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The Methods of Synthesis and Properties of Conjugated Enallenic Hydrocarbons

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The methods of synthesis of conjugated enallenic hydrocarbons are surveyed and their physical and chemical properties are discussed.
The bibliography includes 90 references.

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I. INTRODUCTION

Enallenic hydrocarbons containing the allene group conjugated with a double bond were obtained for the first time (with a rigorous demonstration of their structure) in 1958. The information available at the present time concerning the methods of synthesis and the chemical behaviour of these compounds is limited. However, the available data show that conjugated enallenes are interesting objects of study. The unusual stereochemistry of the allene group, which is particularly clearly manifested in enallenes, determines the ability of only one double bond of this group to participate in conjugation with the α-ethylenic bond, which is the reason for the unusual physical and chemical properties of these hydrocarbons. The likely usefulness of conjugated enallenic hydrocarbons in experimental organic chemistry has been demonstrated by their synthesis from aromatic and methylenecyclohexene compounds, which are relatively difficult to obtain, conjugated cyclopentenones, methylenecyclobutene derivatives, allenic alcohols, epoxides, etc. It has been established that the enallenic conjugated system of bonds occurs in certain natural antibiotics, attractants, and the pigments of algae, sea urchins, and the flowers and leaves of many plants. Allenic compounds with an α-ethylenic bond are also produced by many species of fungi. Since some of these compounds exhibit distinct antimicrobial and fungicidal activities, the study of the structure and biogenesis of natural enallenic derivatives is an important practical task.

The development of the chemistry of enallenic hydrocarbons is mainly due to the development of two fundamental preparative methods for their synthesis: the method of Petrov and Kormer and Bertrand's method. It is to be expected that further research in the chemistry of conjugated enallenic hydrocarbons will lead to the development of new methods of their synthesis and to extensive practical applications of these hydrocarbons.

II. METHODS OF SYNTHESIS

1. THE ANIONOTROPIC REARRANGEMENT OF ENYNE AND PROPARGYL SYSTEMS

(a) The Reduction of Halogenoenynes by Metals

Penta-1,2,4-triene (I), the parent compound of the class of conjugated enallenic hydrocarbons, was obtained for the first time by analogy with Ginzburg's method[1], on treating a mixture of the chloropentenynes (II) and (III)—derivatives of pent-1-en-4-yn-3-ol[2]—with the zinc–copper couple in butanol; the enallene (I) with 94% purity was isolated in 75% yield[3].

$$\underset{\substack{\text{Cl}\\ \text{(II)}}}{CH_2{=}CH{-}CH{-}C{\equiv}CH} + \underset{\text{(III)}}{HC{\equiv}C{-}CH{=}CH{-}CH_2{-}Cl} \xrightarrow[BuOH]{Zn-Cu} \underset{\text{(I)}}{CH_2{=}C{=}CH{-}CH{=}CH_2}.$$

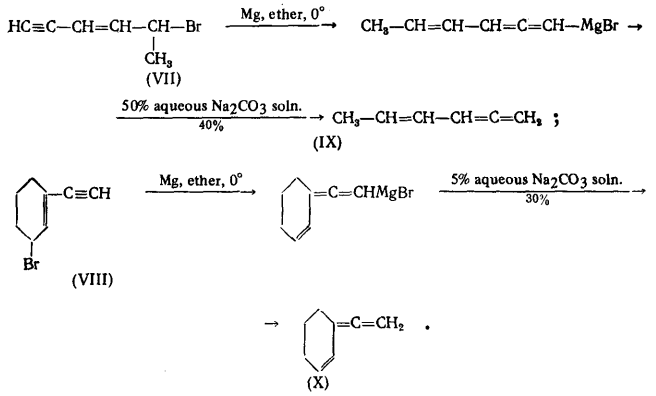
The use of the *trans*-isomer of the chloropentenyne (III) under these conditions made it possible to obtain compound (I) with 97% purity and in 70% yield.

During the reduction of chloroenynes with the zinc–copper couple, accompanied by the anionotropic rearrangement, an organozinc compound is apparently formed as an intermediate[4]. This is confirmed by the experimental observation of the formation of organomagnesium compounds in the reactions of analogues of the chloropentenyne (III) with magnesium. It has been shown[5,6] that the substituted chloropentenynes (IV) react with magnesium in ether at a low temperature to form the derivatives (V), which have the enallenic structure:

$$\underset{\text{(IV)}}{RC{\equiv}C{-}C{=}C{-}CHCl} \qquad \underset{\text{(V)}}{HC{=}C{-}C{=}C{-}C{-}MgCl} \qquad \underset{\text{(VI)}}{HC{=}C{-}C{=}C{=}CH}$$

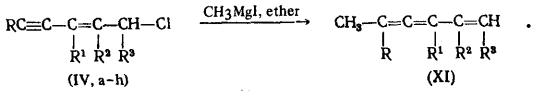
(a) $R{=}R^1{=}R^2{=}R^3{=}H$; (b) $R{=}R^2{=}R^3{=}H$, $R^1{=}CH_3$; (c) $R{=}R^3{=}H$, $R^1{=}R^2{=}CH_3$; (d) $R{=}R^1{=}R^2{=}H$, $R^3{=}CH_3$; (e) $R{=}CH_3$, $R^1{=}R^2{=}R^3{=}H$; (f) $R{=}H$, $R^1{=}R^2{=}R^3{=}CH_3$; (g) $R{=}H$, $R^1+R^2{=}$tetramethylene, $R^3{=}CH_3$; (h) $R{=}H$, $R^1{=}CH_3$, $R^2{+}R^3{=}$tetramethylene.

This discovery made it possible to use the above reaction to synthesise conjugated enallenic hydrocarbons. Thus the primary chloro-derivatives (IV, a–c, e) are converted, on treatment with magnesium and subsequent hydrolysis of the resulting organomagnesium compounds (V), into the corresponding enallenes (VI, a–c, e) in a satisfactory yield (31–55%).[5,6] The secondary chloroenynes (IV, d, f–h) do not react with magnesium either in boiling ether or in tetrahydrofuran (THF). However, the corresponding bromo-derivatives readily form organomagnesium compounds in the cold in ether, which has been demonstrated by the synthesis of the enallenic hydrocarbons (IX) and (X) from the bromo-derivatives (VII) and (VIII):



(b) The Interaction of Propargyl Halides, Halogenoenynes, and Ethers with Grignard Reagents

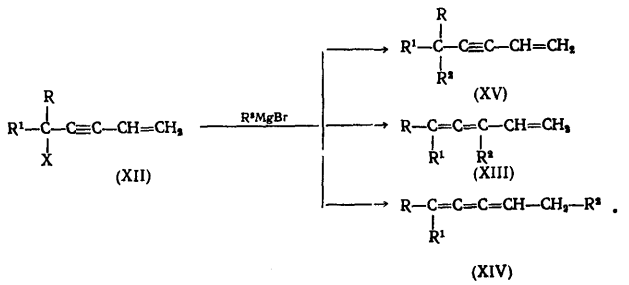
The chloropentenynes (IV, a–h) are converted into conjugated enallenes (XI) in 20–80% yield on treatment with methylmagnesium iodide in boiling† ether over a period of 2–3 h:[6,7]



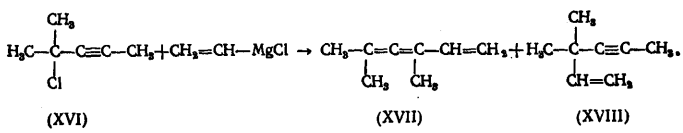
The enallenes (XI) were isolated from the reaction mixture by chromatographic methods. The above treatment of the chloroenyne (IV, f) gave a direct substitution product as the main reaction product. It has been established[6] that conjugated enallenes cannot be obtained from the chloroenynes (IV, a–h) using other Grignard reagents.

Comparison of the above two methods of synthesis of enallenes using chloropentenynes of type (IV) leads to the conclusion that the second method is preferable on the preparative scale, since it makes it possible to obtain the desired products with a higher purity and in higher yields. Furthermore, it permits the use of both primary and secondary chloroenynes.

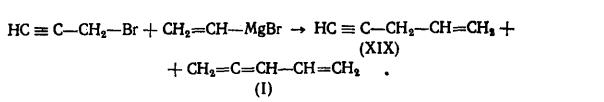
It has been shown[8] that the tertiary chlorides (XII, X = Cl) react with the Grignard reagent to form a mixture of enallenic and cumulenic hydrocarbons [compounds (XIII) and (XIV)], which are obtained from the initial compound as a result of a substitution reaction and the acetylene–allene–cumulene rearrangement. The reaction product contains a certain amount of the enyne hydrocarbon (XV) as a result of the "normal" substitution of chlorine in compound (XII)



The enyne (XV) is absent from the reaction mixture obtained by the analogous treatment of the ethers (XII, X = OAlk) and containing only compounds (XIII) and (XIV).[9] The overall yield and composition of the hydrocarbon mixture formed in the above reaction for different X, R, R^1, and R^2 are presented in Table 1. The reaction of vinylmagnesium chloride and 4-chloro-4-methylpent-2-yne (XVI) yields a mixture of the conjugated enallene (XVII) and the enyne (XVIII):[10]



Vinylmagnesium bromide and propargyl bromide react to form a 2 · 3 mixture of pent-1-en-4-yne (XIX) and penta-1,2,4-triene (I):[11]



Subsequent Bertrand isomerisation[12] of the mixture of hydrocarbons (XIX) and (I) on treatment with NaOH in methanol give the pure enallene (I). The latter can also be isolated by removing the enyne (XIX) from the reaction mixture on treatment with an alcoholic solution of silver nitrate.

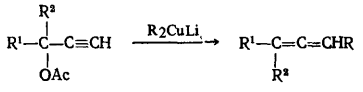
Table 1. The overall yields and compositions of the hydrocarbon mixtures obtained in the reactions of the enynes (XII) with Grignard reagents[9].

Enyne derivative (XII)			R^3MgBr	Content in reaction mixture, %			Overall yield of (XIII) + (XIV) + (XV), %
R	R_1	X	R^3	(XIII)	(XIV)	(XV)	
CH_3	CH_3	Cl	C_2H_5	61	35	4	57
CH_3	n-C_4H_9	Cl	C_2H_5	57	48	5	77
C_2H_5	n-C_4H_9	Cl	C_2H_5	46	38	6	77
CH_3	CH_3	Cl	C_2H_5	54	36	10	46
CH_3	CH_3	CH_3O	C_2H_5	86	14	0	62
CH_3	CH_3	CH_3O	n-C_3H_7	86	14	0	51
CH_3	CH_3	CH_3O	n-C_4H_9	81	19	0	49
CH_3	CH_3	CH_3O	iso-C_3H_7	0	100	0	44
CH_3	CH_3	CH_3O	iso-C_4H_9	0	100	0	40
CH_3	CH_3	CH_3O	t-C_4H_9	0	100	0	40
CH_3	CH_3	C_2H_5O	C_2H_5	77	23	0	66
CH_3	CH_3	n-C_3H_7O	C_2H_5	82	18	0	61
CH_3	CH_3	n-C_4H_9O	C_2H_5	66	34	0	49
CH_3	CH_3	iso-C_3H_7O	C_2H_5	54	46	0	45
CH_3	CH_3	iso-C_4H_9O	C_2H_5	30	70	0	38

† Certain chlorides react at room temperature.

