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THE CHEMISTRY OF ALLENE DERIVATIVES

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I. INTRODUCTION

Research workers studying the chemistry of polyunsaturated compounds have recently been paying increasing attention to substances containing an allenic group in their molecule. This is not only because, from its chemical nature, the allenic double bond system is of great interest in the study of the reactivity of different types of polyunsaturated compounds. The interest is due in considerable measure to the fact that various types of functional derivatives containing this bond system, together with polyyne and diene groups, have been found among plant (including fungal) metabolites. Although the number of these natural compounds is still small, the very presence of such extremely unstable compounds among the products of the vital activity of cells is of great interest to biochemists. Furthermore, these types of compounds have been found to possess high antibacterial and fungicidal activity, which is to a considerable extent associated with the presence of an allene grouping.

Allenic systems are extremely unstable chemically, tending to undergo not only polymerisation and addition reactions but also ready acetylene–allene–diene conversions and various rearrangements. All this greatly hampers the synthesis and the chemical study of functional derivatives of the allene series, and makes it urgently necessary to work out convenient methods for the preparation of such polyunsaturated systems. Since great interest is being shown at the present time in various types of allenic compounds, and previous reviews[1-3] have discussed mainly allenic hydrocarbons, we consider that a literature survey of methods of synthesis and the reactivity of functional derivatives of allenic compounds will be of undoubted interest.

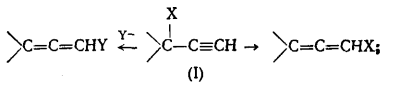
II. METHODS OF PREPARATION

The published information shows that functional derivatives of the allene series are obtained mainly by two methods. One of these is based on various types of acetylene–allene rearrangement of acetylenic systems, whereas 1,4-addition at a butenyne bond system underlies the second method.

1. Isomerisation of Acetylene Derivatives

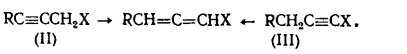
This general method of obtaining allene structures is based on two types of rearrangements characteristic of acetylene derivatives — (*a*) anionotropic rearrangement of

prop-2-ynyl systems of type (I) in the presence of catalysts or in the course of substitution reactions



(I)

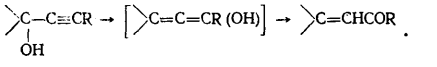
(*b*) prototropic isomerisation of prop-2-ynyl systems of types (II) and (III)



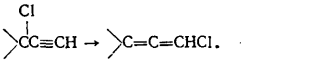
(II) (III)

Methods of synthesising functional derivatives of allene from the corresponding substituted derivatives of acetylene will be examined in this sequence.

(*a*) Anionotropic rearrangement of acetylenic alcohols and their derivatives. Rearrangement of an acetylenic to an allenic system is assumed to be an intermediate stage in the isomerisation, under the influence of acids, of acetylenic tertiary carbinols into unsaturated ketones (the Meyer–Schuster rearrangement)[4] and into $\alpha\beta$-unsaturated aldehydes (the Rupe rearrangement)[5]:

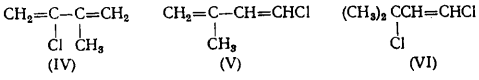


It has subsequently been shown that other acetylenic tertiary alcohols, including butenyne[6] and butadiyne[7] derivatives, are capable of analogous rearrangement. Among prop-2-ynyl derivatives, rearrangements of the chlorides of acetylenic tertiary alcohols have been studied the most thoroughly. Favorskaya and Favorskii[8] were the first to show that 3-chloro-3-methylbut-1-yne isomerises smoothly, under the influence of copper(I) chloride in ammonium chloride and concentrated hydrochloric acid, into 1-chloro-3-methylbuta-1,2-diene:



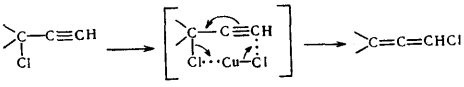
This method has been used to prepare several 1-chloroallene homologues[9–12], including the simplest 1-chloropropadiene[13], from various acetylenic alcohols.

It has subsequently been shown that such isomerisations do not yield unequivocal results: in the isomerisation of 3-chloro-3-methylbut-1-yne[9,14], for example, a mixture of products is formed, containing, together with the halogenoallene, such further isomerisation products as the chlorobutadienes (IV) and (V) and the dichloro-derivative (VI):

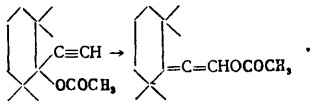


(IV) (V) (VI)

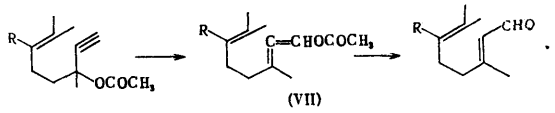
Considerably less work has been done on the rearrangement of acetylenic bromides[13,15–17]. The rearrangement of halogenoprop-2-ynyl systems to halogenoallenes represents a peculiar example of a 1,3-migration occurring by a mechanism of cyclic electron transfer[14]:



The isomerisation of acetates of acetylenic tertiary alcohols has also been described. The Landors[18], for example, observed the formation of an allenic acetate in up to 90% yield in the pyrolysis of 1-ethynyl-2,2,6,6-tetramethylcyclohexyl acetate:



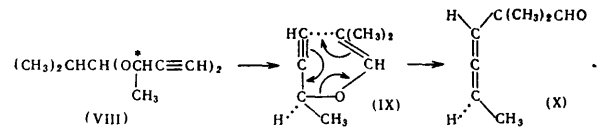
Recently Isler and his coworkers[19] have established that such acetates readily undergo rearrangement when heated in glacial acetic acid in the presence of copper powder or salts of copper or silver:



(VII)

Almost quantitative yields of unsaturated acetates of the type (VII) were obtained in this way. By means of this reaction it has been possible to work out an elegant method for the synthesis of various $\alpha\beta$-unsaturated aldehydes, including citral, farnesal, and phytal [3,7,11,15-tetramethylhexadec-2-enol].

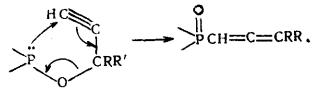
The synthesis has been described[20] of optically active 2,2-dimethylhexa-3,4-dienal (X) by the pyrolysis of dextrorotatory 2-methyl-3,3-bis-(1-methylprop-2-ynyloxy)propane (VIII). Formation of this product probably results from Claisen rearrangement of an intermediate 2-methylprop-1-enyl ether (IX) by a mechanism of cyclic transfer of electrons:



(VIII) (IX) (X)

It has recently been shown that, in the case of vinyl and chloroalkyl prop-2-ynyl ethers, the Claisen rearrangement is a general method for the synthesis of allenic aldehydes[21–23]. Allenic ketones are obtained in a similar manner, but they are very readily isomerised into conjugated dienones[24,25].

Detailed studies have recently been made of other interesting methods of synthesis, in which prop-2-ynyl esters are used for the preparation of allenes containing phosphorus. The prop-2-ynyl esters formed from acetylenic alcohols and halogen derivatives of tervalent phosphorus readily (in ether–pyridine at 20°) undergo intramolecular acetylene–allene rearrangement to give 75–100% yields of the allene derivatives. In view of the structure of the products, the rearrangement is explained by intramolecular migration in the five-centre intermediate system[26–28]:



Primary, secondary, and tertiary acetylenic alcohols can be successfully used in the above reactions[26–31]. Increasing the number of methyl substituents in the prop-2-ynyl portion not only increases the yield but also stabilises the allene derivatives, obviously owing to the inductive effect of the methyl groups, which prevent further prototropic isomerisation.

The rearrangement of prop-2-ynylammonium halides[32] under the influence of sodamide also results in allene derivatives. An interesting sequence of isomerisations into

allene and cumulene systems has been observed in amines containing a butenynyl group[33]:

$$(CH_3)_2CC{\equiv}CCH{=}CH_2 \rightarrow (CH_3)_2C{=}C{=}C{-}CH{=}CH_2 \rightarrow (CH_3)_2C{=}C{=}C{=}CHCH_2NR_2$$
(NR$_2$ and NR$_2$)

It has repeatedly been observed that acetylene–allene isomerisation takes place during the occurrence of substitution reactions. Reaction of 3-chloro-3-methylalk-1-ynes with silver acetate in glacial acetic acid gives a mixture[34] of the allenic acetate (XI) and the normal acetylenic acetate (XII), the latter being the sole product when the reaction is conducted under the influence of potassium acetate:

$$R(H_3C)C{=}C{=}CHOCOCH_3 \xleftarrow{CH_3COOAg} R(H_3C)CCl{-}C{\equiv}CH \xrightarrow{CH_3COOK} R(H_3C)C(OCOCH_3){-}C{\equiv}CH.$$
(XI) (XII)

Silver propionate under similar conditions gave 3-methylbuta-1,2-dienyl propionate[35].

Prop-2-ynyl halides react with metal cyanides in the presence of copper(I) bromide at 60–120° to form allenic nitriles[36,37]. In the case of sterically hindered acetylenic tertiary bromides the yields reach 80%:

$$BrCRR'C{\equiv}CH \xrightarrow{Cu_2CN_2} RR'C{=}C{=}CHCN.$$

Interaction of 3-chloro-3-methylbut-1-yne with trialkyl phosphites at 130–150° results in moderate yields of dialkyl 3-methylbuta-1,2-dienylphosphonites[38]. Primary and secondary amines readily add on to prop-2-ynyl halides, merely forming acetylenic amines[39]. However, Hennion has recently reported[40,41] that, in the alkylation of certain sterically hindered prop-2-ynyl chlorides with tertiary amines, it has proved possible to obtain quaternary salts of allenylamines in 60–80% yields:

$$(CH_3)_2CCl{-}C{\equiv}CH \xrightarrow{(CH_3)_3N} (CH_3)_2C{=}C{=}CH\overset{+}{N}(CH_3)_3\,\overline{Cl}.$$

Not all tertiary amines react in this way, the type of reaction which occurs depending also on the basic strength and the nucleophilic character of the amine[41].

A general method for obtaining allenic acids (XIII) is based on the action of nickel carbonyl and hydrogen chloride on acetylenic alcohols[42–45], but the yields are usually low (10–20%):

$$RR'CC(OH){\equiv}CH \xrightarrow[Ni(CO)_4]{HCl} RR'CCl{-}C{\equiv}CH \xrightarrow[(R''OH)]{} RR'C{=}C{=}CHCO_2R''$$
(XIII)

where R = R′ = H, CH_3, C_2H_5; R = H, R′ = CH_3, C_3H_7, C_6H_5.

The reaction of prop-2-ynyl halides with acetylenic components (in particular with acetylenic alcohols) under the influence of copper salts in an amine medium provides an interesting route for the synthesis of acetylenic–allenic products (the yields reaching 80%)[46]:

$$R_2CC(OH){\equiv}CH + HC{\equiv}CCH_2X \xrightarrow[NH_4OH]{Cu_2Cl_2} R_2CC(OH){\equiv}CCH{=}C{=}CH_2$$

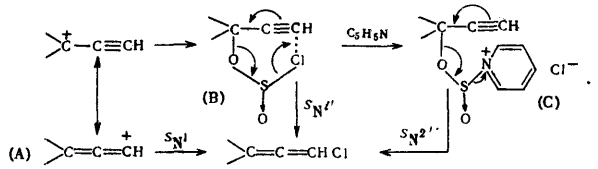
where X = Cl, Br, p-$CH_3C_6H_4SO_2$; R = H, CH_3, C_2H_5.

The isomerisation of acetylenic tertiary alcohols under the influence of concentrated hydrobromic acid in the presence of copper(I) bromide has recently been suggested as a method for the preparation of various 1-bromoallenes[47,48]:

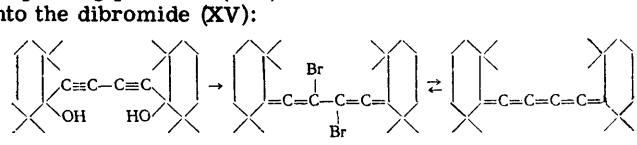
$$RR'CC(OH){\equiv}CH \xrightarrow{HBr/Cu_2Br_2} RR'C{=}C{=}CHBr.$$

This method gives a high yield (60–80%) of quite pure bromoallenes (the content of acetylenic derivatives does not exceed 2–5%). An extremely important feature is that in this case the reaction proceeds stereospecifically, and optically active 3,4,4-trimethylpent-1-yn-3-ol yields the optically active allenic bromide.

Jacobs[49,50] and Landor[51,52] used the reaction of acetylenic alcohols with thionyl chloride for the synthesis of chloroallenes. This reaction is conveniently conducted in dioxan medium, is accelerated by the addition of bases (pyridine), and from sterically hindered alcohols gives good yields (up to 75%) of chloroallenes. Acetylenic secondary alcohols give considerably lower yields, and the reaction is complicated by the formation of byproducts[50,53]. Both the above reactions are characterised by the absence of prop-2-ynyl halides as intermediate products, so that the formation of halogenoallenes is not a result of their anionotropic rearrangement. Furthemore, these reactions proceed stereospecifically, in spite of the disappearance of the centre of asymmetry present in the original acetylenic alcohol. It is hardly possible to explain these results on the assumption that the reaction involves intermediate formation of a carbonium ion (A). Formation of an optically active chloroallene could conceivably occur through a cyclic transition state (B) (by an S_Ni' mechanism). In that case, however, the reaction velocity should be independent of the catalytic action of bases. Nevertheless, in the absence of bases the reaction of acetylenic alcohols with thionyl chloride gives very low yields, even when sterically hindered alcohols are employed. This suggests an S_N2' mechanism, the role of pyridine probably consisting in formation of a pyridinium salt (C), in which the substitution takes place under the influence of chloride ions. Preservation of configuration can then be explained either by a double inversion or by formation of a rigid (undissociated) ion-pair[50]. In either case (S_N2' or S_Ni' mechanism) the chlorine should approach on the hydroxyl side of the alcohol. Thus the available data are not yet sufficient to settle unequivocally the problem of the reaction mechanism between acetylenic alcohols and thionyl chloride:



A few examples have been described of the formation of halogenated allenes by the reaction of acetylenic tertiary alcohols with phosphorus trichloride in pyridine[54] or with phosphorus tribromide[55,56]. By means of the latter reaction Bohlmann[55] obtained from the butadiynylene glycol (XIV), obviously as a result of a double prop-2-ynyl rearrangement, a 70% yield of a diallenic dibromide (XV), whose structure was established by conversion into the corresponding pentaene (XVI) and reconversion of the latter into the dibromide (XV):



(XIV) (XV) (XVI)

The corresponding allenic iodides are formed (mixed with acetylenic and 1,3-diene isomers) by the action of potassium or sodium iodide on the prop-2-ynyl halides[13,16,57,58] or

of hydriodic acid on acetylenic carbinols[59], but it is extremely difficult to isolate these iodides in the pure form owing to their great tendency to undergo polymerisation and rearrangement even on simple distillation. A practical method of synthesis consists in treating acetylenic alcohols with triphenylmethyl phosphite–iodine[60], the yields varying from 20% to 70%:

$$\underset{\underset{OH}{|}}{RCHC{\equiv}CH} \rightarrow RCH{=}C{=}CHI$$

where R = H, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_5.

