Translated from *Uspekhi Khimii*, 50, 1272 - 1303 (1981) U.D.C. 547.1.14;542.91;541.11

The 1,5-Shift Reaction

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Data on the reaction involving the 1,5-shift of hydrogen and substituents in cyclic and acyclic dienes and trienes as well as homodienyl systems published up to June 1979 are considered and treated systematically.
The bibliography includes 197 references.

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I. INTRODUCTION

Since the discovery in 1961 of the 1,5-hydrogen shift reaction[1], isomeric transformations of diene and polyene hydrocarbons have attracted much attention by investigators. Without exaggerating, one may say that studies in this field as well as investigation of other types of thermal intramolecular rearrangements have now become an independent and vigorously developing branch of organic chemistry. Studies in this field are important for the understanding of the general problem of valence tautomerism and valence isomerisation.

In the series of the so-called sigmatropic rearrangements the 1,5-shift of hydrogen and substituents is now the most thoroughly investigated reaction, but there is no review literature of any kind on this problem. The aim of the present review is to fill this gap. The available literature data are classified in terms of different types of hydrocarbon systems; the arrangement of the material corresponds approximately to the chronology of its publication.

The series of cyclopentadienes is historically the first and most thoroughly investigated system in which the 1,5-shift of both hydrogen and substituents has been observed.

II. CYCLOPENTADIENES

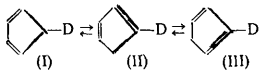
1. The Hydrogen 1,5-Shift

Inspection of early literature data shows that in many instances where the structure of the substituted cyclopentadiene had been sufficiently reliably established the distribution of double bonds in the substance was inconsistent with the expectation based on the synthetic scheme. Thus the decarboxylation of 2,4-diphenylcyclopenta-1,3-diene-1-carboxylic acid[2] yielded 1,4-diphenylcyclopentadiene instead of the expected 1,3-isomer. The cyclopentadienecarboxylic acid formed when cyclopentadienylpotassium is treated with carbon dioxide is the 1-isomer[3] and not the 5-isomer postulated previously. The dehydration of 2,3,4-trimethylcyclopent-2-en-1-ol leads to 1,2,3-trimethylcyclopentadiene instead of the 1,2,5-substituted compound[4]. Methyl cyclopenta-1,3-diene-1-carboxylate reacts partly in the form of the 2-isomer on dimerisation[5-7]. The pyrolysis of 3,3-dichlorocyclopent-1-ene leads to 2-chlorocyclopentadiene and not to the corresponding 1-isomer[8]. Finally, the dehydration of 1-phenylcyclopenta-2-en-1-ol yielded 1-phenylcyclopentadiene instead of 2-phenylcyclopentadiene[9]. Anomalous phenomena have also been observed in the alkylation of sodium, lithium, and magnesium derivatives of the cyclopentadienyl anion. Examination of the mechanism of the above reactions shows that the addition of a substituent to any of the equivalent carbon atoms of the cyclopentadienyl anion should result in the formation of 5-substituted cyclopentadiene. However, in reality the reaction usually gave rise to a mixture of the 1- and 2-isomers,[10-13] while under milder conditions the main products were the 1-isomers[12,14,15].

The independence of the structure of the substituted cyclopentadiene of the method of synthesis has been demonstrated by Mironov and coworkers[16,17], who established that five different synthetic pathways, formally designed to produce 1,4- or 2,5-dimethylcyclopentadienes, in all cases yield only 1,3-dimethylcyclopentadiene. The authors, who had previously observed the above anomalies, either did not attempt to explain them or explained them by the irreversible isomerisation of the substituted cyclopentadiene, formed initially, to the energetically more favourable isomer. The majority of investigators were convinced that the endocyclic double bonds in the cyclopentadiene ring are rigorously fixed; furthermore, the absence of isomerisation of cyclopentadienes was believed to have been proved[18,19].

