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ALLENE HYDROCARBONS

A. A. Petrov and A. V. Fedorova

CONTENTS

I. Introduction 1

II. Methods of preparation 1

III. Physical properties 2

IV. Chemical properties 5

1. Addition reactions without lengthening of the carbon chain 5
2. Addition reactions with lengthening of the carbon chain 8
3. "Ene" and diene synthesis 9
4. Polymerisation of allenes 10
5. Isomeric rearrangement of allenes 10

I. INTRODUCTION

Hydrocarbons of the allene series are the least studied class of diolefins although allene and some of its homologues were described in the sixties of the last century[1]†. In recent years research in this field of organic chemistry has expanded considerably. New methods of preparing allenes have been developed and previously known methods improved. The main features of their physical and chemical properties have been made clearer. Promising new ways of converting allenes into various three-, four-, five-, six-, and eight-membered cyclic carbon compounds have been discovered. Compounds with cumulative double bonds are found in nature[2,3].

Allenes apparently play an important part in a number of chemical processes because they are interconvertible with 1,3-dienes and acetylene compounds[4], isolated representatives of which were widely used some time ago in technical as well as in laboratory work.

There is no doubt that a closer examination of the reactions of allenes will provide not only exceptionally interesting new theoretical data but also valuable practical results. The use of various allene polymers in the production of rubber[5,6] and artificial fibres[7] is already reported in a number of patents. Cyanogen adducts of hydroxy--derivatives of allenes are recommended as insecticides[8].

II. METHODS OF PREPARATION

A good review of methods of preparing allenes[9] is available and we shall therefore limit ourselves to very brief descriptions and the most recent publications.

In the earliest researches allene hydrocarbons were obtained by the preferential elimination of halogens of hydrogen halides from polyhalogeno-compounds of suitable structure (the Gustavson method[10]). In particular, allene was prepared as follows:

$$CH_2Br-CHBr-CH_2Br \xrightarrow{KOH} CH_2=CBr-CH_2Br \xrightarrow{Zn} CH_2=C=CH_2.$$

The hydrocarbon yields were not high. Slobodin and Khitrov[11] recently examined this method in detail and showed that the use of butyl or isopentyl acetate as solvent in the elimination of bromine from 2,3-dibromoprop-1-ene raises the hydrocarbon yield to 95–98%, and the allene so obtained is free from the volatile 2-bromopropene impurity which up till now it has not been possible to remove from allene, even with a distillation apparatus of special design[12].

† Allene was first prepared in 1865.[1]

Cyclic allenes with 9, 10, and 11 carbon atoms in the ring were obtained by eliminating hydrogen chloride from 1-chlorocycloalkenes, or halogens from dihalogenocycloalkenes[12,13]. The action of sodamide in liquid ammonia on 1-chlorocycloheptene and 1-chlorocyclooctene gives dimers of the corresponding allenes[13].

The laboratory method which is most widely used at present for the preparation of allene hydrocarbons with a terminal allene group (1,2-dienes) is reduction of halogenoacetylenes or halogenoallenes with a zinc–copper couple in alcohol (Ginzburg method[14,15]), or with lithium aluminium hydride[16]:

$$\left.\begin{matrix} R_2CBr{-}C{\equiv}CH \\ R_2C{=}C{=}CHBr \end{matrix}\right\} \longrightarrow R_2C{=}C{=}CH_2 + R_2CH{-}C{\equiv}CH.$$

(main product)

Allene hydrocarbons are formed with yields of up to 90% by the reduction of various prop-2-ynyl halides, as a result of the acetylene–allene rearrangement[4,17-19]. Reduction of vinylhalogenoacetylenes and halogenodiacetylenes of the same type gives the corresponding vinylallenes and ethynylallenes[20].

The synthesis of monosubstituted allenes by the reaction of prop-2-ynyl bromide with alkylmagnesium bromides, which is also accompanied by the acetylene–allene rearrangement, is particularly simple[21]. The allene hydrocarbons are formed in yields of over 60% and the acetylene hydrocarbons which are formed at the same time are removed as silver acetylide:

$$HC{\equiv}C{-}CH_2Br + C_4H_9MgBr \begin{cases} \longrightarrow CH_2{=}C{=}CH{-}C_4H_9 & (65\%)\ddagger \\ \longrightarrow HC{\equiv}C{-}CH_2{-}C_4H_9 & (35\%) \end{cases}$$

The acetylene–allene rearrangement also takes place in the action of lithium or sodium acetylide on benzyl chloride[22].

Trisubstituted allenes are obtained in very good yields by the action of alkylmagnesium halides on tertiary halides of the prop-2-ynyl type. The reaction complex is decomposed by water from which traces of acid are absent[23].

A new two-stage method of preparing allenes from olefins is very promising. The first stage involves preparation of derivatives of *gem*-dihalogenocyclopropane from olefins and dihalogenocarbene; the second stage is reaction of the dihalide with sodium or magnesium[24,25], lithium alkyls[26,27], or alkyl- or aryl-magnesium halides[28]:

$$\rangle C{=}C\langle + :CBr_2 \longrightarrow \rangle C{-}C\langle \overset{RLi}{\rightarrow} \rangle C{=}C{=}C\langle .$$

$$\qquad\qquad\quad C$$

$$\qquad\qquad\quad Br_2$$

The best results were obtained using dibromocyclopropanes and lithium alkyls in absolute ether[27]. From substituted 1,1-dichlorocyclopropanes, a mixture of allenes and alkylcyclopropanes is formed, the yield of the former not exceeding 50%.[26,28]

This method is fairly universal, since by starting with different olefins one can obtain allenes with different structures (aliphatic, alicyclic, and aromatic) in yields of about 70–80%. A disadvantage of the method is that the allene–acetylene rearrangement takes place to some extent in the preparation, and the allenes obtained must be purified from acetylenes.

‡ Total yield 95%.

Formation of allenes by the opening of a three-membered ring also occurs in some other instances, *e.g.* diphenylallene is produced by the action of lithium ethoxide on *N*-(2,2-diphenylcyclopropyl)-*N*-nitrosourea[29].

One of the most convenient methods of preparing symmetrical disubstituted allenes is the addition of lithium alkyls to alkylvinylacetylenes[30].

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R'Li} R{-}CLi{=}C{=}CH{-}CH_2{-}R' \xrightarrow{H_2O} R{-}CH{=}C{=}CH{-}CH_2{-}R'.$$

The use of divinylacetylene and its homologues in this reaction gives vinylallenes[30,31]. The hydrocarbon yield is about 80%:

$$CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{RLi} CH_2{=}CH{-}CLi{=}C{=}CH{-}CH_2{-}R \xrightarrow{H_2O}$$

$$\longrightarrow CH_2{=}CH{-}CH{=}C{=}CH{-}CH_2{-}R.$$

The specific mode of the addition of lithium alkyls is apparently connected with formation of an intermediate complex having the lithium atom attached at the triple bond[32].