Another group of substitutions which yield allenic structures involve organometallic compounds (of magnesium, aluminium, and zinc) derived from prop-2-ynyl halides, which have been studied mainly by Prévost and his co-workers[61–63]. On the hypothesis that a free carbanion is formed[61], these workers consider that the MgBr derivatives result from attack by the electrophilic MgBr, so that the structure of the final product should depend on electronic and steric factors. In the case of prop-2-ynyl bromide (XVII, R = H) the carbanion will have the structure (XVIII), and since δ^- far exceeds δ'^- in this instance, the $^+$MgBr should attack the acetylenic carbon atom, which will yield the allenic system (XIX):

$$\underset{\underset{Br}{|}}{RCHC{\equiv}CH} \rightarrow \left[\overset{\delta'-}{RCH}\ \cdots\ \overset{2}{C}\ \cdots\ \overset{\delta-}{\underset{1}{CH}}\right] \xrightarrow{MgBr^+} RCH{=}C{=}CHMgBr$$

(XVII) (XVIII) (XIX)

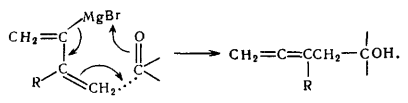
Similar relationships are observed with the bromides (XVII, R = CH_3); here steric hindrance at $C_{(3)}$ is also operative, which should result in the structure (XIX) exclusively. With the isomeric carbanion (XX), on the other hand, the steric factor will act in the opposite direction, and a mixture of acetylenic and allenic MgBr derivatives will be obtained:

$$\underset{\underset{MgBr}{|}}{H_3CC{=}C{=}CH_2} \leftarrow \left[\underset{(XX)}{H_3C\overset{\delta-}{C}\ \cdots\ C\ \cdots\ \overset{\delta'-}{CH_2}}\right] \rightarrow H_3CC{\equiv}CCH_2MgBr.$$

In conformity with these views, it is only in the last case that formation of a mixture of acetylenic and allenic alcohols has been observed[61] on reaction with carbonyl compounds. In all other cases 2-acetylenic alcohols are formed exclusively. The formation of allenic together with acetylenic alcohols has been established in the reaction of prop-2-ynylzinc bromides with ketones[62–65] and in the Reformatskii condensation of prop-2-ynyl bromides with aliphatic and aromatic aldehydes[66–70]. Using condensation with acetone as example, however, it was demonstrated that allenic alcohols are formed, not as a result of reaction of the allenic ZnBr derivative with acetone, but from isomerisation of the acetylenic alcohol under the influence of the zinc salt[63,71]:

$$\underset{H_3C}{\overset{H_3C}{\diagdown}}\overset{OH}{\underset{|}{C}}CH_2C{\equiv}CH \rightarrow \underset{H_3C}{\overset{H_3C}{\diagdown}}\overset{OH}{\underset{|}{C}}{-}CH{=}C{=}CH_2 \xleftarrow{CH_3COCH_3} X \longleftarrow CH_2{=}C{=}CHZnBr.$$

An interesting case of the formation of allenic alcohols has been observed in the reaction of magnesium halide derivatives of diene bromides with carbonyl compounds, which probably occurs by a mechanism of cyclic transfer of electrons[72]:



Formation of an allene derivative has recently been noted in the addition of prop-2-ynyl-lithium to aliphatic aldimines[73] and also in the reaction of orthoformic ester with prop-2-ynyl-magnesium (or -zinc) halides[74,75].

The carboxylation of prop-2-ynylmagnesium halides with carbon dioxide or chloroformic ester has been known for a long time. Marvel[76] described the preparation of allenic acids from acetylenic tertiary chlorides. It was later established that this is a general type of reaction, Grignard reagents derived from prop-2-ynyl primary bromides being most readily carboxylated (in yields of 50–70%)[77–81]:

$$RC{\equiv}CCH_2Br \xrightarrow[2.\ CO_2]{1.\ Mg} RC{\equiv}CCH_2CO_2H + \underset{\underset{CO_2H}{|}}{RC{=}C{=}CH_2} \quad (XXI).$$

Although the reaction is complicated by formation of a dimeric allenic acid (see Section III, 2), in most cases the allenic acids (XXI) can be easily isolated in the pure form. Secondary and tertiary prop-2-ynylmagnesium halides show greater difficulty in reacting with carbon dioxide, but yield pure allenic acids of the type (XXII)[82]:

$$\underset{\underset{Br}{|}}{C_4H_9C{\equiv}CC(R)CH_3} \longrightarrow \underset{\underset{CO_2H}{|}}{C_4H_9C{=}C{=}C\overset{R}{\underset{CH_3}{\diagup}}} \quad (XXII)$$

where R = H, CH_3.

The condensation of dimethylbenzamide with certain substituted prop-2-ynylmagnesium bromides yields mixtures of acetylenic and allenic ketones[83]:

$$RC{\equiv}CCH(R')Br \xrightarrow[2.\ C_6H_5CON(CH_3)_2]{1.\ Mg} \underset{\underset{R}{|}}{C_6H_5COC{=}C{=}CHR'} + \underset{\underset{R'}{|}}{RC{\equiv}CCHCOC_6H_5}$$

(b) **Prototropic rearrangement of acetylenic systems.** Allene derivatives containing COOR, CN, CO, etc. groups have been obtained by the prototropic rearrangement of acetylenic compounds in the presence of bases under comparatively mild conditions. The isomerisation of acetylenic into allenic hydrocarbons is usually reversible[84], although the relative proportions of the acetylene–allene–diene products are greatly dependent on the structure of the initial acetylene, and perhaps on the conditions under which the rearrangement takes place. It might have been expected that the presence of electron-acceptor groups (CN, COOR, CHO, CO) in the allyl position relative to the acetylenic bond would not only facilitate prototropic rearrangement of acetylene to allene but also stabilise the cumulated system. In fact, the acetylenic epoxide (XXIII) readily isomerises under the influence of zinc oxide into the allenic aldehyde (XXIV)[85,86]:

$$\underset{\underset{CH_3}{|}}{RC{\equiv}C{-}C\overset{O}{\diagup\diagdown}CH_2} \rightarrow \underset{\underset{CHO}{|}}{RCH{=}C{=}C\overset{CH_3}{}}.$$

(XXIII) (XXIV)

The oxidation of 2-acetylenic secondary alcohols[67,72,87–90] with chromium trioxide in acetone and sulphuric acid is also accompanied by prototropic rearrangement, giving up to 70% yields of various allenic ketones. Allenic aldehydes and ketones can be obtained by the acid hydrolysis of butenynyl ethers of the type (XXV)[91–94]:

$$\underset{(XXV)}{R'C{\equiv}CCH{=}CR(OC_2H_5)} \rightarrow R'CH{=}C{=}CHCOR$$

where R = H, Alk.

Rearrangement has been observed also in the reaction of prop-2-ynyl halides with copper and potassium cyanides[95-97], by means of which several allenic nitriles have been synthesised in up to 50% yields:

$$RCH{=}C{=}CHCN \xleftarrow{KCN} RC{\equiv}CCH_2Br \xrightarrow{KCN} RC{\equiv}CCH_2CN.$$

The isomerisation of prop-2-ynyl sulphides in the presence of sodium ethoxide yields allenic sulphides[98-100]:

$$HC{\equiv}CCHR(SC_6H_5) \rightarrow H_2C{=}C{=}CR(SC_6H_5).$$

Arens has shown also that substituted 1-ethylthioalkynes (XXVI) on rapid treatment with an equivalent amount of sodamide are capable of giving a carbanion (XXVII), which on hydrolysis or alkylation gives up to 85% yields of the corresponding allenic sulphides[100-103]:

$$RCH_2C{\equiv}CSC_2H_5 \xrightarrow{(NaNH_2)} \underset{\updownarrow}{R\bar{C}HC{\equiv}CSC_2H_5 \;\; RCH{=}C{=}\bar{C}SC_2H_5} \begin{cases} \xrightarrow{H_2O} RCH{=}C{=}CHSC_2H_5 \\ \xrightarrow{R'Br} RCH{=}C{=}CR'SC_2H_5 \end{cases}$$

(XXVI) (XXVII)

Under the same conditions only the branched 2-acetylenic ethers (XXVIII) are converted into allenic ethers[99,104], the 1-acetylenic ethers merely forming 1,3-alkenynes:

$$\underset{(XXVIII)}{RR'CHC{\equiv}CCH_2OC_2H_5} \rightarrow RR'CHCH{=}C{=}CHOC_2H_5.$$

Prototropic rearrangement takes place very readily with $\beta\gamma$-acetylenic acids. Thus but-2(and 3)-ynoic acids are completely isomerised into the allenic acid when heated with 18% potassium carbonate solution to 40°[105] or by the action of sodamide in liquid ammonia[106]. However, 4-phenylbut-3-ynoic acid under the same conditions forms an equilibrium mixture with 4-phenylbut-2,3-dienoic acid in the proportions 2:3.[107] An equilibrium mixture (1:2) is obtained also by the isomerisation of 4-phenylbut-2-ynoic acid[108]:

$$C_6H_5C{\equiv}CCH_2CO_2H \rightleftarrows C_6H_5CH{=}C{=}CHCO_2H \rightleftarrows C_6H_5CH_2C{\equiv}CCO_2H.$$

The esters of these acids undergo rearrangement far more readily. The reaction is almost quantitative in the presence of potassium carbonate solution at 20°.[105] 4-Bromobuta-2,3-dienoic[109] and 2-chlorobuta-2,3-dienoic[110] esters also have easily been obtained in this way:

$$XC{\equiv}CCH_2CO_2R \rightarrow XCH{=}C{=}CHCO_2R$$

where X = H, Br.

The simplest pentynedioic acid (XXXI) does not exist, since, on preparation by oxidising the alcohol (XXX)† with chromium trioxide, it immediately undergoes prototropic isomerisation into penta-2,3-dienedioic acid[111]:

$$\underset{(XXX)}{HOCH_2CH_2C{\equiv}CCO_2H} \rightarrow [HO_2CCH_2C{\equiv}CCO_2H] \rightarrow \underset{(XXXI)}{HO_2CCH{=}C{=}CHCO_2H}.$$

It has been shown that an allenic system can be obtained only when its further isomerisation is difficult or altogether impossible. In this connection it is of interest to note the prototropic rearrangement of octa-3,5-diyne-1,8-dioic acid (XXXII), not into the diallenic acid (XXXIII), but into octa-2,4-dien-6-yne-1,8-dioic acid (XXXIV)[112]:

$$\underset{(XXXIII)}{HO_2CCH{=}C{=}CHCH{=}C{=}CHCO_2H} \leftarrow \chi - \underset{(XXXII)}{HO_2CCH_2(C{\equiv}C)_2CH_2CO_2H} \rightarrow HO_2C[CH{=}CH]_2C{\equiv}CCO_2H.$$

(XXXIV)

† A formula corresponding to (XXIX) does not appear in the Russian text (Ed. of Translation).

Prototropic rearrangement accompanied by migration of the double bond has been observed[66] in the alkaline saponification of the esters (XXXV), but the allenic acids (XXXVI) could not be isolated in the pure form:

$$\underset{(XXXV)}{RC{\equiv}CCH{=}CHCH_2CO_2CH_3} \rightarrow \underset{(XXXVI)}{RCH{=}C{=}CHCH{=}CHCO_2CH_3}.$$

Certain hydroxy-compounds, containing a double bond and a triple bond separated by a methylene group, also rearrange into allenic alcohols when boiled with solutions of bases[72,113-115] or with aluminium oxide[115-117]:

$$\gtrless C{-}C{\equiv}CCH_2CH{=}CH{-}R \rightarrow \gtrless \underset{OH}{\underset{|}{C}}{-}CH{=}C{=}CHCH{=}CH{-}R.$$

2. Addition to Butenyne Systems

The addition of various reactants to a butenyne bond system constitutes a general method for the preparation of allenes. However, in several cases involving the addition of alcohols, halogens, and hydrogen halides, this method is greatly restricted by the difficulty of separating the mixture of acetylenic, allene, and conjugated diene derivatives which is usually formed. Separation may be achieved by careful fractional distillation, in which high temperatures must be avoided as they might cause interconversion of the isomers. On the other hand, such reactions as the reduction of butenyne derivatives and the addition of amines and halide esters usually proceed quite unambiguously, representing convenient and frequently the only possible methods for the synthesis of allene compounds containing these groups in the middle of the chain.

