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# Advances in the Chemistry of α-Halogenoallenes

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Results obtained on the preparation and reactions of α-halogenoallenes are critically surveyed, and the reaction mechanisms are discussed. A list of 224 references is included.

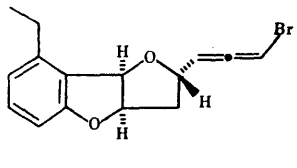
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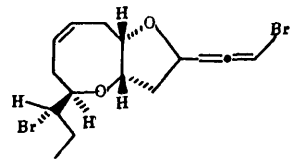
## I. INTRODUCTION

α-Halogenoallenes are important examples of organic compounds having cumulative double bonds. As polyfunctional compounds they have an interesting structure, on whose basis various compounds can be obtained having properties useful in many fields of organic synthesis and practical application.

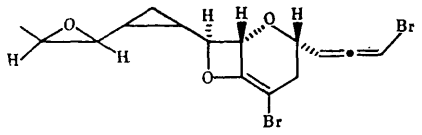
Individual members of this class, containing a terminal bromoallene group, have already been found in Nature. Thus the phenyl ether panacene



panacene



laurallene



okamurallene

has been isolated from the mollusc *Arlysia brasiliana*[1], and the bicyclic diethers laurallene and okamurallene have been obtained[2] from the marine red algae *Laurencia*.

During recent years research in this field has become more active and systematic, but the results have not yet been covered in reviews[3-6].

## II. METHODS OF PREPARATION

Halogenoallenes can be obtained in various ways. In several cases these methods are based on elimination. However, most typically halogen substituents are introduced, and form the basis for various rearrangements of acetylenic compounds.

### 1. 1,2-Elimination

Practical methods for obtaining halogenoallenes by elimination are at present restricted to the dehalogenation and dehydrohalogenation of aliphatic compounds containing mainly halogens as substituents[4].

Mono- and di-fluoropropadienes have been prepared by the action of zinc in alcohol[7] or in dimethylformamide[8]. Debromination of 2,3-dibromo-1,1,3,3-tetrafluoropropene (with magnesium in oxolan) gives a 91% yield of perfluoroallene[9]. Butyl-lithium metallates 2-bromo-3,3,3-trifluoropropene at the bromine, which undergoes elimination when the temperature is allowed to rise from −90 to 20 °C, to give a 72% yield of 1,1-difluoroallene[10]:

$$CF_3C(Br)=CH_2 \xrightarrow{BuLi,\ -90^\circ} CF_3C(Li)=CH_2 \rightarrow CF_2=C=CH_2 .$$

Deiodofluorination in the presence of copper powder at 200 °C has been used to obtain theoretical yields of perfluoro-1,2-dienes[11]:

$$CF_3CCl=C(R)CF_3 \rightarrow CF_2=C=C(R)CF_3 \qquad R=C_2F_5,\ n\text{-}C_3F_7,\ iso\text{-}C_3F_7 .$$

Various basic reagents–alkalis in a solvent[12-15] or in the solid state[16], sodamide in liquid ammonia[17,18], butyl-lithium[19]– are used to effect β′-elimination. This method can be employed to obtain trifluorinated[16], perfluorinated[12-14], perchlorinated[17], and perbrominated[18] allenes.

Dibromoalkenes containing substituents Y = COOR, COR, $PO(OC_2H_5)_2$, which activate an α-hydrogen atom, are readily dehydrobrominated by bases, including amines, to give satisfactory yields of allenes BrCH : C : CHY.[20-24] Potassium or lithium t-butoxide is used at low temperatures to prepare perhalogenoallenes containing electron-accepting groups[25,26]:

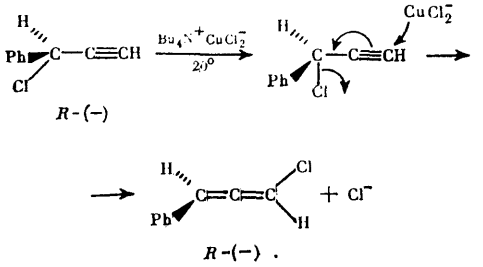
$$CCl_2=C(X)-CH(Cl)Y \xrightarrow{-70^\circ} CCl_2=C=C(Cl)Y \qquad Y=CO_2Et,\ CN,\ CONH_2 .$$

### 2. Prop-2-ynyl Rearrangements

#### Anionotropic conversion

Many reagents are able to convert 3-halogenoalkynes into 1-halogenoallenes, among which the most commonly used are copper(I) salts[27-29]. Although this process is reversible, it is often possible under appropriate experimental conditions to obtain entirely satisfactory yields (40–70%) of α-halogenoallenes[29-32]. Under the influence of the tetrabutylammonium chloride complex of copper(I) chloride(−)-phenylprop-2-ynyl chloride is converted with high stereospecificity into the optically active allene chloride[33]. In view of the first order a single-stage mechanism of $S_N2'$ type with *anti*-attack by

the reagent is assumed for this reaction:



*R*-(−) .

### Prototropic isomerisation

Only a few examples of the prototropic isomerisation of halogeno-compounds have been reported. Thus in the presence of sodium ethoxide a diacetylenic bromide isomerises into an allene[34]:

$$(RC{\equiv}C)_2CHBr \xrightarrow{EtONa} \underset{\underset{Br}{|}}{RC{\equiv}CC{=}C{=}CHR} \qquad R = t\text{-}Bu\ .$$

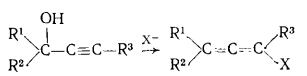
Isomerisation can be arrested at the stage of allene formation when electron-accepting groups activate the initial molecule. For example, halogenoallenecarboxylic esters are formed under very mild condtions[35,36], on brief shaking with dilute potassium carbonate solution at room temperature. Isomerisation is not observed in the absence of stabilising groups, as is clearly shown by the bromoprop-2-ynyl ester[35]:

$$BrC{\equiv}CCH_2\overset{\overset{O}{\|}}{C}OCH_2C{\equiv}CBr \xrightarrow{OH^-} BrCH{=}C{=}CH\overset{\overset{O}{\|}}{C}OCH_2C{\equiv}CBr\ .$$

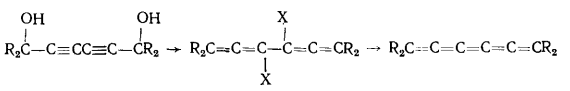
Prototropic isomerisation is possible under radical conditions[31,37]. A photochemically generated bromine atom leads to partial isomerisation of bromoprop-2-ynyl into bromoallenyl[37].

### Anioniotropic rearrangements

It is well known that acetylenic compounds containing a group X = H, Hal, OH, MgZ, etc. in the prop-2-ynyl position are able to give an allene product on undergoing an $S_N2'$ substitution[4,5]. Various α-halogenated allenes can be obtained from acetylenic alcohols as a result of this reaction:



Primary, secondary, and tertiary alcohols having a terminal triple bond and containing various types of alkyl groups near the reaction centre readily undergo the reaction[18,28,38–48]. It has acquired greatest value for the preparation of persubstituted halogenoallenes with aliphatic[43,47,49–51], aromatic[52–55], and alicyclic[56–58] substituents when the yields are 70–90%. Functional halogenoallenes—polyhalogenated[47,59–62], containing ester [63,64] and heteroatomic groups[65–68]—have also been obtained by this method, but side-reactions lower the yields. When two active centres are present, good yields can be obtained of dihalides having conjugated allene groups[51,56,59], which have found application in the synthesis of cumulenes[69,70]:

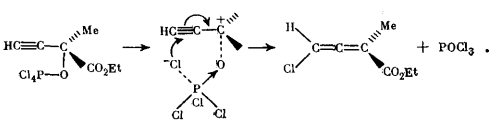


R = t-Bu, Ph, 2,2,6,6-$(CH_3)_4$-cyclo-$C_6H_7$;
X=Cl, Br .

The hydroxy-group is exchanged for a halogen atom when alcohols are treated with hydrohalic acids—hydrochloric[28,44,47,50], hydrobromic[39,40,43,47,59,60,67], and hydriodic[47,60]—phosphorus trichloride[49] and pentachloride[61,64] thionyl chloride[42,44–49,51–55,57,60,61,63], phosphorus tribromide[41,42,46,49,52,53,56,71], sulphuryl bromide[64], phosphorus pentabromide[64,71], and a mixture of triphenyl phosphite and iodomethane[38,68]. The detailed course of the reactions has not been studied, but qualitative observations show the possibility of varying and experimental conditions within each class to enable satisfactory results to be obtained. The yields differ somewhat, but under the most favourable conditions reach 70–90%.

Additional information on the chemistry of the reactions has been gained by the use of optically active substrates. Study of the action of three of the above reagents—thionyl chloride[45,72,73], hydrobromic acid[43], and phosphorus pentachloride[74]—on optically active acetylenic alcohols has shown high stereoselectivity of formation of halogenoallenes, usually with retention of configuration.

Intermediate products in all these reactions are probably chlorosulphite[63,73], a copper complex coordinated with hydroxyl and ethynyl groups[43], or a prop-2-ynyl cation solvated by phosphoryl chloride[74], which break down as a result of internal electron transfer: e.g.



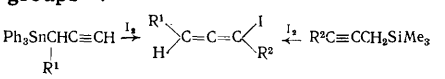
Thus the halogen is introduced as a consequence of *cis*-nucleophilic substitution by an $S_Ni'$ mechanism.

Other reactions are known involving exchange of a prop-2-ynyl function for halogen. Thus the action of iodine on a 4-chlorobut-2-ynoic ester forms the 2-iodobutadienoic ester[75].

Iodoallenes have been obtained by reaction between prop-2-ynyl bromide and iodine in methanolic caustic potash[76,77]; all three hydrogen atoms may be substituted:

$$HC{\equiv}CCH_2Br \xrightarrow{I_2} IC{\equiv}CCH_2I \xrightarrow{I_2} I_2C{=}C{=}CHI \xrightarrow{I_2} I_2C{=}C{=}CI_2\ .$$

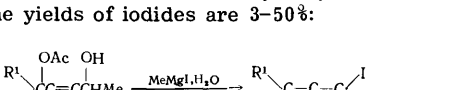
The suggested mechanism involved an intermediate allene carbanion. Similarly, phenylprop-2-ynyl chloride and *para*-substituted phenylprop-2-ynyl sulphide give 40–65% yields of the corresponding tri-iodoallenes[77]. Iodides are formed also by direct replacement of the triphenylstannyl[78] and trimethylsilyl groups[79]:



$R^1$=H, Me; $R^2$=$C_6H_{13}$ .

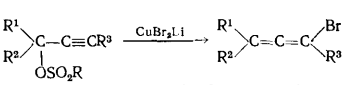
This method is suitable also for obtaining allenyl bromides[79].

Monoacetates of acetylenic t-glycols react with methylmagnesium iodide, but a mixture of products is formed, including allene iodides[80]; after hydrolysis of the reaction mixture the yields of iodides are 3–50%:



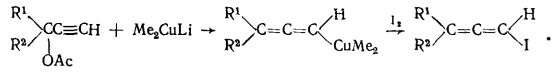
$R^1$, $R^2$=Alk, Ph .

Allene bromides are formed in ~60% yields also from prop-2-ynyl sulphonates by the action of the lithium copper(I) bromide complex in[81]:

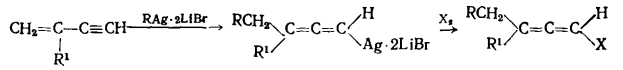


R=Me, *p*-Me-$C_6H_4$; $R^1$, $R^2$, $R^3$=H, Alk, Ph .