The rearrangement of acetylenes on various catalysts, which was studied in detail by Slobodin (on Floridin), in particular, is an equilibrium and gives 1,3-dienes as well as allenes[33,34].

The reaction of prop-2-ynyl halides with arylmagnesium bromides[21,35], the dehydration of some unsaturated alcohols[9], and the prototropic rearrangement of 1,3-arylpropynes over an alkaline alumina catalyst[36] are used to prepare arylallenes.

A mixture of aryl-substituted allenes and arylacetylenes is formed by the chloroarylation of enyne hydrocarbons[37].

Allenes with triphenylmethyl substituents were obtained by the addition of triphenylmethyl free radicals to various enyne hydrocarbons, for example[38,39]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{2(C_6H_5)_3C^{\cdot}} (C_6H_5)_3C{-}CH{=}C{=}CH{-}CH_2{-}C(C_6H_5)_3,$$

and also by the classical method of halogenation and dehalogenation of tetraarylethylenes[40].

Information on the preparation of derivatives of allene hydrocarbons containing halogen, oxygen, and nitrogen atoms can be found in Pansevich-Koleda's review[41].

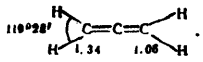
Allenes, like other hydrocarbons, are easily purified chromatographically[42,43]. Melting point curves are recommended as a test for the purity of the preparations[44,45].

III. PHYSICAL PROPERTIES

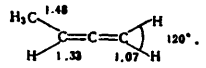
Owing to the two adjacent double bonds, hydrocarbons of the allene series show some peculiarities in their physical properties.

Molecular structure. A stereochemical model of the allene molecule was described by van't Hoff[46]. The three carbon atoms are arranged linearly and the external valencies of the terminal atoms lie in mutually perpendicular planes. Such a structure presupposes the existence of optical isomerism in allenes with two different substituents. Optically active forms of di-α-naphthyldiphenylallene were in fact obtained[47] sixty years after van't Hoff's work. Many examples of optical activity in the allene series are now known[48-51]. Research on the stereochemistry of allenes played an important part in establishing the structure of the natural allenes, mycomycin and isomycomycin[2,3].

Electron-diffraction measurements gave the following parameters for the allene molecule[52,53]:



For methylallene the parameters proposed[54] are:



The central atom in the allene system is in the *sp* state and the outer atoms have sp^2 hybridisation[55].

There are a number of papers on the quantum mechanics and thermodynamics of the allene molecule and its nearest homologues, in which the configuration, symmetry, and energy of the molecule are discussed and thermodynamic constants, many of which feature in the usual handbooks, are given[56-64].

More important constants. From the more important physical constants of allene, and of its homologues and analogues with unsaturated substituents (allyl, prop-2-ynyl, phenyl, naphthyl), given in the Table, the following conclusions can be reached. Allene hydrocarbons usually boil at a higher temperature than paraffins with the same number of carbon atoms and chain structure. As in other homologous series, allene hydrocarbons with the normal structure have higher boiling points than those with a branched chain. Their refractive indices are usually higher than those of the corresponding acetylenes. For the overwhelming majority of known allenes an elevation of the molar refraction of the order of 0.5–1.0 units is observed. The significant discrepancies found possibly indicate inadequate purity of the specimens described. The elevation reaches two units in the conjugated vinylallenes.

The variation of vapour pressure with temperature for allene is given by[82,83]

$$\log P = \frac{0.05233}{T} \times 20.852 + 7.455.$$

There is a definite relation between the boiling point (t_s), specific gravity close to the boiling point (d_s), molecular weight (M), and the number of atoms in the molecule (n)[84]:

$$\frac{t_s}{d_s}\sqrt{\frac{M}{n}} \simeq 1000.$$

TABLE. The more important constants of allene hydrocarbons.

Compound	M.p., °C	B.p., °C	*P*, mm	d_4^t	*t*, °C	n_D^t	*t*, °C	MR_D found	MR_D calc.	Method of preparation*	References
1	2	3	4	5	6	7	8	9	10	11	12
1. Allene and its homologues											
Allene	—136	—34.5	760	0.6575	—30	1.4137	—30	15.30	15.12	I	65,66
				0.7064	—70	1.444	—70				
Buta-1,2-diene	—136.19	10.85	760	0.676	0	1.4205	1.3	20.27	19.74	I	65
				0.652	20						
Penta-1,2-diene	—137.26	44.85	760	0.6926	20	1.4209	20	24.93	24.36	II	65
				0.6876	25	1.4177	25				
Penta-2,3-diene	—125.66	48.26	760	0.6950	20	1.4284	20	25.23	24.36	IV	65
				0.6900	25	1.4251	25				
3-Methylbuta-1,2-diene	—	40	760	0.6800	20	1.4100	20	24.81	24.36	II	65
				0.6759	25	1.4070	25				
Hexa-1,2-diene	—	76	760	0.7140	20	1.4282	20	29.51	28.97	II	66
				0.7102	25	1.4252	25				
3-Methylpenta-1,2-diene	—	70	760	0.715	20	1.4250	20	29.32	28.97	II	65
				0.710	25	1.4220	25				
4-Methylpenta-1,2-diene	—	70	760	0.708	20	1.4240	20	29.55	28.97	II	65
				0.703	25	1.4210	25				
Hexa-2,3-diene	—	68	760	0.6800	20	1.3950	20	28.94	28.97	I	65
				0.6950	25	1.3920	25				
2-Methylpenta-2,3-diene	—	72	760	0.711	20	1.4250	20	29.54	28.97	V	65
				0.706	25	1.4220	25				
Hepta-1,2-diene	—	106	760	0.7374	21	1.4321	21	35.51	33.59	III	21
5-Methylhexa-1,2-diene	—	96	760	0.7225	19	1.4282	19	34.22	33.59	II	67
3,4-Dimethylpenta-1,2-diene	—	—	—	0.751	20	1.4560	20	34.69	33.59	II	19
4,4-Dimethylpenta-1,2-diene	—	80—83	760	0.7184	20	—	—	33.05	33.59	I	33
3-Ethylpenta-1,2-diene	—	97—98	760	0.7423	20	1.4468	20	34.59	33.59	II	14
Hepta-2,3-diene	—	52—53	150	0.7274	20	1.4360	20	34.57	33.59	VI	39
2-Methylhexa-2,3-diene	—	97—100	748	0.7331	20	1.4351	20	34.20	33.59	I	68
2,4-Dimethylpenta-2,3-diene	—	82—84	760	0.7060	20	1.4004	20	33.05	33.59	I	33
Octa-1,2-diene	—	131—132	760	0.7680	15	1.4440	15	38.15	38.21	III	21
3,5-Dimethylhexa-1,2-diene	—	70—71.5	760	0.7435	20	1.4410	20	39.06	38.21	II	19
6-Methylhepta-2,3-diene	—	63—64	100	0.7399	20	1.4380	20	39.03	38.21	VI	39
2,5-Dimethylhexa-2,3-diene	—	119—123	760	0.7637	20	1.4505	20	38.82	38.21	IV	16
Octa-3,4-diene	—	77.5—78	150	0.7443	20	1.4432	20	39.26	38.21	VI	30
3-Methylhepta-3,4-diene	—	30.5	24	—	—	1.4485	18	—	—	III	23
2,2-Dimethylhexa-3,4-diene	—	107.4—108	760	0.7375	25	1.4425	25	39.58	38.21	IV	69
Nona-1,2-diene	—	—	—	0.7581	20	1.4433	20	43.39	42.83	II	19
3-Ethylhepta-1,2-diene	—	145	760	—	—	1.4347	25	—	—	III	70
Nona-2,3-diene	—	64—65	40	0.7555	20	1.4454	20	43.79	42.83	VI	30
2-Methylocta-2,3-diene	—	140—145	744	0.7570	20	1.4370	20	42.91	42.83	I	68
7-Methylocta-2,3-diene	—	62—63	40	0.7525	20	1.4450	20	43.93	42.83	VI	30
6,6-Dimethylhepta-2,3-diene	—	52—53	40	0.7452	20	1.4418	20	44.08	42.83	III	30
Nona-3,4-diene	—	67—68	40	0.7542	20	1.4458	20	43.90	42.83	VI	30
7-Methylocta-3,4-diene	—	60—60.5	40	0.7488	20	1.4430	20	43.98	42.83	VI	30
Deca-3,4-diene	—	82.5—83.5	40	0.7655	20	1.4498	20	48.51	47.45	VI	30
7,7-Dimethylocta-3,4-diene	—	70—70.5	40	0.7555	20	1.4458	20	48.78	47.45	VI	30
2,2-Dimethyldeca-3,4-diene	—	86—87	20	0.7643	20	1.4435	20	57.74	56.68	VI	71
2,2,7,7-Tetramethylocta-3,4-diene	—	74—75	20	0.7645	20	1.4430	20	57.67	56.68	VI	71