Addition of alcohols. This takes place in the presence of alkoxides: hexa-1,5-dien-3-yne reacts with methanol to give 3-methoxyhexa-1,3,4-triene[118]:

$$H_2C{=}CHC{\equiv}CCH{=}CH_2 \rightarrow H_3CCH{=}C{=}\underset{|}{\overset{OCH_3}{C}}CH{=}CH_2.$$

In the case of butenyne the allenic product formed initially is converted at ordinary pressure by allene–diene isomerisation into a 1-alkoxybuta-1,3-diene, and under pressure by allene–acetylene rearrangement into an acetylenic ether[119]:

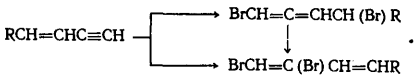
$$HC{\equiv}CCH{=}CH_2 \xrightarrow{CH_3OH} CH_2{=}C{=}CHCH_2OCH_3 \begin{cases} \rightarrow CH_2{=}CHCH{=}CHOCH_3 \\ \rightarrow CH_3C{\equiv}CCH_2OCH_3 \end{cases}.$$

Addition of thiols. In the presence of bases, thiols add to butenyne hydrocarbons mainly at the triple bond[120-122]: allenic sulphides are formed in insignificant quantity, and only in the case of butenyne itself has it been possible to isolate 4-alkylthiobuta-1,2-dienes[120,122]. The addition of thiols under radical conditions also results in partial formation of allenic sulphides[123]:

$$HC{\equiv}CCH{=}CH_2 \xrightarrow{RSH} \begin{cases} \rightarrow H_2C{=}CHCH{=}CHSR \\ \rightarrow H_2C{=}C{=}CHCH_2SR \end{cases}.$$

Addition of halogens. Only the bromination of butenyne and of alkenylacetylenes is of great practical interest[124,125]. In chloroform and at low temperatures butenyne is readily brominated to give a good yield of a

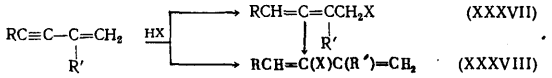
mixture of dibromides in which the allene and diene isomers predominate; with decrease in temperature the relative yield of the allenic dibromide increases:



It is possible that the diene dibromide is formed by allyl isomerisation of the allenic dibromide, which usually takes place very readily.

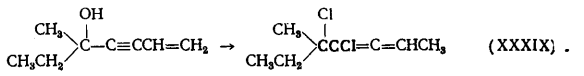
1,4-Addition predominates in the case of silicon-containing alkenynes [126]. The formation of halogenated allenes in small amounts has been noted also in the chlorination, chloroiodination, and halogenoarylation of butenyne and its homologues [119].

Addition of hydrogen halides. In the absence of catalysts, hydrogen chloride and hydrogen bromide add to butenyne [127-129] and its homologues [16,130-135] predominantly in the 1,4-positions to form the corresponding allene derivatives (XXXVII):

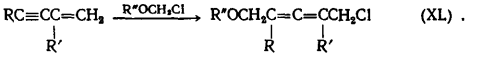


Some formation of halogenated dienes (XXXVIII) also occurs, either as a result of addition at the triple bond or by isomerisation of the halogenated allenes (XXXVII), the latter reaction taking place especially readily in the presence of copper salts (Cu_2Cl_2, Cu_2Br_2). Addition of hydrogen halides in the presence of these catalysts yields only the compounds (XXXVIII) [119]. When butenyne is hydrochlorinated in the presence of aluminium or zinc chloride instead of copper(I) chloride, the chief product is 4-chlorobuta-1,2-diene [129].

Nazarov and his coworkers [6] have established that but-3-en-1-ynylmethanols also add hydrogen halides, the 1,4-addition being preceded by replacement of the hydroxyl by halogen. The resulting allenic dihalide undergoes spontaneous isomerisation to the final conjugated diene products. Vartanyan [136] has recently succeeded in isolating (in 32% yield) the allenic dichloride (XXXIX) by the low-temperature hydrochlorination of 3-methylhept-6-en-4-yn-3-ol (at 18–20°):

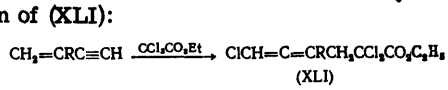


Addition of chloromethyl ethers. In the presence of bismuth trichloride as catalyst, addition to butenyne [137,138], hept-1-en-3-yne [139], 2-methylbutenyne [140], and hepta-1,6-dien-3-yne [141] takes place predominantly in the 1,4-positions to form chlorinated allenic ethers (XL):

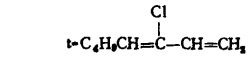


2,3-Dichlorotetrahydrofuran reacts in similar fashion with butenyne [142].

Ethers of secondary and primary alcohols derived from butenyne have recently been studied in this reaction [143]. It is interesting that allenic products are formed also in the reaction of t-alkyl halides with alk-1-en-3-ynes [144] in the presence of zinc chloride, the radical adding on to the double bond to give $C_2H_5CCl{:}C{:}CHCH_2C(CH_3)_3$. The reaction goes in the same direction (alkyl at the double bond) in the addition of trichloroacetic ester to alkenynes [145] with formation of (XLI):

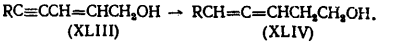


where R = H, CH_3. In contrast to this, addition of t-butyl chloride to butenyne takes place only at the triple bond, with formation of a halogenated diene (XLII) [119]:

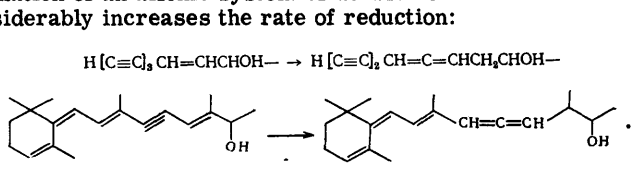


Addition of hydrogen. 1,4-Addition of hydrogen to but-3-en-1-ynylmethanols, with formation of the corresponding allenic alcohols as side-products, has been observed during cathodic reduction [146] and during hydrogenation with coppered zinc dust [147]. However, these reactions have not yet been used successfully for the preparation of allenes.

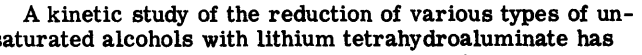
In 1954 Jones and his coworkers [148] studied the reduction of butenyne systems with lithium tetrahydroaluminate. Under these conditions alcohols of the type (XLIII) are selectively reduced (as a result of 1,4-addition) to give good yields of penta-3,4-dien-1-ol derivatives (XLIV) [149-152]:



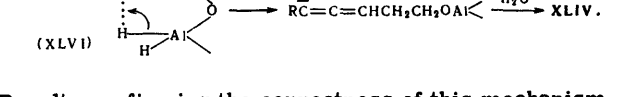
Further investigation of this reaction established that the presence of an allyl hydroxyl is a necessary condition for reduction to an allenic system. The simultaneous presence of allyl and prop-2-ynyl hydroxyls leads to the formation of a mixture of 1,2- and 1,3-diene compounds [149]. A similar type of reduction is observed with butenyne systems containing conjugated double [149,152] or triple [153,154] bonds, the presence of which not only fails to prevent formation of an allenic system of double bonds but in fact considerably increases the rate of reduction:



However, the compound (XLV) could not be reduced in this way [154]:

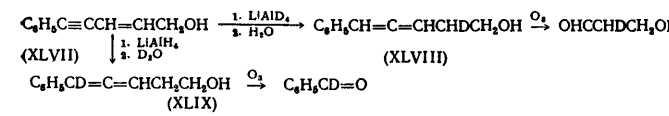


A kinetic study of the reduction of various types of unsaturated alcohols with lithium tetrahydroaluminate has shown [155] that nucleophilic addition of a hydride ion is the rate-determining stage in this reaction. In conformity with this, the mechanism of the reduction of pentenynol derivatives (XLVI) to allenes (XLIV) can be represented by the scheme

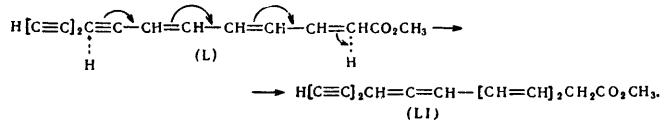


Results confirming the correctness of this mechanism have been obtained in a study of the reduction of 5-phenylpent-2-en-4-yn-1-ol (XLVII) with lithium tetrahydroaluminate and its deuterium analogue followed by decomposition with heavy and ordinary water respectively. The scheme below shows that only with the above reaction mechanism

can deuterated allenes (XLVIII) and (XLIX) be formed, the position of the deuterium in these compounds being proved by ozonisation to the corresponding monodeuterated aldehydes [155]:

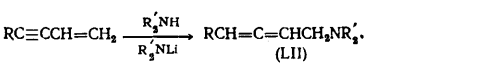


An unusual and extremely simple method of synthesising allenes, suggested by Bohlmann [154], is based on the reduction of alkenyne systems with aluminium amalgam in moist ether by Kuhn's method. Addition of hydrogen to the compound (L) takes place in positions 2 and 9, to give a very good yield of *trans-trans*-mycomycin (LI):

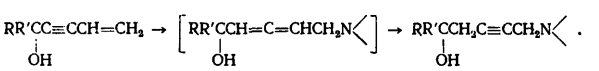


This new method of synthesising allenic structures evidently shows great promise for the preparation of complex natural allenes, and will undoubtedly find wide application.

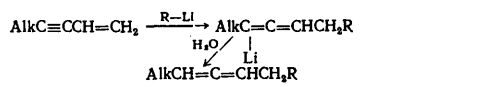
Addition of primary and secondary amines. Addition of these compounds to butenyne usually takes place on heating in an autoclave at 100°, and is a promising method for the preparation of allenic amines (LII, R = H) [156]:



The same reaction has found application in the synthesis of allenic diamines (LII, R = $CH_2N<$) [157]. Alcohols containing the butenyne system and hexa-1,5-dien-3-yne hydrocarbons [157] readily add amines in the 1,4-positions, but, under the reaction conditions with excess of amine present, the resulting allenic amino-alcohols are readily isomerised to acetylenic derivatives:

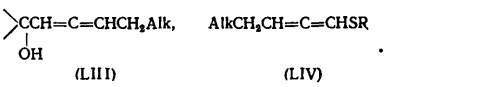


Addition of organolithium compounds. Petrov and Kormer [158] suggested a simple and general route for the preparation of allenes, based on the interaction of alk-1-en-3-ynes with organolithium compounds. This reaction involves an intermediate stage in which an allenyl--lithium is formed (with lengthening of the chain), hydrolysis of which gives good yields of allenic derivatives [159-162]:

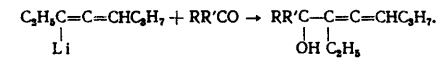


where R = Alk, Ar, pyrid-2-yl, R'_2P, R'_2N, etc.

Addition of lithium alkyls to butenyne alcohols [163] and to alkylthiobutenynes [164] yields allenic alcohols (LIII) and sulphides (LIV) respectively.

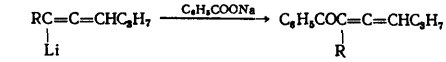


In the case of chlorides and ethers containing a butenyne system the course of the reaction with lithium alkyls is more complicated, a mixture of allenes and cumulenes being obtained [165]. In the above reactions lithium derivatives of allenes are obtained as intermediate products, which opens up wide possibilities for the synthesis of various allenic compounds. Several reactions of 1-ethylhexa-1,2-dienyl-lithium have so far been studied. Its condensation with formaldehyde, oxiran, and many carbonyl compounds, both saturated and unsaturated, has led to the synthesis of a large number of allenic alcohols [166-168]:



It is very significant that addition of allenyl-lithium at the multiple bonds in the starting materials was not observed.

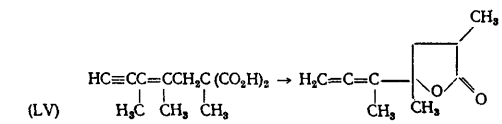
The allenic structure of the initial allenyl-lithium is preserved also during carboxylation [169], addition of pyridine and benzonitrile, and reaction with sodium benzoate [170]:



where R = CH_3, C_2H_5.

Alkenynyl-silicon and -germanium compounds on addition of lithium alkyls [171-174] and dialkyl-lithamides [175] yield mixtures of difficultly separable allenic and acetylenic products.

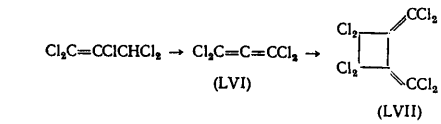
Other instances are known in which allenic derivatives are formed as a result of addition to butenynes. Among them are the reactions of butenyne amines with carbon disulphide [176], and also the formation of allenic lactones by the decarboxylation of malonic acids of the type (LV) [177,178]:



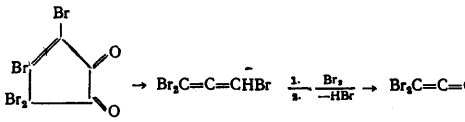
3. Other Methods

Dehydrohalogenation and pyrolysis are widely used for the preparation of polyhalogenated allenes. Blomquist [179] obtained 1,1-difluoroallene from ethylene and dibromodifluoromethane by a series of successive dehydrobrominations and brominations. This product has also been obtained by the pyrolysis of 1,1,2,2-tetrafluoro-3-methylenecyclobutane and of 2,2,3,3-tetrafluorocyclobutylidenemethyl acetate [180].

Dehydrohalogenation of the corresponding halogenated hydrocarbons by means of powdered or alcoholic potassium hydroxide or of sodamide has been used to obtain perfluoroallene [181], halogenoarylallenes [182,183], 4,4,4-trifluorobuta--1,2-diene [184], and alkoxyarylallenes [185-189]. The extremely reactive perchloroallene (LVI), which usually exists in dimeric form (LVII) [190,191], was obtained by Roedig [192] by the dehydrochlorination of pentachloropropene with sodamide in liquid ammonia:



This worker has recently succeeded in obtaining tri- and tetra-bromoallenes [193] by the reactions



Arens [194,195] noted the formation of considerable quantities of allenyl ethers when the *cis*-forms of β-halogenoalkenyl ethers were subjected to prolonged heating with caustic potash. A more unequivocal result is obtained with allenic systems in which the structure is fixed [196-198]:

$$CH_3{=}CBrCH_2CN \rightarrow CH_2{=}C{=}CHCN\ (CO_2CH_3).$$

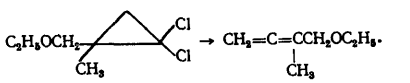
Isolated examples have been reported of the preparation of functional derivatives of allenes by the dehydration of alcohols [199] and the cleavage of acetals [200], nitro-derivatives [201], triglycerides [202], and derivatives of cyclobutane [203] and cyclopropane [204].