In 1961 Mironov and coworkers[20-26] demonstrated that the system of double bonds in the cyclopentadiene ring exhibits an exceptionally high mobility. Special low-temperature methods of synthesis of cyclopentadienes were developed, which made it possible to obtain the individual isomers and

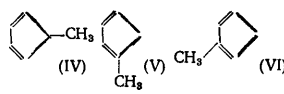
to investigate their thermal transformations. Direct interconversions of the isomeric cyclopentadienes were observed for the first time[20] in relation to 5-deuterocyclopentadiene (I) synthesised by treating cyclopentadienylmagnesium bromide with deuterium oxide at −5 °C. In the course of 1 h at 60 °C the diene (I) was converted into a mixture of equal amounts of 5-, 1-, and 2-deuterocyclopentadienes (I), (II), and (III), the transformation not being accompanied by hydrogen exchange between the molecules[20,26]:



(I) (II) (III)

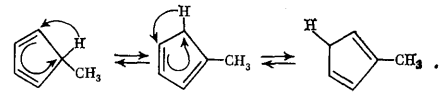
Mironov and coworkers[20,26] explained this process by the irreversible migration of the double bond system with a simultaneous shift of the hydrogen atom from the 5-position of the cyclopentadiene ring, which leads to the establishment of thermodynamic equilibrium involving isomers (I)–(III). In structure (I) a shift of the double bonds is also possible as a result of the analogous migration of the deuterium atom, although such rearrangement is degenerate, since it does not alter the structure of the substance. The measurement of the infrared spectra of diene (I) at successive time intervals during the attainment of the given equilibrium showed[26,27] that the deuterocyclopentadienes isomerise in the following sequence (I) ⇌ (II) ⇌ (III).

Low-temperature methods of synthesis of all three possible isomers of methylcyclopentadiene, namely (IV), (V), and (VI), have been described[22,23]:



(IV) (V) (VI)

It has been established[22,23,26] that at 298 K in the liquid and gas phases 5-methylcyclopentadiene (IV) isomerises to the 1-substituted diene (V). The reaction is virtually completed after 3 h in the liquid phase and after 4 h in the gas phase; 2-methylcyclopentadiene (VI) is then formed only in insignificant amounts (<5%). It has been noted that the concentration of isomer (IV) decreases by a factor of two after equal time intervals (the reaction half-life is constant). The diene (V) isomerises much more slowly but after 2–3 days at 25 °C in the liquid phase (and even more slowly in the gas phase) the substance is transformed into a mixture of approximately equal amounts of the 1-substituted isomer (V) and the 2-substituted isomer (VI) containing <3% of isomer (IV); subsequently the mixture composition no longer changes. Distillation of dienes (IV), (V), or (VI) at atmospheric pressure[22,23,26] (b.p. ~72 °C) leads to the formation of the same mixture of dienes (V) and (VI). The formation on thermal isomerisation of each methylcyclopentadiene of the same mixture, which subsequently does not change, enabled the authors[22,23,26] to conclude that thermodynamic equilibrium is established between the dienes. The formation of homogeneous 1-methylcyclopentadiene (V) at intermediate stages of the transformation of 5-methylcyclopentadiene into a mixture of dienes (V) and (VI) shows that, in the course of equilibration and evidently also in the state of equilibrium, the double bonds migrate selectively via a mechanism corresponding to the migration of hydrogen from the 5-position of the cyclopentadiene ring to a neighbouring carbon atom or via a 1,5-hydrogen shift mechanism†:



(IV) (V) (VI).

Analogous series of experiments were carried out by the same workers in relation to 1,2-dimethyl-,[25] 1,2,3-trimethyl-,[24] and 1,2,3,4-tetramethyl-substituted[21] cyclopentadienes. In each of the instances mentioned above the dienes were found to isomerise readily, the process being completed by the attainment of thermodynamic equilibrium between isomers differing in the position of the system of endocyclic double bonds. The sequence of the interconversions of the isomers, corresponding to the 1,5-hydrogen shift mechanism, has also been observed[24].

