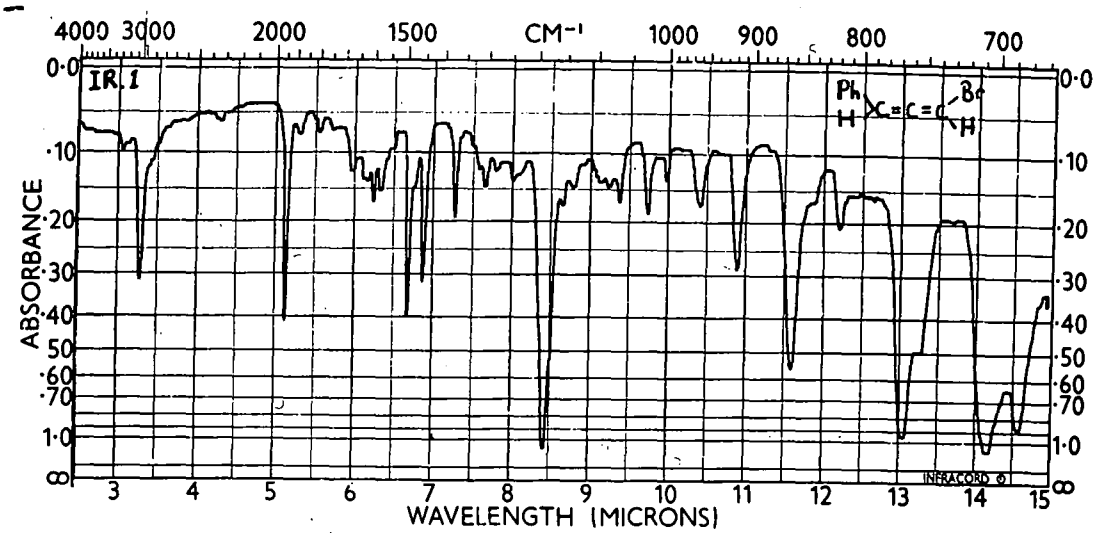
74 4,4,5-Trimethylhexa-2,3-dienoic acid

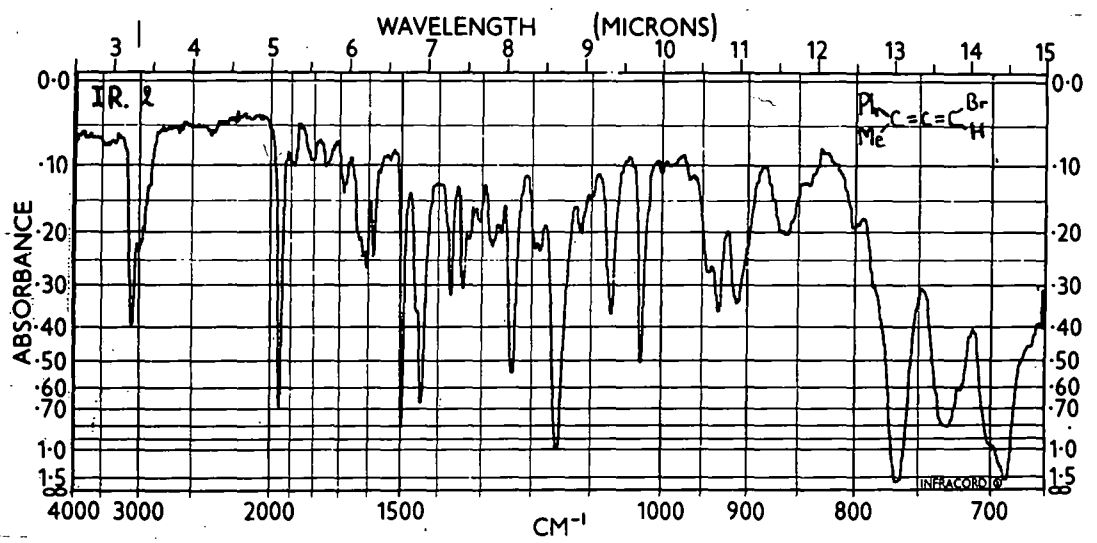
75 4-Isopropyl-5-methylhexa-2,3-dienoic acid

76 4-Phenylbutan-2,3-dienoic acid (Solution in chloroform

77 2,5-dimethylhept-3-yn-2ol

78 Hydrocarbon from coupled Grignard.


IR. 1
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD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ABSORBANCE
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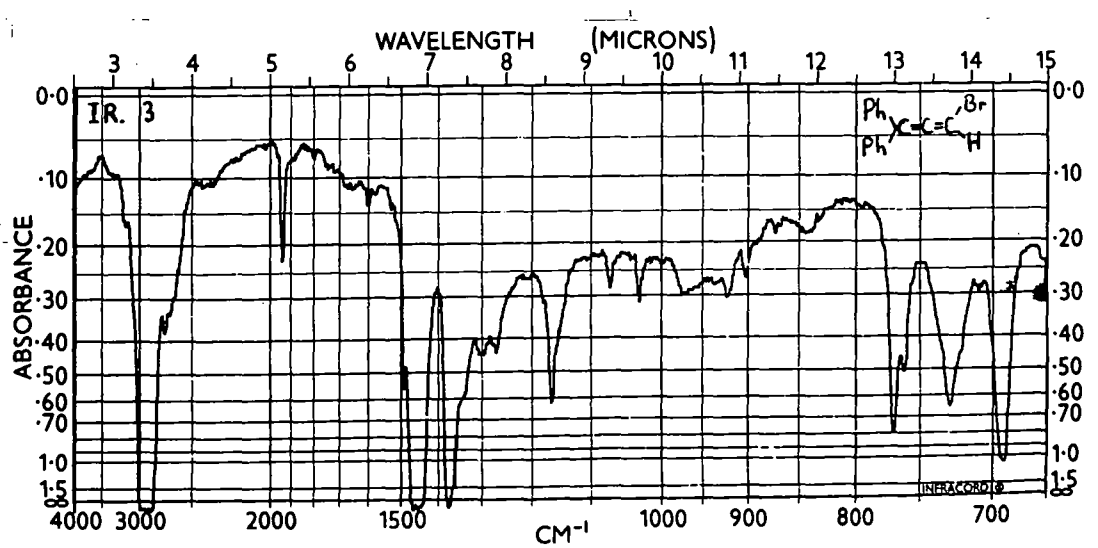
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ABSORBANCE
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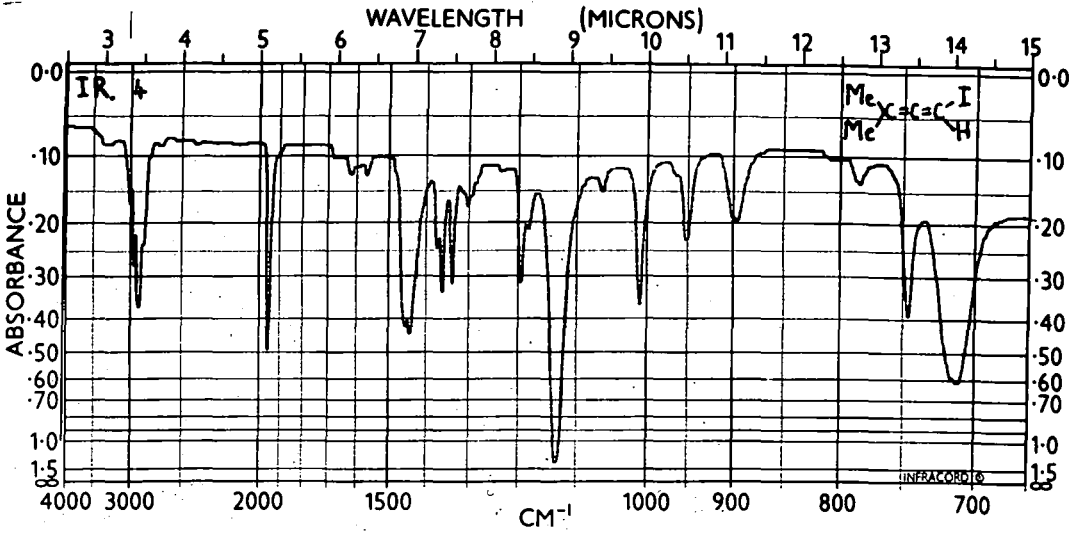
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IR. 4
ABSORBANCE
CM⁻¹
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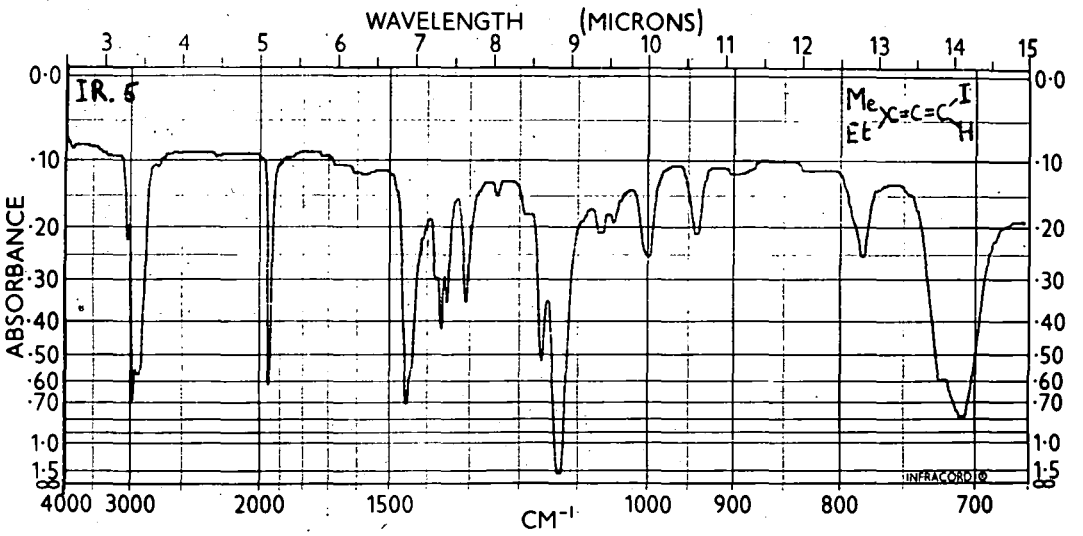
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ABSORBANCE
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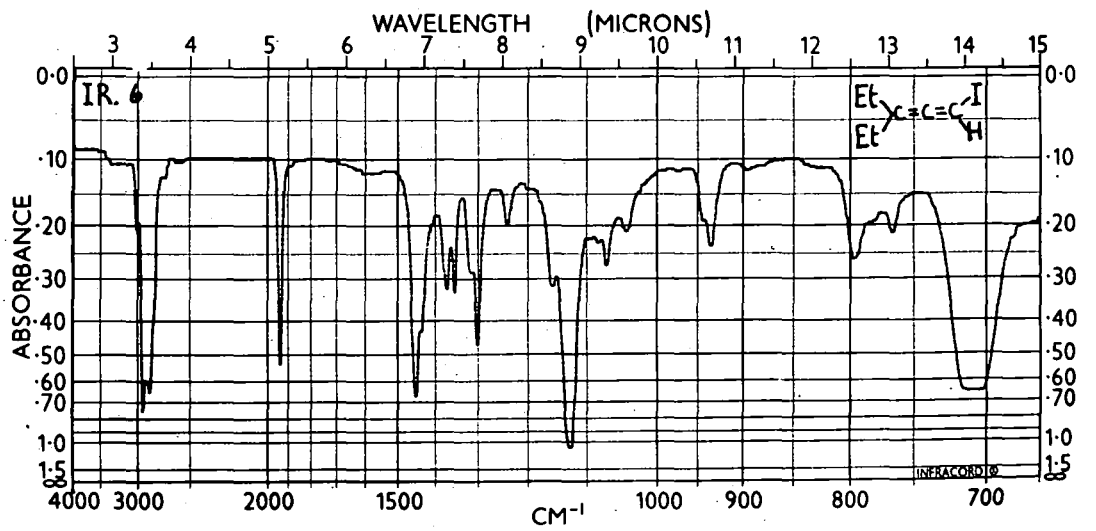
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ABSORBANCE
CM⁻¹
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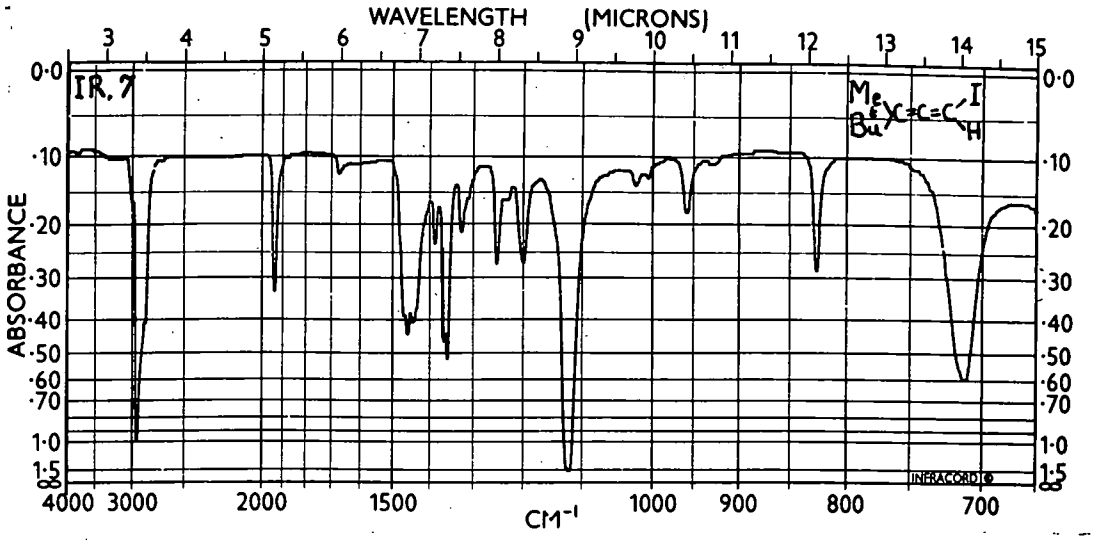
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CM⁻¹
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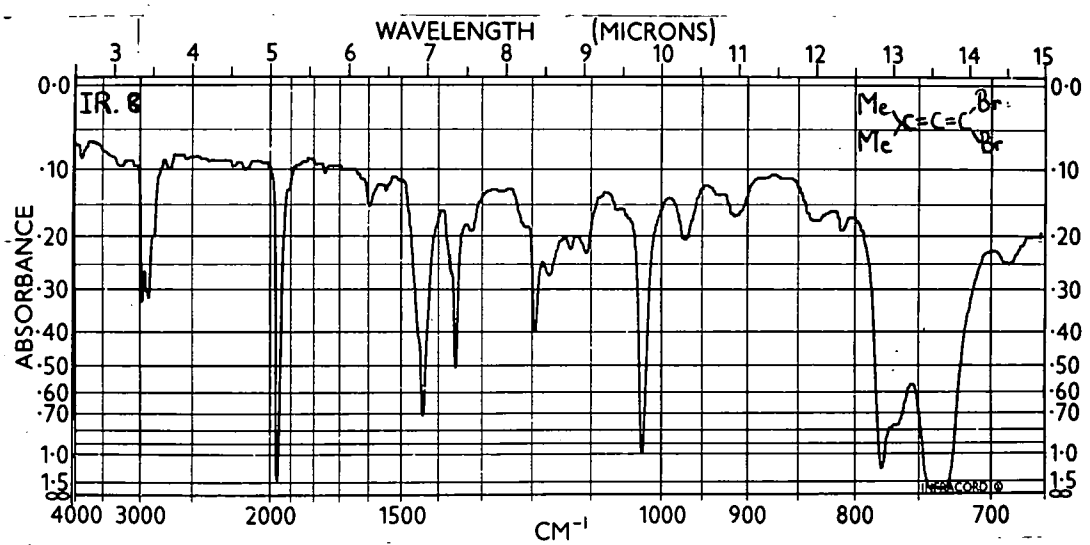
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ABSORBANCE
CM⁻¹
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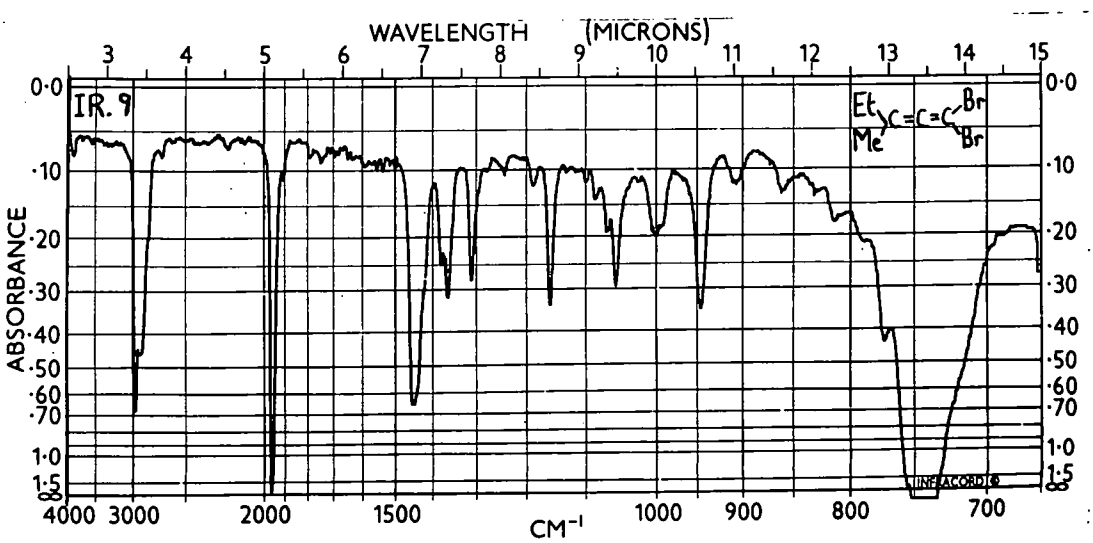
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ABSORBANCE
CM⁻¹
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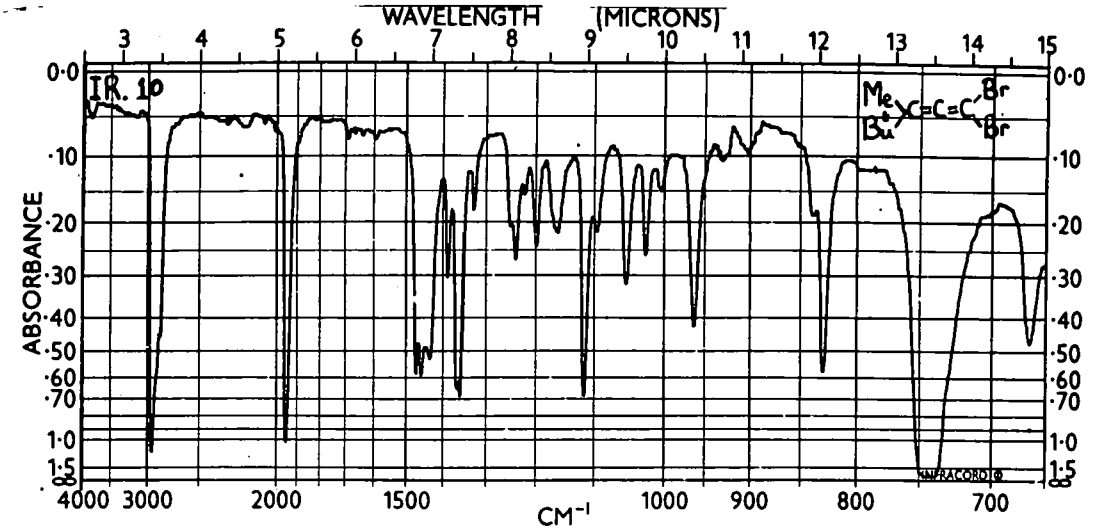
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ABSORBANCE
CM⁻¹
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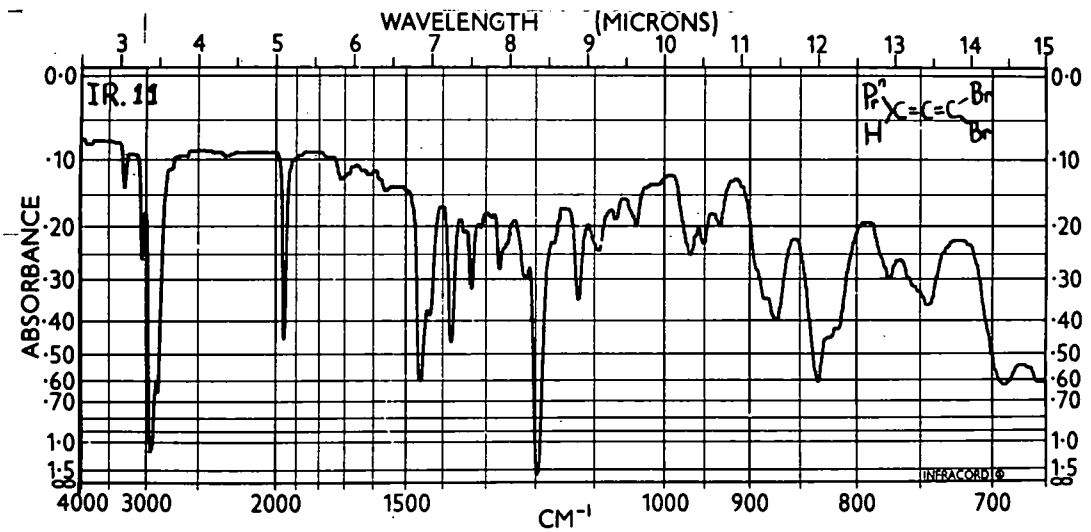
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ABSORBANCE
CM⁻¹
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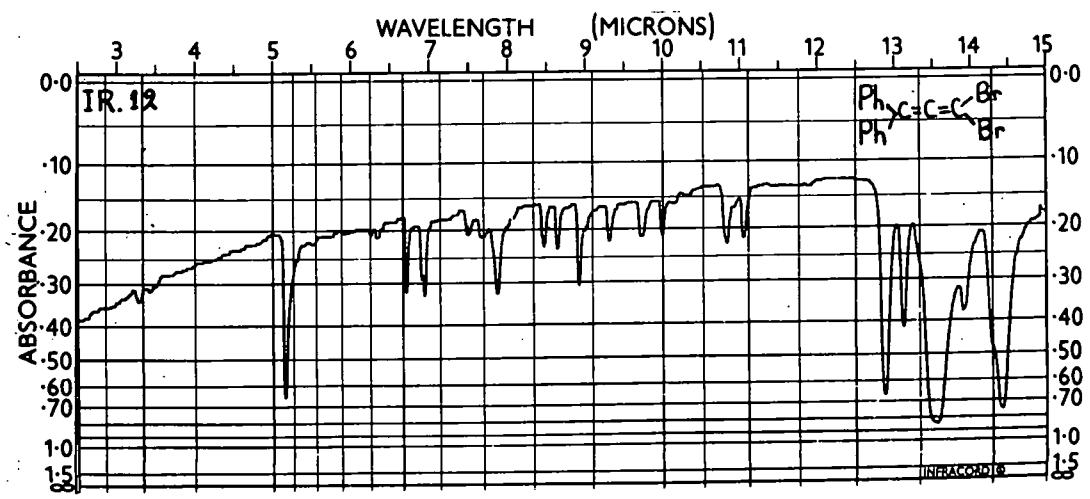
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ABSORBANCE
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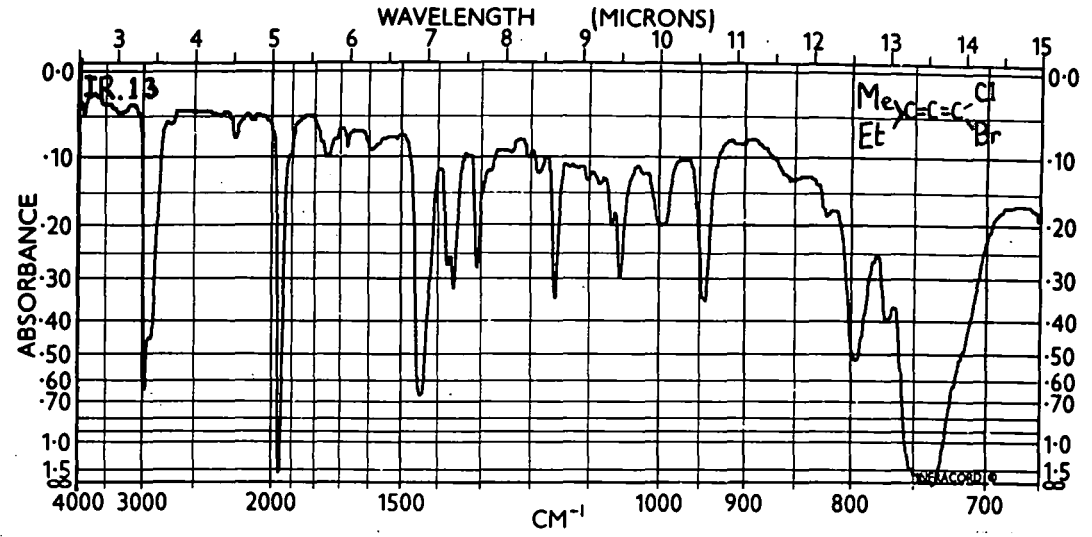
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ABSORBANCE
CM⁻¹
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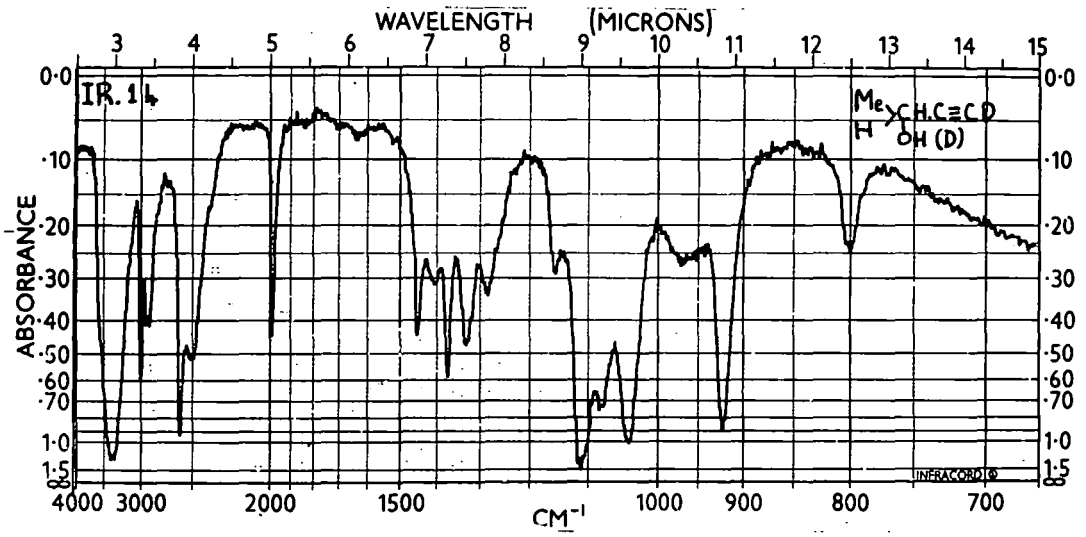
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ABSORBANCE
CM⁻¹
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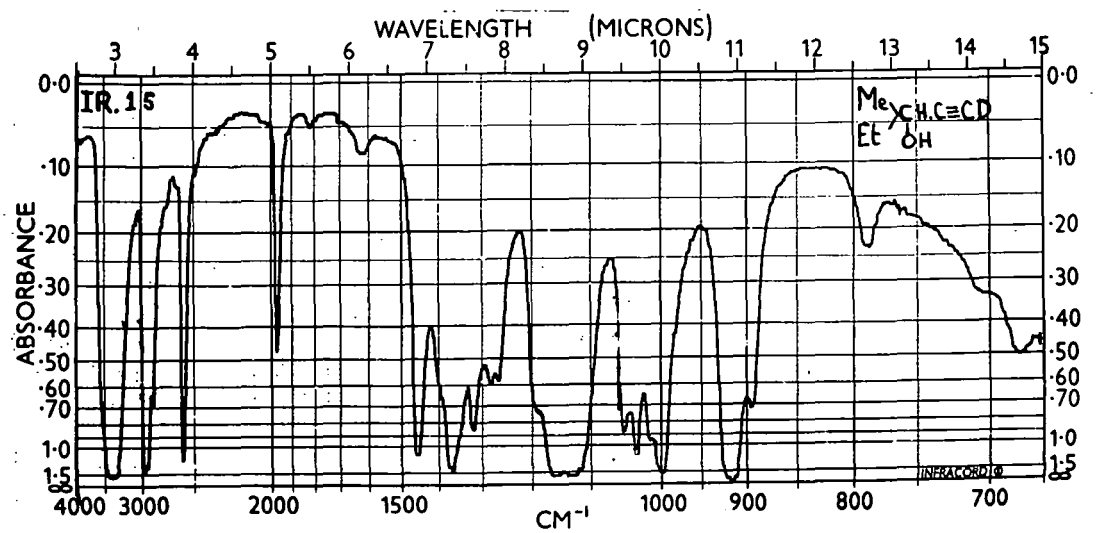
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CM⁻¹
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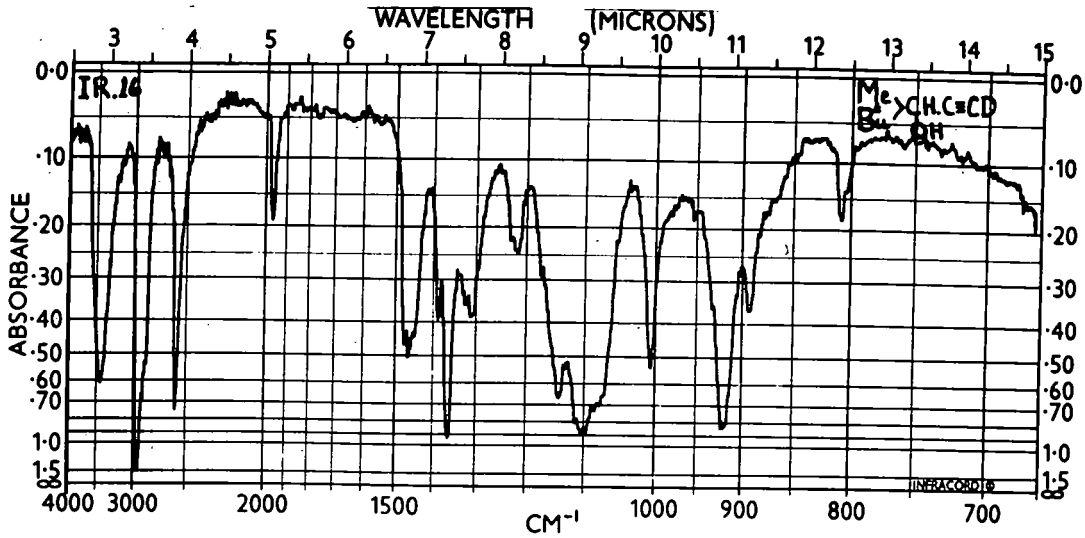
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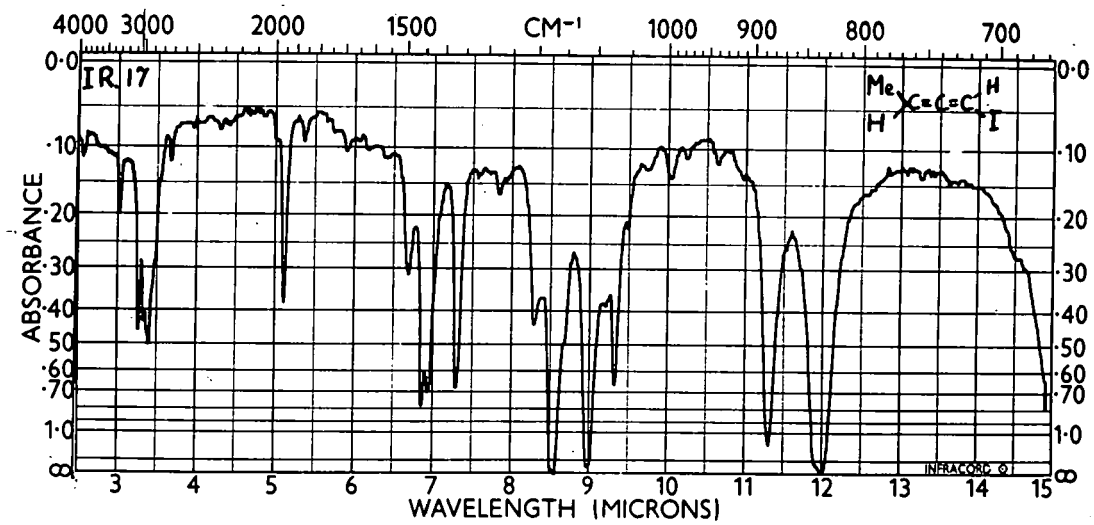
CM⁻¹
IR.17
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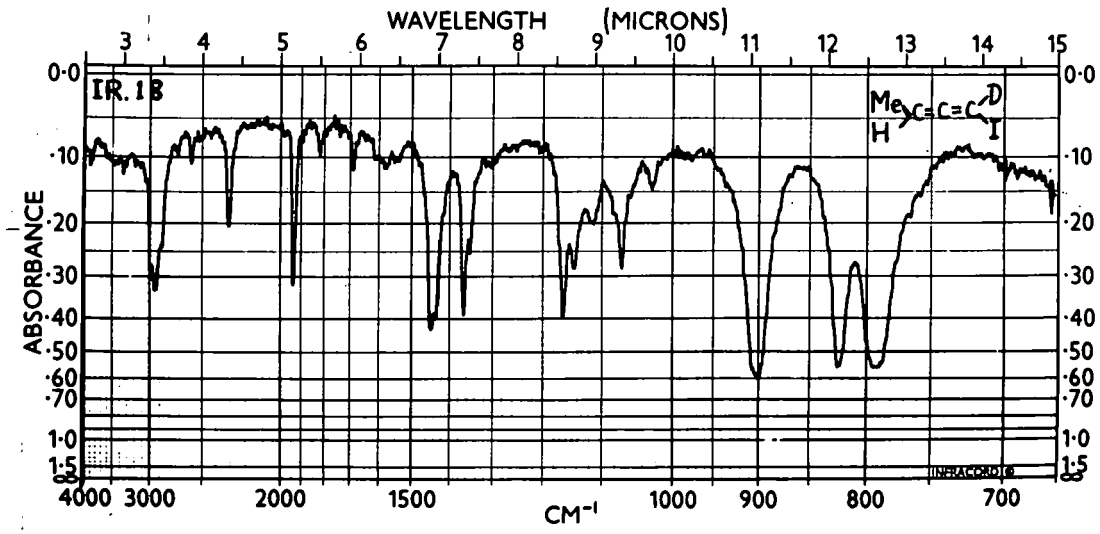
WAVELENGTH (MICRONS)
INFRACORD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CM⁻¹
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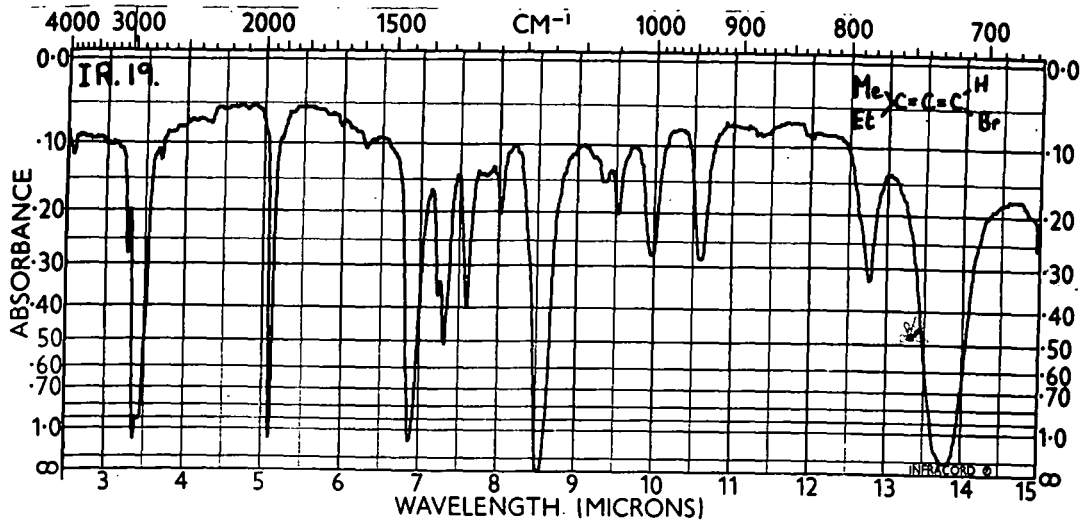
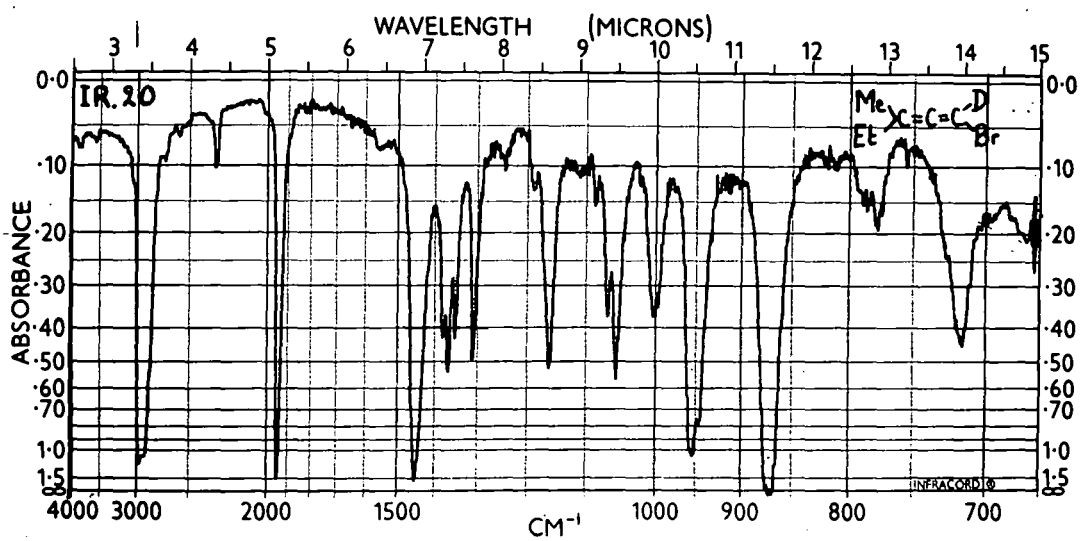