The reaction of but-2-ene-1,4-disulphonyl dichloride with ammonia and primary amines is accompanied by the evolution of hydrogen chloride and sulphur dioxide with the formation of allenic monosulphonamides [205]:

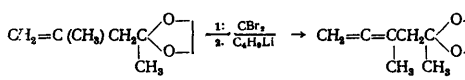
$$ClSO_2CH_2CX{=}CHCH_2SO_2Cl \xrightarrow{RNH_2} CH_2{=}C{=}CXCH_2SO_2NHR$$

where X = H, Cl, CH_3.

The cleavage of *gem*-dihalogenocyclopropane derivatives with lithium alkyls in ethereal solution provides a simple and convenient method of obtaining certain allenic ethers [206,207]:



The successive action of dibromocarbene and butyl-lithium on unsaturated alcohols [208] or 2-substituted dioxolan derivatives [209] yields the corresponding allenic alcohols and acetals in 15–85% yield:



The Wittig reaction has recently found application for the synthesis of 1,2-dienes. It has been used to obtain, from acid chlorides [210] (or ketens) [211] and the appropriate phosphoranes, allenic esters of types (LVIII) and (LIX) respectively.

$$RCH{=}C{=}CCO_2C_2H_5 \quad (C_6H_5)_3C{=}C{=}CHCO_2C_2H_5$$
$$\text{(LVIII)} \qquad\qquad \text{(LIX)}$$

Optically active allene-1-carboxylic acids have recently been prepared in this way [212]. Alka-3,4-dienoic acids (LX, R = H, CH_3) are formed on ultraviolet irradiation of the alka-2,4-dienoic acids [213], but the yields are low:

$$RCH{=}CHCH{=}CHCO_2H \rightarrow RCH{=}C{=}CHCH_2CO_2H. \quad \text{(LX)}$$

Several papers have been published on elimination reactions of enol phosphates (LXI) [108,214,215]:

$$RCH_2COCH_2R' \rightarrow RCH_2C(OPO(OC_2H_5)_2){=}CHR' \rightarrow RCH_2C{\equiv}CR' + RCH{=}C{=}CHR'$$
$$\text{(LXI)} \qquad\qquad \text{(LXII)} \qquad\qquad \text{(LXIII)}$$

These reactions take place under comparatively mild alkaline conditions (at 25°), and simulate the biogenetic path for the synthesis of acetylenes in Nature [108,215]. Cymerman-Craig and Moyle [108] have shown that, in the presence of activating groups (C_6H_5, COOH), enol phosphates (LXI) are extremely readily converted into allenic compounds. The normal acetylenic products (LXII) formed at the same time may isomerise with (LXIII) under less basic conditions than are required for formation of the acetylenic group. The elimination of enol phosphates may, perhaps, be regarded as a chemical model of the biogenetic route for the formation of allenes in Nature.

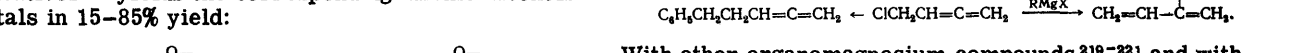
III. CHEMICAL PROPERTIES AND REACTIONS OF FUNCTIONAL DERIVATIVES OF ALLENES

In conformity with the structure of allene [216,217], its functional derivatives are characterised by three types of chemical reactions — (1) reactions of the functional groups, not involving the allenic system, (2) additions at the allenic bonds, and (3) reactions involving isomerisation of the allenic system.

1. Reactions Not Involving the Allene Bond System

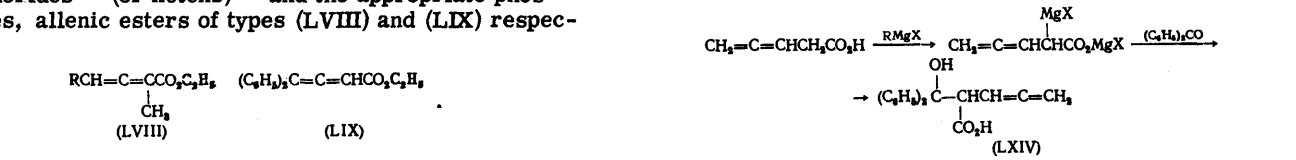
In halogenated allenic derivatives the halogen is extremely mobile, and can undergo various substitutions under the influence of neutral or weakly basic reagents (sodium carbonate, sodium acetate, potassium bromide, potassium iodide) [129,139,143,218]. Thus the action of amines on 4-chlorobuta-1,2-dienes has given various allenic amines [136,139-143,156], the allene group in which is preserved on formation of the derivatives and on reaction with phenyl isocyanate [156]:

4-Chlorobuta-1,2-diene undergoes substitution with benzylmagnesium and especially phenylmagnesium bromide, to give allenic hydrocarbons [219]:



With other organomagnesium compounds [219-221] and with magnesium [222], however, only conjugated dienes are formed.

Penta-3,4-dienoic acid reacts with organomagnesium compounds to form a dimagnesium derivative, which with benzophenone yields an allenic product (LXIV) [223]:



The reduction of 1-halogenoallenes with a zinc–copper couple in alcohol proceeds without affecting the double bonds [224], and provides a general method for the synthesis of allenic hydrocarbons [1]. Roedig [182] succeeded in reducing 1,1-dichloro-3,3-bischlorophenylallene by means of zinc dust in pyridine and glacial acetic acid:

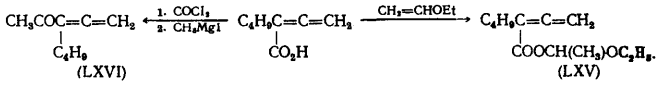
$$(ClC_6H_4)_2C{=}C{=}CCl_2 \rightarrow (ClC_6H_4)_2C{=}C{=}CH_2.$$

The allene group remains unaffected in the reduction of allenic ketones with lithium tetrahydroaluminate [89,90,93,225]. The oxidation of β-allenyl alcohols with chromium trioxide gives moderate yields of the corresponding acids [153,226,227]:

$$RC{\equiv}CCH{=}C{=}CHCH_2CH_2OH \rightarrow RC{\equiv}CCH{=}C{=}CHCH_2CO_2H.$$

2-Butylbuta-2,3-dienoic acid is stable to heating, and with excess of ethyl vinyl ether at 100° gives a quantitative

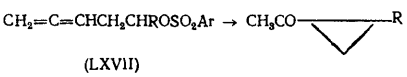
yield of the esterification product (LXV)[228]; the ketone (LXVI)[67] has been obtained by the action of methylmagnesium iodide on the chloride of this acid:



(LXVI) (LXV)

Allenic amides have also been obtained via the acid chlorides[43,78]. Kohler[229] prepared from 4-naphthyl-2,4--diphenylbuta-2,3-dienoyl chloride the corresponding carboxymethyl ester, which he separated into two optical enantiomers. In order to preserve the allene group in the original molecule, reactions must be conducted under mild and rigorously controlled conditions. However, side--reactions involving addition at the allenic bond system frequently occur[69,105,107].

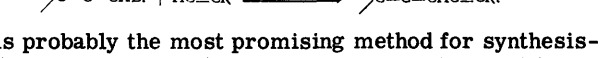
An interesting rearrangement into acetylcyclopropanes[225,230] has recently been observed in the hydrolysis of sulphonates of the type (LXVII):



(LXVII)

where R = H, CH_3.

The allenic system is preserved in the unsymmetrical condensation of 1-halogenoallenes[231] by the Chodkiewicz method:

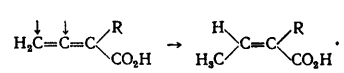


This is probably the most promising method for synthesising allenyne systems related to those occurring in Nature.

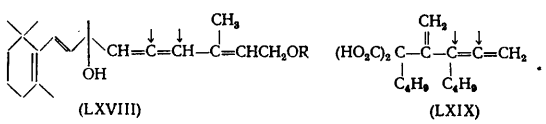
2. Addition Reactions

Reduction. The double bonds in allene readily undergo catalytic hydrogenation over platinum, palladium, or Raney nickel, with high yields of the resulting saturated products, and this method is widely used for the establishment of structure.

Incomplete hydrogenation of buta-2,3-dienoic acid in the presence of 1.5% of palladium on calcium carbonate gave *cis*-crotonic acid exclusively[105], i.e. the product resulting from addition of hydrogen at the $\beta\gamma$-double bond on the side opposite to the carboxyl:



The hydrogenation of 2-butylbuta-2,3-dienoic acid proceeds similarly[232], addition of hydrogen taking place at the less substituted double bond. Addition of hydrogen at one of the double bonds has been observed in the hydrogenation of the polyenol (LXVIII) in the presence of nickel[115], and also in the hydrogenation of the acid (LXIX) over platinum[233]:

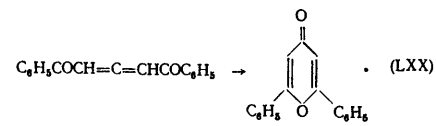


(LXVIII) (LXIX)

The reduction of 1-halogenoallenes with lithium tetrahydroaluminate shows very unusual features. Allenic chlorides[49] give mainly alkenes, alkanes, and small amounts of alkynes. In contrast to this, 1-bromo-3--methylbuta-1,2-diene[16] gives a 75% yield of a mixture of hydrocarbons comprising 61% of 3-methylbutyne, 36% of isopentane, and small quantities of alkenes. A more detailed study has been made of the reduction of 1-chloro--3-methylbuta-1,2-diene[234] with lithium tetrahydroaluminate, when two competitive reactions are involved — (*a*) replacement of chlorine by hydrogen (or deuterium), accompanied by complete allene–acetylene rearrangement, and (*b*) addition of the reagent at the allene double bonds, leading on subsequent hydrolysis to a mixture of the above hydrocarbons.

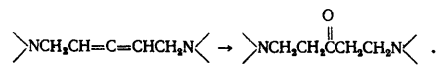
Addition of water, alcohols, thiols, and amines. Addition of these compounds, which is characteristic mainly of the acetylenic bond, takes place readily also with allenes. However, few examples of these reactions are known. 4-Chlorobuta-1,2-diene adds water in the presence of concentrated sulphuric acid[127], and allenic ketones are readily and quantitatively hydrated by dilute acids[72,90].

The action of 30% sulphuric acid on 1,5-diphenylpenta--2,3-diene-1,5-dione gave a 40% yield of the corresponding 4-pyrone (LXX), whose formation probably involves the initial addition of water[87,90]:



(LXX)

1,5-Bisdialkylaminopenta-2,3-dienes are hydrated when heated with mercury salts[157]:

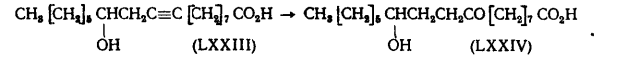


Allenic acids have been found to add water also in alkaline media[105,107]. Extraordinarily ready formation of the hydroxy-ketone (LXXII) was observed[69] on reduction of the sodium salt of the keto-acid (LXXI) with an alcoholic solution of potassium tetrahydroborate:



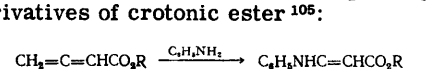
(LXXI) (LXXII)

It is interesting that hydration of the acetylenic acid (LXXIII) by mercury salts in sulphuric acid gives an isomeric hydroxy-keto-acid (LXXIV):



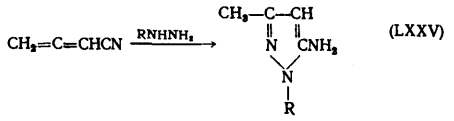
(LXXIII) (LXXIV)

Addition of alcohols and amines to allenes containing electronegative groups (CN, COOR, CO) takes place under considerably milder conditions than with acetylenic derivatives, the addition occurring at the unsubstituted double bond[105,235]. Brief treatment of buta-2,3-dienoic ester with aqueous–alcoholic caustic potash solution gives mainly β-ethoxycrotonic ester[105]. Piperidine and even aromatic amines add vigorously to an allenic ester even at room temperature, with formation of the corresponding β-substituted derivatives of crotonic ester[105]:



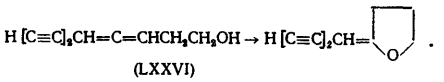
Alcohols, amines, and thiols add at the unsubstituted double bond also in buta-2,3-dienenitrile[97,236]. Addition of

substituted hydrazines is accompanied by ready cyclisation with the formation of an alkylated aminopyrazole (LXXV)[97]:



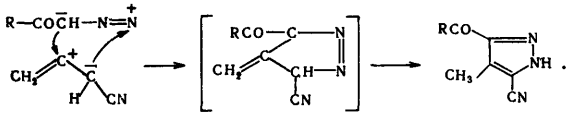
(LXXV)

Allenic ketones give quantitative yields of the corresponding pyrazoles and oxazoles on reaction with hydrazine hydrate[90,94,237] and hydroxylamine[72]. An interesting case of intramolecular addition has been observed with the butadiynylallenic alcohol (LXXVI)[153]:

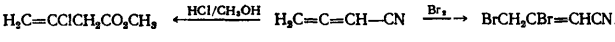


(LXXVI)

Such intramolecular additions may be of interest for the synthesis of various heterocyclic systems[90,97]. 1,3-Dipolar cycloadditions can also be used for this purpose. Success has recently been achieved in condensing buta-2,3--dienenitrile with various diazo-ketones[236] and obtaining the corresponding triazole and pyrazole derivatives:

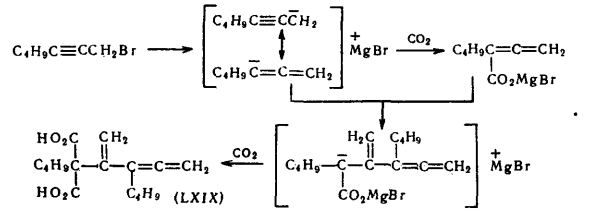


Addition of halogens and hydrogen halides. Addition to allenic compounds usually occurs very easily. Thus perchloroallene[192] and perfluoroallene[181] add two moles of chlorine even at -75°, and with 1,1-dichloro--3,3-di-*p*-chlorophenylallene[182] the reaction goes quantitatively at 20°. In the dark, however, perfluoroallene adds only one mole of chlorine and hydrogen halides[238]. On brominating 1,1-difluoroallene Blomquist[179] obtained a tetrabromide, but 1-chloro-5-ethoxy-4-methoxymethylenepenta-2,3-diene[143] and 1,1-dichloro-3,3-bischlorophenylallene[182] at 20° add bromine at only one double bond. Both the nitrile[97] and the ester[105] of buta-2,3-dienoic acid add only one molecule of bromine, at the unsubstituted double bond:



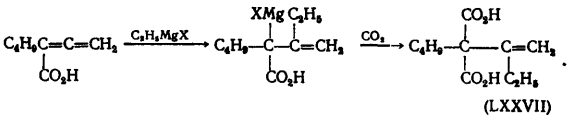
The addition of hydrochloric acid, however, takes place with the formation of $\beta\gamma$-unsaturated derivatives[97,105]. A similar type of addition has been observed also in the acid hydrolysis of the nitrile of octa-1,2-dienedicarboxylic acid[95].