New methods of synthesis are based on reactions of allene organometallic compounds. Thus an organocopper intermediate, prepared regiospecifically from prop-2-ynyl acetates with lithium dimethylcuprate, reacts normally with iodine (at −78 °C) to give allene iodides[82]:



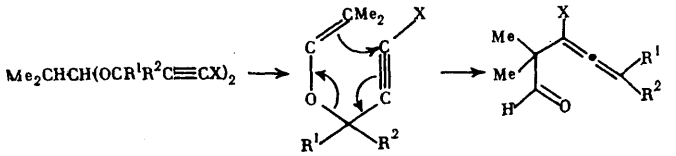
In the same way an allenylsilver salt (obtained by 1,4-addition of an alkylsilver(I)–lithium bromide complex to homologues of butenyne) is able to react with electrophiles (including halogens) to form brominated (iodinated) allenes[83], accompanied by a small quantity of an acetylenic isomer:



R = n-Bu, t-Bu, iso-Pr; $R^1$=H, Me; X=Br, I .

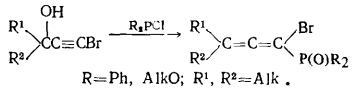
### Other rearrangements

Bishalogenoprop-2-ynylacetals, when heated (to 80–115 °C) in the presence of toluene-*p*-sulphonic acid, rearrange *in situ* into halogenoallene aldehydes[84,85]. It is assumed that a Claisen-type rearrangement takes place with intermediate formation of a prop-2-ynyl vinyl ether:



$R^1$, $R^2$ = H, Alk; X = Cl, Br .

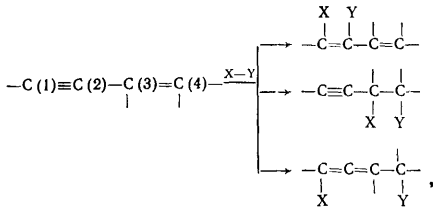
An analogous rearrangement occurs in the reaction between a halogenoprop-2-ynyl alcohol and a dialkyl chlorophosphite[86] or diphenylchlorophosphine[87,88] in the presence of a base, when a halogenoallene derivative is formed in 10–60% yield:



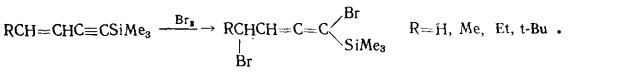
R=Ph, AlkO; $R^1$, $R^2$=Alk .

### 3. Addition to a Conjugated Butenyne System

Addition of molecules X–Y of halogens, hydrogen halides, and other active halogen compounds to conjugated enynes may take place in three main ways[4,89] among which only 1,4-addition yields allenes:

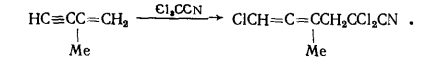


Addition of the different parts of the X–Y molecule obeys the general rule, so that, in conformity with the expected polarisation, the negative group goes to the $C_{(4)}$ atom of the ethylenic double bond. With bromine formation of compounds by 1,4-addition predominates over other directions to such an extent that such addition has preparative value[90–92]:

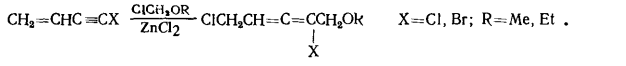


The direction of addition is little affected by the nature of the solvent, although there is a tendency for 1,4-addition to increase with alkenylacetylenes and to a greater extent with trimethylsilyl derivatives[93].

Methylbutenyne reacts with trichloroacetonitrile to give an allene derivative in theoretical yield[94]:

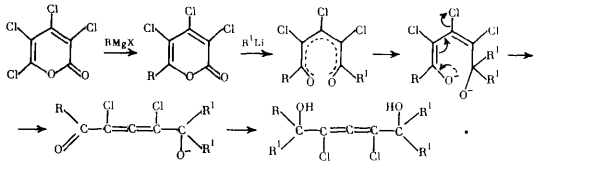


Several examples have been reported of the electrophilic addition of alkyl chloromethyl ethers[95,96] and hydrogen halides[97] to give 30–65% yields of halogenoallenes (although in these cases isomeric dihalides are formed at the same time):

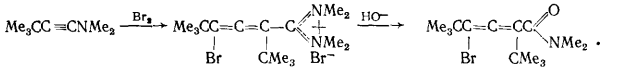


### 4. Other Methods

Perchloro-2-pyrone reacts with Grignard and then organolithium reagents to give tetra-alkyl-2,4-dichloropenta-2,3-diene-1,5-diols[98], most probably by the scheme



In the bromination of a 3,3-dimethylbut-1-ynylamine addition of a second alkynylamine molecule is observed with formation of the corresponding salt, which under alkaline conditions yields the dimethylamide of 4-bromo-2-t-butyl-5,5-dimethylhexadienoic acid[99]:



## III. REACTIONS AND TRANSFORMATIONS

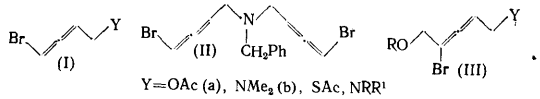
The known chemical reactions of halogenoallenes can be divided into three groups—those leading to functional transformation of substituents without affecting the allene group, cycloaddition, and linear substitution and addition with or without lengthening of the carbon chain.

### 1. Functional Transformations

Halogenoallenes are extremely sensitive to various reagents and to temperature, which cause a change in the allene bond. They can easily be converted into 1,3-dienes by prototropy[65,84]. It must therefore be borne in mind that the problem of

instability is present in all preparations of functional halogenoallenes.

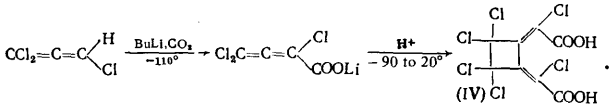
Substitution of the allyl bromine in 1,4-dibromobuta-1,2-diene (I: Y = Br)



Y=OAc (a), $NMe_2$ (b), SAc, $NRR^1$

by primary and secondary amines, potassium acetate and thioacetate, and thiourea under mild conditions gives positive results[67,100]. With benzylamine the reaction yields the bisbromoallene amine (II).[101] Functional derivatives of 5-alkoxy-4-bromopenta-2,3-dienes (IIIa,b) have been obtained similarly[96]. 1,4-Dibromobuta-1,2-diene is not hydrolysed under normal conditions: even mild bases (sodium hydrogen carbonate, calcium oxide, silver(I) oxide, etc.) eliminate hydrogen bromide. The alcohol (I: Y = OH) can readily be obtained in 60–70% yield from the acetate (Ia).[102] Trimethylsilyl and oxanyl protection is also readily introduced and removed[67].

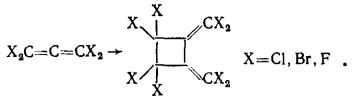
In some cases halogenoallenes undergo deprotonation under the influence of organolithium compounds and form a resonance-stabilised allenylcarbenium ion. But the trichloroallenyl cation reacts in the usual way with carbon dioxide to give the lithium salt of the acid, thermal conversion of which yields (after hydrolysis) and cyclic dimeric product (IV):[19]



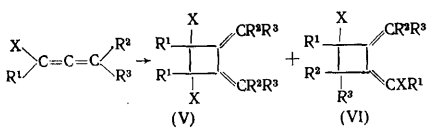
This salt reacts with cyclopentadiene (at −90 to 20 °C) to give in high yield (91%) the adduct of diene synthesis.

## 2. Cycloaddition Reactions

Dimerisation into four-membered cyclic compounds is a general reaction for the allene group, and is undergone also by halogenoallene derivatives. Indeed, polyhalogenoallenes such as the tetrachlorinated[17,103], tetrabrominated[18,104], and tetrafluorinated[12] propadienes are converted extraordinarily readily even at room temperature (which makes it difficult to obtain them in pure form) into 1,2-bisdihalogenomethylenecyclobutanes:



Thermal 2,2-cycloaddition takes place quite readily with unsymmetrical halogenoallenes, and in several cases (Table 1) yields a mixture of the possible isomers (V) and (VI):



(V) (VI)

The orientation of dimerisation undoubtedly depends on the positions of substituents. Experiment shows that halogenoallenes form four-membered rings head to head (V) and head to tail (VI) at the expense of the halogenated double bond preferably with vicinal methylene groups. Examples of the formation of 1,3-dimethylenecyclobutanes are fairly rare[110]. Nor has addition at both double bonds been reported.

**Table 1.** Examples of the 2,2-cycloaddition of halogenoallenes.

| X | $R^1$ | $R^2$ | $R^3$ | t, °C | Total yield, % | Proportions of isomers (V) | Proportions of isomers (VI) | Ref. |
|---|---|---|---|---|---|---|---|---|
| H | H | H | Cl | 60 | — | 100 | — | [105] |
| H | H | F | F | — | — | — | 100 | [106] |
| Cl | Cl | Cl | H | 20 | 100 | + | + | [107] |
| Br | H | Br | Br | 20 | 60 | 100 | — | [25] |
| Cl | Br | Cl | Cl | 20 | 100 | 100 | — | [108] |
| Cl | H | Me | Me | 140 | — | 45 | 55 | [109] |
| Br | H | Me | Me | 80 | 28 | 100 | — | [31] |
| F | $C_2F_5$ | F | F | 20 | 85 | 26 | 74 | [15] |
| F | F | $CF_3$ | $CF_3$ | — | — | — | — | [110] |
| H | H | Cl | $CO_2Et$ | 20 | — | 100 | — | [36] |
| Cl | Cl | Cl | $CO_2Et$ | — | 100 | 100 | — | [25] |
| Cl | Cl | Cl | $CONH_2$ | 20 | — | 100 | — | [26] |
| Cl | Cl | Cl | CN | 20 | — | 100 | — | [26] |
| Cl | H | H | mesityl | 80 | 45 | 41 | 59 | [111] |
| Cl | H | H | adamantyl | 130 | 90 | 41 | 59 | [112] |
| Cl | H | Ph | Ph | — | — | 45 | 55 | [109] |
| Br | H | Ph | Ph | — | — | 45 | 55 | [109] |
| Cl | Cl | Ar | Ar | — | — | 100 | — | [15] |
| Cl | H | fluorenylidene | | — | — | 100 | — | [57] |
| Br | H | fluorenylidene | | 80 | 80 | — | 100 | [57] |
| Cl | t-Bu | T-BuC:C | t-BuC:C | 25 | — | — | 100 | [49] |
| Cl | Cl | Cl | $CCl_2COOH$ | — | — | — | — | [113] |
| F | F | $CF_3$ | $Re(CO)_5$ | — | — | 100 | — | [114] |

Mutual thermal isomerisation of the dimers has been noted in several cases[49,57,110], but the dimer of perfluoroallene in the presence of caesium fluoride isomerises quantitatively into perfluoro-2-methyl-3-methylenecyclobutene[115].

The stereochemistry of dimerisation also depends on the positions of substituents and the degree of substitution of the allene bond. Isomers having a *trans*-arrangement of ring substituents usually predominate in a mixture of stereoisomers[109,112]. Substituents in the two *exo*-methylene groups are arranged mainly in *cis*-positions[111,112]. According to Jacobs[105,111,112] the stereochemical nature of the products of dimerisation is consistent with a biradical mechanism.

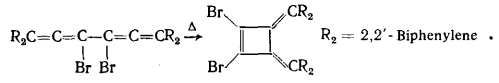
Study of the kinetics and the mechanism of the cyclodimerisation of perhalogenoallenes has shown[103] a second-order reaction. The rate of dimerisation to 1,2-dimethylenecyclobutane derivatives is very strongly dependent on the influence of substituents. Accumulation of electron-acceptors greatly destabilises the system: thus perchloroallene is stable only below −50 °C.[17] Kinetic measurements on a series of halogenoallenes of type $Cl_2C:C:CClX$ show that the rate of dimerisation increases in the sequence of substituents

$$X = H < Br < C_6H_5 \cong Cl < COOC_2H_5 < CN.$$

Among these trichlorobuta-2,3-dienenitrile is the most unstable of all allenes known at the present time[26].

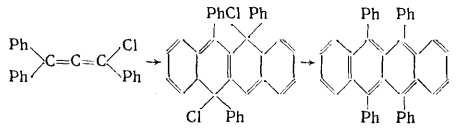
Study of the thermodynamics of cyclodimerisation has revealed a low enthalpy of activation (35.2–62.8 kJ $mole^{-1}$) and high negative entropies of activation (−188 to −146 J $mole^{-1}$ $deg^{-1}$). No paramagnetic intermediate species were detected in the dimerisation of tetrachloroallene, and a non-synchronous two-stage mechanism was assumed[103].