IR. 19.
CM⁻¹
ABSORBANCE
WAVELENGTH (MICRONS)
INFRACORD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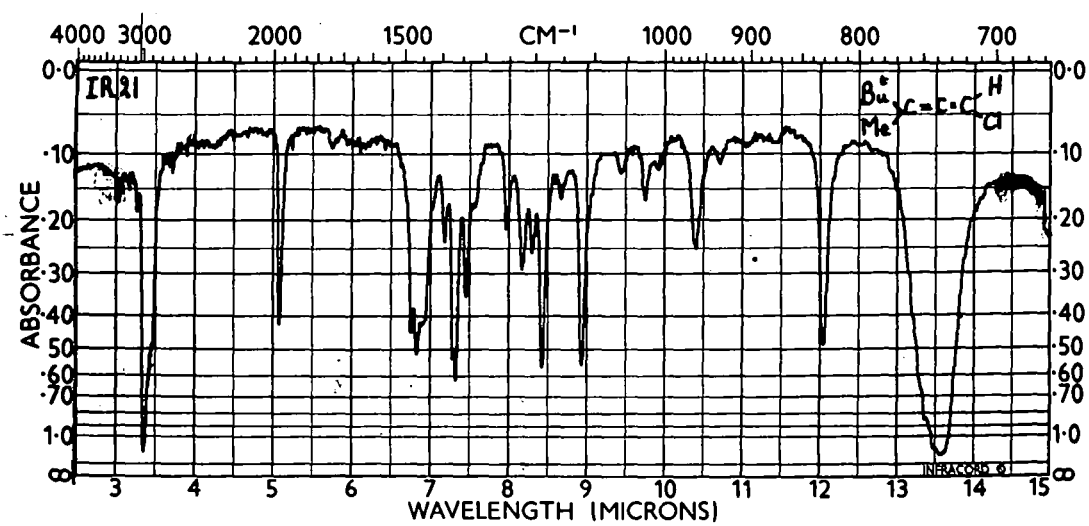
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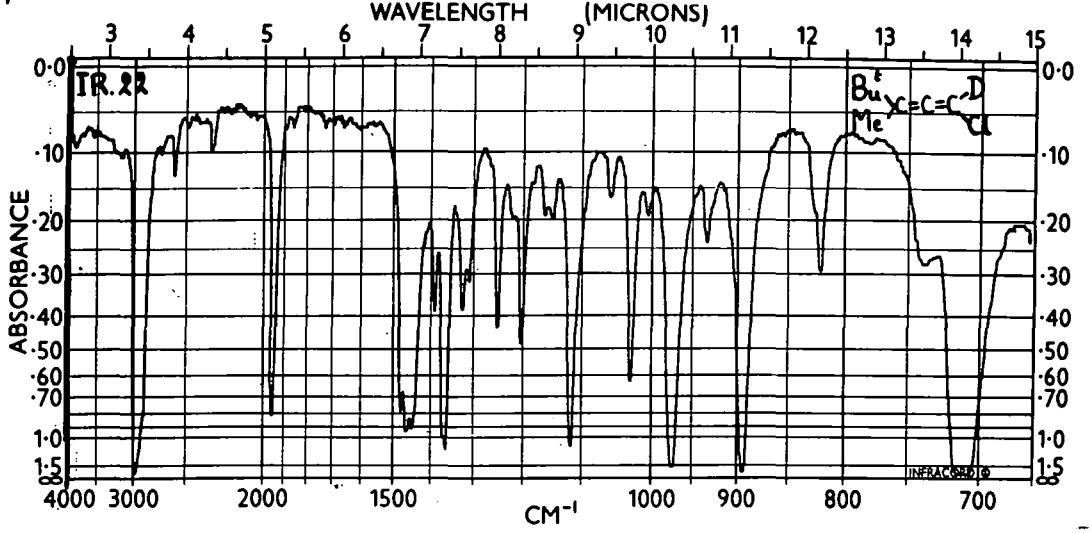
WAVELENGTH (MICRONS)
INFRACORD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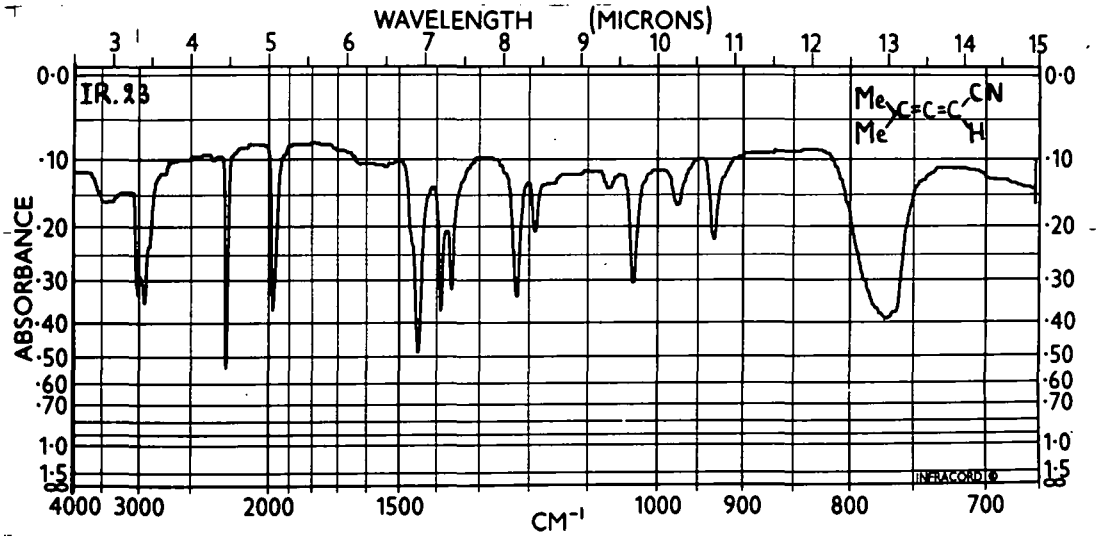
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CM⁻¹
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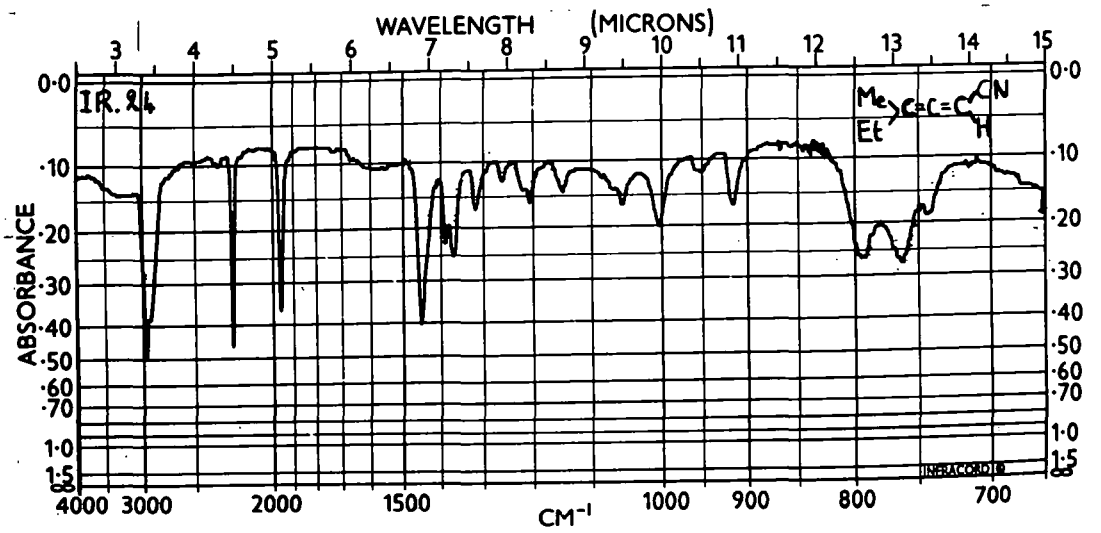
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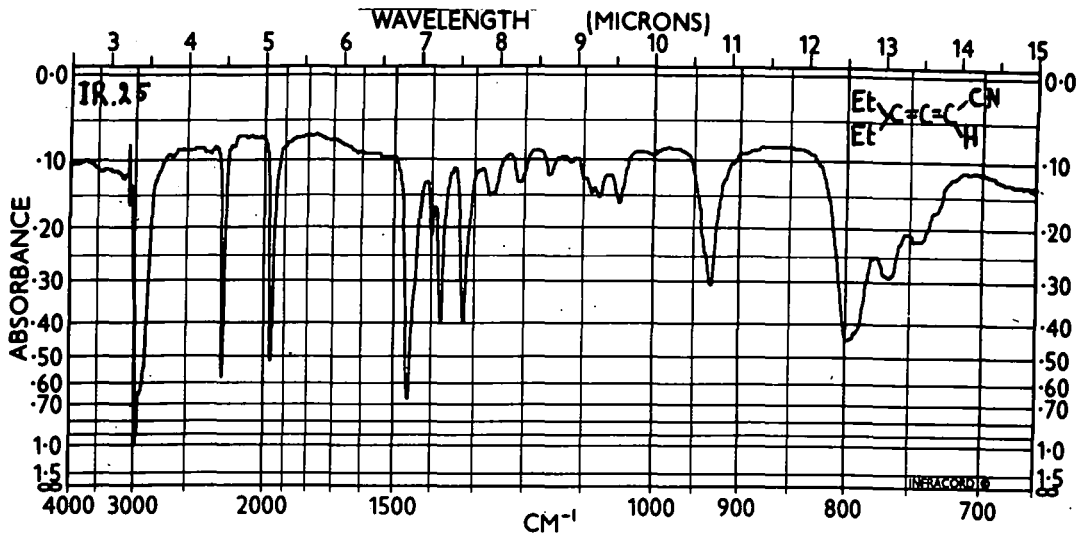
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IR.25
ABSORBANCE
CM⁻¹
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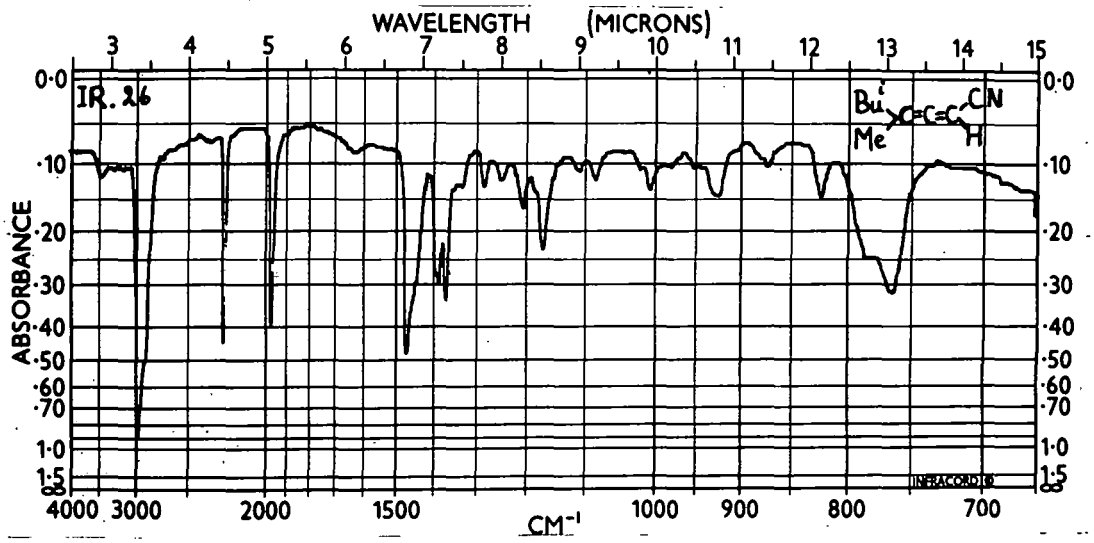
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IR.26
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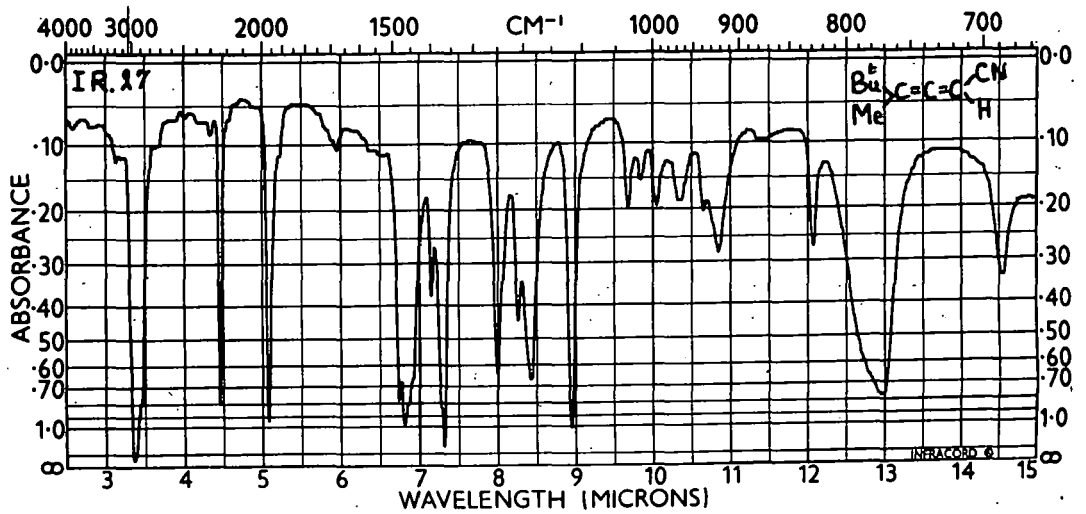
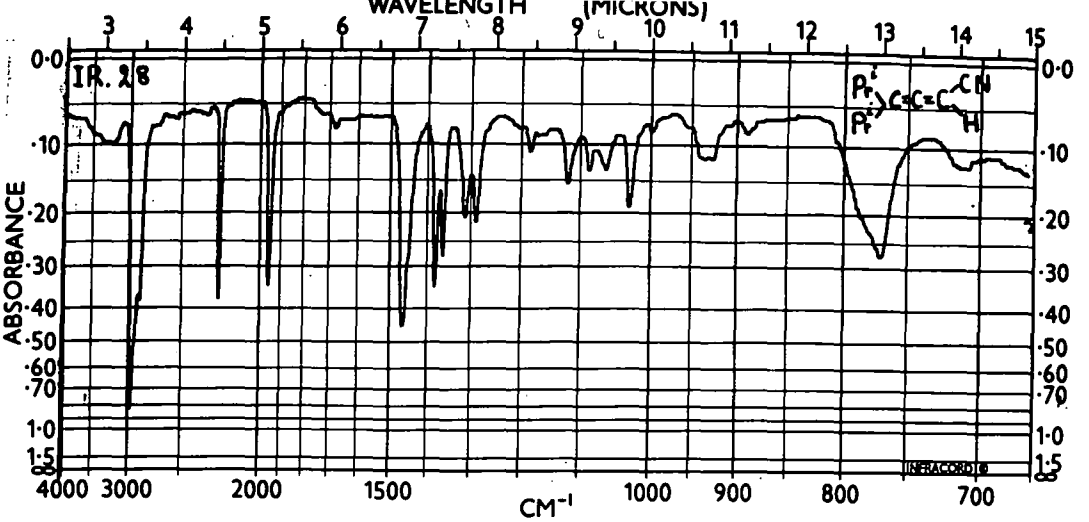

CM⁻¹
IR.27
ABSORBANCE
WAVELENGTH (MICRONS)
INFRACORD


WAVELENGTH (MICRONS)
IR. 28
ABSORBANCE
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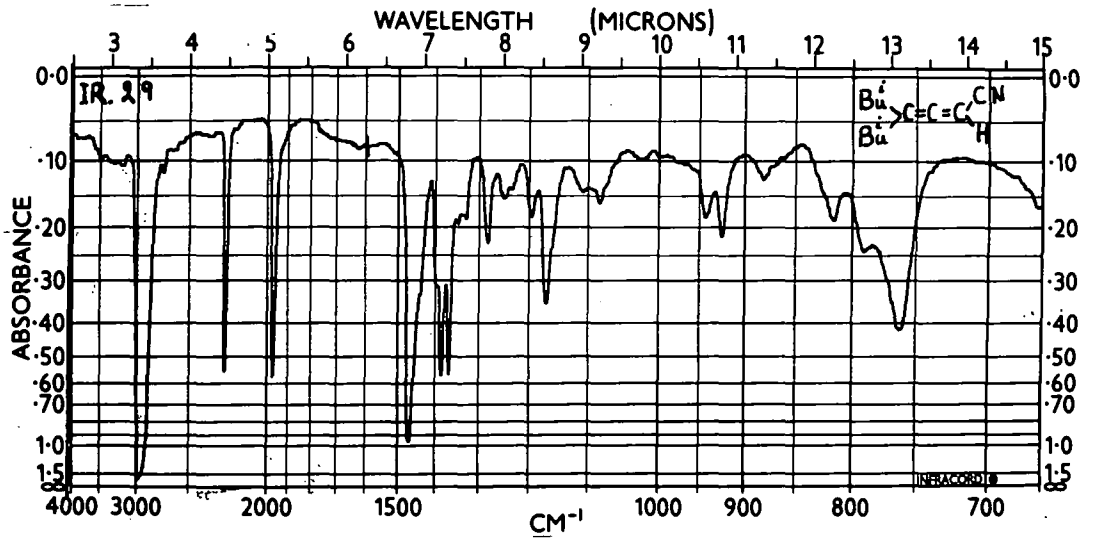
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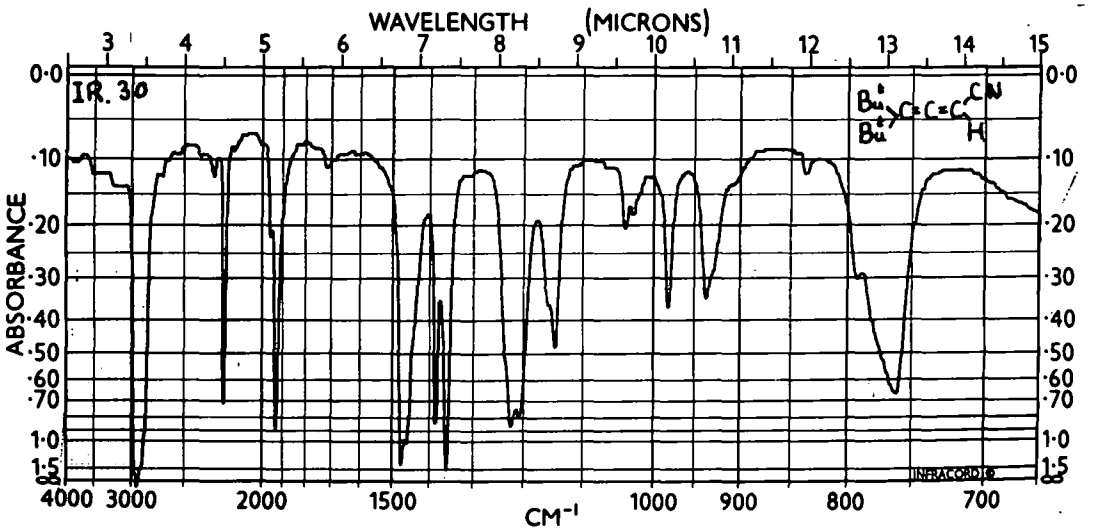
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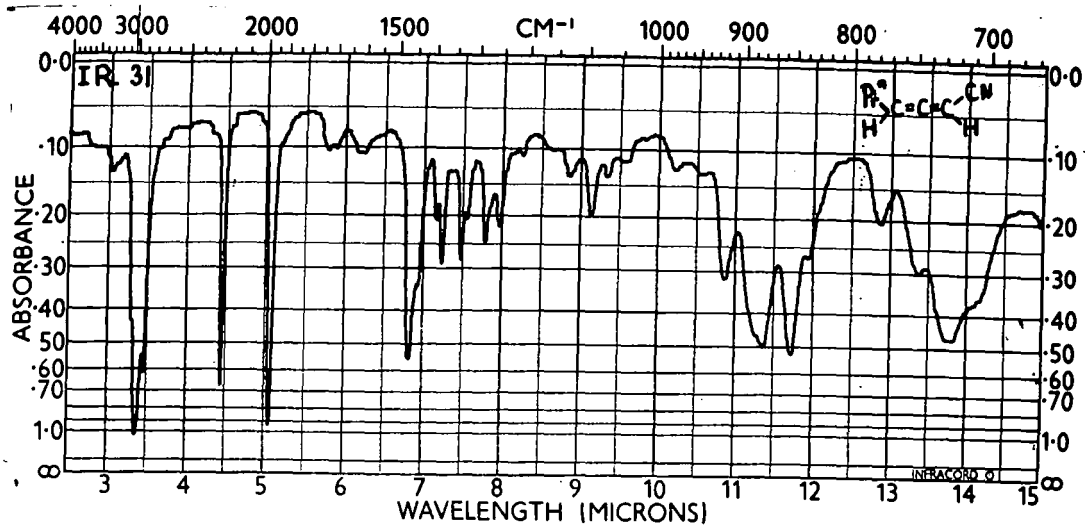
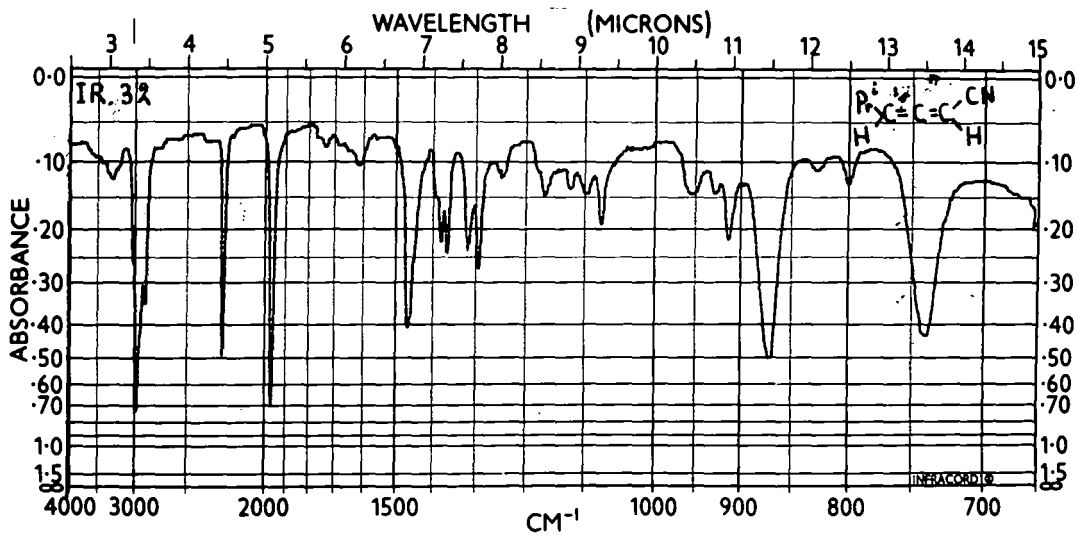
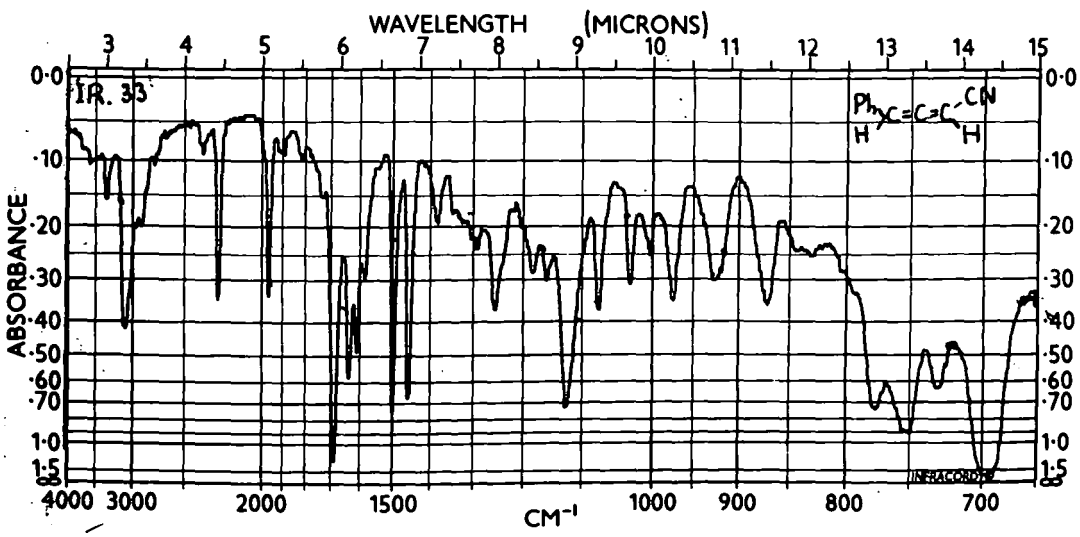
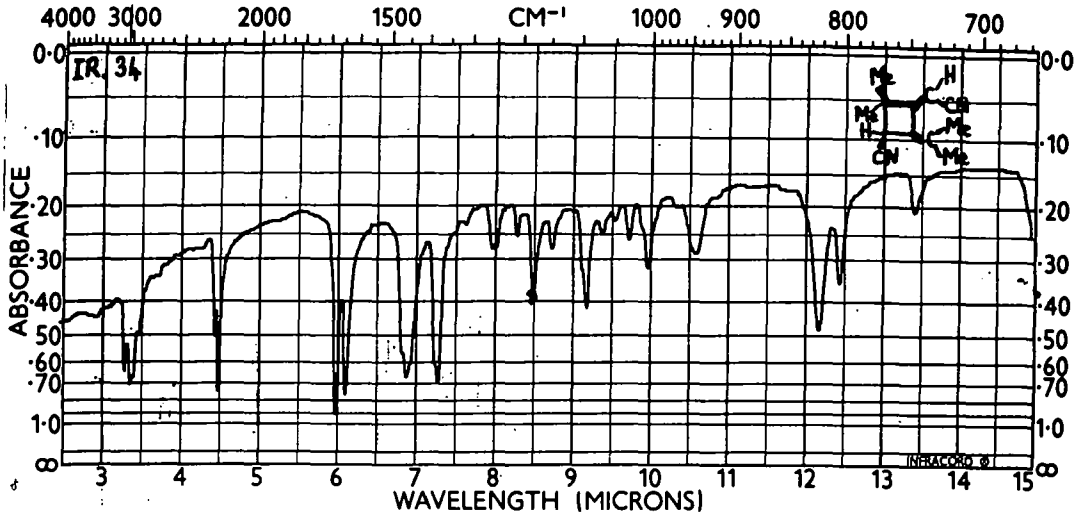
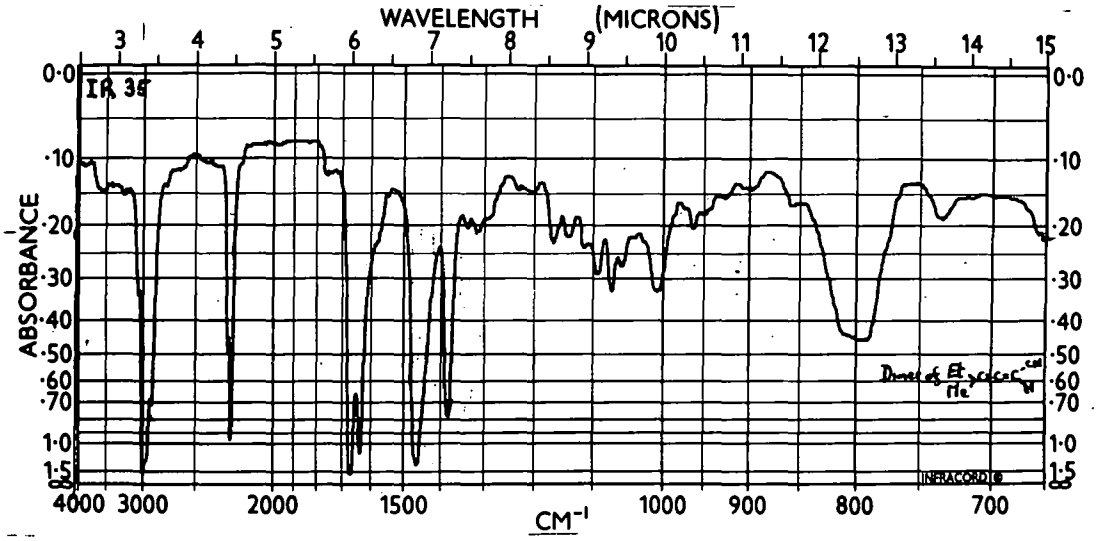
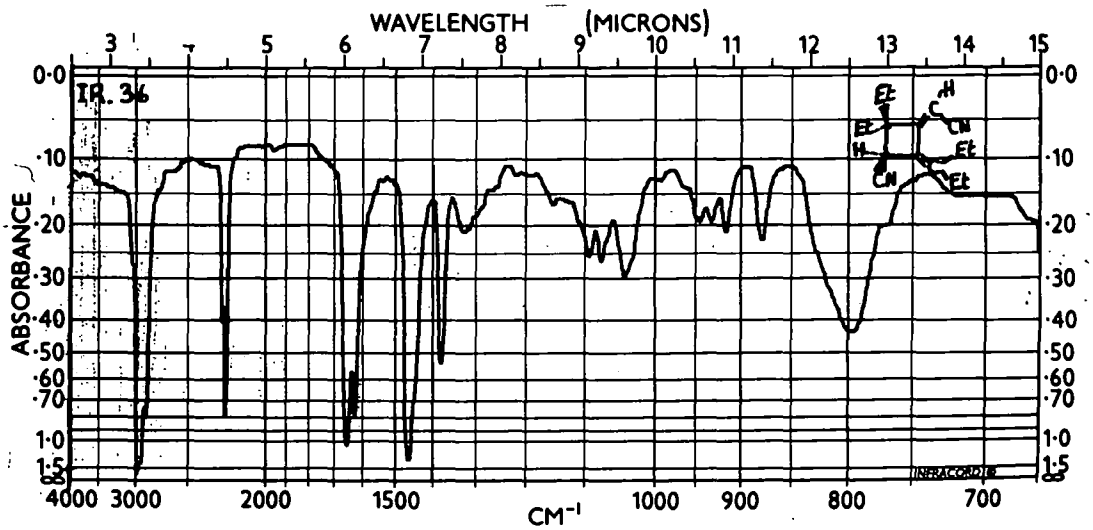

