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Thermal Rearrangements of Vinylcyclopropanes

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Various types of reactions of compounds containing vinylcyclopropane groups are considered, particular attention being devoted to data from which the mechanisms of the rearrangements can be inferred.
The bibliography includes 100 references.

CONTENTS

I. Introduction 469
II. Isomerisation of vinylcyclopropanes to cyclopentenes 469
III. Isomerisation of vinylcyclopropanes involving a 1,5-hydrogen shift 473
IV. Isomerisation of divinylcyclopropanes (the Cope rearrangement) 475

I. INTRODUCTION

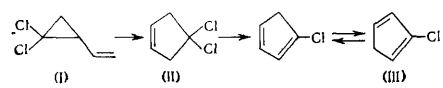
Vinylcyclopropanes are of interest for the investigation of the mutual influence of the cyclopropane ring and an unsaturated group. This influence is illustrated particularly by the relative lability of such systems, which undergo intramolecular rearrangements under various influences (for example, high temperature).

Numerous examples of thermal rearrangements of vinylcyclopropanes are now known. They have been described mainly in the last decade. The types of reactions undergone by the compounds under consideration depend significantly on their structure. In many cases, the isomerisation proceeds with formation of cyclopentenes. When the relative positions of the hydrogen atom in the 1-alkyl substituent and the vinyl group are favourable (*cis*-1-alkyl-2-vinylcyclopropane systems), electrocyclic reactions, including a 1,5-hydrogen shift and yielding dienes, take place. The reactions of divinylcyclopropanes constitute a characteristic example of the Cope rearrangement.

In the present review a systematic account is given of examples of rearrangements of vinylcyclopropanes in accordance with the types of their reactions. Particular attention is devoted to the discussion of studies whose authors attempted to elucidate the mechanisms of the reactions.

II. ISOMERISATION OF VINYLCYCLOPROPANES TO CYCLOPENTENES

The first example of this rearrangement was described in 1959 by Neureiter[1]. In a study of the thermolysis of 1,1-dichloro-2-vinylcyclopropane (I) at 475–500°C, he established that this yields a mixture the main components of which are 4,4-dichlorocyclopentene (II) and 2-chlorocyclopentadiene (III). The latter was obtained via stages involving dehydrochlorination of (II) followed by isomerisation:



(I) (II) (III)

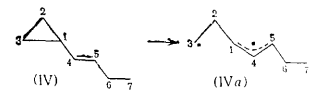
Later it was established that at a lower temperature (200–275°C) the only reaction product is the dichloride (II).[2,3]

Two pathways to the formation of a five-membered ring in this reaction are possible: the biradical pathway (via an intermediate stage involving the opening of the trimethylene ring) and the synchronous pathway (in which there is a simultaneous rupture of the three-membered ring and the formation of a new bond). The latter pathway (a 1,3-suprafacial shift with inversion at the migrating atom or an antarafacial shift with retention of configuration) is allowed on symmetry grounds.

In a number of studies (among which those of Frey must be mentioned), the kinetics of the thermolysis of various substituted monocyclic and bicyclic vinylcyclopropanes were investigated in order to elucidate the mechanism of the rearrangement (Table 1). The results are compared with the kinetic parameters of the thermal rearrangements of the corresponding alkylcyclopropanes in the discussion of the mechanisms of the rearrangements of vinylcyclopropanes. Both biradical[2,3,6,9,10,23,24] and synchronous[4,5,8,12,25] mechanisms for the formation of cyclopentenes have been proposed.

The lower activation energies for the reactions of vinylcyclopropanes compared with the values of E_a for the geometrical and structural isomerisation of alkylcyclopropanes (Table 2) and the low entropies of activation supported the synchronous mechanism[31].

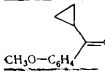
However, the kinetic data obtained could be interpreted also on the hypothesis of the intermediate formation of a biradical. In this case the observed entropy of activation can be attributed to a certain rigidity of the intermediate allyl system. This rigidity is due to the increase of the potential barrier to rotation about the $C_{(1)}-C_{(4)}$ bond from 3.5 to 16.1 kcal on passing from the hydrocarbon (IV) to the corresponding allylically stabilised biradical (IVa):[15]



(IV) (IVa)

On the other hand, the differences between the activation energies for the reactions of monocyclic vinyl- and alkyl-cyclopropane can be attributed to the involvement of the π electrons of the double bonds in the stabilisation of the biradical. Indeed, the difference between the activation energies for the reactions of 1-methyl-1-vinylcyclopropane (Table 1) and 1,1-dimethylcyclopropane (Table 2), amounting to 13.2 kcal mole^{-1}, is close to the resonance energy of the allyl radical (12.6 ± 0.8 kcal mole^{-1}), which Benson and coworkers determined experimentally[24].

Table 1.* Thermal isomerisation of vinylcyclopropanes to cyclopentenes**.

