THE CHEMISTRY OF ALLENES

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CONTENTS

I. INTRODUCTION

A. GENERAL INTRODUCTION

Compounds which contain the $>C{=}C{=}C<$ grouping are known as allenes. Unlike conjugated dienes, they have only recently attracted the attention of chemists, in spite of the fact that the earliest authentic syntheses of allenes were reported nearly 80 years ago (181, 228, 404). As a result of their tedious methods of preparation and the mistaken belief that the cumulated double-bond system would prove to be relatively unstable, allenes came to be regarded as chemical curiosities, mainly of interest for their unusual stereochemistry which van't Hoff successfully predicted as long ago as 1875 (575).

In the last 20 years this situation has entirely changed. Several convenient general methods have been devised for the synthesis of allenes, and an evergrowing volume of publications is unfolding their interesting properties. The industrial potential of such compounds is being examined, and numerous patents cover the use of allenes as dyes (109, 110), drugs (109, 110), antioxidants (109, 110, 474), and in polymers or copolymers suitable for paints (174, 401, 402), fibers (357), elastomers (241), printable films (565, 566), and heat- or corrosion-resistant materials (262). Proof that natural organisms produce compounds containing the allene bond system was first obtained in 1952 (114), and since then numerous other examples of natural allenes have come to light.

B. SCOPE OF THE REVIEW

This article deals with the chemistry of allenes bearing functional groups as well as with hydrocarbon allenes. After a discussion of the main features and limitations of the available synthetic methods, the physical properties and chemical reactions directly related to the allene bond are described. The literature has been searched through May 1966.

The earliest review of Bouis (88) is now quite outdated, and the more recent ones of Pansevich-Kolyada (412), Levina and Viktorova (337), and Petrov and Federova (430) are either not available in translation or are of limited scope. Individual aspects of allene chemistry which have been reviewed recently include rearrangement reactions (277), advances in synthesis (57), polymerization (29), and natural polyacetylenic allenes (97, 278, 279). A comprehensive discussion of all types of cumulenes, including allenes, appeared recently as part of a larger text (191), and supercedes an earlier review of higher cumulenes (102).

C. NOMENCLATURE

The name of the parent hydrocarbon, *i.e.*, allene ($CH_2{=}C{=}CH_2$), has been adopted generally as a class name for all such compounds. Application of the usual conventions leads readily to the correct systematic names of allenes, based on the appropriate alkadiene chain. However, it is often convenient to refer to simple compounds as substitutional derivatives of allene, and both systems are widely used in the literature; some examples are shown in Table I.

The chemist who studies allenes soon realizes that isomeric acetylenes are closely related substances. It should be noted that the term propargyl is used frequently in the literature to refer to the grouping HC≡C—CRR'—, which may be primary (R = R' = H), secondary (R = H; R' = alkyl or aryl), or tertiary (R and R' = alkyl or aryl). This practice will be followed here.

TABLE I
NOMENCLATURE OF ALLENES

Structure	Systematic name	Alternative name
$H_2C{=}C{=}CH_2$	Propadiene	Allene
$H_2C{=}C{=}CHMe$	Buta-1,2-diene	Methylallene
$H_2C{=}C{=}CMe_2$	3-Methylbuta-1,2-diene	1,1-Dimethylallene
$Me_2C{=}C{=}CMe_2$	2,4-Dimethylpenta-2,3-diene	Tetramethylallene
$H_2C{=}C{=}CHCN$	Buta-2,3-dienonitrile	Cyanoallene

D. NATURAL OCCURRENCE

Following at least two earlier incorrect assignments of allenic structures to natural products (321, 506, 543), the first authentic naturally occurring allene, the antibiotic mycomycin (I, R = H; R' = $CH^c{=}CHCH^t{=}CHCH_2CO_2H$), was characterized in 1952 by Celmer and Solomons (114). Mycomycin is a fungal metabolite, apparently produced by the Actinomycete, *Nocardia acidophilus*, although the identity of this source has been questioned (278). Subsequently the Basidomycete fungi have been found to contain nearly 20 allenic metabolites (Table II), all of which contain the characteristic diyne–allene grouping (I).

$$RC{\equiv}CC{\equiv}CCH{=}C{=}CHR'$$

I

Bu'Lock recently suggested that the marked structural similarity of allenes derived from fungi may be due to their biosynthesis from C_{12} and C_{14} acids produced by the organisms from crepenynic acid by dehydrogenation of the chain and β oxidation (98). In some instances isomeric acetylenes, to which the allenes may be related by base-catalyzed rearrangement, occur in the same organism, but it has also been suggested that natural allenes might be formed by the rapid base-promoted cleavage of enol phosphates (131, 132), *e.g.*

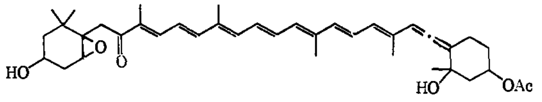
$$MeO_2CCH_2COCH_2CO_2Me \xrightarrow[(EtO)_2POCl]{NaOEt}$$

$$MeO_2CCH_2C({=}CHCO_2Me)OP(O)(OEt)_2 \xrightarrow[25°,\ 90\ min]{aqueous\ Na_2CO_3,\ ether}$$

$$MeO_2CCH{=}C{=}CHCO_2Me$$

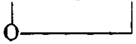
70%

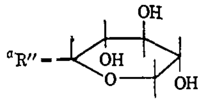
The widespread occurrence of the diyne–allene grouping in fungal allenes has proved of inestimable value in their detection and characterization, owing to its well-known infrared and ultraviolet spectra (96) and characteristic tendency to isomerize (63). However, other types of allenes undoubtedly occur in higher organisms; examples reported recently include fucoxanthin (II), a carotenoid pigment of brown algae (85), labellenic



II

TABLE II
ALLENIC FUNGAL METABOLITES (I)

R	R′	Typical source	Ref
H	CH_2OH	*Cortinellus berkeleyanus*	63
H	CH_2CH_2OH	*Marasmius ramealis*	42
H	CH_2CO_2H	*Aleurodiscus roseus*	103
H	$CH_2CH_2CH_2OH$	*Odontia bicolor*	63
H	$CH(OH)CH_2CH_2OH$	*Odontia bicolor*	63
H	$CH_2CH_2CH_2CH_2OH$	*Odontia bicolor*	63
H	$CH_2CH(OH)CH_2CH_2OH$	*Flammula sapinea*	63
H	$CH(OH)CH_2CH_2CH_2OH$	*Odontia bicolor*	63
H	$CH(OH)CH_2CH_2CO_2H$	"B 841"	99
H	$CH(OH)CH_2CH_2CO_2Me$	*Poria subacida*	64
H	$CH(OR'')CH_2CH_2CO_2H^a$	"B 841"	97
H	 $CHCH_2CH_2CO$	"B 841"	99
H	$CH^c{=}CHCH^t{=}CHCH_2CO_2H$	*Nocardia acidophilus*	114
Me	CH_2CH_2OH	*Daedalea juniperina*	63
Me	$CH(OH)CH_2CH_2CO_2H$	"B 841"	100
Me	 $CHCH_2CH_2CO$	"B 841"	100
$CH^c{=}CHCH_2CO_2H$	H	*Psathyrella (Drosophila) subatrata*	282



acid (III) from the seed oil of *Leonotis nepetaefolia* (20), and an allenic tetraester triglyceride from the

$$Me(CH_2)_{10}CH{=}C{=}CH(CH_2)_3CO_2H$$
III

seed oil of the Chinese tallow tree (539). There seems to be every prospect that many more such compounds will be discovered in the near future.

II. SYNTHETIC ROUTES TO ALLENES

Many of the well-established methods for introducing carbon–carbon double bonds into organic compounds, such as the elimination of halogens, hydrogen halides, or water from adjacent carbon atoms, may also be applied to the synthesis of allenes. Such methods are often laborious, and newer techniques are now available which are specific to the synthesis of allenes, notably the dehalogenation of *gem*-dihalocyclopropanes, the rearrangement of acetylenes, and 1,4 additions to vinylacetylenes.

A. BY DEHALOGENATION

1. *From Dihaloalkenes*

This early method is still the most useful for preparing the parent hydrocarbon, propadiene (136, 228). Very

$$\underset{}{CH_2ClCCl{=}CH_2} \xrightarrow{\text{Zn, EtOH}} \underset{80\%}{CH_2{=}C{=}CH_2} + CH_3CCl{=}CH_2$$

pure allene, not contaminated by 2-halopropene, may be obtained either by zinc debromination of 2,3-dibromopropene in butyl or isoamyl acetate (530), or by treating 2-bromo-3-halopropenes with a 2:1 molar proportion of chromous sulfate (313). Convenient starting materials are allyl chloride or bromide, or less commonly acetone, as in the synthesis of fully deuterated propadiene (388).

$$CD_3COCD_3 \xrightarrow{PCl_5} \underset{30\%}{CD_3CCl{=}CD_2} \xrightarrow{Cl_2,\ SbCl_5}$$
$$\underset{23\%}{CD_2ClCCl_2CD_2Cl} \xrightarrow{\text{Zn, EtOH}} \underset{60\%}{CD_2{=}C{=}CD_2}$$

To apply this method to homologs of propadiene, the corresponding dihaloalkenes must be prepared. Two general approaches are available; in the first, substituted allyl alcohols are converted to the desired dibromoalkenes in three steps, usually in good yield (88).

$$RCH(OH)CH{=}CH_2 \xrightarrow{PBr_3} RCHBrCH{=}CH_2 \xrightarrow{Br_2}$$
$$RCHBrCHBrCH_2Br \xrightarrow{KOH} RCHBrCBr{=}CH_2$$

The second, more recent, procedure involves the reaction of cold concentrated hydrobromic acid with conjugated alkenynes, during which addition occurs both across the triple bond and in a conjugate fashion (57).

$$CH_2{=}CRC{\equiv}CH \xrightarrow[-10°]{\text{concd HBr}} CH_3CR{=}CBrCH_2Br$$

Several fluorinated allenes may be prepared by reaction sequences which culminate in dehalogenation. For example, 1,1-difluoropropadiene is obtainable in 10% over-all yield from ethylene and dibromodifluoromethane (77) (Eq 1), and trifluoromethylallenes may be

$$CH_2{=}CH_2 \xrightarrow[\text{peroxide}]{CF_2Br_2} CF_2BrCH_2CH_2Br \xrightarrow{\text{aq KOH}}$$
$$CF_2BrCH{=}CH_2 \xrightarrow[h\nu]{Br_2} CF_2BrCHBrCH_2Br \xrightarrow{\text{alc KOH}}$$
$$CF_2BrCBr{=}CH_2 \xrightarrow{\text{Zn, EtOH}} CF_2{=}C{=}CH_2 \quad \text{(Eq 1}$$

prepared from the free-radical addition products of trifluoroiodomethane and propargyl halides (15)

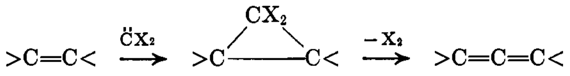
$$\mathrm{RCHXC{\equiv}CH} \xrightarrow[h\nu]{\mathrm{CF_3I}} \mathrm{RCHXCI{=}CHCF_3} \xrightarrow{\mathrm{Zn,\ EtOH}} \underset{85\%}{\mathrm{RCH{=}C{=}CHCF_3}}$$

(R = H or Me; X = Cl or Br). The same intermediate iodoalkenes are produced if propargyl alcohols are treated with trifluoroiodomethane, and the resulting adducts chlorinated by thionyl chloride (15).

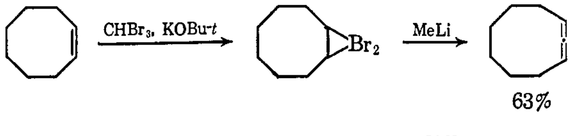
Although arylallenes may be synthesized by zinc dehalogenation, yields are rather low (2, 210), and such compounds are better obtained from arylalkynes by other methods (see sections B and D).

2. *From Dihalocyclopropanes*

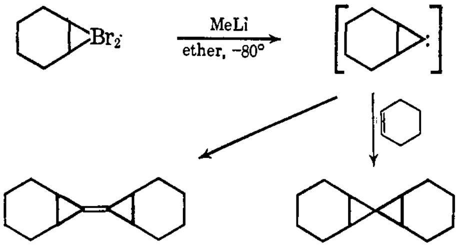
The addition of dichloro- or dibromocarbene across the double bond of an olefin yields 1,1-dihalocyclopropanes (303), which may be converted to allenes simply by treatment with metals or metal alkyls, often in excellent yield (150, 343, 385). Such a procedure has several obvious advantages; acyclic and cyclic olefins are commercially available or easily prepared, and in the absence of labile substituents few side reactions occur. Dibromocarbene, generated from bromoform with potassium *t*-butoxide, is commonly used for the first stage, although it is known that carbenes produced by the decomposition of trihalomethyl mercurials are more reactive with certain olefins (303). The most effective reagent for the dehalogenation appears to be methyllithium in diethyl ether at −30° (386, 520), but alkylmagnesium halides (343), butyllithium (386, 520, 522), sodium (150), and other metals (151) have also been used with varying success. If desired the two steps may be carried out simultaneously, without isolating the intermediate cyclopropane, by treating the olefin with carbon tetrabromide and 2 equiv of a lithium alkyl (520, 574).



Cyclic allenes with eight to eleven carbon atoms in the ring have been synthesized by this route (356, 386, 520, 574), *e.g.*



With smaller rings the reaction takes a different course, presumably because of the rather severe strain which would be imposed on a ring of seven or less carbon atoms by the linear allene arrangement. Thus, if 7,7-dibromonorcarane is treated with methyllithium, only the olefin (IV) is formed, probably by dimerization of an intermediate carbene, and in the presence of olefins products arise which are also conveniently explained in terms of such an intermediate (385).



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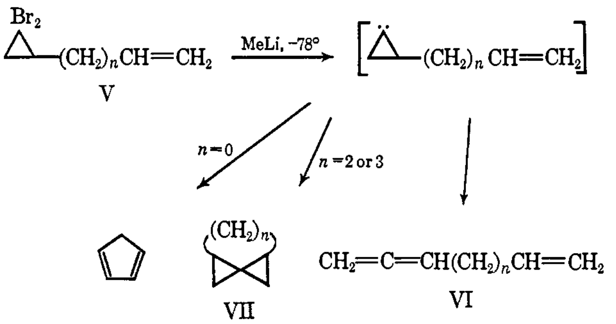
The suggestion that carbenes are intermediates in these dehalogenations, originally made by Doering and LaFlamme (150), is supported by two other observations. When dehalogenation is brought about by methylmagnesium bromide in tetrahydrofuran (511), or by sodium in dimethyl sulfoxide (407), an intermediate monobromocyclopropane may be isolated; such a compound should undergo α elimination readily. Furthermore, in the reaction of alkenyldibromocyclopropanes (V, n = 0, 1, 2, or 3) with methyllithium at low temperature, the amount of the allene (VI, n = 0, 1, 2, or 3) formed varies according to the position of the double bond (519) (Scheme I). The formation of tricyclic compounds (VII, n = 2 or 3) may then be explained by intramolecular addition of an intermediate carbene to the double bond, which can only take place when the two centers are far enough apart.

SCHEME I



Allenes are also formed when diazocyclopropanes decompose, and kinetic data suggest that at least some of the allene forms from an intermediate carbene (290–292, 294). Other reactions in which allenes are formed in small amounts, and which may involve cyclic carbene intermediates, are the photolysis of carbon suboxide with olefins (41, 391), the interaction of "hot" carbon atoms with ethylene (350, 358), the reactions of methylene with ketene (144) and acetylene (276), and the thermal decomposition of triphenylcyclopropylidenephosphorane (60).

A remarkable example of this technique for introducing the allene bond is the conversion of polyisoprene to the corresponding allenic polymer, with only limited chain shortening (452).

$$\text{+}CH_2CMe{=}CHCH_2\text{+}_n \xrightarrow[\text{(ii) MeLi}]{\text{(i) }\ddot{C}Br_2} \text{+}CH_2CMe{=}C{=}CHCH_2\text{+}_m$$

B. BY DEHYDROHALOGENATION

1. *From Haloalkenes*

Allenes may be formed by the base-promoted elimination of hydrogen halides from two types of haloalkene.

$$>CH{-}CX{=}C< \xrightarrow{\text{base}} >C{=}C{=}C< \xleftarrow{\text{base}} >CX{-}CH{=}C<$$

Since such eliminations are initiated by removal of a proton, compounds with the more firmly bound vinyl hydrogen are less easily converted to allenes. In either case, the scope of the method is severely limited by competing side reactions, which are of two types. Firstly, the presence of a suitably placed hydrogen may lead to preferential elimination of HX to give acetylenes or conjugated dienes.

$$>CH{-}CX{=}CH{-} \xrightarrow{\text{base}} >CH{-}C{\equiv}CH$$

$$>\overset{|}{CH}{-}\overset{|}{C}X{-}CH{=}C< \xrightarrow{\text{base}} >C{=}\overset{|}{C}{-}CH{=}C<$$

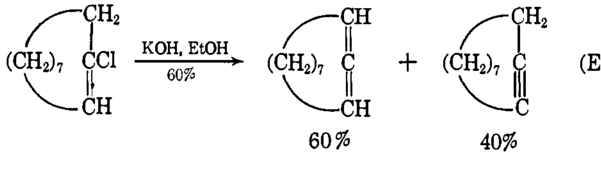
Secondly, the desired allene, once formed, may rearrange to an acetylene or conjugated diene if it bears a hydrogen atom which is labile to the base employed in the elimination.

$${-}CH{=}C{=}C< \xrightarrow{\text{base}} {-}C{\equiv}C{-}CH<$$

$$>CH{-}\overset{|}{C}{=}C{=}C< \xrightarrow{\text{base}} >C{=}\overset{|}{C}{-}CH{=}C<$$

It is not surprising, therefore, that yields of alkylallenes prepared in this way are generally low (10–30%) (18, 184, 336, 413, 529, 558), and alternative routes to such compounds are to be preferred (see sections A and D). However, in most of the examples in the literature large excesses of strong bases were used, and it is possible that a suitable choice of reagent, solvent, and reaction time might lead to greatly improved yields (see, *e.g.*, ref 546).

Dehydrohalogenation is more successful as a method of preparing cyclic allenes containing nine or ten carbon atoms, because isomeric cycloalkynes are more highly strained for such ring sizes, though not in larger rings. Thus, treatment of 1-chlorocyclodecene with alcoholic potash (384) or sodamide in liquid ammonia (32) gives mainly cyclodeca-1,2-diene (Eq 2). The cyclodecyne may be separated by extraction with aqueous methanolic silver nitrate and partially converted to more allene by isomerization with base (387). Prolonged exposure of the cyclic allene to base must be avoided, however, or *cis,cis*-1,3- and *cis,trans*-1,4-cyclodecadiene are formed (384). Such rearrangements become very rapid when a highly polar solvent is used (147). For rings of less than nine carbon atoms, ring strain becomes too high for either acetylenes or allenes to be formed, and dimers or polymers are the only products (32).



(Eq 2)

Elimination of hydrogen halides is not so likely to be attended by rearrangement when the allene to be formed is highly substituted, especially by halogens or aryl groups. Indeed, numerous arylallenes have been synthesized in this way (46, 192, 495, 554, 592, 619). Two new approaches to such allenes were recently reported. In one of these the essential step is the thermal addition of a diphenylmethyl halide to a 1,1-diarylethylene (554).

$$Ph_2C{=}CH_2 \xrightarrow[\text{reflux in }C_6H_6]{Ph_2CHBr} Ph_2CBrCH_2CHPh_2 \xrightarrow{\text{2 steps}}$$

$$Ph_2C{=}CBrCHPh_2 \xrightarrow{\text{alc KOH}} \underset{100\%}{Ph_2C{=}C{=}CPh_2}$$

Alternatively, 1,1-diaryl-2,2-dichloroethylenes may be treated with potassium diphenylmethide in liquid ammonia; initially nucleophilic displacement of chloride by the reagent carbanion must occur, followed by elimination of HCl (302).

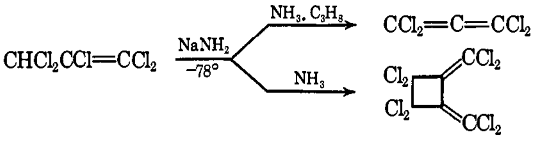
$$Ph_2C{=}CCl_2 \xrightarrow[NH_3,\ -78°]{Ph_2CHK} [Ph_2C{=}CClCHPh_2] \xrightarrow{-HCl} \underset{90\%}{Ph_2C{=}C{=}CPh_2}$$

A similar absence of rearrangement is observed when polyhaloallenes are prepared by dehydrohalogenation, and, although other difficulties arise, all four perhalopropadienes ($CX_2{=}C{=}CX_2$, where X is F, Cl, Br, or I) have now been made in this way. In the case of tetrafluoroallene, obtainable by two successive eliminations of HBr from the adduct of vinylidene fluoride and dibromodifluoromethane, the low yield is due to the reactivity of the allene, which can be destroyed even by water formed in the reaction (34, 36, 261).

$$CH_2{=}CF_2 \xrightarrow[\text{peroxide}]{CF_2Br_2} CF_2BrCH_2CF_2Br \xrightarrow[\text{50°, 36 cm}]{\text{KOH(s)}}$$

$$CF_2BrCH{=}CF_2 \xrightarrow[110°]{\text{KOH(s)}} \underset{35\%}{CF_2{=}C{=}CF_2} \xrightarrow{H_2O} CF_2{=}CHCOF + HF$$

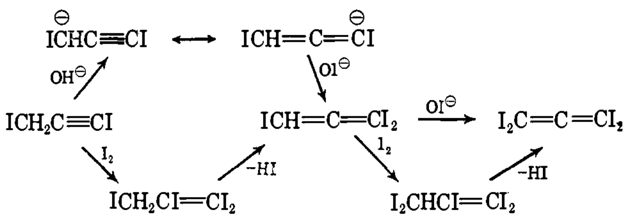
In the case of tetrachloroallene (493) and tetrabromoallene (494), both obtained from the corresponding 3H-pentahalopropenes ($CHX_2CX{=}CX_2$, where X is Cl or Br), rapid dimerization of the allene occurs unless dehydrohalogenation is effected with sodamide at −78° in liquid ammonia, mixed with propane into which the allene rapidly dissolves. A more conventional technique leads only to dimer (492) (Eq 3).



(Eq 3)

It has been claimed that monomeric tetrachloroallene can also be produced in high yield by vapor-phase dehydrochlorination (451). Finally, triiodo- and tetraiodoallene were recently synthesized from 1,3-diiodopropyne and the correct proportions of iodine and potassium hydroxide in methanol (296), a process which could involve addition of iodine and elimination of HI, or iodination by hypoiodite formed *in situ* (Scheme II).