IR. 31
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

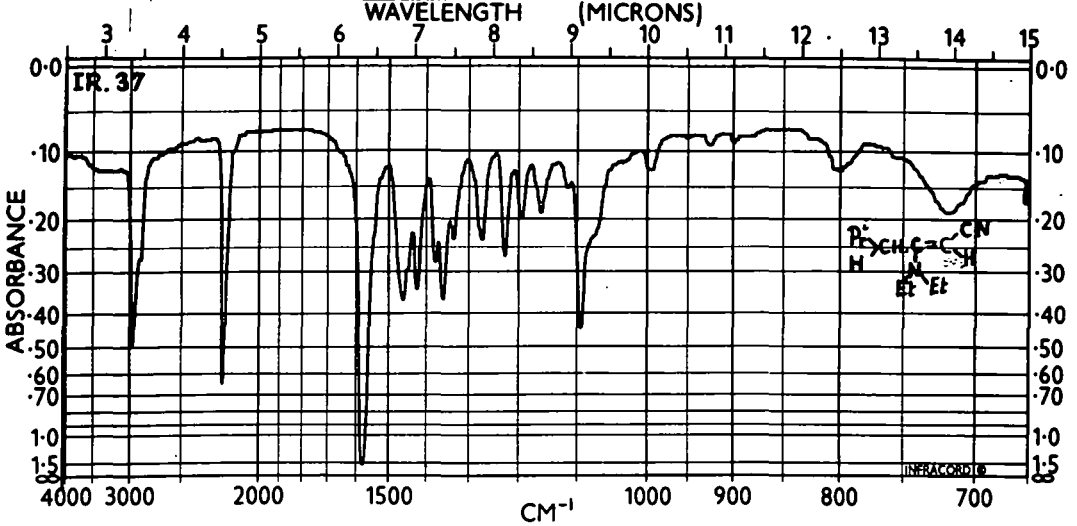

IR. 32
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

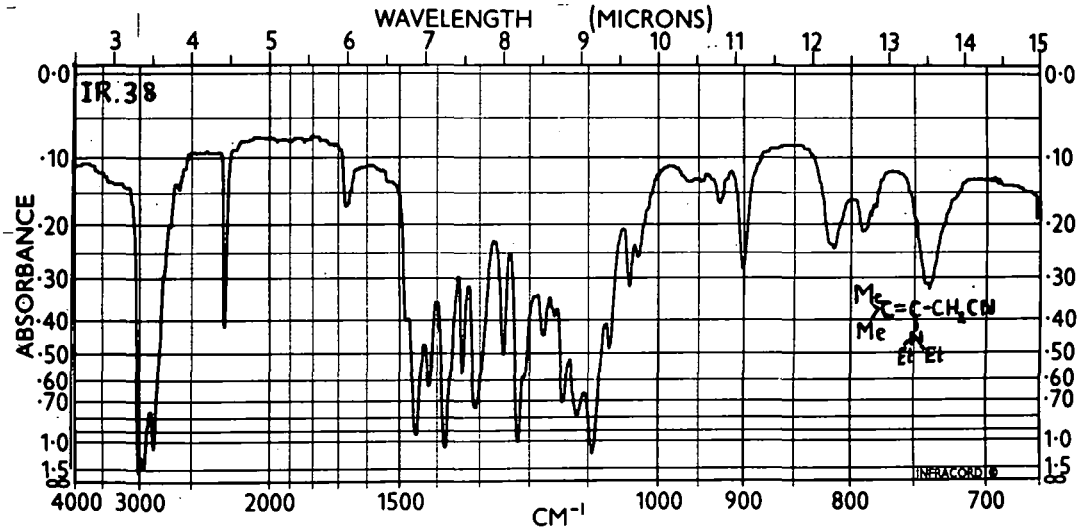

IR. 33
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

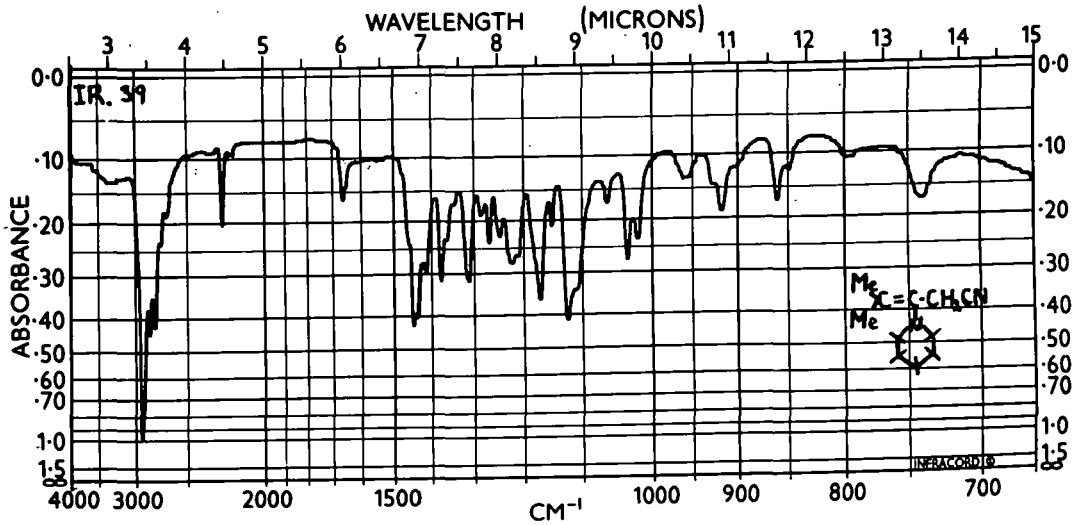

IR. 34
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

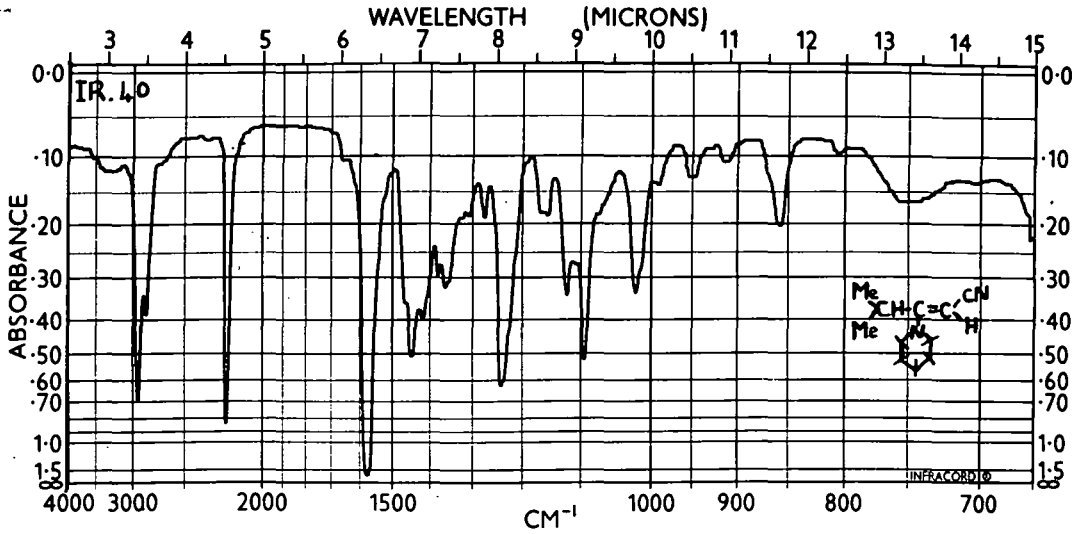

IR. 35
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

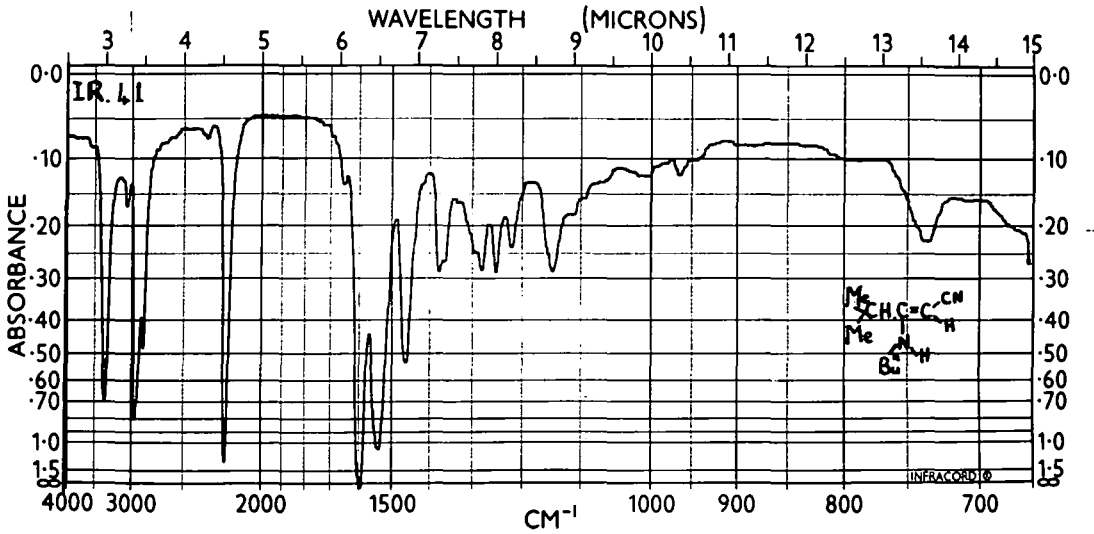

IR. 36
ABSORBANCE
WAVELENGTH (MICRONS)
CM⁻¹
INFRACORD

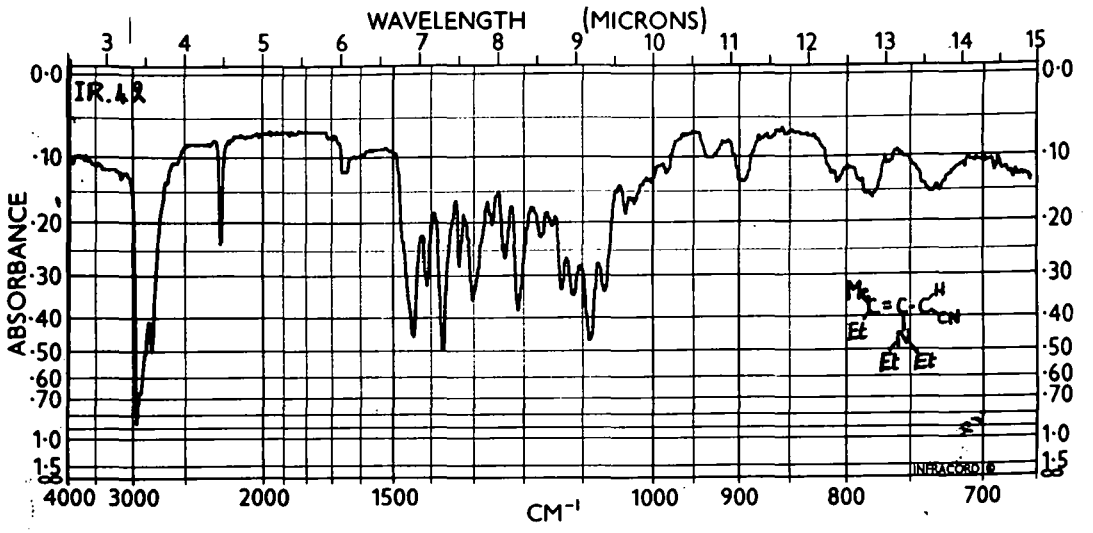

WAVELENGTH (MICRONS)
IR. 37
ABSORBANCE
CM⁻¹
INFRACORD®

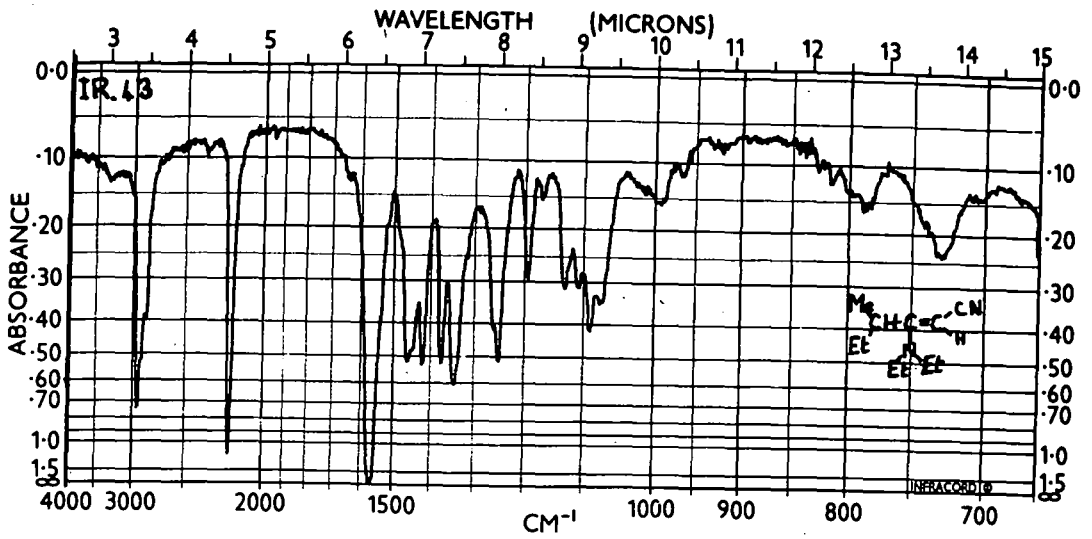

WAVELENGTH (MICRONS)
IR. 38
ABSORBANCE
CM⁻¹
INFRACORD®

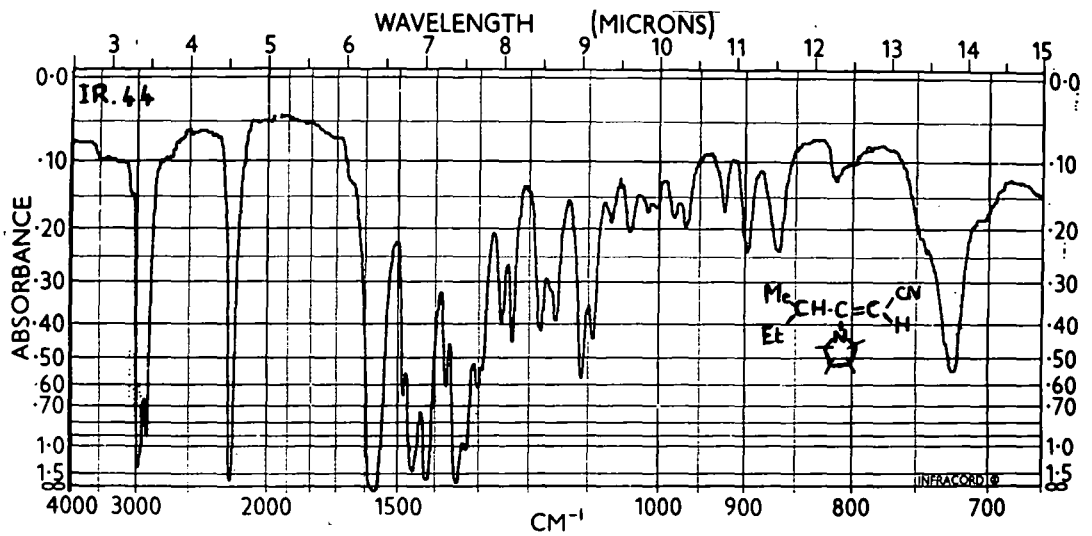

WAVELENGTH (MICRONS)
IR. 39
ABSORBANCE
CM⁻¹
INFRACORD®

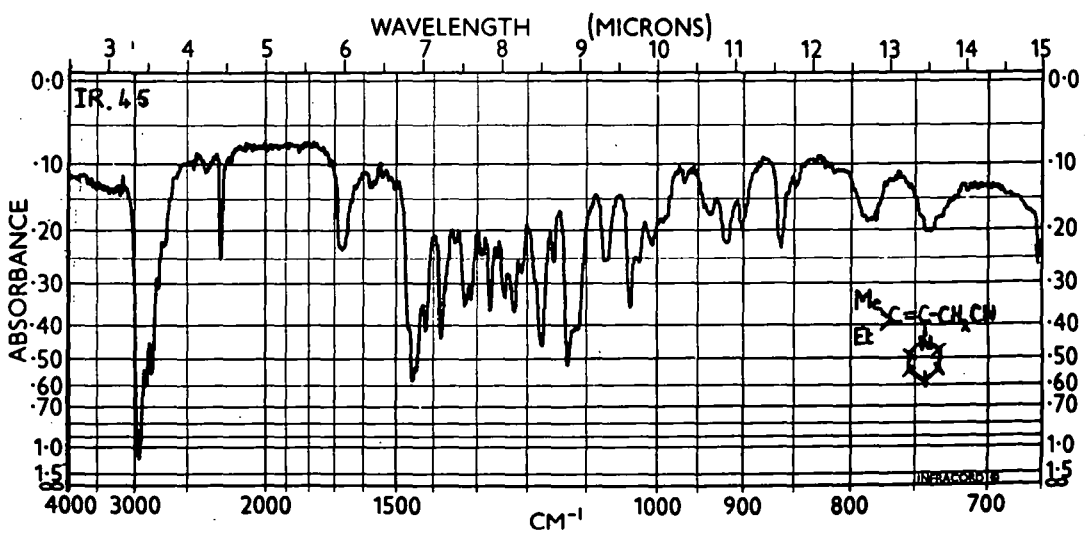

WAVELENGTH (MICRONS)
IR. 40
ABSORBANCE
CM⁻¹
INFRACORD

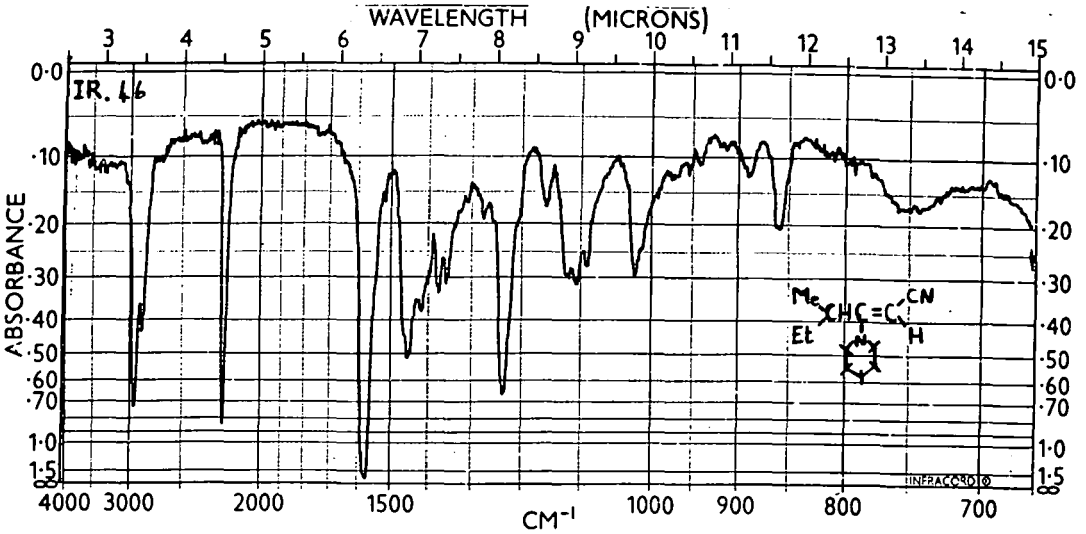

WAVELENGTH (MICRONS)
IR. 41
ABSORBANCE
CM⁻¹
INFRACORD

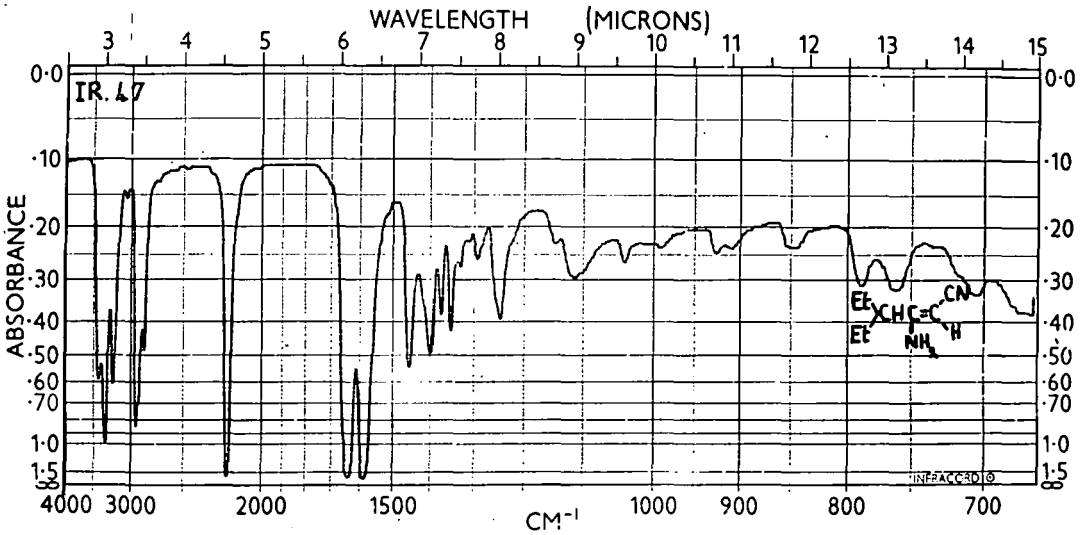

WAVELENGTH (MICRONS)
IR. 42
ABSORBANCE
CM⁻¹
INFRACORD

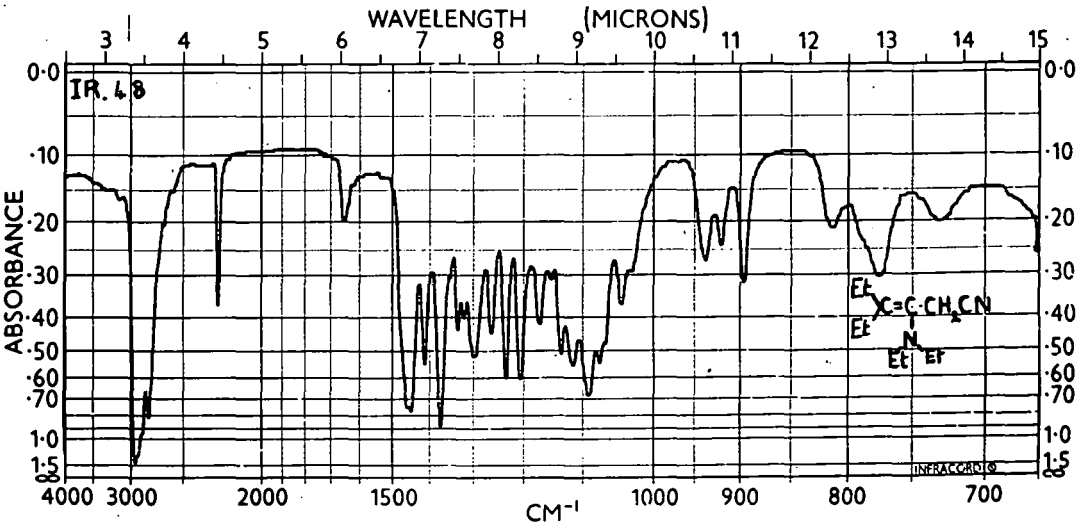

WAVELENGTH (MICRONS)
IR.43
ABSORBANCE
CM⁻¹
INFRACORD

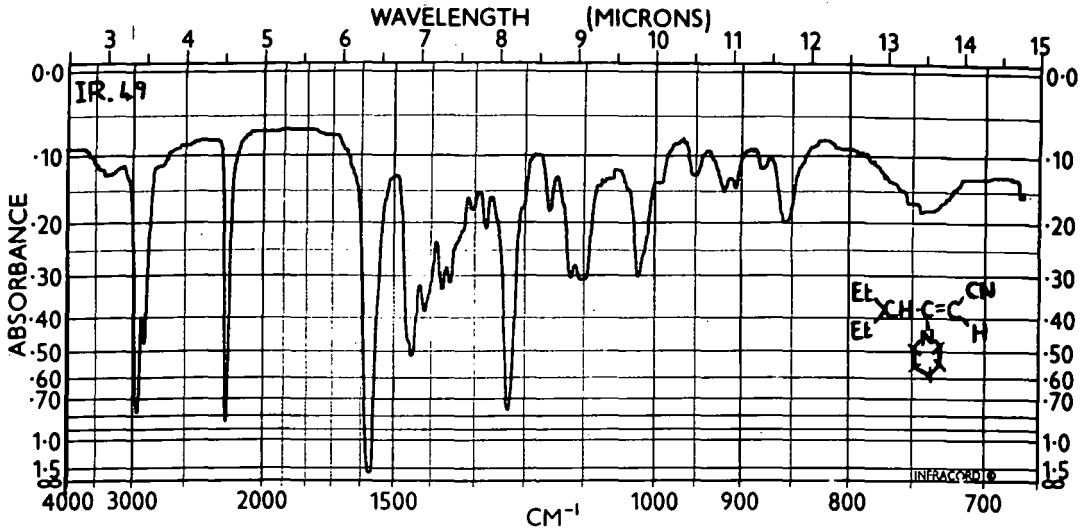

WAVELENGTH (MICRONS)
IR.44
ABSORBANCE
CM⁻¹
INFRACORD

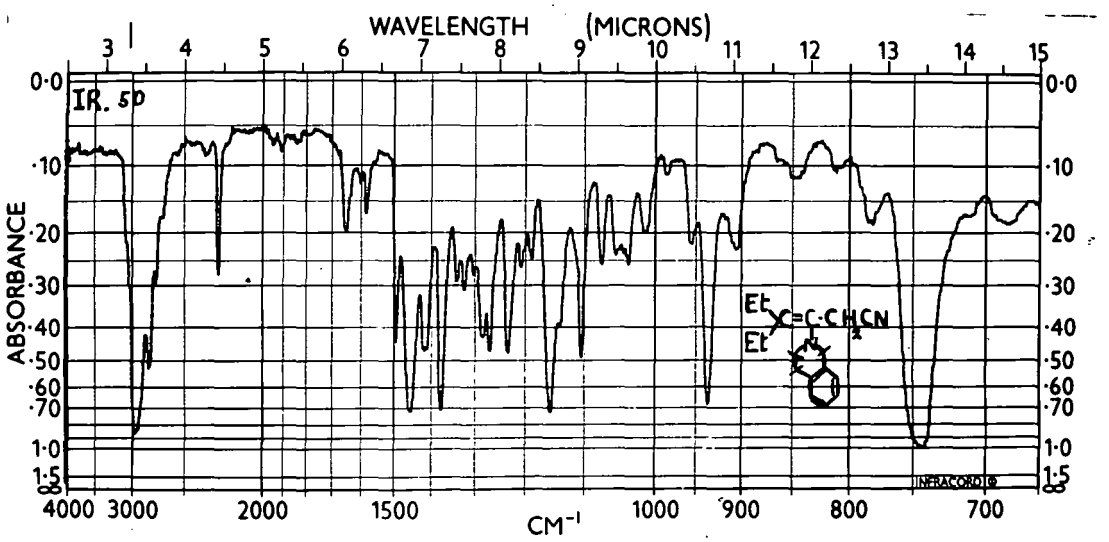

WAVELENGTH (MICRONS)
IR.45
ABSORBANCE
CM⁻¹
INFRACORD

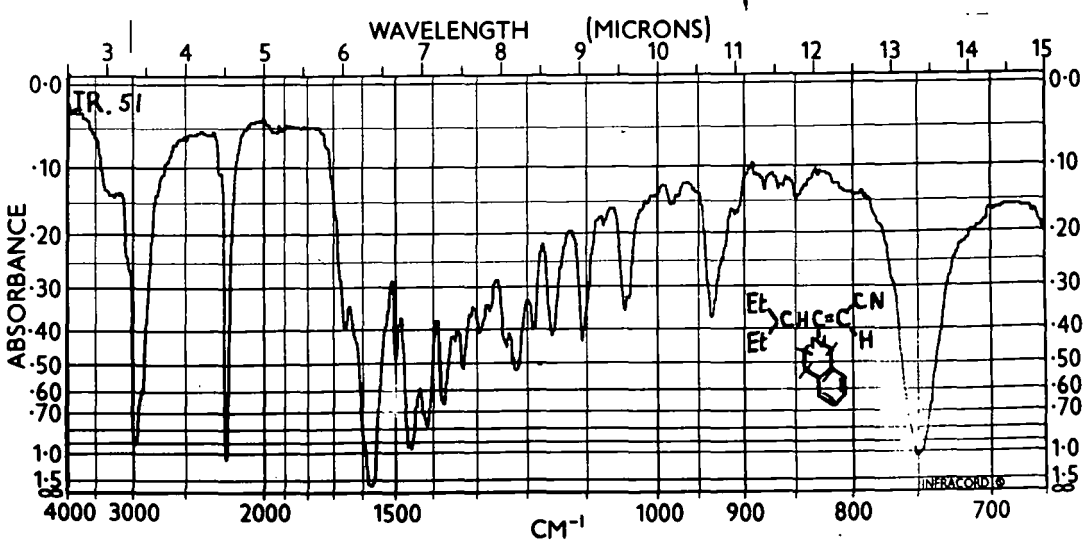

WAVELENGTH (MICRONS)
IR. 46
ABSORBANCE
CM⁻¹
INFRACORD

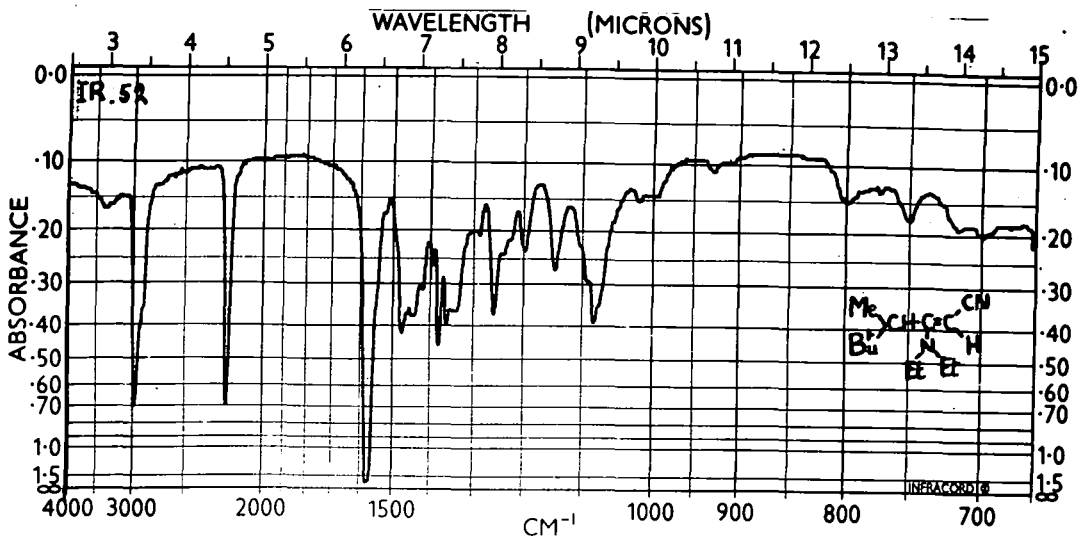

WAVELENGTH (MICRONS)
IR. 47
ABSORBANCE
CM⁻¹
INFRACORD

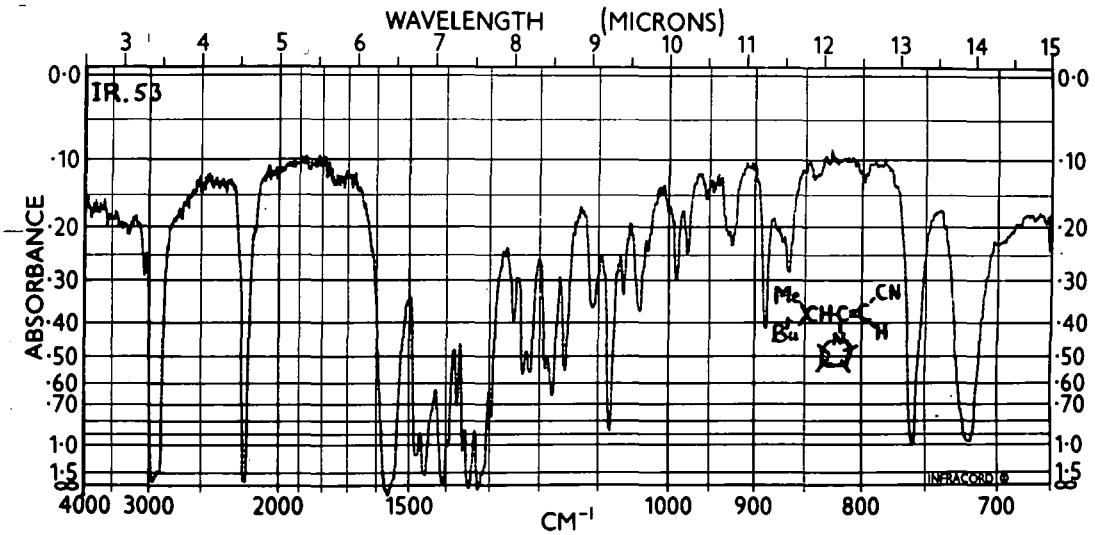

WAVELENGTH (MICRONS)
IR. 48
ABSORBANCE
CM⁻¹
INFRACORD

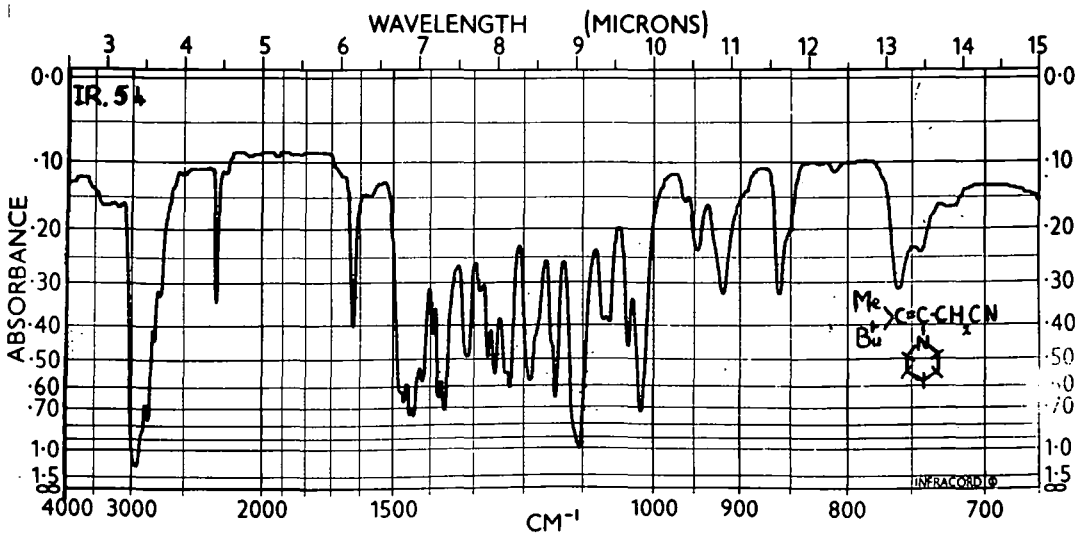

WAVELENGTH (MICRONS)
IR. 49
ABSORBANCE
CM⁻¹
INFRACORD

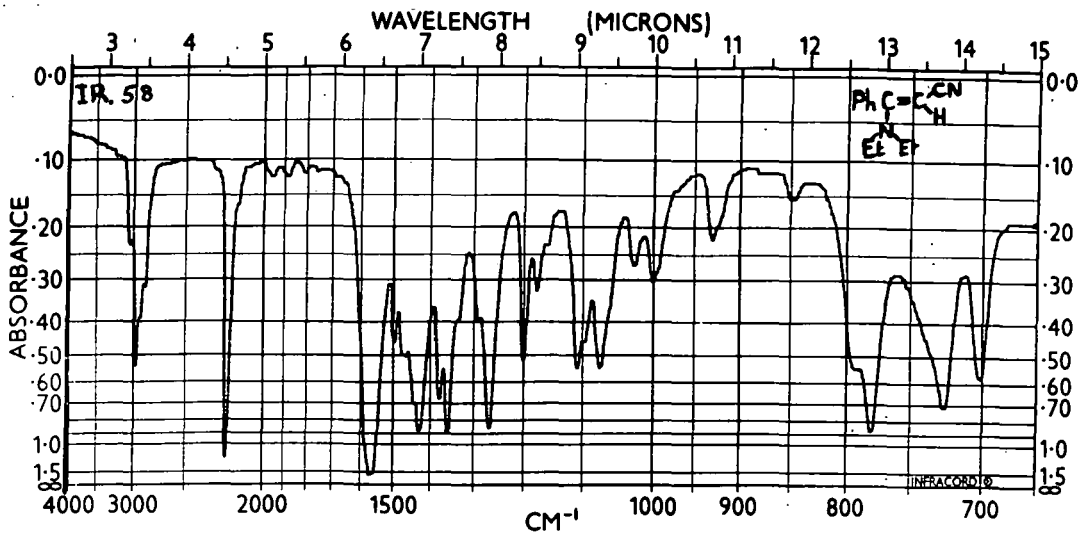

WAVELENGTH (MICRONS)
IR. 50
ABSORBANCE
CM⁻¹
INFRACORD

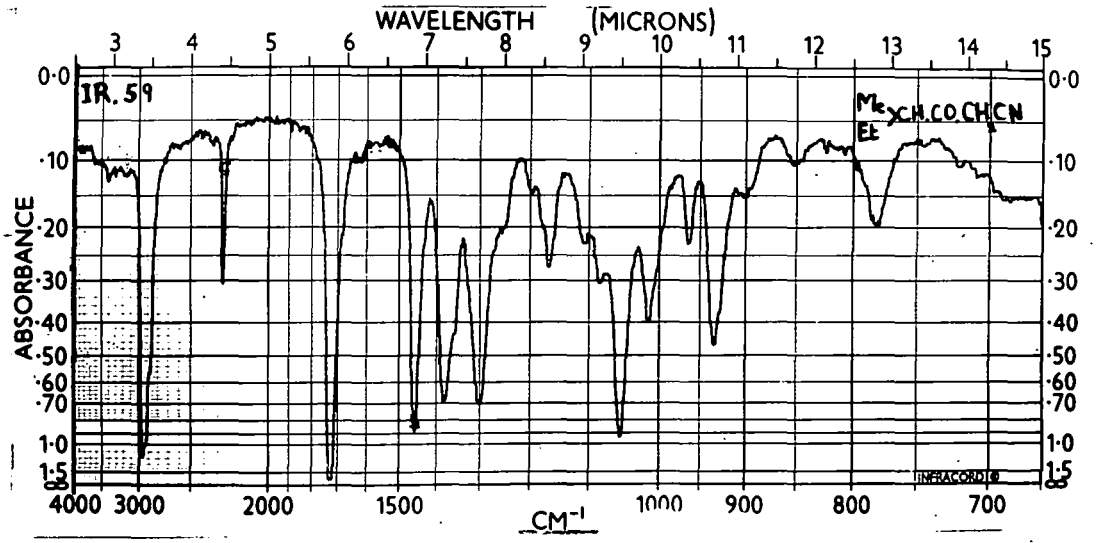

WAVELENGTH (MICRONS)
IR. 51
ABSORBANCE
CM⁻¹
INFRACORD

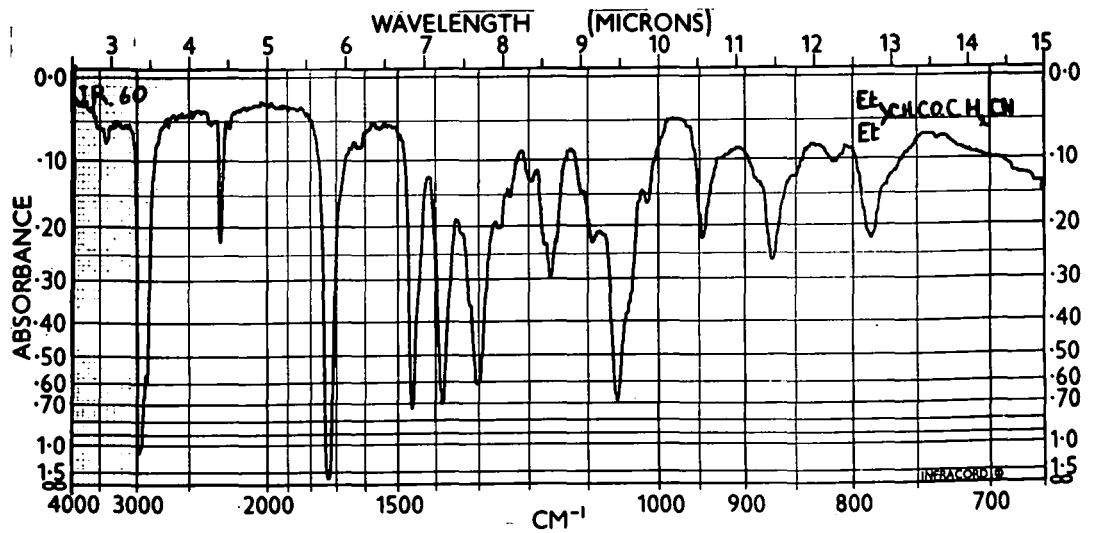

WAVELENGTH (MICRONS)
IR.52
ABSORBANCE
CM⁻¹
INFRACORD

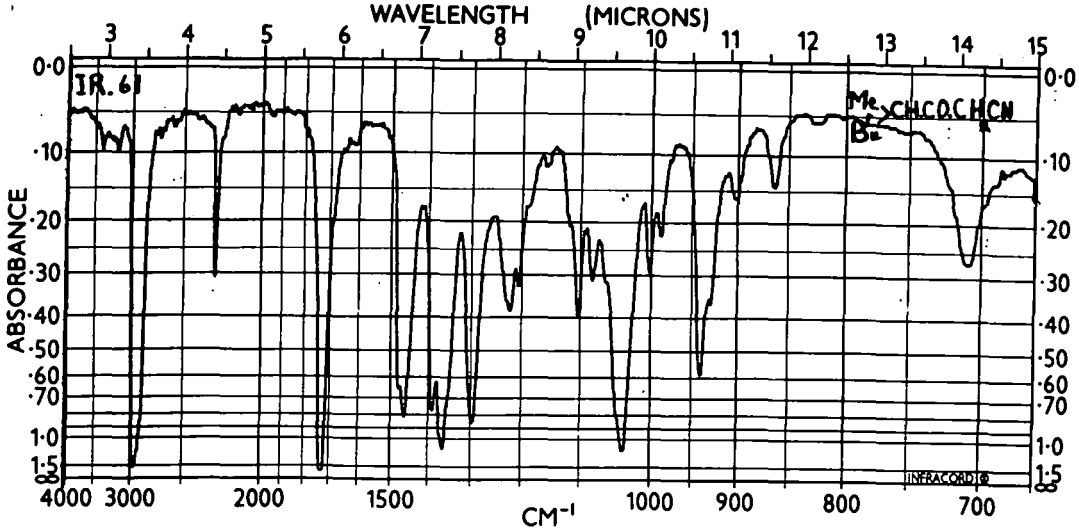