(c) Reduction of Enynyl Acetates with Dialkyl-lithium Cuprates

On treatment with dialkyl-lithium cuprates, propargyl acetates give high yields of alkylallenes[13]:

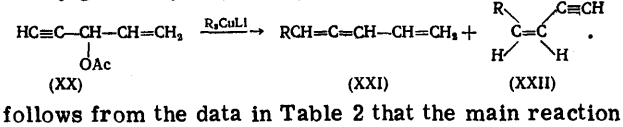


It has been shown[14] that this reaction can also be extended to the synthesis of conjugated enallenes when acetates having the enyne structures are used as the starting compounds.

Table 2. The compositions of the hydrocarbon mixtures obtained on treating the enynyl acetate (XX) with dialkyl-lithium cuprates R_2CuLi.[14]

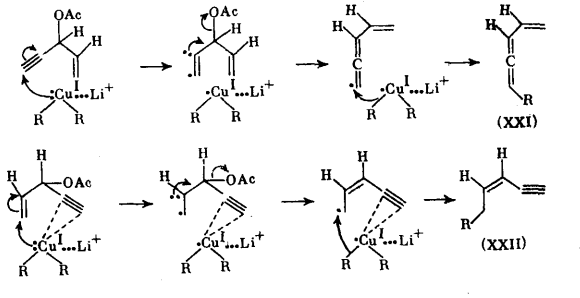
R	Content in reaction mixture, %		Overall yield of (XXI) + (XXII), %
	(XXI)	(XXII)	
CH_3	94	6	42
C_4H_9	80	20	60
C_8H_{17}	90	10	52

Thus the reaction of 3-acetylpent-1-en-4-yne (XX) with R_2CuLi in ether (between −20° and −30°C) results in the formation of the conjugated enallene (XXI) together with the conjugated enyne (XXII) (Table 2):

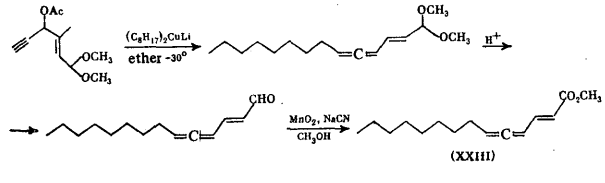


(XX) (XXI) (XXII)

It follows from the data in Table 2 that the main reaction product is the enallenic hydrocarbon (XXI), the formation of which is believed[14] to be the result of the addition of dialkyl-lithium cuprate to the triple bond of the initial acetate (XX), while the enyne (XXII) results from the addition of the cuprate to the double bond:



The ester (XXIII), which is an insect attractant and is therefore of considerable interest, has been synthesised by this method[14]:



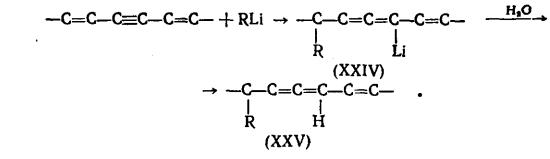
(XXIII)

2. REACTIONS INVOLVING 1,4-ADDITION TO ENYNE AND DIENYNE SYSTEMS

(a) The Addition of Organolithium, Organocalcium, and Organobarium Compounds to Conjugated Dienyne Hydrocarbons

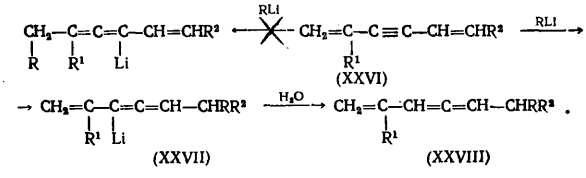
Petrov and Kormer developed a widely used preparative method of synthesising enallenes by treating conjugated dienyne hydrocarbons with alkyl-lithium in ether at a low temperature[15-19]. The following facts were established.

(1) The RLi reagent adds in the 1,4-positions of the enyne fragment of the conjugated dienyne system with formation of the lithium-containing adduct (XXIV) whose hydrolysis yields the enallene (XXV):



(XXIV) (XXV)

(2) The alkyl-lithium undergoes 1,4-addition, leading to the formation of an allenic system, only to the enyne fragments containing an unsubstituted vinyl group. Thus the dienyne (XXVI, $R^1 = CH_3$, $R^2 = H$) reacts with alkyl-lithium to form exclusively the lithio-derivative (XXVII)—the product of the addition of alkyllithium to the "vinyl-acetylene" fragment and not the "isopropenylacetylene" fragment of the dienyne system, as a result of which the enallenic hydrocarbon (XXVIII) is the sole product of the above reaction[16]:

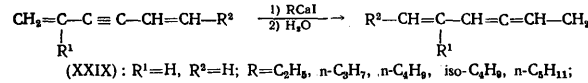


(XXVI) (XXVII) (XXVIII)

(3) The alkyl group of the reagent always adds to the terminal atom of the unsubstituted vinyl group.

The above characteristics of the addition of organolithium reagents to conjugated dienyne hydrocarbons can be accounted for by a coordination reaction mechanism[19]. The same characteristics hold also[20] in the reaction of aryl- and naphthyl-lithium with the dienyne hydrocarbon (XXVI, $R^1 = CH_3$, $R^2 = H$). Because of this, the enallenic hydrocarbon (XXVIII, R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, or α-naphthyl) is the only product of the above reaction.

Conjugated enallenic hydrocarbons can also be obtained by the reactions of the dienyne hydrocarbons (XXIX),[21] (XXVI),[22] and (XXX)[23] with alkyl- and arylcalcium iodides:



(XXIX): R^1=H, R^2=H; R=C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11};

(XXVI): R^1=CH_3, R^2=H; R=C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, C_6H_5, $CH_3C_6H_4$;

(XXX): R^1 = H, R^2 = CH_3; R = C_2H_5, n-C_3H_7, n-C_4H_9.

The above process, which takes place at room temperature over a period of several minutes, is, however, complicated by a competing reaction of the Wurtz type. The yield of enallenes does not exceed 30% in this instance.

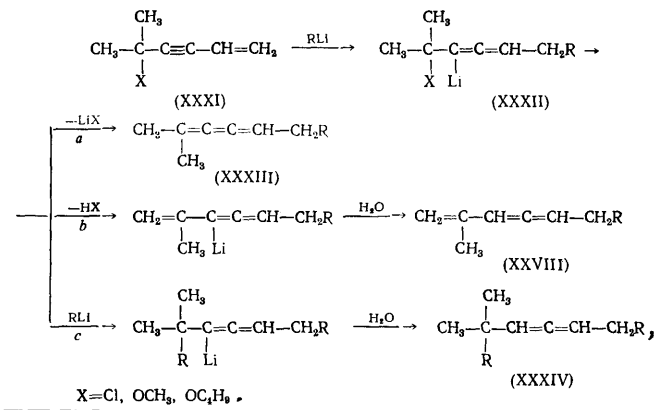
Diethylcalcium[24] and diethylbarium[25] add similarly to the above dienynes. Demetallation of the adducts formed gives conjugated enallenes in 25–30% yield. On the other

hand, the use of organolithium reagents in the reaction with dienynes (the method of Petrov and Kormer[15-19]) makes it possible to obtain conjugated enallenes in 70–80% yield.

However, there are certain limitations imposed by the very nature of the method, which makes it possible to synthesise only disubstituted enallenic hydrocarbons in which the number of carbon atoms in the chain is not less than eight‡.

(b) The Interaction of Organolithium Compounds with Tertiary Enynyl Halides and Ethers

On treatment with alkyl-lithium, tertiary ethers and chlorides having the general formula (XXXI) give rise to conjugated enallenic hydrocarbons (XXVIII) together with cumulenes and allenes[19,26]:



X=Cl, OCH_3, OC_4H_9.

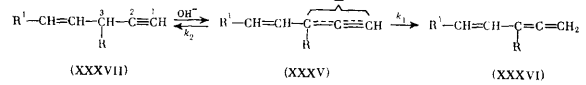
The first stage of the process consists of the 1,4-addition of the alkyl-lithium to the conjugated enyne system of compound (XXXI) with formation of the lithioallene (XXXII). The subsequent reaction of the latter leads to the formation of hydrocarbons (XXXIII) (pathway *a*), (XXVIII) (pathway *b*), or (XXXIV) (pathway *c*). The dependence of the yield of the conjugated enallene (XXVIII) on various factors has been demonstrated in relation to the interaction of the enyne ether (XXXI, X = OCH_3) with organolithium reagents. The most important of these are as follows: solvent polarity, the nature of the alkyl group in the alkyl-lithium, and reaction temperature. It has been shown that a high polarity of the medium leads to the preferential formation of the enallene (XXVIII), because it promotes a greater ease of the dissociation of the C–O bond in the ether. Thus the above ether interacts with n-butyl-lithium in THF at −60°C to form the enallenic hydrocarbon (XXVIII) with a small admixture of the cumulene (XXXIII), while in isopentane the cumulene is the exclusive product. The formation of the cumulene (XXXIII) is fully suppressed on raising the temperature to 0–30°C. In this case the reaction products are the enallene (XXVIII) (in 60% yield) and the hydrocarbon (XXXIV). Higher yields of compound (XXVIII) when the reaction is carried out in ether at −60°C are achieved by using an alkyl-lithium containing secondary or tertiary and not primary alkyl groups.

The influence of the C–O bond strength on the yield of the enallene (XXVIII) in the reactions of tertiary enynyl ethers with alkyl-lithium was discovered on comparing the products of the interaction of n-butyl-lithium with methoxy- and butoxy-derivatives of the hexenyne (XXXI, X = OCH_3 or OC_4H_9). As a result of the greater strength of the C–O bond in the latter ether, the reaction involving the elimination of lithium butoxide in the intramolecular conversion of the adduct (XXXII) predominates over the elimination of butyl alcohol. This is accompanied by the preferential formation of the cumulene (XXXIII). The reaction of the chloride (XXXI, X = Cl) with ethyl-lithium and n-butyl-lithium (in ether, between −30° and −40°C) leads to a mixture of the enallene (XXVIII) in 10–15% yield and the cumulene (XXXIII) in 20–30% yield.

‡ Methyl-lithium does not add to conjugated dienynes[19].