TABLE. (contd.)

1	2	3	4	5	6	7	8	9	10	11	12
2. Aliphatic allenes with unsaturated substituents											
Penta-1,2,4-triene	—	46.5—47.5	760	—	—	1.4710	19	—	—	II	20
Hexa-1,2,5-triene	—	73—73.5	760	0.7450	0	1.4480	20	28.74	28.50	III	72
Hepta-1,2,6-triene	—	102	760	—	—	1.4551	24	—	—	V	27
Octa-1,3,4-triene	—	37—38	20	0.7685	20	1.4742	20	39.57	37.74	VI	30
Nona-2,4,5-triene	—	62	20	0.7826	20	1.4856	20	44.80	42.36	VI	73
8-Methylnona-1,3,4-triene	—	70—70.5	20	0.7787	20	1.4690	20	48.72	46.98	VI	30
Deca-1,3,4-triene	—	75—76	20	0.7815	20	1.4742	20	49.01	46.98	VI	30
Undeca-1,3,4-triene	—	91—92	20	0.7841	20	1.4738	20	53.83	51.60	VI	30
Undeca-2,4,5-triene	—	95—96	20	0.7912	20	1.4818	20	54.12	51.60	VI	73
2-t-Butylocta-1,3,4-triene	—	77—78	10	0.7950	20	1.4690	20	57.45	56.63	VI	74
2-t-Butyldeca-1,3,4-triene	—	104.5—106	10	0.8032	20	1.4690	20	66.57	65.45	VI	74
Penta-1,2-dien-4-yne	—	57	760	—	—	1.4850	16	—	—	II	20
Hexa-1,2-dien-5-yne	—	89—90	760	0.798	20	1.4703	20	27.27	26.97	III	72
3. Alicyclic allenes**											
1,1-Pentamethyleneallene	—	52—53	35	0.8503	20	1.4910	20	36.79	36.03	II	19,20
Cyclonona-1,2-diene	—	62	16	0.8914	25	1.5039	25	—	—	V	13,26,27
Cyclodeca-1,2-diene	—	74	10	0.8918	25	1.5071	25	—	—	V	26
Cyclohexadeca-1,2,9,10-tetraene	80	—	—	—	—	—	—	—	—	V	27
4. Allenes with aromatic radicals											
Phenylallene	—	68	16	0.9370	17	1.5830 1.5630	17 20	41.42	39.23	III	21
Benzylallene	—	72—73	17	0.9220	20	1.5460	20	44.64	43.85	III	75
1-Phenylbuta-1,2-diene		44—47 76—77	0.5—1 10	0.9240	26.5	1.5754 1.5698	20 30	46.33	43.85	I	76
5-Phenylpenta-1,2-diene	—	76—77	7	0.9169	20	1.5400	20	49.28	48.45	III	75
2-Methyl-4-phenylpenta-2,3-diene	—	106—108	20	0.9302	20	1.5470	20	53.89	53.08	III	35
3-Methyl-5-phenylhexa-3,4-diene	—	94—95	7	0.9238	20	1.5436	20	58.74	57.70	III	35
1,1-Diphenylallene	—	80	0.1	—	—	1.6301	20	—	—	V	27
1,3-Diphenylallene	49—51	—	—	—	—	—	—	—	—	VII	36
2,2,3-Trimethyl-5-phenylhexa-3,4-diene	—	118—119	10	0.9101	20	1.5335	20	68.25	66.93	III	35
3,4-Diphenylbuta-1,2-diene	—	135—143	760	—	—	—	—	—	—	V	77
3-Methyl-1,1-diphenylbuta-2,3-diene	—	140—150	18	—	—	—	—	—	—	I	122
Triphenylallene	135	—	—	—	—	—	—	—	—	I	78
1-(*p*-Biphenylyl)-3-phenylallene	94.6—95.5	—	—	—	—	—	—	—	—	VII	36
Tetraphenylallene	165	—	—	—	—	—	—	—	—	I	40,79
2,2,6,6-Tetramethyl-3-phenylhepta-3,4-diene	—	78—80	1	0.8808	20	1.5039	20	76.63	76.17	II	80
4,4-Dimethyl-1,1-diphenylpenta-1,2-diene	25—26	115—118	0.55	0.9661	20	1.5690	20	84.09	81.81	II	81

* I) Dehydrohalogenation of halogeno olefins; II) reduction of acetylenic and allenic halides; III) synthesis using organomagnesium compounds; IV) dehydration of unsaturated alcohols; V) *via gem*-dihalogenocyclopropanes; VI) action of lithium alkyls on alkylvinylacetylenes; VII) isomerisation of acetylenes.

** For preparation of allenes with seven- and eight-membered rings, see Refs.12, 27, and 184.

Dipole moments. Only the moments of allene and methylallene (0.4 *D*) have been determined[54,85].

Polarographic data. Allene is reduced at a dropping mercury electrode, the half-wave potential being -2.29 V.[86]

Ultraviolet spectra. Absorption spectra in the ultraviolet are used little in studying hydrocarbons because the absorption usually occurs in the vacuum region. Monosubstituted allenes have an intense band at 1780 Å (Σ 8000) and another at 1880 Å. In the spectra of disubstituted allenes these bands are displaced 30–40 Å towards longer wavelengths and a third band appears at about 2000 Å.[87] Selection rules have been derived for electronic and electronic-vibrational spectra of allenes[88].