The literature describes several examples of the addition of Grignard reagents at allenic double bonds. Mention has been made above[78] of the preparation of the allenic dicarboxylic acid (LXIX) by carboxylation of the organomagnesium derivative obtained from 1-bromohept-2-yne, the reaction probably being represented by the scheme[233]



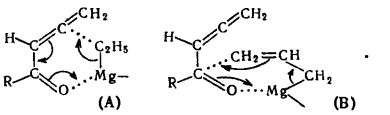
(LXIX)

It has also been shown[232,239] that the addition of organomagnesium compounds to 2-butylbuta-2,3-dienoic acid followed by carboxylation yields the unsaturated acid (LXXVII):



(LXXVII)

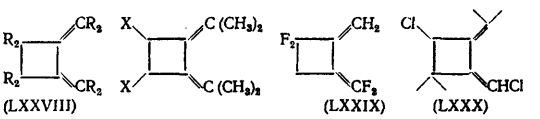
The structure of this acid (LXXVII) shows that the reaction results from addition at the $\alpha\beta$-double bond, not from 1,4-addition. Allenic ketones[72,89,90] with ethylmagnesium bromide also give products in which the ethyl group has been added at the allenic bond system, their formation probably involving a mechanism of cyclic transfer of electrons[72,240] (A):



(A) (B)

This mechanism may be supported by the formation of normal Grignard reaction products of allenic ketones with allyl and prop-2-ynyl halides, which is also interpreted by an electron-transfer scheme. Formation of a six--membered ring is preferable to an eight-membered ring for normal addition at the carbonyl group (B), which might have occurred in addition of allyl (prop-2-ynyl) at the allenic system. Such an explanation, however, is not the only possible one, and the direction of the reaction may also be subject to steric factors[241].

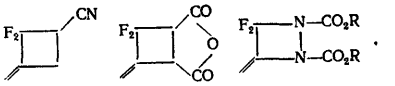
Thermal dimerisation. This is more characteristic of halogenated allenes than of allenic hydrocarbons[3]. The reaction usually occurs even at low temperatures, and results in four-membered dimethylenecycloalkanes[16,110,180-182,190-193,242], whose structure as 1,2:1,2-addition products (LXXVIII) has been established by means of their infrared and nuclear magnetic resonance spectra and their chemical reactions:



(LXXVIII) (LXXIX) (LXXX)

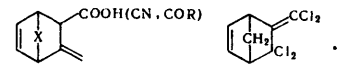
where R = Cl, Br, F and X = Cl, Br. It has recently been shown[56,243] that the dimerisation of 1-halogenoallenes may result in 1,2:2,3-addition products, (LXXIX) and (LXXX). Dimeric products are formed also under the influence of acidic reagents, such as acetic acid, thionyl chloride, and phosphorus tribromide[244,245].

Halogenated allenes can undergo cycloaddition as well as dimerisation. Reaction of 1,1-difluoroallene with acrylonitrile, maleic anhydride, and azoformic ester yields the corresponding four-membered adducts[180]



Wotiz[228] noted that 2-butylbuta-2,3-dienoic acid does not undergo the Diels–Alder reaction, either as a diene or as a dienophile. It was subsequently shown, however, that allenic derivatives can be used as dienophiles of an unusual kind. Buta-2,3-dienoic acid was found[246] to give with cyclopentadiene an adduct of the type (LXXXI). Analogous

products are formed by the condensation of the corresponding nitrile[97] and of allenic ketones[247] with cyclopentadiene, furan, and certain other dienes.



(LXXXI) X = O, CH_2 (LXXXII)

Roedig[192] has been able to effect the diene condensation of perchloroallene with cyclopentadiene (LXXXII) at -10°. The diene condensation of cyclopentadiene with optically active penta-2,3-dienedioic acid has recently been successfully employed[248] to establish the absolute configuration of the acid.

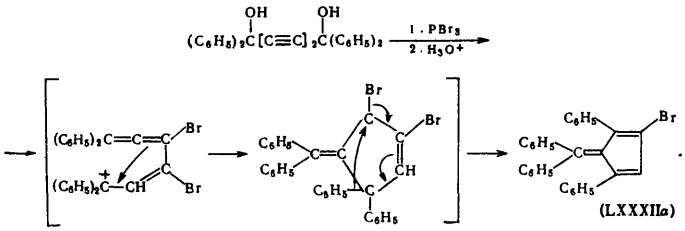
3. Isomerisation of Allenic Compounds

Isomerisation is a most characteristic feature of allenic derivatives. Under the influence of a solution of copper(I) chloride in concentrated hydrochloric acid, 1-halogenoallenes readily isomerise into conjugated 1-halogenobutadienes[8,9,14,64]. Jacobs and Petty[16] obtained a mixture of equal quantities of *cis*- and *trans*-1-bromo-3-methylbuta--1,3-dienes by the thermal isomerisation of 1-bromo-3--methylbuta-1,2-diene:

$$RCH_2CR'=C=CHX \rightarrow RCH=CR'CH=CHX.$$

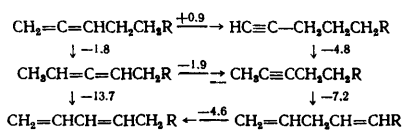
However, certain 1-halogenoallenes could not be isomerised under these conditions[10,136,157].

The interesting isomerisation has recently been described of tetraphenylhexa-2,4-diyne-1,6-diol in the presence of phosphorus tribromide in acetic acid[245], resulting in the fulvene (LXXXII*a*), this reaction undoubtedly involving intermediate allenic structures:



(LXXXII*a*)

Acetylene–allene isomerisations have already been mentioned above. Approximate heats of isomerisation (in kcal mole^{-1}) have been determined[249] for certain types of unsaturated compounds, which permitted these systems to be arranged as follows according to their tendency to interconversion



When discussing isomerisation in a series of functional derivatives of allene, however, we must bear in mind that the direction of isomerisation depends to a certain extent also on the nature of the functional groups. For example, allenic ethers[250] are in equilibrium with alkoxyacetylenic structures:

$$CH_2=C=CHOR \rightleftarrows CH_3C\equiv COR$$

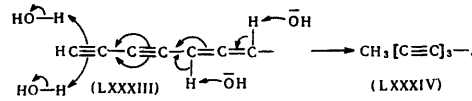
On the other hand, the isomerisation of derivatives of penta-2,3-diene-1,5-diol[139] and of allenic acids[105,227] yields only acetylenic compounds:

$$CH_3CH=C=CHCO_2H \rightarrow CH_3C\equiv CCH_2CO_2H.$$

The isomeric penta-3,4-dienoic acid[138] and other β-functional allenes[20,251] are converted under the same conditions into 2,4-diene derivatives:

$$CH_2=C=CHCH_2CO_2H \rightarrow CH_2=CHCH=CHCO_2H.$$

Allene–acetylene isomerisation plays an important part in establishing the structure of naturally occurring allene-polyynes. The mechanism of this rearrangement includes initial detachment of a proton by a strong base followed by its addition to another carbon atom of the molecule[84]. In the case of mycomycin[252,253] the rearrangement consists in migration of two protons and conversion of the allenediyne grouping (LXXXIII) into the corresponding alkatriyne derivative (LXXXIV):



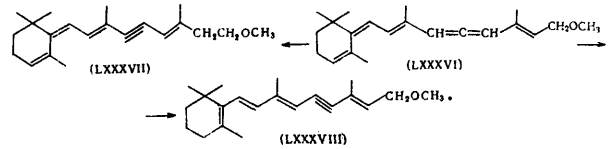
(LXXXIII) (LXXXIV)

However, the methyl ester of *trans*-mycomycin (LI) very readily underwent alkaline isomerisation with the formation of the tridecatetraenediynoic ester (LXXXV), whose structure was proved by an alternative synthesis[154]:

$$H[C\equiv C]_2-CH=C=CH[CH=CH]_2CH_2CO_2CH_3 \rightarrow H[C\equiv C]_2[CH=CH]_4CO_2CH_3.$$

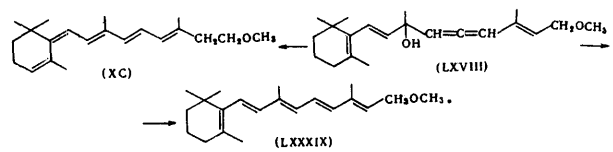
(LI) (LXXXV)

Interesting isomeric rearrangements have been observed with the allenic compound (LXXXVI)[115]. During chromatography on aluminium oxide it could already change into the acetylenic product (LXXXVII), and when boiled with alcoholic caustic soda it gave a mixture of (LXXXVII) and (LXXXVIII):



(LXXXVII) (LXXXVI) (LXXXVIII)

The polyenediol monomethyl ether (LXVIII) when boiled with lithium tetrahydroaluminate in ether isomerises into the methyl ether of vitamin A (LXXXIX), and on treatment with chromium acetate in strongly alkaline medium is converted into the *retro*-compound (XC)[115]:



(XC) (LXVIII) (LXXXIX)

Isomerisation of an allenic system is observed also in the abstraction of hydrogen halide from allenic chlorides[132,254] and dibromides[125,126], and also during the dehydration of allenic alcohols formed by the Reformatskii reaction[68–70]:

$$RCH_2CH=C=CHCH_2Cl \rightarrow RCH=CH-C\equiv CH \leftarrow RCHCH=C=CH_2$$

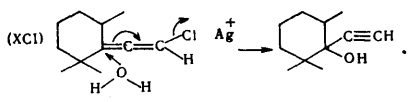
(OH)

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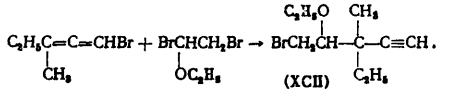
The cleavage of allenyl sulphides with sodamide[255], which gives 80–90% yields of a mixture of *cis*- and *trans*--isomers, may be of value for the preparation of substituted butenynes:

$$CH_3CH{=}C{=}C(R)SR' \xrightarrow{2\ equiv.\ NaNH_2} RCH{=}CH{-}C{\equiv}CH.$$

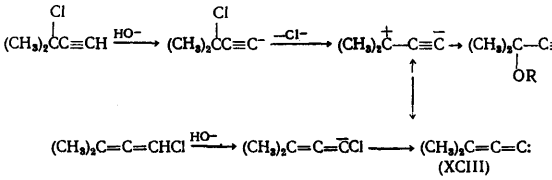
Substitutions in the halogenated allene series are often accompanied by isomerisation of the allenic system of double bonds. Although 1-chloro-3-methylbuta-1,2-diene does not react with silver acetate[34] and undergoes practically no solvolysis in 80% alcohol at 25°,[256] the allenyl chloride (XCI) is 90% converted into an acetylenic alcohol when heated with an alcoholic solution of silver nitrate[52]:



1-Bromo-3-methylbuta-1,2-diene reacts similarly with sodium iodide and with sodium phenyl sulphide, giving the corresponding acetylenic derivatives[16]. The action of ethoxy-1,2-dibromoethane on 1-bromo-3-methylpenta-1,2--diene also yields mainly acetylenic derivatives (XCII)[257]:

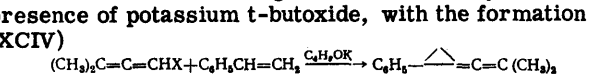


Interesting results have been obtained in a study of the solvolysis of 1-halogenoallenes. It has already been remarked above that 1-chloro-3-methylbuta-1,2-diene undergoes practically no solvolysis in 80% alcohol. In the presence of bases, however, the reaction is greatly accelerated, with the formation of 2-methylbut-3-yn-2-ol and its ethyl ether. A similar result is obtained with 3-chloro--3-methylbut-1-yne[256]. To explain these results, it was suggested that the rate-determining stage of the reaction was abstraction of a proton with formation of an intermediate carbene (XCIII):



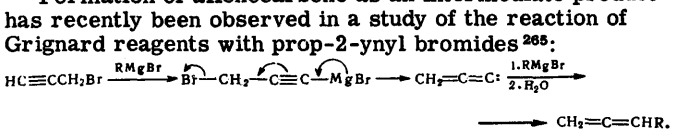
where R = H, C_2H_5. This mechanism of allene–acetylene rearrangement has found further support in the detailed work of Shiner and Wilson[17], who studied the kinetics, salt effect, deuterium exchange with the solvent, and the relative proportions of the reaction products.

The reaction of 1-halogenoallenes with styrene in the presence of potassium t-butoxide, with the formation of (XCIV)



where X = Cl, Br, also takes place by a carbene mechanism[258,259]. Alkynes of various structures[258,260–262] and dicarbene (:C=C=C:)[263,264] have also been used as starting materials in the above reaction with cyclohexene, isomeric butenes, and other alkenes.

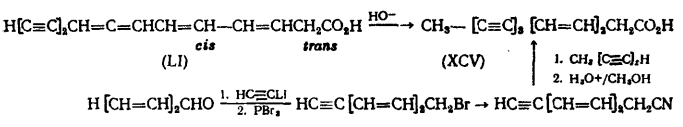
Formation of allenecarbene as an intermediate product has recently been observed in a study of the reaction of Grignard reagents with prop-2-ynyl bromides[265]:



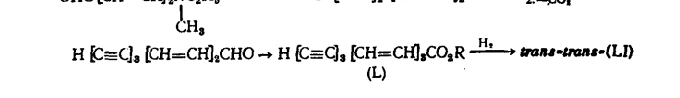
The accompanying formation of allenic hydrocarbons can best be explained by means of an intermediate allenecarbene.