3. THE PROTOTROPIC REARRANGEMENT OF NON-CONJUGATED ENYNE HYDROCARBON (ALK-1-EN-4-YNES)

Bertrand and coworkers developed a preparative method for the synthesis of conjugated enallenic hydrocarbons by the prototropic rearrangement of alk-1-en-4-ynes[12,27,28]. The rearrangement is catalysed by a base, which attacks the active methylene group of the enyne with formation of the ambident carbanion (XXXV). The stabilisation of the latter by the addition of a proton to the $C_{(1)}$ or $C_{(3)}$ atom leads to the enallene (XXXVI) or to the initial enyne (XXXVII) respectively:



(XXXVII) (XXXV) (XXXVI)

(a) R=R¹=H; (b) R=H, R¹=CH_3; (c) R=H, R¹= iso-C_3H_7;
(d) R=CH_3, R¹=H; (e) R=CH_3, R¹=CH_3; (f) R=H, R¹=C_2H_5;
(g) R=n-C_3H_7, R¹ = H.

The proposed mechanism of the rearrangement[28] has been fully confirmed[29-31] in a study of the kinetics and in the determination of the thermodynamic parameters of the process involving enyne hydrocarbons (XXXVII, a–e) substituted in different ways. It has been established that the rate of conversion of the carbanion (XXXV) into the enallene (XXXVI) is many times higher than the rate of its conversion into the initial enyne (XXXVII), i.e. $k_1 \gg k_2$. The application of ultraviolet spectroscopy in combination with gas–liquid chromatography (GLC) made it possible to follow the content in the reaction mixture of both the initial enyne and the enallene formed and to establish that the rate of this reaction may be described by the second-order equation

$$v = k\,[OH^-][\text{alk-1-en-4-yne}].$$

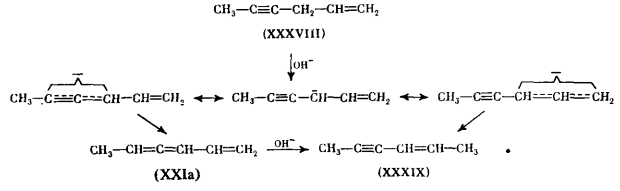
In conformity with the proposed mechanism, the activation energy $E^{\neq}$ and activation enthalpy $\Delta H^{\neq}$ of the isomerisation of the enynes (XXXVIId) and (XXXVIIe), containing the alkyl substituent at the $C_{(3)}$ atom, are much higher than for compound (XXXVII, a–c).

In all the cases investigated the activation entropy $\Delta S^{\neq}$ is negative owing to the restriction in the transition state of free rotation about the $C_{(2)}$–$C_{(3)}$ bond due to the change in the hybridisation of the $C_{(3)}$ atom. The latter promotes a certain degree of separation of the substituents at $C_{(3)}$ owing to the increase of the valence angle resulting in higher values of $\Delta S^{\neq}$ for the isomerisation of the enynes (XXXVIId) and (XXXVIIe) compared with the hydrocarbon unsubstituted at $C_{(3)}$ [$\Delta S^{\neq}$ = −5.1 e.u. for the reaction (XXXVIId) → (XXXVId) and −45.6 e.u. for (XXXVIIa) → (XXXVIa)]. The transition of the $C_{(3)}$ atom from the sp^3

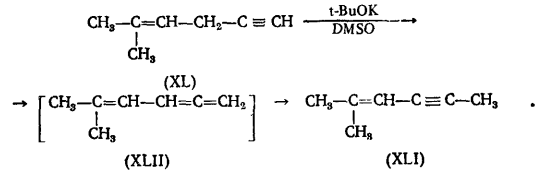
to the sp^2 state on formation of the carbanion (XXXV) greatly reduces the steric interaction of the methyl and ethynyl groups of the *cis*-isomer of the enyne (XXXVIIb), as a result of which the rate of isomerisation of the latter to the enallenic hydrocarbon exceeds by a factor of 3 the rate of isomerisation of the *trans*-isomer ($\Delta S^{\neq}_{cis} > \Delta S^{\neq}_{trans}$).

The intermediate formation of the carbonion (XXXV) explains the stereospecificity of the prototropic rearrangement of alk-1-en-4-ynes in the course of which the configuration of the double bond is maintained. It has been established for a large number of compounds that the above rearrangement takes place smoothly when alk-1-en-4-ynes are refluxed for 3–4 h with a 5% methanolic solution of NaOH, which results in the formation of enallenes with a high degree of purity[27,30].

In contrast to this, the prototropic rearrangement of hex-1-en-4-yne (XXXVIII), carried out under the same conditions, leads to the formation of a mixture of the enallene (XXIa) and the conjugated enyne (XXXIX), the latter being the main reaction product[32]. At 112°C the hydrocarbon (XXXVIII) is converted quantitatively into the enyne (XXXIX). The study of the time course of this process showed that in this case too the reaction takes place with participation of the enallene (XXIa), which isomerises rapidly at the given temperature to the enyne (XXXIX). It has been shown that the enallene is not a necessary precursor of the latter and that direct isomerisation of the initial hexenyne into the enyne (XXXIX) also occurs. Thus the reaction takes place as a parallel-consecutive process in conformity with the mechanism

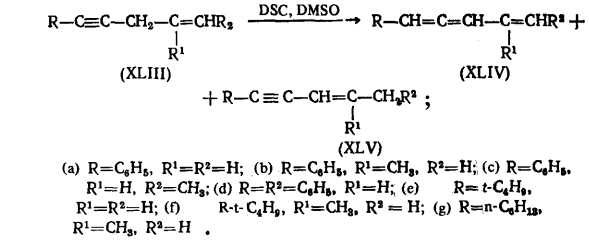


When 2-methylhex-2-en-5-yne (XL) was treated with t-BuOK in dimethyl sulphoxide (DMSO), the conjugated enyne (XLI) was the only product[33]. It has been suggested[33] that the intermediate enallene (XLII) is converted under the experimental conditions into the enyne (XLI) via the classical mechanism of the Favorskii allene–acetylene rearrangement:

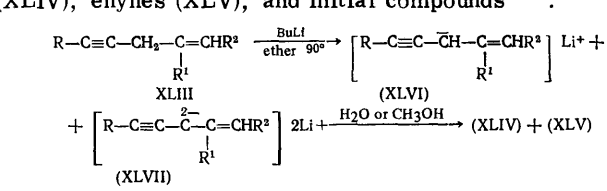


The unstable enallene (XLII) can be obtained[33] by carrying out the reaction under the conditions proposed by Bertrand.

The instantaneous isomerisation of alk-1-en-4-ynes (XLIII) in DMSO, catalysed by the dimethylsulphenyl carbanion (DSC), has been investigated[34] and it has been established that the conjugated enallenes (XLIV) can be obtained only when alk-1-en-4-ynes containing a symmetrically substituted double bond, as in compounds (XLIII, c, d), are used. The conjugated enynes (XLV) are obtained by the isomerisation of the enynes (XLIII, a, b, e, f, g) with a terminal C=C bond under the same conditions, as a result of the subsequent prototropic transformation of the enallenes formed:



Klein and Brenner described[34-36] the metallation of alk-1-en-4-ynes (XLIII) with butyl-lithium in ether at −90°C, leading to the intermediate formation of the mono- and di-lithio-derivatives (XLVI) and (XLVII). Protonation of the latter leads to a mixture of conjugated enallenes (XLIV), enynes (XLV), and initial compounds[34,35]:

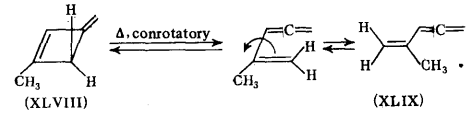


The composition of the reaction mixture depends on the reaction conditions and also on which lithio-derivative, (XLVI) or (XLVII), is protonated[35].

4. PERICYCLIC REACTIONS

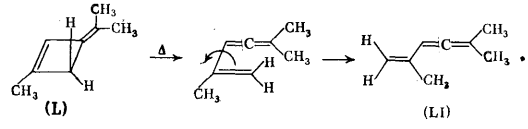
(a) Electrocyclic Transformation of Methylenecyclobutenes

The thermal conversion of methylenecyclobutenes into enallenes is analogous to the electrocyclic conversion of cyclobutenes into butadienes[37]. The opening of the ring of methylenecyclobutenes, which has a 4π-electron system, under thermally controlled conditions is conrotatory[38] and leads to the formation of enallenic hydrocarbons. For example, the pyrolysis (at 350–400°C) of 1-methyl-3-methylenecyclobutene (XLVIII) yielded 2-methylpenta-1,3,4-triene (XLIX):[39]



The process is reversible; the equilibrium reaction mixture contains ~51% of the enallene (XLIX) and ~49% of the methylenecyclobutene (XLVIII). It has been noted that[39] the latter is thermally more stable than alkylcyclobutenes as a result of the stabilising influence of the exocyclic C=C bond.

3-Isopropylidene-1-methylcyclobutene (L) is similarly converted into 2,5-dimethylhexa-1,3,4-triene (LI):[40]

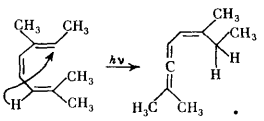


Data indicating the reversibility of this process are lacking; it was carried out by injecting compound (L) into the evaporator of the chromatograph (at 340°C) and trapping the reaction product (yield 45–55%) in a cooled trap.

Since methylenecyclobutenes are not readily available, this method of synthesis of conjugated enallenic hydrocarbons cannot be regarded as preparative.

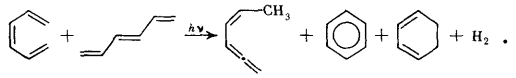
(b) The Sigmatropic Rearrangement of Conjugated Trienes

Conjugated enallenes are formed as a result of the photochemical sigmatropic rearrangement of conjugated trienes. This reaction includes a [1,5]-shift of hydrogen, which is symmetry-allowed as an antarafacial displacement[41]. According to Crowly's data[42,43], the photolysis of allo-ocimene (LII) gives a 37% yield of the unstable enallene (LIII):



(LII) (LIII)

The enallene (IX), cyclohexa-1,3-diene (LV), benzene, and hydrogen have been obtained as the main reaction products by the vapour-phase photolysis of a mixture of the geometrical isomers of hexa-1,3,5-triene (LIV):[44]



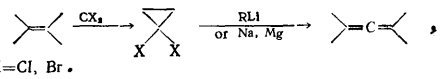
(LIV) (IX) (LV)

Similar products are obtained in the photolysis of cyclohexa-1,3-diene (LV).[45,46] The enallene (IX) was obtained in this instance as a result of the electrocyclic conversion of the cyclohexadiene (LV) into the conjugated triene (LIV)[47] and the [1,5]-sigmatropic rearrangement of the latter.

The isomerisation of conjugated trienes to conjugated enallenes is of considerable interest, since it may be responsible for the biogenic synthesis of natural enallenes[42].