Infrared spectra. The problem of identifying different allenes is at present solved mainly by infrared spectroscopy. Allene, its homologues, and derivatives are characterised by an intense band due to asymmetric stretching vibrations of the C=C=C group in the 1950 cm^{-1} region, with some variations depending on the position and nature of substitutents. This band can be used to detect allenes in the presence of other types of dienes and acetylenes[89–96].

When electron-accepting groups are present in the molecule, this band splits into two (at 1930 and 1950 cm^{-1}). Its intensity falls as substitution in allene by electronically similar groups is increased. It is absent from the spectrum of tetraphenylallene, for example; the presence of the allene grouping is demonstrated in this case by nuclear magnetic resonance spectra. If the substituents are of different types they hardly affect the intensity of the band.

The intense band in the 850 cm^{-1} region corresponds to CH deformation vibrations of a terminal allene group. An analogous band appears in the 870 cm^{-1} region of the spectra of symmetrically disubstituted allenes. Different types of allenes can easily be distinguished by these deformation vibration bands.

Raman spectra. There are two intense lines, in the 1100 and 1130 cm^{-1} regions, in the Raman spectra of allene hydrocarbons; their use for analytical purposes has been suggested[89,97–99].

Nuclear magnetic resonance spectra. The chemical shift of the CH_2= group in the spectrum of allene is in a higher-field region than in the spectra of alkenes[100]. The existence of 1,4-spin-spin interaction through the allene

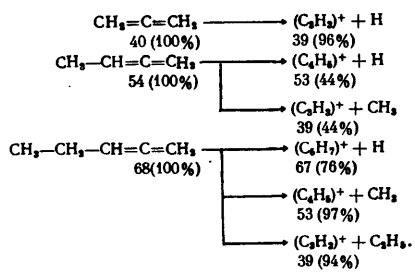
system with constants up to 7 c/s is very characteristic of allene compounds [101,102]. This confirms the *sp* hybridisation of the orbitals of the central atom of the allene system.

Mass spectra. The mass spectra of a number of allenes have been studied in recent years and interesting mechanisms of disintegration of these hydrocarbons under electron impact established [55,103-109].

In the mass spectrum of allene the peak for $(C_3H_4)^+$ ions is the most intense, but that for $(C_3H_3)^+$ ions, which are stabilised either through conjugation or as a result of transition to a cyclic three-carbon ion, is almost as intense. The ionisation potential of allene is 1·2.02 ± 0.03 eV. [55,103]

The highest peak in the mass spectra of methylallene and ethylallene also corresponds to the molecular ions, and the peak for $(C_3H_3)^+$ ions has a high intensity. In methylallene disintegration with loss of hydrogen or methyl to form $(C_4H_5)^+$ or $(C_3H_3)^+$ ions occurs with considerably lesser, and approximately equal, probabilities.

For ethylallene there is approximately equal and high probability of loss of methyl or ethyl higher than of ionisation with loss of hydrogen [55,108].



As the number of carbon atoms in the chain increases, the stability of the molecular ions falls and ions originating through rupture of C–C bonds predominate in the spectra of higher allenes. The formation of many of the fairly intense ions cannot be explained by simple dissociation at one bond; the latter is accompanied either by migration of hydrogen or by simultaneous rupture of two bonds [108,109].

The mass spectra of 2,3- and 3,4-dienes are characterised by specific features which are related to their structure. In 2,3-dienes disintegration to form the most intense ions takes place chiefly at the bond in the β position with respect to the allene system and is accompanied by migration of hydrogen. With 3,4-dienes, however, it occurs mainly at the α bond and without migration of hydrogen. This difference in the dissociative ionisation of allenes can be explained as follows. The ion formed by dissociation of 3,4-dienes achieves the stable prop-2-ynyl structure without migration of hydrogen:

$$R'—CH=C=CH—R \longrightarrow R'—CH=C=CH^+ + R \longrightarrow R'—\overset{+}{C}H—C\equiv CH.$$

whereas on rupture of the β bond of 2,3-dienes stabilisation is possible only with migration of hydrogen.

If the allene system contains a tertiary butyl radical, dissociative ionisation produces mainly $(C_4H_9)^+$ and $(t\text{-}C_4H_9)^+$ ions.

IV. CHEMICAL PROPERTIES

Owing to structural peculiarities, allene hydrocarbons possess specific properties with respect to a number of reagents and therefore occupy a special place among unsaturated compounds.

1. Addition Reactions without Lengthening of the Carbon Chain

Even unsubstituted allene shows unusual features in its addition reactions. Because of its symmetry the molecule is non-polar, but the central atom must be positively polarised with respect to the outer atoms, owing to conjugation and the inductive effect of the C–H bonds.

$$\overset{\delta-}{CH_2}=\overset{\delta+}{C}=\overset{\delta-}{CH_2}.$$

In the reactions of allene with hydrogen halides, water, alcohols, and free radicals, and in diene syntheses, when dipolar-1,3-addition takes place the positions of the added molecules correspond to the formula shown above. However, the course of the addition of mixed halogens, hypohalous acids, and their derivatives does not conform to the polarisation proposed.

The sharp disagreement between the course of addition of halogens and of hydrogen halides is typical only of allenes and is not observed with olefins, acetylenes, or 1,3-dienes. The reason for this can be sought in the geometry of the allene molecule and in the addition mechanism.

It is still more difficult to explain the rules in the addition reactions of allene homologues. They apparently proceed through formation of an intermediate state stabilised above all by hyperconjugation.

Hydrogenation. It is impossible, on the basis of available data on the hydrogenation of allene hydrocarbons in the presence of various catalysts, to reach definite conclusions as to where the first two hydrogen atoms are added. In most cases the hydrogenation was exhaustive and had the aim of establishing the structure of the hydrocarbon. The corresponding saturated compounds were formed in the hydrogenation of allene over palladium [110], 2,4-dimethylpenta-2,3-diene in the presence of platinum [111], tetraphenylallene on boiling with hydriodic acid and phosphorus in glacial acetic acid or by the action of sodium in alcohol [112], and also in the reduction of 1-(*p*-biphenyl)-3-phenylpropadiene under the same conditions [36].

Propene and tetraphenylpropene were obtained by the incomplete hydrogenation of allene [110] and tetraphenylallene [112]. Hexa-1,2-diene was incompletely hydrogenated on nickel to a mixture of hex-1-ene and hex-2-ene with the latter predominating [17]. Hydrogenation of 2-methyl-4-phenylpenta-2,3-diene using sodium in alcohol also gave a mixture of olefins [113].