The conjugated 1,6-dibiphenylene-3,4-dibromohexa-1,2,4,5-tetraene when heated undergoes intramolecular cycloaddition with formation of a 3,4-dimethylenecyclobutene derivative[57]:

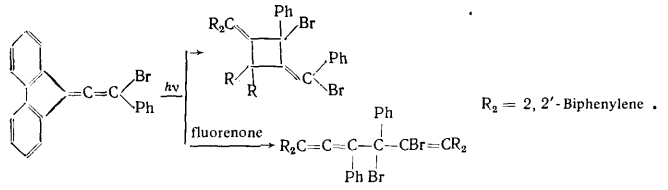


$R_2$ = 2,2′-Biphenylene .

However, dimerisation of triphenylchloropropadiene takes place preferentially by a Diels–Alder type of reaction accompanied by elimination of hydrogen chloride to form rubrene[116]:



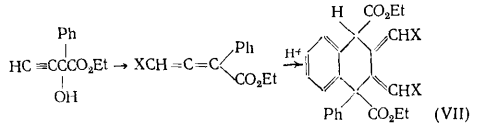
Depending on the conditions photochemical treatment yields various products, including those of 2,2-cycloaddition[111,117]. Thus exposure of 1,1-biphenylene-3-bromo-3-phenylallene in benzene to ultraviolet radiation yields a 1,3-divinylcyclobutane derivative[117]:



$R_2$ = 2, 2′-Biphenylene .

The action of ultraviolet radiation in the presence of fluorenone as sensitiser forms only a product of linear dimerisation of the bromoallene[117].

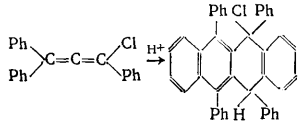
In several cases the reactions are complicated by interesting rearrangements of the resulting halogenoallenes under the influence of electrophiles. With a 2-hydroxy-2-phenylbut-3-ynoic ester the main product is the cyclic dimer (VII) as a mixture of geometrical isomers relative to the double bond[63,118]:



X = Cl, Br .

Formation of such a product can be explained by addition of the cation $XCH:C^+C(C_6H_5):C(OH)OC_2H_5$, formed by protonation of the ester group of the halogenoallene, to the central atom of another molecule of the latter followed by an electrophilic substitution type of cyclisation to an aromatic ring[118].

Under the influence of acids triphenylchloroallene undergoes cycloaddition to a tetracyclic compound (VIII):

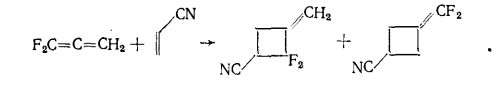


(VIII)

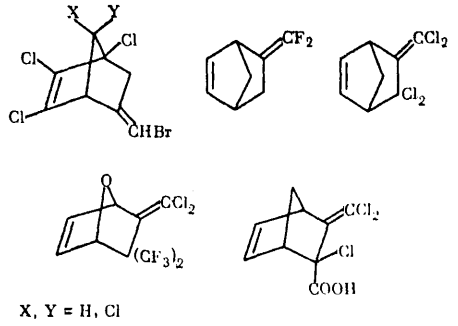
The reaction is assumed to involve interaction of a delocalised carbenium ion formed by protonation of the central carbon atom[119].

The possibility of the codimerisation of halogenoallenes with other dienophiles (X = Y) is strongly dependent on the position and the character of the substituent. The thermal codimerisation of perfluoroallene with hexafluorobutyne at 80–85 °C in the presence of a free-radical scavenger gives a 50% yield of perfluoro-1,2-dimethyl-3-methylenecyclobutene mixed with a dimer of allene (yield 42%) and other minor products[120].

With typical dienophiles (acrylonitrile, azodicarboxylic ester) 1,1-difluoroallene forms a four-membered rings predominantly by means of the fluorinated double bond[7,106]. In the case of acrylonitrile[7] the proportions of isomeric products are 5 : 1:



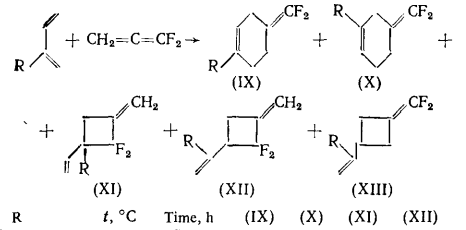
Halogenoallenes react quite well also with various 1,3-dienes, but in this case adducts of diene synthesis are formed primarily, together with 2,2-cycloaddition products[7,17,121]. The diene condensation has been reported of bromopropadiene[122], 1,1-difluoroallene[7,106], perchloroallene[17], trichlorobutadienoic acid[19], and 1,1-dichloro-3,3-bistrifluoromethylpropadiene[123] with cyclic dienes. These reactions always lead to the formation of only one of the isomers having an exocyclic halogenomethylene group



X, Y = H, Cl

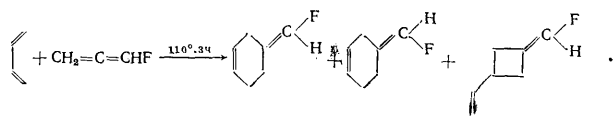
and may be of synthetic value for their preparation.

**Table 2.**



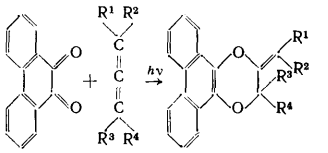
| R | *t*, °C | Time, h | (IX) | (X) | (XI) | (XII) |
|---|---|---|---|---|---|---|
| R=H | 110 | 7 | 63 | — | 37 | — |
| R=$CH_3$ | 110 | 7.5 | 29 | 35 | 26 | 10 |
| R=$(CH_3)_3SiO$ | 140 | 5.5 | 23 | 23 | 37 | 17 |

Addition of fluoroallene to butadiene forms a mixture of isomers at the *exo*-fluoromethylene group (yield 57%), the proportions of the reaction products being 2 : 2 : 1: [7]



Addition of 1,1-difluoroallene to alkylated dienes is still less selective: the yield of the adducts (IX) and (XIII) fluctuates between 60% and 90% (Table 2).[121] It is interesting that in both cases[7,121] an appreciable difference is observed in the addition of fluoroallenes: whereas 2,4-adducts are formed solely with an exocyclic mono- or di-fluoromethylene group, 2,2-adducts appear almost exclusively with an endocyclic difluoromethylene group; the proportions are (XI) + (XII) : (XIII) = 20 : 1.

Cycloaddition often occurs in photochemical processes. For example, 2,4-cycloaddition of 9,10-phenanthraquinone to dimethylbromoallene[124] leads to a roughly equally probable mixture of structural and geometrical cycloadducts of type (XIV: $R^1 = Br$, 9%; $R^2 = Br$, 7%; $R^4 = Br$, 13%):



(XIV)

When bromopropadiene is used under the same conditions[125], only one bond is involved in the reaction, with formation of a methylene-containing isomer (XIV: $R^1 = R^2 = R^3 = H$ and $R^4 = Br$).

Similarly, 4-chloro(and bromo)methylenetetramethyl-1-pyrazolines have been obtained (in respective yields 18% and 28%) from diazopropane and 1-chloro(and bromo)-3-methylbuta-1,2-dienes. The orientation in these examples corresponds to a hindered mode of cycloaddition[126,127].

The photoinduced addition of dehydrobenzene to chloroallene with formation of a chloromethylenebenzocyclobutane has been reported, but the yield is low (12%).[128]

### 3. Substitution of Halogen

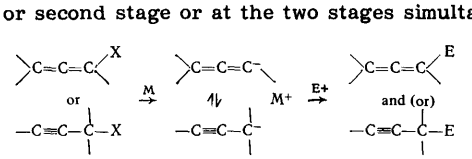
The ability of a halogen atom to be replaced by a nucleophilic species is directly dependent on the structure of the substrate. The presence of two electrophilic centres in a molecule is responsible for their peculiar reactivity, which depends in complicated fashion on the relative electrophilic properties of the centres, the nature of the nucleophilic, and solvolytic effects.

Subsequent discussions of α-halogenoallenes in nucleophilic reactions include consideration of parallel reactions of isomeric alkyne halides. This is necessary, since from the character of the changes they often lead to the formation of intermediate species that are resonance forms.

Reactions of halogenoallenes have been studied with water, alcohols, C–H acids, organometallic compounds, amines, metal hydrides, etc. The experimental results indicate that these reactions are governed by similar laws, and enable their most characteristic mechanisms to be examined.

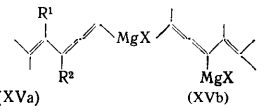
#### Organometallic derivatives

Halogenoallenes (and prop-2-ynyls) give with such metals as magnesium, zinc, aluminium, lithium, etc. organometallic derivatives, which then react with an electrophilic (E) with preservation and/or rearrangement of the initial molecule at the first or second stage or at the two stages simultaneously:



Reviews have recently appeared on this topic[129,130]. Not all the reactions have been discussed exhaustively, only the fundamental principles from the point of view of applying the especially valuable magnesium– and lithium–allene derivatives. It is considered at present that formation of Grignard reagents from halogenoallenes and the corresponding prop-2-ynyls is facilitated on the introduction of mercuric chloride or the addition of magnesium amalgam by the use of low temperatures (0–5 °C) and high-dilution technique[3,131,132].

1-Chloro- and 1-bromo-propadienes, as also the corresponding propynes, give with magnesium in ether a Grignard reagent, according to the infrared spectrum identical with the allene form but according to nuclear magnetic resonance data containing a greater proportion of the latter[3]. The preparation of α-deuteroallenylmagnesium bromide has been described[133]. Grignard reagents of vinylallenyl structure

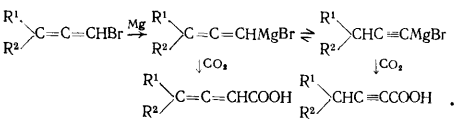


(XVa) (XVb)

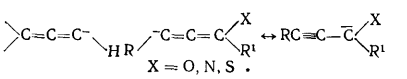
can be obtained by the action of magnesium on conjugated[129,134] and non-conjugated[135,136] vinylprop-2-ynyl halides. This method has wide application for the synthesis of diverse systems, in particular of phenomones and jasminoids[134–136].

Substitution of organo-magnesium and -zinc derivatives of allene in reactions involving electrophiles (water, aldehydes, ketones, epoxides, carbon dioxide, etc.) leads to their functionalisation. Attack takes place in general either at $C_{(1)}$ or at $C_{(3)}$. The regioselectivity of these reactions is ambiguous, and variations can be observed in the dependence on the nature of the metal (aluminium, magnesium, zinc)[137] and in the effects of various steric and electronic factors[138].

Sometimes competing side-reactions also lead to the formation of allene and/or acetylene derivatives. For example, hydrolysis of allenylmagnesium halides always occurs with partial formation of dimers of the hydrocarbon part of the initial halide[131,132]. Carbon dioxide gives exclusively or preponderantly allenic acids[43,48,49,131], the formation of acetylenic acids being explained by a slow prototropic shift in the allenylmagnesium bromide formed[131]:



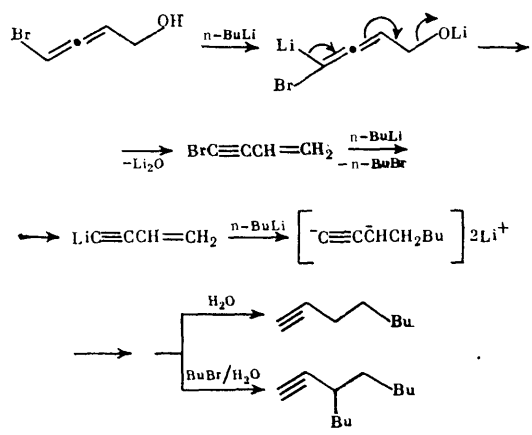
Lithiation of halogenoallenes gives good yields of lithium allenyls[59,139,140]; in many other cases the latter are generated by deprotonolysis[139–142], which occurs especially readily with hetero-substituted prop-2-ynyls:



In such reactions lithium reagents are especially attractive as synthons for organic synthesis. Reactions with diverse electrophiles clearly indicate the dual nature of the reagent, although in most cases they take place with retention of the allene structure[139–147].