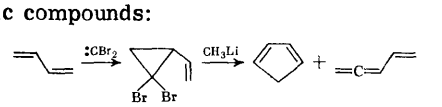
5. DEHALOGENATION OF *GEM*-DIHALOGENOCYCLOPROPANES

The dehalogenation by organolithium reagents[48-52] or active metals[53,54] of *gem*-dihalogenocyclopropanes, obtained by the addition of dihalogenocarbenes to olefins, is one of the best methods of synthesising allenes:

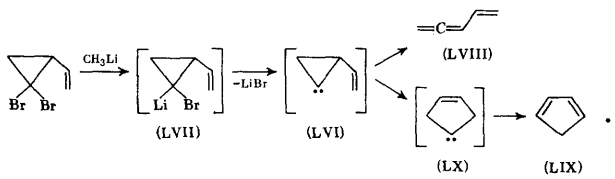


X=Cl, Br.

It might have been expected that conjugated enallenic hydrocarbons can also be synthesised from conjugated dienes by the above procedure. However, Skatteboel showed[55,56] that, when *gem*-dibromovinylcyclopropanes are treated with methyllithium, cyclopentadienes are formed in 70–90% yield together with only small amounts of enallenic compounds:



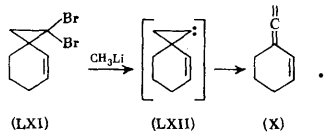
This anomalous course of the reaction can be tentatively[55] regarded as a result of reactions of cyclopropylidene [the carbene§ (LVI)], generated when lithium bromide is eliminated from the intermediate (LVII). Two products of the above reaction—the enallene (LVIII) and the cyclopentadiene (LIX)—correspond to two different pathways in the transformation of the above carbene. On the one hand, it has been firmly established[48,51,59] that cyclopropylidene can be converted directly into allene as a result of ring opening. On the other hand, there is a possibility of an intramolecular interaction of the carbene with the double bond, leading to a new carbene (LX). The latter is stabilised by forming the cyclopentadiene (LIX):



(LVII) (LVI) (LVIII) (LX) (LIX)

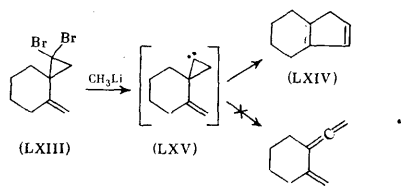
It has been shown[60] that the preferential formation of an enallene or cyclopentadiene in the above reaction depends on the strain energy in the system formed and the stereochemistry of the intermediate cyclopropylidene. The *s-cis*-conformation of the latter promotes its intramolecular interaction with the double bond and hence the formation of the cyclopentadiene. The *s-trans*-conformation of cyclopropylidene (LVI) favours the direct opening of the three-membered ring with formation of the enallene.

The foregoing findings have been confirmed by the synthesis of the enallene (X), without an admixture of a cyclopentadiene derivative, from the dibromo-compound (LXI), which is an isomer with a rigidly fixed *s-trans*-structure and which gives rise to the intermediate cyclopropylidene (LXII) having the same conformation:



(LXI) (LXII) (X)

It has also been established that the dibromo-compound (LXIII) gives rise exclusively to the cyclopentadiene (LXIV) under the above conditions, which is promoted by the *s-cis*-conformation of the intermediate cyclopropylidene (LXV):



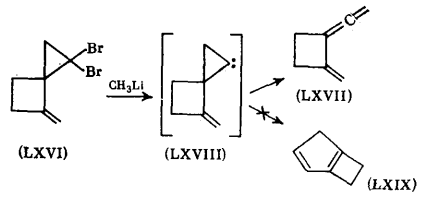
(LXIII) (LXV) (LXIV)

From this point of view, the formation of a mixture of enallenes and cyclopentadienes has been explained logically[55] by the fact that the initial *gem*-dibromovinylcyclopropanes were mixtures of the *s-cis*- and *s-trans*-conformers.

The adduct of the carbene CBr_2 and 1,2-dimethylenecyclobutane (LXVI) reacts with CH_3Li to form exclusively the enallene (LXVII), despite the fact that this compound

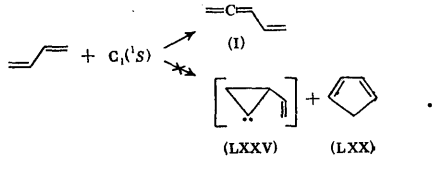
§ It has been suggested[57,58] that the cyclopropylidene obtained under these conditions is not a free carbene, but forms part of a carbene–lithium halide complex.

and the cyclopropylidene (LXVIII) are *s-cis*-conformers[60]:



The formation of the cyclopentadiene derivative (LXIX) is prevented in this case by the high strain energy of the system.

The data of Skell and Engel[61] are of theoretical interest in connection with the problem of the intermediate formation of cyclopropylidene as the precursor of enallene. It has been established that the reaction of buta-1,3-diene with a carbon atom in the metastable ^1S energy state in a neopentane matrix gives rise to penta-1,2,4-triene (I) only. The cyclopentadiene (LXX) is absent from the reaction mixture:



It follows from calculations[62] by the MINDO/2 method that the activation energy for the opening of the cyclopropylidene (LXXI) ring to give the allene (LXXII) is much higher than the activation energy for the formation of strained systems such as spiropentane (LXXIII) and cyclopropene (LXXIV):

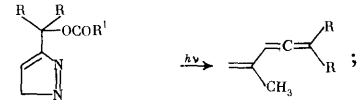


The ring strain energy in cyclopentadiene (LXX) is less than the strain energies in the above system, as a result of which its formation from the postulated intermediate cyclopropylidene (LXXV) apparently requires a smaller activation energy than the formation of enallene (I).

The fact that cyclopentadiene (LXX) is not formed in the reaction under consideration rules out, in our view, the possibility of the formation of enallene (I) from the cyclopropylidene (LXXV)¶.

6. SPECIFIC METHODS OF SYNTHESIS

Penta-1,2,4-triene is formed on dehydrobromination of 1,4-dibromopent-2-ene[63]. The latter is a readily available product of the bromination of piperylene. The mixture formed on dehydrobromination of the hydrocarbon contains 12.3% of enallene. 2,5-Dimethylhexa-1,3,4-triene has been obtained by a prototropic rearrangement from 2,5-dimethylhexa-2,3,4-triene under the influence of sodium methoxide or hydride[64]. It has been established[65] that the reaction mixture formed on solvolysis of 1-chloromethylene-2,2-dimethylcyclopropane contains 9% of 2-methylpenta-1,3,4-triene. 2,5-Dimethylhexa-1,3,4-triene (LXXVI) and 5-ethyl-2-methylhepta-1,3,4-triene (LXXVII) are obtained in 5% yield on photolysis of the pyrazolenine derivatives (LXXVIII, a, b) and (LXXIX) respectively[66]:

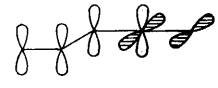


(LXXVIII): (a) $R = R^1 = CH_3$, (b) $R = CH_3$, $R^1 = C_2H_5$; (LXXVI): $R = CH_3$; (LXXVII): $R = C_2H_5$

(LXXIX): $R = C_2H_5$, $R^1 = CH_3$.

III. PHYSICAL PROPERTIES

The characteristics of the physical properties of the conjugated enallenic hydrocarbons are due to two factors: the cumulation of bonds and conjugation. According to the molecular orbital theory, the planes of two cumulated bonds are mutually perpendicular and the central carbon atom of the allene group, which is in the sp-hybridised state, is located on the same straight line with the extreme sp^2-hybridised carbon atoms in this group. Owing to the non-coplanarity of the cumulated bonds, only one of them can be involved in $\pi-\pi$ conjugation with the α-ethylenic bond of enallene:



The conjugation† of the double bonds in enallenic hydrocarbons is manifested most clearly by the considerable increase of molecular refraction, by the increased magneto-optical molecular rotation, and by the intense absorption in the ultraviolet spectrum, characteristic of conjugated dienes.

1. MOLECULAR REFRACTION

Among all the allenic compounds without an additional double bond in the molecule, only disubstituted allenes with strongly branched groups exhibit a significant exaltation of molecular refraction (ΔMR).[68] It has been suggested[67] that the latter is due to the $\sigma-\pi$ conjugation of the substituents with the coplanar double bond of the allene group and does not exceed unity as a rule. The occurrence of $\pi-\pi$ conjugation in enallene molecules is responsible for the higher values of ΔMR of these compounds, which reach 2.5 in individual instances (Table 5).

2. MAGNETO-OPTICAL MOLECULAR ROTATION

According to Labarre's data[69,70], the experimental magneto-optical molecular rotations (MOMR) of conjugated enallenic compounds greatly exceed the calculated values. Unfortunately penta-1,2,4-triene is the only enallene whose properties have been investigated. Other data quoted in the above reports refer to conjugated enallenic alcohols. However, since the OH group does not influence the magneto-optical properties of these compounds significantly,

¶ We have in mind "free" cyclopropylidene generated in the absence of Lewis bases.

† The specific influence of the cumulation of bonds on the physical properties of allenes has been described in an extensive review[67].

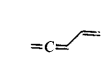
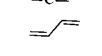
one may assume that the MOMR exaltation is due to the conjugated enallene group and amounts to ~110 μrad, as can be seen from the data in Table 3.

Table 3. The magneto-optical properties of enallene structures.

Compound	A^*, μrad	B^*, μrad	$E^*=A-B$, μrad
$CH_2=CH-CH=C=CH_2$	664	559	+105
$C_2H_5CH(OH)-CH=C=CH-CH=CH-CH_3$	965	854	+111
$C_2H_5C(OH)(CH_3)-CH=C=CH-CH=CH_2$	985	882	+103
$CH_3-C(OH)(CH_3)-CH=C=CH-CH=CH_2$	935	816	+119

*A is the experimental MOMR, B the calculated MOMR, and E the exaltation of MOMR.

Table 4. The magneto-optical properties of certain conjugated systems.

Conjugated system	E_{av}, μrad	Designation	Conjugated system	E_{av}, μrad	Designation
	+110	E_1		+63	E_3
	+119	E_2		+211	E_4

Labarre[70] also quotes the MOMR exaltations for certain other conjugated systems, which makes it possible to compare them with the values of E found for conjugated enallenes (Table 4). It also follows from the data in Table 4 that E_1 is close to E_2, but differs sharply from E_4. This finding constitutes additional confirmation of the fact that only one C=C bond in the cumulated system of enallene is involved in conjugation. The MOMR exaltation can also serve as a criterion whereby one can distinguish the conjugated enallene system from the conjugated triene and enyne system.

3. ULTRAVIOLET, INFRARED, AND ^{1}H NMR SPECTRA

Ultraviolet Spectra

The ultraviolet absorption spectra are widely used to investigate conjugated enallenic hydrocarbons. As expected, the conjugated enallene group behaves as a chromophore similarly to the conjugated diene system, exhibiting an intense absorption in the range 215–230 nm ($\epsilon \simeq 20\,000$) depending on the nature and number of substituents (Table 5). The absorption is due to a $\pi-\pi^*$ electronic transition.