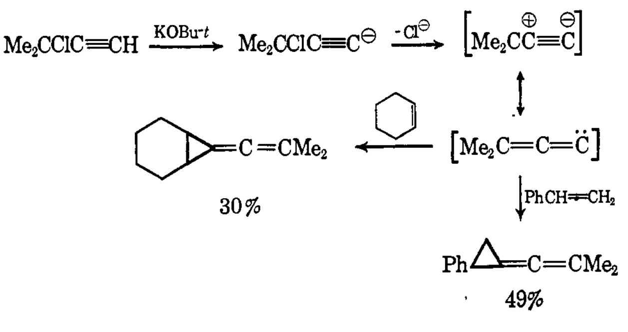
SCHEME II

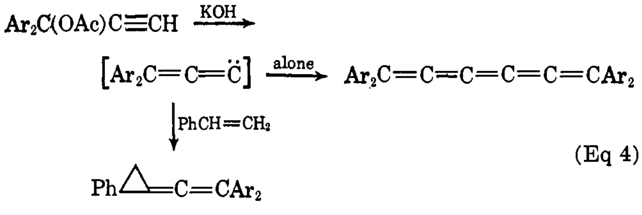


2. *From Propargyl Halides*

An unusual type of dehydrohalogenation occurs when propargyl halides ($R_2CXC{\equiv}CH$) are treated with strong bases (75, 89, 238, 239). It appears that allenic carbenes are formed, which are readily trapped by means of added olefins, giving cyclopropylideneallenes (Scheme III). The intermediate carbenes add stereospecifically to *cis*- and *trans*-but-2-ene (239) and, like dihalocarbenes, react more readily with highly substituted olefins (240).

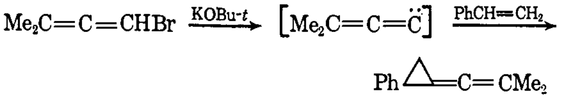
SCHEME III





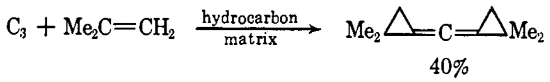
(Eq 4)

The potential of this technique for synthesizing allenes of unusual structure is enhanced because such allenic carbenes may also be generated from the acetates of diarylpropynols (101, 238) (Eq 4) or from 1-haloallenes by α elimination (240, 327) (Eq 5).



(Eq 5)

Still more complicated cyclic allenes are formed when triatomic carbon, which is produced in carbon arcs and behaves like a dicarbene ($\ddot{C}{=}C{=}\ddot{C}$), interacts with olefins (524) or imines (145). Although the scale is necessarily small, moderate yields have been obtained in some cases, *e.g.*



C. BY DEHYDRATION

The synthesis of allenes by dehydration of α,β-unsaturated alcohols is closely allied to the previous method, though of more limited application. Propadiene is not conveniently prepared by dehydrating allyl alcohol, although it is formed in small amounts when allyl alcohol or its ethers are reduced (201, 202). Nor is dehydration suitable for the synthesis of simple alkylallenes, because when β-hydrogen atoms are present the loss of water takes place in such a way that conjugated dienes are the main products, *e.g.* (157)

$$>C{=}CH{-}C(OH)< \xrightarrow{-H_2O} >C{=}C{=}C<$$

$$MeCH_2CH(OH)CH{=}CH_2 \xrightarrow[250\text{–}280^\circ]{Al_2O_3} MeCH{=}CHCH{=}CH_2$$

Even when such elimination is prevented by the presence of highly branched substituents, as in

$$MeCH{=}CHCH(OH)Bu\text{-}t$$

the yield of the corresponding allene is disappointing (392).

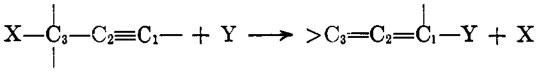
Dehydration is therefore mainly used for the preparation of polyarylallenes in which at least three aryl groups are directly attached to the allene bond (47, 570, 618). Thus, tetraphenylallene may be obtained in up to 53% yield by heating the corresponding alcohol [$Ph_2C(OH)CH{=}CPh_2$] with acetic anhydride (197, 588, 592) or potassium bisulfate (166), or simply by heat alone since the hydroxyl group is comparatively labile (616). Even for polyarylallenes the method has disadvantages: under the acid conditions usually needed to effect loss of water, such allenes tend to rearrange to form indenes or, especially in the case of triarylallenes, to dimerize rapidly (601, 616, 617).

A useful modification avoids the need to isolate the unsaturated alcohols; instead the corresponding carbonium ion perchlorates are prepared from the reaction of 1,1-diarylethylenes with diaryl ketones in perchloric acid, and then treated with a base (601).

$$\mathrm{Ar_2C{=}CH_2} \xrightarrow[\mathrm{HClO_4,\ AcOH}]{\mathrm{Ar_2CO}} \mathrm{[Ar_2CCH{=}CAr_2]^{\oplus}ClO_4^{\ominus}} \xrightarrow{\text{base}} \mathrm{Ar_2C{=}C{=}CAr_2}$$

D. BY THE PROPARGYL REARRANGEMENT

The term propargyl rearrangement refers to processes of the type



$$\mathrm{X{-}\overset{|}{\underset{|}{C_3}}{-}C_2{\equiv}C_1{-} + Y \longrightarrow {>}C_3{=}C_2{=}\overset{|}{C_1}{-}Y + X} \qquad \text{(Eq 6)}$$

which closely resemble the better known allylic rearrangement. Because the synthesis of acetylenes is generally easier than allenes, such processes are often of great value. In the following discussion, a classification of propargyl rearrangements similar to that proposed by Jacobs (259) has been adopted, and four general types are differentiated, namely, prototropic (Eq 6, $X = Y = H$), anionotropic ($X = Y =$ anion), displacement ($X \neq Y$), and intramolecular rearrangements.

1. *Prototropic Rearrangements*

Terminal aliphatic acetylenes undergo simultaneous polymerization, isomerization, and degradation at temperatures of 500–600°, but under the influence of suitable catalysts, or in basic media such as alcoholic potash, the isomerization takes place at lower temperatures and allenes may be formed. The rearrangement is reversible and may also proceed further to give conjugated dienes or alk-2-ynes, so that worthwhile yields of terminal allenes are seldom obtained unless substitution prevents further isomerization, as in Favorsky's early synthesis of 1,1-dimethylallene (182).

$$\mathrm{Me_2CHC{\equiv}CH} \xrightarrow[150°,\ 6\ \text{hr}]{\mathrm{KOH,\ EtOH}} \mathrm{Me_2C{=}C{=}CH_2}$$

In such reactions the choice of reagent is critical; the same acetylene affords mainly isoprene when heated over alumina (159).

An interesting procedure was reported recently which does enable the conversion of alk-1-ynes to terminal allenes in good yields, and without the simultaneous formation of alk-2-ynes and 1,3-dienes. The acetylene is treated with phosphorus pentachloride, the adduct hydrolyzed, and the resulting phosphonic acid cleaved with alkali (371) (Eq 7). Unfortunately, treatment of corresponding diethyl phosphonates with bases does not lead to allene formation, but to mixtures of allenic and propargyl phosphonates (371, 403).

$$\mathrm{Me(CH_2)_nCH_2C{\equiv}CH} \xrightarrow[\text{then } \mathrm{H_2O}]{\mathrm{PCl_5,}} \mathrm{Me(CH_2)_nCH{=}CClCH_2P(O)(OH)_2} \xrightarrow{\mathrm{NaOH}} \mathrm{Me(CH_2)_nCH{=}C{=}CH_2} \qquad \text{(Eq 7)}$$

Alk-2-ynes also undergo base-catalyzed rearrangement, but to a lesser extent than terminal acetylenes. For example, the equilibrium mixture obtained by treating either pent-1-yne or pent-2-yne with alcoholic potash contains 95% pent-2-yne, 1% of pent-1-yne, and only 4% of penta-1,2-diene (260).

As mentioned earlier (section B), cycloalkynes are converted by bases to equilibrium mixtures containing cyclic allenes, which predominate only if the ring size is favorable (C_9 or C_{10}). Evidence that the equilibrium concentration of the allenic components in these mixtures is greater in nonpolar solvents has been obtained (387).

If the migrating hydrogen is initially adjacent to a second multiply bonded carbon atom, the greater mobility of the proton enables milder conditions to be used. Moreover, the allenic bond which forms in such a rearrangement is stabilized by conjugation and resists further isomerization. For example, a simple method of preparing di- and triarylallenes consists of the isomerization of arylacetylenes on columns of alumina impregnated with base (264, 265, 273).

$$\mathrm{ArC{\equiv}CCH_2Ar'} \xrightarrow[20°,\ 20\ \text{min}]{\mathrm{Al_2O_3,\ KOH}} \underset{80\%}{\mathrm{ArCH{=}C{=}CHAr'}}$$

Yields are excellent and if an optically active base (*e.g.*, brucine) is used on the column, a partially asymmetric synthesis can be achieved. Similarly, allylacetylenes are very readily isomerized to alkenylallenes, and further rearrangement occurs only under forcing conditions (50, 73, 377, 406), *e.g.*

$$\mathrm{Me_2C(OH)C{\equiv}CCH_2CH{=}CH_2} \xrightarrow[20°,\ 3\ \text{hr}]{5\%\ \mathrm{KOH,\ MeOH}} \underset{88\%}{\mathrm{Me_2C(OH)CH{=}C{=}CHCH{=}CH_2}}$$

A second triple bond can facilitate proton migration in the same way; in the case of nona-1,4-diyne the resulting allene rearranges nearly 20 times slower than the diyne (208).

$$n\text{-}\mathrm{BuC{\equiv}CCH_2C{\equiv}CH} \xrightarrow[\text{rapid}]{\text{aq } \mathrm{KOH,\ EtOH}} \underset{71\%}{n\text{-}\mathrm{BuC{\equiv}CCH{=}C{=}CH_2}} \xrightarrow[\text{slow}]{} n\text{-}\mathrm{BuC{\equiv}CC{\equiv}CCH_3}$$

Clearly, any functional group which renders adjacent hydrogen atoms more acidic will assist the formation of substituted allenes by prototropic rearrangement of the corresponding β,γ-acetylene isomer. Such reactions are therefore useful for the preparation of allenic nitriles (317, 536), carboxylic acids (280, 284, 286, 354), and esters (131, 280, 590). However, allenic acids of the type $\mathrm{RCH{=}C{=}CHCO_2H}$ are obtained in worthwhile amounts from the corresponding acetylenes

($RC{\equiv}CCH_2CO_2H$) only if the group R is hydrogen, phenyl, or carboxyl, but not when R is alkyl. No doubt the rearrangement in alkaline solution proceeds *via* a carbanion, and the nature of the group R decides whether the allenic form of this carbanion is stable enough for allene formation to occur in preference to hydration or further isomerization (280, 286) (Eq 8).

$$\begin{array}{lcl} RC{\equiv}CCH_2CO_2H & \xrightarrow{\text{aq } K_2CO_3} & [RC{\equiv}C\overset{\ominus}{C}HC\overset{\ominus}{O_2}] \\ & & \updownarrow \\ RCH{=}C{=}CHC\overset{\ominus}{O_2} & \xleftarrow[\text{(R not alkyl)}]{H_2O} & [R\overset{\ominus}{C}{=}C{=}CHC\overset{\ominus}{O_2}] \end{array} \qquad \text{(Eq 8)}$$

When α,β-acetylenic acids are isomerized by sodamide in liquid ammonia, only butadienoic acid is found to be sufficiently resistant to further rearrangement for its isolation to be practicable (130).

$$RCH_2C{\equiv}CCO_2H \xrightarrow[-70^\circ,\ 2\text{ hr}]{NaNH_2,\ NH_3} RCH{=}C{=}CHCO_2H \xrightarrow{(R \neq H)} RC{\equiv}CCH_2CO_2H$$

During the last 5 years the interesting chemistry of allenic thioethers has been developed, based on their reversible formation by prototropic rearrangement of acetylenic thioethers (90, 91, 382, 458–461) (Eq 9).

$$RSCHR'C{\equiv}CR'' \rightleftharpoons RSCR'{=}C{=}CHR'' \overset{R'=H}{\rightleftharpoons} RSC{\equiv}CCH_2R'' \qquad \text{(Eq 9)}$$

If R′ and R″ are both hydrogen, the above equilibria lie to the right unless sufficient base is present to lead to quantitative formation of the acetylide ($RSCH_2C{\equiv}C^-$), which forces the equilibria to the left. Therefore, when R′ is other than hydrogen, allenes are obtainable using catalytic amounts of base and prove to be comparatively stable, though readily oxidized to sulfones (459) (Eq 10). However, phenyl propadienyl

$$PhSCHMeC{\equiv}CH \xrightarrow{KOH,\ THF} PhSCMe{=}C{=}CH_2 \xrightarrow{H_2O_2,\ AcOH} PhSO_2CMe{=}C{=}CH_2 \qquad \text{(Eq 10)}$$

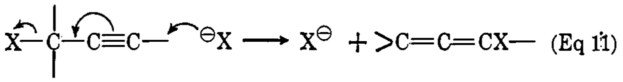
sulfone ($PhSO_2CH{=}C{=}CH_2$) is best obtained by the alumina-catalyzed rearrangement of phenyl propargyl sulfone, since the allenic thioether in that case is unstable (545).

When R′ is hydrogen in Eq 9, the allenic isomers are obtainable either by stopping the reaction after a suitable time (458), or by using an equimolar amount of alkali metal amide in liquid ammonia and rapidly intercepting the allenic carbanion (VIII) with water, an alkyl halide, or a carbonyl compound (90, 91, 382). A further application becomes possible when R″ is methyl, because treatment of the resulting thioethers with excess of sodamide then leads to vinylacetylenes by elimination of alkylthiol (90, 382) (Scheme IV).

Allenic derivatives of oxygen, selenium, and tellurium have also been synthesized by prototropic rearrangement (86, 458, 461). Alkoxyallenes appear to be relatively unstable, and evidence for their formation rests mainly on spectroscopic data (86, 361) and on their hydrolysis to substituted crotonaldehydes (86, 522).

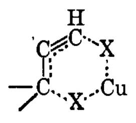
2. *Anionotropic Rearrangements*

Anionotropic propargyl rearrangements are those in which the migrating group X is an anion such as halide or acetate.



$$X{-}\overset{|}{\underset{|}{C}}{-}C{\equiv}C{-}\ {}^{\ominus}X \longrightarrow X^{\ominus} + {>}C{=}C{=}CX{-} \qquad \text{(Eq 11)}$$

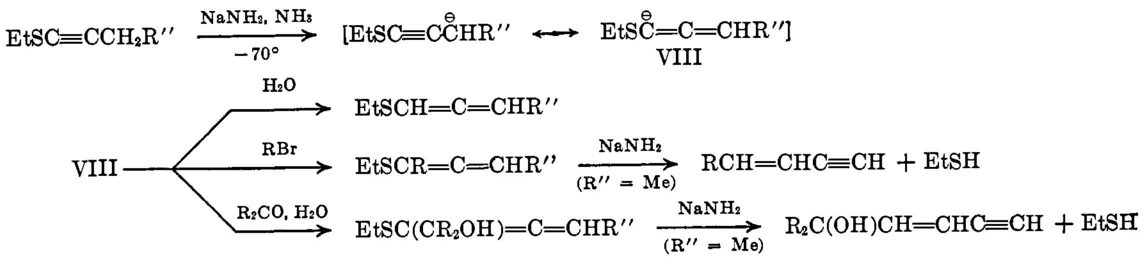
Such reactions are frequently catalyzed by cuprous salts, but in few cases has the mechanism been firmly established. Intermediate carbonium ion formation by a unimolecular process is considered unlikely on theoretical grounds (322) and from studies on the solvolysis of propargyl halides (247, 248, 513); the simplest alternative is the S_N2' displacement represented in Eq 11. However, it seems very likely that the role of the cuprous catalyst in the rearrangement is to set up a cyclic transition complex (IX), and several of the displacement rearrangements to be discussed in sections 3 and 4 almost certainly involve such intermediates as well.



IX

This type of reaction is useful for the synthesis of α-haloallenes. Chloroallene and bromoallene are obtained by treating the corresponding propargyl halide

SCHEME IV



$$EtSC{\equiv}CCH_2R'' \xrightarrow[-70^\circ]{NaNH_2,\ NH_3} [EtSC{\equiv}C\overset{\ominus}{C}HR'' \longleftrightarrow Et\overset{\ominus}{SC}{=}C{=}CHR''] \ \text{VIII}$$

$$\text{VIII} \xrightarrow{H_2O} EtSCH{=}C{=}CHR''$$

$$\text{VIII} \xrightarrow{RBr} EtSCR{=}C{=}CHR'' \xrightarrow[(R''\,=\,Me)]{NaNH_2} RCH{=}CHC{\equiv}CH + EtSH$$

$$\text{VIII} \xrightarrow{R_2CO,\ H_2O} EtSC(CR_2OH){=}C{=}CHR'' \xrightarrow[(R''\,=\,Me)]{NaNH_2} R_2C(OH)CH{=}CHC{\equiv}CH + EtSH$$

with an acid solution of cuprous halide (263).

$$HC\equiv CCH_2X \xrightarrow[(X = Cl,\ Br)]{aq\ HX,\ CuX} CHX=C=CH_2$$

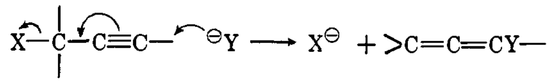
Complete conversion is not achieved and, although the yield of bromoallene is satisfactory (60%), chloroallene is more economically prepared by treating propargyl chloride with aqueous hydroxide (368). Secondary and tertiary propargyl halides are also rearranged by cuprous salts (176, 178, 179, 271, 416), but the reaction is often complicated by further isomerization of the desired allene to a conjugated diene, *e.g.* (176)

$$Me_2CClC\equiv CH \xrightarrow[Cu\ bronze]{aq\ HCl,\ CuCl} Me_2C=C=CHCl \longrightarrow CH_2=CMeCH=CHCl$$

Cesium fluoride has been cited as a heterogeneous catalyst for the anionotropic rearrangement of perfluorinated acetylenes and dienes, and in one instance a perfluoroallene was identified in the product mixture (379).

3. *Displacement Rearrangements*

A very similar group of propargyl rearrangements comprises those in which the incoming and outgoing groups are different anions.



$$X—\overset{|}{\underset{|}{C}}—C\equiv C—{}^{\ominus}Y \longrightarrow X^{\ominus} + >C=C=CY—$$

A variety of techniques for effecting such conversions are known. Some are mainly of interest from a mechanistic standpoint, but many are useful for the synthesis of allenes. For convenience, the field will be subdivided according to the nature of the leaving group (X), which is usually either halide or hydroxide.

a. Propargyl Halides

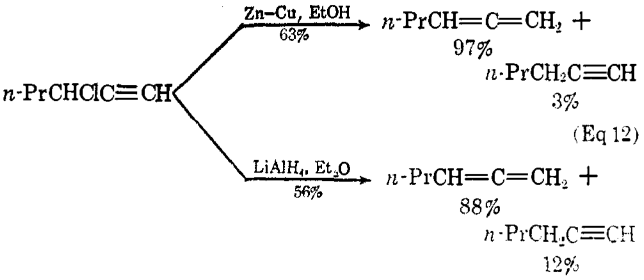
In 1940 Ginzburg reported a most useful method for the preparation of allenic hydrocarbons, in which propargyl halides are reduced by means of a zinc–copper couple (211, 212).

$$Me_2CClC\equiv CH \xrightarrow{Zn–Cu,\ EtOH} \underset{64\%}{Me_2C=C=CH_2}$$

Some years elapsed before this work received general attention but, following its successful application to the synthesis of hexa-1,2-diene (249), it has been widely applied. It leads to good yields of terminal allenes (48), and also of allenes with neighboring double and triple bonds (281). The solvent is usually ethanol or butanol, but, if deuterium oxide is used, deuterioallenes are obtained (388).

$$HC\equiv CCH_2Cl \xrightarrow{Zn,\ D_2O} CHD=C=CH_2 + HC\equiv CCH_2D$$

Ginzburg's procedure may be modified so that allenes are prepared directly from propargyl alcohols without isolating the intermediate propargyl halides, which are instead treated *in situ* with lithium aluminum hydride (23). However, a thorough study of these alternative techniques has shown that the zinc–copper couple has definite advantages for the preparation of alka-1,2-dienes, because smaller amounts of by-products are formed (274, 275), as the results of Eq 12 show for the reduction of 3-chlorohex-1-yne.



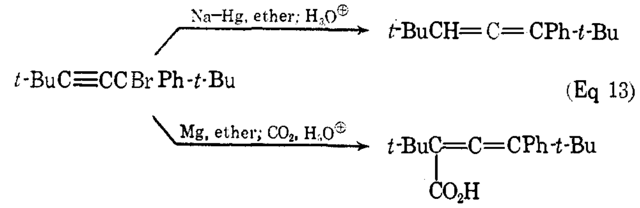
$$n\text{-}PrCHClC\equiv CH \xrightarrow[63\%]{Zn–Cu,\ EtOH} \underset{97\%}{n\text{-}PrCH=C=CH_2} + \underset{3\%}{n\text{-}PrCH_2C\equiv CH}$$

$$n\text{-}PrCHClC\equiv CH \xrightarrow[56\%]{LiAlH_4,\ Et_2O} \underset{88\%}{n\text{-}PrCH=C=CH_2} + \underset{12\%}{n\text{-}PrCH_2C\equiv CH}$$

(Eq 12)

The two types of reduction probably proceed by different mechanisms; lithium aluminum hydride can bring about rearrangement by an S_N2′ displacement of halide by hydride ion (275), but with the metallic couple the formation of intermediate organozinc compounds seems more likely, with the solvent participating in the rearrangement through a cyclic transition complex (423).

The postulation of organozinc intermediates in such reductions is in line with another fascinating type of propargyl rearrangement, namely the interaction of propargyl halides with metals. The first to report such reactions was Marvel (196, 542), who treated α-bromoacetylenes with sodium amalgam or magnesium and obtained allenes and allenic acids when the resulting solutions were hydrolyzed or carbonated (Eq 13).



$$t\text{-}BuC\equiv CCBrPh\text{-}t\text{-}Bu \xrightarrow{Na–Hg,\ ether;\ H_3O^{\oplus}} t\text{-}BuCH=C=CPh\text{-}t\text{-}Bu$$

$$t\text{-}BuC\equiv CCBrPh\text{-}t\text{-}Bu \xrightarrow{Mg,\ ether;\ CO_2,\ H_3O^{\oplus}} t\text{-}Bu\underset{CO_2H}{\underset{|}{C}}=C=CPh\text{-}t\text{-}Bu$$

(Eq 13)

Subsequent work on reactions of this type has led to a general method for the synthesis of allenecarboxylic acids, which consists of the treatment of propargyl bromides with magnesium, followed by carbonation of the resulting Grignard solution (205, 462, 605, 606, 608, 609) (Eq 14).

$$BrCRR'C\equiv CR'' \xrightarrow{Mg,\ ether} \text{“Grignard”} \xrightarrow{CO_2,\ H_3O^{\oplus}} \underset{10–40\%}{RR'C=C=CR''CO_2H} \quad (Eq\ 14)$$

Unfortunately the allenic acids are usually contaminated with varying amounts of the isomeric acetylenic acids.