Initial hydrocarbon	Isomerisation products	Temperature, °C	lg A (s^{-1})	E_a, kcal mole^{-1}	References
		339—391	13.5	49.60	4
		324.7—390.2	13.6	49.7±0.3	5
		»	14.4	57.3±1.0	5
		»	13.0	53.6±0.8	5
		»	13.9	56.2±0.8	5
		296—328	13.67	48.64	6
		270—290	12.5	45.7±0.6	7
		332.7—373.3	13.79	49.98	8
		332—386	13.89	50.9	9
		313—357	14.11	49.35	10
		325—368	14.14	50.50	11
		350—390	14.00	54.60	12
		»	14.61	56.65	»
		»	13.39	53.00	»
		»	13.25	52.10	»
		332—371	—	50.4	13
		341.9—388.5	14.3	51.1	14
		»	14.0	51.3	14
		271—316	13.36±0.1	44.47±0.26	15
		233—257	12.57	39.6±1.0	16
		201.6—258.6	14.33±0.24	43.41±0.54	17, 18
		—	14.6	44.00	19
		144—180	12.6	32.4	19
		132—160	9.69	26.3	20
		—	13.7	33.5	21
		108—138	13.4	34.3±1.4	22
		—	13.9	33.9	21
		108—138	17.1	39.6±1.4	22

*Tables 1, 3, and 4 list only those examples of the reactions for which the kinetic parameters have been determined.

**Quantitative parameters of the simultaneous isomerisation to other olefins are quoted for some of the hydrocarbons.

Thus the kinetic data do not allow an unambiguous choice between the synchronous and biradical mechanisms of the thermal isomerisation of vinylcyclopropanes. In recent years, there has been an increase in the number of facts supporting the biradical reaction pathway.

Table 2. Thermal isomerisation of cyclopropanes.

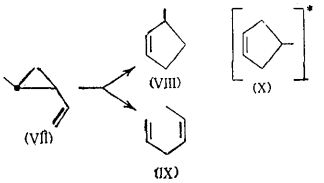
Initial hydrocarbon	Isomerisation products	Temperature, °C	lg A (s^{-1})	E_a, kcal mole^{-1}	References
		445	16.41	66.1±0.5	26
	CHD=CH—CH_2D	»	15.12	65.4±1.1	26
		380—420	15.35	60.5±1	27
	CH_3CH=CHD—CH_2D	420—475	14.43±0.16	62.3±0.5	»
	CHD=CD—CH_2—CH_3	»	14.4	62.3±0.5	»
		380—453	15.25	59.42	28
	CH_2=CH—CH(CH_3)—CH_3	»	14.1	61.8	»
	CH_3—C(CH_3)=CH—CH_3	»	14.1	61.8	»
		447—511	15.05	62.6	29
		»	»	»	»
		395—452	15.78	60.95	30

Willcott and Cargle investigated the thermal transformations of 1-(*trans*-2-deuterovinyl)-*trans*, *trans*-2,3-dideuterocyclopropane (V), and *trans*-2-deuterovinylcyclopropane (VI):

(V)

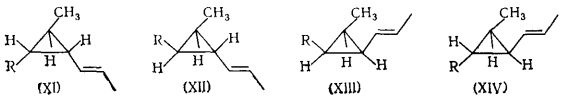
Here structural isomerisation is accompanied by a degenerate *cis*—*trans* isomerisation [32,33]. It was established that (1) the rearrangement takes place with inversion of configuration at two carbon atoms and (2) the geometrical isomerisation is at least five times faster than the formation of cyclopentenes. The results led to the conclusion that kinetically independent intermediate compounds are formed in the reaction investigated in accordance with the scheme below:

The study of the thermal isomerisation of *trans*-1-methyl-2-vinylcyclopropane (VII), the reactions of which at 270–330°C proceed with the same activation parameters via two pathways, led to a similar conclusion[6,7]:

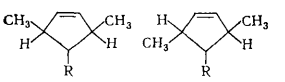


Methylcyclopentene is the "usual" product of the rearrangement of vinylcyclopropanes. The diene (IX) can be formed only from *cis*-1-methyl-2-vinylcyclopropane (this will be discussed in greater detail below). Thus, the isomerisation to cyclopentene is accompanied by *trans–cis* isomerisation in this case too.

Data obtained in the study of the thermal transformations of the esters (XI)–(XIV) also constitute evidence against the synchronous mechanism[34]:

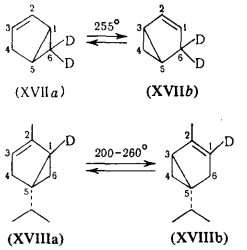


It was found that the above compounds readily undergo isomeric interconversions, the two isomeric cyclopentenes (XV) and (XVI) being also obtained, together with dienes, in various proportions (depending on the structure of the initial vinylcyclopropane).



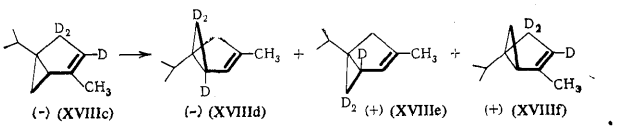
The composition of the reaction product would have been different if one of the possible symmetry-allowed 1,3-sigmatropic shifts occurred. However, according to Mazzocchi and Tamburin[34], the available data are insufficient to rule out the possibility that the reaction proceeds via a combined (concerted and non-concerted) pathway.