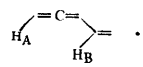
Infrared Spectra

Because of the presence of characteristic intense absorption bands in the infrared, conjugated enallenic hydrocarbons can be reliably identified or detected in a mixture of unsaturated hydrocarbons by infrared spectroscopy. The infrared spectra of these compounds contain absorption bands characteristic of the allene group[71–73] and a conjugated double bond. The bands associated with the allene group include one in the range 1930–1950 cm^{-1} due to the assymetric stretching vibrations of the $-C=C=C-$ system, a band in the region of 850 cm^{-1} due to the out-of-plane deformation vibrations of the C–H bonds of the terminal $C=C=C\langle^{H}_{H}$ group (overtone at ~1700 cm^{-1}), and absorption at 875 cm^{-1} due to the analogous vibrations of the C–H bonds of the symmetrically disubstituted allene group. The last band is frequently not resolved or appears as a shoulder on the much more intense band close to it and due to the deformation vibrations of the C–H bond of the terminal α-ethylene group. On the other hand, the absorption band at 850 cm^{-1} is of great analytical value and its presence in the spectrum confirms reliably the presence of a terminal allene group in the enallene molecule.

The stretching and deformation vibration frequencies of the α-ethylenic bond in conjugated enallenes are the same as the corresponding vibration frequencies of the conjugated C=C bond in diene hydrocarbons. As an example, one may quote the characteristic positions in the spectrum in the range 1600–1640 cm^{-1} of the band due to the stretching vibrations of the α-ethylenic bond in enallenes[16,19].

Proton Magnetic Resonance Spectra

The ^{1}H NMR spectra of conjugated enallenes are complex and their interpretation is frequently difficult. It has been established[74] that the protons of the allene group located in the positive part of the anisotropy cone are subjected to a positive shielding effect and because of this their signals appear in a stronger field compared with the signals of olefinic protons. Among all the protons of the allene group, the H_A protons, attached to the atoms involved in the double bond of this group, which is non-coplanar with the α-ethylenic bond of the enallene (δ_{H_A} = 4.8 p.p.m.), absorb in the strongest field. The signal in the weakest field (δ_{H_B} = 5.9–6.3 p.p.m.) corresponds to the H_B proton[27]:



A characteristic feature of enallenic hydrocarbons and of all allenes is the occurrence of a strong proton–proton interaction via the allene system, which can be accounted for by the interaction of the σ electrons of the C–H bond and the π electrons of the double bond, which are in the same plane[67].

The physical properties of conjugated enallenic hydrocarbons are compiled in Table 5.

Table 5. Conjugated enallenic hydrocarbons.

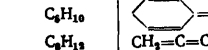
Overall formula	Hydrocarbon*	B.p., °C (pressure, mmHg)	n_D (t, °C)	d_4 (t, °C)	ΔMR_D	Ultraviolet absorption		Method of synthesis**	References
						λ_{max}, nm	ϵ_{max}		
C_6H_8	$CH_2=C=CH-CH=CH_2$	48.0—48.5 (760)	1.4685 (25)	0.7133 (25)	1.85	225	13 100	3	27,12,28
	ditto	49	1.4719 (19)	0.7174 (19)	—	—	—	(1*b*)	11
	»	47.5—48.0	1.4750 (18)	—	—	216.5	15 600	1*a*, 5, (6)***	3,6,55, (63)
C_6H_8	$CH_3-C=CH-CH=CH-CH_3$	80 (760)	1.4790 (25)	0.749 (25)	1.80	228	18 000	3, 1*a*, (4*b*)	27,12,28, 5, (6,44—46)
C_6H_8	$CH_3-CH=C=CH-CH=CH_2$	84—85 (775)	1.4861 (20)	0.7449 (20)	2.37	214	22 050	3, (1*a*,*b*,*c*)	32, (6,14)
C_6H_8	$CH_2=C=C(CH_3)-CH=CH_2$	71 (760)	1.4780 (20)	0.725 (20)	—	226	11 500	3, 1*a*, (5)	27,5, (6,55)
C_6H_8	$CH_2=C=CH-C(CH_3)=CH_2$	—	—	—	—	220	17 380	4*a*, (6)	39, (65)
C_7H_{10}	$CH_2=C=C(CH_3)-CH=CH-CH_3$	62 (260)	1.4925 (20)	0.768 (20)	—	228	17 500	3	27
C_7H_{10}	$CH_2=C=CH-CH=C(CH_3)-CH_3$	55 (60)	1.4997 (22)	—	—	230.5	25 700	3	33
C_7H_{10}	$CH_3-CH=C=CH-CH=CH-CH_3$	—	1.4922 (25)	—	—	219	25 400	5, (1*b*)	55, (6,7)
C_7H_{10}	$CH_2=C=CH-CH=CH-C_2H_5$	56.0—57.5 (98)	1.4800 (24)	0.764 (24)	1.85	227	20 000	3	27,12,28
C_8H_{10}		—	—	—	—	227	7 350	5, (1*a*)	60, (5,6)
C_8H_{12}	$CH_3-C=CH-CH=CH-$ iso-C_3H_7	—	1.4786 (20)	0.767 (20)	—	—	—	3	27
C_8H_{12}	$CH_2=C=C(n\text{-}C_3H_7)-CH=CH_2$	56 (180)	1.4765 (20)	0.759 (20)	—	230	23 000	3	27
C_8H_{12}	n-C_3H_7-$CH=C=CH-CH=CH_2$	37—38 (20)	1.4742 (20)	0.7685 (20)	1.83	—	—	2*a*	15,21,24
	ditto	37—38 (20)	1.4773 (20)	0.7688 (20)	—	—	—	2*a*	25
C_8H_{12}	$CH_3-C(CH_3)=C=CH-CH=CH_2$	—	1.4857 (20)	0.773 (20)	2.22	—	—	1*b*	10
C_8H_{12}	$CH_3-C(CH_3)=C=CH-C(CH_3)=CH_2$	46 (45)	1.4808 (18)	—	—	219	11 700	6	66
	ditto	—	1.4617 (25)	—	—	218	22 000	4*a*	40
	»	—	1.4765 (24)	—	—	220	24 000	5, (6)	55, (64)
C_9H_{14}	n-C_3H_7-$CH=C=CH-C(CH_3)=CH_2$	54—55 (20)	1.4790 (20)	0.7775 (20)	2.21	—	—	2*a*, (2*b*)	16,22,24, 25, (26)
C_9H_{14}	n-C_3H_7-$CH=C=CH-CH=CH-CH_3$	62 (20)	1.4856 (20)	0.7826 (20)	2.44	—	—	2*a*	17,23—25
C_9H_{14}	n-C_4H_9-$CH=C=CH-CH=CH_2$	56 (20)	1.4742 (20)	0.7755 (20)	—	—	—	2*a*, (1*c*)	21, (14)
C_9H_{14}	$CH_3-C(CH_3)=C=CH-CH=CH_2$	42—44 (20)	1.4825 (20)	0.8021 (20)	—	—	—	1b	9,8
$C_{10}H_{16}$	n-C_5H_{11}-$CH=C=CH-CH=CH_2$	75—76 (20)	1.4742 (20)	0.7815 (20)	2.03	—	—	2*a*	15,21
$C_{10}H_{16}$	n-C_4H_9-$CH=C=CH-CH=CH-CH_3$	79—80 (20)	1.4837 (20)	0.7869 (20)	—	—	—	2*a*	23
$C_{10}H_{16}$	iso-C_4H_9-CH_2-$CH=C=CH-CH=CH_2$	70.0—70.5 (20)	1.4690 (20)	0.7787 (20)	1.74	—	—	2*a*	15,21
$C_{10}H_{16}$	n-C_4H_9-$CH=C=CH-C(CH_3)=CH_2$	71—72 (20)	1.4790 (20)	0.7834 (20)	2.33	—	—	2*a*	16,22
$C_{10}H_{16}$	$C_2H_5-C(CH_3)=CH-CH=C=C(CH_3)-CH_3$	23.8—24.1 (0.45)	1.4989 (25)	—	—	225	24 600	4*b*	42,43
$C_{10}H_{16}$	$C_2H_5-C(CH_3)=C=CH-C(CH_3)=CH_2$	50—52 (11)	1.4819 (18)	—	—	220	15 900	6	66
$C_{10}H_{16}$	iso-C_3H_7-CH_2-$CH=C=CH-C(CH_3)=CH_2$	67.5—68.5 (20)	1.4750 (20)	0.7793 (20)	2.24	—	—	2*a*	16
$C_{10}H_{16}$	$CH_3-C(CH_3)=C=C(n\text{-}C_3H_7)-CH=CH_2$	56—58 (20)	1.4790 (20)	0.7794 (20)	—	—	—	1*b*	9
$C_{10}H_{16}$	$CH_3-C(CH_3)=C=C(iso\text{-}C_3H_7)-CH=CH_2$	42—43 (10)	1.4830 (20)	0.7633 (20)	—	—	—	1*b*	9
$C_{11}H_{18}$	n-C_6H_{13}-$CH=C=CH-CH=CH_2$	91—92 (20)	1.4738 (20)	0.7841 (20)	2.23	—	—	2*a*	15,21
$C_{11}H_{18}$	n-C_5H_{11}-$CH=C=CH-CH=CH-CH_3$	95—96 (20)	1.4818 (20)	0.7912 (20)	2.52	—	—	2*a*	17,23
$C_{11}H_{18}$	n-C_5H_{11}-$CH=C=CH-C(CH_3)=CH_2$	89.5—90.5 (20)	1.4795 (20)	0.7898 (20)	2.40	—	—	2*a*, (2*b*)	16,22, (26)
$C_{11}H_{18}$	t-C_4H_9-CH_2-$CH=C=CH-C(CH_3)=CH_2$	76.5—77.5 (20)	1.4719 (20)	0.7852 (20)	2.52	—	—	2*a*	16
$C_{11}H_{18}$	iso-C_4H_9-CH_2-$CH=C=CH-C(CH_3)=CH_2$	83.0—83.5 (20)	1.4762 (20)	0.7853 (20)	2.39	—	—	2*a*	16,22
$C_{11}H_{18}$	$CH_3-C(CH_3)=C=C(n\text{-}C_4H_9)-CH=CH_2$	66—68 (12)	1.4770 (20)	0.8181 (20)	—	—	—	1*b*	9
$C_{11}H_{18}$	$CH_3-C(CH_3)=C=C(C_4H_9\text{-}iso)-CH=CH_2$	57—58 (10)	1.4870 (20)	0.7950 (20)	—	—	—	1*b*	9
$C_{12}H_{20}$	n-C_3H_7-$CH=C=CH-C(t\text{-}C_4H_9)=CH_2$	77—78 (10)	1.4690 (20)	0.7950 (20)	0.82	—	—	2*a*	18
$C_{12}H_{20}$	n-C_6H_{13}-$CH=C=CH-C(CH_3)=CH_2$	78 (5)	1.4798 (20)	0.7960 (20)	—	—	—	2*a*	22

Table 5 (contd.)