WAVELENGTH (MICRONS)
IR.53
ABSORBANCE
CM⁻¹
INFRACORD

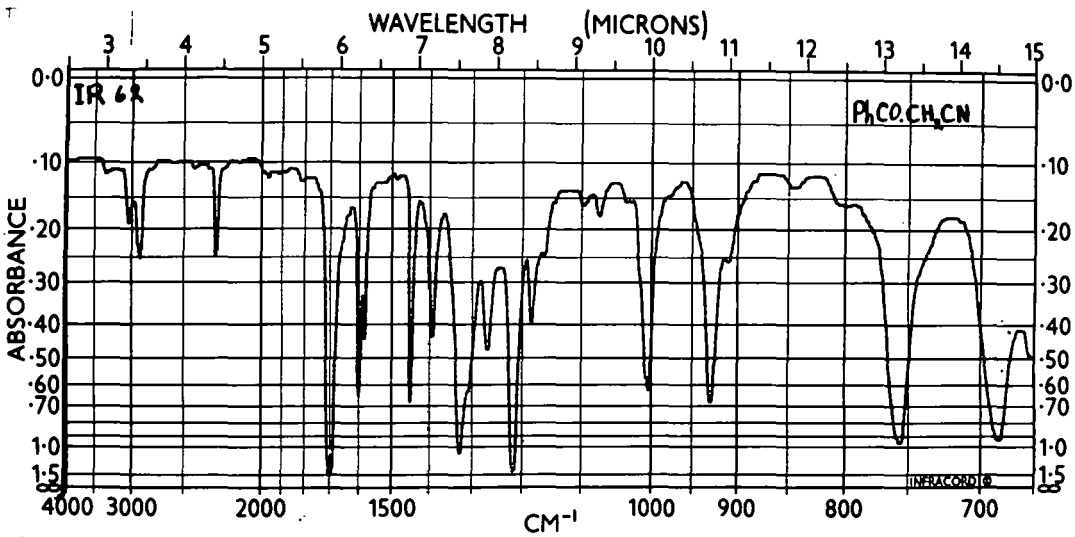

WAVELENGTH (MICRONS)
IR.54
ABSORBANCE
CM⁻¹
INFRACORD

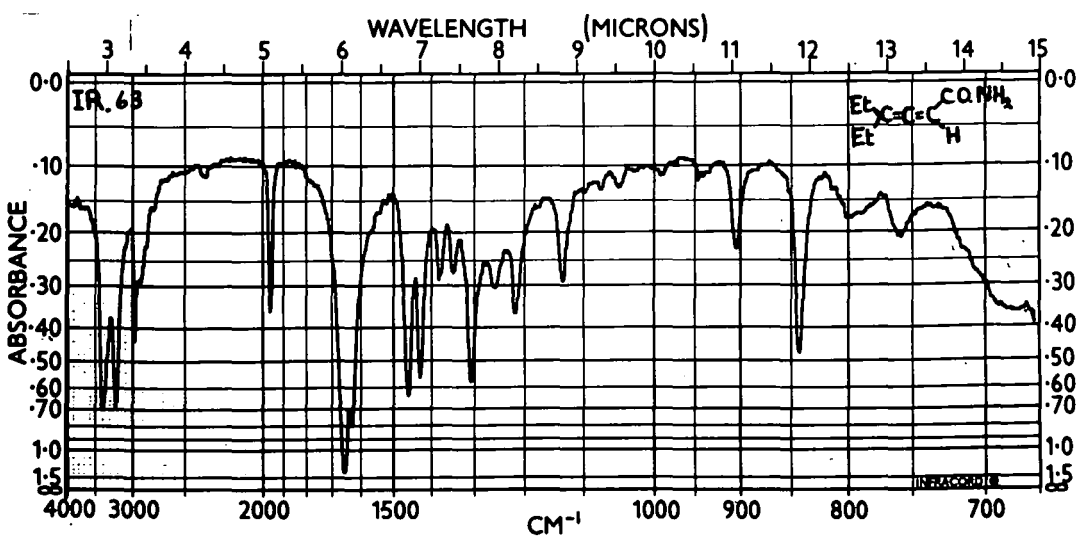

WAVELENGTH (MICRONS)
IR. 58
ABSORBANCE
CM⁻¹
INFRACORD

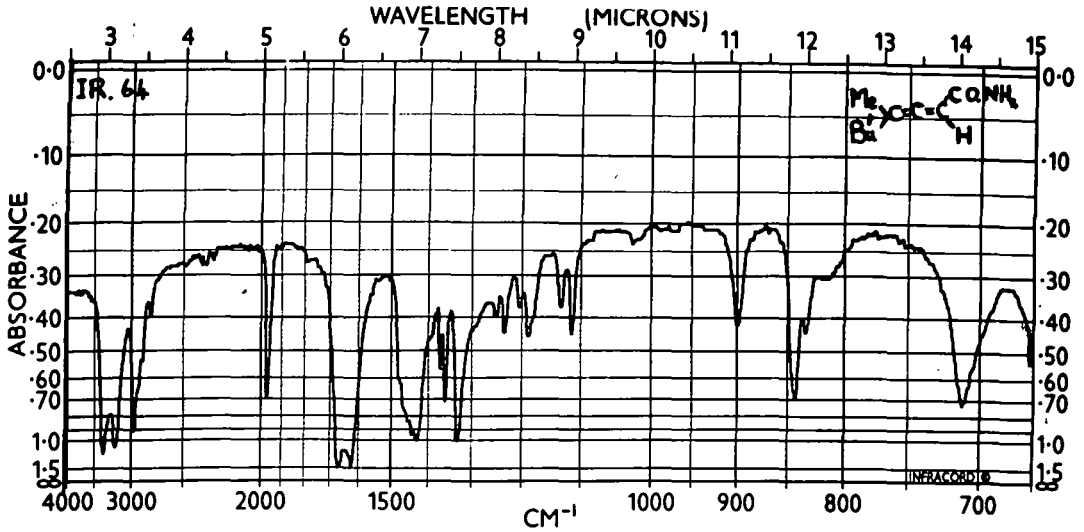

WAVELENGTH (MICRONS)
IR. 59
ABSORBANCE
CM⁻¹
INFRACORD

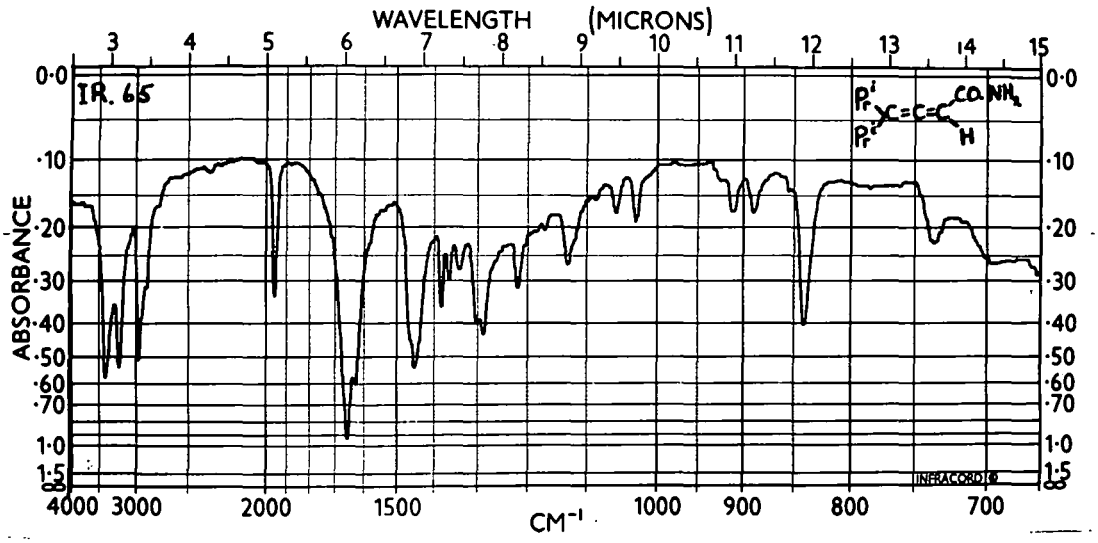

WAVELENGTH (MICRONS)
IR. 60
ABSORBANCE
CM⁻¹
INFRACORD

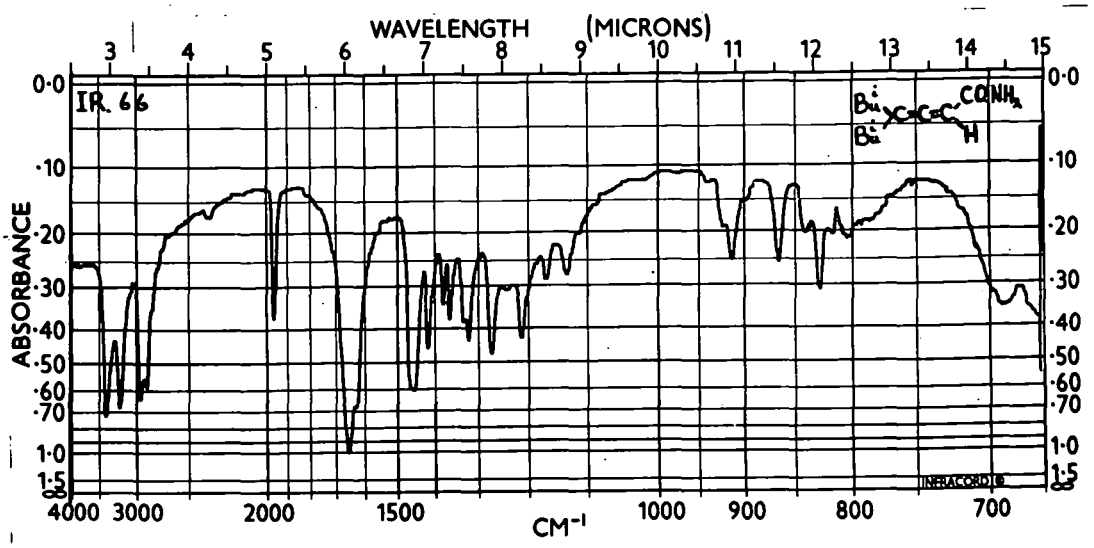

WAVELENGTH (MICRONS)
IR. 61
ABSORBANCE
CM⁻¹
INFRACORD

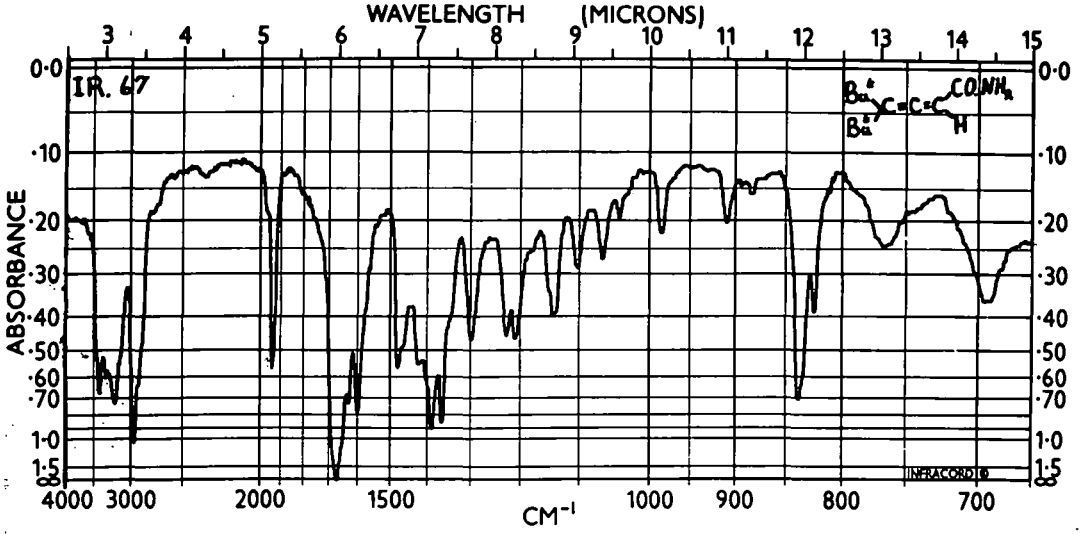

WAVELENGTH (MICRONS)
IR 62
PhCO.CH2CN
ABSORBANCE
CM⁻¹
INFRACORD

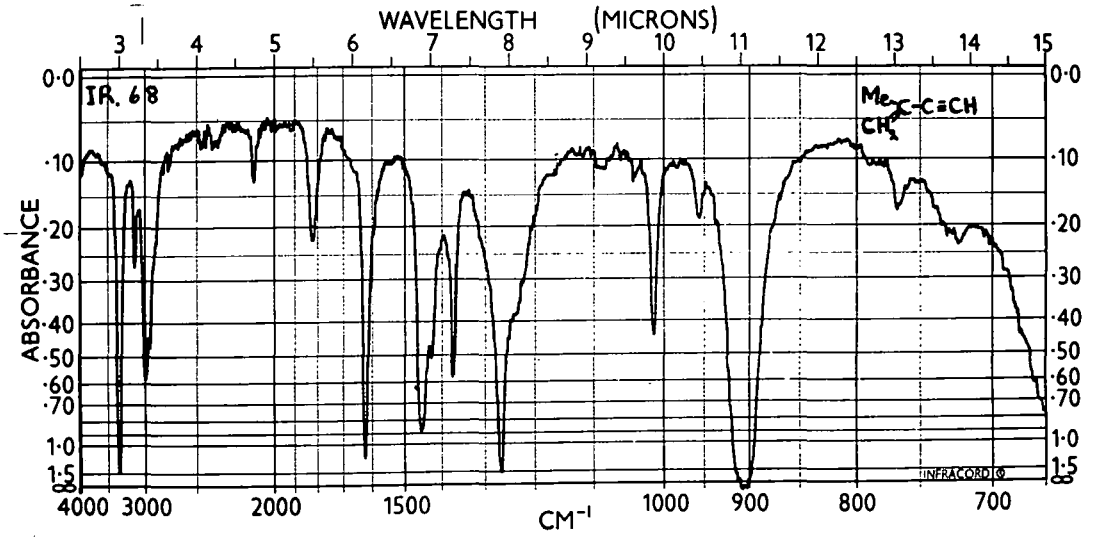

WAVELENGTH (MICRONS)
IR. 63
ABSORBANCE
CM⁻¹
INFRACORD

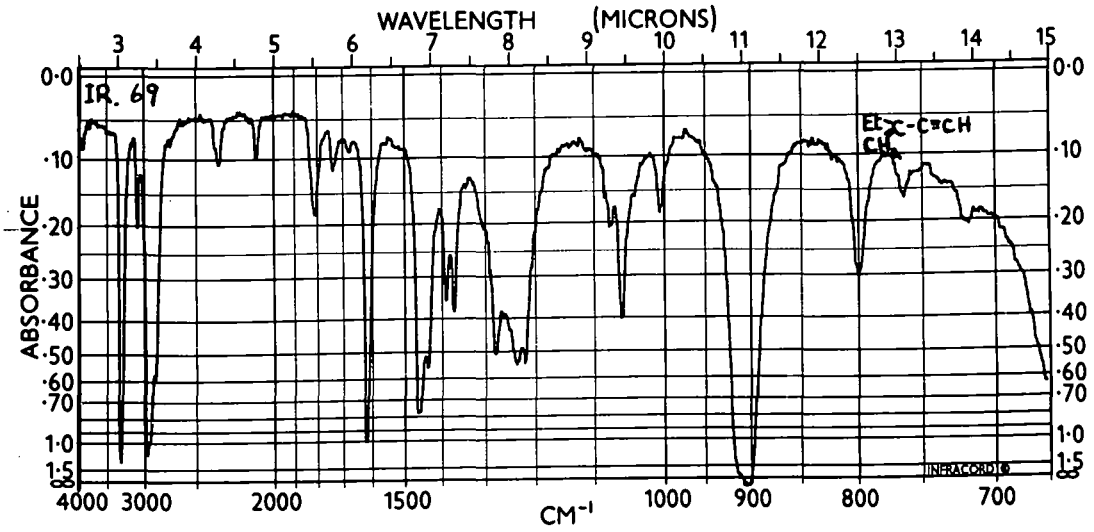

IR. 64
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

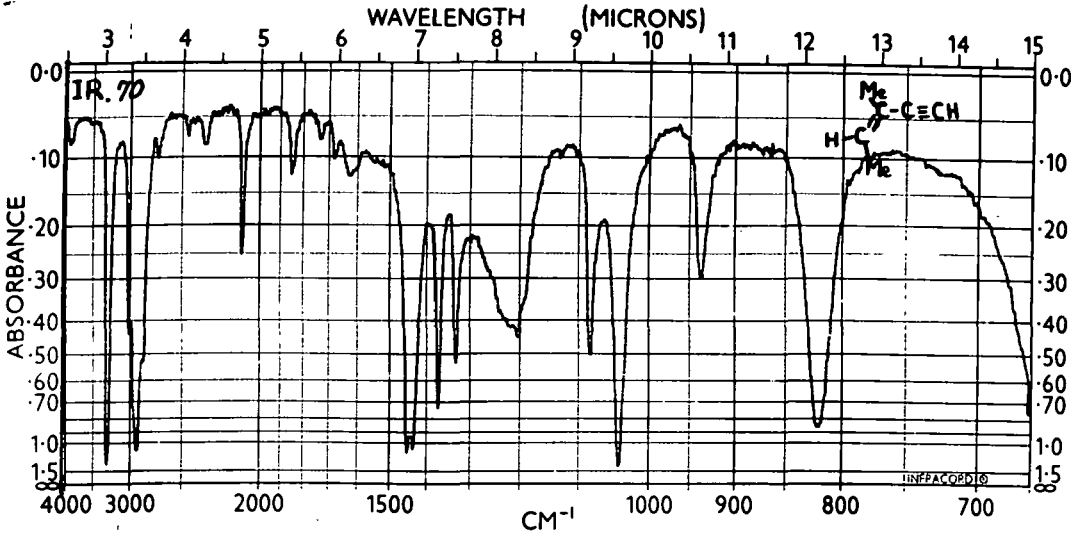

IR. 65
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

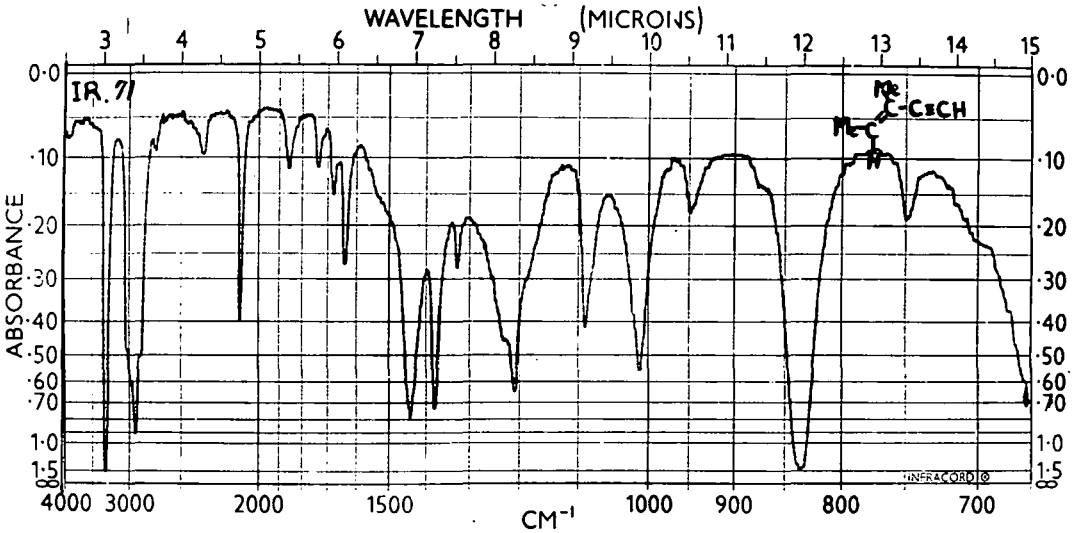

IR. 66
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

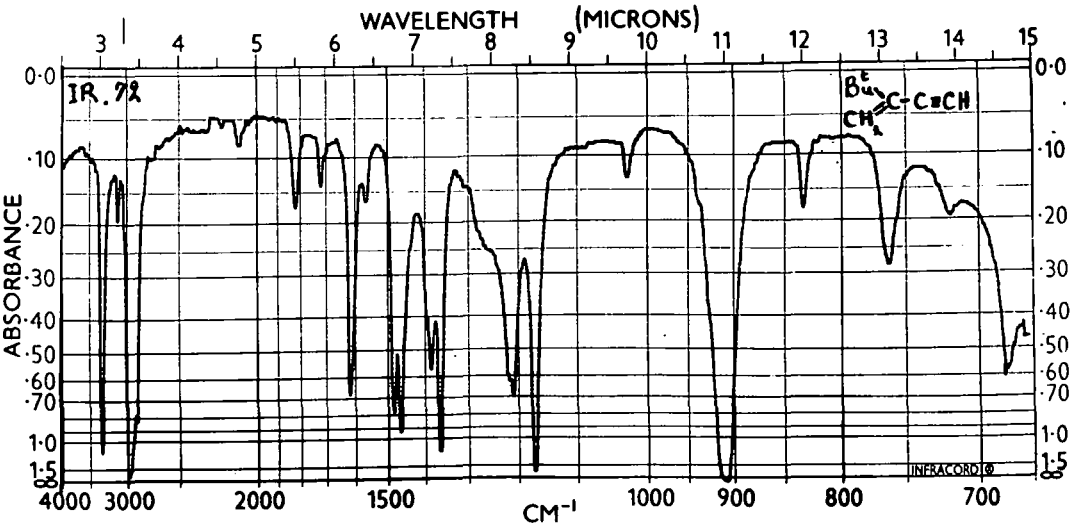

WAVELENGTH (MICRONS)
IR. 67
ABSORBANCE
CM⁻¹
INFRACORD

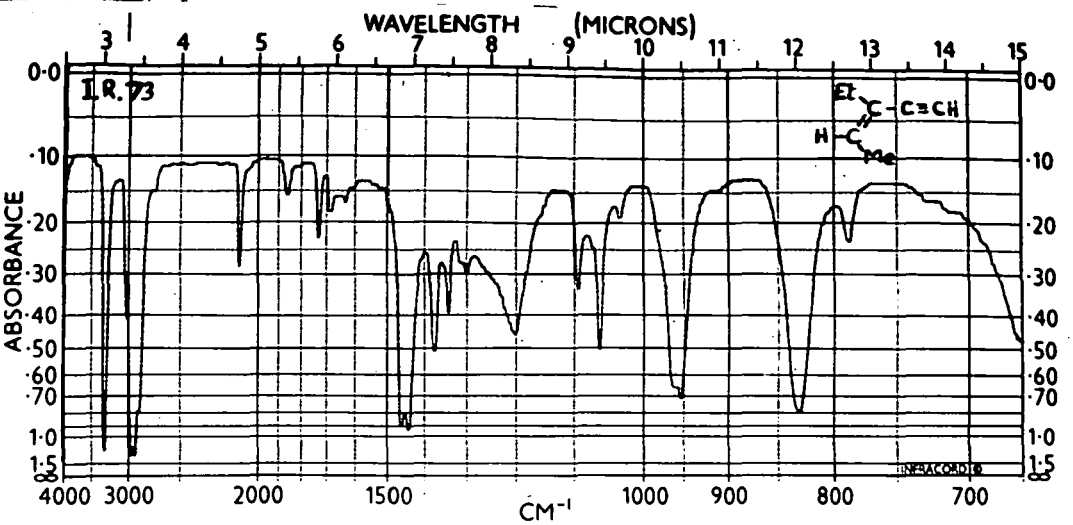

WAVELENGTH (MICRONS)
IR. 68
ABSORBANCE
CM⁻¹
INFRACORD

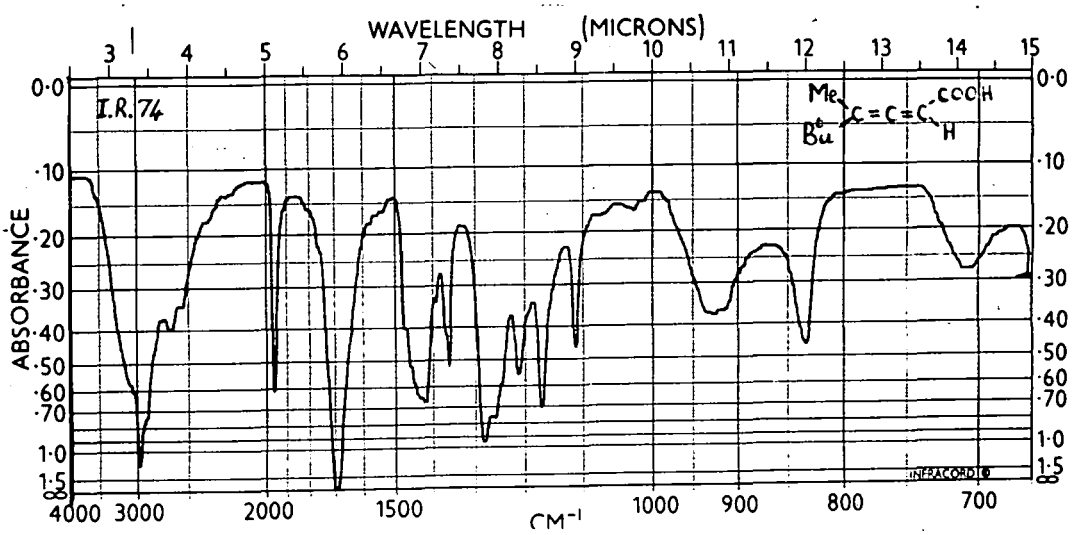

WAVELENGTH (MICRONS)
IR. 69
ABSORBANCE
CM⁻¹
INFRACORD

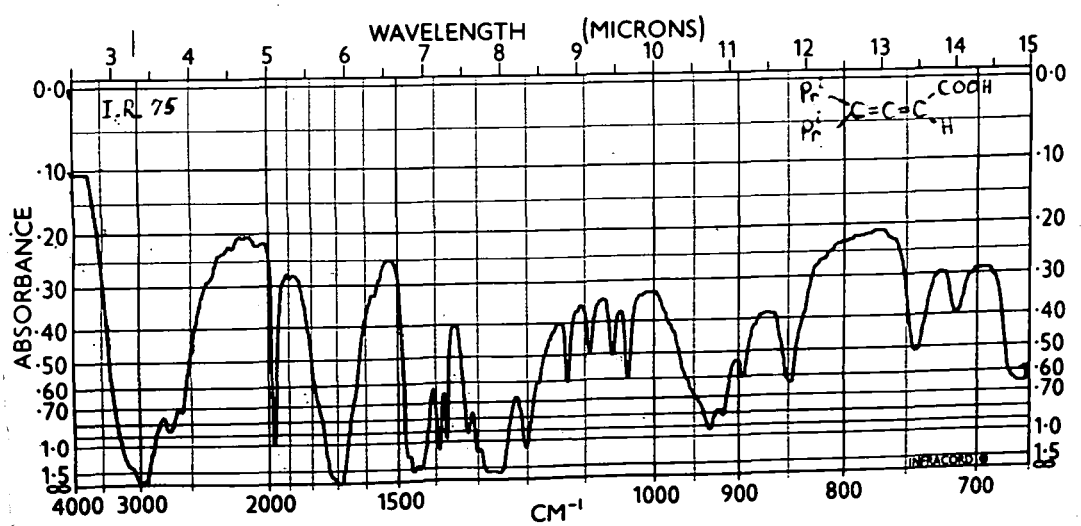

IR. 70
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

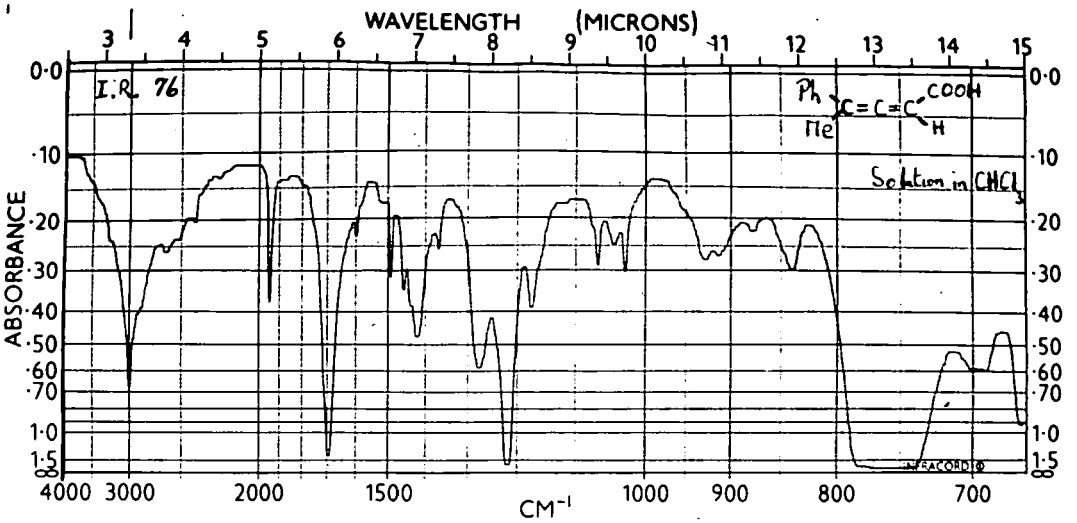

IR. 71
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

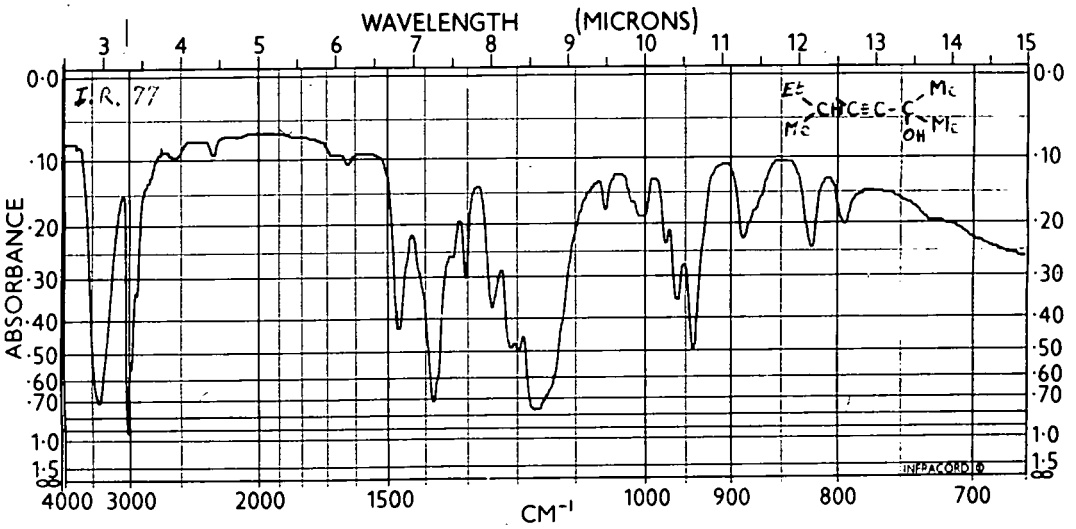

IR. 72
WAVELENGTH (MICRONS)
ABSORBANCE
CM⁻¹
INFRACORD

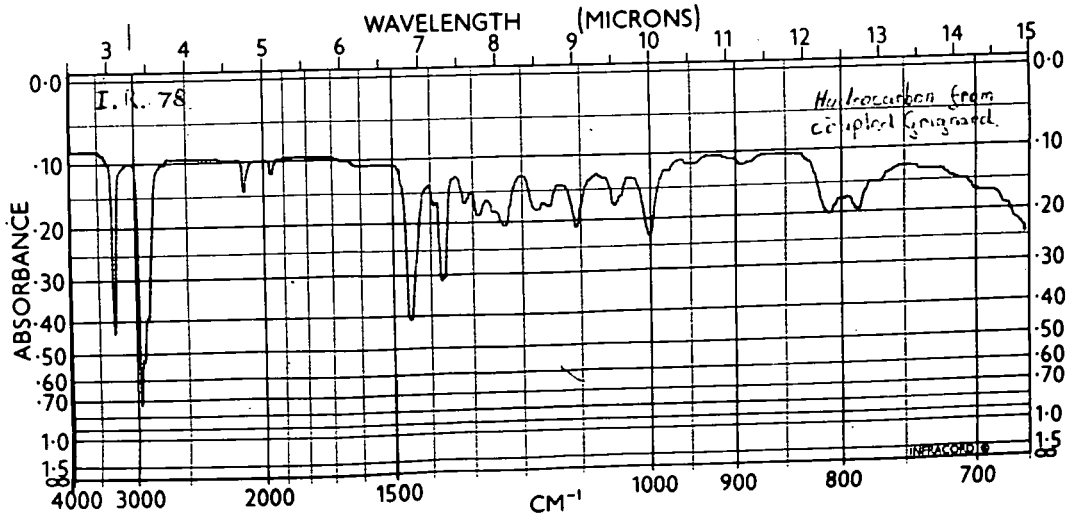

WAVELENGTH (MICRONS)
I.R. 73
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
I.R. 74
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
I.R. 75
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
I.R. 76
Ph
Me
C=C=C
COOH
H
Solution in CHCl3
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
I.R. 77
Et
Me
CH
C≡C-C
Me
OH
Me
ABSORBANCE
CM⁻¹
INFRACORD


WAVELENGTH (MICRONS)
I.R. 78
Hydrocarbon from
coupled Grignard.
ABSORBANCE
CM⁻¹
INFRACORD