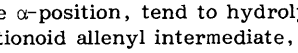
A curious rearrangement takes place in the action of butyl-lithium on 4-bromobuta-2,3-diene-1-ol. The reaction produces not only buta-2,3-dienol (in ~25% yield) but also a mixture of acetylenic hydrocarbons. An intermediate bromobutenyne is formed, which then reacts with butyl-lithium to form a dilithium prop-2-ynyl derivative that is converted into

the final hydrocarbons[148]:



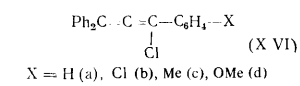
## Hydrolysis (solvolysis) of allenyl halides

Allenyl halides, especially those containing electron-donor substituents in the α-position, tend to hydrolyse by an $S_N1$ mechanism via a cationoid allenyl intermediate, which is a resonance form of an alkynylcarbenium ion



The latter is formed also by heterolysis of the C–X bond in prop-2-ynyl substrates, and its structure has been reliably confirmed by the $^1$H n.m.r. spectra of diarylalkynols in a strongly acid medium[149]. Jacobs and Fenton[52] were the first to suggest formation of an intermediate allenyl cation during hydrolysis.

Finally, a fairly recent study of the solvolysis of various triarylchloroallenes



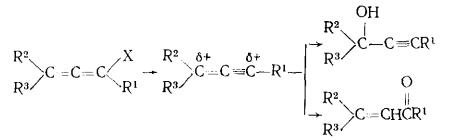
(XVI)

X = H (a), Cl (b), Me (c), OMe (d)

has shown that all these processes are unimolecular[54,150]. First-order kinetics has been established right up to 90% conversion, when reaction rates are independent of addition of a base. Solvolysis is characterised by a considerable accelerating effect of the ionic strength of the solvent [$m = 0.69$ and 0.77 for (XVIa) and (XVId) respectively] and a retarding effect of a salt having a common ion: the initial rate of solvolysis of triphenylchloroallene decreases by 29% in the presence of 0.1m lithium chloride[150]. The relative rates of reaction of the halogenoallenes (XVIa-d) in 80% aqueous acetone are 1 : 0.57 : 3.7 : 37.5. The element effect of the leaving group lies in the range $k_{Br}/k_{Cl} = 20$–58.

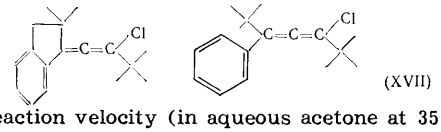
Similar rules have been illustrated by the solvolysis of a wide range of di- and tri-alkylated halogenoallenes with the alkyl groups in different positions ($R^1$, $R^2 = CH_3$, t-$C_4H_9$)[42,55]. The rate of solvolysis depends on the type and the number of substituents: on passing to bromopropadiene the rate constant decreases by a factor of $10^9$.[151] The appearance of an element effect $k_{Br}/k_{Cl} = 20$–58, the reaction constant of arylated chloroallenes $\rho = -2.0$, and the entropy of activation of these reactions (−42 to +37 J mole$^{-1}$ deg$^{-1}$) also agree well with substitution by an $S_N1$ mechanism.

In conformity with this the solvolysis of optically active 1-bromo-3-methylpenta-1,2-diene gives racemic products[152]. Finally, the effect of a salt on the observed solvolysis rate constant[152] and stereochemical data on recovery of the allenyl halide (complete retention of configuration)[153] indicate directly the possibility that the intimate ion-pair of the allenyl cation is involved in the transition state:



Substitution in allene derivatives by an $S_N1$ mechanism obeys different rules, since selectivity of attack is then determined by competition of the carbenium ion from two sides. The main products are acetylenic alcohols (yield 40–60%): i.e. preferential attack at the prop-2-ynyl centre of the cation is observed. Furthermore, addition takes place at the sterically less hindered carbenium centre, for unsaturated ketones are formed in the case of halogenoallenes having the substituents $R^2 = R^3 = t\text{-}C_4H_9$.[53,55]

An aromatic ring is more effective in influencing the rate of solvolysis when attached to $C_{(1)}$ than to $C_{(3)}$ (nine times as rapid)[55]. This is obviously due to the inability of such a ring at position 3 to attain a planar arrangement in order to act effectively on formation of a cationic centre and on its reactivity. It has been shown for the sterically fixed chloroallene



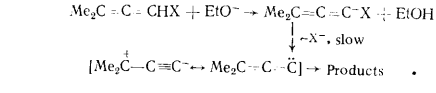
(XVII)

that the reaction velocity (in aqueous acetone at 35 °C) is higher than that of the open-chain analogue by a factor of 6800.[58]

An aromatic 3-substituent may be expected to have a greater influence in stabilising an allenyl than a vinyl cation. Stang[154] estimated this effect by comparing the reaction rate constants of triphenylallenyl and tri-p-methoxyphenylvinyl chlorides in 90% aqueous ethanol. The considerable kinetic effect of $10^6$–$10^9$ in the rate constant can be explained by direct attachment of the aryl substituent to the carbon atom, which in a unimolecular process becomes a cation.

The influence of isotopes on reaction velocity has also been studied[42,155]. Replacement of α-hydrogen by deuterium in 1-bromo-3,4,4-trimethylpenta-1,2-diene lowers the rate, with an α-secondary isotope effect $k_H/k_D = 1.22$,[155] which far exceeds the usual isotope effect of hydrogen substitution in the solvolysis of alkyl bromides. Solvolysis of the above bromo-compound labelled with deuterium in the β′-position ($CD_3$) gave considerable secondary isotope effects (1.23). These results can be explained by additional stabilisation of the transition state and the intermediate carbenium ion by a greater contribution from the prop-2-ynyl structure.

The solvolysis of terminal halogeno allenes and prop-2-ynyl halides under conditions of catalysis by bases is of especial interest, since it enabled the possibility of substitution via an intermediate vinylidenecarbene—a zwitterion—to be demonstrated for the first time[156]. Mainly prop-2-ynyl substitution products are formed from a 3,3-dialkylated bromoallene:



There is no doubt about the mechanism of this reaction, at least in relation to the formation of vinylidenecarbene[157,158]. It is supported by physical and chemical tests: the reaction is not catalysed by bases when the acetylenic hydrogen is replaced by an alkyl group[159]; and the change in the activation volume indicates that water plays no part in the transition state. The positive but small activation volume

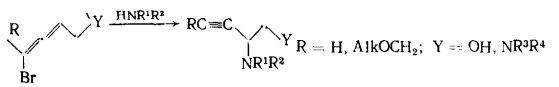
(+1.8 $cm^3$ $mole^{-1}$) is consistent with equally probable contributions by the two resonance structures[160].

From data on recovery of the allenyl halide (with the use of 1,4-disubstituted adamantanes as stereochemical label) it was concluded that a carbene–anion pair was involved in the reaction[153].

A carbene mechanism has been attributed to other reactions of halogenoallenes—with amines[156,161] C–H acids[162,163], Grignard reagents[164]—mainly by analogy with the mechanism of solvolysis. These reactions also take place in basic media, which favour carbene formation, e.g. under conditions of phase-transfer catalysis[165]. However, because of inadequate study of these reactions, there is no complete certainty that a carbene mechanism is involved.

## Substitution by amines

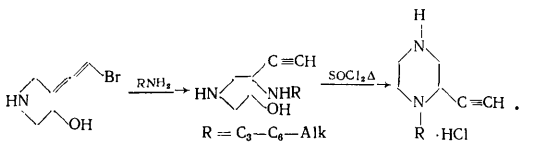
Replacement of halogen by an amine in a prop-2-ynyl halide is one of the most widely used methods for obtaining many aminoacetylenes, which show promise in research on physiologically active substances[166]. Halogenoallenes have been less investigated. It has proved possible to use these reactions, not with halogenoallenes themselves but with their functional derivatives. Examination of the reactions of allene bromides (I: R = H) and (III: R = AlkOCH$_2$)



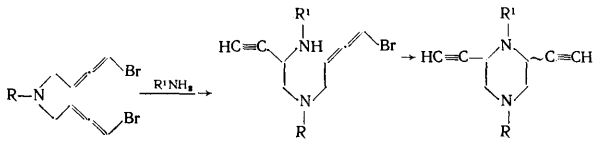

(I), (III)

with primary and secondary amines have shown that the sole process is replacement of the bromine atom by an amino-group. Substitution takes place at the γ-position, i.e. with simultaneous allene–acetylene rearrangement, to give vicinal difunctional acetylenes in ~40–70% yields[100,167,168].

Aminoalkylation also occurs with 1-bromo-4-2′-hydroxyethylaminobuta-1,2-diene[169]; although yields are not high, the resulting acetylenic diamino-alcohols can be converted by simple transformations into 2-ethynylpiperazines, which are difficultly accessibled by other means (yield ~30%):



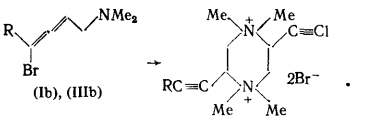

However, results for the heterocyclisation of *NN*-bis-4-bromobutadienylamines (II) are most interesting for preparative purposes; the only products are 2,6-diethynylpiperazines (an equimolecular mixture for *cis*- and *trans*-isomers) in 40–60% yield, apparently by intramolecular replacement of an atom in an intermediate diaminobromoallene[101,170]:




R=CH$_2$Ph, HOCH$_2$CH$_2$; R$^1$=C$_2$–C$_8$–Alk, CH$_2$Ph, 1-adamantyl .

This unusual, but smooth and obviously general reaction provides a good method for obtaining *C*-alkynyl derivatives of other heterocycles (nitrogen, oxygen, sulphur) and merits further study.

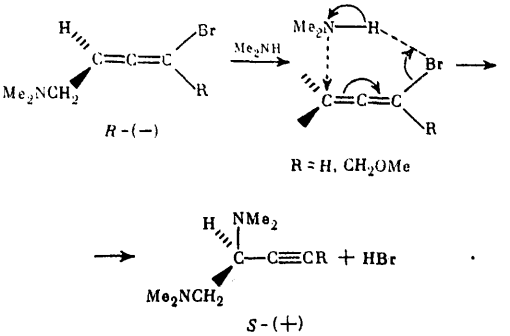
Finally, the dimerisation of bromo-*NN*-dimethylbuta-2,3-dienylamines (Ib, IIIb) (dimethylformamide at 20 °C) yields the corresponding salt of the quaternised 2,5-dialkynylpiperazine (which may be explained as both an intermolecular and an intramolecular process, in which a three-membered ring should be obtained)[170]:



(Ib), (IIIb)

The mechanism deserves special consideration. To elucidate the effect of the degree of substitution in the bromomethylene group on the direction, kinetics, and stereochemistry of substitution, two types of α-bromoallenes were used (Ib: R = H) and (IIIb: R = CH$_2$OCH$_2$). In the former case the reaction could occur via a carbene, and in the latter an allenyl cation could be formed. As noted above, the reaction is not complicated by secondary processes, gives the same regioselective substitution product in the two cases, and has overall second order (first with respect to the halogenoallene and first with respect to the amine)[171]. Even from these results it could be concluded that interaction with amines involves neither $S_N1$ alkylation nor a carbene stage.