When symmetrically disubstituted allenes are exhaustively hydrogenated on colloidal palladium, the process takes place at an increasing rate until half the theoretical quantity of hydrogen has been absorbed, after which addition of hydrogen occurs very slowly [114]. The ultimate reduction products are saturated hydrocarbons. The rate of hydrogenation depends on the structure of the hydrocarbons: it increases more rapidly for those with a branched structure. If the process is stopped after absorption of the first mole

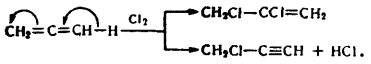
of hydrogen, at the point when the reaction slows down, a mixture of olefins which does not contain the original allene hydrocarbon is isolated§.

Cyclic allenes are easily hydrogenated to cycloolefins on palladium poisoned with pyridine [26].

The heat of hydrogenation of allene to propene at 355°K is 41.265 kcal mole^{-1}, and to propane 71.280 kcal mole^{-1}.[57]

Halogenation. The available data on halogenation relate mainly to allene and some of its simplest homologues.

When allene is chlorinated in chlorine-containing solvents, 2-chloropropene and prop-2-ynyl chloride are formed in equimolar quantities. The latter is a primary product of the reaction and is not formed by elimination of hydrogen chloride from 2,3-dichloropropene under the conditions used [115]:



When allene is brominated in acetic acid in the presence of potassium bromide, addition of rather more than one mole of bromine takes place rapidly, and then the reaction becomes very slow. The action on allene of solutions of iodine chloride in acetic acid and carbon tetrachloride is similar [115]. Complete bromination of allene is achieved by the bromide–bromate method [116], and also with bromine in chloroform [10].

2-Bromo-3-chloroprop-1-ene is formed by the action of bromine chloride on allene, *i.e.* the central atom in allene displays negative polarisation [115].

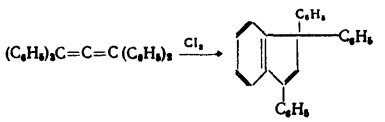
Addition of bromine to methylallene gave 2,3-dibromobut-1-ene, which easily isomerises even at room temperature to 1,2-dibromobut-2-ene [117]. Complete bromination gave 1,2,2,3-tetrabromobutane [33].

Bromination of ethylallene and propylallene also takes place at the substituted double bond to form respectively 2,3-dibromopent-1-ene and 2,3-dibromohex-1-ene, and then the tetrabromides [67,117,118]. Unsymmetrical dimethylallene is brominated to 3,4-dibromo-2-methylbut-1-ene which is capable of the allylic rearrangement to 1,2-dibromo-3-methylbut-2-ene [118]. The latter dibromide was obtained in earlier work, apparently because the possibility of a rearrangement was not considered [119,120]. Bromination of 1-phenylbuta-1,2-diene gives 2,3-dibromo-1-phenylbut-1-ene [76].

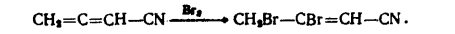
The addition of halogens preferentially at the more substituted double bond is possibly explained by the latter's high polarisation under the influence of the $+I$ effect of the radicals.

Addition of bromine to symmetrically disubstituted allenes occurs preferentially at the bond which is further removed from the end of the molecule. 3,4-Dibromopent-2-ene was obtained from symmetrical dimethylallene [76].

Phenyl radicals in the molecule reduce the rate of bromination considerably. Tetrabromides were, however, obtained from phenylallene, phenyltrimethylallene, and methyldiphenylallene [113,121,122]. Bromine is added with difficulty to triphenylallene [78], and indenes are formed by the action of halogens on tetraphenylallene [112]:



Addition of halogens (chlorine or bromine) to allenes containing electronegative groups takes place at the unsubstituted double bond, for example [123]:



Addition of hydrogen halides. Whereas in halogenation of allenes the two possible monoadducts are interconvertible by the allylic rearrangement and the discrepancies between the results of different authors can be explained by small changes in the conditions of preparation or treatment of the reaction products, in the addition of hydrogen halides only two of the four possible adducts can be interconverted by the allylic rearrangement. The published data here indicate reliably that there are fundamental differences in the course of addition, depending on the structure of the allene hydrocarbons.

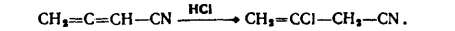
With hydrogen fluoride allene forms 2,2-difluoropropane, and with hydrogen chloride 2-chloroprop-1-ene and 2,2-dichloropropane [124,125]. The addition thus obeys Markovnikov's rule.

Addition of hydrogen chloride to methylallene (giving 2-chlorobut-2-ene and 2,2-dichlorobutane) [125] and propylallene (giving 2-chlorohex-2-ene and 2,2-dichlorohexane) in the presence of bismuth trichloride [17] is similar.

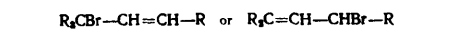
With unsymmetrical dimethylallene addition of hydrogen chloride occurs in a different way, mainly 3-chloro-3-methylbut-1-ene being formed. The ratio of the allylic isomers is 64:36. [125] When hydrogen chloride is added to homologues of allene partial isomerisation to 1,3-dienes takes place.

In earlier work it was suggested that 1-chloro-3-methylbut-2-ene is formed on addition of hydrogen chloride to dimethylallene [126]. Allylic rearrangement evidently occurs under the conditions of the reaction.

Addition of hydrogen chloride to allenes with electronegative substituents takes place at the substituted double bond [123]:



Addition of hydrogen bromide to allenes proceeds in the same way: the peroxide effect was not observed. Ethylallene gives 2-bromopent-2-ene and also 2-bromopent-1-ene and 2,2-dibromopentane [67,127], propylallene gives 2-bromohex-2-ene and the corresponding dihydrobromide [118], and unsymmetrical dimethyl-, diethyl-, and trimethyl-allenes give, depending on the conditions, one or two linked hydrobromides, interconvertible by the allylic rearrangement:



and also dihydrobromides with bromine atoms in the 1,3-positions [118,128,129]. The latter are often used for the synthesis of cyclopropane hydrocarbons [130].

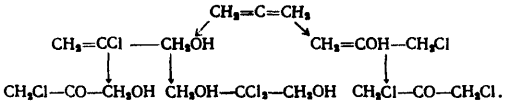
§ When disubstituted allenes are hydrogenated by the action of lithium or sodium in liquid ammonia, mainly alk-2-enes are formed [185].

In the electrophilic addition of hydrogen halides the proton attacks the outer carbon atoms in the case of alkylallenes and the middle carbon atom in the case of unsymmetrical dialkylallenes. Evidently in the two cases the intermediate ion is formed which is the more stabilised by hyperconjugation.

Hydrogen chloride and hydrogen bromide are added to symmetrically disubstituted allenes to form a mixture of hydrobromides in which the hydrogen is attached both to the outer and to the middle carbon atoms of the allene system [118].

Tetraphenylallene gives with hydrogen halides dark unstable products [112].

Addition of hypohalous acids and their esters. The action of hypochlorous acid on allenes was studied long ago but only in two cases. Mainly a chloro--keto-alcohol (3-chloro-1-hydroxypropan-2-one), dichloroacetone (15%), and chloroallyl alcohol (10%) were obtained from allene [131].