Overall formula	Hydrocarbon*	B.p., °C (pressure, mmHg)	n_D (t, °C)	d_4 (t, °C)	ΔMR_D	Ultraviolet absorption		Method of synthesis**	References
						λ_{max}, nm	ϵ_{max}		
$C_{13}H_{14}$	$C_6H_5-CH_2-CH=C=CH-C(CH_3)=CH_2$	50—51 (0.05)	1.5615 (20)	0.9401 (20)	1.47	—	—	2a	20,22
$C_{14}H_{16}$	m-$CH_3-C_6H_4-CH_2-CH=C=CH-C(CH_3)=CH_2$	64—65 (0.06)	1.5530 (20)	0.9796 (20)	—	—	—	2a	20,22
$C_{14}H_{16}$	o-$CH_3-C_6H_4-CH_2-CH=C=CH-C(CH_3)=CH_2$	63—64 (0.06)	1.5575 (20)	0.9894 (20)	—	—	—	2a	20
$C_{14}H_{24}$	n-$C_6H_{11}-CH=C=CH-C(t\text{-}C_4H_9)=CH_2$	104.5—106.0 (10)	1.4690 (20)	0.8032 (20)	1.12	—	—	2a	18
$C_{17}H_{16}$	α-naphthyl$-CH_2-CH=C=CH-C(CH_3)=CH_2$	123—124	1.6150	1.0060	—	—	—	2a	20

*The following enallenes have been characterised solely by spectroscopic methods: 1-methylene-2-vinylidenecyclobutane[60]; 3,4-dimethylpenta-1,2,4-triene[5,6,55]; 3-methylhexa-1,3,4-triene[6,7]; 5-methylhexa-1,3,4-triene[6]; 2,3-dimethylhexa-1,3,4-triene[6,7]; 6,6-dimethylhepta-1,3,4-triene[34]; 4,5-dimethylhepta-2,3,5-triene[6,7]; 2,6,6-trimethylhepta-1,3,4-triene[34]; 1-phenylpenta-1,2,4-triene[34]; 1-ethylidene-2-propenylidenecyclohexane[6,7]; 2-cyclohexenylpenta-2,3-diene[6,7]; 4-methyl-1-phenylpenta-1,2,4-triene[34]; 1-phenylhexa-1,2,4-triene[34]; 3-ethyl-5-methylnona-1,3,4-triene[8]; 5-methyl-3-phenylhexa-1,3,4-triene[8]; trideca-1,3,4-triene[14]; 3,5-diethylnona-1,3,4-triene[8]; 1,5-diphenylpenta-1,2,4-triene[34].

**The designations of the methods of synthesis correspond to those in Section II.

***The references to studies (and to the methods of synthesis employed in them) in which the physical constants of the given enallene are not quoted are enclosed in brackets.

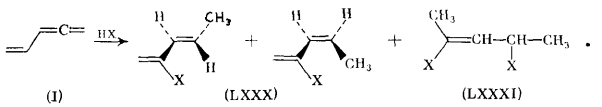
IV. CHEMICAL PROPERTIES

1. ELECTROPHILIC ADDITION

(a) The Addition of Hydrogen Halides[30,75]

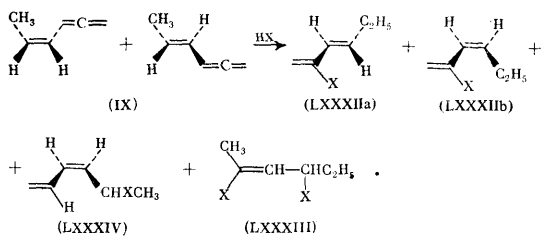
When enallene (I) was treated with concentrated HCl, a 3 : 2 mixture of a monoadduct and a diadduct was obtained in 60% yield. The monoadduct is a mixture of the *cis*- and *trans*-isomers of 2-chloropenta-1,3-diene (LXXX, X = Cl) with a threefold excess of the latter isomer. Both geometrical isomers have been isolated by preparative GLC and characterised by infrared, ultraviolet, and ^{1}H NMR spectroscopy. The diadduct (LXXXI, X = Cl) has been identified as 2,4-dichloropent-2-ene.

The result of the addition of HBr to this enallene is quite analogous as regards the nature of the products and their proportions in the reaction mixture:



(I) (LXXX) (LXXXI)

When the enallene (IX) is acted upon by concentrated HCl, a mixture of a monoadduct and a diadduct is again formed. The former, which makes up 65% of the product, is the virtually pure *trans*-isomer of 2-chlorohexa-1,3-diene (LXXXII, a; X = Cl). The *cis*-isomer of this compound has not been isolated, because of its low content in the reaction mixture. The diadduct has the structure of 2,4-dichlorohex-2-ene (LXXXIII, X = Cl):



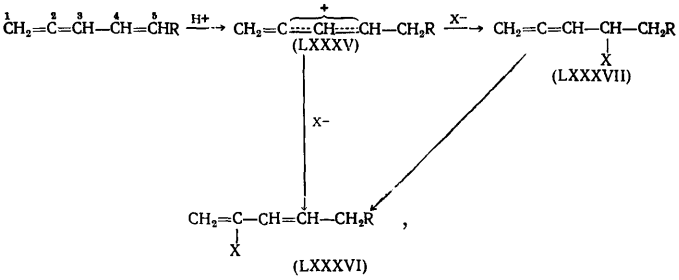
(IX) (LXXXIIa) (LXXXIIb)

(LXXXIV) (LXXXIII)

A more complex mixture of adducts was obtained (in 50% yield) when the enallene (IX) was acted upon by hydrobromic acid. According to GLC data, the mixture consists of five monobromides and two dibromides. Three monobromides were isolated by preparative GLC and one of the dibromides was isolated by fractional distillation; 70% of the mixture of monobromides consists of *trans*- and *cis*-2-bromohexa-1,3-dienes in the proportions (LXXXIIa) : (LXXXIIb) = 17 : 3; here X = Br. The third monobromide, which is 5-bromohexa-1,3-diene (LXXXIV, X = Br), was isolated in only a small amount. The structure of 2,4-dibromohex-2-ene (LXXXIII, X = Br) was assigned to the diadduct.

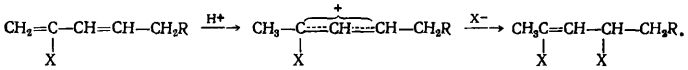
Thus hydrogen halides add to the enallenes (I) and (XIX) in the 1,4-positions in the conjugated ethylene–allene system, and there is also secondary 1,4-addition with formation of diadducts. The reaction mechanism[30,75] consists in the protonation of the $C_{(5)}$ atom of the enallene with formation of the carbonium ion (LXXXV). The latter is attacked by the reagent in the 2- or 4-position, which

leads to the halogeno-derivatives (LXXXVI) and (LXXXVII) respectively:



where R = H or CH_3 and X = Cl or Br.

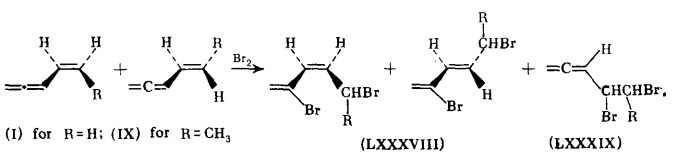
The halogenoallene (LXXXVII) was not detected in the reaction mixture probably owing to the rapid anionotropic rearrangement to the thermodynamically more stable halide (LXXXVI).[75] When a second HX molecule is added, the attack by the proton is directed by the halogen:



The interaction of 3-methylpenta-1,2,4-triene and 3-methylhexa-1,2,4-triene with hydrogen halides has also been investigated[30]. However, owing to the rapid polymerisation of these hydrocarbons and the halogeno-derivatives formed, the nature of the processes occurring has not been established.

(b) The Addition of Bromine[30]

The study of the interaction of bromine with conjugated enallenic hydrocarbons is complicated by the difficulty of separating the products. Thus, when penta-1,2,4-triene (I) was brominated, a mixture of three dibromo-derivatives, which could not be separated by distillation, was obtained in 40% yield. According to spectroscopic data, it contained the *cis*- and *trans*-isomers of 1,4-dibromopenta-2,4-diene (LXXXVIII, R = H) and 1,2-dibromopenta-3,4-diene (LXXXIX, R = H):

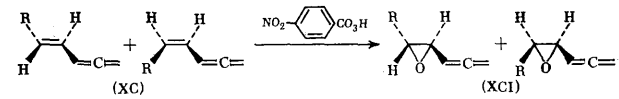


(I) for R=H; (IX) for R=CH_3 (LXXXVIII) (LXXXIX)

The bromination of hexa-1,2,4-triene (IX) also led to a mixture of two dibromo-derivatives (in 30% yield), which could not be separated by distillation. In conformity with spectroscopic data, the structures of the *cis*- and *trans*-isomers of 2,5-dibromohexa-1,3-diene (LXXXVIII, R = CH_3) was attributed to them, the latter being the main product; the 1,2-adduct is not formed in this case.

(c) Epoxidation By Peracids

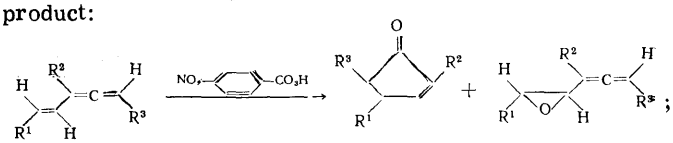
This reaction of conjugated enallenic hydrocarbons was investigated for the first time in relation to the epoxidation of the enallene (XC) by *p*-nitroperbenzoic acid[76]. In all cases the only reaction products are the epoxy-derivatives of α-allenes (XCI), which were not described previously:



(XC) (XCI)

R = H, CH_3, C_2H_5, or n-C_3H_7.

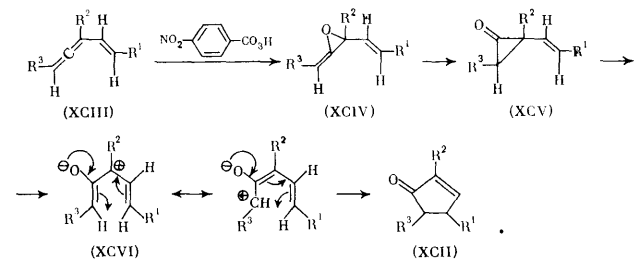
Their geometrical isomers were separated by preparative GLC. It was shown that the ratio of these isomers is determined solely by the ratio of the *cis*- and *trans*-isomers of the initial enallenes, which confirms the stereospecificity of this reaction. It was subsequently established[30,77,78] that the alkylation of the allene group alters the course of the reaction and leads to the formation of the conjugated cyclopentenone (XCII) as the sole or main product:



(XCIII) (XCII) (XCVII)

R^2 or R^3=Alk.