For some time it was assumed that the organometallic intermediate in such reactions is an acetylenic Grignard reagent, but extensive study has shown that in many cases, if not in all, it contains the allenic bond system (194, 245, 270, 376, 418, 463). Thus, the same organomagnesium bromide is obtained whether bromopropadiene or 3-bromopropyne is treated with magnesium, and its infrared absorption at 1880 cm^{-1} is thought to be characteristic of such an allene (270, 463). Confusion sometimes arises because the allenic Grignard disproportionates on standing into propadiene, propyne, and a difunctional acetylenic Grignard (X) (270) (Eq 15). The difunctional Grignard (X) is

$$H_2C{=}C{=}CHBr \text{ (or } HC{\equiv}CCH_2Br) \xrightarrow{\text{Mg, ether}} H_2C{=}C{=}CHMgBr \longrightarrow H_2C{=}C{=}CH_2 + CH_3C{\equiv}CH + \underset{\text{X}}{BrMgCH_2C{\equiv}CMgBr} \quad \text{(Eq 15)}$$

also formed when the initial, allenic Grignard is treated immediately with alkylmagnesium halides; it reacts normally, *i.e.*, without rearrangement, with aldehydes and ketones to give acetylenic diols (205, 463). However, when the first-formed allenic Grignard is treated directly with carbonyl compounds other than carbon dioxide, rearrangement does occur, so that allenic alcohols cannot be made in this way (49, 194, 205, 270, 376, 463) (Eq 16). Fortunately allenic alcohols may

$$\begin{tikzcd}
CH_2{=}C{=}CHMgBr \arrow[r, "RR'CO"] \arrow[d, "R''MgBr"] & RR'C(OH)CH_2C{\equiv}CH & \\
R''H + \underset{\text{X}}{BrMgCH_2C{\equiv}CMgBr} \arrow[r, "RR'CO"] & RR'C(OH)CH_2C{\equiv}CCRR'OH & \text{(Eq 16)}
\end{tikzcd}$$

be synthesized quite easily by two procedures, conveniently mentioned here. They are produced either by reduction ($LiAlH_4$) of conjugated allenic ketones, derived by oxidation of acetylenic alcohols such as those obtained above (37, 51, 52)

$$RCH(OH)CH_2C{\equiv}CH \xrightarrow[0-5°]{\text{chromic acid}} RCOCH{=}C{=}CH_2 \xrightarrow{LiAlH_4} RCH(OH)CH{=}C{=}CH_2$$

(*e.g.*, where R = Me, Et, *n*-Pr), or by the hydrolysis of alkoxyalkenynes (XI, R = H or Et and R′ = Me, Et or *n*-Pr) (58).

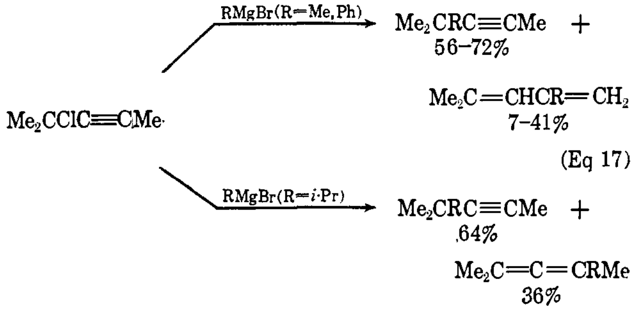
$$\underset{\text{XI}}{RCH(OH)C{\equiv}CCH{=}CR'OEt} \xrightarrow{\text{aq } HClO_4} EtOH + \underset{20-80\%}{RCH(OH)CH{=}C{=}CHCOR'}$$

When zinc or aluminum replaces magnesium in the above reactions, the results are very similar. For example, bis(propadienyl)zinc is produced by treating either bromopropadiene or propargyl bromide with zinc; like its magnesium analog, the organozinc compound reacts with carbonyl compounds to give mainly acetylenic alcohols (205, 206, 230, 442, 449, 463).

$$BrCH_2C{\equiv}CH \xrightarrow[-5 \text{ to } -10°]{\text{Zn, THF}} (CH_2{=}C{=}CH)_2Zn \xrightarrow{RR'CO,\ H_3O^{\oplus}} RR'C(OH)CH_2C{\equiv}CH$$

To sum up, the treatment of propargyl halides with metals appears to be useful for the synthesis of allenes only if the resulting organometallic species are treated, before disproportionation occurs, with water, carbon dioxide, and with certain halogen compounds such as allyl or propargyl bromide (245, 270, 376, 422).

An excellent route to branched allenic hydrocarbons, discovered by Zakharova (612, 614, 615), consists of the reaction between propargyl halides and alkyl- or arylmagnesium halides. Early claims that tetraalkylallenes could be made in this way have been found unreliable (269), and the actual products appear to be acetylenes and conjugated dienes, in one case containing some allenic isomer (Eq 17). Nevertheless, Zakharova's technique is successful when applied to the synthesis of alkyl (205, 507), dialkyl (375, 606), and trialkylallenes (205, 415). Yields of the more highly substituted allenes are greatly improved by effecting the final hydrolysis with the minimum amount of pure water, rather than with dilute acid (415). 2-Methylhexa-2,3-diene may be prepared almost quantitatively if this is borne in mind.



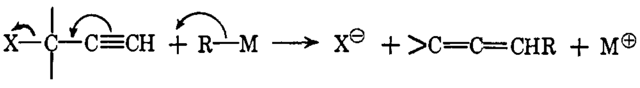
(Eq 17)

$$Me_2CBrC{\equiv}CH \xrightarrow[\text{(ii) } H_2O]{\text{(i) EtMgBr, ether}} \underset{99\%}{Me_2C{=}C{=}CHEt}$$

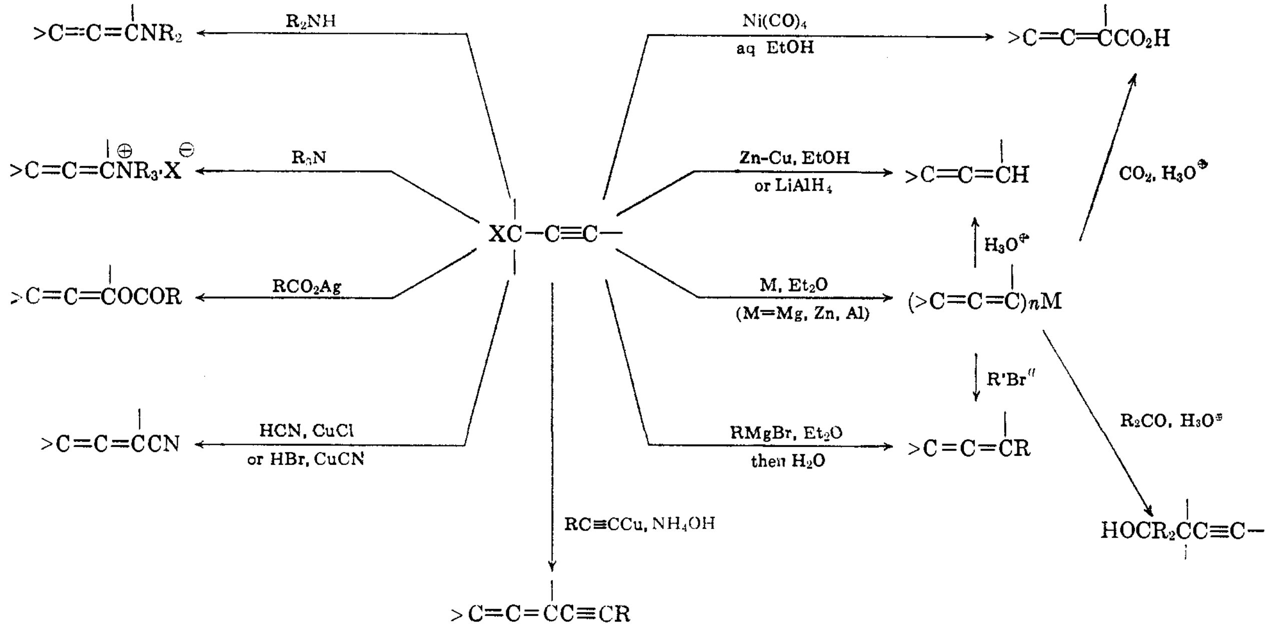
A rather similar type of rearrangement, recently reported (509), occurs when propargyl halides are treated with ammoniacal solutions of cuprous acetylides, so that good yields of alkynylallenes [XII, where R = Ph, $CH_2{=}CMe$–, $HOCH_2$–, MeCH(OH)–, or $Me_2C(OH)$–] may be obtained.

$$RC{\equiv}CH + BrCH_2C{\equiv}CH \xrightarrow{Cu^I,\ NH_4OH} \underset{\text{XII, } 60-80\%}{RC{\equiv}CCH{=}C{=}CH_2}$$

It is tempting, but probably erroneous, to assume that these reactions lead to allenes by straightforward S_N2' displacement of halide by carbanion



An alternative mechanism, in keeping with the behavior of propargyl halides with strong bases (238, 239, 247, 248), could lead to the observed products through an intermediate carbene such as that formed



^{a} $\mathrm{R' = -CH_2CH{=}CH_2}$ or $\mathrm{-CH_2C{\equiv}CH}$ only

Figure 1.—Displacement rearrangements of propargyl halides.

by α elimination when haloallenes are treated with phenyllithium (327) (Eq 18). When the choice of solvent for such reactions favors nucleophilic substitution, acetylenes and not allenes are the main products, and to obtain best yields of allenes less polar solvents and lower temperatures should be used (507).

$$\begin{tikzcd}
\mathrm{XCR_2C{\equiv}CH} \arrow[r, "B^{\ominus}"] & {} & {} \\
\mathrm{XCR_2C{\equiv}C^{\ominus}} \arrow[r, "-X^{\ominus}"] & \mathrm{R_2C{=}C{=}\ddot{C}} \arrow[d, "R'M"] & \mathrm{R_2C{=}C{=}CHX} \arrow[l, "PhLi"'] \\
\mathrm{R_2C{=}C{=}CHR'} & \mathrm{R_2C{=}C{=}\overset{\ominus}{C}R' + M^{\oplus}} \arrow[l, "H_2O"'] & \text{(Eq 18)}
\end{tikzcd}$$

Allenic nitriles (220, 317, 417, 536), esters (142, 611, 613), and amines (246, 579, 581) have all been reported from reactions involving nucleophilic attack on propargyl halides. Usually the unrearranged acetylenic isomers are also formed, as in the synthesis of the allenic ester (XIII), required as a possible precursor of the sex attractant of the American cockroach (142).

$$\mathrm{Me_2CClC{\equiv}CH} \xrightarrow[\mathrm{EtCO_2H,\ 60^\circ}]{\mathrm{EtCO_2Ag}} \mathrm{Me_2C(OCOEt)C{\equiv}CH} + \underset{\mathrm{XIII}}{\mathrm{Me_2C{=}C{=}CHOCOEt}}$$

Rather low yields of allenic acids are obtainable by a modified Reppe reaction, in which α-haloacetylenes are treated with nickel carbonyl in buffered solution (287). If an overpressure of carbon monoxide is built up, further carbonylation is liable to occur (120).

$$\mathrm{RC{\equiv}CCH_2Cl} \xrightarrow[\text{buffered aq EtOH}]{\mathrm{Ni(CO)_4}} \mathrm{RC(CO_2H){=}C{=}CH_2} \xrightarrow[(\mathrm{R\ =\ H})]{\mathrm{CO,\ H_2O}} \mathrm{CH_2{=}C(CO_2H)CH_2CO_2H}$$

The various processes by which allenes are produced from propargyl halides by this general type of rearrangement are represented schematically in Figure 1.

b. Propargyl Alcohols

The displacement rearrangements of propargyl alcohols provide useful routes to halo- and cyanoallenes and to allenic phosphorus derivatives.

Many secondary and tertiary propargyl alcohols are converted directly into haloallenes by treatment with concentrated aqueous hydrogen halides in the presence of the corresponding cuprous halide (176, 178, 179, 250, 394). Yields are especially good when the end product is a bromoallene (70, 271, 326). Intermediate propargyl bromides, which could be formed by direct substitution and subsequently rearrange under the influence of the cuprous salt, cannot be detected by infrared spectroscopy, and the stereospecificity of the reaction suggests that direct S$_N$2' or S$_N$i' substitution is more likely. When the end product is a chloroallene, several isomers are often formed, *e.g.* (250)

$$\mathrm{RR'C(OH)C{\equiv}CH} \xrightarrow[(\mathrm{X\ =\ Cl\ or\ Br})]{\mathrm{aq\ HX,\ CuX}} \mathrm{RR'C{=}C{=}CHX}$$

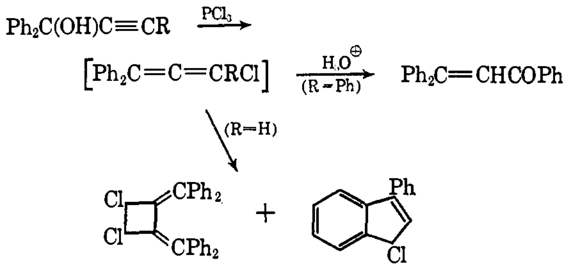
$$\mathrm{Me_2C(OH)C{\equiv}CH} \xrightarrow{\mathrm{aq\ HCl,\ CuCl}} \mathrm{Me_2C{=}C{=}CHCl} + \mathrm{Me_2CClC{\equiv}CH} + \mathrm{CH_2{=}CMeCH{=}CHCl}$$

Good yields of cyanoallenes are readily obtained in the same way, by treating substituted propargyl alcohols with acid solutions of cuprous and potassium cyanides (220). Under the same conditions unsub-

$$\mathrm{Et_2C(OH)C{\equiv}CH \xrightarrow[\text{aq HBr}]{\text{CuCN, KCN}} \underset{75\%}{Et_2C{=}C{=}CHCN}}$$

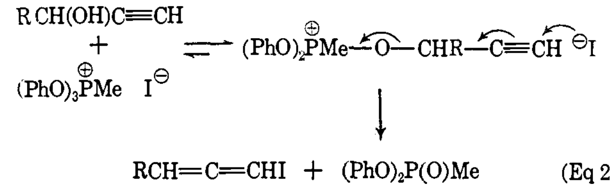
stituted propargyl alcohols give poor yields of cyanoallenes.

Chloroallenes are also produced when propargyl alcohols are treated with thionyl chloride, usually in pyridine (69, 266, 272), triethylamine (515), or an ether (69, 272); the yield of chloroallene varies with the choice of solvent, as does the steric course of the reaction. In ethers it is stereospecific, suggesting an SNi′ pathway *via* intermediate chlorosulfinates (161, 170, 272), but in the presence of bases stereospecificity is lost, perhaps because a simple SN2′ rearrangement occurs (kinetic data are lacking). Phosphorus trihalides have also been used to rearrange propargyl alcohols to chloro- and bromoallenes (152, 266, 362, 514, 555), usually in the presence of a base. If acid is present, side reactions tend to occur with either thionyl or phosphorus halides; for example, the dimerization (152, 362) and intramolecular cyclization (325, 514, 555) of diarylhaloallenes are catalyzed by traces of acid, and, if aqueous acid is present, unsaturated ketones are also produced by the Meyer–Schuster reaction (266, 325, 514, 515) (Eq 19).



(Eq 19)

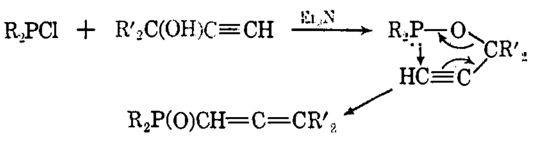
Iodoallenes are best prepared from propargyl alcohols by means of an unusual reaction with phosphonium iodides produced *in situ* from triphenyl phosphite and methyl iodide (26) (Eq 20, where R = H, alkyl, or aryl). Only small amounts of the isomeric iodoacetylenes are formed in this process.



$$\mathrm{RCH(OH)C{\equiv}CH + (PhO)_3\overset{\oplus}{P}Me\ I^{\ominus} \rightleftharpoons (PhO)_2\overset{\oplus}{P}Me{-}O{-}CHR{-}C{\equiv}CH\ {}^{\ominus}I \rightarrow RCH{=}C{=}CHI + (PhO)_2P(O)Me}$$

(Eq 20)

Propargyl alcohols react in the normal way with tervalent P-Cl compounds, but the phosphorus esters so formed rearrange on standing, or thermally, to give corresponding allenic derivatives (XIV, where R is aryl or alkoxy, and R′ is H or alkyl) of pentavalent phosphorus (82, 83, 117, 355, 468–470) (Eq 21). If a dichlorophosphine or phosphorus trichloride is used, the resulting di- or triester contains only one allene unit (83, 117).



$$\mathrm{R_2PCl + R'_2C(OH)C{\equiv}CH \xrightarrow{Et_3N} R_2P{-}O{-}CR'_2{-}C{\equiv}CH \rightarrow R_2P(O)CH{=}C{=}CR'_2}$$

(Eq 21)

XIV

A final example of displacement rearrangements undergone by propargyl alcohols is the conversion of aldehydes or ketones, often as their enol ethers, to allenic carbonyl compounds (*e.g.*, XV, where R, R′, or R″ are H or alkyl) (255, 295, 561, 562).

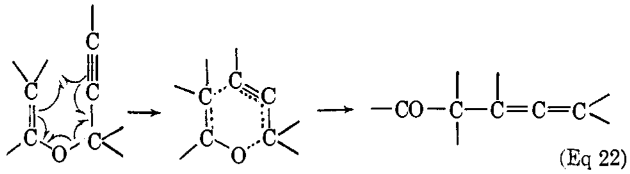
$$\mathrm{RR'C(OH)C{\equiv}CH + CH_2{=}C(OEt)R'' \xrightarrow{\text{acid catalyst}} RR'C{=}C{=}CHCH_2COR''}$$

XV

All of the above rearrangements of propargyl alcohols are shown diagrammatically in Figure 2.

4. *Intramolecular Rearrangements*

Several examples of thermal propargyl rearrangements are now known which seem to proceed through cyclic transition states. The Claisen rearrangement of propargyl vinyl ethers is such a process (71, 283) (Eq 22). This isomerization, carried out at 140–250°, provides a convenient route to unconjugated allenic aldehydes. Yields are highest when the vinyl ether is highly substituted, *e.g.* (71)

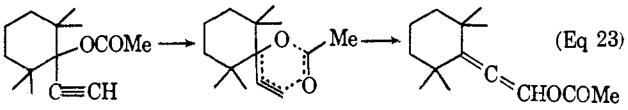


(Eq 22)

$$\mathrm{Me_2C{=}CHOCMe_2C{\equiv}CH \xrightarrow{140°,\ 15\ min} \underset{76\%}{Me_2C{=}C{=}CHCMe_2CHO}}$$

and for this reason a heterolytic mechanism is considered less likely than a series of one-electron shifts. The vinyl group may not be replaced by an aromatic ring, even when catalysts are present (71). The cyclic nature of the transition state is confirmed by the fact that the reaction is quite stereospecific when the tetrahedral carbon of the ether is asymmetrically substituted (283).

An allied type of rearrangement of highly substituted ethynyl esters leads to the migration of the acetate group, through internal displacement in a cyclic transition state (253, 324) (Eq 23).



(Eq 23)

Finally, a single example of a Cope type of isomerization has been observed to occur when diethyl isobutenylpropargyl malonate (XVI) is heated (71).

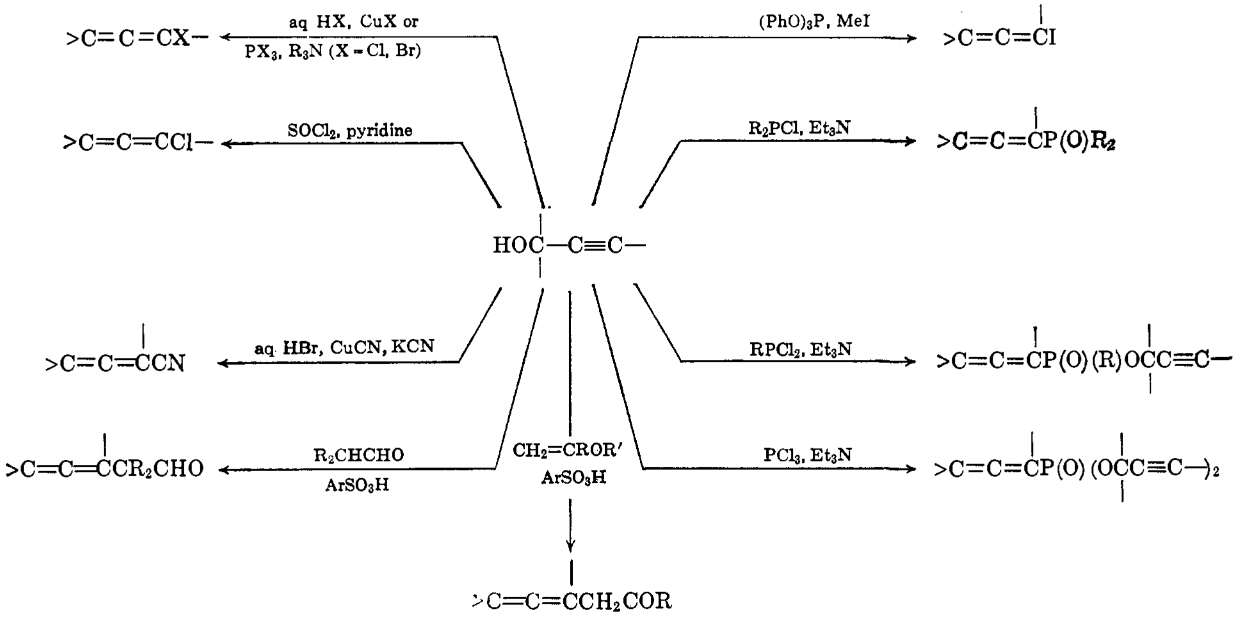
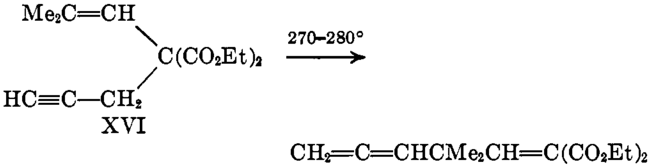


Figure 2.—Displacement rearrangements of propargyl alcohols.



XVI

$$\mathrm{Me_2C{=}CH\,C(CO_2Et)_2CH_2C{\equiv}CH}\ \xrightarrow{270\text{–}280°}\ \mathrm{CH_2{=}C{=}CHCMe_2CH{=}C(CO_2Et)_2}$$

E. BY ADDITIONS TO VINYLACETYLENES

Allenes may be formed by reactions in which 1,4 addition takes place across the conjugated system of

$$>\mathrm{C_1{=}\overset{|}{C_2}{-}C_3{\equiv}C_4{-}}\ \xrightarrow{XY}\ >\mathrm{C_1X{-}\overset{|}{C_2}{=}C_3{=}C_4Y{-}}$$

1,3-alkenynes. If 1,2 or 3,4 addition occurs, acetylenes or 1,3-dienes are produced, respectively, so that mixtures of isomers frequently result from such reactions; the choice of the reagent XY and the nature of the substituents at C_1, C_2, and C_4 may then be critical if acceptable yields of allenes are to be realized.