Investigation of the stereochemistry of amino-substitution[172] involving optically active (–)-bromobuta-2,3-dienylamines (Ib) and (IIIb) has shown that the reaction with dimethylamine involves transfer of chirality with formation of (+)-acetylenic diamines†. Such constancy of structural, kinetic, and stereochemical relations indicates that the same type of transition state is involved in the two cases. From these facts a model of this complex was suggested with *cis*-orientation of entering and leaving groups, according to which aminoacetylenes should be formed with positive specific rotation for the *S*-configuration#:



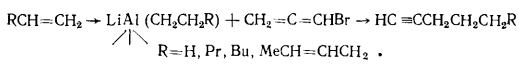

Since the retroprop-2-ynyl rearrangement accompanying substitution involves essentially an $S_Ni'$ mechanism, it is interesting that such reactions in the acyclic allyl system lead to predominance of the *cis*-isomer when the attacking nucleophile is neutral[173], and the *trans*-isomer if the nucleophile is ionic in character ($RS^-$).[174]

† The degree of stereospecificity of the analogous reaction of (–)-(Ib) with (–)-α-methylbenzylamine is ≥80% (according to capillary gas–liquid chromatography)[170].

# Erroneously termed an *R*-configuration in Ref. 172.

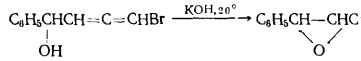
### Other nucleophiles

Individual studies have been made of the conversion of allenyl halides in the Meyer reaction[175] with metal phosphides and arsenides[176] and with lithium tetrahydroaluminate[177], leading to the formation solely of acetylenic derivatives§. A novel method for obtaining terminal acetylenes (in 50–60% yield) is based on the hydroalumination of bromopropadiene[178]:

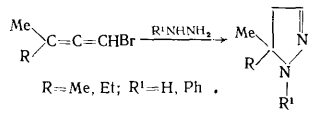


Under similar conditions prop-2-ynyl bromide yields terminal allenes[178].

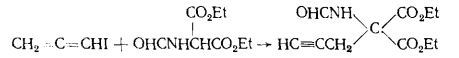
Halogen can be replaced by hydroxyl under suitable conditions[44,179]. A case has been reported of intramolecular substitution—rearrangement with formation of *trans*-2-ethynyl-3-phenyloxiran (yield 34%) from 4-bromo-1-phenylbuta-2,3-dien-1-ol in the presence of caustic potash[180]:



Substitution of dialkylallenyl bromides by hydrazines is accompanied by intramolecular cyclisation with formation of a 2-pyrazolines (yield 60–70%), reaction being facilitated by catalytic additions of copper(I)[181]:

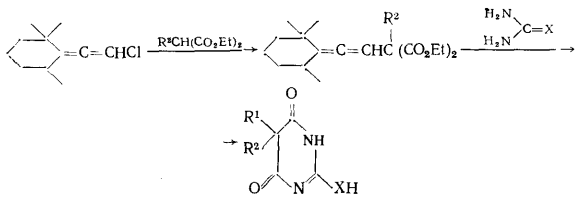


Compounds containing active hydrogen can be used. With acetoacetic ester halogenoallenes are assumed to undergo reactions having $S_N2$ and/or $S_N2'$ mechanisms[182,183]. Under these conditions the isomeric 1-bromoallene and 3-bromopropyne give a moderate yield of a like mixture of mono and disubstitution products and cyclic compounds formed from them[182,183]. From iodoallene (mixed with 25% of 3-iodopropyne) with formamidomalonic ester in the presence of sodium ethoxide as base are formed the corresponding prop-2-ynyl derivatives in 67% yield[162]:



Similar reactions occur with alkylated halogenoallenes, but the proportion of isomeric allenic keto-esters[183] or diesters[162] increases with the steric hindrance of the halides.

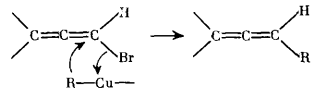
Similarly, alkylmalonic esters react with sterically hindered allenyl halides in the presence of sodium ethoxide to form allenic diesters, from which several allenic barbiturates (and thiobarbiturates) have been obtained by the action of urea (thiourea)[163]:



$R^1$ = t-BuCH = C = CH, t-BuC (Me) = C = CH, (iso-Pr)$_2$ C = C = CH, $Et_2C{=}C{=}CH$; $R^2$ = Et, n-Bu; X = O, S .

§ Reactions of iodoallenes with vinyl cuprates have been used also for the synthesis of dehydroarachidonic acids[224].

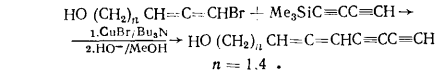
Halogenoallenes are converted by lithium dialkylcuprates[184,185] and copper cyanide[186] into allenic derivatives with replacement of the halogen via a four-centre transition state:



R = Alk, CN, $(AlkO)_2P(O)CH_2$ .

The allenic structure is retained during cathodic reduction[187] and on reaction with lithium alkyls[188] and with a Grignard reagent in the presence of catalytic quantities of palladium chloride[189].

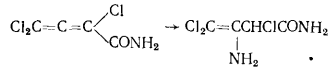
We note in conclusion that bromo- and iodo-allenes condense smoothly with terminal acetylene in the presence of copper salts and an amine (as a base) to form conjugated allene–acetylenes[67,190]. This process has been used to synthesise allene-diyne metabolites produced by micro-organisms[67]:



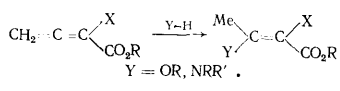
Under the influence of copper salts α-bromoallenes are converted into conjugated diallenes, the course of the reaction being strictly regioselective[191].

### 4. Linear Addition of Nucleophilic Reagents

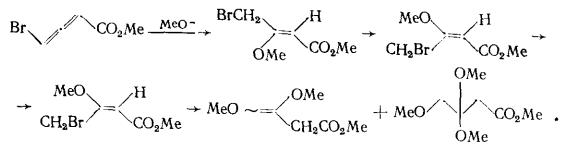
The allene group in α-halogeno-derivatives is usually resistant to attack by nucleophiles, and addition reactions have been little studied. Among them we may note firstly those of halogenoallenes containing electron-accepting substituents (alkoxycarbonyl, diethylphosphono, carbonyl). As might be expected, attack by the nucleophile (amine or alcohol) takes place exclusively at the carbon atom of the more electrophilic αβ-double bond, with formation of adducts corresponding to a protonated carbanion at the outer carbon atoms of the allene group. Adducts of crotonic type, being thermodynamically stable, may of course result also from prototropic isomerisation of vinylacetic adducts. 2,4,4-Trichlorobut-2,3-dienamide and ammonia form only the vinylacetic amino-derivative[26]:



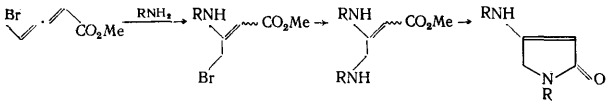
Primary and secondary amines and also alcohols (in the presence of an alkoxide) react smoothly with 2- [192] and 4-4-halogenobutadienoic esters[24,35,193] to give high yields of β-substituted derivatives of crotonic type:



However, involvement of γ-halogen in the reaction leads to formation of bisadducts. Thus mono-, di-, and tri-alkoxy-derivatives are formed with alcohols depending on the proportions of the components[193]: for the addition of methanol the reactions are

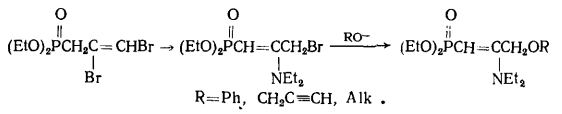


When excess of a primary amine is used, the resulting diaminocrotonic ester then undergoes cyclisation to form γ-alkylamino-substituted α-pyrrolinones, which cannot be obtained in other ways[35]:



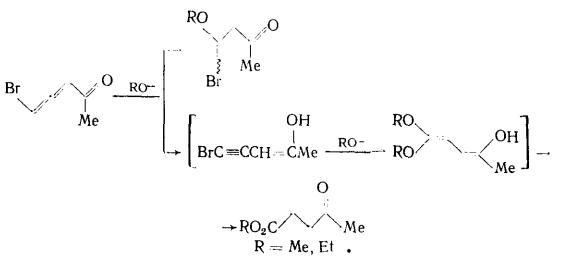
R=Et, n-Bu, t-Bu, $CH_2Ph$ .

Several nucleophilic additions of amines and alcohols have been reported for βγ-dibromoalkenylphosphonates. The reactions involve an intermediate bromoallenylphosphonate. The method enables addition to be conducted selectively, and phosphonates to be synthesised to contain various functional substituents[21-23]:



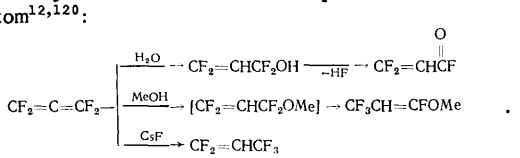
R=Ph, $CH_2C{\equiv}CH$, Alk .

The interaction of halogenoallenyl ketones with amines and alcohols has been studied considerably less. 5-Bromopenta-3,4-dien-2-one with alcohols gives only a small proportion of alkoxy-derivatives, the main reaction products being laevulinic esters. It is assumed that an intermediate ketenic acetal is formed by substitution at the *sp*-hybridised carbon atom[194]:



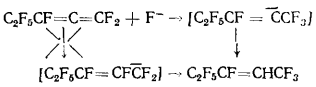
R = Me, Et .

Somewhat different rules are observed in the orientation of addition of nucleophilic reagents to perfluoroallene compounds, whose reactions have been widely studied. Tetrafluoroallene reacts with such reagents as water, methanol, and moist caesium fluoride under exceptionally mild conditions to give monoadducts. Elimination or rearrangement of the initial adducts can be observed at the same time, but the regioselectivity is such that the nucleophile adds to a terminal carbon atom[12,120]:

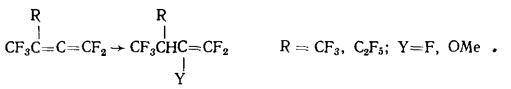


Similarly, perfluoropenta-1,2-diene gives monoadducts formed by attack at a terminal difluoromethylene group, with simultaneous formation of products of retroprop-2-ynyl rearrangement[195].

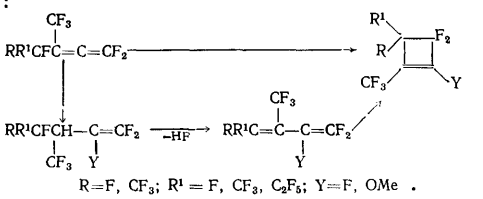
The orientation of nucleophilic addition to tetrafluoroallene and perfluoropenta-1,2-diene is directly opposite to that observed with halogenated buta-2,3-dienoic acids and related compounds discussed earlier. Such a course is not surprising, since attack by a nucleophile at the central carbon atom should produce an α-fluorocarbanion, which is unable to destabilise the positive charge on the fluorinated carbon atom[196]. In such cases only derivatives at a terminal carbon atom are formed: i.e. addition takes place at the double bond with formation of the most stable carbanion, stabilised by the perfluoroalkyl group:



Increasing the chain length of perfluoroalkyl-substituted allenes leads to a change in the orientation of addition. Their reactivity diminishes, but with increase in reaction time quantitative yields can be obtained even here[11]. The perfluorinated analogues of 1,1-methyl(alkyl)- and tetramethylallenes react with nucleophiles (methanol, caesium fluoride) to form monoadducts corresponding to regioselective attack at the central carbon atom[11,13,197]; hydrogen is directed solely to the end of the double bond substituted by the perfluoroalkyls:

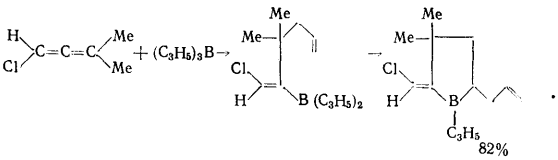


The monoadducts formed may undergo further changes, as e.g. in the reactions of 1,1-dialkylperfluoroallenes, when the resulting derivatives are dehydrofluorinated and spontaneously cyclised with high yields into the corresponding cyclobutenes[11]:



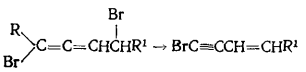
R=F, $CF_3$; $R^1$ = F, $CF_3$, $C_2F_5$; Y=F, OMe .