A similar rearrangement has been observed also in a series of bicyclic condensed compounds containing a three-membered ring and a double bond in the larger ring. An example of such rearrangements is provided by the degenerate isomerisation of bicyclo[3,1,0]hex-2-ene (XVII)[35] and Δ^3-thujene (XVIII).[17,18,35,36] (At higher temperatures, the three-membered ring is opened—see below.)



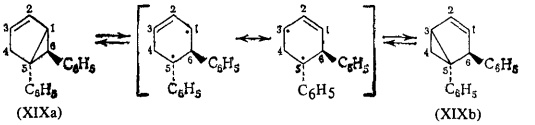
† The formation of 3-methylcyclopentene (VIII)[6] and of 4-methylcyclopentene (X)[7] has been noted. Somewhat different activation parameters were obtained in these reactions (see Table 1).

In a detailed study of the reactions of optically active deuterated Δ^3-thujene (XVIIIc) at 240°C, Doering[17] concluded that the reaction proceeds with intermediate formation of biradicals, since the reaction products (XVIII, *d–f*) are inconsistent with the predicted formation of the single compound (XVIII*f*) (via a concerted mechanism in accordance with the Woodward–Hoffmann rules):

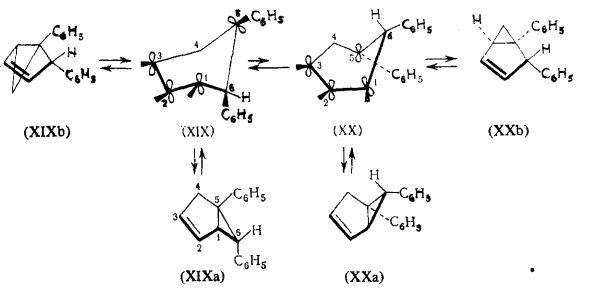


In order to elucidate the pathway whereby vinylcyclopropanes rearrange to cyclopentenes, two methods were used in the above investigations: (1) comparison of the activation parameters for the reaction with those for the simultaneous geometrical isomerisation, for which the mechanism may be regarded as established; (2) comparison of the observed composition of the reaction products and the composition postulated on the basis of the synchronous mechanism. To prove the proposed mechanism, one frequently investigates the stereospecificity of the reaction. Stereospecificity is an invariable consequence of the concerted mechanism. However, stereospecificity alone cannot serve as an adequate evidence for the synchronous mechanism[17].

For example, the stereospecificity of the reversible thermal isomerisation of *trans*-5,6-diphenylbicyclo[3,1,0]hex-2-ene (XIXa) and *trans*-4,5-diphenylbicyclo[3,1,0]hex-2-ene (XIXb)[19,37] can be a result of either the synchronous reaction or a process which may proceed via an intermediate biradical stage in which the rate of closure of the new ring is higher than that of the inversion of the configuration at $C_{(5)}$:



The calculated minimum activation energy for the conversion of (XIXa) into (XIXb) via the biradical (31.5 kcal mole^{-1}) proved to be very close to the experimental value E_a = 32.4 kcal mole^{-1}.[19] The stereospecificity of this reaction is apparently determined by the high energy barrier separating the radicals (XIX) and (XX). In the transformation (XIX) → (XX), there is an appreciable enhancement of the steric interaction between the two phenyl groups, which leads to the breakdown of the coplanarity of the phenyl group and the radical centre at $C_{(5)}$ and hence to decreased conjugation:

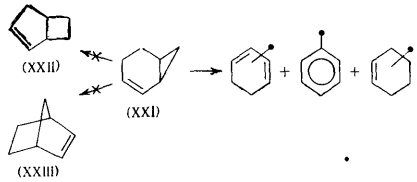


This is probably why the activation energy for the thermolysis of (XXa) is higher (36.7 kcal mole^{-1}). It has also been noted that the rate of isomerisation of (XXa) is

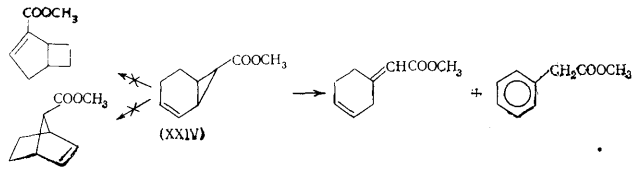
appreciably lower than the rate of reaction of (XIXa). Thus Swenton and Wexler's experimental data[19] confirm the biradical reaction mechanism which they proposed.

The lower activation energies and reaction temperatures for bicyclo[3,1,0]hex-2-ene systems are striking (Table 1). The observed lower activation energy compared with E_a for the rearrangement of monocyclic vinylcyclopropanes has been attributed to the contribution of the strain energy of the five-membered ring (+6.8 kcal mole^{-1}) [17,38] and, in the presence of substituents, to the additional stabilisation of the biradical state due to the involvement of the substituents[19,20].