When the addition of XY takes place by an ionic process, the orientation of addition is usually predictable on the basis of the known polarization of vinylacetylene, bearing in mind that alkylation at C_4, and

$$\mathrm{CH_2{=}CH{-}C{\equiv}CH} \longleftrightarrow \mathrm{\overset{\oplus}{C}H_2{-}CH{=}C{=}\overset{\ominus}{C}H}$$

to a lesser extent at C_2, will oppose this polarization. This and other aspects of vinylacetylene chemistry have been adequately reviewed (428, 576).

One of the advantages of this route to allenes, especially those containing functional groups, is that the reagent XY can be varied widely. If allenic hydrocarbons are desired, XY may be hydrogen (over an iron catalyst) (92, 559); a similar reduction is also effected by complex aluminum hydrides (40, 68, 169). Lithium alkyls react to give, after hydrolysis of the initial adducts, allenes in which the alkyl radical is attached to the vinyl methylene group (433, 436, 437, 439, 475)

$$\mathrm{RC{\equiv}CCH{=}CH_2}\ \xrightarrow[\text{(ii) } \mathrm{H_3O^{\oplus}}]{\text{(i) R'Li}}\ \mathrm{RCH{=}C{=}CHCH_2R'}$$

(where R may be alkyl, alkenyl, hydroxyalkyl, or alkylthiyl, and R′ is alkyl). A useful extension of this technique allows α- or β-hydroxyallenes and allenecarboxylic acids or amides to be synthesized from alkenynes; after addition of the lithium alkyl, but before hydrolysis, other reactive substances such as carbon dioxide, ketones, epoxides, and nitriles are added (118, 119, 425–427). The synthetic possibilities are shown in Figure 3.

If haloallenes are desired, a variety of reagents may be used. Carothers and his colleagues obtained 4-halobuta-1,2-dienes (XVII, X = Cl or Br) and haloprenes by treating vinylacetylene with hydrogen chloride or bromide (107, 112, 113). A recent reinvestigation of these reactions showed that optimum conditions for haloallene formation are low temperature and a low conversion rate (153). Cuprous chloride catalyzes the reaction with hydrogen chloride, but also leads to rapid rearrangement of the chloroallene to chloroprene. Alkenylacetylenes react in a similar manner, but amounts of bromoallenes obtained tend to be lower because the addition of hydrogen bromide occurs in three ways (568).

$$\mathrm{CH_2{=}CHC{\equiv}CH}\ \xrightarrow{\text{aq HX}}\ \underset{\text{XVII}}{\mathrm{CH_2XCH{=}C{=}CH_2}} + \mathrm{CH_2{=}CHCX{=}CH_2}$$

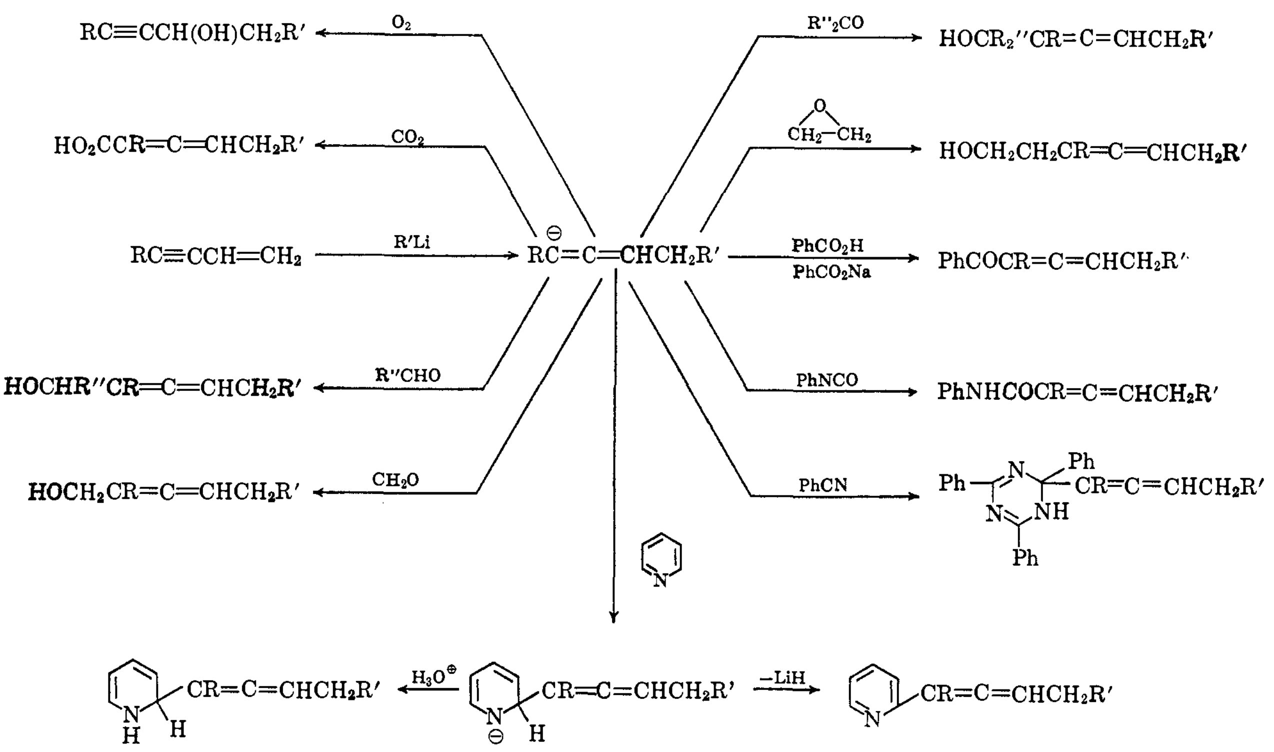


Figure 3.—Synthesis with allenic carbanions.

$$CH_2{=}CMeC{\equiv}CH \xrightarrow{\text{aq HBr}} \begin{array}{ll} CH_2BrCMe{=}C{=}CH_2 & (55\%) \\ CH_2{=}CMeCBr{=}CH_2 & (35\%) \\ CH_3CMeBrC{\equiv}CH & (10\%) \end{array}$$

The formation of conjugated halodienes in the above reactions is not without advantage, because recent work has shown that they are potentially useful for the synthesis of hydroxyallenes, undergoing rearrangement when treated with magnesium and carbonyl compounds (57, 418)

$$RCH{=}CR'CBr{=}CH_2 \xrightarrow{\text{Mg, R}''\text{CHO}} R''CH(OH)CHRCR'{=}C{=}CH_2$$

(where R = H or Me; R′ = Me; and R″ = Me or Et).

Low yields of chloroallenes are also obtained when vinylacetylenes react with aryl diazonium salts, but the main products are acetylenes formed by 1,2 addition (429, 431). On the other hand, 1,4 addition predominates when alkenynes react with chloromethyl ethers in the presence of Lewis acids (499, 582–584, 587). The chloroallenes formed rearrange rather easily to 1,3-dienes, especially in the presence of cuprous halides.

$$CH_2{=}CHC{\equiv}CH \xrightarrow[\text{BiCl}_3]{\text{ROCH}_2\text{Cl}} CH_2ClCH{=}C{=}CHCH_2OR \xrightarrow[\text{2 hr, 20°}]{\text{HCl, CuCl}} CH_2{=}CHCCl{=}CHCH_2OR$$

Dihaloallenes may be prepared by 1,4 addition of halogens to vinylacetylenes, but only when the halogen is bromine or ICl is the reaction useful for synthesis. Chlorine is too reactive and affords mainly tetrachlorides even at low temperatures, and iodine or iodine bromide add mainly to the triple bond (428, 443). Even when using bromine or iodine chloride, the amount of dihaloallene formed depends on the structure of the alkenyne; thus, whereas alkenylacetylenes ($RCH{=}CR'C{\equiv}CH$) give mainly allenes, vinylacetylene reacts with bromine to give all three possible isomers (444) (Eq 24). In the case of alkylvinylacetylenes ($CH_2{=}CHC{\equiv}CR$), addition of bromine takes place mainly at the double bond (440), unless R is a trialkylsilyl group, when 1,4 addition again predominates and silylallenes are the main products (541).

$$CH_2{=}CHC{\equiv}CH \xrightarrow[-25°]{\text{Br}_2\text{, CHCl}_3} \begin{array}{ll} CH_2BrCH{=}C{=}CHBr & (56\%) \\ CH_2{=}CHCBr{=}CHBr & (34\%) \\ CH_2BrCHBrC{\equiv}CH & (10\%) \end{array} \qquad \text{(Eq 24)}$$

Allenic amines are obtainable in up to 60% yield when vinylacetylenes are treated with secondary amines (164, 165, 577, 578) or their lithium salts (432, 434, 438, 446). The reaction was first reported by Engelhardt (165) and is exemplified by thesynthes is of N,N-dimethylbuta-2,3-dienylamine (XVIII). The

$$CH_2{=}CHC{\equiv}CH \xrightarrow[\text{100°, 10 hr}]{\text{aq Me}_2\text{NH}} \underset{\text{XVIII, 56\%}}{Me_2NCH_2CH{=}C{=}CH_2}$$

exact amount of amine should be taken, since any excess leads to rapid isomerization of the allenic amine.

If primary amines are used, the initially formed aminoallene reacts further to produce a bis(allenyl)-amine (165). Similar reactions between amines and

$$CH_2{=}CHC{\equiv}CH \xrightarrow{MeNH_2} MeNHCH_2CH{=}C{=}CH_2 \xrightarrow{C_4H_4} MeN(CH_2CH{=}C{=}CH_2)_2$$

hydroxyalkenynes have now been reported (580).

The use of a lithium amide instead of an amine enables the reaction to be effected under much milder conditions and is therefore to be preferred when the orientation of the addition is favorable (432, 434, 438, 446). In a similar fashion lithium salts of secondary phosphines add to give allenic phosphines, though these are rather unstable and rapidly polymerize when exposed to the atmosphere (435)

$$CH_2{=}CHC{\equiv}CR \xrightarrow[H_3O^{\oplus}]{Et_2MLi} Et_2MCH_2CH{=}C{=}CHR$$

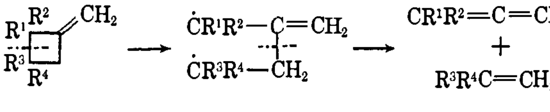
(where R is alkyl and M is N or P).

Very few examples of free-radical additions to conjugated alkenynes are known, though such reactions may well afford allenes and their derivatives. For example, it is possible to obtain good yields of allenes by the conjugate addition of two triphenylmethyl radicals to alkenynes, the radicals being produced thermally from hexaphenylethane or by the reaction of chlorotriphenylmethane with mercury (445, 448, 560), *e.g.*

$$CH_2{=}CHC{\equiv}C\text{-}t\text{-}Bu \xrightarrow[\text{reflux } C_6H_6]{Ph_3CCl,\ Hg} \underset{53\%}{Ph_3CCH_2CH{=}C{=}C\text{-}t\text{-}BuCPh_3}$$

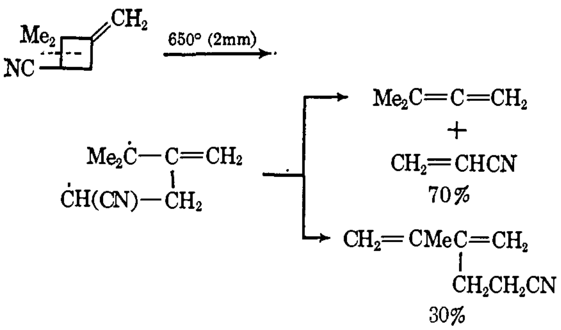
F. BY PYROLYSIS AND PHOTOLYSIS

Although most allenes dimerize and polymerize when strongly heated, there are several ways in which allenes may usefully be synthesized by pyrolysis of larger molecules, usually ring compounds. Thermal cleavage of methylenecyclobutanes yields mixtures of allenes and olefins, the initial opening of the ring taking place between the most substituted carbon atoms, perhaps because a more stable intermediate diradical is then formed (Eq 25). If the cyclobutane is suitably



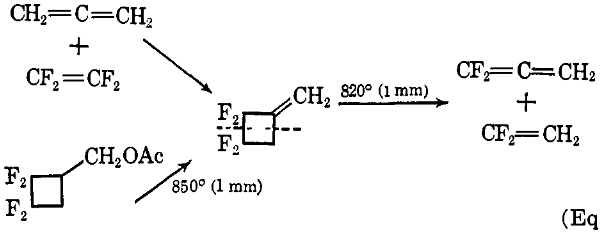
(Eq 25)

substituted, 1,3- or 1,4-dienes are formed as well as allenes and olefins, a process which may be explained on the basis of rearrangement of the intermediate diradical (156) (Eq 26).



(Eq 26)

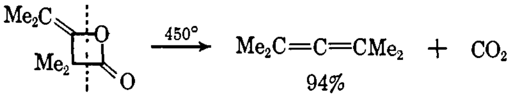
Since one way to prepare methylenecyclobutanes is the codimerization of an allene with an electron-deficient olefin, only a few useful applications of this method are known. One instance is the preparation of 1,1-difluoroallene from 3-methylene-1,1,2,2-tetrafluorocyclobutane, which may be obtained by codimerizing allene with tetrafluoroethylene (13, 121) or by the pyrolysis of the cyclic acetate (XIX) (308) (Eq 27).



XIX

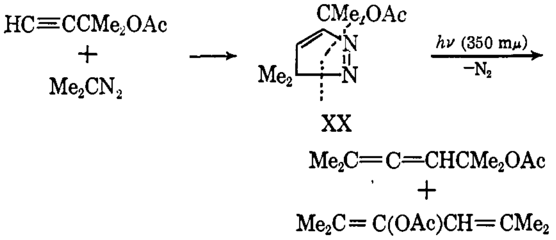
(Eq 27)

Diketene and other alkylidene β-lactones may also be cleaved thermally to allenes, the other fragment being carbon dioxide. Yields are high when the allene is highly substituted (359), but yields of allene obtained



in this way from diketene are low (8–18%) (193), although allene is one of the minor gaseous products formed during the pyrolysis of monomeric ketene (227).

An unusual way of progressing from a tertiary propargyl ester to a more highly substituted allenic ester involves the preliminary synthesis of pyrazolenines (XX), which are broken down with loss of nitrogen when photolyzed at wavelengths corresponding to their n → n* transitions (141) (Eq 28).



(Eq 28)

Certain esters (9, 301, 525) and salts (592) of carboxylic acids have been reported to yield allenes on pyrolysis, though in small amounts. Similarly, bis(hydroxytrimethylammonium)alkanes decompose to allenes on pyrolysis (257).

$$\mathrm{Me_3\overset{\oplus}{N}(\overset{\ominus}{O}H)CH_2CHEt\overset{\oplus}{N}Me_3\overset{\ominus}{O}H} \xrightarrow{(-\mathrm{Me_3N},\ -\mathrm{H_2O})} \underset{56\%}{\mathrm{CH_2{=}C{=}CHCH_3}} + \underset{44\%}{\mathrm{EtC{\equiv}CH}}$$

Such reactions are rarely useful, since the precursors are not readily available and isomeric products are also formed.

G. BY THE WITTIG OLEFIN SYNTHESIS

The Wittig synthesis of olefins may be applied to the synthesis of allenes from ketenes (116, 594, 600), Schiff's bases (62), or acyl halides (61). The most general method appears to be the treatment of phosphinemethylenes with acyl halides, *e.g.*

$$\begin{matrix}\mathrm{C_5H_{11}CH_2COCl} \\ + \\ \mathrm{Ph_3P{=}CMeCO_2Et}\end{matrix} \longrightarrow \underset{80\%}{\mathrm{C_5H_{11}CH{=}C{=}CMeCO_2Et}}$$

H. INDUSTRIAL METHODS

Although not attractive for laboratory syntheses of allene hydrocarbons, prototropic or thermal catalytic rearrangement of alkynes are of potential value as industrial processes, since they are adaptable to large-scale continuous operation. Catalysts cited for the partial conversion of propyne into propadiene include active carbon (126), Floridin (a siliceous sand) (527), alumina (124, 125), and aluminates (143). Calculations based on spectroscopic data and heats of hydrogenation show that the percentage of propadiene at equilibrium with propyne increases with rising temperature (195), but a practical limit of about 350° is imposed by the onset of dimerization and polymerization.

Numerous reports testify to the formation of allenes in small amounts during the flow pyrolysis of alkanes (235, 421, 477), alkenes (11, 216, 236, 300, 397, 486, 505, 552), and halogen compounds (79, 215, 556, 557), and during continuous dehydrohalogenation of aliphatic dihalides and halopropenes (22, 558). Such processes may offer the best hopes for large-scale synthesis of allenes, should this become desirable.

III. PHYSICAL PROPERTIES OF ALLENES

A. BONDING AND STEREOCHEMISTRY

Before the general behavior of allenes can be understood properly, their peculiar geometry, which is a consequence of the cumulated bond system, must be appreciated. A molecular orbital treatment of the allene molecule correctly predicts that the most stable bonding arrangement involves two mutually perpendicular π bonds, with the central carbon atom (sp-hybridized) joined in a straight line to the two terminal carbon atoms (sp^2-hybridized) (252, 473, 504).

As a result, only the hydrogen atoms at one end project above and below the plane containing the rest of the molecule (Figure 4), and the two π bonds are not conjugated with each other because they are not coplanar. In a completely coplanar arrangement,

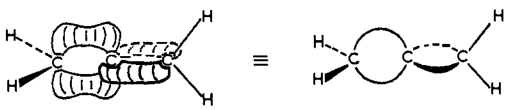
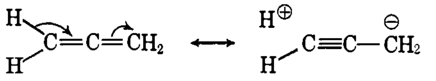


Figure 4.—Arrangement of allenic π bonds.

Figure 5.—Bonding in planar allene diradical.

the stabilization by π bonding would be around 2.4 ev lower (191), and in such a molecule there would be two unpaired electrons (Figure 5).

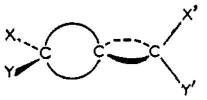
Exact dimensions for the allene molecule (C=C = 1.309 −1.312 A; C—H = 1.061 − 1.082 A; H-C-H bond angle = 116–118°) have been determined from Raman spectra (547), from study of infrared perpendicular vibration bands (380, 409, 480), and by electron diffraction (10). Earlier, higher values of the double-bond length therefore seem to be in error (171, 419). The contraction of the double bond in allene, relative to that in ethylene (1.33 A), is in accord with results obtained for other cumulene compounds such as ketene. It is considered to indicate the occurrence of hyperconjugation (σ–π overlap) which suggests partial triple-bond character (289, 464, 473, 508) (Eq 29). Such σ–π overlap is particularly favorable in



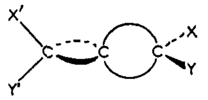
$$\mathrm{H_2C{=}C{=}CH_2} \longleftrightarrow \mathrm{H^{\oplus}}\quad \mathrm{HC{\equiv}C{-}\overset{\ominus}{C}H_2} \qquad \text{(Eq 29)}$$

allene, because the C–H σ bonds at one end lie in the plane of the C=C π bond at the other end of the molecule (Figure 4). The dimensions and bond angles of buta-1,2-diene have also been determined (339), and in this case a more normal value was obtained for the double-bond length.

The stereochemical consequences of the bonding in allenes were predicted by van't Hoff (575), who foresaw that optical isomerism due to a lack of molecular symmetry is possible if the terminal carbon atoms bear two different substituents. Thus, the mirror images XXI and XXII differ even if X = X′ and Y = Y′; they become identical only if X = Y (or X′ = Y′). Experimental proof of this prediction proved so difficult (329, 619) that as recently as 1930 the suggestion that allenes adopted planar configurations was still being made (172). Since then, however, van't Hoff's conclusions have been amply verified by meas-



XXI



XXII

urements of the dipole moments of tetraarylallenes (46) and bromoallene (496), and by the resolution of many asymmetric allenes.

Two general approaches have been adopted in the isolation of enantiomers of optically active allenes. The most obvious is the synthesis of racemic mixtures, followed by their resolution by such standard procedures as reaction with optically active acids or bases (310, 311, 609). Thus, the allenic acid (XXIII), obtained from 2-bromo-oct-3-yne by treatment with magnesium and carbon dioxide, was resolved by separation of its strychnine salts (609).

$$n\text{-BuC}\equiv\text{CCHBrMe} \xrightarrow{\text{Mg, CO}_2} \underset{\substack{\text{XXIII} \\ [\alpha]^{25}\text{D} \pm 30.7^\circ}}{n\text{-BuC(CO}_2\text{H)=C=CHMe}}$$

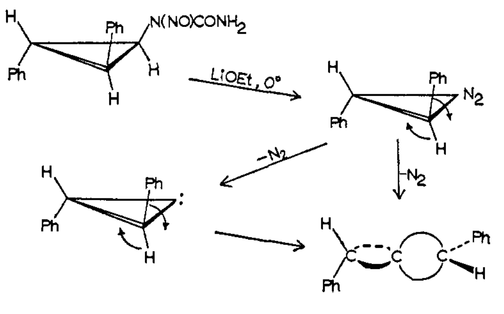
A more direct approach is that of stereospecific synthesis, pioneered by Maitland and Mills in their dehydration of the unsaturated alcohol (XXIV, Ar = α-naphthyl) with (+)- or (−)-camphor-10-sulfonic acid, whereby they obtained in each case a predominance of one stereoisomer of the tetraarylallene (351, 352). The allene has a very high specific rotation and

$$\underset{\text{XXIV}}{\text{ArCPh=CHC(OH)PhAr}} \xrightarrow[\text{sulfonic acid}]{(+)\text{-camphor-}} \underset{[\alpha]\text{D} +437^\circ}{\text{ArCPh=C=CPhAr}}$$

only racemizes at temperatures above 160°.

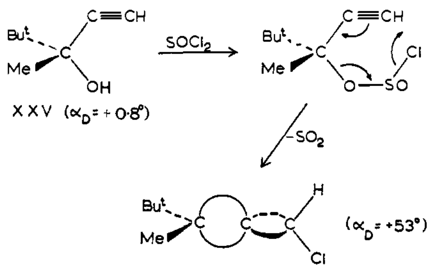
Other stereospecific syntheses of allenes include the rearrangement of 1,3-diarylacetylenes on columns of alumina coated with optically active base (264), the displacement rearrangement reaction of propargyl alcohols and thionyl chloride (161, 170), thermal rearrangements of propargyl vinyl ethers (169, 283), reduction of conjugated alkenynes by highly hindered complex aluminum hydrides (169), and the Wittig olefin synthesis (567). A particularly interesting instance is the preparation of (+)-1,3-diphenylallene ($[\alpha]^{24}$D +797°) by the decomposition of (−)-*trans*-2,3-diphenyldiazocyclopropane (294). The steric course of this reaction is known with precision, because the absolute configuration of both the diazo compound (293) and the allene formed (365) have been established, in the latter case by the study of its optical rotary dispersion (Scheme V).

SCHEME V



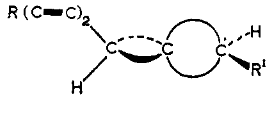
The absolute configuration of several optically active allenes has been determined, usually by making the allenic enantiomer from a compound of known absolute configuration by a stereospecific synthesis (168, 169, 283, 567). Thus, (+)-1-chloro-3,4,4-trimethylpenta-1,2-diene has been prepared (170) from the dextrorotatory propargyl alcohol (XXV), which has been shown to have *S* configuration by application of Brewster's rules (93, 161) and by its oxidation to (*S*)-(+)-*t*-butyllactic acid (168). When the propargyl alcohol is treated with thionyl chloride in an ether, formation of the chloroallene follows by SNi′ substitution in the intermediate chlorosulfinate; the dextrorotatory allene must therefore have the *R* configuration shown in Scheme VI.