This reaction pathway was explained by the authors as the results of a series of consecutive processes: (1) the epoxidation of the alkylated and therefore fairly nucleophilic allene group of the enallene (XCIII) with formation of the epoxide (XCIV); (2) the tautomeric transformation of the epoxide (XCIV) into the cyclopropanone (XCV); (3) the electrocyclic transformation of the latter into the 1,3-dipole (XCVI) and the subsequent intramolecular 1,3-dipole cycloaddition leading to the formation of the conjugated cyclopentenone (XCII):



(XCIII) (XCIV) (XCV) (XCVI) (XCII)

Table 6 presents the results of the study of the above reaction.

Table 6. The epoxidation of the conjugated enallenes (XCIII) by *p*-nitroperbenzoic acid[30].

Enallene (XCIII)	Content in reaction mixture, %		Overall yield of (XCII) + (XCVIII), %
	(XCVII)	(XCII)	
(a) R^1=R^3=H, R^2=CH_3	0	100	60
(b) R^1=R^3=H, R^2 = n-C_3H_7	0	100	60
(c) R^1=R^2=CH_3, R^3 = H(*trans*)	35	65	60
(d) R^1=R^2=H, R^3 = n-C_3H_7	5	95	55

It is noteworthy that, when both the allene group and the α-ethylenic bond are alkylated in the enallene, they are both acted upon, in competition, by the electrophile, which

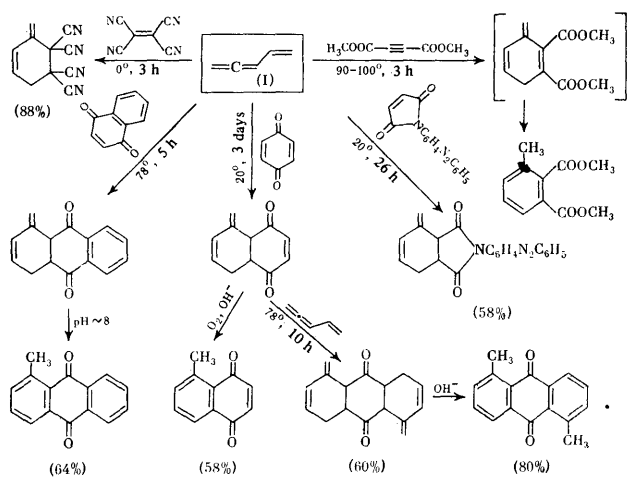
leads to the formation of a mixture of the cyclopentenone (XCII) and the allene epoxide (XCVII). The epoxidation reaction of the enallene (XCIIIc) may serve as an example. It has been shown[30,79] that allene epoxides are valuable starting materials for the synthesis of many hitherto unknown or difficult to obtain compounds such as α- and β-allenic alcohols, vicinal allenic diols, enynyl alcohols, etc. Furthermore, the epoxidation of enallenes by peracids can serve as a method of synthesis of compounds with the hydrindan structure.

2. PERICYCLIC REACTIONS

(a) Thermal Cycloaddition

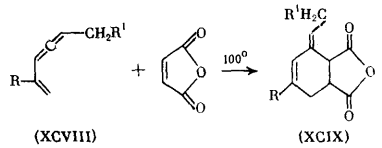
Conjugated enallenes are formally capable of participating in thermal cycloaddition reactions of two types: $[\pi 2 + \pi 2]$ and $[\pi 4 + \pi 2]$. A characteristic feature of compounds with a cumulated system of double bonds is known to be the first of the above transformations, which results in the formation of cyclobutane derivatives[80], while dienes with a conjugated system of bonds are involved preferentially in the $[\pi 4 + \pi 2]$ cycloaddition reaction, which leads to the formation of cyclohexene derivatives. The simultaneous presence in the molecule of the conjugated enallene of cumulated and conjugated diene systems constitutes an interesting problem as regards their competition in the cycloaddition reaction.

The possibility of the involvement of conjugated enallenes in the Diels–Alder reaction, which is a type of $[\pi 2 + \pi 2]$ cycloaddition, was demonstrated for the first time[3] in relation to the reaction of penta-1,2,4-triene (I) with different dienophiles. This hydrocarbon reacts under mild conditions with tetracyanoethylene and derivatives of maleic and acetylenedicarboxylic acids and quinone. The reactions which have been carried out and the products obtained are indicated schematically below:



Many of the adducts indicated in the above scheme are methylenecyclohexene derivatives, which are difficult to obtain in other ways. The ready aromatisation of certain compounds makes enallene (I) a valuable starting material for the synthesis of aromatic compounds which are difficult to obtain.

Fedorova and Petrov[18] investigated the reactions of the enallenes (XCVIII) and maleic anhydride at 100°C. Homologues of the anhydride of 3-alkylidene-4-cyclohexene-1,2-dicarboxylic acid (XCIX) were obtained in all cases:



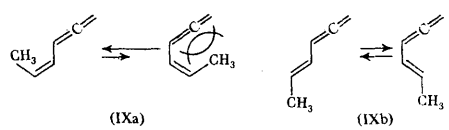
(XCVIII) (XCIX)

(a) R = CH_3, R^1 = C_2H_5; (b) R = CH_3, R^1 = n-C_4H_9;
(c) R = t-C_4H_9, R^1 = C_2H_5;
(d) R = t-C_4H_9, R^1 = n-C_4H_9.

Further condensation does not take place despite the presence in the adduct (XCIX) of a conjugated diene group, which is believed[18] to be due to steric factors.

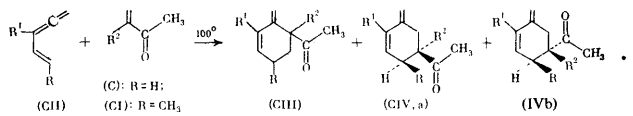
The mechanism of the thermal $[\pi 4 + \pi 2]$ cycloaddition of conjugated enallenes has been determined in a study of their reactions with but-1-en-3-one (C) and 2-methylbut-1-en-3-one (CI).[30,81,82] It has been shown that the reaction proceeds via a concerted cyclic mechanism, which is symmetry-allowed as a $[\pi 4_S + \pi 2_S]$ process, in which all the π orbitals are involved suprafacially. A direct consequence of this mechanism is the requirement of a definite, namely cisoid, conformation of the reacting enallene, so that the addition of the dienophile must be preceded by the conversion of the energetically more favourable transoid conformation of the hydrocarbon into the cisoid conformation.

Such transformation of the *cis*-isomer of hexa-1,2,4-triene (IXa) is difficult for steric reasons and it does not therefore react with the above ketones. Under these conditions, the *trans*-isomer of the enallene (IXb) actively interacts with the ketones:



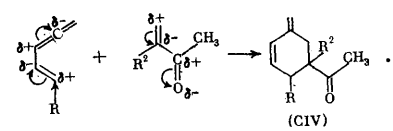
(IXa) (IXb)

The conjugated enallenes (CII) react with $\alpha\beta$-unsaturated ketones as the diene components in accordance with the mechanism



(CII) (C): R = H; (CI): R = CH_3 (CIII) (CIV, a) (IVb)

The experimental data obtained are compiled in Table 7. The structures of the products have been reliably demonstrated by spectroscopic methods (infrared, ^{1}H NMR, and ultraviolet), by mass spectrometry, and by their conversion into the corresponding aromatic compounds in order to determine the position of the acetyl group in the adduct which indicates the relative orientations of the dienophile and enallene in the transition state. This orientation is unambiguous and leads to the exclusive formation of the adduct (CIV) subject to the condition that the terminal $C_{(5)}$ atom of the α-ethylenic bond of the enallene (CII) has an alkyl substituent (i.e. R $\neq$ H):



(CIV)

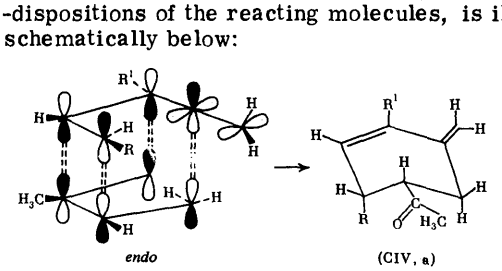
Otherwise a mixture of the adducts (CIII) and (CIV) is formed with the latter greatly predominating. The ratio of the adducts depends little on whether there is an alkyl substituent at the $C_{(3)}$ atom of the hydrocarbon and on whether the C=C bond of the ketone is alkylated, which rules out a zwitter-ionic mechanism of the cycloaddition.

Table 7. The compositions of the reaction mixtures obtained in the interaction of the enallenes (CII) with $\alpha\beta$-unsaturated ketones[82].

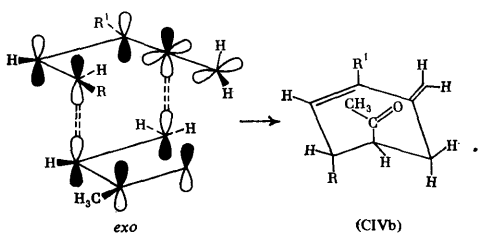
Groups in (CII)–(CIV)			Overall yield of (CIII) + (CIV), %	Fraction of adduct (CIII), %	Fraction of adduct (CIV), %	Fraction of adduct (CIVa) in (CIV), %	Fraction of adduct (CIVb) in (CIV), %
R	R^1	R^2					
H	H	H	60	28	72	—	—
H	CH_3	H	75	20	80	—	—
H	n-C_3H_7	H	70	15	85	—	—
H	H	CH_3	40	21	79	—	—
CH_3	H	H	50	0	100	75	25
iso-C_3H_7	H	H	65	0	100	82	18
CH_3	CH_3	H	75	0	100	80	20
CH_3	H	CH_3	35	0	100	100	0

In the reaction of the enallenes (CII, R ≠ H) with the ketone (C) the adduct (CIV) was obtained as a mixture of the *cis*- and *trans*-isomers, (CIVa), and (CIVb), respectively. It was established that the former is the kinetically controlled product and the latter the thermodynamically controlled product of the reaction. The fact that the kinetically controlled *cis*-adduct greatly predominates (Table 7) supports the concerted mechanism. If a two-stage mechanism operated, the ratio of the geometrical isomers (CIVa) and (CIVb) would have been determined by the thermodynamic equilibrium.