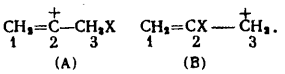
The addition of hypochlorous acid to unsymmetrical dimethylallene was even more complex, giving a mixture of products from which were isolated in the largest amounts a chloro-keto-alcohol (1-chloro-3-hydroxy-3-methylbutan--2-one), a dichloro-ketone (1,3-dichloro-3-methylbutan-2--one), and a dichloro-glycol (2,2-dichloro-3-methylbutane--1,3-diol). [131] The first and last products are assumed to be formed through intermediate products of the following structures:

$$(CH_3)_2COH{-}CCl{=}CH_2 \text{ and } (CH_3)_2C{=}CCl{-}CH_2OH,$$

which are produced by addition of one molecule of hypochlorous acid. Thus in both cases addition of hypochlorous acid to the allene system took place contrary to Markovnikov's rule, *i.e.* differently from the addition of other electrophilic reagents.

Combined hypobromination by the action of bromine and methanol on allenes also mainly occurs contrary to Markovnikov's rule [76].

Addition of electrophilic reagents to allene may be accompanied by formation of two types of ion in the transition state:



At the time when ion B is formed in the transition state conjugation cannot take place because the positive charge and the electron pair are in different planes. In order to achieve conjugation, atom C_3 must be rotated about the C_2-C_3 axis, which requires expenditure of energy. Ion A is stabilised through hyperconjugation. Ion B is consequently not always more stable than ion A and it is, in principle, possible for either to be formed. Comparison of the reactions described above suggests that the reactions which are accompanied by considerable heat usually occur through formation of ion B. It is possible that in reaction complexes which are richer in energy, conditions obtain for achieving conjugation and ion B is more favoured.

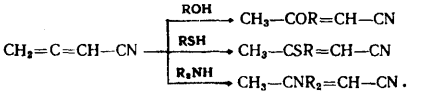
Addition of water, alcohols, acids, and their sulphur analogues. Hydration of allene and its homologues which have one or two radicals attached to the cumulative bond system occurs easily by the action of 80% sulphuric acid or under the conditions of the Kucherov reaction, only ketones being formed [10,17,28,67,132,133].

Water is added, irrespective of the structure of the allene, in strict accordance with Markovnikov's rule. The ease of hydration distinguishes allenes from other dienes; in this respect they are more like acetylenes.

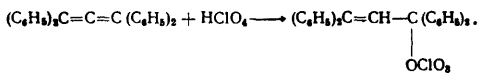
Research on the reactions of allene hydrocarbons with alcohols in the presence of alkali formed part of the major research carried out by Favorskii and his students on the isomeric rearrangements of hydrocarbons of the C_nH_{2n-2} series [134]. Addition of an alcohol in the presence of alkali is possible with allenes, as with acetylenes, but not with olefins and dienes with conjugated or isolated double bonds. This is due to the special "acetylenic" nature (*sp* hybridisation) of the central atom of the allene system. The reaction is usually carried out by heating to 150–170°. Allene gives ethyl isopropenyl ether. Methylallene and symmetrical and unsymmetrical dimethylallenes isomerise under these conditions to disubstituted acetylenes. t-Butylallene is unchanged [120,135-137].

Addition of alcohols to allenes in the presence of boron trifluoride and mercuric oxide, studied using propylallene, follows the same path, with formation of acetals [17].

Addition of alcohols, mercaptans, and amines to allenes containing electronegative substituents takes place at the unsubstituted double bond [123]:



The addition of perchloric acid to tetraphenylallene occurs in a different way [138]:



This reaction needs further study.

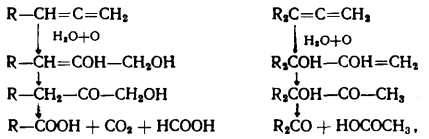
The crystalline addition products of 2,4-dinitrobenzenesulphenyl chloride and cyclic allenes have been used for identification of the latter [26].

Addition of peroxide compounds and oxidative cleavage.

(a) Action of potassium permanganate solutions. Many allene hydrocarbons have been oxidised using potassium permanganate with the aim of establishing their structures. Although the glycols (or rather keto-alcohols) which are first formed were not isolated, it is nevertheless possible to judge from the reaction products to which of the double bonds the elements of hydrogen peroxide were added first.

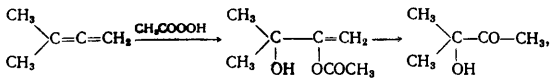
In the oxidation of monosubstituted allenes (t-butyl- and phenyl-allenes) formic acid was obtained, but not acetic acid; this indicates that the oxidant acts first at the outer double bond [113,121,139]. With unsymmetrically disubstituted

allenes (dimethylallene) it is the double bond at the most substituted carbon atom which undergoes oxidation, since acetic acid is a reaction product [14,140]. With trimethylallene the oxidation products agree with both possible modes of oxidation [140].

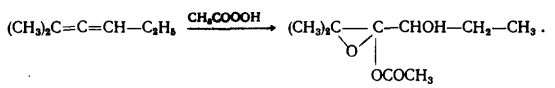


(b) Action of ozone. Ozonisation of allenes has also been studied only as a means of demonstrating their structures. The formation of a monoozonide has never been recorded and it is therefore impossible to draw conclusions as to the way in which ozone is added to allenes [33,121,140].

(c) Action of hydroperoxides. Addition of hydroperoxides either takes place at the more substituted double bond as, for example, in the reaction of unsymmetrical dimethylallene with acetyl hydroperoxide:



or acts at both bonds forming epoxides of glycol esters [141]:



Pansevich-Koleda has examined this reaction in detail [68], and has reviewed the subject [41].

(d) Action of lead tetraacetate. This reaction has been studied for a few hydrocarbons, but the mode of addition of the acetoxy-group has not been proved rigorously [142].

(e) Addition of the elements of hydrogen peroxide to ethylallene by the action of an aqueous solution of silver perchlorate on ethylallene in the presence of osmium tetroxide took place at the more substituted double bond [143].

Addition of alkyldichlorosilanes. The mode of addition of methyldichlorosilane to propyl-, butyl-, methylpropyl-, methylpentyl-, and ethylpropyl-allenes and of ethyldichlorosilane to propyl- and butyl-allenes in the presence of chloroplatinic acid has been investigated. The silicon-containing chlorides obtained were alkylated with methyl- or ethyl-magnesium bromide without being isolated [144].

Silylolefins of the type $R-CH=CH-CH_2-SiR_3$ were obtained by the addition of methyl- or ethyl-dichlorosilanes to monosubstituted allenes. Disubstituted allenes gave mainly adducts with a silyl group at the smaller radical.

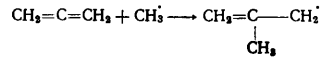
The mode of addition of alkyldichlorosilanes to allenes was thus found to be different from that for the addition of water or hydrogen halides. The results obtained are best explained by a radical mechanism for the reaction.

Addition of nitrogen trioxide. Allene gives a pseudonitrosite with nitrogen trioxide [145].