SCHEME VI



An SN2′ attack by chloride ion on the same side as the -OSOCl residue, which could lead to the same result, seems less likely because stereospecificity is lost when a tertiary amine is added to the reaction mixture (170).

Deductions regarding the absolute configuration of allenes have also been made on the basis of their conversion to compounds of known geometry (4, 168) and by measurements of optical rotatory dispersion (209, 365). A simple rule for predicting the absolute configuration of an allene from its direction of optical rotation was proposed recently (348). When applied to naturally occurring allenes, most of which are fungal metabolites with the rigid diyne–allene system (section I.D), it appeared that dextrorotatory isomers have the *S* configuration (XXVI, R = H or Me) in almost all cases (348).



XXVI

The application of rules of configurational nomenclature to allenes and other aspects of their stereochemistry have been thoroughly discussed by Eliel (162).

B. PHYSICAL CONSTANTS

A recent tabulation of the principal constants of a large number of allene hydrocarbons (430) permitted the following generalizations to be made: (i) allenes boil at higher temperatures than paraffins with the same skeleton, and branching of the chain increases the boiling point even further; (ii) allenes have higher refractive indices than the corresponding acetylenes; (iii) allenes show very small exaltations of molar refraction of 0.5 to 1.0 unit.

The negligible exaltation of molar refraction (256, 430) and the slight exaltation of diamagnetic susceptibility (38, 231, 319) shown by allenes confirm the predictions made on the basis of molecular orbital theory that no conjugation or delocalization of electrons occurs between the two π bonds, which are mutually perpendicular. However, alkenylallenes in which one of the allenic double bonds is conjugated with a substituent double bond do show the exaltation of refraction (430) and diamagnetic susceptibility (319) typical of conjugated compounds.

C. THERMOCHEMICAL DATA

Thermochemical measurements, such as heat capacities (304, 305, 309, 498, 538, 549), heats of combustion (309, 465–467), heats of hydrogenation (306, 467), and heats of isomerization (465–467), have been reported only for propadiene and a few of its homologs. Vapor pressure curves have been obtained (232, 251, 323) and virial coefficients estimated (146, 497). From such measurements and from data obtained by spectroscopic techniques, various thermodynamic functions have been calculated; they include entropies (16, 342, 498), free energies (309, 342, 498), and enthalpies (21, 309, 342, 466, 467, 498) of formation. The position of equilibrium between propadiene and propyne at various temperatures has also been predicted and verified by experiment (195).

Comparison of the heats of hydrogenation and combustion of allenes with those of isomeric 1,3- and 1,4-dienes leads to the conclusion that compounds such as allenes, with cumulated double bonds, are less stable than those with isolated double bonds, and that conjugated 1,3-dienes are the most stable isomers (306, 465, 467, 498); in fact, allenes show negative departures from additivity of heats of formation (21). The difference in the C–H bond dissociation energy between propadiene and propyne has been calculated from their heats of formation, on the assumption that dissociation leads to the same radical

$$HC{\equiv}C{-}\dot{C}H_2 \longleftrightarrow HC{=}C{=}CH_2$$

suggesting that a propargyl C–H bond is 1.7 kcal mole^{-1} stronger than an allenic C–H bond (553). Heats of hydrogenation have also been used to calculate the bond energy of the allenic double bond (213), the value being 133.97 kcal mole^{-1}. The rather high bond energies of allenes, satisfactorily explained by a molecular orbital treatment (307), have led to their consideration as welding gases (604).

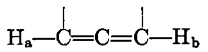
D. MASS SPECTRA

The first ionization potentials of allene and its lower homologs have been determined by electron impact in a mass spectrometer (122, 123, 454, 455); they are all close to 10 ev, in good agreement with theoretical values (414, 548). The first ionization potential of propadiene (10.16 ev) lies between that of propene (9.94 ev) and propyne (10.32 ev), suggesting that the π electrons in the allene are in molecular orbitals of intermediate energy (122), and lending weight to the suggestion that σ–π overlap leads to partial triple-bond character. The first ionization potential of buta-1,2-diene is slightly lower, perhaps because the polarity of the $CH_3{-}CH{<}$ bond tends to repel nearby π electrons.

The mass spectra of simple allene hydrocarbons show the following general trends (455): (1) the intensity of the parent ion decreases with increasing molecular weight; (2) breaking of carbon–carbon single bonds is easier than C–H rupture and is accompanied by migration of hydrogen or further single-bond fission; (3) ions containing three to five carbon atoms predominate. Further detailed discussion of the mass spectra of allenes is given by Petrov and Federova in their review (430).

E. NUCLEAR MAGNETIC RESONANCE SPECTRA

The proton magnetic resonance spectra of a number of allenes have been reported and are of considerable interest. Allenes of the type



$$H_a{-}\overset{|}{C}{=}C{=}\overset{|}{C}{-}H_b$$

show exceptionally large coupling constants between the protons H_a and H_b (6–7 cps), in spite of their separation by four bonds (190, 269, 326, 353, 461, 483, 537, 597). This is one of the largest long-range couplings so far observed and is comparable with the coupling through three bonds observed in acetylene (9 cps). The large coupling is attributed to σ–π interaction between the electrons of the C–H bond and the double bond furthest from it, as already mentioned in relation to the bond length and ionization potential (297, 298). Moreover, the rigid nature of the allene bond will minimize steric hindrance of resonance (489). A preliminary study of the effect of substituents on the value of the four-bond coupling constant has been made (312).

The position of the vinyl proton resonance in allenes is to higher field than in simple olefins and indicates that the central sp-hybridized carbon atom exerts a long-range shielding of the terminal protons. Solvent effects on the value of the shift are apparently negligible (502). ^{13}C resonance spectra have also been examined for some allenes and compared with those of other olefinic compounds (200). The central carbon of the allenic system resonates at −15 ppm (from CS_2), a frequency well removed from that of the terminal nuclei (100–125 ppm) or from that observed for an acetylenic sp-hydridized carbon nucleus (*ca.* 115 ppm). These observations have been related to theory by Pople (457).

Magnetic nonequivalence has been observed in the pmr spectra of allenic ethers and thioethers of the type $PhCH{=}C{=}CR{-}Y{-}CH_2Me$, where R is Me or *i*-Pr and Y is O or S (361). Their molecular asymmetry is revealed, for example, by the observation of ABX_3 patterns for the methylene hydrogens of the ethyl group, the difference in chemical shift being greater when Y is oxygen.

F. ELECTRONIC SPECTRA

Very few thorough studies of the ultraviolet spectra of allenes have been undertaken, no doubt because the lower hydrocarbons such as propadiene and buta-1,2-diene do not show any intense absorption maxima in the 200–400-mμ range (249). Molecular orbital calculations (414, 508) show that the first allowed π–π^* transition will have an energy difference of 7.05 to 8.90 ev in propadiene; it should therefore appear in the far-ultraviolet. This conclusion agrees with experiment, since there is an intense absorption at 1710 A (7.25 ev) in the vacuum ultraviolet spectrum of the allene (550), which is accompanied by weak, continuous absorption in the range 1770–2030 A. Strong, discrete bands are also observed between 1200 and 1550 A, which belong to two Rydberg series converging to a limit at 10.19 ev, a value close to the ionization potential measured by mass spectrometry (122).

Substitution of the hydrogens of allene by alkyl groups shifts the ultraviolet maximum to longer wavelength (1780–1830 A) (288, 550), as is the case with olefins. Pure α-haloallenes show a maximum at 2000–2070 A, accompanied by a shoulder or a maximum when the halogen is bromine (at 2150–2270 A) or iodine (at *ca.* 2390 A), thought to be due to nonbonded interactions between the halogen and a π bond (326). In tetrafluoroallene a single maximum is observed at 2090 A (34).

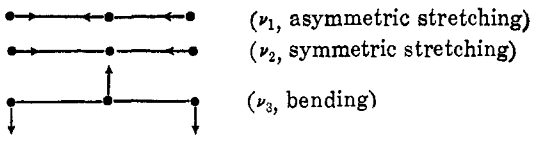
Cyclopropylideneallenes show a sharp maximum at 2030–2040 A (ϵ 2400), due possibly to overlap between the bent σ bonds of the ring and the π bond system of the allene (327). Alkenylallenes (68, 281, 540), alkynylallenes (24, 25, 208, 281), arylallenes (264, 265, 290), and α-cyanoallenes (220), in which the allenic π bond is conjugated with a substituent π bond, all show intense ultraviolet absorptions typical of conjugated systems. Most of the naturally occurring allenes so far known contain the diyne–allene chromophore ($RC{\equiv}CC{\equiv}CCH{=}C{=}CHR'$), readily characterized by the presence of about six intense absorptions in the range 2000–3000 A (63, 96).

G. VIBRATIONAL SPECTRA

The vibrational spectra of allenes are of considerable interest because of the simple molecular structure. Allene belongs to the D_{2d} point group; four of its fifteen ($3N - 6$) vibrational modes belong to the doubly degenerate E class, so that eleven fundamental vibrational frequencies are to be expected. These have all been observed and assigned to their particular vibrations, together with many combination and difference bands. The Raman spectra of allene and deuterioallene (95, 167, 342, 346, 547) have been reported and used to calculate molecular dimensions and vibrational force constants (547, 564). Similarly, their infrared spectra have been recorded both on prism (167, 342, 347, 563) and grating (171, 378, 411, 481, 516) spectrometers, and rotational fine structures have been observed for some of the bands (347, 378, 410, 411). A useful table of Raman and infrared assignments for allene is given by Blanc and co-workers (72), together with a discussion of the crystal structure of the compound at 95°K.

From such spectroscopic data the molecular geometry (380, 409, 480), force constants (84), and bond dissociation energies (400) of propadiene have been calculated and compared with theoretically predicted values (139, 140, 589). More limited studies have been made for monohaloallenes (405) and buta-1,2-diene (16, 482, 551).

The organic chemist is mainly interested in applying infrared spectroscopy to the analysis of product mixtures, and to this end certain generalizations may prove helpful. To a first approximation the allenic bond system in a symmetrically substituted allene may be regarded as a triatomic linear vibrator, for which three vibrational frequencies are to be expected, two of the possible modes being degenerate.



The symmetric stretching mode (ν_2) involves no change in dipole moment, so that it will not be infrared active in symmetrically substituted allenes, though it should appear in their Raman spectra just as it does in that of allene (95, 547) at *ca.* 1074 cm^{-1}. In asymmetrically substituted allenes, this mode is also active in the infrared, appearing as a doublet (*ca.* 1100–1130 cm^{-1}) in the spectra of alka-1,2-dienes (450). The bending vibration (ν_3), which occurs in allene (72, 347) at 354 cm^{-1}, is useless for identification purposes since it is usually masked by stronger bands. For such purposes the asymmetric stretching mode (ν_1) is much to be preferred; it is generally observed as a strong infrared band in the 1930–1980-cm^{-1} region. The intensity of this band should be greatest when the allene is symmetrically substituted, because the change in dipole moment is then at a maximum, but this is not entirely in accord with experiment (191, 192, 430, 607). Commonly called the allene band, its frequency is not greatly affected by terminal substitution by alkyl (450), acyl (49, 51), vinyl (281), aryl (265, 266), or alkynyl groups (25, 281), or by terminal cyanide (220) or halogens other than fluorine (26, 243, 326, 492–494). However, it is displaced to shorter wavelength by terminal fluorine substitution, as in 1,1-difluoroallene (2020 cm^{-1}) (77) and tetrafluoroallene (2065–2070 cm^{-1}) (34, 261), and to a lesser degree by fusing the allene system to a cyclopropane ring (1980–2025 cm^{-1}) (327, 518). It is unaffected by incorporating the allene bond system into a carbocyclic ring (384, 386). When bound to a metal such as magnesium or zinc, this asymmetric stretching mode appears at 1880–1910 cm^{-1} (206, 463). It is split into a doublet (separation 20–50 cm^{-1}) when certain electron-withdrawing substituents are present, as in (287, 607) $CH_2{=}C{=}CRCO_2H$, although this generalization has recently been challenged (327).

Another band useful for diagnostic purposes is that due to the out-of-plane deformation mode of the $=CH_2$ group, which occurs in olefins at *ca.* 890 cm^{-1}; in alka-1,2-dienes this band is observed at *ca.* 850 cm^{-1} (607); and in the spectra of conjugated allenic ketones it appears at 860 cm^{-1} (51). A similar deformation mode occurs at 870 cm^{-1} in the infrared spectra of nonterminal allenes with vinyl C–H bonds (430). Other bands which have been suggested for the identification of allenes are C–H frequencies at *ca.* 3000 cm^{-1} (450, 518), C–H deformations (447), and an overtone of the symmetric stretching mode at *ca.* 550 cm^{-1} (450). Some of these points are discussed in more detail elsewhere (191, 607).

IV. REACTIONS OF ALLENES

This section is largely confined to those reactions of allenes which directly involve the unsaturated bond system, and the behavior of functional groups elsewhere in the molecule will be considered only if the cumulene bond is also affected.

The following simple generalizations may be made concerning the chemical behavior of allenes and result from their bonding and stereochemistry, already discussed.

(1) A relatively high degree of unsaturation and a readily accessible π-bond system lead to facile addition reactions.

(2) Electrophilic additions are particularly favored.

(3) Because of the geometry and polarizability of the π bonds, the orientation of ionic and free-radical additions is strongly affected by groups already attached to the cumulene bond. Thus, in propadiene the central carbon atom is electrophilic, whereas in tetramethylallene the same carbon is nucleophilic.

(4) Allenes show a pronounced tendency to undergo ring-forming reactions such as dimerization.

(5) Rearrangements to isomeric acetylenes and conjugated dienes are common, and their occurrence during addition and substitution reactions has always to be borne in mind as a possible complication.

(6) There is little interaction between the two π bonds, although one or both of them may conjugate with the π bonds of adjacent groups, as in α-ketoallenes and vinylallenes.

A. OXIDATION

Reagents which oxidize olefins will also attack allenes, and their degradation to carbonyl compounds is readily effected by potassium permanganate, ozone, or chromic acid.

Reactions between allenes and potassium permanganate probably occur by initial formation of unstable glycols, which either react at once with more oxidant or first rearrange to α-hydroxy ketones (Eq 30 and 31).

$$\begin{tikzcd}
R_2C{=}C{=}CR'_2 \arrow[r, "KMnO_4,\ H_2O"] & {} & \\
{[R_2C(OH)C(OH){=}CR'_2]} \arrow[r, "KMnO_4"] \arrow[d] & R_2CO + CO_2 + R'_2CO & \text{(Eq 30)} \\
{[R_2C(OH)COCHR'_2]} \arrow[r, "KMnO_4"] & R_2CO + R'_2CHCO_2H & \text{(Eq 31)}
\end{tikzcd}$$

Different products are thus formed according to which pathway is followed, and this depends in turn upon the conditions. Alkaline (112, 249) or concentrated aqueous permanganate (2, 570) or permanganate in acetic acid (20), pyridine (352), and acetone (2, 495) lead to reaction as in Eq 30. Aldehydes are not isolated under these conditions but are converted to the corresponding acids, *e.g.* (2)

$$PhCH{=}C{=}CHMe \xrightarrow{\text{aq } KMnO_4} PhCO_2H + CH_3CO_2H$$

Such forcing conditions are to be preferred when the purpose of oxidation is to determine the structure of the allene, because an isomeric acetylene (for example, $PhCH_2C{\equiv}CCH_3$) would give different products. When very dilute aqueous permanganate is used, reaction proceeds as in Eq 31, *e.g.* (180)

$$Me_2C{=}C{=}CH_2 \xrightarrow{1\%\ KMnO_4} [Me_2C(OH)C(OH){=}CH_2] \longrightarrow Me_2CO + CH_3CO_2H$$

Such products reveal that a more alkylated double bond is hydroxylated preferentially, in accordance with an electrophilic addition mechanism.

Ozone cleaves allenes smoothly to carbonyl compounds and carbon dioxide; the detection of carbon dioxide serves as a simple diagnostic test for the presence of an allene or similar cumulene compound. In partially substituted allenes the carbonyl fragments are aldehydes, which may be isolated under reducing conditions (384) or converted *in situ* to acids (180).

$$RCH{=}C{=}CHR' \xrightarrow{O_3} RCHO + CO_2 + R'CHO \xrightarrow{[O]} RCO_2H + R'CO_2H$$

Some doubt has recently been cast on the reliability of this widely used method for confirming the structure of allenes. When the volatile fragments from the ozonolysis of three 1,2-dienes (XXVII, R = Et, *n*-Pr, *n*-Bu) were examined by gas chromatography, rather large amounts of acetaldehyde were detected, in addition to formaldehyde (535). The authors

$$\underset{\text{XXVII}}{RCH{=}C{=}CH_2} \xrightarrow{O_3} RCHO + CO_2 + \underset{40\text{–}53\%}{CH_2O} + \underset{32\text{–}40\%}{CH_3CHO}$$

concluded that partial rearrangement of the allenes to alk-2-ynes occurs during ozonolysis. This is not the only instance of anomalous analytical results being obtained by ozonolyzing acetylene–allene mixtures (32, 384).

A few instances of peracid oxidation of allenes have been reported (80, 413), and one group has described the use of lead tetraacetate (320). Hydroxy ketones are obtained in both cases and, in accord with an electrophilic mechanism, alkylated double bonds are attacked preferentially, *e.g.*

$$Me_2C{=}C{=}CH_2 \xrightarrow{AcOOH} Me_2C(OH)COCH_3$$

B. REDUCTION

Catalytic hydrogenation of allenes to saturated compounds has been used extensively for structural determinations, although it fails to distinguish allenes from isomeric acetylenes or conjugated dienes. Convenient catalysts include various forms of platinum (3, 20, 40, 83, 249) and palladium (165, 192, 310, 315), but iron is ineffective (92, 559). Certain polyarylallenes resist catalytic reduction altogether, or require very vigorous conditions (310, 495). It seems unlikely that such compounds are resistant through steric hindrance, because branched alkylallenes take up the first molecule of hydrogen more rapidly than unbranched isomers (33).

The presence of traces of allenes adversely affects the rate and degree of polymerization of olefins and conjugated dienes (12, 344); as a result, numerous catalysts have been developed for selective partial hydrogenation of allenes (14, 30, 94, 163, 198, 217, 233, 314, 340, 484, 596). In some of these partial reductions, addition of hydrogen occurs mainly at the least substituted double bond (249, 254, 280, 301, 373). Thus, hexa-1,2-diene is hydrogenated over Raney nickel to a mixture of hex-1-ene and (mainly) hex-2-ene (249). Such reductions are frequently stereospecific, *e.g.* (280)

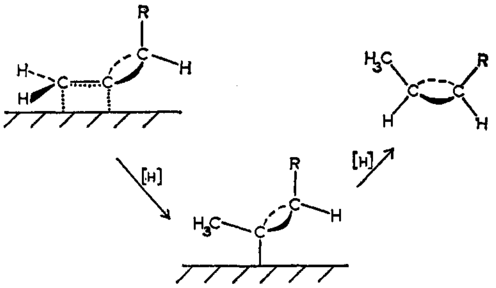
$$CH_2{=}C{=}CHCO_2H \xrightarrow{H_2,\ Pd\text{–}CaCO_3} cis\text{-}CH_3CH{=}CHCO_2H$$

Similarly, *cis*-cycloolefins are the main products of the reduction of cyclic allenes over palladium catalyst (204, 383).

A careful study of the partial hydrogenation of buta-1,2-diene over palladium on alumina has shown that terminal addition predominates, but is not wholly stereospecific (373). Probably the allene becomes attached to the surface mainly at the least hindered double bond, and attack by hydrogen then occurs mainly at the terminal, surface-bound carbon atom (Scheme VII).

$$MeCH{=}C{=}CH_2 \xrightarrow{H_2,\ Pd\text{-}Al_2O_3} \underset{cis,\ 53\%;\ trans,\ 7\%}{MeCH{=}CHCH_3} + \underset{40\%}{MeCH_2CH{=}CH_2}$$

SCHEME VII



In contrast to catalytic hydrogenation, partial reduction of acyclic allenes by metals in liquid ammonia leads to nonstereospecific addition of hydrogen, mainly at the most hindered double bond (148), but cyclic allenes again give *cis*-cycloolefins preferentially (204, 517).

$$Me_2C{=}C{=}CHMe \xrightarrow{Na,\ NH_3} \underset{trans,\ 48\%;\ cis,\ 34\%}{Me_2CHCH{=}CHMe} + \underset{18\%}{Me_2C{=}CHCH_2Me}$$

Recently it was found that when tetraphenylallene is treated with sodium in ether at temperatures greater than −30°, and the resulting red solution quenched with deuterium oxide, 3-deuteriotetraphenylpropene is formed (154). It was suggested that an initially formed dianion rapidly abstracts a proton from ether. When other alkali metals are used, unusual rearrangement products are isolated.

$$Ph_2C{=}C{=}CPh_2 \xrightarrow[\text{ether}]{Na} [Ph_2C{=}CH\overset{\ominus}{C}Ph_2 \cdot \overset{\oplus}{Na}] \xrightarrow{D_2O} Ph_2C{=}CHCDPh_2$$

The allene bond is unaffected by lithium aluminum hydride or zinc–copper couple reduction, which fortunately permits these reagents to be used for the synthesis of allenes by the reduction of acetylenic or allenic halides (23, 274, 275), allenic ketones (37, 52, 58), and certain conjugated alkenynes (40, 68). Butadienoic acid and its esters are exceptions to this rule, being more susceptible to nucleophilic attack, and are reduced by lithium aluminum hydride at the conjugated double bond (280).

$$CH_2{=}C{=}CHCO_2R \xrightarrow{LiAlH_4} CH_2{=}CHCH_2CH_2OH$$

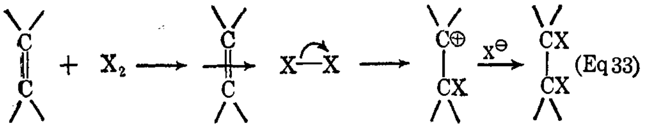
C. IONIC ADDITIONS

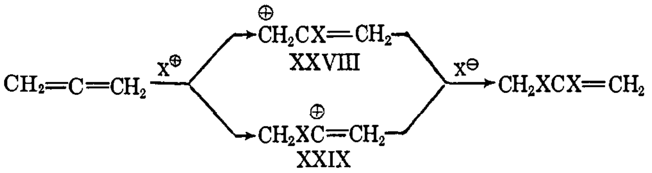
1. *Halogenation*

Even under mild conditions most allenes react rapidly with chlorine or bromine to form 2,3-dihalopropenes, and then more slowly with a second molecule of halogen, *e.g.* (420) Eq 32. Only certain polyarylallenes appear to resist the initial addition (374, 593), but saturation often requires more forcing (*e.g.*, free-radical) conditions, especially for polyfluoroallenes (34).