The kinetic control of the ratio of the stereoisomeric adducts in the reaction under consideration can be accounted for on the basis of the Woodward–Hoffmann rules[38], which take into account the interaction between the frontal orbitals of the reacting molecules. The interaction between the lowest unoccupied orbital (LUMO) of the conjugated diene system of the enallene and the highest occupied orbital (HOMO) of the ethylenic system of the $\alpha\beta$-unsaturated ketone in the transition state, with *endo*- and *exo*-dispositions of the reacting molecules, is illustrated schematically below:



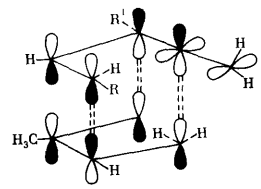
endo (CIV, a)



exo (CIVb)

The more effective overlapping of the π orbitals of the two systems in the case of the *cis*-adduct (*endo*-addition)‡ leads to a decrease of the activation energy for its formation relative to that for the *trans*-adduct (*exo*-addition). Because of this, the *cis*-adduct (CIVa) is the kinetically controlled main product of the reaction.

An alternative treatment of the interaction of the LUMO of the ethylenic bond of the dienophile and the HOMO of the diene system of the enallene leads to the conclusion that such interaction is energetically less favourable owing to a smaller secondary orbital effect even for the most favourable *endo*-disposition of the reacting molecules:



HOMO

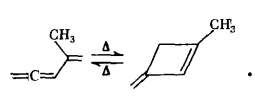
LUMO .

The absence of compounds with the cyclobutane structure among the products shows that, under the experimental conditions, there is no competition between the allene and conjugated groups of the conjugated enallenes, i.e. the reaction proceeds solely via the $[\pi 4_S + \pi 2_S]$ cycloaddition mechanism.

It is noteworthy that this reaction is of great interest for synthesis. The thermal cycloaddition of enallenes to unsaturated ketones can be widely used in the synthesis of monocyclic terpenoids, particularly derivatives of β-phellandrene[30,81]. Furthermore it has been shown[30] that the base-catalysed prototropic rearrangement of certain adducts with structure (CIII) easily leads to cyclic conjugated trienones.

(b) Electrocyclic Reactions

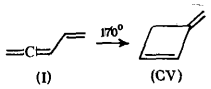
Much interest has been aroused recently by uncatalysed thermal reactions of triene hydrocarbons containing the allene group[84]. The electrocyclic transformation of the latter has become a preparative method for the synthesis of certain exotic cyclic hydrocarbons. However, there are few data concerning the thermal behaviour of conjugated enallenes. It has been established[39] that pyrolysis of 2-methylpenta-1,3,4-triene (XLIX) in pentane at 350–450 °C leads to the formation of 1-methyl-3-methylene cyclobutene (XLVIII). With increase of the duration of pyrolysis, the fraction of the hydrocarbon (XLVIII) in the reaction mixture remained constant, which indicated the attainment of equilibrium. The reversibility of the process was also demonstrated by the pyrolysis of methylenecyclobutene (XLVIII) and the discovery that the ratio of the hydrocarbons (XLIX) and (XLVIII) in the reaction mixture remains constant:



(XLIX) (XLVIII)

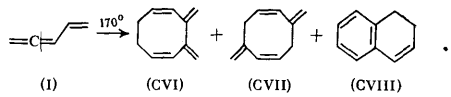
‡ $\alpha\beta$-Unsaturated dienophiles react with dienes in the cisoid conformation[83].

At 170°C penta-1,2,4-triene undergoes analogous cyclisation to methylenecyclobutene (CV):[85]



(I) (CV)

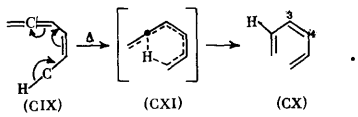
However, the content of the cyclic hydrocarbon (CV) in the reaction mixture does not exceed 10%. The main pathway in the thermal transformation of enallene (I) is its dimerisation, leading to the formation of at least seven hydrocarbons having the composition $C_{10}H_{12}$. Only three have been specified as the most interesting[85]—compounds (CVI), (CVII), and (CVIII):



(I) (CVI) (CVII) (CVIII)

(c) Sigmatropic Rearrangements

Apart from the intramolecular cyclisation discussed above, the thermal transformation of an enallene can involve a sigmatropic rearrangement to a conjugated triene accompanied by a [1,5]-H-shift:

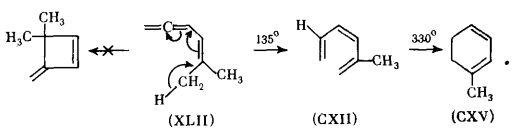


(CIX) (CXI) (CX)

Since this process involves three electron pairs, the synchronous migration of hydrogen takes place suprafacially[86].

The sigmatropic rearrangement of the enallene system (CIX) to the conjugated triene system (CX) is believed to take place[87] as a result of a rearrangement of the orbitals in the six-centre transition state (CXI). The latter is possible only provided that the initial enallene has the *cis*-configuration of the α-ethylenic bond. The experimental observation that the 3,4-bond in the resulting triene (CX) is a *cis*-C=C bond confirms the cyclic process mechanism.

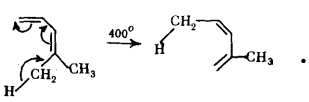
The sigmatropic rearrangement of 5-methylhexa-1,2,4-triene (XLII) takes place similarly[33], the compound being rapidly converted into *cis*-2-methylhexa-1,3,5-triene (CXII) at 135°C:



(XLII) (CXII) (CXV)

A methylenecyclobutene derivative is not formed under these conditions. The above process has an activation energy of 24.6 kcal mole^{-1} and proceeds at an anomalously low temperature.

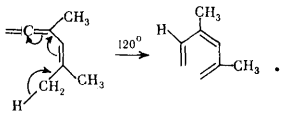
The analogous thermal rearrangement of acyclic conjugated dienes requires much more severe conditions. Thus the sigmatropic rearrangement of 4-methylpenta-1,3-diene (CXIII) to *cis*-2-methylpenta-1,3-diene (CXIV) proceeds at a temperature not less than 400°C (E_a = 32.8 kcal mole^{-1}):[88]



(CXIII) (CXIV)

The thermal transformation of the enallene (XLII) at 330°C leads to the exclusive formation of the cyclohexadiene derivative (CXV), which is a consequence of the intramolecular cyclisation of the hexatriene (CXII), having the *cis*-configuration which favours the electrocyclic process.

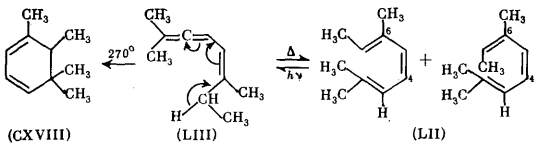
The conjugated enallene (CXVI) rearranges to the conjugated triene (CXVII) at the instant of distillation[33,55]:



(CXVI) (CXVII)

It is of interest to compare the thermally controlled transformation of conjugated enallenes into conjugated trienes with the opposite process which is photochemically controlled. Thus 2,6-dimethylocta-2,3,5-triene (LIII), obtained by the photochemical [1,5]-sigmatropic rearrangement of 2,6-dimethylocta-2,4,6-triene (LII), was reconverted into the initial triene (LIII) after heating for 8 min at 112–114°C as a result of a thermal [1,5]-H-shift (degree of conversion 93%).[42,43] The triene (LII) is formed as a mixture of the 4-*cis*-6-*cis*- and 4-*cis*-6-*trans*-isomers, the latter greatly predominating owing to favourable steric factors. As already mentioned above, the *cis*-configuration of the central double bond of the triene (LII) is a consequence of a cyclic mechanism of the rearrangement.

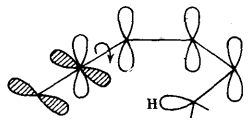
As expected, at a higher temperature (270°C) the enallene (LIII) is converted into the cyclohexadiene (CXVIII):



(CXVIII) (LIII) (LII)

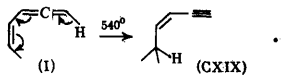
It has been established[43] that the 4-*trans*-6-*trans*- and 4-*trans*-6-*cis*-isomers of the hydrocarbon (LII) are formed when the enallene (LIII) is stored for several years at room temperature.

It has been suggested[33] that the unusual ease with which the thermal sigmatropic rearrangement of conjugated enallenes takes place (compared with conjugated dienes) can be accounted for by the specific influence of the allene group. In the case of a [1,5]-H-shift in the enallene the hydrogen atom migrates to the C atom in the *sp* state, which is more electronegative than the C atom in the sp^2 state to which the hydrogen atom migrates in the diene. Furthermore, the sigmatropic rearrangement of the enallene results in the dissociation of the C_{sp^3}–H bond and the formation of a stronger C_{sp^2}–H bond. These effects lead to an appreciable decrease of the process activation energy. The stabilisation of the transition state during the rearrangement of the enallene to a conjugated triene can take place as a result of the partial involvement in the conjugation of the π orbitals of the terminal C=C bond of the allene group:



A new type of [1,5]-sigmatropic rearrangement of penta-1,2,4-triene (I), in which hydrogen migrates from the terminal carbon atom of the allene group to the terminal carbon atom of the α-ethylenic bond, was established recently[85]. The rearrangement, occurring at a

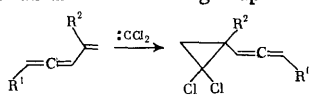
very high temperature (540°C), results in the formation of pent-2-en-4-yne (CXIX):



(I) (CXIX)

(d) Cheletropic Reactions

Conjugated enallenes react with carbenes. This reaction, which belongs to the class of non-linear cheletropic processes[38], has been investigated in relation to the interaction of dichlorocarbene with penta-1,2,4-triene (I) [89] and 2-methylocta-1,3,4-triene (CXX).[90] It was carried out with an equimolar enallene–dichlorocarbene mixture, the dichlorocarbene being generated from t-BuOK and chloroform. It was shown that in both cases the dichlorocarbene attacks the α-ethylenic bonds of enallenes, which shows that it has more pronounced nucleophilic properties than the C=C bonds in the allene group:



(I): $R^1 = R^2 = H$; (CXXI): $R^1 = R^2 = H$;
(CXX): $R^1 = n\text{-}C_3H_7$, $R^2 = CH_3$; (CXXII): $R^1 = n\text{-}C_3H_7$, $R^2 = CH_3$.

The selective addition of CCl_2 to the α-ethylenic bonds of enallenes (I) and (CXX) resulted in the synthesis of new derivatives of *gem*-dichlorocyclopropane, (CXXI) and (CXXII), containing an allene group conjugated with the cyclopropane ring.

The more marked nucleophilic properties of the α-ethylenic bond of enallene (I), manifested in its reaction with dichlorocarbene, have also been confirmed by the results of the epoxidation of this hydrocarbon with *p*-nitroperbenzoic acid.

3. CATALYTIC HYDROGENATION

Selective stepwise hydrogenation of conjugated enallenes has not been studied. Exhaustive hydrogenation of these compounds proceeds smoothly in the presence of palladium and platinum catalysts, which has been used to demonstrate the structures of many conjugated enallenes[15,17,42,43].

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