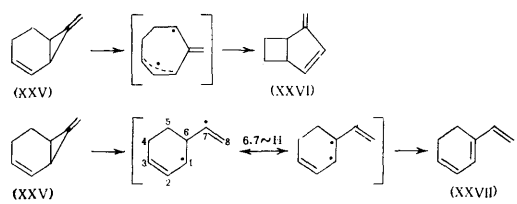
It is noteworthy that the thermal transformations of condensed compounds in the bicyclo[4,1,0]hept-2-ene series {in contrast to bicyclo[3,1,0]hexenes} do not proceed via the mechanism of the rearrangement of vinylcyclopropanes discussed above. Thus a complex mixture of hydrocarbons, the main components of which are methylcyclohexadienes, is formed from bicyclo[4,1,0]hept-2-ene (XXI) at 300–500°C: [39]



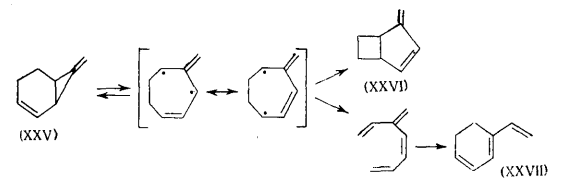
Bicyclo[3,2,0]hex-2-ene (XXII) and bicyclo[2,2,1]-heptene (XXIII), the formation of which would have been expected if there were a rearrangement to the corresponding cyclopentene system, were not detected over the entire experimental temperature range. This applies also to the transformations of the ester (XXIV): [3]



7-Methylenebicyclo[4,1,0]hept-2-ene (XXV), which contains both vinyl and methylenecyclopropane fragments, constitutes an exception in the above series of compounds[21,22]. The methylenecyclopropane fragment is in fact responsible for the specific features of the behaviour of this hydrocarbon. 7-Methylenebicyclo[4,1,0]hept-2-ene isomerises under comparatively mild conditions (at a temperature as low as 110°C) in two independent ways with formation of 4-methylenebicyclo[3,2,0]hept-2-ene (XXVI) and 1-vinylcyclohexa-1,3-diene (XXVII) in proportions of 4 : 1. The ratio of the reaction products changes with increase of temperature above 300°C in favour of the hydrocarbon (XXVII).[22] The activation parameters for the two types of reaction differ appreciably from one another according to one of the investigations (Table 1), which may be due to the fact that the reactions proceed via different transition states, formed in accordance with the mechanism indicated below:



An alternative reaction mechanism corresponds to the identical activation parameters for reactions of both types obtained by Billups et al.[21]:



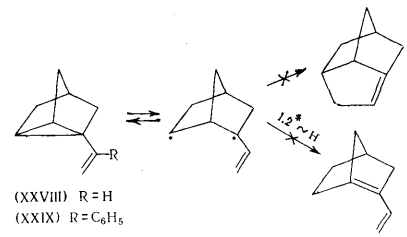
In conclusion of this section, examples of the "anomalous" behaviour of certain vinylcyclopropanes at an elevated temperature will be quoted.

(1) Cases are known where compounds containing the vinylcyclopropane systems do not isomerise to cyclopentenes. These include the following:

(a) the compounds of the bicyclo[4,1,0]hept-2-ene series already mentioned;

(b) 1-alkyl-2-vinyl- and 1,2-divinyl-cyclopropanes, the rearrangements of which take place in a different way (see below);

(c) the hydrocarbons (XXVIII) and (XXIX) do not change up to 475°C, i.e. under conditions such that even cyclopropanes isomerise. This is probably due to the fact that the rearrangements would necessarily lead to the formation of strained compounds with a double bond at the bridgehead.

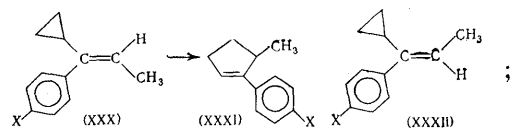


(2) The presence at the $C_{(4)}$ atom of the vinyl group and in the cyclopropane ring of substituents, such as the alkyl group (Table 1), the phenyl[2,41–43], cyclopropyl[2,14,35,44], vinyl[15,25,35,45], and ester[34,46,47] groups and chlorine atoms in the cyclopropane ring[1–3] does not affect the mode of rearrangement of monocyclic vinylcyclopropanes.



At the same time the introduction of substituents at the $C_{(5)}$ atom involved in a double bond has a significant influence on the behaviour of vinylcyclopropanes.

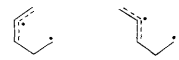
Thus the *trans*-isomer (XXX) is converted almost quantitatively into the substituted cyclopentene (XXXI) in the temperature range 360–390°C. On the other hand, a complex mixture of products, in which the content of the expected cyclopentene does not exceed 20%, is formed from the *cis*-isomer (XXXII); the process is accompanied by intense polymerisation (up to 60%) [41]:



X = H, CH_3, $CH(CH_3)_2$, OCH_3 .

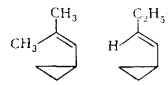
‡ The symbol ~H denotes a hydrogen shift.