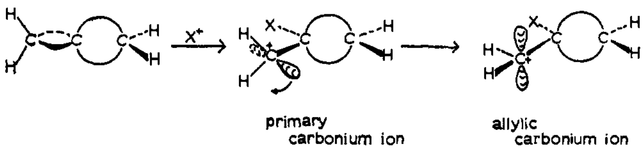
$$CH_2{=}C{=}CH_2 \xrightarrow[KBr,\ AcOH]{Br_2} CH_2BrCBr{=}CH_2 \xrightarrow[KBrO_3,\ H_3O^{\oplus}]{Br_2} CH_2BrCBr_2CH_2Br \quad \text{(Eq 32)}$$

The commonly accepted ionic mechanism for the addition of halogens such as bromine and chlorine to a double bond involves initial attack by a cation to give, *via* a π complex, a carbonium ion which reacts with halide ion or halogen molecule (Eq 33). The application of such a mechanism to the halogenation of allene is complicated by the possible intervention of two carbonium ions (XXVIII and/or XXIX), the relative stabilities of which are not easily predicted. Carbonium ion XXVIII is not necessarily allylic, because of the initially mutually perpendicular orientation of the two π bonds in allene; it will only gain the resonance stabilization which is a characteristic feature of allyl carbonium ions if the final attack by halide ion is sufficiently delayed to permit a 90° rotation of the electron-deficient end group (Scheme VIII).





Scheme VIII



It has been claimed that allene reacts with a mixture of bromine and chlorine under ionic conditions (*i.e.*, $^{+}$Br–Cl^{-}) to give only 2-bromo-3-chloropropene (420). If this is correct it suggests that the more stable carbonium is XXVIII (X = Br), but this need not necessarily mean that allylic stabilization is achieved.

Further evidence on this problem is provided by some careful studies of the halogenation products of unsymmetrically substituted allenes (185, 186). It is found that 1-alkylallenes (XXX, R^1 = alkyl; R^{2-4} = H), 1,1-dialkylallenes (XXX, $R^{1,2}$ = alkyl; $R^{3,4}$ = H), and certain 1,3-dialkylallenes (XXX, $R^{1,3}$ = alkyl; $R^{2,4}$ = H; $R^1 > R^3$), all afford 1,2-dihalides (XXXII) preferentially. Presumably such reactions proceed *via* carbonium ion XXXI, which, even if there is insufficient time for 90° rotation of the end group, is likely to be the most stable intermediate when R^1 and R^2 are more electron releasing than R^3 and R^4. In fact, there is evidence to suggest that final attack by halide precedes any rotation of the end group. The dibromide obtained by low-temperature bromination of 3-methylbuta-1,2-diene undergoes rearrangement at 20°, almost certainly by ionization to an allylic carbonium ion (186, 322) (Eq 34).

$$\underset{\text{XXX}}{R^1R^2C{=}C{=}CR^3R^4} \xrightarrow{X^{\oplus}} \underset{\text{XXXI}}{R^1R^2\overset{\oplus}{C}CX{=}CR^3R^4} \xrightarrow{X^{\ominus}} \underset{\text{XXXII}}{R^1R^2CXCX{=}CR^3R^4}$$

$$Me_2C{=}C{=}CH_2 \xrightarrow[-10°]{Br_2,\ CHCl_3} \underset{\text{nonallylic}}{Me_2\overset{\oplus}{C}{-}CBr{=}CH_2} \xrightarrow[\text{fast}]{Br^{\ominus}}$$

$$Me_2CBrCBr{=}CH_2 \xrightarrow[-Br^{\ominus}]{20°} \underset{\text{allylic}}{Me_2\overset{\delta+}{C}{\cdots}CBr{\cdots}\overset{\delta+}{C}H_2} \xrightarrow{Br^{\ominus}}$$

$$Me_2C{=}CBrCH_2Br \quad \text{(Eq 34)}$$

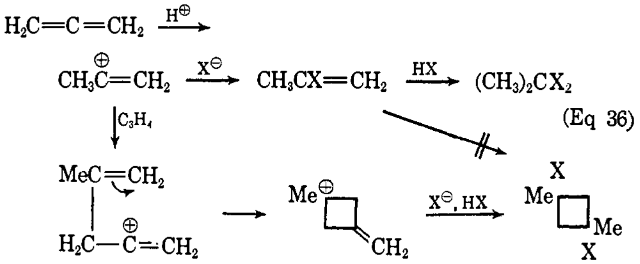
In some cases substantial amounts of by-products are formed during halogenation; chlorination of allene in solution gives as much 3-chloropropyne as 2,3-dichloropropene (420), and bromination at high temperatures also leads to complex product mixtures, presumably by free-radical processes (335).

2. *Other Electrophilic Additions*

Addition reactions of olefins with reagents of the type HX, where X is F, Cl, Br, I, OH, OEt, etc., are generally considered to proceed by initial protonation of the double bond. The orientation of such additions to unsymmetrical olefins may then be predicted from the relative stabilities of the possible intermediate carbonium ions, leading to Markovnikov's rule for hydrocarbon olefins. When allene reacts with an electrophile HX, the proton bonds to a terminal carbon atom, and it may therefore be argued that an intermediate vinyl carbonium ion is the more stable form (Eq 35), in surprising contrast to the apparent mechanism of halogenation. Certainly allene is hydrated

$$H_2C{=}C{=}CH_2 \xrightarrow{H^{\oplus}} CH_3\overset{\oplus}{C}{=}CH_2 \xrightarrow{X^{\ominus}} CH_3CX{=}CH_2 \quad \text{(Eq 35)}$$

in dilute acid to give acetone (*via* the enol) (229), and it reacts with hydrogen fluoride (17) and hydrogen iodide (223) to give 2-halopropenes, and 2,2-dihalopropanes by further addition. When allene is treated with hydrogen chloride or bromide, however, an unusual ionic cyclization occurs and 1,3-substituted cyclobutanes are formed as well as the expected 1:1 adducts (222, 223) (Eq 36). These cyclic products, formed in greater amounts at lower temperatures in the range −70 to 20°, are considered to arise by attack of the vinyl carbonium ion upon a second allene molecule, and not by acid-catalyzed dimerization of 2-halopropene.



(Eq 36)

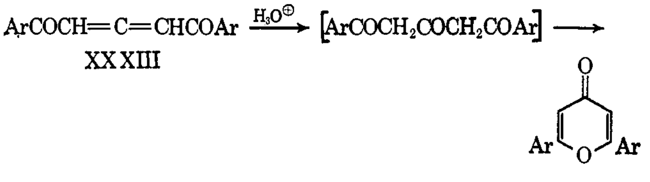
Terminal allenes ($RCH{=}C{=}CH_2$) are also protonated at the 1 position, giving methyl ketones by hydration (56, 88, 268) and mainly 2-haloalk-2-enes ($RCH{=}CXCH_3$) by addition of hydrogen halides (186, 249, 268). Some but-2-yne is formed when buta-1,2-diene is treated with hydrogen chloride at low temperature (268). The adduct does not, however,

$$MeCH{=}C{=}CH_2 \xrightarrow[\text{20\% conversion}]{HCl,\ -78^\circ} \underset{62\%}{MeCH{=}CClCH_3} + \underset{38\%}{MeC{\equiv}CCH_3}$$

form by addition of hydrogen chloride to but-2-yne, a much slower process. Similarly, the acid-catalyzed addition of alcohols to allenes gives acetals of the corresponding ketones (249), *e.g.*

$$n\text{-}PrCH{=}C{=}CH_2 \xrightarrow[HgO]{MeOH,\ BF_3} n\text{-}PrCH_2C(OMe)_2CH_3$$

and 1,3-dialkylallenes ($RCH{=}C{=}CHR'$) are hydrated to the corresponding ketones (RCH_2COCH_2R') in strong aqueous acid, even in the absence of mercuric salts (187). Occasionally these reactions take interesting alternative pathways; thus 1,3-dibenzoylallenes (XXXIII, Ar = Ph or *p*-tolyl) form pyrones when treated with aqueous acid (37).



XXXIII

In all the above reactions the first step seems to be protonation of the terminal carbon atom of the allene, to form a vinyl carbonium ion. Nevertheless, the structure of the allene may affect the orientation of addition in some cases. For example, certain 1,3-dialkylallenes (XXXIV, R = *i*-Bu or *n*-Am) react with hydrogen bromide to give products of mixed orientation (185), and cyclic allenes behave similarly

$$\underset{\text{XXXIV}}{RCH{=}C{=}CHMe} \xrightarrow{HBr,\ -40^\circ} RCH{=}CBrCH_2Me + RCH{=}CHCHBrMe$$

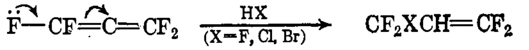
with hydrogen chloride, though giving mainly the 3-chlorocycloolefins (512). This changeover to protonation of the central carbon atom of the allene, no doubt induced by increasing electron density at that position, is complete in 3-methylbuta-1,2-diene, which gives only allylic halides with hydrogen halides (186, 268).

$$Me_2C{=}C{=}CH_2 \xrightarrow[(X\ =\ Br\ or\ Cl)]{HX} Me_2C{=}CHCH_2X$$

Allenes bearing electron-withdrawing substituents protonate at the substituted carbon atom, as might be expected, *e.g.* (317)

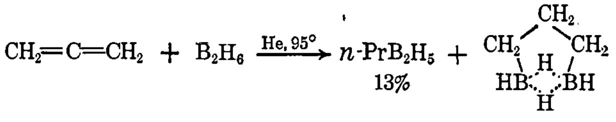
$$H_2C{=}C{=}CHCN \xrightarrow{HCl} H_2C{=}CClCH_2CN$$

but when there is the possibility of back-donation to increase the electron density at the central carbon atom, as in 1,1-dichloroallenes (394, 495) and tetrafluoroallene (34), the orientation of the addition of hydrogen halides is reversed. However, the possibility that such additions proceed nucleophilically or by a four-center process cannot be excluded.



$$F{-}CF{=}C{=}CF_2 \xrightarrow[(X=F,\ Cl,\ Br)]{HX} CF_2XCH{=}CF_2$$

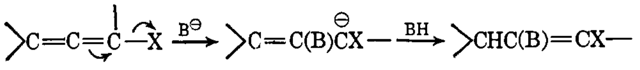
Hydroboration of several allenes has been reported, but the exact nature of the products has not always been determined. Thus there are conflicting claims that ketones, secondary alcohols, and olefins are formed from cyclic and acyclic allenes (149) and, on the other hand, that the products are 1,2- and 1,3-glycols, at least from acyclic allenes (127). The situation regarding the allene–diborane reaction was recently clarified; in a gas-phase flow system trimethylenediborane (XXXV), which polymerizes reversibly, is the main product (341). Spectroscopic evidence was obtained that the ring structure is preserved in the polymer, which depolymerizes at 60°, and this accords with the observation that peroxide degradation of the polymer leads to trimethyleneglycol (500).



XXXV, 42%

3. *Nucleophilic Additions*

There is no evidence to suggest that allene or its lower homologs are susceptible to nucleophilic attack, but the presence of strongly electron-withdrawing groups leads to additions initiated by a nucleophile attacking the central carbon atom (Eq 37). The



$$>C=C=\overset{|}{C}-X \xrightarrow{B^{\ominus}} >C=C(B)\overset{\ominus}{C}X- \xrightarrow{BH} >CHC(B)=CX-$$

(Eq 37)

final products are those in which the intermediate carbanion gains a proton at the unsubstituted carbon atom. Typical electron-withdrawing groups (X) are nitrile (317), carboxylic acid and ester (156, 280), carbonyl (37, 54, 598), and $(RO)_2P(O)-$ (471), which activate the allenic bond to attack by amines, alkoxides, sodio diethyl malonate, etc. A useful example is the synthesis of enol ethers from ketoallenes (XXXVI, R = Et, *n*-Pr, or *i*-Pr) (54).

$$\underset{\text{XXXVI}}{RCOCH=C=CH_2} \xrightarrow[-40°]{\text{MeONa, MeOH}} \underset{95\%}{RCOCH=C(OMe)CH_3}$$

Nucleophilic additions may also occur in highly fluorinated allenes. Thus, neutral methanol adds to both perfluoro(tetramethylallene) (116) and tetrafluoroallene (34), though the site of attack varies.

$$(CF_3)_2C=C=C(CF_3)_2 \xrightarrow{\text{MeOH}} (CF_3)_2CHC(OMe)=C(CF_3)_2$$

$$CF_2=C=CF_2 \xrightarrow{\text{MeOH}} MeOCF_2CH=CF_2$$

D. FREE-RADICAL ADDITIONS

Much interest has been shown recently in free-radical additions to allenes. The orientation of such additions depends on both the nature of the attacking radical and the degree and type of substitution of the allene; it may also be affected by reaction parameters such as temperature, solvent, and initial concentrations.

The reactions of allene with twelve different free radicals have so far been examined (Table III). Theoretically, two 1:1 adducts (XXXVII and XXXVIII) and three 2:1 adducts (XXXIX, XL, and XLI) may be formed by random terminal and central attack on the allene bond (Eq 38). Superficially it might be assumed that attack would always take place at the center carbon to give the more stable allylic intermediate radical ($CH_2=CR\dot{C}H_2$); reflection shows that an allene, which has orthogonal π bonds, will convert to such a radical only if it exists long enough to permit 90° rotation of the orbital containing the unpaired electron (Scheme IX).

SCHEME IX

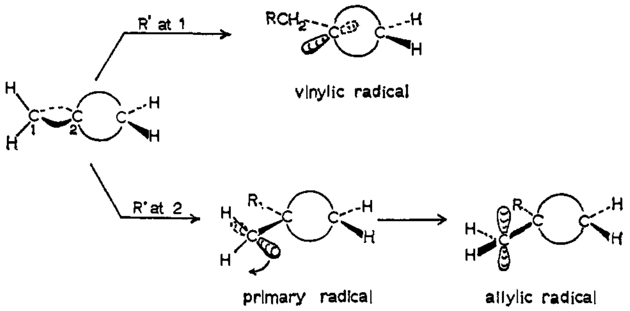
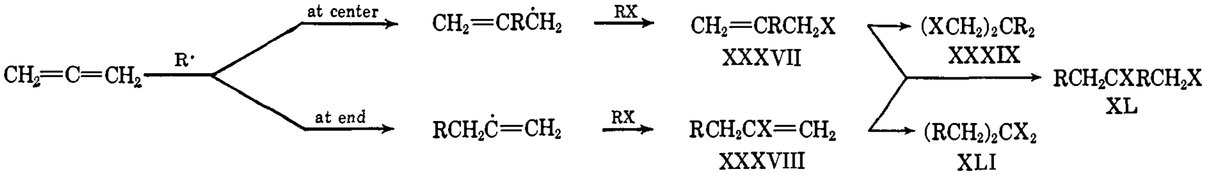


TABLE III
FREE-RADICAL ADDITIONS TO ALLENE

Attacking radical	Source	Max yield of adducts, %	Site of attack % at center	 % at ends	Ref
$F_3C\cdot$	CF_3I	96	0	100	242
$Cl_3C\cdot$	CCl_3Br	...	0	100	244
$H_2P\cdot$	PH_3	3	0	100	214
$Et_2N\cdot$	Et_2NCl	58	0	100	399
$F_5S\cdot$	S_2F_{10}	...	0	100	569
$HS\cdot$	H_2S	95	≤2	≥98	225
$MeCOS\cdot$	MeCOSH	92	9	81	226
$MeS\cdot$	MeSH	88	6–14	86–94	226
$EtS\cdot$	EtSH	...	13	87	267
$PhS\cdot$	PhSH	97	20–30	70–80	226, 244
$Me_3Sn\cdot$	Me_3SnH	67	45	55	316
$Br\cdot$	HBr	92	≥52	≤48	1, 224

The results in Table III show that, in fact, most free radicals attack allene mainly at the two terminal carbon atoms; this agrees with calculations of the radical localization energies of allene (472). There is, however, an increasing tendency for central attack to occur along the series HS· < MeCOS· < alkyl-S· < PhS· < $Me_3Sn\cdot$ < Br·. Polar and steric factors do not provide a satisfactory explanation for this sequence; one would not expect trimethyltin radicals to lie between thiyl radicals and bromine atoms on either consideration. The best solution may arise from the possibility that reversible addition of the radical takes place in some cases, so that dissociation of the intermediate radicals competes with chain transfer (Eq 39). Careful studies of the addition of benzene-



(Eq 38)

$$\begin{array}{l} \nearrow \mathrm{CH_2{=}CRCH_2\cdot \xrightarrow{RX} CH_2{=}CRCH_2X + R\cdot} \\ \mathrm{CH_2{=}C{=}CH_2 + R\cdot} \qquad\qquad\qquad\qquad \text{(Eq 39)} \\ \searrow \mathrm{RCH_2\dot{C}{=}CH_2 \xrightarrow{RX} RCH_2CX{=}CH_2 + R\cdot} \end{array}$$

thiol and hydrogen bromide to allene (1, 224, 226, 244) suggest that, although terminal attack is freely reversible, central attack is followed by rapid achievement of allylic structure by a 90° rotation about the C–C single bond in the intermediate radical. Central attack by these radicals is then essentially irreversible, because chain transfer is energetically favored. As a result, the product distribution shows a preference for central attack, especially in the absence of a large excess of chain-transfer agent, and the effects of temperature and concentration are thereby rationalized (244).

TABLE IV

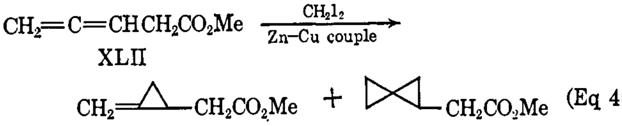
EFFECT OF ALKYLATION ON THE ORIENTATION OF ADDITION

Allene $C_1{=}C_2{=}C_3$	Attacking radical	Yield of adducts, %	Site of attack (%) C_1	C_2	C_3	Ref
$CH_2{=}C{=}CH_2$	$EtS\cdot$	...	43	13	43	267
	$Me_3Sn\cdot$	67	27	45	27	316
$MeCH{=}C{=}CH_2$	$EtS\cdot$	...	6	48	46	267
	$Me_3Sn\cdot$	73	0	86	14	316
$Me_2C{=}C{=}CH_2$	$EtS\cdot$	...	0	100	0	267
	$Me_3Sn\cdot$	72	0	100	0	316
$MeCH{=}C{=}CHMe$	$Me_3Sn\cdot$	65	0	100	0	316
$Me_2C{=}C{=}CHMe$	$Me_3Sn\cdot$	83	0	100	0	316

A careful examination of the radical additions of ethanethiol (267) and trimethylstannane (316) to propadiene and allenes, in which the terminal hydrogens are successively replaced by methyl groups, shows that the effect of substitution is a progressive increase in the amount of products from central attack (Table IV). It is not possible to explain this effect on the basis of the changing polarity of the allenes, since alkylthiyl radicals are relatively electrophilic and trimethyltin radicals are relatively nucleophilic. Steric hindrance at C_1 and C_3 may be responsible for increased attack at C_2, especially in the case of the bulky trimethyltin radicals, or it may be that the relative stabilities of the intermediate radicals are changed, for example, by hyperconjugation of terminal methyl groups with the π bond of an allylic intermediate.

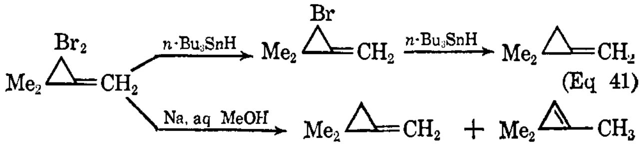
More observations of this type are required before firm conclusions are possible regarding the detailed factors which control the orientation. However, it is now clear that the absence of a blocking effect on the rate of additions to allene and methylallenes is no guide to the orientation, since without full product analysis one cannot tell whether a changeover from terminal to central attack is occurring (478, 479, 544).

Allenes react with diradicals (*e.g.*, carbenes) to give methylenecyclopropanes or spirobicyclopentanes. The carbenoids may be made from ketenes or diazo compounds (76, 199), by treatment of methylene iodide with a zinc–copper couple (476, 572, 591), by thermal decomposition of halomercurials (510), or by treatment of haloforms with base (31, 65, 66, 476, 591), of which the last has been most widely used. Methylene adds to the more substituted double bond of the allenic ester (XLII) (572) (Eq 40), and this appears to be a general tendency, since dihalocarbenes add preferentially to the more alkylated double bonds of a series of mono-, di-, and trialkylallenes (31, 65, 66, 476, 591). This is perhaps surprising, because competition experiments show that bulky substituents retard the rate of addition of carbenes to allenes (67).

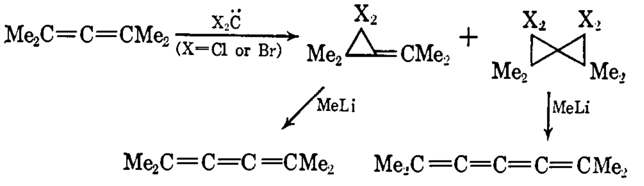


(Eq 40)

The products obtained by addition of dihalocarbenes to allenes are useful synthetic intermediates, which may be reduced either in a stepwise fashion with tributylstannane (476) or converted by more vigorous reducing agents to mixtures of methylenecyclopropanes and methylcyclopropenes (66) (Eq 41). Alternatively, they may be dehalogenated by lithium alkyls to higher cumulenes; tetramethylallene was recently used as a source of both tetramethylbutatriene and tetramethylpentatetraene in this way (521) (Eq 42). A recently developed technique for ring expansion also utilizes carbene addition to a cyclic allene (389).

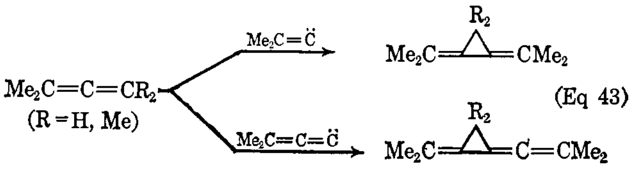


(Eq 41)



(Eq 42)

Vinylidene and allenylcarbenes, made from 1,1-dibromoethylenes and tertiary propargyl halides, respectively, react with allenes to give novel ring compounds (75) (Eq 43).

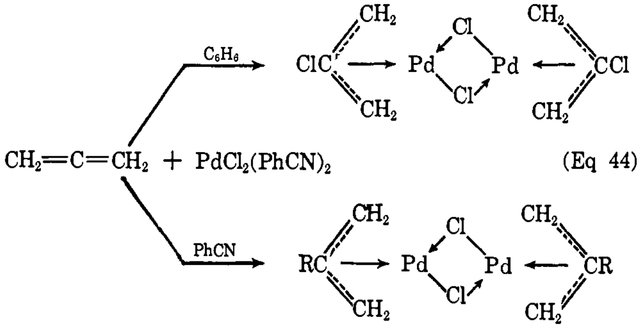


(Eq 43)

E. FORMATION OF π COMPLEXES

Those addition reactions of allenes which might afford π complexes have not been extensively studied, and gas chromatographic retention data for alkylallenes on silver nitrate indicate that allenic π complexes are likely to be less stable than those from olefins and acetylenes (390). Nevertheless, when tetraphenylallene is treated with iron pentacarbonyl a red, diamagnetic, air-stable solid is formed, from which the allene may be recovered on heating or by treatment with triphenylphosphine (396). The formula of the complex $[Ph_4C_3Fe(CO)_3]$ suggests that the allene here functions as a bidentate ligand. Although tetraphenylallene fails to react with nickel or cobalt carbonyl (221, 396), it is converted in low yields to complexes of unknown structure with cyclopentadienylcobalt dicarbonyl and chromium hexacarbonyl; in these cases the allene seems to act as a monodentate ligand (396), although the exact structures are not known. Propadiene reacts with iron dodecacarbonyl, and the resulting complex is interesting in that it exists as an equilibrium mixture of two forms even at −10°, both of which contain two allene residues linked at their central carbons (395). Complexes of unknown structure have also been obtained from β-aminoallenes and transition metal chlorides (19).