At 20 °C reaction takes place between triallylborane and dimethylchloroallene at the substituted double bond; the resulting diallylborane undergoes intramolecular cyclisation[198]:



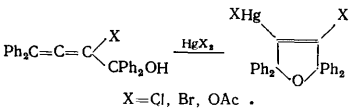
## 5. Other Reactions

Derivatised halogenoallenes exhibit specific properties towards several reagents in virtue of their structural features. Thus 1,4-dibromoallenes are sensitive to alkalis and readily undergo dehydrobromination involving the allyl bromine atom[90-92]:



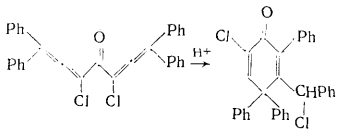
R=H, $SiMe_3$; $R^1$=H, Me, Et .

Treatment of halogenoallenes with acidic reagents[46,119,199,200] or with mercury salts[201] leads to unusual reactions, probably involving carbocation intermediates, which may be cyclised, depending on the presence of a functional group (hydroxy, phenyl), into derivatives of indene[46,119,201] or of dihydrofuran[199-201]:

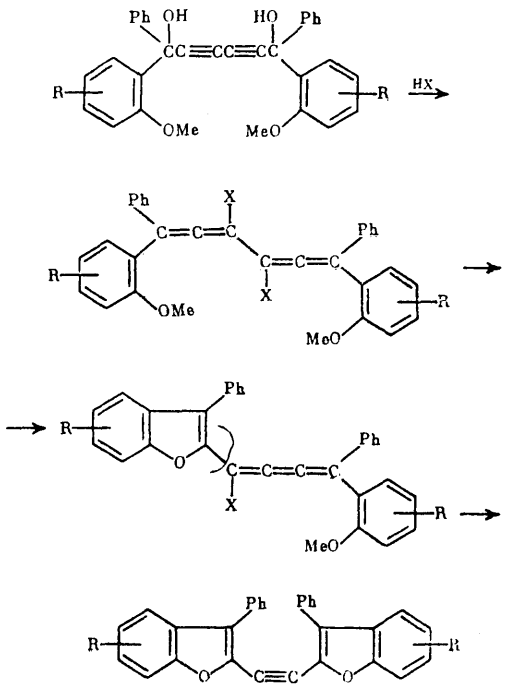


X=Cl, Br, OAc .

αβ-Unsaturated aldehydes and ketones are obtained under the same conditions[46,119,132]. Bis-3,3-diphenyl-1-chloroallenyl ketone is smoothly cyclised into cyclohexadienone in the presence of an acid[202]:

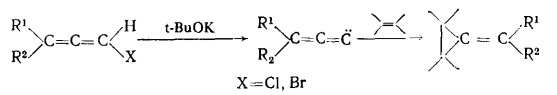


Symmetrical tetraphenylhexadiynediol under the influence of hydrogen halides undergoes two-stage cyclisation with formation of bisbenzofurylacetylenes[203]; study of this curious reaction showed the intermediate formation of a halogenobutatriene, which in the presence of activated alumina gives the final product in 35–45% yield:



R = H, Me, Cl, OMe; X = Cl, Br .

Under alkaline conditions halogenoallenes are able to eliminate a hydrogen halide containing the allenyl halogen atom. For example, heating bromoallenes with copper cyanide in dimethylformamide gives 45–65% yields of butenynes[39,204]. The most interesting is the 1,1-elimination of α-halogenoallenes. The method consists in acting on the latter with a strong base (usually potassium t-butoxide) with generation of a carbene; subsequent reactions with alkenes yield the corresponding cyclopropanes[205,206]:

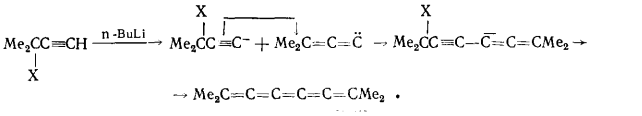


X = Cl, Br

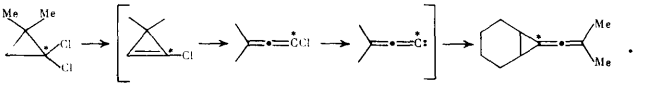
Better yields of carbene intermediates are observed if phase transfer is used in the presence of butyltriethylammonium chloride[165,166,207] or a crown ether[208,209].

Another method of generating carbenes consists in the intermediate formation of products of lithiation of halogenoacetylenes at the carbon-hydrogen bond. Under mild conditions isomerisation of the triple bond does not occur.

Above 25 °C, however, the lithium halogenoalkynides undergo unambiguous conversion into carbenes[210], which under the reaction conditions are often transformed into hetero-substituted (methylated, phenylated) hexapentaenes[47,211]:



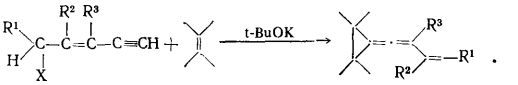
In a limited number of cases carbenes could be obtained from such compounds as 1,2-dibromo-3,3-diphenylallene (by the action of lithium alkyls[47]) and 3-alkyl-1-bromopropynes (by the action of alkoxides)[212,213]. The most interesting case was the preparation of dimethylvinylidenecarbene by the action of potassium t-butoxide (in Hexametapol) on dichlorocyclopropane (yield at most 6%), with intermediate formation of a chlorocyclopropene[214]:



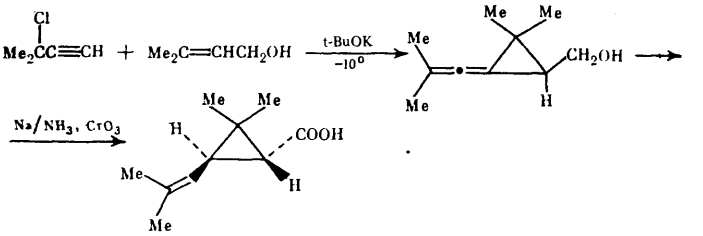
Such reactions constitute a special case, and can be used only for compounds analogous to those described above.

Towards alkenes allenylcarbenes behave as strong electrophiles, and undergo exclusively *cis*-addition, as has been demonstrated for dimethylvinylidenecarbene with *cis*- and *trans*-but-2-enes[209,215]. Study of the reactions of this carbene generated in different ways (from chloroprop-2-ynyl with potassium 2-butoxide or from bromoallene by the phase-transfer method) showed good agreement between the relative rate constants of the carbene with different alkenes[209].

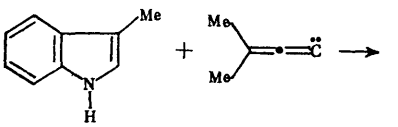
Various allenylcyclopropanes are readily formed, usually in satisfactory yield, also in the generation of allenylcarbenes from available halogenoprop-2-ynyl derivatives, which is of great value for their synthesis[216–218]. Analogous schemes are suitable also for the generation of vinylvinylidenecarbene[219]:

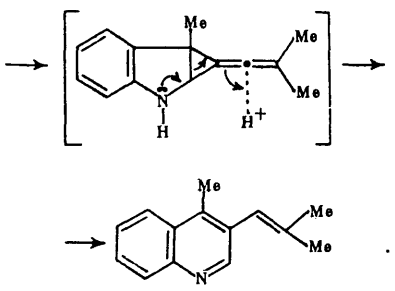


An interesting example is the stereospecific synthesis of *trans*-chrysanthemic acid by use of this carbene[220]:

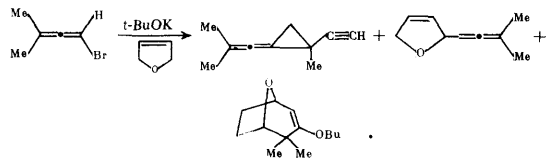


1-Bromoallenes react in basic medium (via the carbenes) with methylindoles to give alkynyl(allenyl)-3*H*-indoles[221] and alkenylquinolines—products of the ring expansion of allene intermediates:

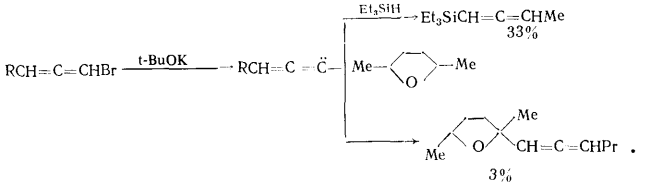




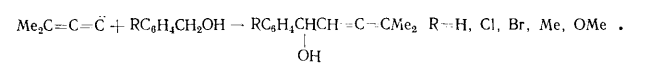
Dimethylvinylidenecarbene (generated from a halogenoallene by the action of potassium t-butoxide) reacts with dihydrofuran[222] to form, together with cyclopropanation products (yield 22%), also unsaturated compounds corresponding to incorporation of the carbene at a carbon-hydrogen bond:



The action of potassium t-butoxide on alkylallenyl bromides led to isolation of a carbene, which added to 2,5-dimethyloxolan and triethylsilane to give products involving incorporation at carbon-hydrogen and silicon-hydrogen bonds respectively[214]:



The action of dimethylvinylidenecarbene on alcohols (reaction between halogenoallenes and sodium ethoxide in alcoholic solution) usually gives satisfactory yields of products involving incorporation at a carbon–hydrogen bond, i.e. α-allenyl alcohols[223]:



---oOo---

As the above survey shows, α-halogenoallenes can be used to obtain many aliphatic, carbocylic, and heterocyclic functional derivatives belonging to various classes of organic compounds. Halogenoallenes can therefore be rightly regarded as effective and multipurpose starting materials for the synthesis of diverse compounds of theoretical and practical value.