This finding has been explained by the fact that the steric interaction of the cyclopropane ring and the alkyl substituent in the *cis*-isomer prevents the formation of a *cis*-allyl biradical of type (XXXIIIa), which precedes cyclopentene. A *trans*-allyl biradical of type (XXXIIIb) should be formed from compound (XXXII).[48,49]



(XXXIIIa) (XXXIIIb)

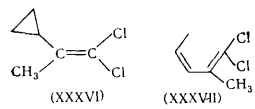
That the transformation of hydrocarbon (XXXIV) has the highest known activation energy of all the thermal isomerisations of vinylcyclopropanes (Table 1) is a consequence of the steric influence of the *cis*-methyl group.



(XXXIV) (XXXV)

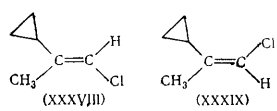
On the other hand, the activation energy for the transformation of hydrocarbon (XXXV), containing the *trans*-ethyl group, does not differ from the value of E_a for the unsubstituted vinylcyclopropane (Table 1).

The transformation of 1,1-dichloro-2-cyclopropylprop-1-ene (XXXVI) takes place at 450°C with formation of a complex mixture, the main component of which is the dichloro-derivative (XXXVII):[3]



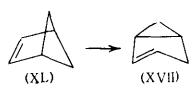
(XXXVI) (XXXVII)

Thus the introduction of two electron-accepting substituents hinders the involvement of the π electrons of the double bond in the opening of the cyclopropane ring. In this case, the usual thermal decomposition of the three-membered ring takes place, namely a reaction which has a higher activation energy than that for the rearrangement of vinylcyclopropanes. The study of the thermal transformations of the isomeric monochloro-derivatives (XXXVIII) and (XXXIX) showed that the electronic influence of the chlorine atom prodominates over the steric influence[3]:



(XXXVIII) (XXXIX)

(3) The rearrangement of vinylcyclopropanes is an exothermic reaction (by approximately 25 kcal mole^{-1}) and the reverse reaction is not, as a rule, observed[17]. Systems characterised by a higher strain energy are an exception[50-54]. For example, bicyclo[2,1,1]hex-2-ene (XI) is converted into bicyclo[3,1,0]hex-2-ene (XVII),[50,51] while the reverse process does not take place:

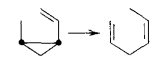


(XL) (XVII)

This reaction probably proceeds via a synchronous mechanism, like the 1,3-suprafacial shift with inversion of configuration at the migrating atom, which is confirmed by the stereospecificity[52,54] and the kinetic parameters of the reactions[51,54].

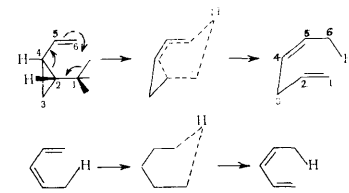
III. ISOMERISATION OF VINYLCYCLOPROPANES INVOLVING A 1,5-HYDROGEN SHIFT

When the steric configuration of 1-alkyl-2-vinylcyclopropanes is favourable, suitable conditions are created for the occurrence of the electrocyclic reaction, involving a 1,5-hydrogen shift and the opening of the cyclopropane ring and leading to isomeric dienes. The simplest case of a rearrangement of this type is the quantitative conversion of *cis*-1-methyl-2-vinylcyclopropane (XLI) above 160°C into *cis*-hexa-1,4-diene (XLII):[6,7,55]



(XLI) (XLII)

The structural requirements and the geometry of the transition state for the 1,5-hydrogen shift in *cis*-1-alkyl-2-vinylcyclopropanes and *cis*-1,3-dienes are illustrated below:

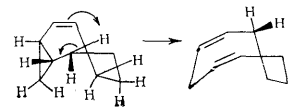


This rearrangement proceeds via a suprafacial mechanism in accordance with the Woodward–Hoffmann rules for the conservation of orbital symmetry[56].

Table 3 presents the activation parameters for the reactions of vinylcyclopropanes occurring with a 1,5-hydrogen shift (data for certain 1,3-dienes are presented for comparison).

It is striking that the activation energy for the above transformation is much lower than the values of E_a for the rearrangement of vinylcyclopropanes into cyclopentenes. The factors A are also lower and correspond in magnitude to the values of A for the Cope rearrangement (Section IV). The low value of A suggests a rigid transition complex in which the free rotations of the methyl and vinyl groups have been lost.

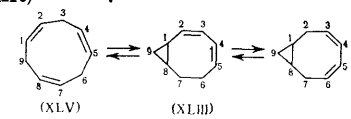
The 1,5-hydrogen shift takes place readily in bicyclo[n,1,0]olefins (n = 5, 6, or 7), which have a saddle-shaped conformation.



The migrating hydrogen atom is in the *trans*-position relative to the cyclopropane methylene group and this is why a *cis*-diolefin is formed. The thermal opening of the cyclopropane ring in bicyclo[n,1,0]olefins (n = 5, 6, or 7) proved to be a convenient method for the synthesis of *cis*,*cis*-1,4-diene systems.