The only complexes of allenes for which good structural evidence is available are those obtained by passing alkylallenes into solutions of palladium salts (349, 503). The structure of the complex is found to depend on the solvent and allene concentration, *e.g.*, Eq 44 (where R = $CH_2{=}C(CH_2Cl){-}$).



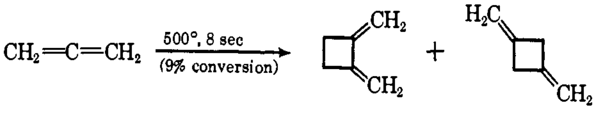
(Eq 44)

Carbonylation of the allene–palladium dichloride complex in ethanol provides a route to ethyl 3-chlorobut-3-enoate ($CH_2{=}CClCH_2CO_2Et$) (571). Carbonylation of allene has also been effected using ruthenium salts and similar catalysts and leads to derivatives of methacrylic acid (299).

$$CH_2{=}C{=}CH_2 \xrightarrow[\text{(B = OH, NHR, OR)}]{\text{CO, BH}} \underset{16\text{–}50\%}{CH_2{=}CMeCOB}$$

F. DIMERIZATION

Allene may be dimerized thermally, either in sealed tubes at 110–160° when the yield of dimers is low (332, 532), or in flow reactors at 400–510° when yields rise to 50% if a low conversion per pass is achieved (78, 531, 599). Contrary to Lebedev's early report (332) the dimer is a mixture of two isomers, in which 1,2-dimethylenecyclobutane (XLIII) predominates. The proportion of the other isomer, 1,3-dimethylenecyclobutane (XLIV), increases as the reaction temperature is raised, especially in static reactors (532).

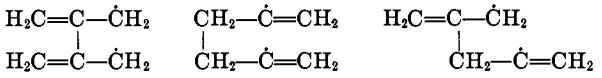


XLIII, 34%   XLIV, 11%

The formation of an end–center linked dimer (XLIV) from allene is unique; all other symmetrically substituted allenes so far examined afford only center–center linked dimers similar to XLIII. These include penta-2,3-diene (332), tetramethylallene (368), bis(fluorenylidene)allene (192), and certain cycloalka-1,2-dienes (523). Tetrafluoroallene, which dimerizes rather slowly at 20° (34), and tetrachloro- and tetrabromoallene, both of which dimerize rapidly at or below ambient temperatures (451, 493, 494), also give only perhalo-(1,2-dimethylenecyclobutanes); tetraiodoallene does not dimerize readily (296).

Dimerization of unsymmetrically substituted allenes is usually found to give only one or two of the three possible center–center linked dimers, and none of the possible 1,3-dimethylenecyclobutanes are observed (see XLV and XLVI in Table V).

Any mechanism for the dimerization must account for the predominance of 1,2-dimethylenecyclobutane dimers, and for the more specific preferences for certain dimers shown by unsymmetrically substituted allenes. Two mechanisms merit discussion, both currently debated in the literature in relation to Diels–Alder and other cycloaddition reactions (39, 345, 381, 490, 602, 603). The first postulates the intermediate formation of the most stable possible diradical (129). When applied to the dimerization of propadiene, however, it becomes hard to assess the relative stabilities of the three possible diradicals (XLVII, XLVIII, XLIX).



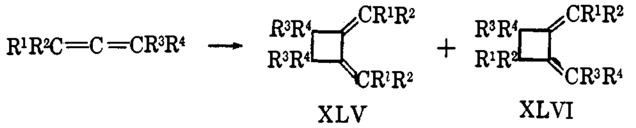
$$\begin{array}{ccc} H_2C{=}C{-}\dot{C}H_2 & CH_2{-}\dot{C}{=}CH_2 & H_2C{=}C{-}\dot{C}H_2 \\ | & | & | \\ H_2C{=}C{-}\dot{C}H_2 & CH_2{-}\dot{C}{=}CH_2 & CH_2{-}\dot{C}{=}CH_2 \end{array}$$

XLVII   XLVIII   XLIX

Because of the initially orthogonal arrangement of the π bonds in the monomer, allylic p–π overlap and stabilization are only attained in XLVII and XLIX if 90° rotation about their C–$\dot{C}H_2$ bonds is allowed (*e.g.*, Scheme X). In view of the observed predominance of terminal free-radical attack on propadiene, such free rotation cannot be assumed to occur.

The second mechanism involves a four-center transition state (603) and is distinguished from the first by

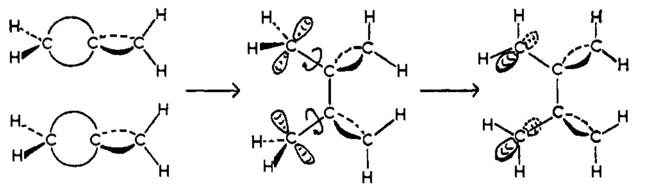
TABLE V
DIMERIZATION OF UNSYMMETRICALLY SUBSTITUTED ALLENES



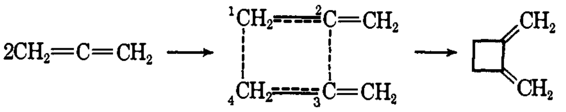
Allene substituents				Temp, °C	Yield, %	Composition			Ref
R^1	R^2	R^3	R^4			% XLV	% XLVI	Others[a]	
Cl	H	H	H	60	25	78	16	7	368
Br	H	H	H	60	...	80	16	4	368
F	F	H	H	300	30	0	100[b]	...	308
Cl	CO_2Et	H	H	20	...	100	0	...	590
Me	Me	H	H	150	...	64	34	2	368
Et	Et	H	H	...	...	100	0	...	372
Me	Me	Me	H	150	...	[d]	...	[d]	332
Me	Me	Cl	H	60	...	90	10	...	368
Me	Me	Br	H	60	48	88	10	2	368
Br	Br	Br	H	40	60	100	0	...	494
CN	H	Me	Me	...	...	[d]	...	...	417
CN	H	Et	Me	...	...	100	0	...	220
Ph	Ph	Cl	H	...	49[c]	59	0	41	325
				...	...	[d]	[d]	...	152
p-ClC_6H_4	p-ClC_6H_4	Cl	H	...	29[c]	100	0	...	325
Fluorenylidene		Cl	H	...	74[c]	100	0	...	393
Ph	Ph	Br	H	20	...	[d]	[d]	...	362
Ph	Ph	Fluorenylidene		200	40	100	0	...	192
Ph	Ph	Cl	Cl	...	[c]	100	0	...	495
p-FC_6H_4	p-FC_6H_4	Cl	Cl	...	9[c]	100	0	...	495
p-ClC_6H_4	p-ClC_6H_4	Cl	Cl	100	40	100	0	...	495
p-BrC_6H_4	p-BrC_6H_4	Cl	Cl	100	78	100	0	...	495

[a] Refers to other dimers and in some cases rearrangement products. [b] Dimerized in a flow system. [c] Starting material formed *in situ* and not isolated. [d] Identified but not estimated.

SCHEME X



the fact that both of the bond-forming processes follow so closely after the bond-breaking steps that no rotation about the bonds C_1–C_2 and C_3–C_4 can occur (Eq 45). This process is sometimes termed the "virtual

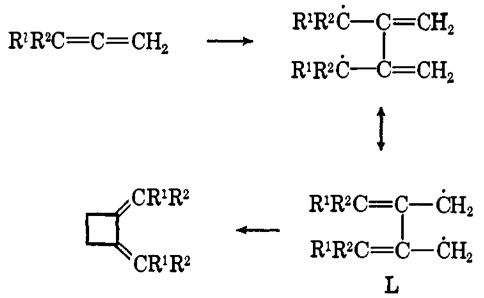


(Eq 45)

diradical" mechanism, to draw attention to the fact that, if the bonding between C_1 and C_4 is incomplete when the C_2–C_3 bond is almost fully formed, the intermediate resembles a diradical even though the electrons remain paired and free rotation is forbidden. In such a process free-valence indices and steric and polar factors may determine the orientation of addition, though they are usually hard to predict. In the case of allenes, conjugation of the exocyclic π bonds may occur in the transition state, so leading to preferred formation of 1,2-dimethylenecyclobutanes.

It is known that terminal alkylation of allene leads to a changeover in the site of free-radical attack to mainly the center carbon (see section D), and this is clearly consistent with the exclusive formation of center-center linked dimers from substituted allenes. In the author's opinion, if an intermediate diradical is formed during dimerization of an unsymmetrically substituted allene (see Table V), allylic p–π overlap must be attained, because those substituents R^1 and R^2 which could best stabilize an unpaired electron do not become attached to the ring, but to the exocyclic methylene groups (Scheme XI, where R^1 = H, R^2 =

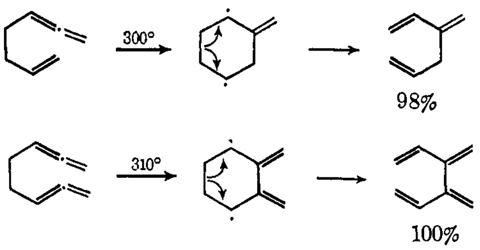
SCHEME XI



L

Cl, Br, CN; R^1 = CO_2Et, R^2 = Cl; or R^1 = R^2 = Me, Et, aryl). Dimerization from L is more likely because of π–π, p–π, or σ–π overlap between the substituents and the π bonds. It would obviously be of value to know the orientation of free-radical additions to a greater variety of allenes, and also to determine the steric outcome of the dimerization of pure enantiomers of asymmetric allenes, which would indicate the degree of permitted rotation during ring formation.

A recent study of the dimerization of cyclic allenes and of the intramolecular cyclizations of unsaturated allenes tended to confirm that allylic intermediate radicals are formed (523). For example, hepta-1,2,6-triene and octa-1,2,7-triene afford only methylenehexadienes after thermal rearrangement; these products are consistent with initial cyclizations by attack at the central allenic carbon (Eq 46). However, no evidence of discrete intermediates was obtained, and a concerted Cope-type rearrangement seems quite plausible in the case of such allenes.

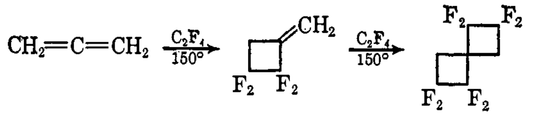


(Eq 46)

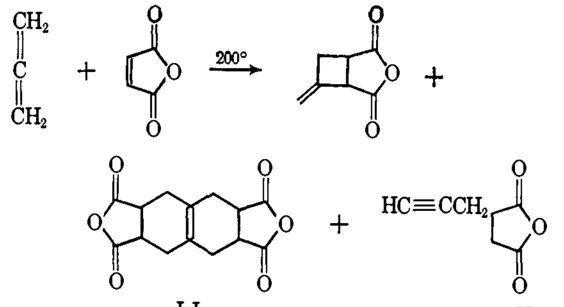
The dimerization of arylallenes is complicated by a tendency to rearrange to indene derivatives, especially in the presence of acids (see section J), and their dimers have seldom been carefully characterized (210, 264, 265, 273, 601, 617, 618). Early work in this area will almost certainly reward further investigation using modern analytical techniques (*e.g.*, ref 487). A further type of dimerization is shown by 1,3-dibenzoylallene, which forms a methylenepyran by a Diels–Alder process (5).

G. CODIMERIZATION

In spite of its fairly rapid self-dimerization, allene codimerizes with electron-deficient olefins. With tetrafluoroethylene it is claimed that simple stepwise addition takes place (121) (Eq 47), but with other olefins the reaction is more complicated. Thus, allene and maleic anhydride codimerize at 175–200° to give, besides the expected methylenecyclobutane anhydride, a 2:2 adduct which proves to be an octalin derivative (LI), and a 1:1 adduct in which rearrangement has occurred (LII) (6, 134, 137) (Eq 48), and similar products are observed when penta-1,2-diene is treated with maleic anhydride (7). The octalin (LI) almost certainly arises from the dimer of allene, by Diels–Alder addition followed by ring opening and further addition; it may also be obtained by treating the dimer with maleic anhydride (MA) at 150° (78) (Eq 49).

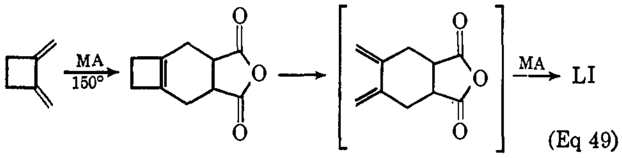


(Eq 47)



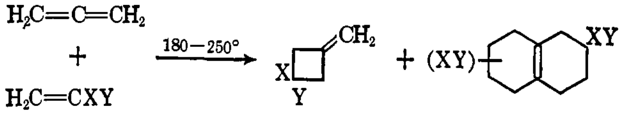
LI LII

(Eq 48)



(Eq 49)

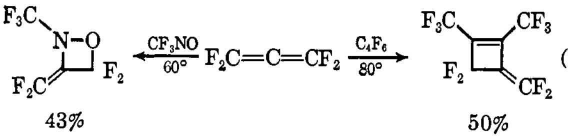
Many substituted methylenecyclobutanes and octalins are obtainable by treating allene with a variety of olefins (LIII, X = H, Y = CN, CO_2H, CO_2Me, CHO, Ph, py; X = Me, Y = CN, CO_2Me, Ph; X = OAc, Y = CN; X = CH_2CO_2Et, Y = CO_2Et) (134, 137).



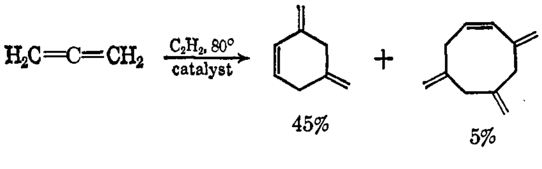
LIII

Optimum yields (up to 75%) of octalins are realized if the reactants are in equimolar proportions, whereas if the olefin is in excess methylenecyclobutanes are the main products. Other allenes which have been codimerized with olefins include alkylallenes (7, 74, 137) and 1,1-difluoroallene (308).

Tetrafluoroallene codimerizes both with trifluoronitrosomethane (in the vapor phase at 60°) and with hexafluorobut-2-yne (in the liquid phase at 80°) (35, 36) (Eq 50). The latter reaction is unusual, in that allenes cannot usually be codimerized with acetylenes, although if suitable catalysts are present six- and eight-membered rings are produced (44, 45), *e.g.*

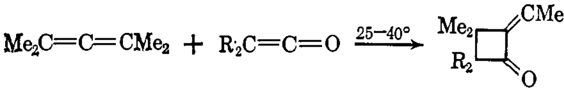


(Eq 50)



(Eq 51)

Recently it was found that polar codimerizations occur between allenes and ketenes (218, 360) (Eq 52, where R = Me or Ph).

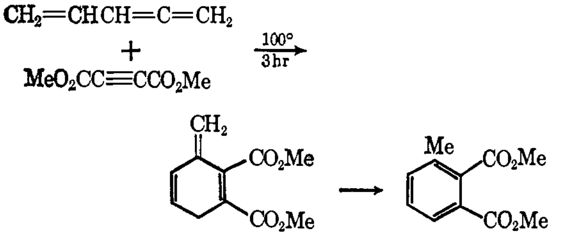


(Eq 52)

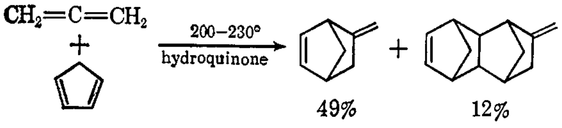
70%

H. DIELS–ALDER REACTIONS

Allenes participate in Diels–Alder reactions in two ways. First, if one of the allenic π bonds is conjugated with a double bond, as in vinylallene, the behavior on treatment with dienophiles is typical of a conjugated diene (188, 281); rearrangement is liable to follow addition, owing to the presence of the remaining allenic π bond (281) (Eq 53). Secondly, allenes frequently behave as dienophiles, especially if they bear electron-withdrawing substituents such as halogen (308, 493), carboxyl (4, 285), carbonyl (53), or nitrile (317). Even propadiene behaves as a dienophile, perhaps because the central sp carbon atom renders the π bonds electron-deficient (104, 135, 160, 453) (Eq 54).



(Eq 53)

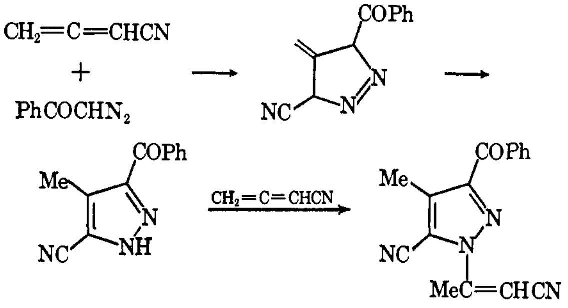


(Eq 54)

49% 12%

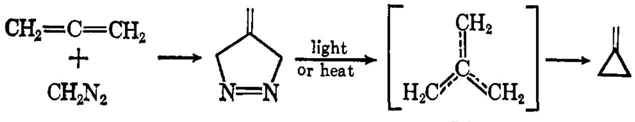
I. 1,3-DIPOLAR ADDITIONS

Diazo compounds such as diazoalkanes (128, 133, 155, 158), diazoacetic esters (128, 158), and diazo ketones (488) react with alkylallenes and with allenic acids, esters, and nitriles to produce ring compounds by 1,3-dipolar additions. As with Diels–Alder additions, the primary product frequently rearranges and may also react further with the allene to form 2:1 adducts (488) (Eq 55).



(Eq 55)

The reaction between propadiene and diazomethane, first examined by D'yakonov (158), was recently shown to give as the sole initial product 4-methylene-1-pyrazoline (133, 155), the specific orientation of addition being in line with other polar additions to the allene. Pyrolysis (133) or photolysis (155) of this pyrazoline leads to elimination of nitrogen to give methylenecyclopropane. Evidence was obtained that the theoretically interesting trimethylenemethane (LIV) is an intermediate in the decompositions (Eq 56).



LIV (Eq 56)

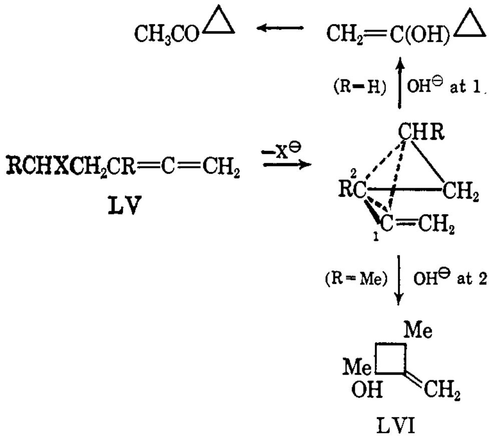
Butadienonitrile also undergoes dipolar additions with cyclic enamines (487), but such additions cannot always be facile, because a recent report indicates that a variety of enamines are obtainable in high yield by the addition of secondary amines to 1-cyanoallenes (219), apparently without further dipolar cyclization, *e.g.*

$$Me_2C{=}C{=}CHCN \xrightarrow{Et_2NH} \underset{75\%}{Me_2C{=}C(NEt_2)CH_2CN}$$

J. INTRAMOLECULAR CYCLIZATIONS

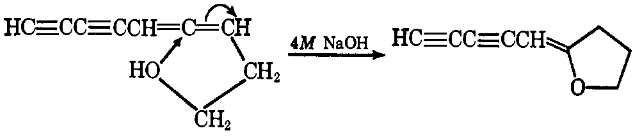
Both alicyclic and heterocyclic compounds have been obtained from suitably substituted allenes by internal ring closure. The formation of acetylcyclopropane from the reaction of 5-bromopenta-1,2-diene (LV, R = H; X = Br) with silver oxide, or in better yield by formolysis of the naphthalenesulfonate of the corresponding alcohol (LV, R = H; X = OH), is of interest because a nonclassical carbonium ion of unusual structure could be involved (234) (Scheme XII).

SCHEME XII



Alkylation of the allene affects the way in which the supposed carbonium ion reacts with hydroxyl ion, since solvolysis of the tosylate of the alcohol (LV, R = Me; X = OH) leads as shown to the dimethylmethylenecyclobutanol (LVI) (59).

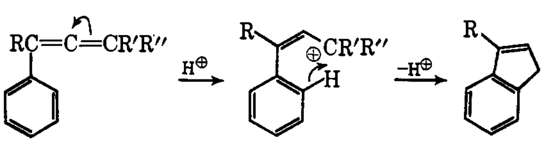
A somewhat simpler type of intramolecular cyclization occurs when a suitably placed nucleophile is present in an allene. For example, the naturally occurring polyacetylenic hydroxyallene, Marasin (LVII), cyclizes in aqueous alkali to a methylenefuran (81).



LVII

A similar cyclization has recently been reported in propadienyl trimethylene glycol monoether (87).

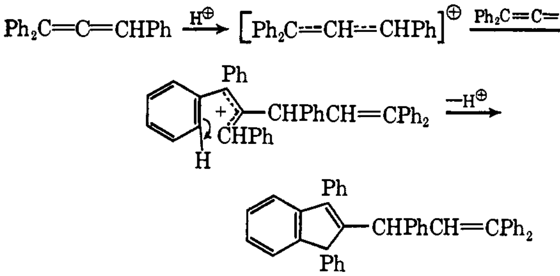
In the presence of acids, arylallenes undergo rapid isomerization to indenes; a plausible mechanism involves protonation of the center carbon, followed by internal electrophilic substitution of one of the phenyl groups (Eq 57). For example, tetraphenylallene



(Eq 57)

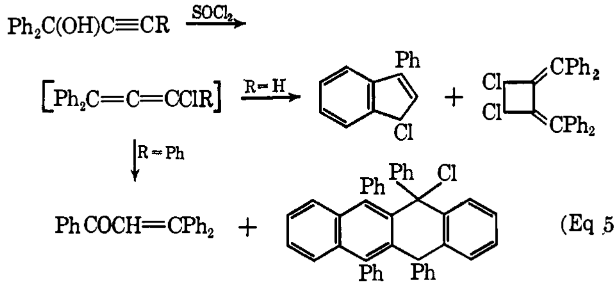
affords 1,1,3-triphenylindene (Eq 57, R, R', R'' = Ph) when treated with hydrogen halides or acetic acid (592), and naphthindenes (352) and fluorenylindenes (192) may be obtained in the same way. The structure of the indene so formed has not always been established (see, *e.g.*, ref 619).