## REFERENCES


1. R.Kinnel, A.J.Duggan, T.Sisner, J.Meinwald, and I.Miura, Tetrahedron Letters, 1977, p.3913.
2. A.Fukuzawa and E.Kurosawa, Tetrahedron Letters, 1979, p.2797; M.Suzuki and E.Kurosawa, Tetrahedron Letters, 1981, **22**, p.3853.
3. J.H.Wotiz, in "Chemistry of Acetylenes", edited by H.G.Viehe, Marcel Dekker, New York, 1969, p.365.
4. M.V.Mavrov and V.F.Kucherov, in "Reaktsii i Metody Issledovaniya Organicheskikh Soedinenii" (Reactions and Methods of Investigation of Organic Compounds), Khimiya, Moscow, 1970, Book 21, p.90.
5. D.R.Taylor, Chem.Rev., 1967, **67**, 317.
6. T.Okamoto, Bull.Inst.Chem.Res., 1972, **50**, 450.
7. W.R.Dolbier Jr. and C.R.Burkholder, Tetrahedron Letters, 1980, **21**, 785.
8. M.J.Bunegar, R.Fields, and R.N.Haszeldine, J. Fluorine Chem., 1980, **15**, 497.
9. R.E.Banks, M.G.Barlow, W.D.Davies, R.N.Haszeldine, and D.R.Taylor, J.Chem.Soc.. 1969, 1104.
10. F.G.Drakesmith, O.J.Stewart, and P.Tarrant, J. Org.Chem., 1968, **33**, 280.
11. P.W.L.Bosbury, R.Fields, and R.N.Haszeldine, J.Chem.Soc.Perkin Trans.I, 1978, 422.
12. R.E.Banks, R.N.Haszeldine, and D.R.Taylor, J. Chem.Soc., 1965, 978.
13. R.E.Banks, A.Braithwaite, et al., J.Chem.Soc.(C), 1969, 996.
14. R.E.Banks, A.Braithwaite, R.N.Haszeldine, and D.R.Taylor, J.Chem.Soc.(C), 1968, 2593.
15. A.Roedig and H.Niedenbrück, Chem.Ber., 1957, **90**, 673.
16. A.P.Zens, P.D.Ellis, and R.Ditchfield, J.Amer. Chem.Soc., 1974, **96**, 1309.
17. A.Roedig, F.Bischoff, B.Heinrich, and G.Märke, Annalen, 1963, **670**, 8.
18. A.Roedig and N.Detzer, Annalen, 1967, **710**, 1.
19. G.Köbrich and E.Wagner, Chem.Ber., 1970, **103**, 2515.
20. M.V.Mavrov and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1442.
21. M.Baboulene and G.Sturtz, Compt.rend., 1975, **280C**, 149.
22. M.Baboulene, A.Belbeoch, and G.Sturtz, Synthesis, 1977, p.240.
23. G.Sturtz, Bull.Soc.chim.France, 1967, 1345.
24. J.Tendil, M.Verny, and R.Vessiere, Bull.Soc.chim. France, 1977, 565.
25. A.Roedig and N.Detzer, Annalen, 1971, **749**, 153.
26. A.Roedig, N.Detzer, W.Mann, and W.Ritschel, Annalen, 1979, 1969.
27. T.A.Favorskaya and A.E.Favorskii, Zhur.Obshch. Khim., 1939, **9**, 386.
28. G.F.Hennion, J.J.Seehan, and D.E.Maloney, J.Amer.Chem.Soc., 1950, **72**, 3542.
29. T.L.Jacobs and W.F.Brill, J.Amer.Chem.Soc., 1953, **75**, 1314.
30. G.M.Mkryan, N.A.Papazyan, G.B.Arsenyan, E.A.Avetisyan, V.F.Zhurba, and A.A.Nazaryan, Zhur.Org.Khim., 1971, **7**, 2466.
31. T.L.Jacobs and W.L.Petty, J.Org.Chem., 1963, **28**, 1360.
32. M.L.Poutsma and P.A.Ibarbia, J.Org.Chem., 1970, **35**, 4038.
33. O.J.Muscio, Y.M.Jun, and J.B.Philip, Tetrahedron Letters, 1978, 2379.
34. H.Hauptmann, Tetrahedron Letters, 1974, 3593.
35. M.V.Mavrov and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1763.
36. R.Vessiere and M.Verny, Compt.rend., 1965, **261**, 1868.
37. H.G.Meunier and P.I.Abell, Tetrahedron Letters, 1967, 3633.
38. C.S.L.Baker, P.D.Landor, P.D.Landor, and A.N.Patel, J.Chem.Soc., 1965, 4348.

39. P.R.Ashurst and D.R.J.Laws, J.Chem.Soc.(C), 1966, 1615.
40. S.R.Landor, A.N.Patel, P.F.Whiter, and P.M.Greaves, J.Chem.Soc.(C), 1966, 1223.
41. T.L.Jacobs and S.Hoff, J.Org.Chem., 1968, **33**, 2986.
42. M.D.Schiavelli, T.C.Germroth, and J.W.Stubbs, J.Org.Chem., 1976, **41**, 681.
43. S.R.Landor, B.Demetriou, R.J.Evans, R.Grzeskowiak, and P.Davey, J.Chem.Soc.Perkin Trans.II, 1972, 1995.
44. Y.R.Bhatia, P.D.Landor, and S.R.Landor, J.Chem. Soc., 1959, 24.
45. W.J.Le Noble, D.M.Chiou, H.Matuszynska, and Y.Okaya, Tetrahedron Letters, 1977, 3865.
46. H.Tani and F.Toda, Bull.Chem.Soc.Japan, 1964, **37**, 470.
47. H.Kollmar and H.Fischer, Tetrahedron Letters, 1968, 4291.
48. K.Shingu, S.Hagishita, and M.Nakagawa, Tetrahedron Letters, 1967, 4317.
49. C.K.Tseng, K.G.Migliorese, and S.I.Miller, Tetrahedron 1974, **30**, 377.
50. Yu.P.Artsybasheva, B.L.Andonskaya, and B.V.Ioffe, Zhur.Org.Khim., 1968, **4**, 155.
51. A.N.Patel, Zhur.Org.Khim., 1977, **13**, 2046, 2226.
52. T.L.Jacobs and D.M.Fenton, J.Org.Chem., 1965, **30**, 1908.
53. T.L.Jacobs, C.Hall, D.A.Bable, and P.Prempree, J.Org.Chem., 1967, **32**, 2283.
54. M.D.Schiavelli, S.C.Hixon, and H.W.Moran, J.Amer. Chem.Soc., 1970, **92**, 1082.
55. M.D.Schiavelli, R.P.Gilbert, W.A.Boynton, and C.J.Boswell, J.Amer.Chem.Soc., 1972, **94**, 5061.
56. F.Bohlmann and K.Kieslich, Chem.Ber., 1954, **87**, 1363.
57. F.Toda, H.Motomura, and H.Oshima, Bull.Chem. Soc.Japan, 1974, **47**, 467.
58. M.D.Schiavelli, P.L.Timpanaro, and R.J.Brewer, J.Org.Chem., 1973, **38**, 3054.
59. T.B.Patrick, E.C.Haynie, and W.J.Probst, J.Org. Chem., 1972, **37**, 1553.
60. S.R.Landor, P.M.Greaves, and M.Kalli, J.Chem. Soc.(C), 1971, 667.
61. E.W.Reeve and T.F.Steckel, Canad.J.Chem., 1973, **51**, 2017.
62. R.E.A.Dear and E.E.Gilbert, J.Org.Chem., 1968, **33**, 819.
63. M.Dugat, M.Verny, and R.Vessiere, Bull.Soc.chim. France, 1976, 1903.
64. M.Verny and R.Vessiere, Bull.Soc.chim.France, 1968, 2578, 2585.
65. L.N.Yakhontov, L.I.Mastafanova, K.F.Turchin, Yu.N.Sheinker, and M.V.Rubtsov, Dokl.Akad. Nauk SSSR, 1966, **168**, 1085.
66. W.Jasiobedzki, A.Sinniak, and T.Glinka, Dokl. Akad.Nauk SSSR,[sic], 1975, **49**, 111
67. P.D.Landor, S.R.Landor, and P.Leighton, J. Chem.Soc.Perkin Trans.I, 1975, 1628.
68. A.N.Patel, Zhur.Org.Khim., 1977, **13**, 2227.
69. T.Negi, T.Kaneda, H.Mizuno, et al., Bull.Chem. Soc.Japan, 1974, **47**, 2398.
70. F.Bohlmann and K.Kieslich, Chem.Ber., 1955, **88**, 1211.
71. M.Verny and R.Vessiere, Bull.Soc.chim.France, 1967, 2210.
72. R.J.D.Evans and S.R.Landor, J.Chem.Soc., 1965, 2553.
73. R.J.D.Evans, S.R.Landor, and R.Taylor-Smith, J.Chem.Soc., 1963, 1506.
74. D.Dugat and M.Verny, Bull.Soc.chim.France, 1971, 4532.
75. J.Tendil, M.Verny, and R.Vessiere, Bull.Soc. chim.France, 1972, 4027.
76. F.Kai and S.Seki, Chem.Pharm.Bull., 1965, **13**, 1374.
77. F.Kai and S.Seki, Chem.Pharm.Bull., 1966, **14**, 1122.
78. M.S.Simo, A.Jean, and M.Lequan, J.Organomet. Chem., 1972, **35C**, 23.
79. T.Flood and P.E.Peterson, J.Org.Chem., 1980, **45**, 5006.
80. R.Baudouy, J.Core, and M.L.Roumestant, Bull. Soc.chim.France, 1973, 2506.
81. M.Montury and J.Gore, Synth.Comm., 1980, **10**, 873.
82. J.M.Dollat, J.L.Luche, and P.Crabbe, Chem. Comm., 1977, 761.
83. H.Westmijze, H.Kleijn, et al., J.Organomet.Chem., 1980, **199**, 293.
84. M.V.Mavrov, I.S.Runge, A.P.Rodionov, and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1971, 883.
85. Sh.O.Badanyan and G.R.Mkhitaryan, Arm.Khim. Zhur., 1973, **26**, 649.
86. V.M.Ignat'ev, V.I.Ionin, and A.A.Petrov, Zhur. Obshch.Khim., 1967, **37**, 2135.
87. J.Berlan, M.L.Capmau, and W.Chodkiewicz, Compt. rend., 1971, **273C**, 1107.
88. J.Berlan, M.L.Capmau, and W.Chodkjewicz, Bull. Soc.chim.France, 1975, 2259.
89. A.A.Petrov, Uspekhi Khim., 1960, **29**, 1049 [Russ. Chem.Rev., 1960(9)].
90. A.A.Petrov, G.I.Semenov, and N.P.Sopov, Zhur. Obshch.Khim., 1957, **27**, 928.
91. A.A.Petrov and Yu.I.Porfir'eva, Zhur.Obshch. Khim., 1957, **27**, 1805.
92. M.D.Stadnichuk and A.A.Petrov, Zhur.Obshch. Khim., 1961, **31**, 411.
93. G.D.Mel'nikov and Yu.I.Porfir'eva, Zhur.Org.Khim., 1972, **8**, 1344.
94. Sh.O.Badanyan, K.L.Sarkisyan, and A.A.Gevorkyan, Zhur.Org.Khim., 1970, **6**, 397.
95. A.A.Gevorkyan, S.O.Badanyan, and A.A.Manukyan, Arm.Khim.Zhur., 1972, **25**, 851.
96. M.V.Mavrov, A.P.Rodionov, V.M.Shitkin, S.D.Kulomzina, and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 948.
97. Yu.N.Shmatov, Yu.I.Porfir'eva, and A.A.Petrov, Zhur.Org.Khim., 1976, **12**, 305.
98. A.Roedig, M.Forsch, H.Abel, and S.Bauer, Chem. Ber., 1977, **110**, 1000.
99. R.Fuks and H.G.Viehe, Bull.Soc.Chim.Belg., 1977, **86**, 219.
100. M.V.Mavrov, E.S.Voskanyan, and V.F.Kucherov, Tetrahedron, 1969, **25**, 3277.
101. M.V.Mavrov and V.F.Kucherov, USSR P.492 518 (1975); Byull.Izobr., 1975, **43**, 63.
102. M.V.Mavrov et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1967, 2774.
103. N.Detzer,and A.Roedig, Tetrahedron, 1971, **27**, 5697.
104. A.Roedig and N.Detzer, Annalen, 1967, **710**, 7.
105. T.L.Jacobs, J.R.McClenon, and O.J.Muscio, J. Amer.Chem.Soc., 1969, **91**, 6038.
106. W.H.Knoth and D.Coffman, J.Amer.Chem.Soc., 1960, **82**, 3973.