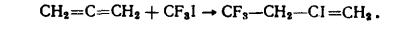
2. Addition Reactions with Lengthening of the Carbon Chain

Addition of free radicals. Divinyl hydrocarbons are the most reactive towards free radicals. This is explained by the high stability of the allyl radicals formed.

Addition of the methyl radical, which is nucleophilic, to allene takes place more slowly than to dienes or even to olefins. Substitution of the hydrogen atoms of allene by alkyl or phenyl radicals has little effect on the reactivity of the allene system. In this respect allenes differ markedly from conjugated dienes and olefins, the reactivity of which towards methyl radicals depends very much on the position and nature of the substituents. The lack of relation between the rate of reaction and the type of substituent indicates that only the central atom of the allene system undergoes attack [146].



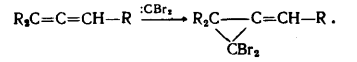
Addition of the electrophilic trifluoromethyl radical occurs only at the outer carbon atoms of allene. Thus allene and CF_3I gave, by a radical reaction, 1,1,1-trifluoro-3-iodobut-3-ene: [147]



Radicals thus behave towards the allene system in the same way as hydrogen halides. In reactions with radicals and hydrogen halides a higher electron density is found on the outer carbon atoms of the cumulative system.

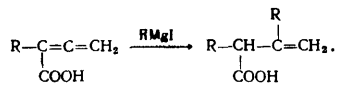
Methylene radicals, produced in the photolysis of ketene and diazomethane, form methylenecyclopropane and methylallene with allene [148].

It was shown recently that addition of dibromocarbene to allene hydrocarbons occurs at the most substituted double bond [149,150]:



This reaction provided a new method of synthesising derivatives of methylenecyclopropane which is difficult to prepare in other ways.

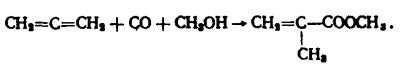
Addition of organometallic compounds. There are no published data on the mode of addition of organometallic compounds to allene hydrocarbons. The addition of alkylmagnesium halides to allene acids takes place at the double bond which carried the carboxy-group [151,152]:



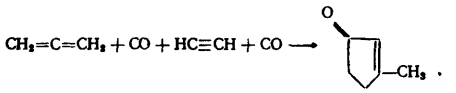
These acids do not react as dienophiles and polymerisation can occur [153].

Reaction with carbon monoxide. Like acetylene, allene adds on carbon monoxide in the presence of metals which are able to form carbonyls (ruthenium). Water, alcohols, ammonia, amines, or acetylene can be used as the second component [154].

Methyl methacrylate was obtained from allene, carbon monoxide, and methanol:



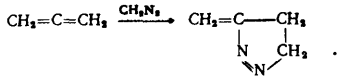
Acetylene, carbon monoxide, and allene gave 3-methylcyclopent-2-en-1-one:



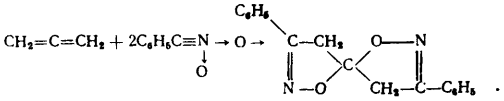
Allene hydrocarbons which have a hydrogen atom in the position α to the cumulative bonds (allene, butylallene, etc.) can react with cobalt carbonyl at room temperature with liberation of carbon monoxide and formation of organometallic complexes which cause polymerisation of the original hydrocarbon[155].

Reaction with tetranitromethane. Allenes, like other unsaturated compounds, give yellow products with tetranitromethane. Introduction of a phenyl radical into the molecule deepens the colour while a t-butyl radical makes it paler. The nature of the products has not been determined[156].

Dipolar 1,3-addition also produces lengthening of the carbon chain. With diazomethane allene forms methylenepyrazoline but the position of the substituent has not been established precisely[157]:

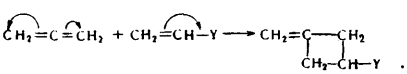


Benzonitrile oxide is added to both double bonds of allene to form 3,3′-diphenyl-5,5′-spirobi-(4*H*,5*H*-isoxazoline)[158]:



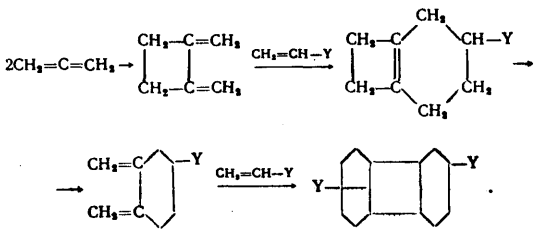
3. "Ene" and Diene Synthesis

Allene hydrocarbons are involved in diene synthesis as dienes and dienophiles. Allene and a number of its homologues give cyclobutane-type condensation products with many typical dienophiles (maleic anhydride, acrylonitrile and methacrylonitrile, methyl acrylate and methyl methacrylate, methacrylic aldehyde, itaconic ester, α-methylstyrene, etc.) by the following mechanism (for allene)[159-161]:

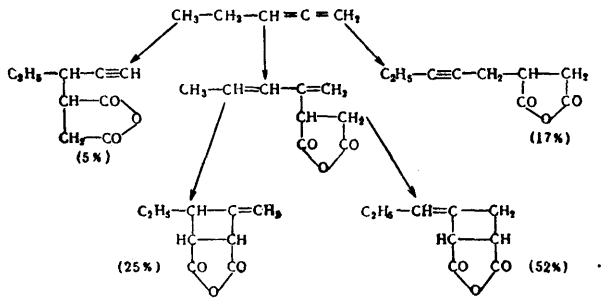


Derivatives of octalin and acetylene compounds are formed as by-products.

The formation of octalin derivatives is explained by partial dimerisation of allenes under the conditions of the reaction. The dimers then take part in diene synthesis in the usual way:



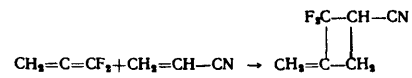
The formation of acetylene compounds indicates an unusual mechanism for the condensation of allenes with dienophiles. The reaction evidently occurs not by "diene", but by "ene" synthesis. For example, condensation of ethylallene with maleic anhydride gives products corresponding to all three possible paths for "ene" synthesis:



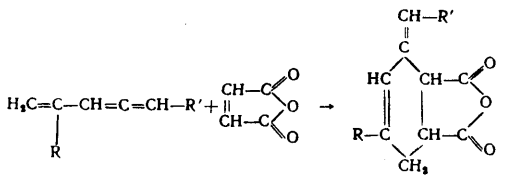
Addition of maleic anhydride occurs at both double bonds but the outer double bond is more than twice as reactive as the middle bond.

With tetrafluoroethylene allene gives methylenetetrafluorocyclobutane and spirobistetrafluorocyclobutane[162].