IV. NATURALLY OCCURRING COMPOUNDS OF ALLENIC STRUCTURE

The number of compounds of this type is not yet large, but they constitute a very interesting group of optically active compounds exhibiting a broad spectrum of antimicrobial and fungicidal action. In chemical structure these compounds are polyunsaturated functional derivatives containing acetylenic, polyene, and allenic groups. The first representative of these substances was *mycomycin* (LI), which was isolated from the mould *Nocardia acidophylus* by Johnson and Burdon[266] in 1947. This antibiotic is very unstable in the crystalline state, and can be stored only in solution at -40°; it decomposes explosively at 75°. The structure of mycomycin was elucidated by Celmer and Solomons[252,267], who established that it contains an unbranched chain of carbon atoms with the empirical formula $C_{13}H_{10}O_2$. Absorption bands in the ultraviolet and infrared spectra[66,267] indicate the presence of diene and diyne groupings, unconjugated carboxyl, an allenic group, and ethynyl hydrogen. This together with other data has enabled mycomycin to be assigned the structure trideca--*trans*-3,*cis*-5,7,8-tetraene-10,12-diynoic acid (LI). In the presence of small amounts of alkalis, mycomycin undergoes isomerisation into the optically inactive isomycomycin (XCV), whose structure as trideca-*trans*--3,*trans*-5-diene-7,9,11-triynoic acid was confirmed by spectroscopic data and its complete synthesis by Bohlmann and Viehe[268] in 1954:



Bohlmann and Sugrow[154] synthesised *trans*-*trans*-mycomycin by reducing with aluminium amalgam the trideca--2,4,6-triene-8,10,12-triynoic esters (L) obtained by the reactions



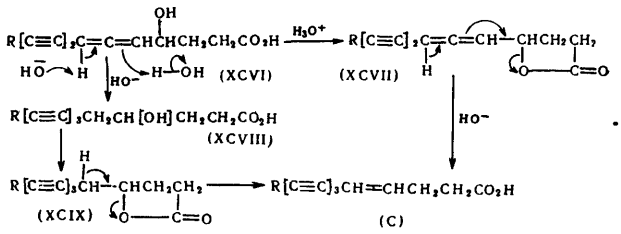
Synthetic *trans*-mycomycin is more stable towards alkalis, and its isomerisation half-life at pH 7.5 is 115 h, compared with the 3 h for natural *cis*-mycomycin[154].

Two other antibiotics having an allenic structure — *nemotin* (XCVII) and *nemotinic acid* (XCVI) — have been isolated from cultures of *Poria tenuis*, *P. corticola*, and the fungus B-841 (an unidentified Basidiomycete from white cedar)[269–271]. These two biologically active substances are very similar in their bactericidal spectrum, but differ considerably in fungicidal activity; they are very toxic, and cause contact dermatitis[269].

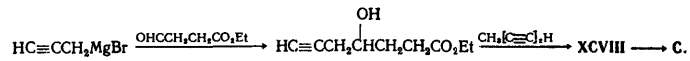
Both substances are extremely unstable, and can be prepared only in solution. When an attempt is made to isolate them from solution by lyophilic drying, they are converted into a dark polymeric mass[270]. Their ultraviolet and infrared spectra, catalytic hydrogenation, and chemical behaviour in alkaline and acid media[253,272] indicate that

nemotinic acid is a 4-hydroxyundeca-5,6-diene-8,10-diynoic acid (XCVI, R = H), while nemotin is its lactone.

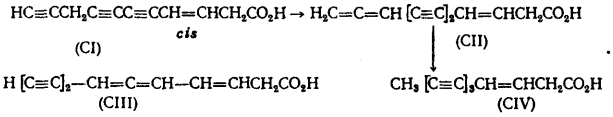
Study of the chemical transformations of these antibiotics showed[253] that at pH 10 nemotin undergoes rearrangement with cleavage of the lactone ring and formation of nemotin A (C, R = H). In contrast to this, nemotinic acid, which contains the same chromophoric group as does nemotin, is converted in alkaline medium into isonemotinic acid (XCVIII, R = H), from which the alkatriynoic lactone (XCIX) is readily formed; this compound can be further converted into nemotin A (C, R = H):



Odyssin (XCVII, R = CH_3) and *odyssic acid* (XCVI, R = = CH_3) are homologues of nemotin and nemotinic acid respectively, and are present with them in the culture liquid of the Basidiomycete B-841.[272,273] They are similar in chemical and physicochemical properties to the latter compounds, while their transformation products (R = CH_3) are more stable; the final structure of the compounds (XCVIII)–(C) has been proved by synthesis[177]:

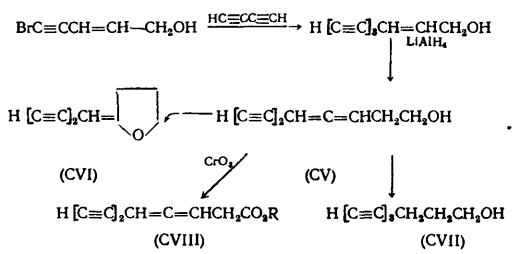


In addition to the above, two related polyunsaturated antibiotics — *drosophilins C* and *D* — have been isolated from the culture medium of the fungus *Drosophilia subatrata*[274,275] and *D. semivestita*[276]. It was formerly supposed that drosophilin C contained an allenic group and had the structure (CIII). However, Jones et al.[277] have shown that its structure is (CI), and that it is converted into drosophilin D (CII) by alkalis:



Thus drosophilin D (CII) contains a terminal allene group. It can be converted by further isomerisation into the alkenetriynoic acid (CIV).

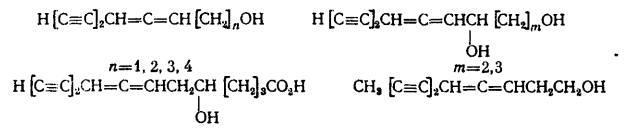
Marasin (CV) is the only allenic antibiotic at present known in both optically active forms. In 1959 (-)-marasin was isolated from a culture of *Marasmius ramealis*[278], and quite recently (+)-marasin has been obtained from the culture medium of *Aleurodiscus roseus*[226]. The formula (CV) was assigned to marasin on the basis of a study of the chemical transformations and the infrared and ultraviolet spectra; this has subsequently been confirmed by a complete synthesis of the racemate[153].



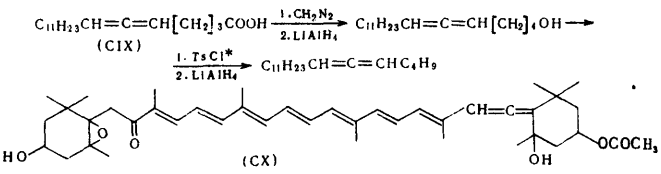
In alkaline media all three forms of marasin are readily converted into the corresponding cyclic enolic ether, isomarasin (CVI), which on hydrogenation absorbs five moles of hydrogen with the formation of n-butyltetrahydrofuran, identified by gas–liquid chromatography. It is interesting that the alkaline isomerisation of (+)-marasin yields also a small amount of the alkatriynol (CVII).

Two new allenic antibiotics — nona-3,4-diene-6,8--diynoic acid (CVIII) and its methyl ester — have been isolated, together with (+)-marasin, from the culture medium of *Aleurodiscus roseus*[226], and have been isolated from natural marasin.

It has recently been noted that *Odontia bicolor*[279] manufactures mycomycin and certain other allenic antibiotics, to which can be assigned the structures



Among natural allenic compounds the simplest is labal-lenic (octadeca-5,6-dienoic) acid (CIX), which has been isolated from the oil of *Leonotis nepetaefolia*[280]. This acid is extremely stable to alkalis and, in conformity with its structure, can be readily converted into octadeca-5,6-diene.



* Ts = p-$CH_3C_6H_4SO_2$ (Ed. of Translation).

The first allenic carotenoid to be isolated was fucoxanthin (CX), from seaweed[281]. Its proposed structural formula (CX) is extremely reliable[282,283], and agrees well with experimental results hitherto obtained.

Further investigation will undoubtedly lead to the isolation of other natural allenic compounds, which will enable us to elucidate the routes of their biogenesis and their role in the vital activities of micro-organisms.

1. R. Ya. Levina and E. A. Viktorova, Uspekhi Khim., 27, 162 (1958).
2. V. I. Pansevich-Kolyada, Beloruss. Politekh. Inst., Sbornik Nauch. Trudov, No. 87 (1959).
3. A. A. Petrov and A. V. Fedorova, Uspekhi Khim., 33, 3 (1964) [Russ. Chem. Rev., 1 (1964)].
4. K. Meyer and K. Schuster Ber., 55, 819 (1922).
5. W. Jasiobedzki, Wiadomosci Chem., 17, 647 (1963).
6. S. A. Vartanyan, Uspekhi Khim., 32, 1137 (1964) [Russ. Chem. Rev., 529 (1962)].
7. W. Chodkiewicz, P. Cadiot, and A. Willemart, Compt. rend., 250, 150 (1960).
8. T. A. Favorskaya and A. E. Favorskii, Zhur. Obshch. Khim., 9, 386 (1939).
9. T. A. Favorskaya and A. I. Zakharova, Zhur. Obshch. Khim., 10, 446 (1940).
10. T. A. Favorskaya, Zhur. Obshch. Khim., 12, 638 (1942).
11. T. A. Favorskaya, Zhur. Obshch. Khim., 18, 52 (1948).
12. T. D. Nagibina, Zhur. Obshch. Khim., 10, 427 (1940).
13. T. L. Jacobs and W. F. Brill, J. Amer. Chem. Soc., 75, 1314 (1953).