Thus at 130–200°C bicyclo[5,1,0]oct-2-ene[35,61], bicyclo[6,1,0]non-2-ene[35,60], bicyclo[6,1,0]nona-2,5-diene[62], bicyclo[6,1,0]nona-2,4-diene[60,62,63], and bicyclo[7,1,0]dec-2-ene[17] isomerise smoothly to the corresponding monocyclic compounds.

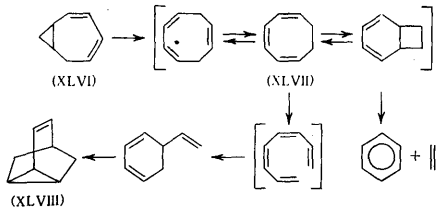
In system (XLIII), the $C_{(7)}-C_{(3)}$ hydrogen shift (a homodienyl shift), competes with the $C_{(6)}-C_{(2)}$ hydrogen shift (a dienyl shift)[60,62,63]:



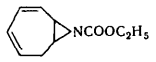
(XLV) (XLIII)

Above 160°C the equilibrium is displaced towards the cyclononatriene (XLV). For example, at 170°C we have the ratios (XLV) : (XLIII) : (XLIV) = 93 : 6 : 1.[62]

A mixture of hydrocarbons (XLVII) and (XLVIII) and benzene was obtained from bicyclo[5,1,0]octa-2,4-diene (XLVI) at 225°C in accordance with the following reaction mechanism[47]:

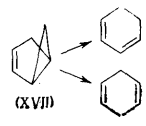


The corresponding heteroanalogue (XLIX) undergoes a similar isomerisation[64]:



(XLIX)

The non-planar conformation necessary for the 1,5-hydrogen shift is not achieved in bicyclo[n,1,0]olefins (n = 3 or 4). Thus bicyclo[3,1,0]hex-2-ene (XVII) isomerises to a mixture of cyclohexa-1,3-diene and cyclohexa-1,4-diene above 300°C:[7,65–67]

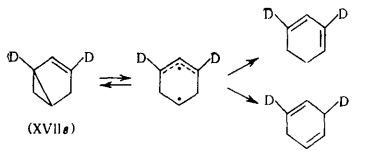


$\lg A = 14.28$ s^{-1}; $E_a = 50.2$ kcal mole^{-1};

$\lg A = 14.095$ s^{-1}; $E_a = 50.2$ kcal mole^{-1}.

The activation energies quoted are much higher than the values of Ea for reactions proceeding via a 1,5-hydrogen shift (Table 3). Furthermore, this mechanism does not explain the preferential formation of a conjugated diene on isomerisation (cyclohexa-1,3-diene and cyclohexa-1,4-diene do not undergo thermal isomeric interconversions[68]).

Data obtained in 1973 in studies on the thermolysis of deuterated bicyclo[3,1,0]hex-2-ene (XVIIc) support the biradical mechanism of reactions via a 1,2-hydrogen shift[67]:



Evidently, enormous distortions are needed in system (XXI) with n = 4 in order that a transition state be formed for which an electrocyclic reaction involving a 1,5-hydrogen shift is possible. The thermal transformations of bicycloheptene (XXI) take place only via the radical mechanism[39] (see Section II).

Certain substituted derivatives of bicyclo[4,1,0]hept-2-ene [(L) and (LI)][59,69–72] and bicyclo[3,1,0]hex-2-ene[73] are partly isomerised via a six-unit electrocyclic transition state involving a 1,5-hydrogen shift (which is confirmed by the stereospecificity of the reactions and the kinetic parameters):

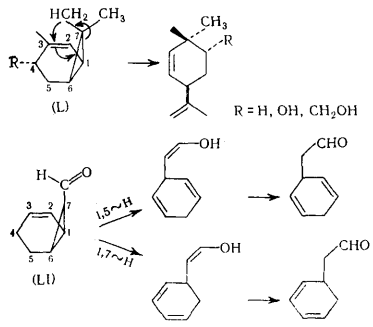


Table 3. Thermal isomerisation of *cis*-1,3-dienes and *cis*-1-alkyl-2-vinylcyclopropanes.

Initial hydrocarbon	Isomerisation product	Temp., °C	lg$A$ (s^{-1})	E_a, kcal mole^{-1}	$\Delta H^{\neq}$, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	References
		185—205	11.93	36.3	—	—	57
		»	11.86	37.7	—	—	»
		202—245	10.80	32.50	—	—	58
		166—220 170—190	11.03 10.95	31.24 31.1±0.6	30.3 30.2	—11.6 —11.0	6.55 7
		—	11.41	33.54	—	—	31
		— —	11.32 11.27	33.7 33.6	— —	— —	31 31
 R=H		200—240	—	—	27.2	—17.2	59
R=OH		»	—	—	33.0	—8.8	59
R=CH2OH		»	—	—	28.6	—6.5	59
		»	—	—	28.0	—6.7	59
		125—150	—	—	31.4	—6	60
		125—150 »	— —	— —	29.3 32.5	—7 —5	60 60

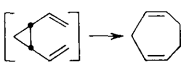
However, these reactions bear only a formal analogy to the isomerisation considered in this Section, since in the case of hydrocarbon (L) the hydrogen atom of the $C_{(7)}-CH_3$ side chain migrates and in the case of aldehyde (LI) the hydrogen atom attached to the carbon atom in the 4- or 5-position relative to the carbonyl group migrates.