The experimental data described enabled the authors[26] to reach the following conclusions. At a relatively low temperature (20–80 °C) the system of endocyclic double bonds in the cyclopentadiene ring migrates and the reaction results in the formation of equilibrium mixtures of isomers. The interconversions of the isomeric cyclopentadienes take place rigorously selectively as a result of the migration of hydrogen from the 5-position in the cyclopentadiene ring to a neighbouring carbon atom (in the 1-position), which is consistent with the 1,5-hydrogen shift mechanism. The reaction proceeds via an intermolecular mechanism, since it is not accompanied by hydrogen exchange between the molecules and is of first order (the half-life of the reaction is constant and the rates of isomerisation in the liquid and gas phases are comparable).

By using procedures analogous to those of Mironov and coworkers[20,26], Roth[28] synthesised in 1964 1,2,3,4,5-pentadeuterocyclopentadiene and established that, when it is heated to 45–65 °C, the hydrogen atoms are distributed uniformly among the 1-, 2-, and 5-positions of the cyclopentadiene ring and the reaction is not accompanied by hydrogen exchange. This confirmed the conclusions of Mironov et al.[20,26] Roth[28] obtained the kinetic parameters of the isomerisation of pentadeuterocyclopenadiene: $\Delta G^{\neq} = 24.3$ kcal mol^{-1}# and $\lg A = 12.06$.

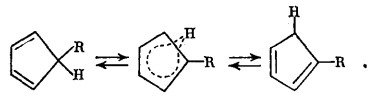
The experiments of Mironov and coworkers[22,23,26] on the synthesis and isomeric transformations of diene (IV) were reproduced[29–31], the first order of the reaction was confirmed, and $\Delta H^{\neq} = 20.4$ kcal mol^{-1} and $\Delta S^{\neq} = -10$ e.u. were found for the transformation (IV) → (V). It has been established[29] that the rate of reaction does not change when the sample of the given substance is diluted with carbon tetrachloride or when the reaction is carried out in a platinum vessel. The data of Mironov and coworkers[16,22,25,26] concerning the composition of the equilibrium mixtures of mono- and di-methylcyclopentadienes were also confirmed[29,30]. The same workers[31] reproduced the earlier experiments[20,26] on the synthesis of isomerisation of 5-deuterocyclopentadiene.

Using a method similar to that described by Mironov and coworkers[22,23,26], McLean et al.[32] synthesised in 1969 2-methylpentadeuterocyclopentadiene, compared the kinetic parameters of its conversion into the 1-isomer ($\Delta H^{\neq} = 22.35$ kcal mol^{-1}, $\Delta S^{\neq} = -6.2$ e.u.) with the corresponding values for 2-methylcyclopentadiene ($\Delta H^{\neq} = 19.9$ kcal mol^{-1}, $\Delta S^{\neq} = -10.8$ e.u.), and calculated the isotope effect $k_H/k_D = 6$. The measured quantity represents the sum of the primary kinetic isotope effect and the secondary effect generated by the four D atoms attached to the double bonds, but the latter hardly constitutes 10% of the value quoted. Thus the

† The non-traditional designation of electron transfer in this review (and in the papers quoted) is used in order to emphasise that the essential feature of the 1,5-shift is the migration of precisely the system of two double bonds.

Here and henceforth, the conversion of the values of $\Delta G^{\neq}$, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ quoted in this review to the SI system requires their multiplication by 4.18.

primary kinetic isotope effect of the 1,5-hydrogen shift in the series of cyclopentadienes greatly exceeds the value which might have been expected from the difference between the dissociation energies of the C–D and C–H bonds. This shows that in the transition state the migrating hydrogen (deuterium) atom is equidistant from the initial ($C_{(5)}$) and final ($C_{(1)}$) migration centres:



This mechanism has also been confirmed by the high negative entropy of activation for the reaction $\Delta S^{\neq} = -8$–10 e.u., corresponding to a rigorously ordered transition state, which also explains satisfactorily the rigorous sequence of the interconversions of the isomers.

Virtunlly all subsequent studies[33–50] on cyclopentadiene derivatives were carried out taking into account the high rate of their isomerisation. The rate of the isomeric transformations of cyclopentadienes depends significantly on the nature of the substitution. Thus in 5-substituted cyclopentadienes the 1,5-shift of hydrogen takes place at a rate much higher than in their isomers with a free methylene group[22,23]. The accumulation of alkyl groups in the cyclopentadiene ring lowers the rate of reaction appreciably[26,30]. Electron-accepting substituents apparently exert the opposite effect[5].