ULTRA-VIOLET SPECTRA

U.V. 1 1-Bromo-3-phenylbuta-1,2-diene

2 1-Bromo-3,3-diphenylpropa-1,2-diene

3 1-Iodo-3-methylbuta-1,2-diene

4 1-Iodo-3-methylpenta-1,2-diene

5 1-Iodo-3-ethylpenta-1,2-diene

6 1-Iodo-3,4,4-trimethylpenta-1,2-diene

7 1,1-Dibromo-3-methylbuta-1,2-diene

8 1,1-Dibromo-3-methylpenta-1,2-diene

9 1,1-Dibromo-3,4,4-trimethylpenta-1,2-diene

10 1-Cyano-3-methylpenta-1,2-diene

11 1-Cyano-3,5-dimethylhexa-1,2-diene

12 1-Cyano-3-t-butyl-4,4-dimethylpenta-1,2-diene

13 1-Cyano-3-(ciscyanomethylene)-4,4-dimethyl-2-isopropylidenecyclobutane

14 1-Cyano-3-cyanomethylene-4-ethyl-4-methyl-2-(2'butylidene)cyclobutane

15 1-Cyano-3-cyanomethylene-4,4-diethyl-2-(3'pentylidene)-cyclobutane

U.V. 16 1-Cyano-3-methyl-2-piperidinobut-2-ene

17 1-Amino-1-cyano-3-ethylpent-1-ene

18 1-Cyano-2-(diethylamino)-3-ethylpent-2-ene

19 1-Cyano-3-ethyl-2-piperidinobut-1-ene

20 1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene

21 β-Diethylamino-β-phenylacrylonitrile

22 β-Cyanophenylacetylene

23 1-Cyano-3-ethylpentan-2-one

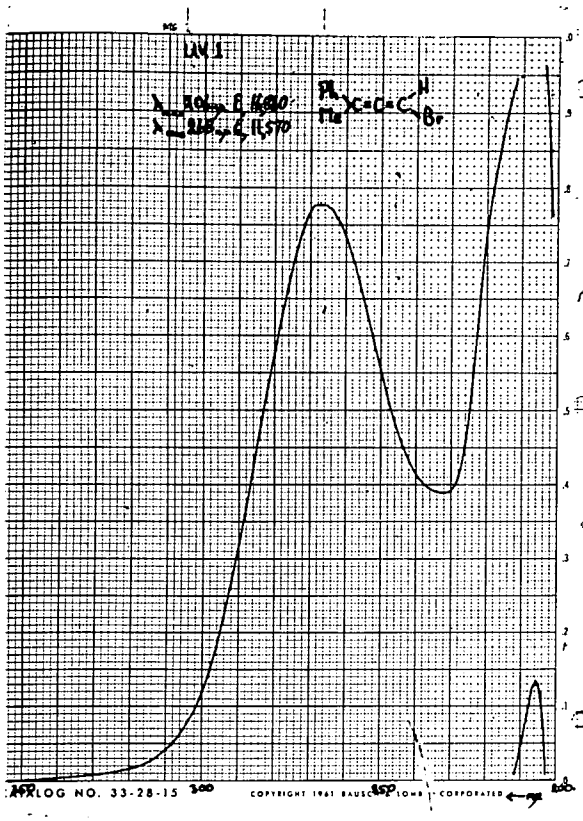
24 4-Ethylhexa-2,3-dienamide

25 4,5,5-Trimethylhexa-2,3-dienamide

26 3-t-Butylbut-3-en-1-yne

27 4,5,5-Trimethylhexa-2,3-dienoic acid

28 4-Isopropyl-5-methylhepta-2,3-dienoic acid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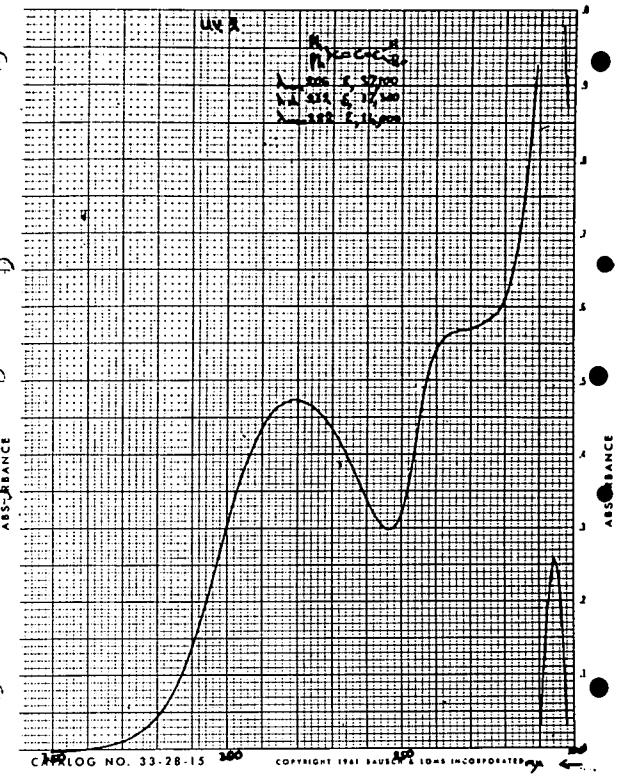
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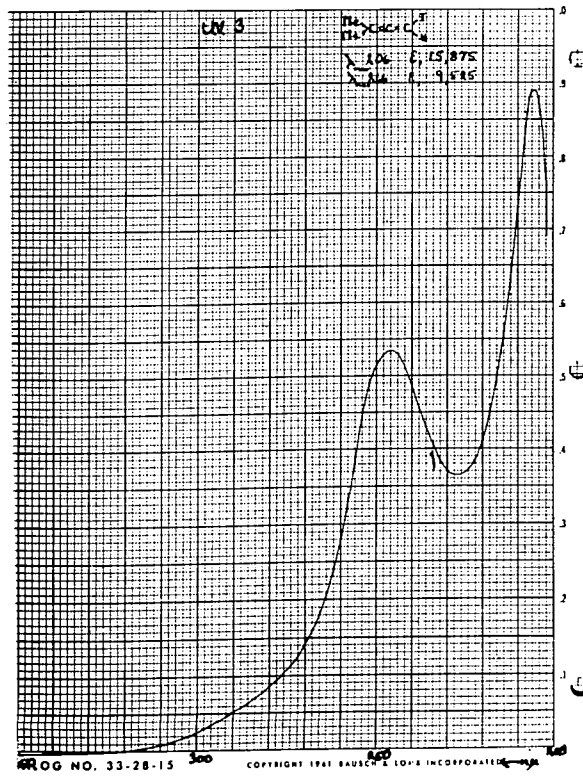
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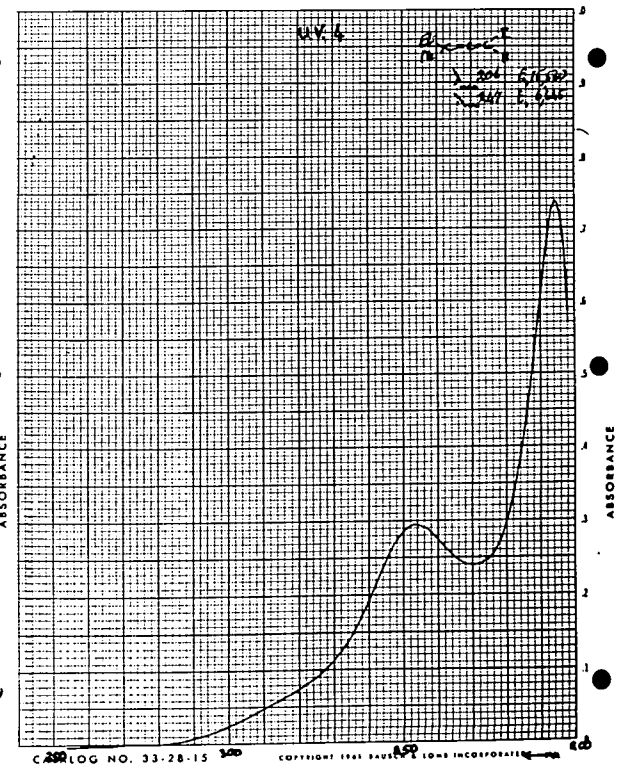
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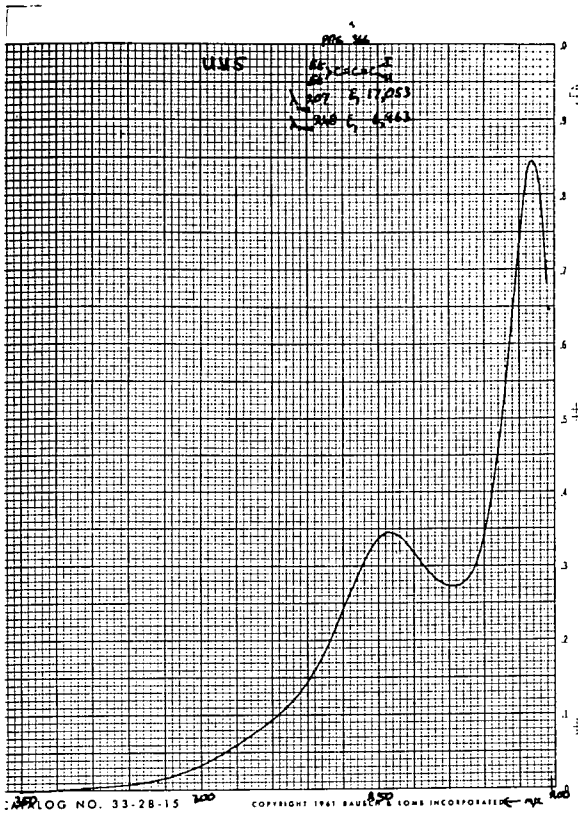
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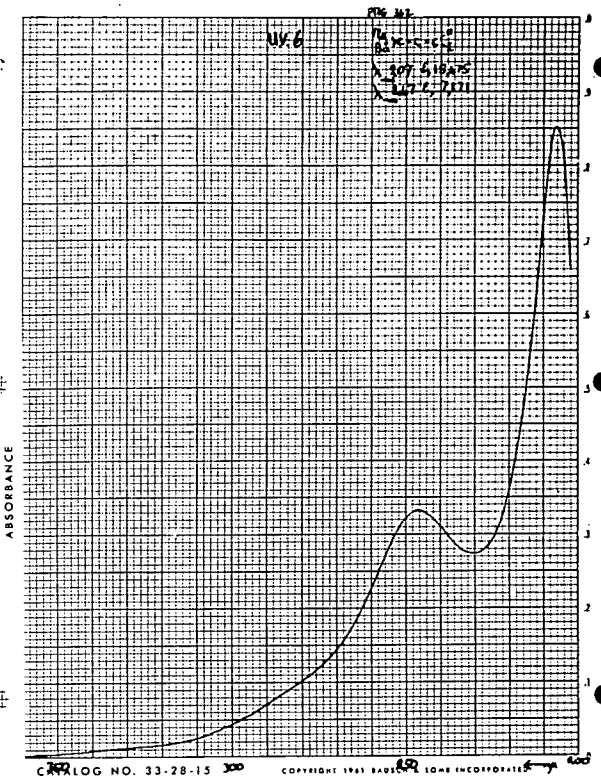
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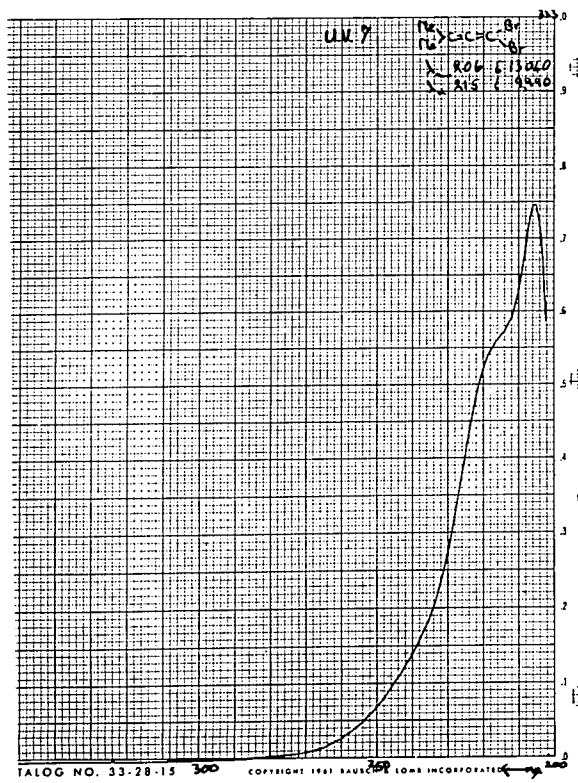
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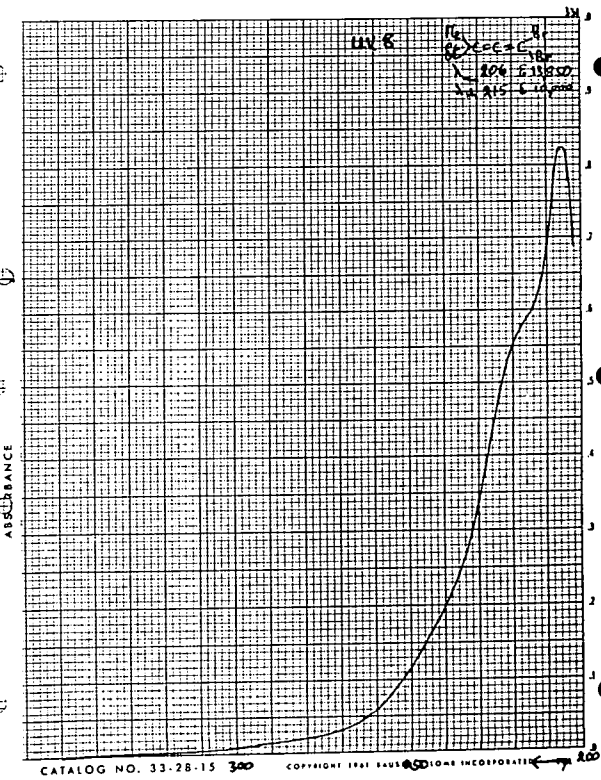
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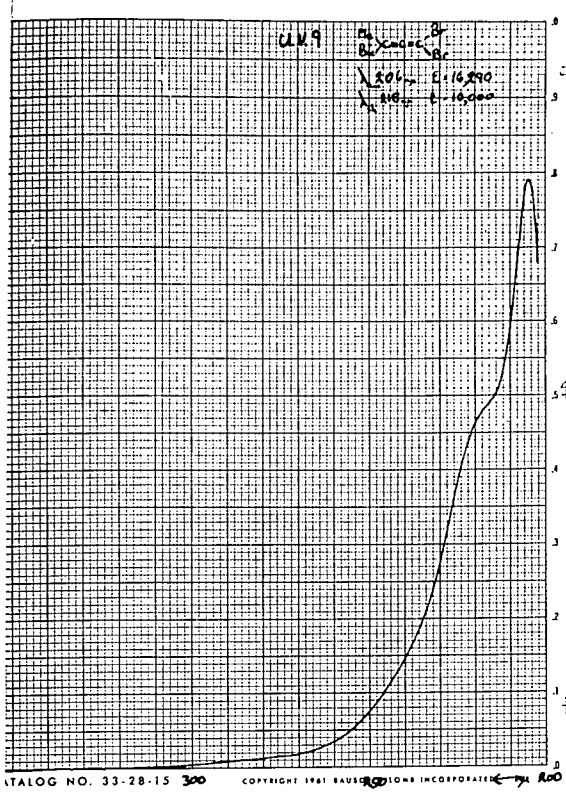
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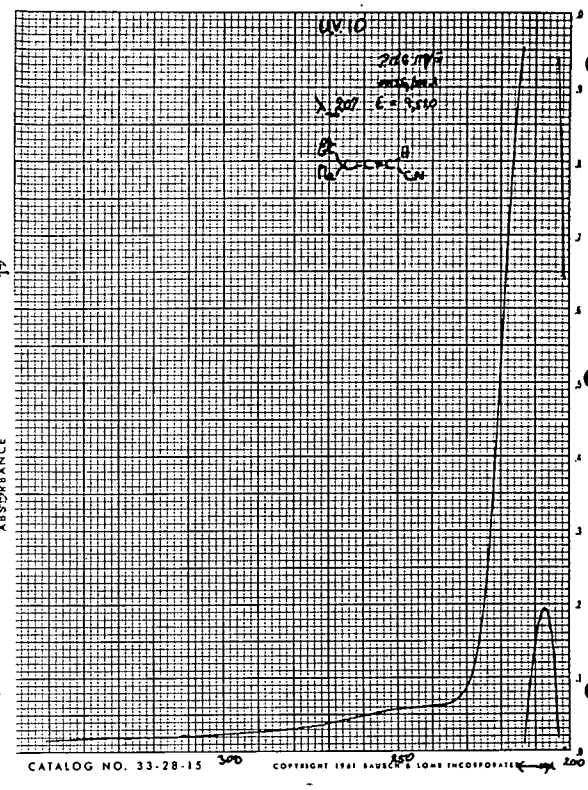
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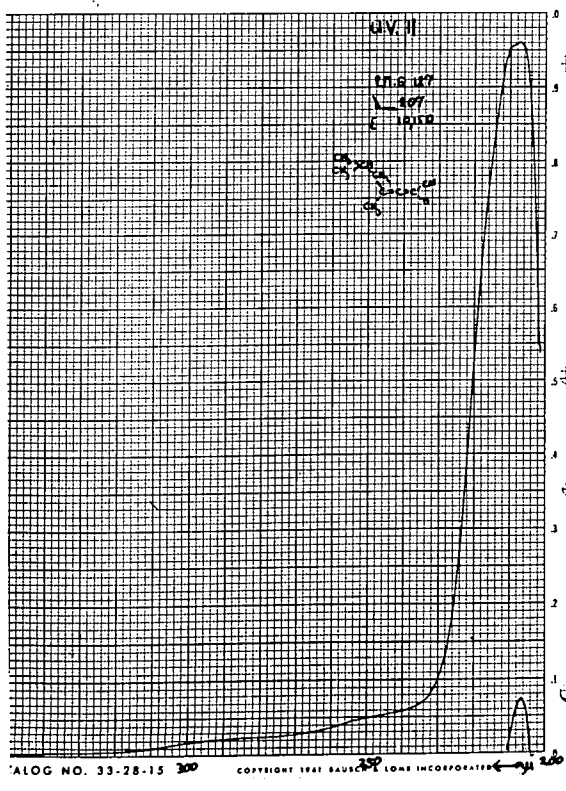
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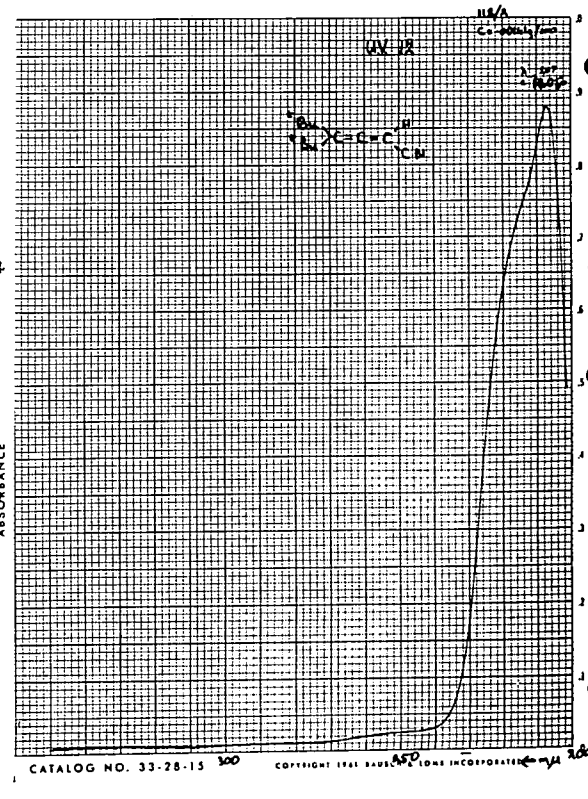
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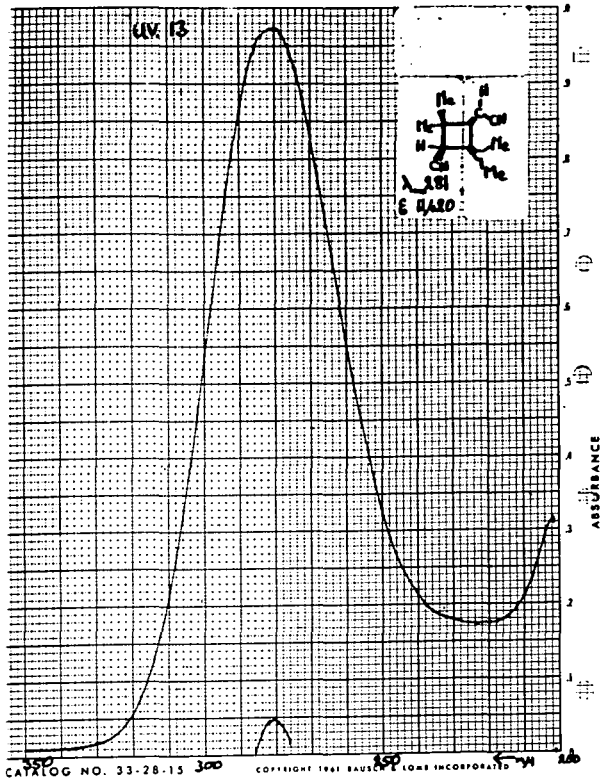