IV. ISOMERISATION OF DIVINYLCYCLOPROPANES (THE COPE REARRANGEMENT)

1. *cis*-Divinylcyclopropanes

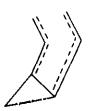
The isomerisation of *cis*-divinylcyclopropanes, which may be regarded as a special case of the Cope rearrangement of 1,5-dienes, is an interesting example of the [3,3] sigmatropic rearrangement.

The *cis*-isomer of divinylcyclopropane (LII) is so labile that it rearranges to cyclohepta-1,4-diene already under the conditions of its formation [42,49,74,75]:



(LII)

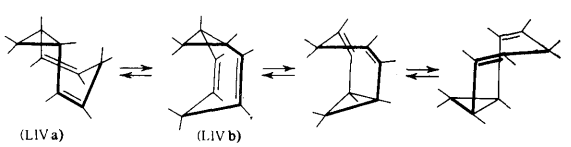
Examination of the geometry of divinylcyclopropane leads to the conclusion that the only possible transition state in the rearrangement investigated is the quasi-boat structure (LIII) in which the vinyl groups overhang the plane of the three-membered ring:



(LIII)

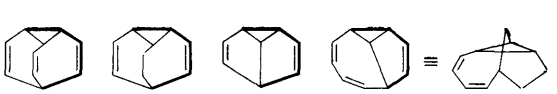
Any other orientations of the vinyl groups would have led to the *trans,trans*- or *cis,trans*-heptadienes which are not observed. Since only slight changes in the position of the vinyl groups are necessary in the *cis*-isomer in order to attain such a transition state, the rearrangement takes place readily. The reversible degenerate rearrangements of a series of bicyclic and tricyclic unsaturated hydrocarbons belong to the same type of reactions.

The *cis*- and *trans*-isomers of bicyclo[5,1,0]hepta-2,5-dienes (LIVb) and (LIVa) isomerise at room temperature via the stage involving the formation of the thermodynamically less favourable *cis*-form [35,49]:



(LIVa) (LIVb)

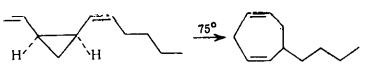
The allyl groups in bullvalene are rigidly fixed in the cisoid conformation. Rapid reversible isomerisation leads to the approximate equivalence of all the carbon atoms of bullvalene [35,49,76–79]:



(LV) (LVI) (LVII) (LVIII)

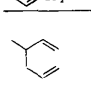
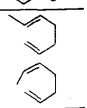
Bullvalene analogues, namely dihydrobullvalene (LVI), [79] semibullvalene (LVII), [80,81] and isobullvalene (LVIII), [82,83] isomerise similarly. Table 4 lists the kinetic parameters of the isomerisation of *cis*-divinylcyclopropanes (data for certain 1,5-dienes and *cis*-divinylcyclobutane are included for comparison). The Cope rearrangement is characterised by comparatively low activation energies and low negative activation entropies.

More stable (stable at room temperature) *cis*-1,2-divinylcyclopropanes are also known: *cis*-1-(*cis*-hex-1-enyl-)2-vinylcyclopropane (LIX) [89] and the bicyclic hydrocarbons (LX), [62,87,90,91] (LXI) [88] (Table 4), (LXII), and (LXIII):

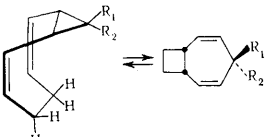


(LIX)

Table 4. Thermal isomerisation of 1,5-dienes and *cis*-divinylcycloalkanes.

Initial hydrocarbon	Isomerisation product	Temperature, °C	lg*A* (s^{-1})	E_a, kcal mole^{-1}	$\Delta S^{\neq}$, e.u.	Ref.
		—	11.1	35.5	—	84
		220—300	10.5±0.1	34.2	—	85
		220—300	10.5±0.1	35.7	—	86
		65.4—108.5	10.7	22.4	—11.7	86
 (LII)		5—20	—	—	—5.3	75
 (LV)		10—83	12.0	11.8±1.0	—5.0	77
		25—123	12.9	12.8±0.1	—2.3	78
 (LVIII)		11—30	—	—	—10	83
 (LX)		35—48	13.2	25.0±0.5	—	87
 (LXI)		—	11.7	22.9	—7.2	88

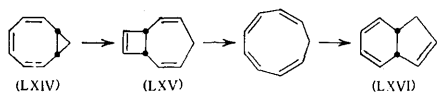
The latter isomerise only at 150—180°C. The rearrangement is difficult owing to the steric hindrance by the methyl groups in the *cis*-conformations [89]:



(LXII) R_1=H; R_2=CH_3;
(LXIII) R_1=R_2=CH_3.