14. G. F. Hennion, J. J. Sheehan, and D. E. Maloney, J. Amer. Chem. Soc., 72, 3542 (1950).
15. Y. Pasternak, Compt. rend., 257, 2121 (1963).
16. T. L. Jacobs and W. L. Petty, J. Org. Chem., 28, 1360 (1963).
17. V. J. Shiner and J. W. Wilson, J. Amer. Chem. Soc., 84, 2402 (1962).
18. P. D. Landor and S. R. Landor, J. Chem. Soc., 1015 (1956).
19. G. Saucy, R. Marbet, H. Lindlar, and O. Isler, Helv. Chim. Acta, 42, 1945 (1959).
20. E. R. H. Jones, J. D. Loder, and M. C. Whiting, Proc. Chem. Soc., 180 (1960).
21. B. Thompson, B. P. 1 012 475 (1966); Chem. Abs., 64, 6498 (1966).
22. D. K. Black and S. R. Landor, J. Chem. Soc., 6784 (1965).
23. P. Cresson, Compt. rend., 261, 1707 (1965).
24. R. Marbet and G. Saucy, Chimia, 14, 362 (1960).
25. S. Julia, M. Julia, and P. Graffin, Bull. Soc. chim. France, 3218 (1964).
26. A. P. Boisselle and N. A. Meinhardt, J. Org. Chem., 27, 1828 (1962).
27. V. Mark, Tetrahedron Letters, 281 (1962).
28. A. N. Pudovik and I. M. Aladzheva, Zhur. Obshch. Khim., 33, 707 (1963); A. N. Pudovik, I. M. Aladzheva, and L. N. Yakovenko, Zhur. Obshch. Khim., 35, 1210 (1965).
29. A. N. Pudovik and I. M. Aladzheva, Dokl. Akad. Nauk SSSR, 151, 1110 (1963).
30. A. N. Pudovik and O. S. Durova, Zhur. Obshch. Khim., 36, 1460 (1966).
31. V. M. Ignat'ev, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., 36, 1505 (1966).
32. I. Iwai and T. Hiraoka, Chem. Pharm. Bull. (Japan), 11, 1556 (1963).
33. S. A. Vartanyan and Sh. O. Badanyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 16, 547 (1963).
34. A. I. Zakharova, Zhur. Obshch. Khim., 15, 429 (1945); 17, 83 (1947).
35. A. C. Day and M. C. Whiting, J. Chem. Soc., (C), 464 (1966).
36. Y. Pasternak and G. Peiffer, Compt. rend., 259, 1142 (1964).
37. P. M. Greaves, S. R. Landor, and D. R. J. Laws, Chem. Comm., 321 (1965).
38. A. N. Pudovik, Zhur. Obshch. Khim., 20, 92 (1950).
39. G. F. Hennion and K. W. Nelson, J. Amer. Chem. Soc., 79, 2142 (1957).
40. G. F. Hennion and C. V. DiGiovanna, J. Org. Chem., 30, 3696 (1965).
41. G. F. Hennion and C. V. DiGiovanna, J. Org. Chem., 31, 1977 (1966).
42. P. J. Ashworth, G. H. Whitham, and M. C. Whiting, J. Chem. Soc., 4633 (1957).
43. E. R. H. Jones, G. H. Whitham, and M. C. Whiting, J. Chem. Soc., 4628 (1957).
44. R. W. Rosenthal and L. H. Schwartzman, J. Org. Chem., 24, 836 (1959).
45. G. P. Chiusoli, Chimica e Industria, 41, 513 (1959).
46. A. Sevin, W. Chodkiewicz, and P. Cadiot, Tetrahedron Letters, 1953 (1965).
47. D. K. Black, S. R. Landor, and A. N. Patel, Tetrahedron Letters, 483 (1963).
48. S. R. Landor, A. N. Patel, P. F. Whiter, and P. M. Greaves, J. Chem. Soc., (C), 1223 (1966).
49. T. L. Jacobs, E. G. Teach, and D. Weiss, J. Amer. Chem. Soc., 77, 6254 (1955).
50. T. L. Jacobs, W. L. Petty, and E. G. Teach, J. Amer. Chem. Soc., 82, 4094 (1960).
51. R. J. D. Evans, S. R. Landor, and R. T. Smith, J. Chem. Soc., 1506 (1963).
52. Y. R. Bhatia, P. D. Landor, and S. R. Landor, J. Chem. Soc., 24 (1959).
53. G. F. Hennion and C. A. Lynch, J. Org. Chem., 25, 1330 (1960).
54. C. W. Shoppee, J. Cymerman-Craig, and R. E. Lack, J. Chem. Soc., 1311, 2291 (1961).
55. F. Bohlmann and K. Kieslich, Chem. Ber., 87, 1363 (1954).
56. P. Martinet and H. Doupeux, Compt. rend., 261, 2498 (1965).
57. L. F. Hatch and D. J. Mangold, J. Amer. Chem. Soc., 77, 176 (1955).
58. F. Kai and S. Seki, Chem. Pharm. Bull. (Japan), 13, 1374 (1965).
59. T. A. Favorskaya, Zhur. Obshch. Khim., 10, 461 (1940).
60. C. S. L. Baker, P. D. Landor, S. R. Landor, and A. N. Patel, J. Chem. Soc., 4348 (1965).
61. C. Prévost, M. Gaudemar, L. Miginiac, F. Bardone-Gaudemar, and M. Andrac, Bull. Soc. chim. France, 679 (1959).
62. M. Gaudemar, Bull. Soc. chim. France, 1475 (1963).
63. M. Gaudemar, Ann. Chim. (France), [13], 1, 161 (1956).
64. M. Gaudemar, Bull. Soc. chim. France, 974 (1962).
65. M. Andrac, Ann. Chim. (France), [13], 9, 287 (1964).
66. W. D. Celmer and I. A. Solomons, J. Amer. Chem. Soc., 75, 3430 (1953).
67. J. H. Wotiz and D. E. Mancuso, J. Org. Chem., 22, 207 (1957).
68. L. Crombie and A. G. Jacklin, J. Chem. Soc., 1622 (1957).
69. L. Crombie and A. G. Jacklin, J. Chem. Soc., 1740 (1955).
70. A. A. Petrov, Zhur. Obshch. Khim., 29, 2101 (1959).
71. M. Andrac, Compt. rend., 248, 1356 (1959).
72. M. Bertrand, Y. Pasternak, J. C. Traynard, J. de Gras, and A. Guillemonat, Ann. Fac. Sci. Marseille, 35, 85, 109 (1964).
73. J. Huet, Bull. Soc. chim. France, 952 (1964).
74. Y. Pasternak and J. C. Traynard, Bull. Soc. chim. France, 356 (1966).
75. R. Gélin, S. Gélin, and A. Arcis, Compt. rend., 263, 499 (1966).
76. J. H. Ford, C. D. Thompson, and C. S. Marvel, J. Amer. Chem. Soc., 57, 2619 (1935).
77. G. R. Lappin, J. Amer. Chem. Soc., 71, 3966 (1949).
78. J. H. Wotiz, J. Amer. Chem. Soc., 72, 1639 (1950).
79. J. H. Wotiz, J. S. Matthews, and J. A. Lieb, J. Amer. Chem. Soc., 73, 5503 (1951).
80. C. Prévost, M. Gaudemar, and M. Andrac, Compt. rend., 245, 2054 (1957).
81. V. K. Jones and A. J. Deutschman, J. Org. Chem., 30, 3978 (1965).
82. J. H. Wotiz, J. Amer. Chem. Soc., 73, 1971 (1951).
83. F. Bardone-Gaudemar, Compt. rend., 243, 1895 (1956).
84. T. L. Jacobs, R. A. Akawie, and R. G. Cooper, J. Amer. Chem. Soc., 73, 1273 (1951).
85. A. E. Favorskii and P. A. Tikhomolov, Zhur. Obshch. Khim., 10, 1501 (1940).
86. F. Ya. Perveev, Zhur. Obshch. Khim., 18, 686 (1948).
87. F. Bardone-Gaudemar, Compt. rend., 242, 2471 (1956).
88. M. Bertrand, Compt. rend., 244, 1790 (1957).
89. M. Bertrand and J. Le Gras, Compt. rend., 255, 1305 (1962).
90. F. Bardone-Gaudemar, Ann. Chim. (France), [13], 3, 79, 93 (1958).
91. E. M. Kosower and T. S. Sorensen, J. Org. Chem., 28, 687 (1963).
92. M. Winter, Helv. Chim. Acta, 46, 1749, 1754 (1963).
93. M. Bertrand and C. Rouvier, Compt. rend., 260, 209 (1965).
94. C. Rouvier and M. Bertrand, Compt. rend., 259, 1530 (1964).
95. J. H. Wotiz and E. S. Hudak, J. Org. Chem., 19, 1580 (1954).
96. L. I. Smith and J. S. Swenson, J. Amer. Chem. Soc., 79, 2962 (1957).
97. P. Kurtz, H. Gold, and H. Disselnkötter, Annalen, 624, 1 (1959).
98. G. Pourcelot, M. Le Quan, M.-P. Simonnin, and P. Cadiot, Bull. Soc. chim. France, 1278 (1962); G. Pourcelot and C. Georgoulis, *ibid.*, 866 (1964).
99. H. Normant and R. Montione, Compt. rend., 259, 1635 (1964).

100. L. Brandsma, H. E. Wijers, and J. F. Arens, Rec. Trav. chim., 82, 1040 (1963).
101. A. Schaap, L. Brandsma, and J. F. Arens, Rec. Trav. chim. 84, 1200 (1965).
102. J. H. van Boom, L. Brandsma, and J. F. Arens, Rec. Trav. chim., 85, 580 (1966).
103. H. E. Wijers, L. Brandsma, and J. F. Arens, Rec. Trav. chim., 85, 601 (1966).
104. J. H. van Boom, P. P. Montijn, L. Brandsma, and J. F. Arens, Rec. Trav. chim., 84, 31 (1965).
105. G. Eglinton, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, J. Chem. Soc., 3197 (1954).
106. J. Cymerman-Craig and M. Moyle, J. Chem. Soc., 4402 (1963).
107. G. H. Mansfield and M. C. Whiting, J. Chem. Soc., 4761 (1956).
108. J. Cymerman-Craig and M. Moyle, J. Chem. Soc., 5356 (1963).
109. M. V. Mavrov and V. F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1494 (1965).
110. R. Vessière and M. Verny, Compt. rend., 261, 1868 (1965).
111. E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, J. Chem. Soc., 3208 (1954).
112. E. R. H. Jones, B. L. Shaw, and M. C. Whiting, J. Chem. Soc., 3212 (1954).
113. M. Bertrand, Compt. rend., 247, 824 (1958).
114. J. Blanc-Guénée, M. Duchon d'Engenières, and M. Miocque, Bull. Soc. chim. France, 603 (1964).
115. W. Oroshnik, A. D. Mebane, and G. Karmas, J. Amer. Chem. Soc., 75, 1050 (1953).
116. T. L. Jacobs and S. Singer, J. Org. Chem., 17, 475 (1952).
117. T. L. Jacobs, D. Dankner, and S. Singer, Tetrahedron, 20, 2177 (1964).
118. A. L. Klebanskii, D. M. Krasinskaya, and L. G. Safonova, Zhur. Obshch. Khim., 16, 1213 (1946).
119. A. A. Petrov, Uspekhi Khim., 29, 1049 (1960) [Russ. Chem. Rev., 489 (1960)].
120. B. S. Kupin and A. A. Petrov, Zhur. Org. Khim., 1, 244 (1965).
121. A. A. Petrov and B. S. Kupin, Zhur. Org. Khim., 2, 1904 (1966).
122. E. N. Prilezhaeva and V. N. Petrov, Izv. Akad. Nauk SSSR, Ser. Khim., 1494 (1966).
123. I. G. Sulimov and A. A. Petrov, Zhur. Org. Khim., 2, 767 (1966).
124. A. A. Petrov, G. I. Semenov, and N. P. Sopov, Zhur. Obshch. Khim., 27, 928 (1957).
125. A. A. Petrov and Yu. I. Porfir'eva, Zhur. Obshch. Khim., 27, 1805 (1957).
126. T. V. Stadnichuk and A. A. Petrov, Zhur. Obshch. Khim., 31, 411 (1961).
127. W. H. Carothers, G. J. Berchet, and A. M. Collins, J. Amer. Chem. Soc., 54, 4066 (1932).
128. W. H. Carothers and G. J. Berchet, J. Amer. Chem. Soc., 55, 2807 (1933).
129. S. A. Vartanyan and Sh. O. Badanyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 15, 231 (1962).
130. J.-C. Traynard, Compt. rend., 249, 136 (1959).
131. E. D. Bergman and D. Herrman, J. Amer. Chem. Soc., 73, 4013 (1951).
132. D. D. Coffman and W. H. Carothers, J. Amer. Chem. Soc., 55, 2040 (1933).
133. A. E. Akopyan, Zhur. Prikl. Khim., 27, 639 (1954).
134. A. A. Petrov and Yu. I. Porfir'eva, Zhur. Obshch. Khim., 27, 2076 (1957).
135. J.-C. Traynard, Bull. Soc. chim. France, 19 (1962).
136. S. A. Vartanyan, G. A. Musakhanyan, and L. O. Avetyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 17, 164 (1964).
137. S. I. Sadykh-zade, A. Z. Shikhmamedbekova, S. D. Yul'chevskaya, S. Kh. Salakhova, and A. S. Rzaeva, Azerb. Khim. Zhur., No. 2, 37 (1963).
138. H. B. Dykstra, J. Amer. Chem. Soc., 58, 1747 (1936).
139. S. A. Vartanyan and A. O. Tosunyan, Izv. Akad. Arm. SSR, Khim. Nauki, 15, 337 (1962).
140. S. A. Vartanyan, A. O. Tosunyan, and S. A. Melkonyan, Izv. Akad. Arm. SSR, Khim. Nauki, 17, 184 (1964).
141. S. A. Vartanyan and F. V. Dangyan, Izv. Akad. Arm. SSR, Khim. Nauki, 18, 269 (1965).
142. S. A. Vartanyan, A. O. Tosunyan, L. G. Mesropyan, and R. A. Kuroyan, Izv. Akad. Arm. SSR, Khim. Nauki, 18, 227 (1965).
143. S. A. Vartanyan and A. O. Tosunyan, Izv. Akad. Arm. SSR, Khim. Nauki, 16, 499 (1963).
144. A. A. Petrov and K. V. Leets, Zhur. Obshch. Khim., 26, 407 (1956).
145. S. A. Vartanyan, Sh. O. Badanyan, and R. T. Agababyan, Arm. Khim. Zhur., 19, 66 (1966).
146. A. P. Golovchanskaya, Zhur. Obshch. Khim., 10, 435 (1940).
147. I. N. Nazarov and L. B. Fisher, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 71 (1944).
148. E. B. Bates, E. R. H. Jones, and M. C. Whiting, J. Chem. Soc., 1854 (1954).
149. W. Oroshnik, J. Amer. Chem. Soc., 77, 4048 (1955).
150. R. G. Powell, C. R. Smith, C. A. Glass, and I. A. Wolff, J. Org. Chem., 30, 610 (1965).
151. S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, Chem. Comm., 585 (1966).
152. K. R. Bharucha and B. C. L. Weedon, J. Chem. Soc., 1584 (1953).
153. F. Bohlmann, P. Herbst, and H. Gleinig, Chem. Ber., 94, 948 (1961).
154. F. Bohlmann and W. Sugrow, Chem. Ber., 97, 1846 (1964).
155. F. Bohlmann, R. Enkelmann, and W. Plettner, Chem. Ber., 97, 2118 (1964).
156. V. A. Engelhardt, J. Amer. Chem. Soc., 78, 107 (1956).
157. S. A. Vartanyan, Sh. O. Badanyan, and R. G. Agababyan, Izv. Akad. Nauk Arm. SSR, Khim. Nauki, 17, 407 (1964).
158. V. A. Kormer and A. A. Petrov, Zhur. Obshch. Khim., 30, 2160 (1960).
159. A. A. Petrov and V. A. Kormer, Dokl. Akad. Nauk SSSR, 132, 1095 (1960).
160. L. N. Cherkasov, V. A. Kormer, Kh. V. Bal'yan, and A. A. Petrov, Zhur. Org. Khim., 2, 1573 (1966).
161. L. N. Cherkasov and Kh. V. Bal'yan, Zhur. Org. Khim., 2, 1751 (1966).
162. V. A. Kormer and A. A. Petrov, Zhur. Obshch. Khim., 30, 918 (1960).
163. V. A. Kormer and A. A. Petrov, Zhur. Obshch. Khim., 30, 3890 (1960).
164. S. I. Radchenko and A. A. Petrov, Zhur. Org. Khim., 1, 993 (1965).
165. T. V. Stadnichuk, V. A. Kormer, and A. A. Petrov, Zhur. Obshch. Khim., 34, 3279, 3284 (1964).
166. O. V. Perepelkin, V. A. Kormer, and Kh. V. Bal'yan, Zhur. Obshch. Khim., 35, 957 (1965).
167. O. V. Perepelkin, L. N. Cherkasov, V. A. Kormer, and Kh. V. Bal'yan, Zhur. Obshch. Khim., 35, 574 (1965).
168. L. N. Cherkasov, V. A. Kormer, and Kh. V. Bal'yan, Zhur. Obshch. Khim., 35, 616 (1965).
169. O. V. Perepelkin, V. A. Kormer, Kh. V. Bal'yan, and A. A. Petrov, Zhur. Org. Khim., 1, 1705 (1965).
170. L. N. Cherkasov and Kh. V. Bal'yan, Zhur. Org. Khim., 1, 1811 (1965).
171. M. D. Stadnichuk and A. A. Petrov, Zhur. Obshch. Khim., 35, 700 (1965).
172. M. D. Stadnichuk, Zhur. Obshch. Khim., 36, 937 (1966).
173. A. A. Petrov, V. A. Kormer, and M. D. Stadnichuk, Zhur.