Dimerization of the arylallene may occur concurrently with indene formation (175, 196, 363, 364, 542, 617). Acid-catalyzed dimerization of triphenylallene was recently reinvestigated and shown to lead to triphenylallyldiphenylindene (485), possibly as shown in Eq 58. Unidentified high molecular weight products,



(Eq 58)

possibly also allylindenes, are formed along with 3-chloro-1-phenylindene and a conventional dimer when unstable 1,1-diphenylchloroallene is formed from the corresponding acetylene alcohol (325). More highly arylated allenes, such as triphenylchloroallene, are liable to undergo Meyer-Schuster rearrangements, giving vinyl ketones (266, 325, 514, 620), and also form rubrene derivatives (325) (Eq 59). Unusual polycyclic products are also obtained when tetraphenylallene is treated with lithium or potassium and then quenched with water (154).

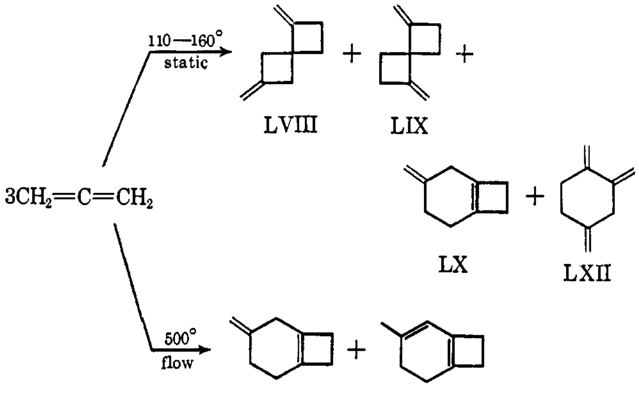


(Eq 59)

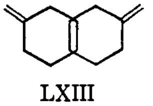
K. POLYMERIZATION

Although it has often been noted that allenes polymerize readily, even under mild conditions, to give material of higher molecular weight than dimers, few systematic studies of such reactions have been undertaken. One of the first investigators, Lebedev, examined the thermal polymerization of allene and some of its simple homologs (331–334); from allene he isolated fractions containing low molecular weight oligomers such as dimers (5%), trimers (15%), tetramers (27%), pentamers (18%), and hexamers (10%), and a 25% yield of high molecular weight polymer thought to arise by polymerization of the dimer, now known to be a mixture of 1,2- and 1,3-dimethylenecyclobutane (599).

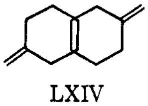
More recently, two groups have reinvestigated the low molecular weight oligomers (189, 533, 595). The trimer fraction appears to be a mixture of spiro[3.3]-heptanes (LVIII and LIX), bicyclo[4.2.0]octenes (LX and LXI), and trimethylenecyclohexane (LXII), the relative amounts of which vary according to the conditions and duration of the polymerization. The β tetramer, originally thought to have a dispirodecane structure, is now known to be a mixture of 2,6- and 2,7-dimethylene-$\Delta^{9,10}$-octalins (LXIII and LXIV), converted by chloranil to dimethylnaphthalenes and on reduction eventually to dimethyldecalins (189). The formation of these octalin tetramers is not unexpected since such compounds are also formed when allene reacts with dienophiles (section G).



LVIII LIX LX LXII LX LXI

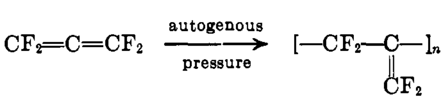


LXIII



LXIV

On the basis of Lebedev's data, Gapon calculated initial rate constants for the polymerization of allene and its homologs and found that alkylation had little effect on the rate (203). A recent study of the thermal polymerization of chloro- and bromoallene has shown that the rate of consumption of these allenes is governed by a first-order law and is unaffected by radical initiators or scavengers. Dimers, trimers, and tetramers are the main products, and it appears that the small amounts of high molecular weight polymer form mainly by polymerization of the dimers, as in the case of allene, and probably by a free-radical chain mechanism (330). 1,1-Difluoroallene (77) and tetrafluoroallene (34, 261) both polymerize under autogenous pressure, whereas tetrachloroallene does not polymerize readily in spite of its facile dimerization (493). In fact, the polymer of tetrafluoroallene has a linear structure which cannot arise from the dimer (369)



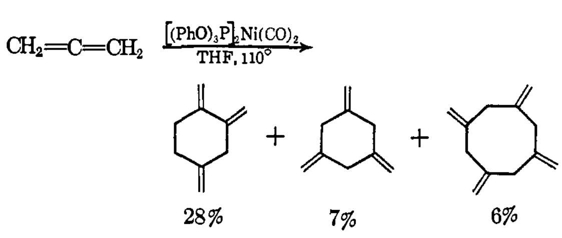
$$CF_2{=}C{=}CF_2 \xrightarrow[\text{pressure}]{\text{autogenous}} [-CF_2-\underset{\underset{CF_2}{\|}}{C}-]_n$$

and there is evidence that it forms from the monomer by a free-radical chain mechanism (34). A highly crystalline polymer of similar structure has quite recently been obtained by stereoregular polymerization of allene over π complexes of nickel (408).

Phenylallene (328), which structurally resembles styrene, and 1,1-diphenylallene (520) both polymerize readily to materials of unknown structure.

Few copolymerizations of allenes have been investigated with any thoroughness. Chloroallene and styrene copolymerize, but the allene has a much lower reactivity ratio than either styrene or the dimer of the allene, so that under conditions in which dimerization competes with polymerization, the polymer incorporates the dimer as well as monomer units (330).

A variety of catalysts initiate allene polymerizations and copolymerizations. They include peroxides (173, 174), alkali metals (501, 610), and Ziegler catalysts which induce stereoregular linear polymerization of allene (27, 408, 456, 491), and assist its copolymerization with ethylene (366, 367, 565) and ethylene–propylene mixtures (28). When allene, allenic carboxylic acids, or alkylallenes are treated with cobalt carbonyl, a reaction takes place in which one carbon monoxide unit is displaced; the initial product catalyzes the linear polymerization of excess of the allene without intermediate dimerization (221). In contrast, allene is converted into trimers and tetramer when heated with catalysts based on nickel carbonyl (43) (Eq 60).



(Eq 60)

L. REARRANGEMENT REACTIONS

The rearrangements of allenes to acetylenes and conjugated dienes is one of the most interesting facets of their chemistry and needs to be considered as a possible complication in their synthesis and in any study of their reactions. The prolific literature on this subject will be subdivided according to the mechanism, *i.e.*, into prototropic and anionotropic (including displacement) rearrangements, irrespective of the type of product formed. Isomerizations of arylallenes to indenes have already been discussed and will not be dealt with here (see section J).

1. *Prototropic Rearrangements*

Calculations based on heats of formation and hydrogenation establish the following order of thermodynamic stability for the acyclic hydrocarbons C_nH_{2n-2} (387): alk-1-yne < 1,2-diene < 2,3-diene < alk-2-yne < 1,4-diene < 1,3-diene < 2,4-diene. The greater stability of allenes relative to terminal acetylenes has already been discussed in relation to the synthesis of allenes; such preparative rearrangements are reversible and allenes are completely converted to alk-1-ynes if the equilibrium is displaced by formation of the acetylide (88, 183), *e.g.*

$$EtCH{=}C{=}CH_2 \xrightarrow[\text{ligroin, 140°}]{NaNH_2} EtCH_2C{\equiv}CNa$$

Normally, however, terminal allenes are converted by bases and other catalysts to alk-2-ynes (Eq 61) and conjugated dienes (Eq 62). Propadiene is exceptional

$$RCH{=}C{=}CH_2 \longrightarrow RC{\equiv}CCH_3 \qquad \text{(Eq 61)}$$

$$R_2CHCR'{=}C{=}CH_2 \longrightarrow R_2C{=}CR'CH{=}CH_2 \qquad \text{(Eq 62)}$$

in that it can only afford propyne; it is found that the equilibrium mixture obtained from propadiene over active carbon at 300° contains 81% of the acetylene (126). Numerous other catalysts are suitable for such prototropic rearrangements, including silicates (526–529), Fuller's earth (79), activated alumina (8, 398), chromic oxide (338), and quinoline salts (318). Frequently the allenes are formed *in situ* by rearrangement of alkynes (338) (Eq 63).

$$n\text{-}BuC{\equiv}CH \xrightarrow[250°]{Cr_2O_3\text{-}Al_2O_3} [n\text{-}PrCH{=}C{=}CH_2] \longrightarrow$$

$$n\text{-}PrC{\equiv}CCH_3 \xrightarrow[250°]{Cr_2O_3\text{-}Al_2O_3} [EtCH{=}C{=}CHMe] \longrightarrow$$

$$EtC{\equiv}CCH_2Me + MeCH{=}CHCH{=}CHMe \qquad \text{(Eq 63)}$$

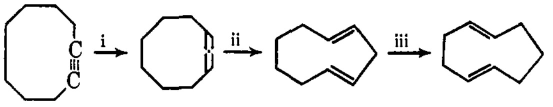
The use of potassium ethoxide, pioneered by Favorsky (182), has been reinvestigated and extended to other alkoxides (534). At first it was thought that such isomerizations, proceeding *via* carbanion intermediates, terminate with the formation of methylacetylenes (260) (Eq 64). However, a more thorough study

$$\mathrm{EtCH{=}C{=}CH_2} \xrightarrow[170^\circ]{\text{KOH, EtOH}} \begin{array}{ll} \mathrm{EtCH{=}C{=}CH_2} & (4\%) \\ + & \\ \mathrm{EtCH_2C{\equiv}CH} & (1\%) \\ + & \\ \mathrm{EtC{\equiv}CCH_3} & (95\%) \end{array} \quad \text{(Eq 64)}$$

of the *t*-butoxide-catalyzed rearrangement of allenic *n*-heptadienes has revealed that a suitable choice of conditions leads to successive equilibria containing (i) mainly hept-2-yne, (ii) mainly hept-2-yne and hept-3-yne, and (iii) exclusively conjugated heptadienes, irrespective of the nature of the starting material (534). Potassium *t*-butoxide proved to be the most effective of the bases examined, especially in aprotic solvents. These isomerizations greatly enhance the value of allenes as synthetic intermediates, *e.g.* (534).

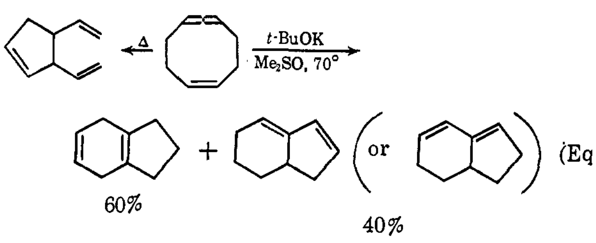
$$n\text{-}\mathrm{BuCH{=}C{=}CH_2} \xrightarrow[245^\circ,\ 3\ \mathrm{hr}]{1.4\ M\ t\text{-BuOK, }t\text{-BuOH}} \underset{97\%}{\mathrm{EtCH{=}CHCH{=}CHMe}}$$

When their unsaturated bonds are part of a ring system, the relative stabilities of allenes, acetylenes, and 1,3-dienes depend upon the size of the ring (387). This is hardly surprising, since in an acetylene four carbon atoms are held in a straight line, whereas in an allene only three are collinear, and in other dienes even less strain is entailed. In rings of eleven or more carbon atoms, allenes are less stable than acetylenic isomers, but in nine- or ten-membered rings the reverse is true. In either case prolonged equilibration over bases leads to the formation of less-strained dienes (147, 384, 387) (Eq 65). When additional unsaturation is present, particularly in a transannular position, bicyclic compounds can be produced by base-catalyzed isomerization (147), and thermal rearrangements of the Cope type may lead to ring contraction (237, 523, 573) (Eq 66).



(Eq 65)

(i) NaNH$_2$, NH$_3$, −33°, 3 hr, 95%
(ii) *t*-BuOK, Me$_2$SO, 70°, 1 hr, 98%
(iii) *t*-BuOK, Me$_2$SO, 70°, 143 hr, 94%



(Eq 66)

Prototropic rearrangements of haloallenes (176–179, 271), allenic alcohols (111), amines (164, 576, 580), thioethers (91, 459–461), and phosphonates (258, 470, 471) have all been reported, and usually lead to the formation of nonterminal acetylenic isomers or to conjugated dienes. Such rearrangements are also particularly facile when the functional group is suitably placed to activate the migrating proton, as in α-allenic carboxylic acids or esters, *e.g.* (280)

$$\mathrm{CH_2{=}C{=}CHCO_2H} \xrightarrow[90^\circ,\ 6\ \mathrm{hr}]{18\%\ \mathrm{K_2CO_3}} \underset{60\%}{\mathrm{CH_3C{\equiv}CCO_2K}}$$

or if, as in certain naturally occurring allenes, the allenic bond is part of a long conjugated system, when the rearrangement may extend right along the chain (114).

$$\mathrm{HC{\equiv}CC{\equiv}CCH{=}C{=}CH(CH{=}CH)_2CH_2CO_2H} \xrightarrow{\mathrm{NaOH}} \mathrm{CH_3(C{\equiv}C)_3(CH{=}CH)_2CH_2CO_2H}$$

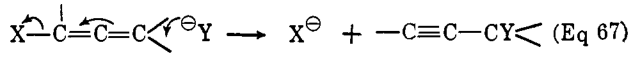
If a methylene group interposes between the allene bond and an activating group, migration of one of the methylene protons usually occurs, leading to conjugated dienes, *e.g.* (138)

$$\mathrm{CH_2{=}C{=}CHCH_2CO_2H} \xrightarrow[70^\circ,\ 15\ \mathrm{min}]{10\%\ \mathrm{NaOH}} \underset{83\%}{\mathrm{CH_2{=}CHCH{=}CHCO_2Na}}$$

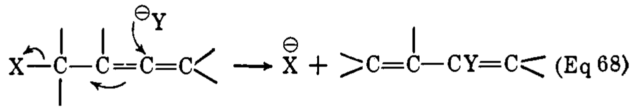
In the example cited the reverse reaction was also observed when the 1,3-diene acid was photolyzed in dilute solution.

2. *Anionotropic Rearrangements*

Suitable derivatives of allenes may be converted to the corresponding acetylenic or conjugated diene isomers by the migration or displacement of an anion. If the anion was initially bound directly to the allenic system, acetylenes are formed (the retropropargyl rearrangement) (Eq 67). On the other hand, conjugated dienes arise if the anion lies initially at the β position (Eq 68), in which case the isomerization is a variant of the well-known allylic rearrangement (322).



$$\mathrm{X{-}\overset{|}{C}{=}C{=}C{<}\ ^{\ominus}Y} \longrightarrow \mathrm{X^{\ominus}} + \mathrm{{-}C{\equiv}C{-}CY{<}} \quad \text{(Eq 67)}$$



$$\mathrm{X{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{C}{=}C{=}C{<}\ ^{\ominus}Y} \longrightarrow \overset{\ominus}{\mathrm{X}} + \mathrm{{>}C{=}\overset{|}{C}{-}CY{=}C{<}} \quad \text{(Eq 68)}$$

So far the only examples of anionic retropropargyl rearrangements (Eq 67) involve allenic halides (X = F, Cl, or Br). Ginzburg (211, 212), and later Jacobs and his co-workers (271, 274, 275), examined the reduction of α-haloallenes and found that partial rearrangement accompanies the reduction if a zinc–copper couple is used. Because identical mixtures of isomers are produced, whether the starting material is an allene or an acetylene, and the products fail to interconvert under these conditions, a common intermediate seems likely and is possibly an organozinc halide (274) (Eq 69). It is found that alkylation

$$\begin{matrix}CH_2{=}C{=}CHBr\\ \text{or}\\ BrCH_2C{\equiv}CH\end{matrix} \xrightarrow{Zn\text{–}Cu,\ EtOH} (CH_2{=}C{=}CH)ZnBr \xrightarrow{EtOH} \underset{67\%}{CH_2{=}C{=}CH_2} + \underset{33\%}{CH_3C{\equiv}CH} \quad \text{(Eq 69)}$$

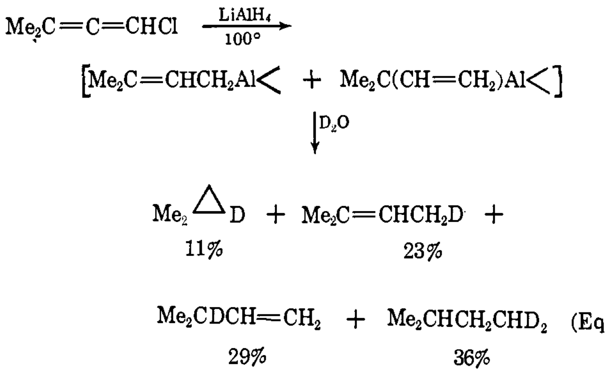
of the haloallene increases the proportion of the allenic isomer produced (274).

The likelihood of a common organozinc intermediate is enhanced by the observation that α-haloallenes and their corresponding acetylenic isomers are converted by metals such as zinc or magnesium to identical organometallic species, which, although of allenic structure, are converted mainly to acetyic lenhydrocarbons or alcohols when treated with alkyl halides or carbonyl compounds, respectively (194, 207, 270, 418, 424) (Eq 70).

$$\begin{matrix}CH_2{=}C{=}CHBr\\ \text{or}\\ BrCH_2C{\equiv}CH\end{matrix} \xrightarrow[THF,\ -10^\circ]{Zn} (CH_2{=}C{=}CH)_2Zn \xrightarrow{Me_2CO} HC{\equiv}CCH_2CMe_2OH \quad \text{(Eq 70)}$$

In contrast to their behavior with a zinc–copper couple, α-haloallenes are reduced by lithium aluminum hydride to complex mixtures of acetylenes, olefins, and alkanes, without the formation of allenic isomers (271, 274, 275). Probably addition of the reagent to a double bond, followed by hydrolysis, competes with hydride ion attack in an SN2′ fashion. With bromopropadiene the latter process occurs mainly, and a high yield of propyne is obtained (275), but with increased alkylation of the allene the main process is addition and hydrolysis, as is shown by studies with heavy water (275) (Eq 71).

$$CH_2{=}C{=}CHBr \xrightarrow[26^\circ]{LiAlH_4} \underset{60\%}{CH_3C{\equiv}CH} + \underset{1\%}{CH_3CH{=}CH_2}$$



(Eq 71)

An α-haloallene possesses a relatively unreactive halogen, but nevertheless a few other cases are known in which the halogen is displaced in an anionic rearrangement. For example, bromoallene is slowly isomerized over cuprous bromide and by potassium iodide in solution (263) (Eq 72), and 1,1-dialkyl-3-chloroallenes isomerize slowly in the presence of aqueous carbonate, though in this medium some prototropy also occurs (177) (Eq 73).

$$CH_2{=}C{=}CHBr \begin{cases}\xrightarrow{CuBr} BrCH_2C{\equiv}CH\\ \xrightarrow{KI} ICH_2C{\equiv}CH + CH_2{=}C{=}CHI\end{cases} \quad \text{(Eq 72)}$$

$$Me_2C{=}C{=}CHCl \xrightarrow[80^\circ]{aq\ CaCO_3} Me_2CClC{\equiv}CH + CH_2{=}CMeCH{=}CHCl \quad \text{(Eq 73)}$$

When treated with an alkoxide in methanol, the rearrangement of α-haloallenes produces acetylenic ethers by a second-order rate equation (370). This need not imply an SN2′ mechanism, but may be due to initial rate-determining prototropic rearrangement or carbene formation.

An interesting example of the use of α-bromoallenes in synthesis was reported recently (24, 25). The bromoallenes are treated with alk-1-ynes in the presence of cuprous bromide and amines, giving alkynylallenes in excellent yield.

$$RR'C{=}C{=}CHBr + R''C{\equiv}CH \xrightarrow[Et_3N]{CuBr} \underset{15\text{–}82\%}{RR'C{=}C{=}CHC{\equiv}CR''}$$

β-Haloallenes, which may be obtained from alkenynes and hydrogen halides, are much more reactive. They are easily converted into conjugated dienes (Eq 68) by cuprous halides in acid solution, a reaction which forms the basis of Carothers' synthesis of chloroprene and bromoprene (106, 107, 112). Reinvestigations of this reaction have led to the suggestion that cuprous chloride, or a complex of the type CuCl·HCl, participates directly in the transition state of the rearrangement; the rate of isomerization depends not only upon the concentration of the chloroallene but shows first-order dependence on the cuprous chloride concentration (115, 153). The reaction is quite general, since alkenylacetylenes also react with bromine (441), hydrogen bromide (568), and chloromethyl ethers (585–587), giving allenes (by 1,4 addition) which are readily isomerized by cuprous salts or by zinc halides (Eq 74).

$$CH_2{=}CHC{\equiv}CH \xrightarrow[-15^\circ]{aq\ HCl} CH_2ClCH{=}C{=}CH_2 \xrightarrow[aq\ HCl]{CuCl} CH_2{=}CHCCl{=}CH_2$$

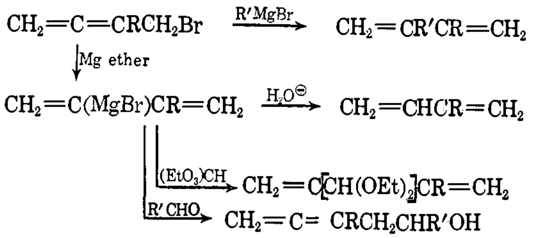
$$CH_2{=}CMeC{\equiv}CH \xrightarrow[ZnCl_2]{MeOCH_2Cl} CH_2ClCMe{=}C{=}CHCH_2OMe \xrightarrow[ZnCl_2]{CuCl\ or} CH_2{=}CMeCCl{=}CHCH_2OMe \quad \text{(Eq 74)}$$

No rearrangement occurs when β-haloallenes undergo nucleophilic substitution by acetate or hydroxide ions, or with neutral nucleophiles such as amines (109–111, 583, 584). However, when reduced by a zinc–copper couple they are isomerized and yield conjugated dienes (568).

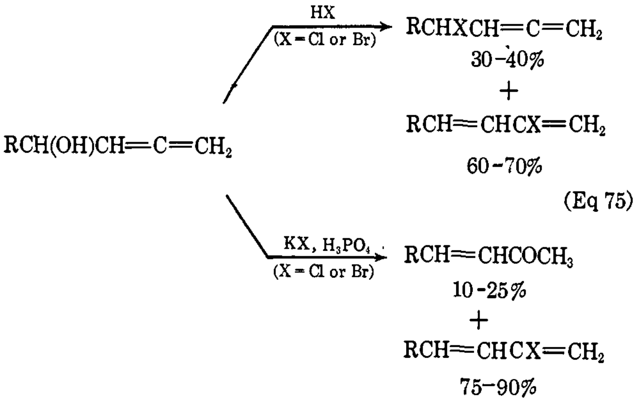
$$CH_2{=}C{=}CMeCH_2Br \xrightarrow[EtOH]{Zn-Cu} CH_2{=}CHCMe{=}CH_2$$

Similar rearrangements have been observed when β-haloallenes are treated with Grignard reagents (105, 108), or with magnesium in ether followed by hydrolysis or addition of a carbonyl compound (57, 418) (Scheme XIII).

SCHEME XIII



Both β-halo- and β-hydroxyallenes rearrange to *cis*- and *trans*-halodienes when treated with potassium halides in acid solution (56), and β-hydroxyallenes also rearrange partially during halogenation (55) (Eq 75). Such rearrangements offer possible routes to a variety of new conjugated dienes.



(Eq 75)

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