Bicyclo[6,1,0]nonatriene (LXIV) is converted at 90°C into hydrocarbon (LXVI). However, it has been established that the reaction proceeds in succession via a number of stages, each of which takes place with conservation

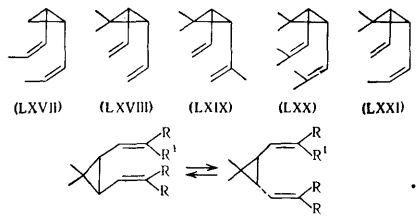
of orbital symmetry[92]. The first stage is the Cope rearrangement to bicyclo[5,2,0]nona-2,5,8-triene (LXV):



Thus the analogy between the transformations of hydrocarbon (LXIV) and the vinylcyclopropane rearrangement to cyclopentenes, discussed in certain reviews[17,93], is purely formal.

In contrast to unsubstituted divinylcyclopropane, substituted *cis*-divinylcyclopropane systems do not change even under fairly severe conditions.

Hydrocarbons (LXVII)–(LXXI), which are stable at room temperature, undergo geometrical isomerisation on heating to 170–180°C, yielding a mixture of *trans*- and *cis*-olefins instead of the expected Cope rearrangement[94-97]:

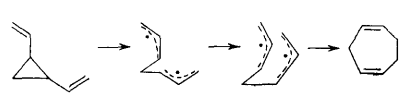


The activation energy observed for the transformation of hydrocarbon (LXX) [E_a = 33 kcal mole^{-1}; lg$A$ (s^{-1}) = 12.4; ΔS = −3.8 e.u.][97] is one of the lowest for the homolytic dissociation of the C–C bonds in cyclopropane (Table 2), which can be accounted for by the involvement of two allyl groups in the stabilisation of the transition state.

The difference in the behaviour of substituted and unsubstituted *cis*-divinylcyclopropanes is due to the steric interactions of the substituents in the transition state.

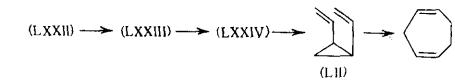
2. *trans*-Divinylcyclopropanes

Since the discovery of the rearrangement of *trans*-1,2-divinylcyclopropane (LXXII)[42] and the determination of its Arrhenius parameters [lg$A$ = 12.09 (s^{-1}) and E_a = 32.10 kcal mole^{-1}],[98] studies on this subject have not been continued. Since the rearrangement hydrocarbon (LXXII) led to the same product as the Cope rearrangement of *cis*-divinylcyclopropane (LII), it has been suggested that the central linkage dissociates owing to the rigid geometry of the cyclopropane ring with formation of the *trans*-allyl biradical (LXXIII), the two allyl components of which then assume the *cis*-positions as in (LXXIV):[35,49]

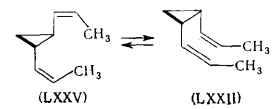


However it remained obscure whether the isomerisation proceeds only via intermediate biradicals or whether biradical (LXXIV) cyclises to *cis*-divinylcyclopropane (LII) with its subsequent rearrangement via a quasi-boat six-unit transition state.

Products containing *trans*-1,2-dialkenylcyclopropane fragments have been isolated in recent years from the oil of *Distyopteris* and the seaweed *Ectocarpus siliculosees*; this aroused more interest in the study of the mechanism of the transformations of *trans*-divinylcyclopropanes. It has been established that at 150–205°C the racemisation of (−)-*trans*-1,2-divinylcyclopropane (LXXII) is accompanied by the geometrical isomerisation to the corresponding *cis*-isomer (LII), which is in its turn rapidly and quantitatively converted into cyclohepta-1,4-diene; here the opening of the cyclopropane ring in the *trans*-isomer is a biradical and not an electrocyclic process[99]:



At 180°C, the *trans*-isomer (LXXV) underwent only geometrical isomerisation with formation of an equilibrium mixture of the *trans*- and *cis*-isomers; the resistance of the latter to the Cope rearrangement was discussed previously[94]:



The study of the stereochemical specificity of the thermolysis of other isomeric *trans*-1,2-dialkenylcyclopropanes yielded additional evidence ruling out the possibility of the direct formation of cycloheptadienes from the intermediate *cis*-allyl biradicals of type (LXXIV).[94,100]

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Thus data obtained in kinetic studies on the thermal transformations of vinylcyclopropanes with formation of cyclopentenes can be interpreted both on the basis of ideas involving the synchronous mechanism and on the hypothesis of the intermediate formation of a biradical. However, the results obtained in recent years in studies on the stereochemical specificity of the thermolysis and of the transformations of deutero-derivatives of vinylcyclopropanes are more consistent with the biradical mechanism of the vinylcyclopropane rearrangement.

When the specific configuration of the vinylcyclopropane systems is favourable (*cis*-1-alkyl-2-vinylcyclopropanes and *cis*-divinylcyclopropanes), suitable conditions are created for the occurrence of concerted sigmatropic reactions proceeding via a six-membered cyclic transition state.

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