Obshch. Khim., 30, 2243 (1960).
174. A.A. Petrov, V.A. Kormer, and M.D. Stadnichuk, Zhur. Obshch. Khim., 31, 1135 (1961).
175. M.D. Stadnichuk and A.A. Petrov, Zhur. Obshch. Khim., 32, 2490 (1962).
176. I. Bell, R. Madroñero, and M.C. Whiting, J. Chem. Soc., 3195 (1958).
177. E.R.H. Jones, J.B. Jones, L. Skattebøl, and M.C. Whiting, J. Chem. Soc., 3489 (1960).
178. M.V. Mavrov and V.F. Kucherov, Izv. Akad. Nauk SSSR, Ser. Khim., 1653 (1964).
179. A.T. Blomquist and D.T. Longone, J. Amer. Chem. Soc., 79, 4981 (1957).
180. W.H. Knoth and D.D. Coffman, J. Amer. Chem. Soc., 82, 3873 (1960).
181. T.L. Jacobs and R.S. Bauer, J. Amer. Chem. Soc., 81, 606 (1959).
182. A. Roedig and H. Niedenbruck, Chem. Ber., 90, 673 (1957).
183. E. Bergmann and G.C. Hampson, J. Chem. Soc., 989 (1935).
184. R.N. Haszeldine, K. Leedham, and B.R. Steele, J. Chem. Soc., 2040 (1954).
185. L.F. Hatch and H.D. Weiss, J. Amer. Chem. Soc., 77, 1798 (1955).
186. K. Ziegler, Annalen, 434, 34 (1923).
187. K. Ziegler and C. Ochs, Ber., 55, 2257 (1922).
188. W. Tadros, A.B. Sakla, and A.A.A. Helmy, J. Chem. Soc., 2687 (1961).
189. R. Wizinger and G. Renckhoff, Helv. Chim. Acta, 24, 369E (1941).
190. K. Pilgram and F. Korte, Tetrahedron Letters, 883 (1962).
191. A. Roedig and P. Bernemann, Annalen, 600, 1 (1956).
192. A. Roedig, F. Bischoff, B. Heinrich, and G. Marke, Annalen, 670, 8 (1963).
193. A. Roedig, N. Detzer, and H.J. Friedrich, Angew. Chem., 76, 379 (1964).
194. J.R. Nool and J.F. Arens, Rec. Trav. chim., 78, 284 (1959).
195. J.F. Arens, Rec. Trav. chim., 74, 271 (1955).
196. A.T. Bottini and E.F. Bottner, J. Org. Chem., 31, 385 (1966).
197. C.K. Ingold and C.W. Shoppee, J. Chem. Soc., 1619 (1930).
198. R. Vessière and F. Théron, Compt. rend., 255, 3424 (1962).
199. J.-C. Cognaq and W. Chodkiewicz, Bull. Soc. chim. France, 1999 (1966).
200. L.N. Parfent'ev and A.M. Mirzaev, Zhur. Obshch. Khim., 11, 707 (1941).
201. F.G. Bordwell and E.W. Garbisch, J. Org. Chem., 27, 3049 (1962).
202. S. Skraup and L. Hedler, Chem. Ber., 85, 1161 (1952).
203. J.J. Drysdale, H.B. Stevenson, and W.H. Sharkey, J. Amer. Chem. Soc., 81, 4908 (1959).
204. J. Meinwald, J.W. Wheeler, A.A. Nimetz, and J.S. Liu, J. Org. Chem., 30, 1038 (1965).
205. G.T. Esayan and E.E. Oganesyan, Dokl. Akad. Nauk Arm. SSR, 33, 111 (1961).
206. L. Skatteböl, J. Org. Chem., 31, 1554 (1966).
207. L. Skatteböl, Acta Chem. Scand., 17, 1683 (1963).
208. M. Bertrand, Compt. rend., 260, 6122 (1965).
209. M. Santelli, Compt. rend., 261, 3150 (1965).
210. H.J. Bestmann and H. Hartung, Angew. Chem., 75, 297 (1963).
211. W.S. Wadsworth and W.D. Emmons, J. Amer. Chem. Soc., 83, 1733 (1961).
212. I. Tömösközi and H.J. Bestmann, Tetrahedron Letters, 1293 (1964).
213. K.J. Crowley, J. Amer. Chem. Soc., 85, 1210 (1963).
214. J. Cymerman-Craig and M. Moyle, J. Chem. Soc., 3712 (1963).
215. I. Fleming and J. Harley-Mason, J. Chem. Soc., 4771 (1963).
216. J. Collin and F.P. Lossing, J. Amer. Chem. Soc., 79, 5848 (1957).
217. J.H. van't Hoff, "La Chimie dans l'Espace" (Translated into Russian), Inostr. Lit., Moscow, (1911).
218. I.N. Nazarov and A.I. Kuznetsova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 431 (1941).
219. W.H. Carothers and G.J. Berchet, J. Amer. Chem. Soc., 55, 2813 (1933).
220. Y. Pasternak, Compt. rend., 255, 1750 (1962).
221. I.M. Dolgopol'skii, Yu.V. Trenke, and M.Kh. Blyumental', Zhur. Obshch. Khim., 33, 1071 (1963).
222. C.A. Aufdermarsh, J. Org. Chem., 29, 1994 (1964).
223. D. Ivanov and B. Blagoev, Compt. rend. Acad. bulg. Sci., 15, 751 (1962).
224. Ya.I. Ginzburg, Zhur. Obshch. Khim., 10, 573 (1940).
225. M. Bertrand and S. Maurice, Compt. rend., 259, 2251 (1964).
226. R.C. Cambie, A. Hirschberg, E.R.H. Jones, and G. Lowe, J. Chem. Soc., 4120 (1963).
227. E.R.H. Jones, G.H. Whitham, and M.C. Whiting, J. Chem. Soc., 3201 (1954).
228. J.H. Wotiz and N.C. Bletso, J. Org. Chem., 19, 403 (1954).
229. E.P. Kohler, J.T. Walker, and M. Tishler, J. Amer. Chem. Soc., 57, 1743 (1935).
230. M. Hanack and J. Haffner, Tetrahedron Letters, 2191 (1964).
231. C.S.L. Baker, P.D. Landor, and S.R. Landor, Proc. Chem. Soc., 340 (1963); J. Chem. Soc., 4659 (1965).
232. J.H. Wotiz and H.E. Merrill, J. Amer. Chem. Soc., 80, 866 (1958).
233. J.H. Wotiz, J.S. Matthews, and H.E. Merrill, J. Org. Chem., 23, 1817 (1958).
234. T.L. Jacobs and R.D. Wilcox, J. Amer. Chem. Soc., 86, 2240 (1964).
235. M. Bertrand and J. LeGras, Compt. rend., 260, 6926 (1965).
236. W. Ried and H. Mengler, Annalen, 678, 95 (1964).
237. M. Bertrand, Compt. rend., 245, 2306 (1957).
238. R.E. Banks, R.N. Haszeldine, and D.R. Taylor, J. Chem. Soc., 978 (1965).
239. J.H. Wotiz and J.S. Matthews, J. Amer. Chem. Soc., 74, 2559 (1952).
240. M. Bertrand and J. LeGras, Bull. Soc. chim. France, 2136 (1962).
241. J. Klein, Tetrahedron, 20, 465 (1964).
242. W.J. Sparks and C.S. Marvel, J. Amer. Chem. Soc., 58, 866 (1936).
243. M. Bertrand, H. Reggio, and G. Leandri, Compt. rend., 259, 827 (1964).
244. R.D. Landor and S.R. Landor, J. Chem. Soc., 2707 (1963).
245. H. Tani and F. Toda, Bull. Chem. Soc. Japan, 37, 470 (1964).
246. E.R.H. Jones, G.H. Mansfield, and M.C. Whiting, J. Chem. Soc., 4073 (1956).
247. M. Bertrand and J. LeGras, Compt. rend., 259, 404 (1964).
248. W.C. Agosta, J. Amer. Chem. Soc., 86, 2638 (1964).
249. W.R. Moore and H.R. Ward, J. Chem. Soc., 85, 86 (1963).
250. J.F. Arens, Adv. Org. Chem. (Translated into Russian, Inostr. Lit., Moscow), 2, 117 (1960).
251. M. Julia and C. Descoins, Bull. Soc. chim. France, 2541 (1964).
252. W.D. Celmer and I.A. Solomons, J. Amer. Chem. Soc., 75, 1372 (1953).
253. J.D. Bu'Lock, E.R.H. Jones, P.R. Leeming, and J.M. Thompson, J. Chem. Soc., 3767 (1956).
254. A.A. Petrov, Zhur. Obshch. Khim., 25, 1483 (1955).
255. P.P. Montijn and L. Brandsma, Rec. Trav. chim., 83, 456 (1964).
256. G.F. Hennion and D.E. Maloney, J. Amer. Chem. Soc., 73, 4735 (1951).
257. G. Peiffer, Compt. rend., 258, 3499 (1964).
258. H.D. Hartzler, J. Org. Chem., 29, 1311 (1964).
259. S.R. Landor and P.F. Whiter, J. Chem. Soc., 5625 (1965).
260. H.D. Hartzler, J. Amer. Chem. Soc., 83, 4990, 4997 (1961).

261. R. F. Bleiholder and H. Schechter, J. Amer. Chem. Soc., 86, 5032 (1964).
262. A. F. Bramwell, L. Crombie, and M. H. Knight, Chem. and Ind., 1265 (1965).
263. P. S. Skell and L. D. Wescott, J. Amer. Chem. Soc., 85, 1023 (1963).
264. P. S. Skell, L. D. Wescott, J. P. Golstein, and P. R. Engel, J. Amer. Chem. Soc., 87, 2829 (1965).
265. F. Serratosa, Tetrahedron Letters, 895 (1964).
266. E. A. Johnson and K. L. Burdon, J. Bact., 54, 281 (1947).
267. W. D. Celmer and I. A. Solomons, J. Amer. Chem. Soc., 74, 1870, 2245 (1952).
268. F. Bohlmann and H. G. Viehe, Chem. Ber., 87, 712 (1954).
269. F. Kavanagh, A. Hervey, and W. J. Robbins, Proc. Nat. Acad. Sci. USA, 36, 1 (1950).
270. M. Anchel, J. Polatnick, and F. Kavanagh, Arch. Biochem., 25, 108 (1950).
271. J. D. Bu'Lock and E. F. Leadbeater, Biochem. J., 62, 476 (1956).
272. J. D. Bu'Lock, E. R. H. Jones, and P. R. Leeming, J. Chem. Soc., 4270 (1955).
273. J. D. Bu'Lock, E. R. H. Jones, and P. R. Leeming, J. Chem. Soc., 1097 (1957).
274. F. Kavanagh, A. Hervey, and W. J. Robbins, Proc. Nat. Acad. Sci. USA, 38, 555 (1952).
275. M. Anchel, Arch. Biochem. Biophys., 43, 127 (1953).
276. M. Anchel, Science, 126, 1229 (1957).
277. E. R. H. Jones, P. R. Leeming, and W. A. Remers, J. Chem. Soc., 2257 (1960).
278. G. Bendz, Arkiv Kemi, 14, 305, 475 (1959).
279. J. D. Bu'Lock, Progr. Org. Chem., 6, 86 (1964).
280. M. O. Bugby, C. R. Smith, and I. A. Wolff, J. Org. Chem., 30, 4227 (1965).
281. P. Karrer and E. Jucker, "Carotinoide", Birkhäuser, Basle, 1948, p. 318.
282. R. Bonnett, A. A. Spark, J. L. Tee, and B. C. L. Weedon, Proc. Chem. Soc., 419 (1964).
283. A. Jensen, Acta Chem. Scand., 18, 2005 (1964).

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ORGANOPHOSPHORUS COMPOUNDS CONTAINING ACETYLENIC AND DIENE SUBSTITUENTS

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I. INTRODUCTION

The interest taken by research workers in the chemistry of unsaturated organophosphorus compounds, which has increased extraordinarily during recent years, is explained by the potentialities of these compounds for use as monomers in the manufacture of plastics[1], intermediates in the synthesis of plasticisers[2], solvents for the extraction of compounds of the rare metals[3], finishing agents for textiles[4], additives to lubricating oils[5], and also as starting materials for the synthesis of various biologically active compounds[6-10]. Besides this, the great reactivity and the accessibility of unsaturated organophosphorus compounds of various classes makes them valuable materials for the study of the interaction of atoms in organic compounds of elements in the Third Period, in particular for elucidating the role of the vacant *d*-orbitals in the transmission of electronic influences in the molecule[11-14].

The first attempts to prepare acetylenic derivatives of phosphorus were made in 1921.[15] More recent work on the synthesis of tertiary acetylenic phosphines and of phosphonic esters containing 1,3-diene substituents attached to the phosphorus atom has been summarised in Gefter's monograph[1] (up to 1958) and in several reviews[16,17]. This section of the chemistry of organophosphorus compounds has developed so rapidly since 1958 that the number of compounds synthesised has more than doubled. During the past seven years original new routes have been worked out for the synthesis of highly unsaturated compounds containing acetylenic, allenic, and 1,3-diene substituents attached to the phosphorus atom. Data obtained from the study of unsaturated organic compounds of phosphorus by modern physical methods (ultraviolet, infrared, and nuclear magnetic resonance spectroscopy, dipole moments) have enabled certain conclusions to be drawn concerning the way in which phosphorus-containing groups are conjugated with multiple bonds. The present review summarises all these fresh results.

II. PREPARATION AND CHEMICAL PROPERTIES

1. Phosphines

Primary phosphines are usually obtained by the reduction of halogenophosphines and by the reaction of phosphine and its metal derivatives with alkyl halides and carbonyl compounds[18]. None of these methods has been used to obtain acetylenic or diene phosphines. Attempts to use the reduction of phenylethynylphosphonic ester with lithium tetrahydroaluminate to obtain a primary phosphine containing the phosphino-group directly linked to a triple bond were unsuccessful. Besides cleavage of the phosphorus–carbon bond, the triple bond was hydrogenated to a double bond with formation of α-styrylphosphine[19,20]:

$$C_6H_5C{\equiv}CPO(OC_2H_5)_2 \rightarrow C_6H_5CH{=}CHPH_2.$$

Two of the primary acetylenic phosphines which have been described were obtained by the reaction of sodium phosphide with acetylenic α-epoxides in liquid ammonia[21]:

$$RC{\equiv}C{-}\underset{CH_2}{\overset{O}{C}}{-}CH_2 \xrightarrow[NH_3]{NaPH_2} RC{\equiv}CC(OH)(CH_3)CH_2PH_2$$

where R = CH_3 or C_4H_9.

No secondary phosphines have been described containing acetylenic or diene substituents. Tertiary phosphines,