107. A.Roedig and N.Detzer, Angew.Chem., 1968, **80**, 482.
108. A.Roedig, N.Detzer, and G.Bonse, Annalen, 1971, **752**, 60.
109. E.V.Dehmlow, Tetrahedron Letters, 1969, 4283.
110. P.W.L.Bosbury, R.Fields, et al., J.Chem.Soc.Perkin Trans.I, 1976, 1173.
111. O.J.Muscio and T.L.Jacobs, Tetrahedron Letters, 1969, 2867.
112. T.L.Jacobs and O.J.Muscio, Tetrahedron Letters, 1970, 4829.
113. A.Roedig, M.Försch, G.Geiger, and G.Zaby, Annalen, 1977, 1267.
114. M.E.Green, N.Meyne, and F.G.A.Stone, Chem.Comm., 1966, 755.
115. R.E.Banks, M.G.Barlow, W.R.Deem, R.N.Haszeldine, and D.R.Taylor, J.Chem.Soc.(C), 1966, 981.
116. C.Dufraisse, J.Mathieu, and J.Valls, Compt.rend., 1958, **246**, 661.
117. K.Ueda and F.Toda, Chem.Letters, 1975, 257.
118. M.Dugat, M.Verny, and R.Vessiere, Bull.Soc.chim. France, 1976, 1909.
119. P.D.Landorè and S.R.Landor, J.Chem.Soc., 1963, 2707.
120. R.E.Banks, W.R.Deem, R.N.Haszeldine, and D.R.Taylor, J.Chem.Soc.(C), 1966, 2051.
121. W.R.Dolbier and C.Piedrahita, Tetrahedron Letters, 1978, 2231.
122. R.Alexander and D.I.Davies, J.Chem.Soc.(C), 1971, 5.
123. B.L.Dyatkin, N.I.Delyagina, et al., Tetrahedron, 1974, **30**, 4031.
124. J.S.M.Boleij and H.J.T.Bos, Rec.Trav.chim., 1972, 91, 1212.
125. J.S.M.Boleij and H.J.T.Bos, Tetrahedron Letters, 1971, 3201.
126. S.D.Andrews and A.C.Day, J.Chem.Soc.(B), 1968, 1271.
127. S.D.Andrews, A.C.Day, and R.N.Inwood, J.Chem. Soc.(C), 1969, 2443.
128. H.H.Wasserman and L.S.Keller, Chem.Comm., 1970, 1483.
129. Sh.O.Badanyan, M.G.Voskanyan, and A.A.Pashayan, Arm.Khim.Zhur., 1980, **33**, 38.
130. J.L.Moreau, in "The Chemistry of Ketenes, Allenes and Related Compounds" edited by S.Patai, John Wiley, New York, 1980, p.363.
131. P.M.Greaves, S.R.Landor, and M.M.Lwanga, Tetrahedron, 1975, **31**, 3073.
132. R.Barlet, Bull.Soc.chim.France, 1979, 132.
133. R.Couffignal and M.Gaudemar, Bull.Soc.chim.France, 1969, 3218.
134. F.Delbecq, R.Baudouy, and J.Gore, Nouv.J.Chim., 1979, **3**, 321.
135. P.Place, M.L.Roumestant, and J.Gore, Tetrahedron, 1978, **34**, 1931; M.Malacria and M.L.Roumestant, Tetrahedron, 1977, **33**, 2813.
136. M.L.Roumestant, M.Malacria, J.Gore, J.Grimaldi, and M.Bertrand, Synthesis, 1976, 755.
137. R.Couffignal and M.Gaudemar, Bull.Soc.chim. France, 1970, 3157.
138. J.L.Moreau and M.Gaudemar, Bull.Soc.chim.France, 1970, 2171, 2175.
139. J.C.Clinet, et al., Nouv.J.Chim., 1977, 1, 373; Synthesis, 1981, 875.
140. D.Michelot and G.Linstrumelle, Tetrahedron Letters, 1976, 275.
141. X.Greary, J.Amer.Chem.Soc., 1977, **99**, 7632.
142. R.Baudouy, F.Delbecq, and J.Core, J.Organomet. Chem., 1979, **177**, 39.
143. Y.Leroux and C.Roman, Tetrahedron Letters, 1973, 2585.
144. B.W.Metcalf and P.Casara, Tetrahedron Letters, 1975, 3337.
145. R.C.Cookson and P.J.Parsons, Chem.Comm., 1978, 821, 822.
146. G.Köbrich and E.Wagner, Angew.Chem., 1970, **82**, 548.
147. R.Epstein and F.Mercier, Synthesis, 1977, 183.
148. M.V.Mavrov, A.P.Rodionov, E.P.Prokof'ev, and V.F.Kucherov, Zhur.Org.Khim., 1973, **9**, 658.
149. G.A.Olah, R.J.Spear, P.W.Westerman, and J.M.Denis, J.Amer.Chem.Soc., 1974, **96**, 5855.
150. M.D.Schiavelli, S.C.Hixon, H.W.Moran, and C.J.Boswell, J.Amer.Chem.Soc., 1971, **93**, 6989.
151. C.V.Lee, R.J.Hargrove, T.E.Dueber, and P.J.Stang, Tetrahedron Letters, 1971, 2519.
152. D.Scheffel, P.J.Abbott, G.J.Fitzpatrick, and M.D.Schiavelli, J.Amer.Chem.Soc., 1977, **99**, 3769.
153. W.J.le Noble, D.M.Chiou, and Y.Okata, J.Amer. Chem.Soc., 1979, **101**, 3244.
154. P.J.Stang, Prog.Phys.Org.Chem., 1973, **10**, 205.
155. M.D.Schiavelli and D.E.Ellis, J.Amer.Chem.Soc., 1973, **95**, 7916.
156. G.F.Hennion and D.E.Maloney, J.Amer.Chem.Soc., 1951, **73**, 4735.
157. V.J.Shiner and J.W.Wilson, J.Amer.Chem.Soc., 1962, **84**, 2402, 2408.
158. V.J.Shiner and J.S.Humphrey, J.Amer.Chem.Soc., 1967, **89**, 662.
159. A.Burawoy and E.Spinner, J.Chem.Soc., 1954, 3752.
160. W.J.le Noble, J.Amer.Chem.Soc., 1965, **87**, 2434.
161. G.F.Hennion and R.S.Hanzel, J.Amer.Chem.Soc., 1960, **82**, 4908.
162. D.K.Black and S.R.Landor, J.Chem.Soc.(C), 1968, 283.
163. S.R.Landor, P.D.Landor, and R.F.Whiter, J. Chem.Soc.Perkin Trans.I, 1977, 1710.
164. D.J.Pasto, R.H.Shultz, J.A.McGrath, and A.Waterhouse, J.Org.Chem., 1978, **43**, 1382.
165. T.B.Patrick Tetrahedron Letters, 1974, 1407.
166. H.E.Schulte and G.Rücker, in "Progress in Drug Research" Basel and Stuttgart, 1970, Vol.14, p.387.
167. M.V.Mavrov et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1968, 834.
168. M.V.Mavrov, A.P.Rodionov, and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2633
169. V.F.Kucherov, N.V.Stolyarenkova, and M.V.Mavrov, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 124.
170. M.V.Mavrov, Doctoral Thesis, Institute of Organic Chemistry of the USSR Academy of Sciences, Moscow, 1980.
171. M.V.Mavrov, A.P.Rodionov, V.P.Gul'tyai, and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1977, 564.
172. M.V.Mavrov and V.F.Kucherov, Zhur.Org.Khim., 1977, **13**, 1871.
173. R.M.Magid and O.S.Fruchey, J.Amer.Chem.Soc., 1977, **99**, 8368.
174. G.Stork and A.F.Kreft, J.Amer.Chem.Soc., 1977, **99**, 3851.
175. Ts.D.Mechkov, I.G.Sulimov, and N.V.Usik, in "Metody Sinteza, Stroenie i Khimicheskie Prevrashcheniya Nitrosoedinenii" (Preparation, Structure, and Chemical Reactions of Nitro-compounds), Izd. LGPI, Leningrad, 1980, p.16.

176. M.Arthurs, S.M.Nelson, and B.J.Walker, Tetrahedron Letters, 1978, 1153.
177. J.K.Crandall, D.J.Keyton, and J.Kohne, J.Org. Chem., 1968, **33**, 3655.
178. F.Sato, H.Kodama, and M.Sato, Chem.Letters, 1978, 789.
179. F.Toda and K.Akagi, Tetrahedron, 1969, **25**, 3795.
180. J.C.Paladini and J.Chuche, Bull.Soc.chim.France, 1974, 192.
181. M.G.Voskanyan, G.G.Khudoyan, and Sh.O.Badanyan, Khim.Geterotsikl.Soed., 1974, 822.
182. D.Plouin, C.Coeur, and R.Glenat, Bull.Soc.chim. France, 1973, 1043.
183. D.Plouin, C.Coeur, and R.Glenat, Bull.Soc.chim. France, 1974, 244.
184. M.Kalli, P.D.Landor, and S.R.Landor, J.Chem. Soc.Perkin Trans.II, 1973, 1347.
185. P.Savignac, A.Breque, C.Charrier, and F.Mathey, Synthesis, 1979, 832.
186. P.M.Greaves, S.R.Landor, and D.R.J.Laws, J. Chem.Soc.(C), 1968, 291.
187. H.Doupeux, P.Martinet, and J.Simonet, Bull.Soc. chim.France, 1971, 2299.
188. B.Schaub and M.Schlosser, Helv.Chim.Acta, 1975, **58**, 556.
189. T.Jefferyluong and G.Linstrumelle, Tetrahedron Letters, 1980, **21**, 5019.
190. C.S.L.Baker, P.D.Landor, and S.R.Landor, J. Chem.Soc., 1965, 4659.
191. T.Toda and Y.Takehira, Chem.Comm., 1975, 174.
192. M.Verny and R.Vessiere, Bull.Soc.chim.France, 1967, 2508.
193. M.V.Mavrov and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 1440.
194. M.V.Mavrov and V.F.Kucherov, Izv.Akad.Nauk SSSR, Ser.Khim., 1973, 1279.
195. R.E.Banks, A.Braithwaite, R.N.Haszeldine, and D.R.Taylor, J.Chem.Soc.(C), 1969, 454.
196. D.Holtz, Prog.Phys.Org.Chem., 1971, **8**, 1.
197. Yu.A.Cheburkov, Yu.E.Aronov, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1966, 582.
198. B.M.Mikhailov and V.N.Smirnov, Izv.Akad.Nauk SSSR, Ser.Khim., 1974, 1137.
199. P.P.Montijn, L.Brandsma, and J.F.Arens, Rec. Trav.chim., 1967, **86**, 129.
200. J.A.Gautier, Compt.rend., 1967, 264, 224.
201. F.Toda, Bull.Chem.Soc.Japan, 1971, **44**, 1050.
202. W.Ried and A.Marhold, Chem.Ber., 1973, **106**, 2455.
203. S.Kobayashi, M.Shinya, T.Nakana, and H.Taniguchi, J.Chem.Soc.Japan, 1971, **92**, 644.
204. P.M.Greaves, S.R.Landor, and D.R.J.Laws, J. Chem.Soc.(C),1966, 1976.
205. H.D.Hartzler, J.Org.Chem., 1964, **29**, 1311.
206. S.R.Landor and P.F.Whiter, J.Chem.Soc., 1965, 5625.
207. T.Sasaki, S.Eguchi, and T.Ogawa, J.Org.Chem., 1974, **39**, 1927.
208. T.Sasaki, S.Eguchi, M.Ohno, and F.Nakata, J.Org.Chem., 1976, **41**, 2408.
209. T.B.Patrick and D.J.Smidt, J.Org.Chem., 1977, **42**, 3354.
210. J.B.Battioni and W.Chodkiewicz, Bull.Soc.chim. France, 1969, 911.
211. L.T.Scott and G.J.DeCicco, Tetrahedron Letters, 1976, 2663.
212. C.D.Beard, J.Craig Cymerman, and M.D.Solomon, J.Amer.Chem.Soc., 1974, **96**, 7944.
213. C.D.Beard and J.C.Craig, J.Amer.Chem.Soc., 1974, **96**, 7950.
214. L.Crombie, P.J.Griffiths, and B.J.Walker, Chem. Comm., 1969, 1206.
215. H.D.Hartzler, J.Amer.Chem.Soc., 1961, **83**, 4997.
216. S.Julia, D.Michelot, and G.Linstrumelle, Compt. rend., 1974, **278C**, 1523.
217. I.H.Sadler and J.A.G.Stewart, Chem.Comm., 1970, 1588.
218. L.Crombie, P.J.Maddocks, and G.Pattenden, Tetrahedron Letters, 1978, 3479, 3483.
219. A.Doutheau and J.Gore, Bull.Soc.chim.France, 1976, 1189.
220. R.W.Mills, R.D.H.Murray, and R.A.Raphael, J. Chem.Soc.Perkin Trans.I, 1973, 133.
221. S.R.Landor, V.Rogers, and H.R.Sood, J.Chem.Soc. Perkin Trans.I, 1976, 2103.
222. S.R.Landor, V.Rogers, and H.R.Sood, Tetrahedron, 1977, **33**, 73.
223. T.B.Patrick and D.L.Schutzenhofer, Tetrahedron Letters, 1975, 3259.
224. R.J.Corey and J.Kang, Tetrahedron Letters, 1982, **23**, 1651.

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