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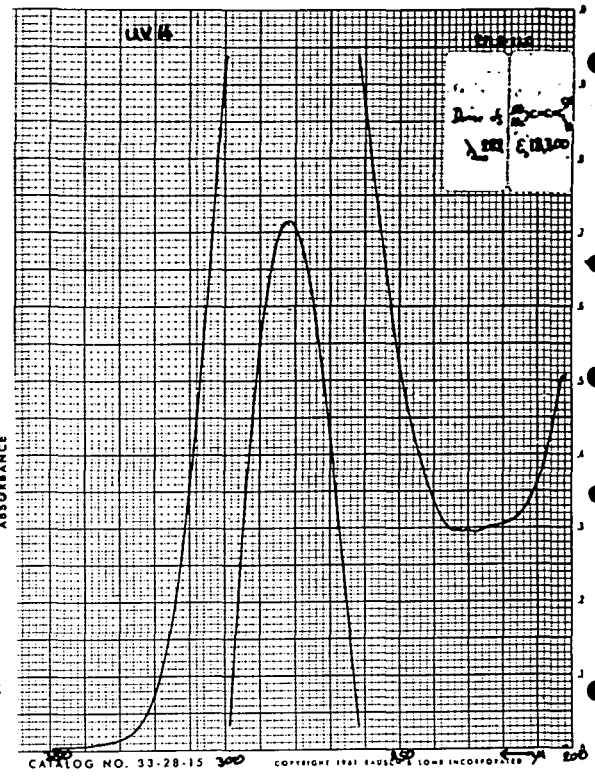
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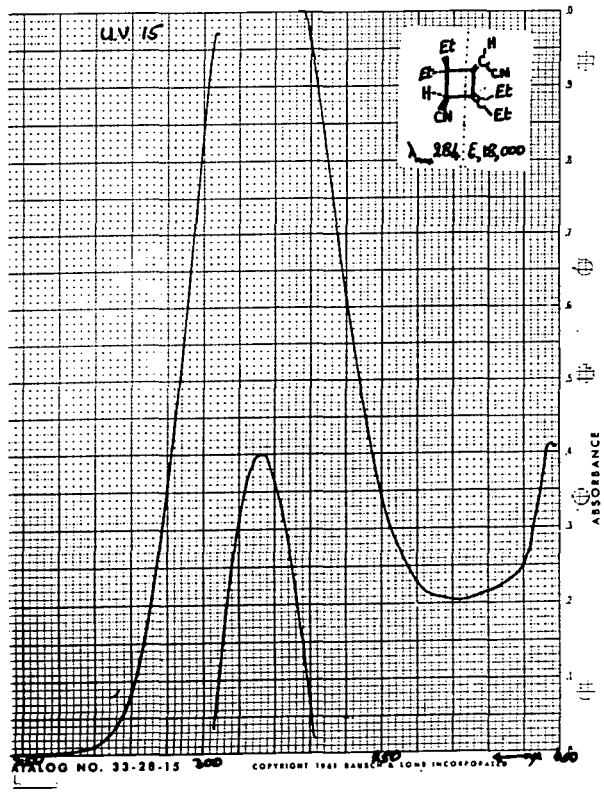
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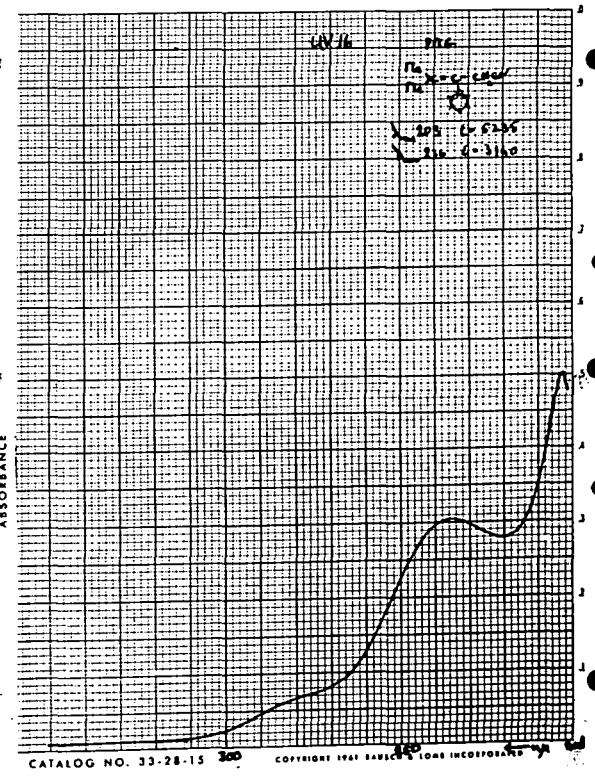
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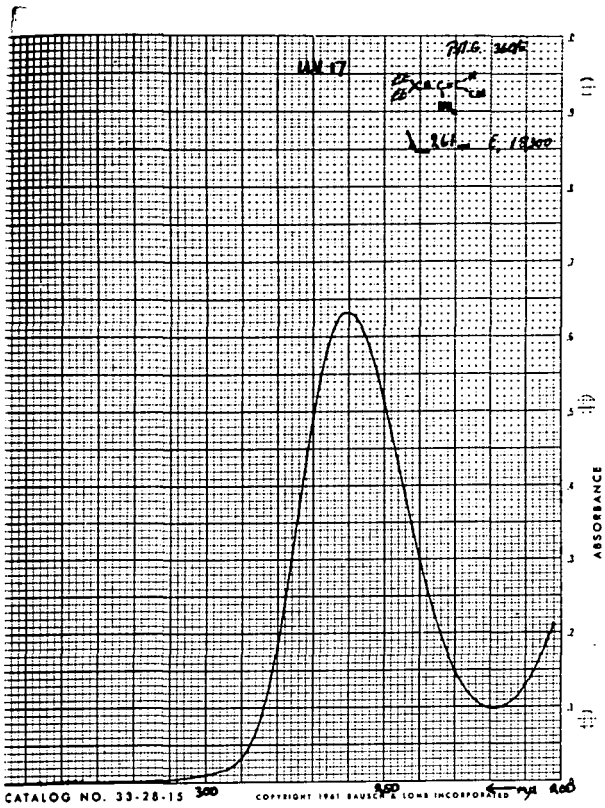
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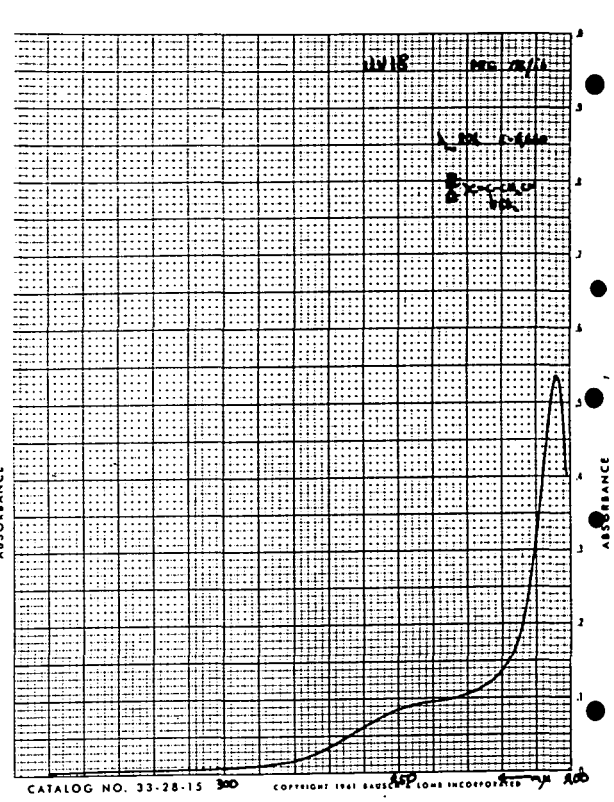
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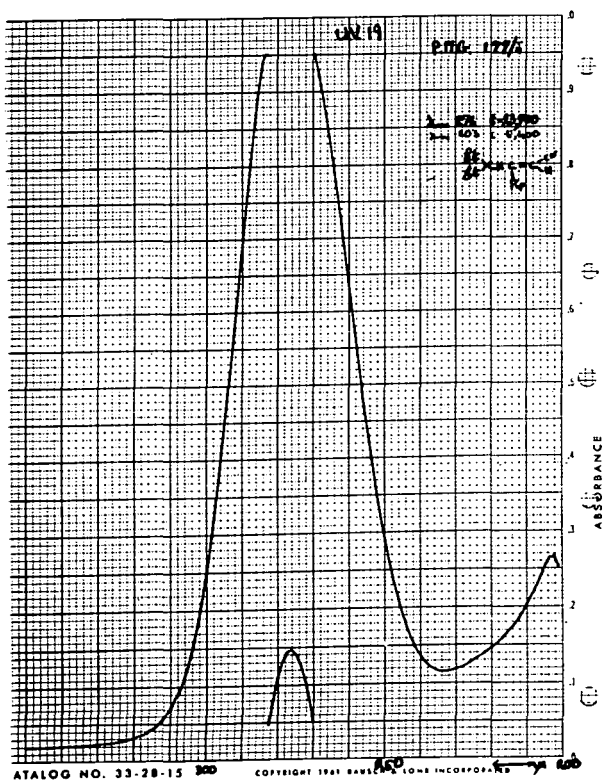
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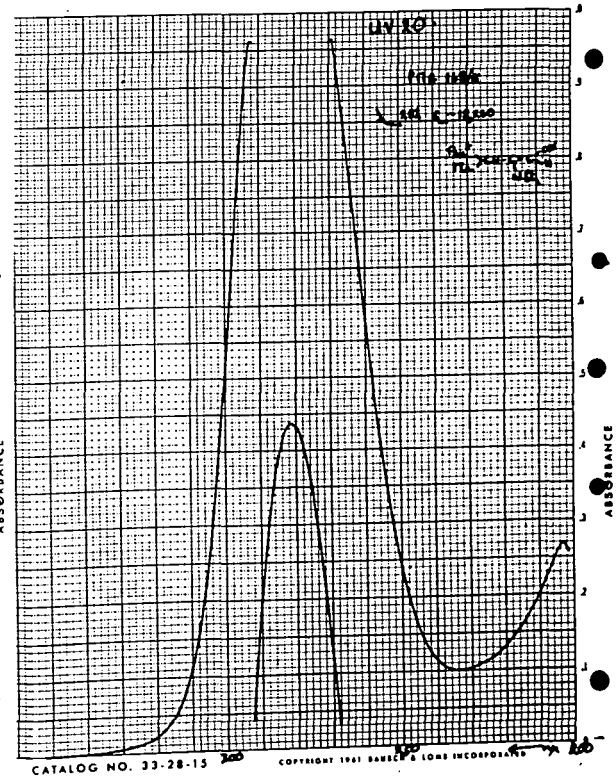
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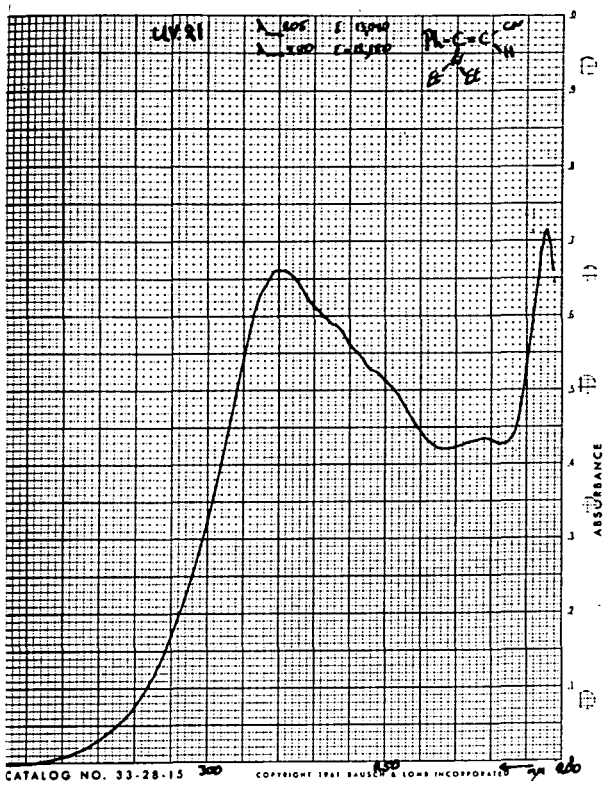
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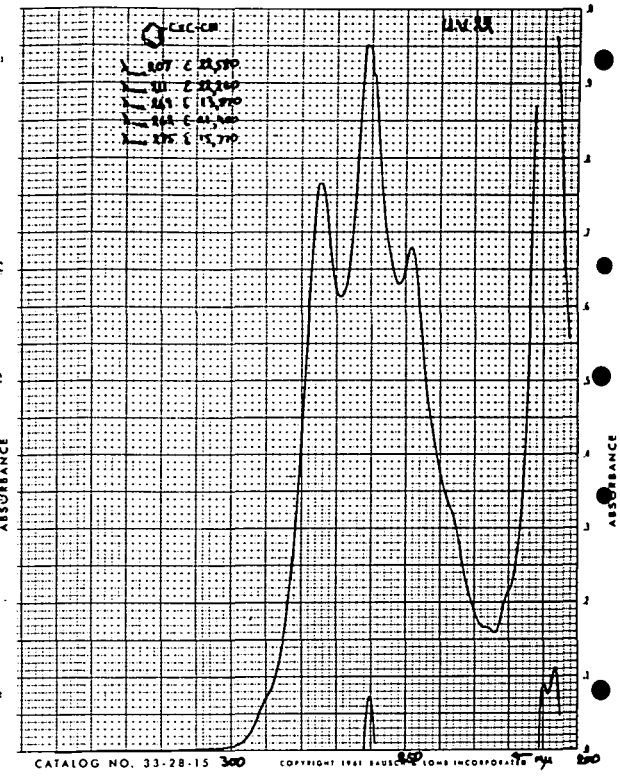
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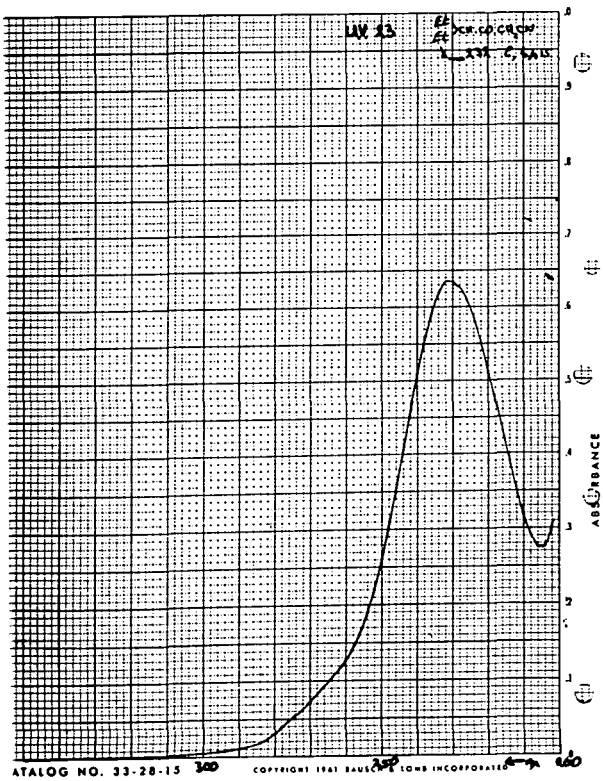
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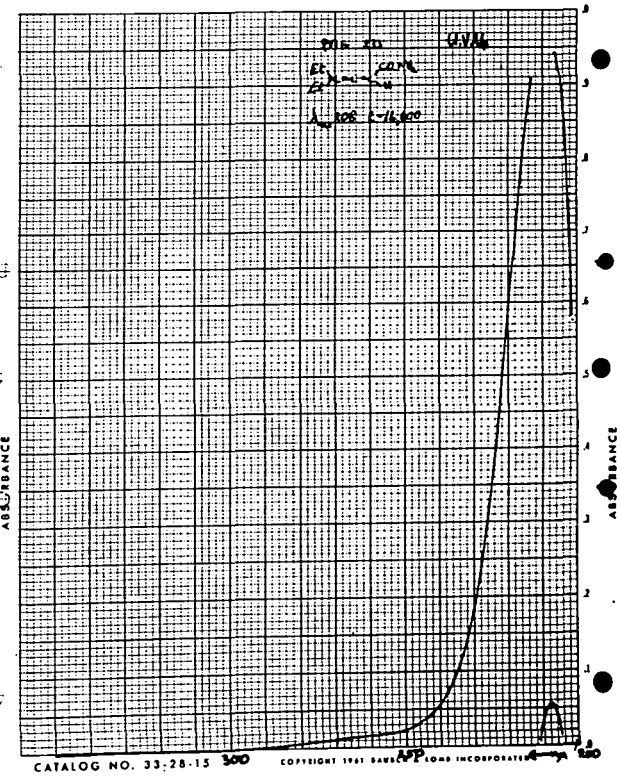
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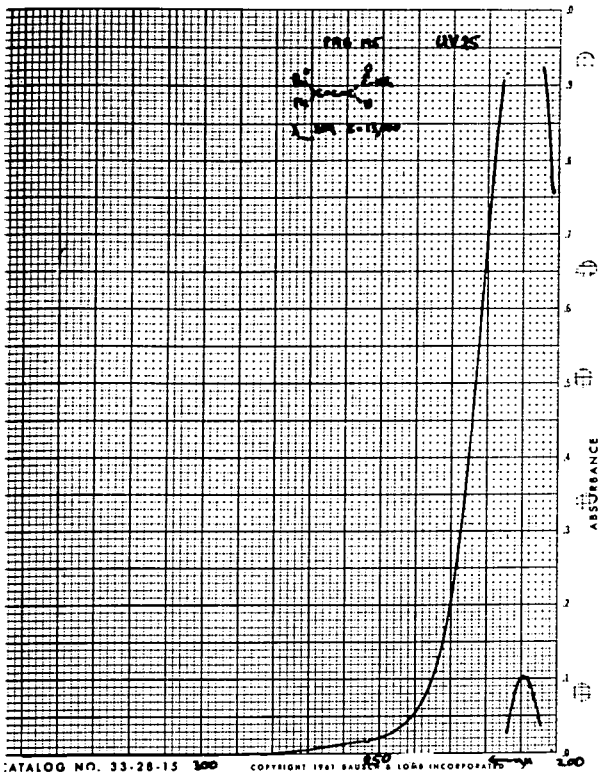
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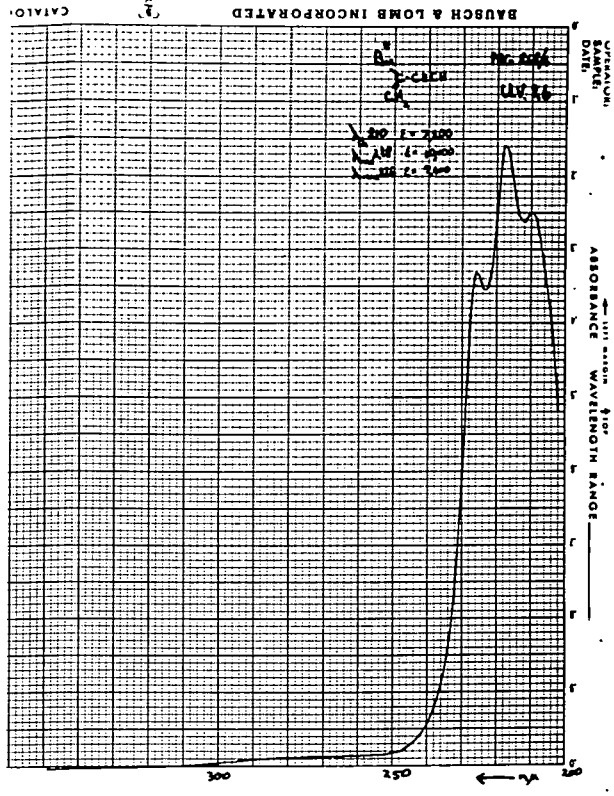
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ABSORBANCE
WAVELENGTH RANGE
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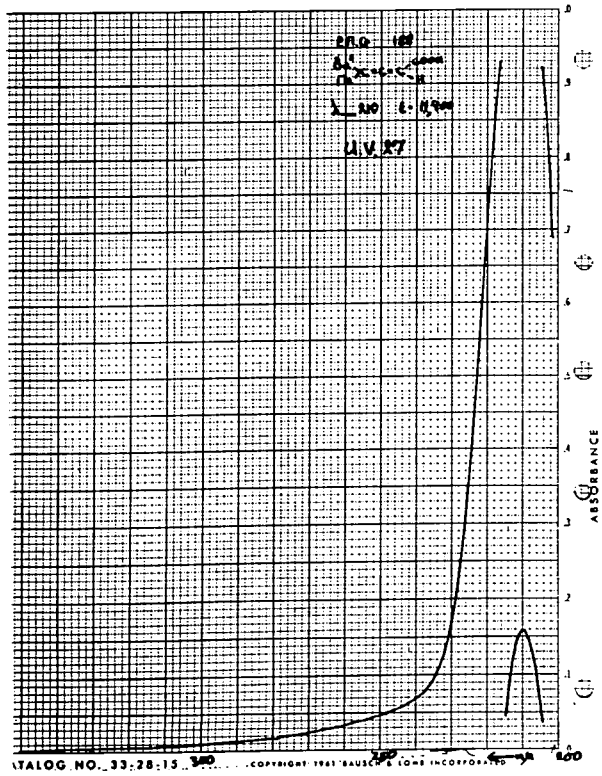
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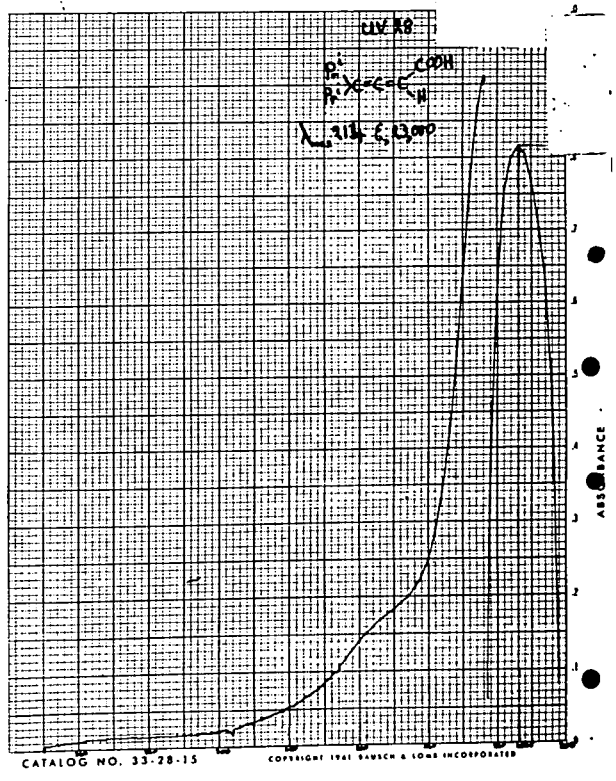
UV 28
COOH
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CATALOG NO. 33-28-15
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NUCLEAR MAGNETIC RESONANCE SPECTRA

N.M.R.	1	1-Bromo-3-methylpenta-1,2-diene
	2	1-Bromo-3-ethylpenta-1,2-diene
	3	1-Bromo-3,3-diphenylpropa-1,2-diene
	4	1-Iodo-3-methylbuta-1,2-diene
	5	1-Iodo-3-methylpenta-1,2-diene
	6	1-Iodo-3,4,4-trimethylpenta-1,2-diene
	7	1,1-Dibromo-3-methylpenta-1,2-diene
	8	1,1-Dibromo-3,4,4-trimethylpenta-1,2-diene
	9	1-Deutero-3-methylbat-1-yn-3-ol
	10	1-Deutero-3-methylpent-1-yn-3-ol
	11	1-Deutero-3,4,4-trimethylpent-1-yn-3-ol
	12	1-Deutero-1-iodobuta-1,2-diene
	13	1-Bromo-1-deutero-3-methylpenta-1,2-diene
	14	1-Chloro-1-deutero-3,4,4-trimethylpenta-1,2-diene
	15	1-Cyano-3-methylpenta-1,2-diene
	16	1-Cyano-3-ethylpenta-1,2-diene
	17	1-Cyano-3,4,4-trimethylpenta-1,2-diene
	18	1-Cyano-3-t-butyl-4,4-dimethylpenta-1,2-diene