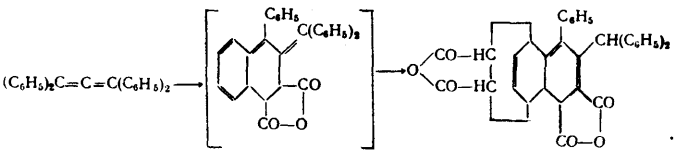
Condensation of difluoroallene with dienophiles takes place at the substituted doubled bond[163]:



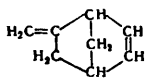
Vinylallene and its homologues can be condensed with maleic anhydride at the 1,3-conjugated system to form substituted methylenecyclohexenes[20,74]:



Phenyl-substituted allenes behave differently from aliphatic allenes in that two molecules of maleic anhydride are added to them to give derivatives of phenylnapthalene[164].

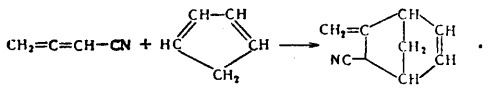


Allenes react as "dienophiles" with 1,3-dienes; for example, with cyclopentadiene the following adduct is formed[165]:



as well as derivatives of naphthalene and anthracene and products of further addition of cyclopentadiene to this adduct.

Condensation of allene nitriles with cyclopentadiene takes place at the substituted double bond[123]:



4. Polymerisation of Allenes

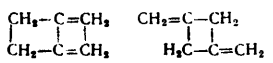
The ability to polymerise on heating is characteristic of allenes to no less an extent than of dienes with conjugated double bonds. The principal features of the thermal polymerisation of allenes were established by Lebedev for allene, symmetrical and unsymmetrical dimethylallenes, and trimethylallene[166].

In contrast to 1,3-dienes, allenes polymerise on heating at almost identical rates, irrespective of structure. The rate constants for the polymerisation of three of the allenes mentioned above were calculated by Gapon[167] from Lebedev's data. This feature [identical rates (Ed. of Translation)] indicates that at the beginning of the polymerisation process two hydrocarbon molecules combine through the two central carbon atoms.

A distinctive feature of the allene type of polymerisation is also the formation of a continuous series of compounds containing cyclobutane rings, from dimer to hexamer and beyond.

The process is complicated by polymerisation of a type characteristic of 1,3-dienes, owing to partial isomerisation of allenes to 1,3-dienes on heating.

In the case of allene, dimers, trimers, tetramers, pentamers, and hexamers have been isolated. The dimer is a mixture of the following two substances:

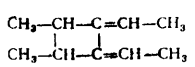


the former predominating[168,169].

The tetramer is also obtained in two forms, one of which is produced by condensation with transition to a divinyl structure.

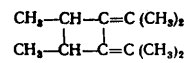
At 500–550° methylallene gives mainly a mixture of dimers together with gaseous hydrocarbons (methane, ethane, ethylene, propene, allene, and methylacetylene)[170].

Only one dimer and one trimer are obtained from symmetrical dimethylallene:



Unsymmetrical dimethylallene gives the two possible dimers. Only one trimer with a definite structure was isolated from a mixture of trimers[171].

One dimer, which makes up 90% of the crude polymer, was obtained from trimethylallene:

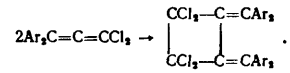


Allenes with seven- and eight-membered rings can polymerise to dimers under the action of alkali[26].

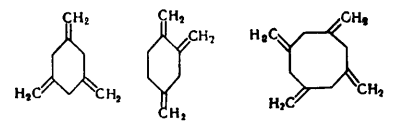
Fluorinated allenes also give dimers containing a cyclobutane ring. 1,2-Bis(difluoromethylene)tetrafluorocyclobutane was obtained from tetrafluoroallene[172], and 2-difluoromethylene-1-methylenedifluorocyclobutane from 1,1-difluoroallene[163]:



Diaryldihalogenoallenes form four-membered rings through the halogen-substituted bonds[173]:

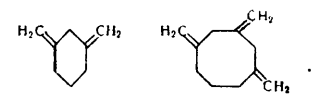


A new type of cyclopolymerisation of allene in the presence of nickel complexes which gives polymers containing six- and eight-membered rings was discovered recently[174]:



This type of trimerisation indicates the similarity between the structures of allene and acetylene.

It is of interest that in the presence of nickel catalysts allene enters into joint cyclopolymerisation with acetylene hydrocarbons (acetylene, and methyl-, phenyl-, and vinyl-acetylenes) in the ratios 2 : 1 and 3 : 1, with formation of six- and eight-membered rings, *e.g.* for allene[174]:



Photopolymerisation of allene[175] and polymerisation under the action of radon[176] have also been investigated.

5. Isomeric Rearrangement of Allenes

Since the discovery of the allene–acetylene–1,3-diene rearrangement the interconversion of acetylenes and dienes has been the subject of innumerable researches. Allene hydrocarbons can isomerise in three ways: to monosubstituted acetylenes, to disubstituted acetylenes, or to conjugated dienes.

Conversion of allenes into monosubstituted acetylenes is easily achieved by heating with sodium metal or sodamide[10,67,111,135,137,139]. In this case the isomerisation is irreversible because the monosubstituted acetylene is removed from the reaction as the sodium derivative.

The use of other catalysts (Floridin, metal oxides) allows this reaction to be carried out reversibly, as has been demonstrated for allene, methylallene, and unsymmetrical dimethylallene[33,34]. The allene–methylacetylene equilibrium constant depends only on temperature[34].

Conversion of allenes into disubstituted acetylenes takes place when they are heated with alcoholic alkali[25,120,135-137], and into conjugated dienes under the action of various catalysts and at an elevated temperature[33,34,98,177-182]. The heat of isomerisation of buta-1,2-diene to divinyl is 12.78 ± ± 0.16 kcal mole^{-1}.[177] Floridin, metal oxides, and halide salts of quinoline were used as catalysts.

Cyclic allenes can isomerise to 1,3-dienes under the action of alkali[26].

Isomeric rearrangements of allenes involve, in all probability, removal of a proton by the base and its addition to another part of the molecule[183].

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Lensovet Leningrad Institute of Technology

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MECHANISM OF THE OXIDATIVE THERMAL DEGRADATION AND OF THE STABILISATION OF POLYMERS

M. B. Neiman

CONTENTS

1. Oxidation in gas and liquid phases 13
2. Oxidation in the solid phase 14
3. Oxidation of polypropylene 15
4. Critical antioxidant concentration 18
5. Initiation of oxidation by antioxidants 20
6. Theory of synergism 21
7. Free radicals as stabilisers 23
8. Borate stabilisers 25

1. OXIDATION IN GAS AND LIQUID PHASES

After Bakh[1] and Engler[2] had formulated the peroxide theory of oxidation, many papers appeared on the oxidation of hydrocarbons and other organic compounds. Many oxidations were found to be autocatalytic and characterised by well-defined induction periods. Work in this field entered a new phase of development with the theory of chain branching[3], and especially the theory of degenerate explosions[4]. The principal results obtained on oxidation were generalised on the basis of the theory of chain reactions[5]. Under the influence of the work done by the Semenov and Hinshelwood schools, a great deal of research effort was devoted to the mechanism of the oxidation of organic compounds in the gas and liquid phases.

Shortly afterwards it was suggested that the main task of research in this field was to determine the rate constants of the elementary reactions in a complicated radical-chain