N.M.R. 19 1-Cyano-3-(ciscyanomethylene)-4,4-dimethyl-2-isopropylidenecyclobutane

20 1-Cyano-3-(ciscyanomethylene)-4,4-diethyl-2-(3-pentylidene)-cyclobutane

21 2-(n-Butylamino)-1-cyano-3-methylbut-1-ene

22 1-Cyano-2-(diethylamino)-3-methylpent-2-ene

23 1-Cyano-2-(diethylamino)-3-methylpent-1-ene

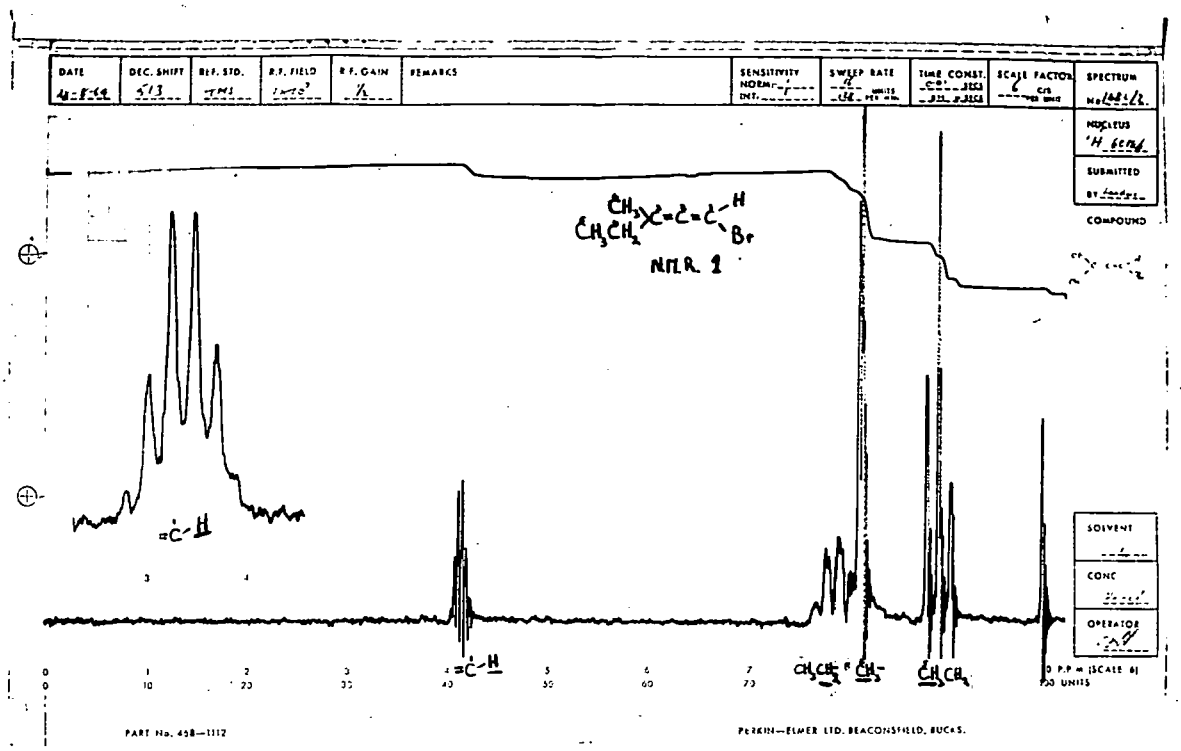
24 1-Cyano-3-methyl-2-piperidinopent-1-ene

25 2-Amino-1-cyano-3-ethylpent-1-ene

26 1-Cyano-2-(diethylamino)-3,4,4-trimethylpent-1-ene

27 4,5,5-Trimethylhexa-2,3-dienamide

28 1-Ethynyl-1-t-butylethylene oxide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R.F. GAIN
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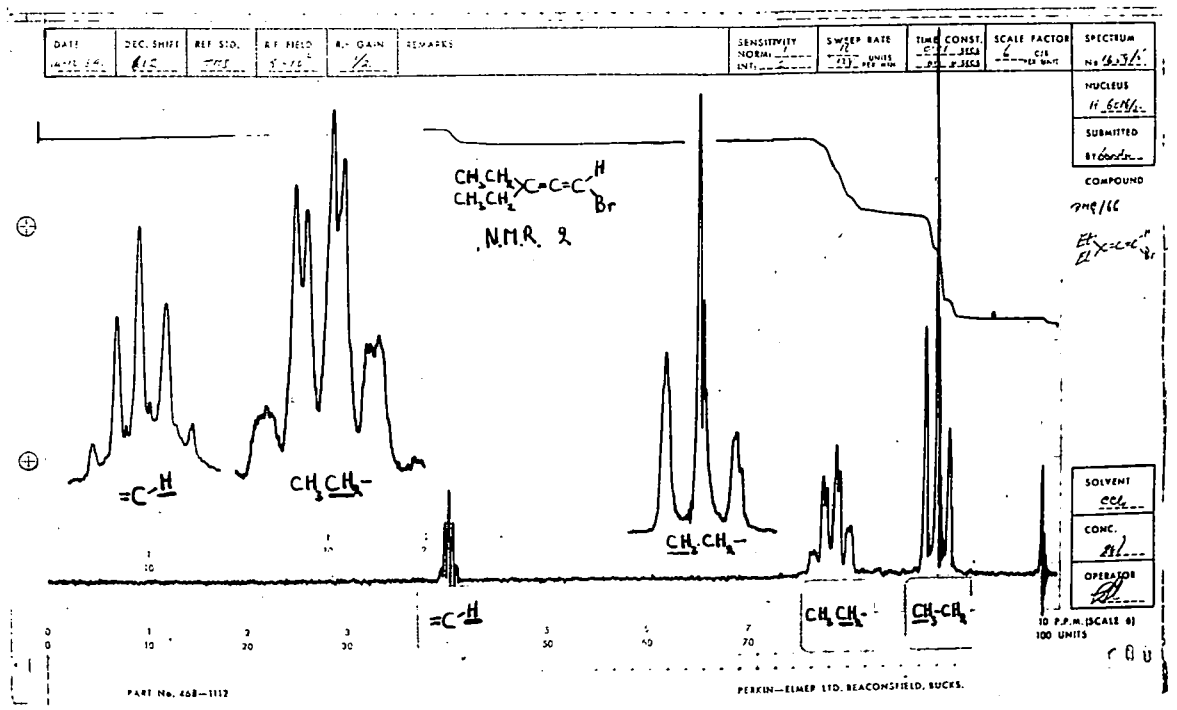
SENSITIVITY
SWEEP RATE
TIME CONST.
SCALE FACTOR
SPECTRUM
NUCLEUS
SUBMITTED
COMPOUND
N.M.R. 1
=C-H
CH3CH2-
SOLVENT
CONC
OPERATOR
10 P.P.M. (SCALE 6)
100 UNITS
PART No. 468—1112
PERKIN—ELMER LTD. BEACONSFIELD, BUCKS.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SPECTRUM
NUCLEUS
SUBMITTED
COMPOUND
N.M.R. 2
=C-H
CH3CH2-
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100 UNITS
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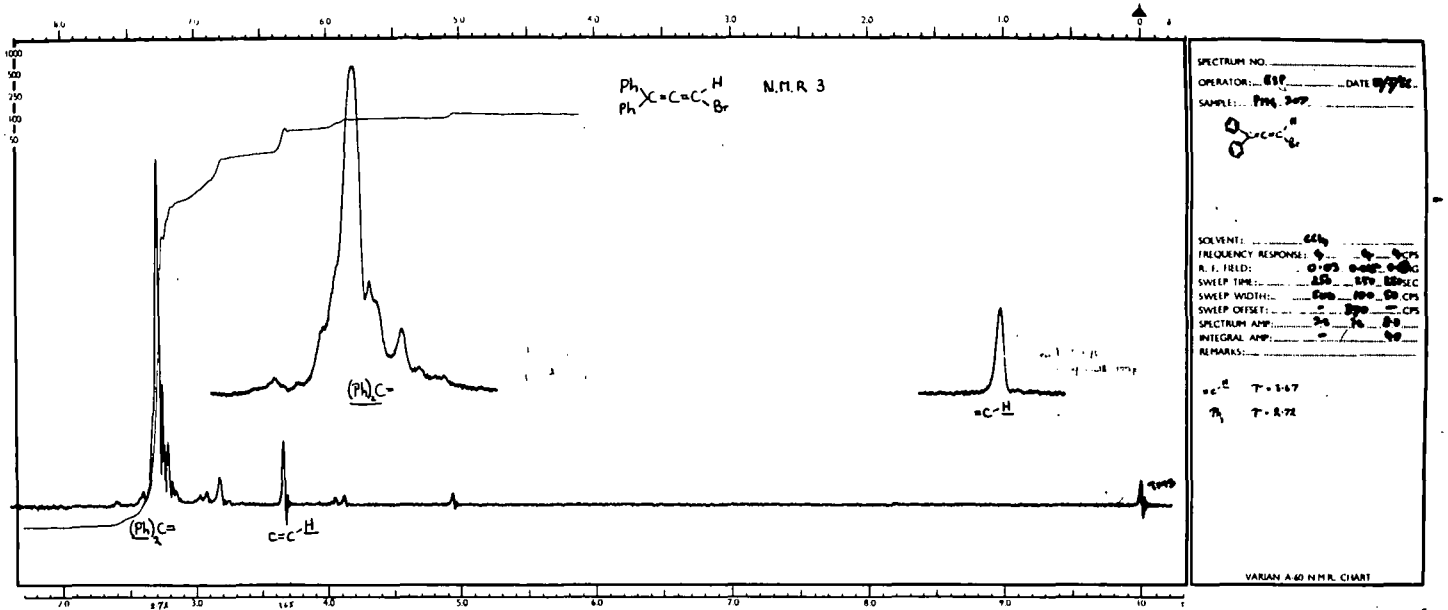
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OPERATOR:
DATE
SAMPLE:
SOLVENT:
FREQUENCY RESPONSE:
R. F. FIELD:
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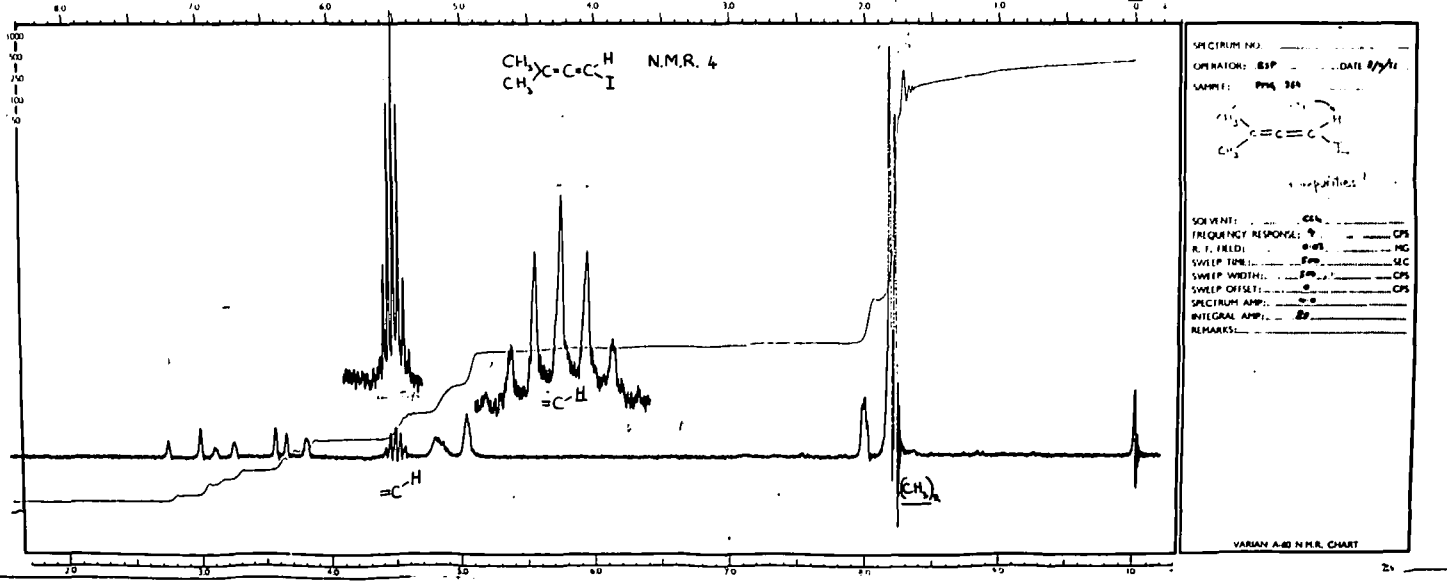
REMARKS:
VARIAN A-60 N.M.R. CHART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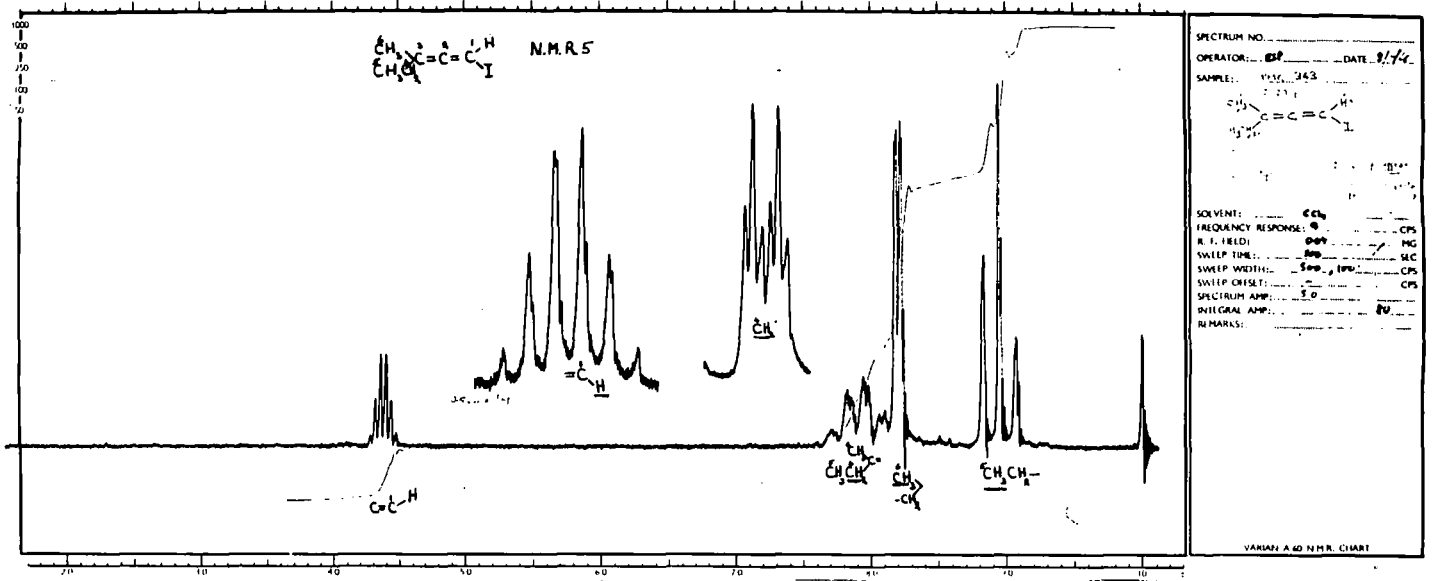
REMARKS:
VARIAN A-60 N.M.R. CHART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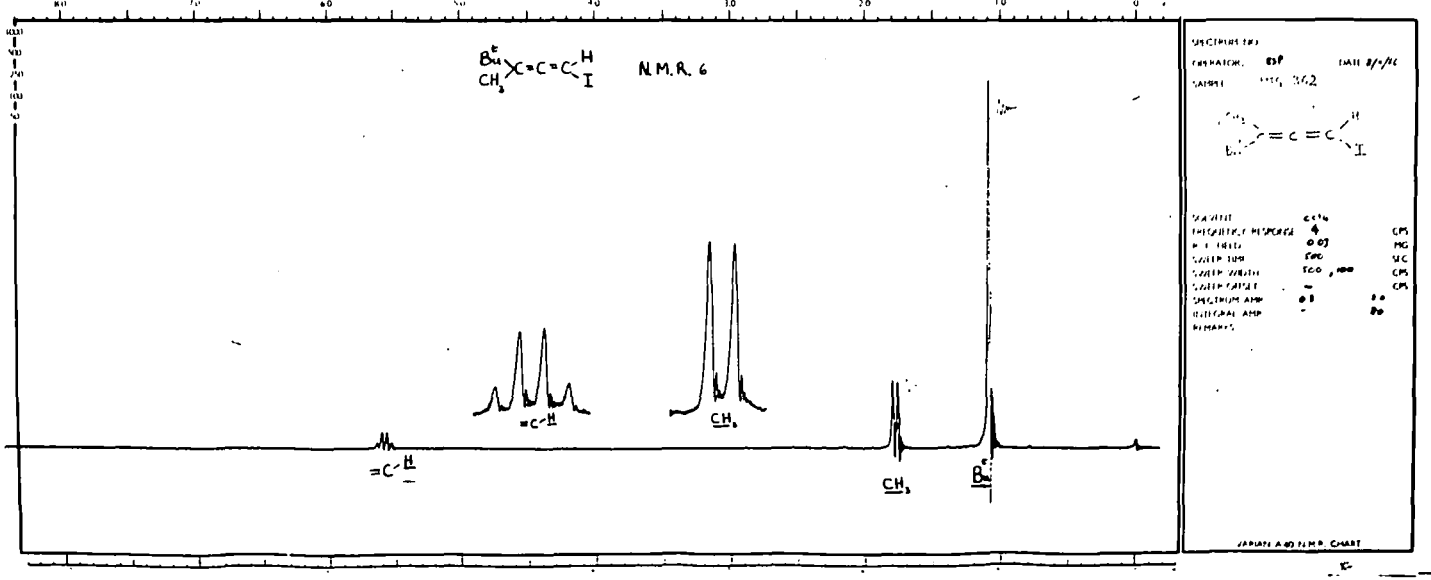
REMARKS:
VARIAN A60 N.M.R. CHART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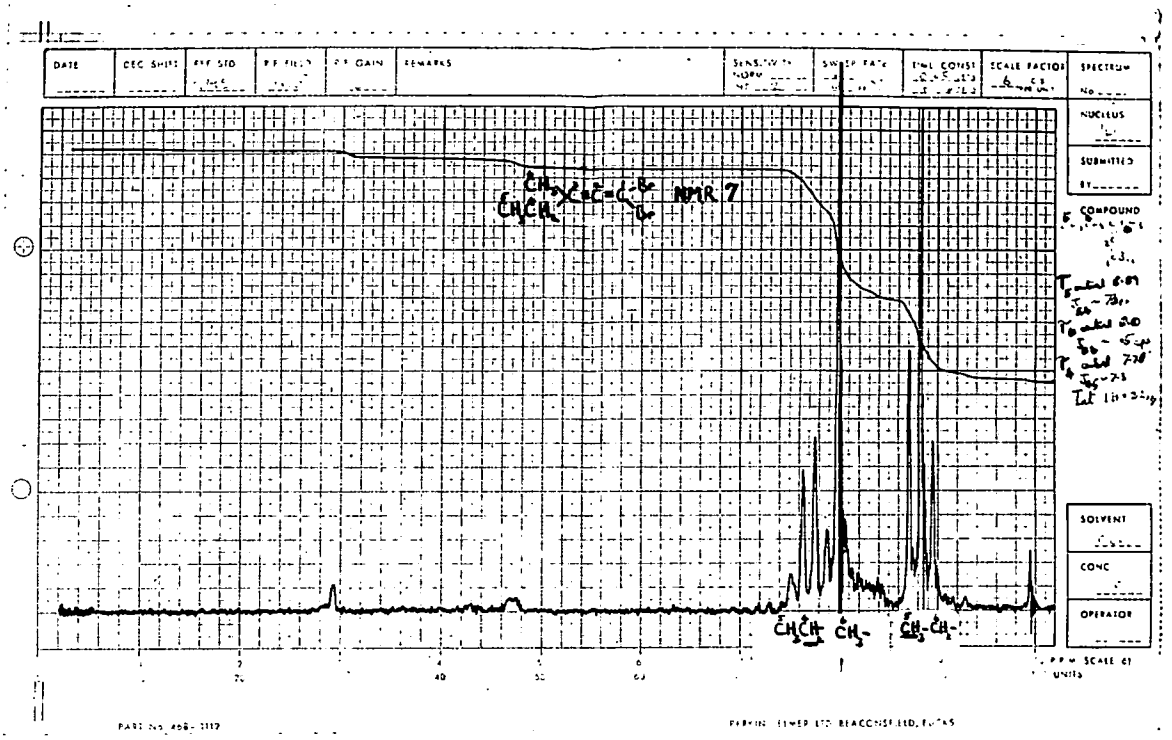
VARIAN A60 N.M.R. CHART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TIME CONST
SCALE FACTOR
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NUCLEUS
SUBMITTED
COMPOUND
NMR 7
SOLVENT
CONC
OPERATOR
P.P.M. SCALE 6
UNITS
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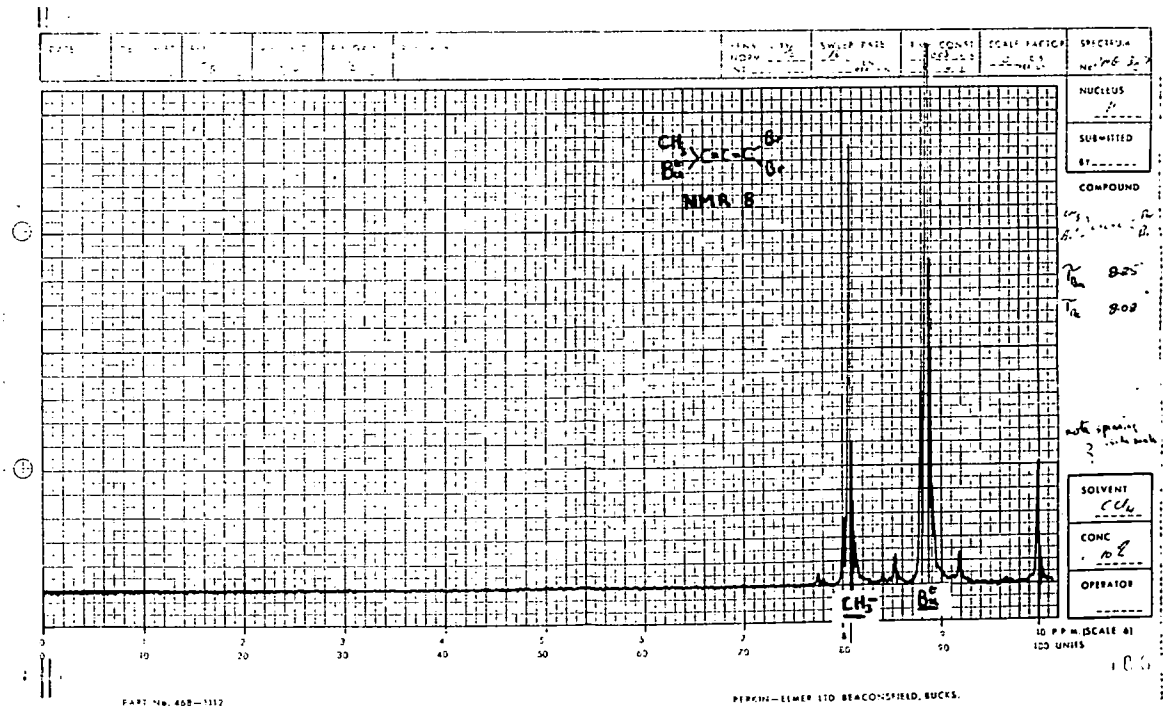
PERKIN-ELMER LTD. BEACONSFIELD, BUCKS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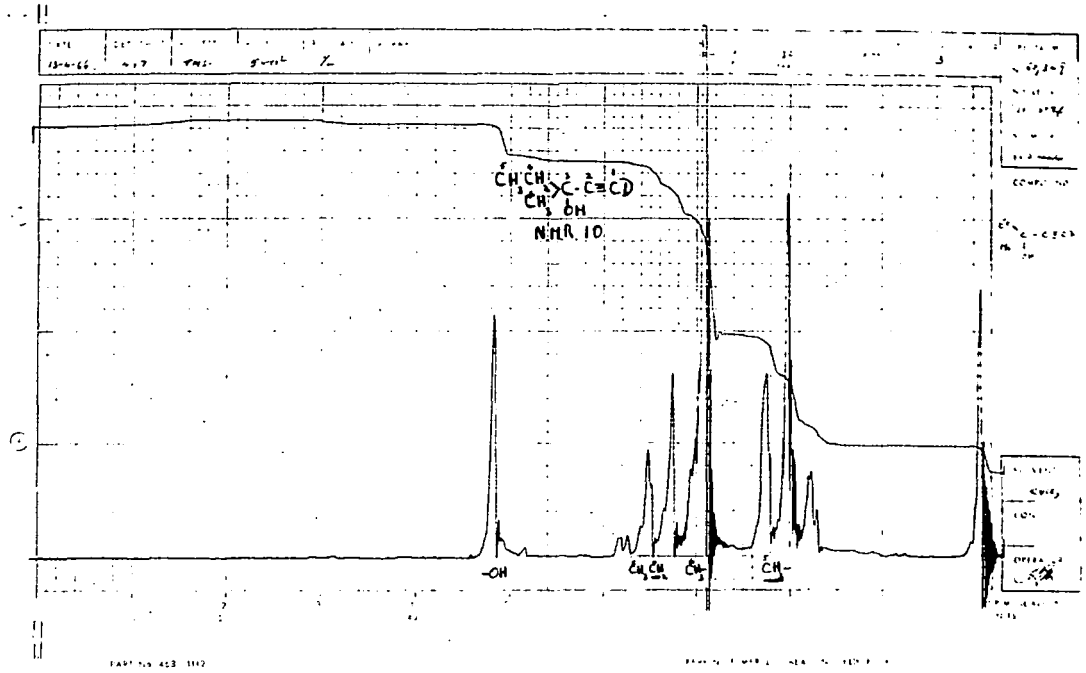
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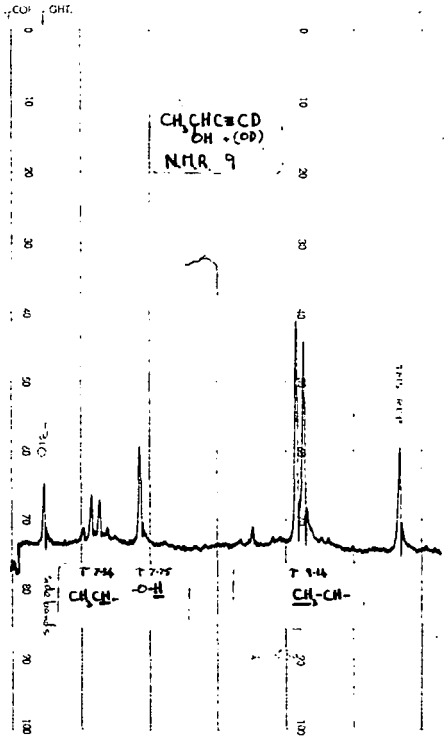
CH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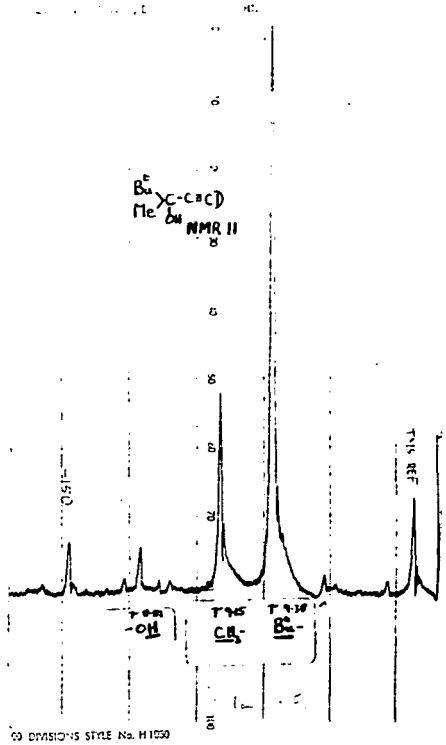
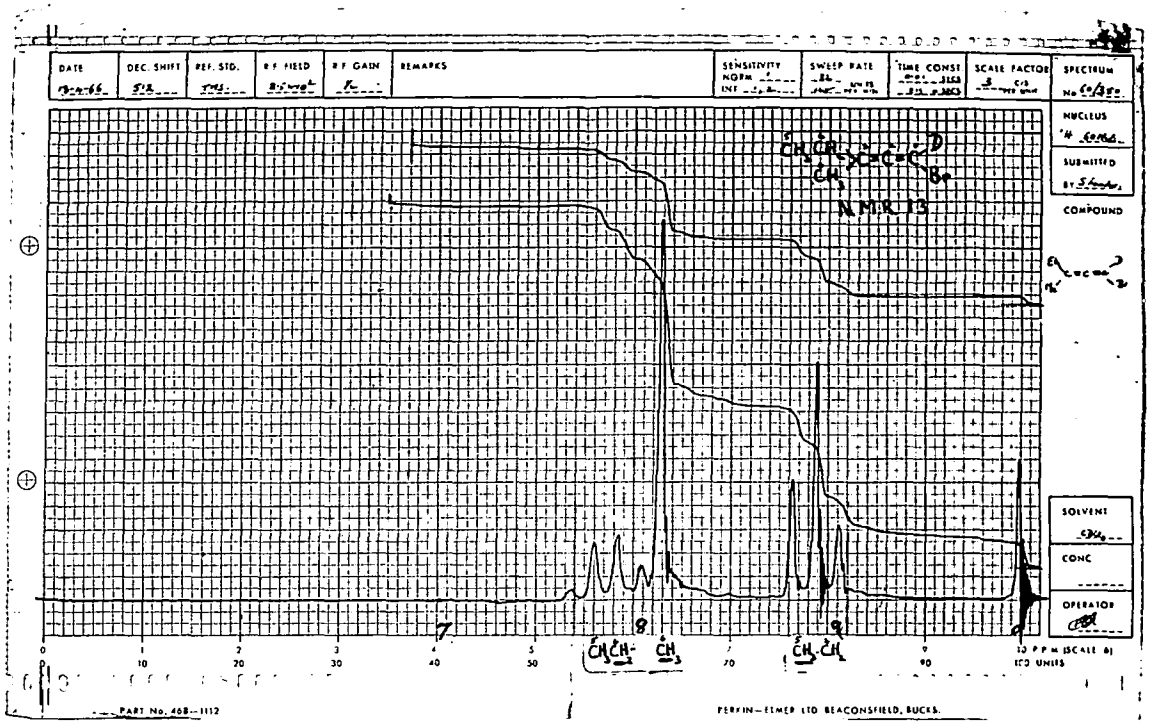
CH3CH-
-O-H
CH3-CH-


NMR 11
-OH
CH3-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R F GAIN
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SWEEP RATE
TIME CONST
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SPECTRUM
NUCLEUS
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COMPOUND
SOLVENT
CONC
OPERATOR
N.M.R. 13
PART No. 468-1112
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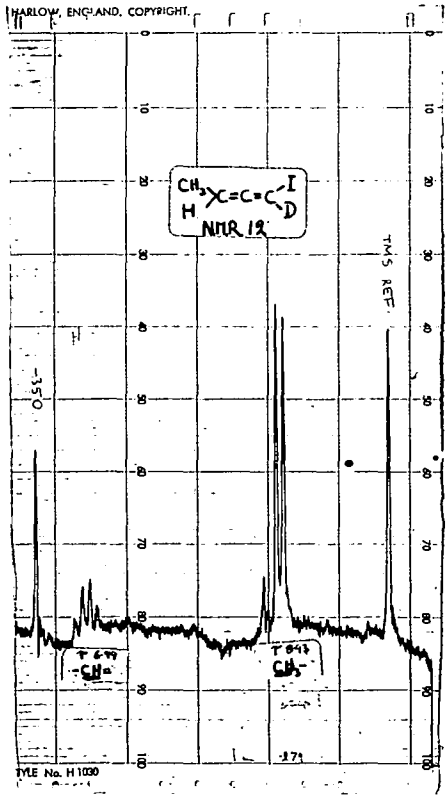
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NMR 12
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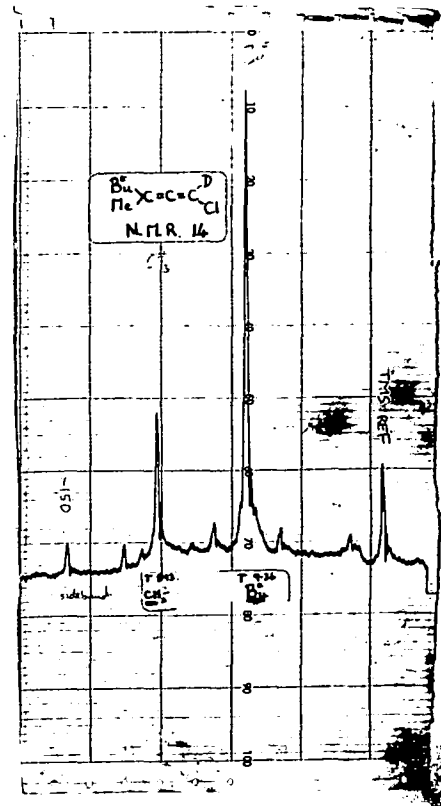
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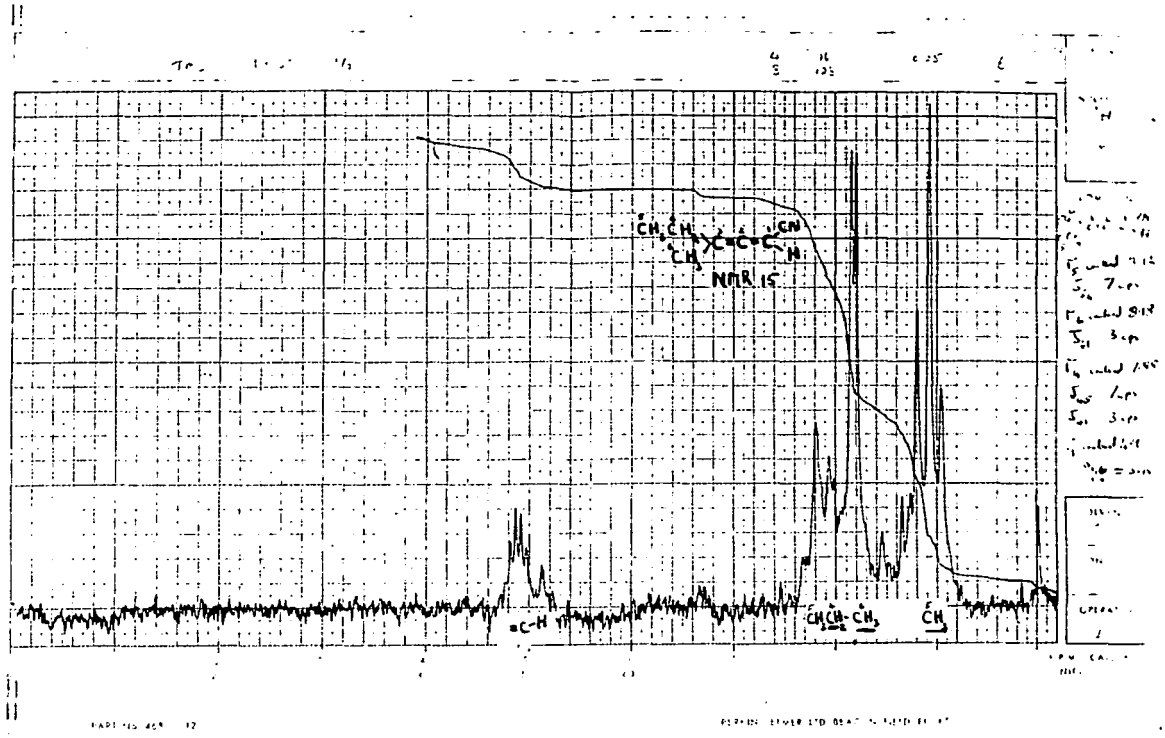
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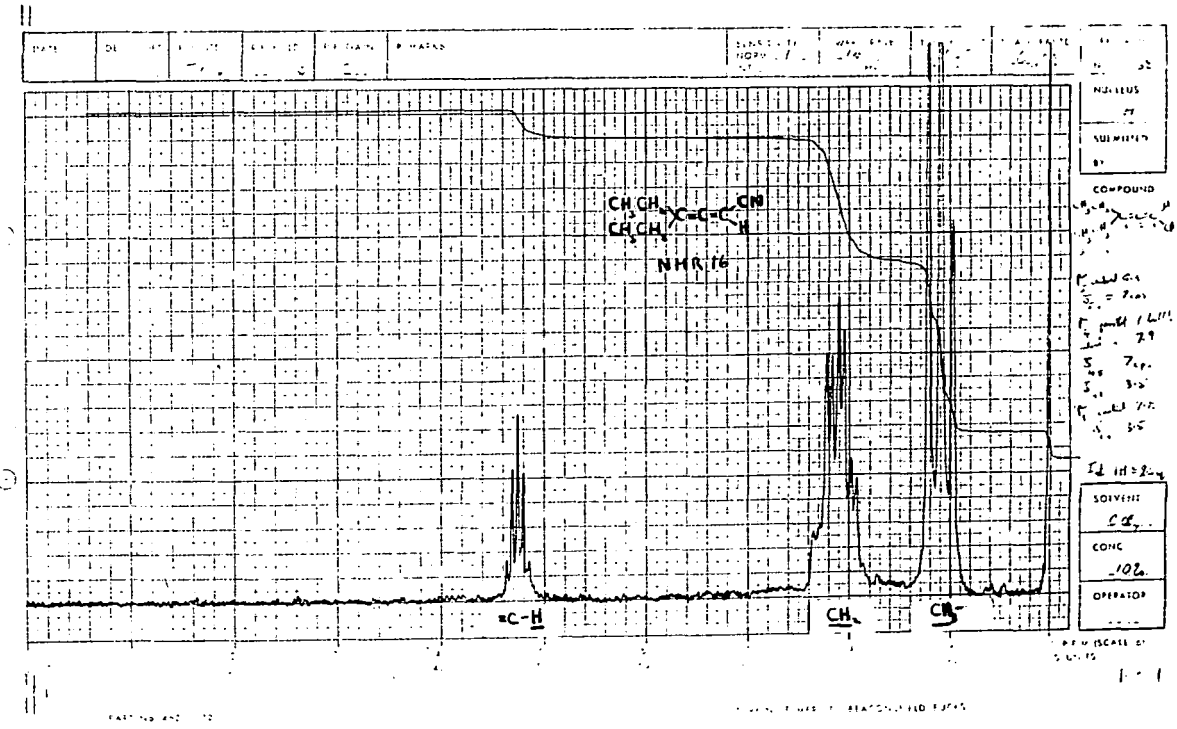
CH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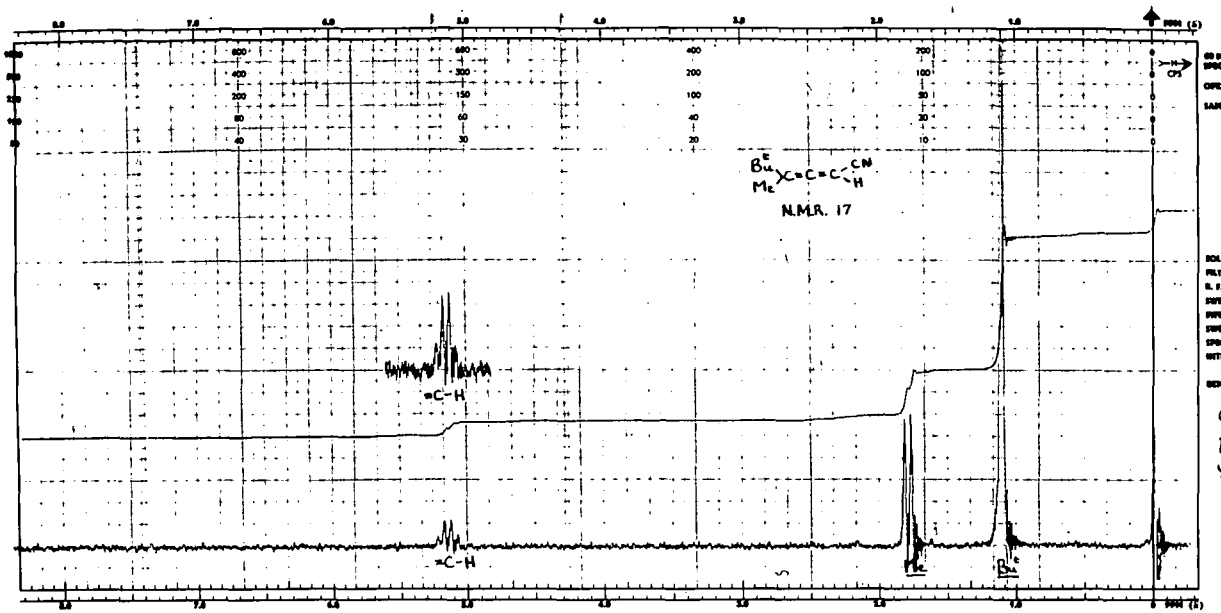
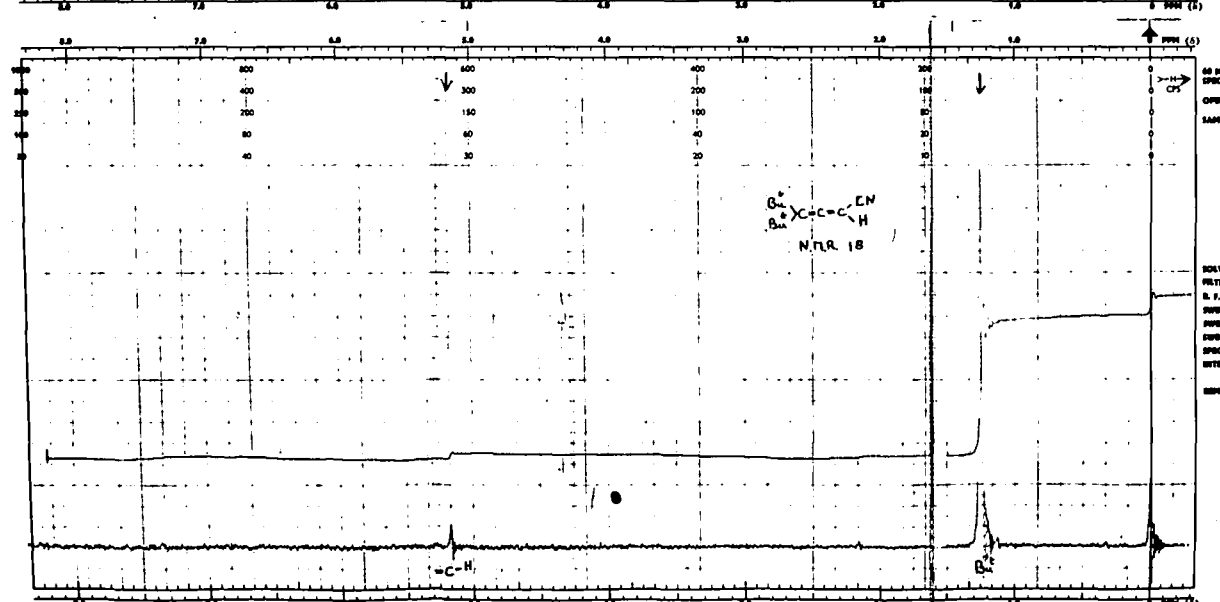
CH
CH
SOLVENT
CONC
OPERATOR


N.M.R. 17
=C-H
=C-H
Quintet 1331 by $CH_3 \rightarrow H$.
Doublet 11 by $H \rightarrow CH_3$
Singlet by Bu^t
$J_{CH_3 H}$ = 3/cps
$J_{H CH_3}$ = 3.4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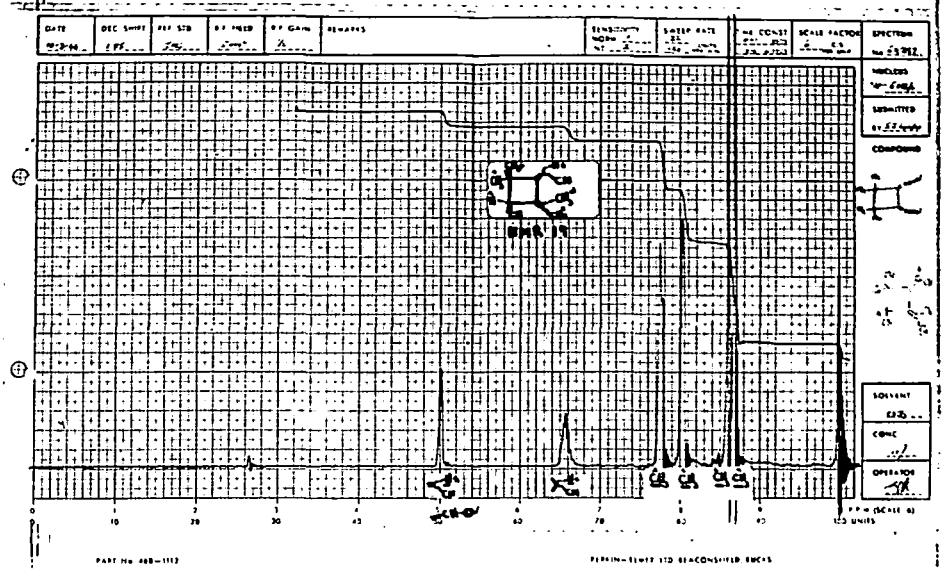
=C-H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SWEEP RATE
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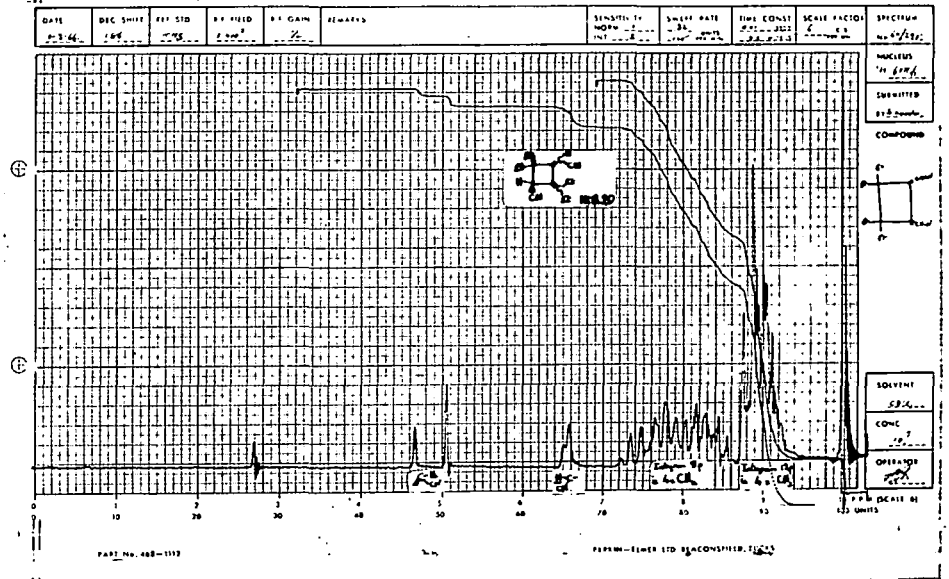
NMR 19
PERKIN-ELMER LTD BEACONSFIELD, BUCKS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REMARKS
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SWEEP RATE
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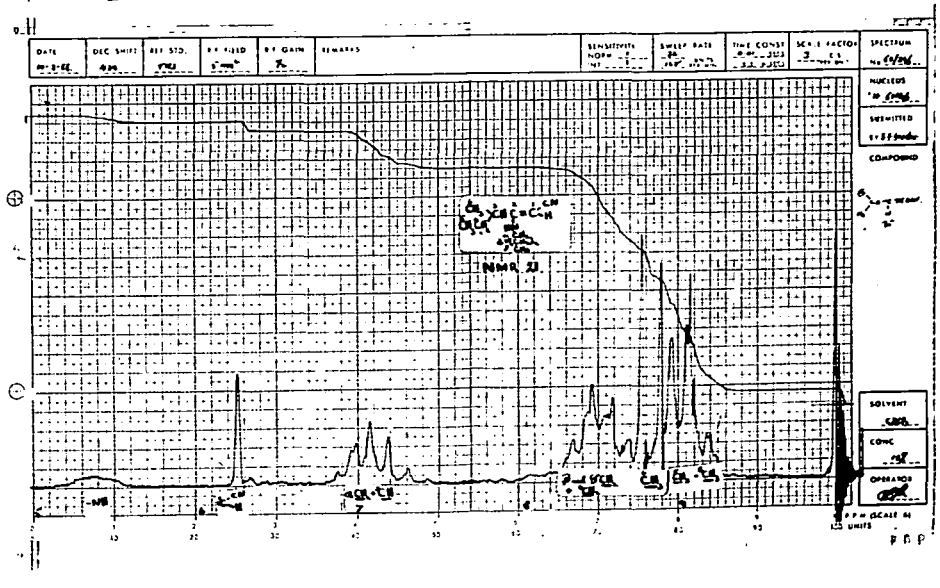
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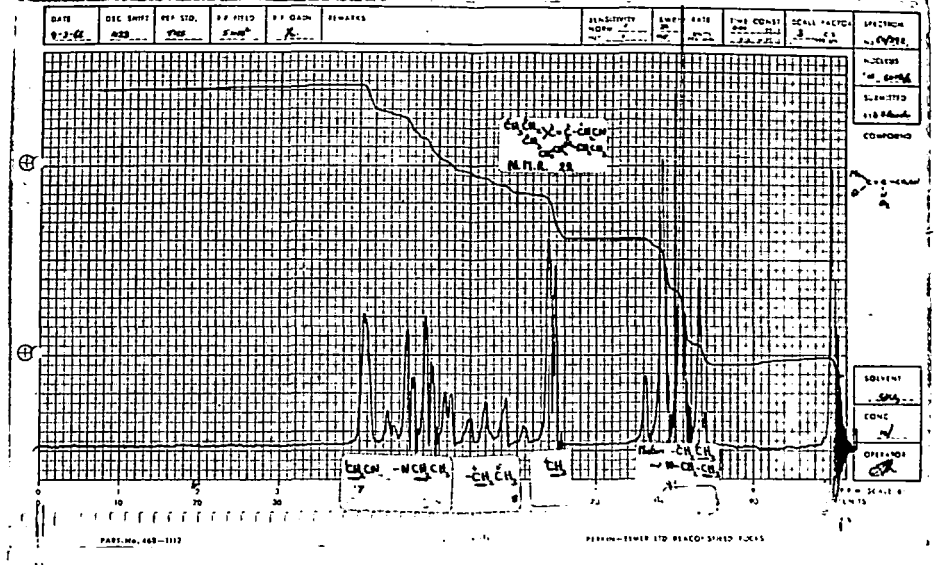
OPERATOR
NMR 21


NMR 22
SOLVENT
CONC
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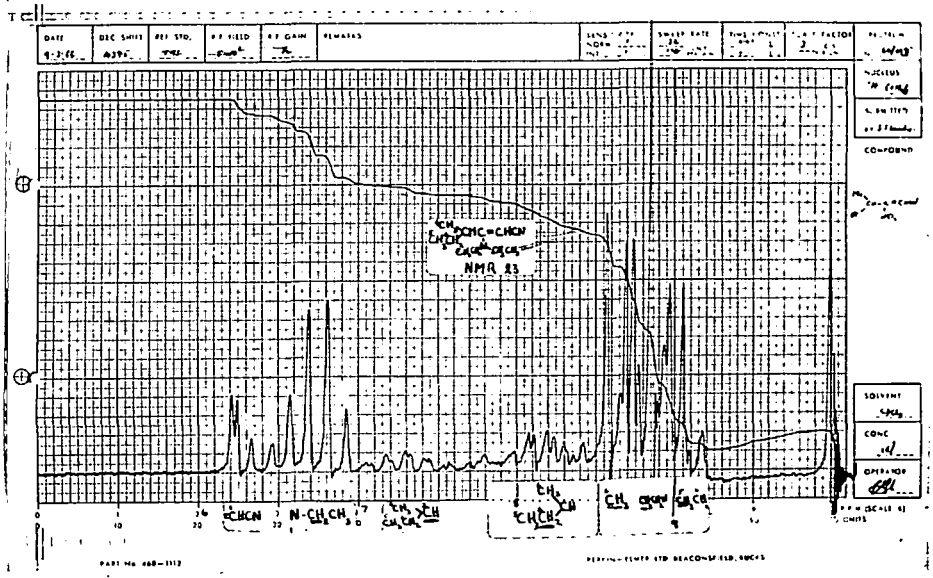
NMR 23
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CONC
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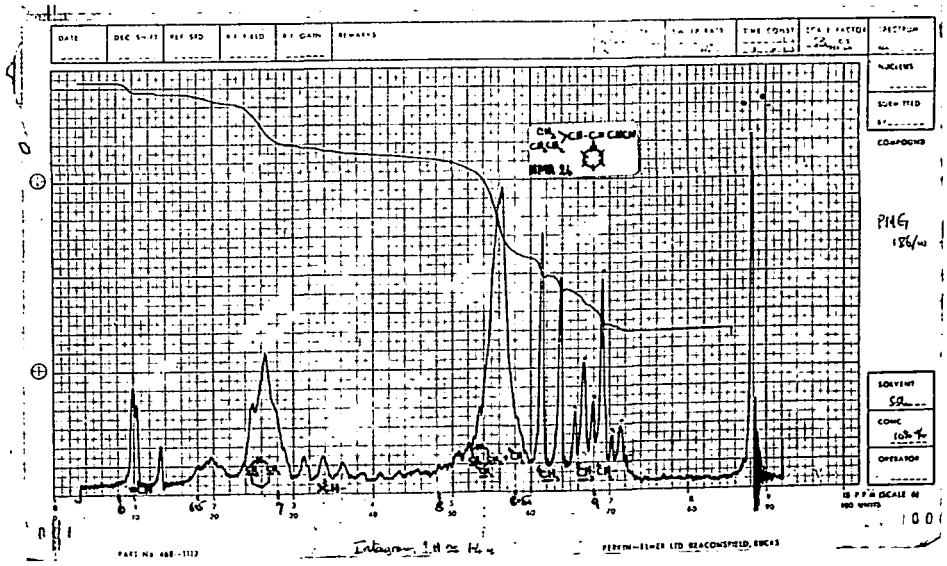
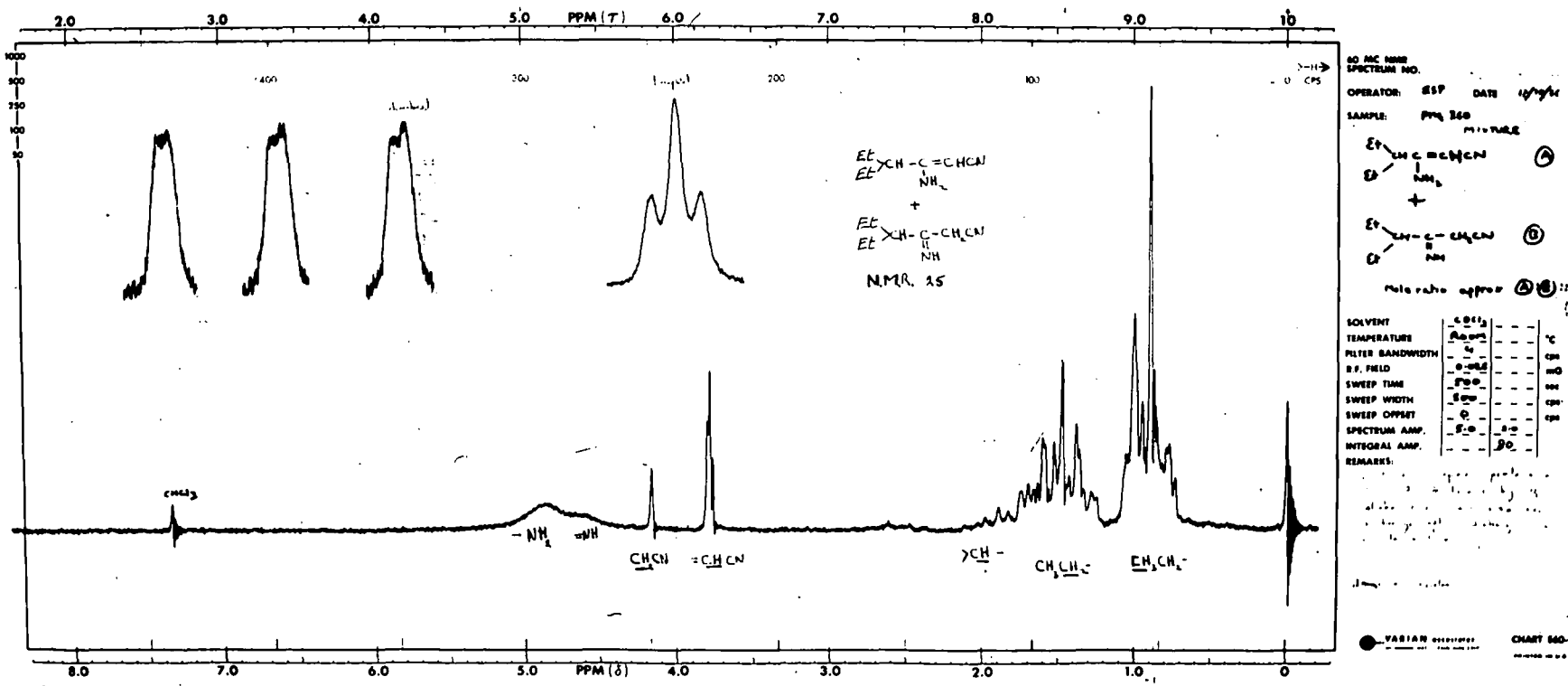
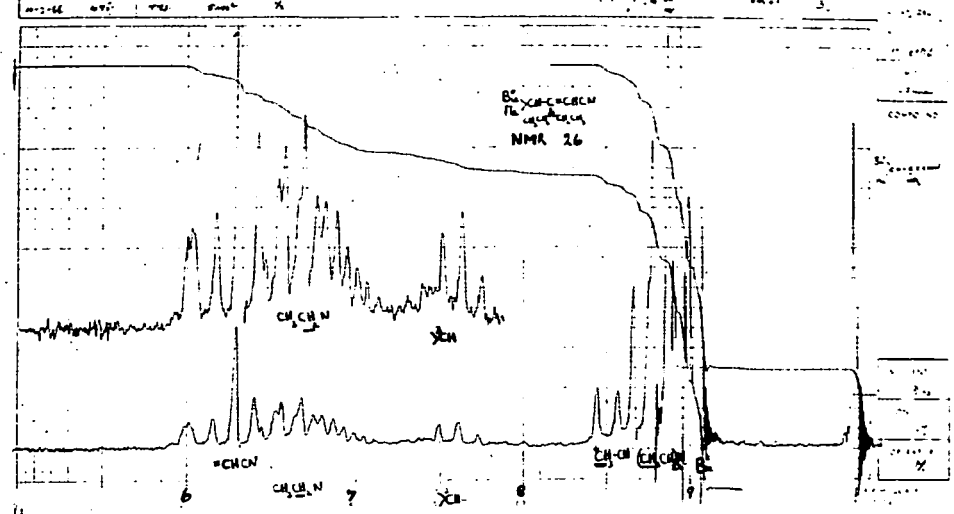
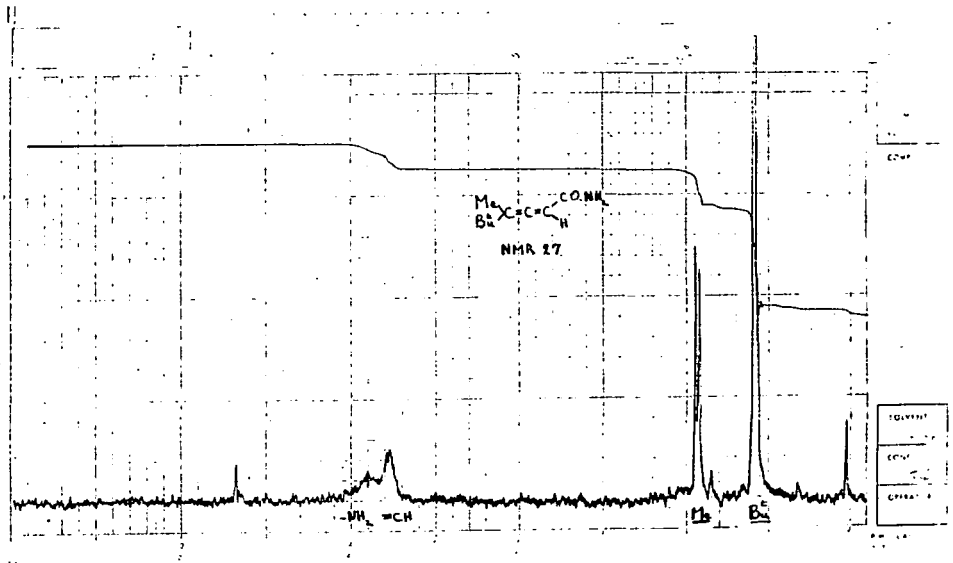
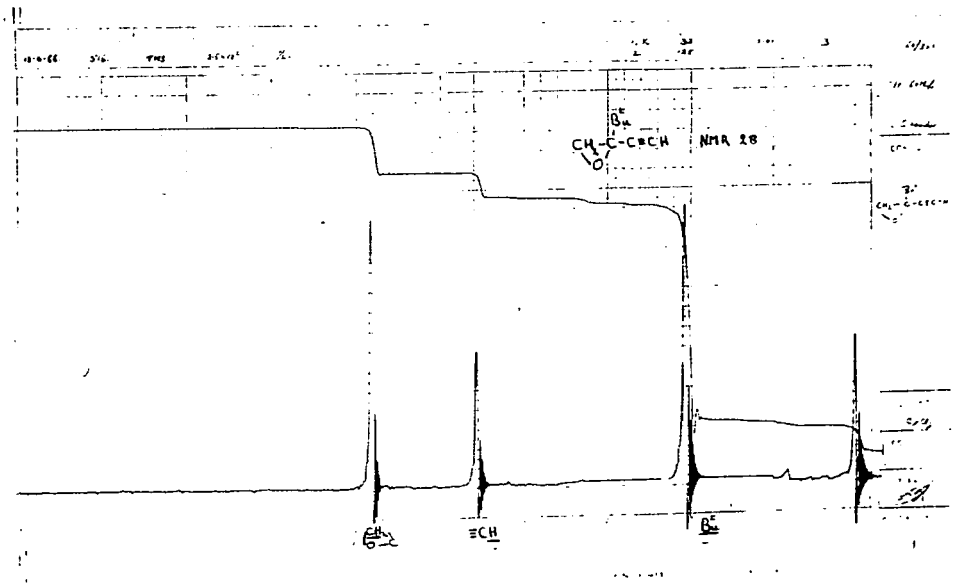

NMR 24
SOLVENT
CONC
OPERATOR
PERKIN-ELMER LTD BEACONSFIELD BUCKS


PPM (τ)
PPM (δ)
NMR. 25
-NH2
=NH
CH2CN
=CHCN
>CH-
CH3CH2-
CH3CH2-
60 MC NMR SPECTRUM NO.
OPERATOR:
DATE
SAMPLE:
SOLVENT
TEMPERATURE
FILTER BANDWIDTH
R.F. FIELD
SWEEP TIME
SWEEP WIDTH
SWEEP OFFSET
SPECTRUM AMP.
INTEGRAL AMP.
REMARKS:
VARIAN
CHART


NMR 26
=CHCN
6
7
8
9


NMR 27
=CH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