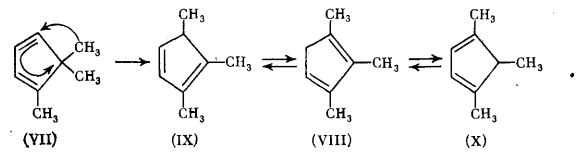
The kinetic measurements described above were performed for the virtually irreversible reaction (IV) → (V). Recently a study has been made[51] of the kinetics of the reversible isomerisation of thermodynamically stable cyclopentadienes, namely (V) ⇌ (VI), starting with the pure diene, at 50–80 °C. The values obtained were $\Delta H^{\neq} = 20.5$ kcal mol^{-1} and $\Delta S^{\neq} = -15.7$ e.u. for the reaction (VI) → (V) and $\Delta H^{\neq} = 20.6$ kcal mol^{-1} and $\Delta S^{\neq} = -15.1$ e.u. for the reaction (V) → (VI). It is striking that, within the limits of the accuracy of the measurements, the enthalpies of activation for the reactions (IV) → (V) [29,32] and (V) → (VI) [51] are the same. This permitted the conclusion[51] that the sharp difference between the rates of the above processes is virtually caused solely by the entropy factor. In other words, the difference between the rates of the 1,5-shift of hydrogen in cyclopentadienes which are isomeric as regards the position of the system of endocyclic double bonds is determined mainly by the entropy of activation. Hence the relative thermodynamic stability of isomers and correspondingly their concentrations in the equilibrium mixture should depend to a large extent on their entropies.

The compositions of the equilibrium mixtures of substituted cyclopentadienes have now been fairly thoroughly investigated and the general trend is known—5-substituted cyclopentadienes are energetically less favourable than their isomers with a free methylene group[26]. The change in the nature of the alkyl group in monoalkylcyclopentadienes is not reflected in the composition of the equilibrium mixture (1- and 2-alkylcyclopentadienes in proportions of 44 : 56).[52] As a result of the presence in the cyclopentadiene ring of substituents lengthening the conjugation chain, the dominant isomer (not lets than 95%) in the mixture has the structure of the 1-isomer (phenylcyclopentadiene[9], cyclopentadienecarboxylic acid[3,7,53], its methyl ester[3,7], and chloride[54]). However, the introduction of the same groups in the side chain of an alkylcyclopentadiene, even in the α-position, hardly affects the composition of the equilibrium mixture compared with alkylcyclopentadienes[55].

It is known[31,56] that the migration of the system of double bonds in cyclopentadienes is accelerated by strong bases. Thus, in the presence of sodium amide in liquid ammonia, the alkylation of the cyclopentadienyl anion leads directly to equilibrium mixtures of alkylcylopentadienes even at 240 K.[52,56,57] Sodium hydroxide in methanol also catalyses the isomeric transformations of cyclopentadienes[31]. However, under the conditions of alkaline catalysis hydrogen exchange takes place in cyclopentadienes[31]; presumably in this instance the reaction proceeds via a mechanism different from that indicated above, namely via the heterolytic dissociation of the C–H bond in the 5-position in the cyclopentadiene ring with subsequent protonation of the resulting cyclopentadienyl anion.

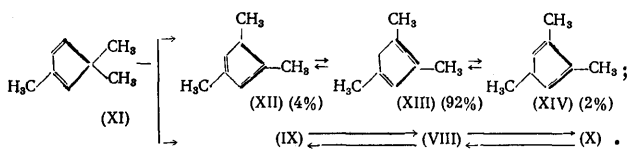
2. The 1,5-Shift of the Alkyl Group

The irreversible thermal isomerisation of 1,5,5-trimethylcyclopentadiene (VII) to 1,2,3-trimethylcyclopentadiene (VIII) in the gas phase at 623 K has been observed[4]. It was subsequently established[56,58–61] that this reaction leads to an equilibrium mixture of vicinally substituted trimethylcyclopentadienes, in which isomer (VIII) predominates[24]:



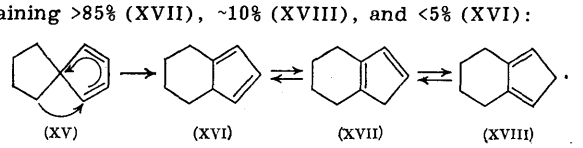
The following kinetic parameters have been obtained for this reaction: $\Delta H^{\neq} = 40.3$ kcal mol^{-1} and $\Delta S^{\neq} = -1$ e.u. (350° to 400 °C) according to the data of de Haan and Kloosterzieb[58,59] and $\Delta H^{\neq} = 43.8$ kcal mol^{-1} and $\Delta S^{\neq} = 0.7$ e.u. (328–430 °C) according to the data of Herndon and Manion[60,61].

Isomerisation of the same type has been observed[59] in relation to 2,5,5-trimethylcyclopentadiene [$\Delta H^{\neq} = 44.2$ kcal mol^{-1} and $\Delta S^{\neq} = 6$ e.u. for the reaction (XI) → (VIII) + (IX) + (X) and $\Delta H^{\neq} = 44.4$ kcal mol^{-1} and $\Delta S^{\neq} = 3$ e.u. for the reaction (XI) → (XII) + (XIII) + (XIV)]:



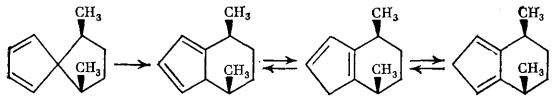
Like compound (XI), 5,5-dimethylcyclopentadiene[56,62] is converted at 220–330 °C into a mixture of 1,2- and 2,3-dimethylcyclopentadienes ($\Delta H^{\neq} = 43.3$ kcal mol^{-1} and $\Delta S^{\neq} = 3$ e.u.[62]).

Isomerisation involving spiran cyclopentadienes can proceed via the same mechanism; thus spiro[4,4]nona-2,4-diene (XV) is smoothly converted at 503–593 K in the gas phase[63,64] into an equilibrium mixture of compounds of the tetrahydroindene series—bicyclo[4,3,0]nonadienes (XVI), (XVII), and (XVIII), containing >85% (XVII), ~10% (XVIII), and <5% (XVI):



The results of Mironov and coworkers[63,64] were subsequently confirmed[65]; the following kinetic parameters were obtained for the reaction (XV) → (XVI) + (XVII) + (XVIII): $\Delta H^{\neq} = 34.6$ kcal mol^{-1} and $\Delta S^{\neq} = -1$ e.u. The study of the same reaction in relation to the *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-2,4-dienes showed[66] that the isomerisation

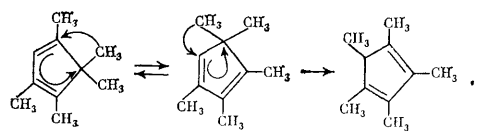
takes place rigorously stereospecifically with retention of the configuration of the initial compound, for example:



An analogous isomerisation has been observed for spiro-[4,5]deca-2,4-diene[65] ($\Delta H^{\neq} = 45.5$ kcal mol^{-1} and $\Delta S^{\neq} = 6$ e.u.). The composition of the equilibrium mixture of bicyclo[5,3,0]decadienes formed [90% of the 1(5),2-isomer] is extremely close to that mentioned above for the analogue with a six-membered ring. It is of interest that the isomerisation of spiro[4,3]octa-2,4-diene to a mixture of bicyclo-[3,3,0]octadienes [the 1,4- and 1(5),2-isomers in proportions of 1 : 1.3], with conversion of the four-membered ring into a five-membered ring[67], takes place already at 100 °C, i.e. much more readily than for the analogues described above ($\Delta G^{\neq} = 29.2$ kcal mol^{-1}, $\lg A = 13.8$)§. This reaction is virtually irreversible, because the isomers of cyclopentadienes containing two alkyl groups in the 5-position are thermodynamically unstable (cf. the 5-substituted cyclopentadienes described above).

In all the cases mentioned above the isomerisation of 5,5-disubstituted cyclopentadienes takes place selectively via the intramolecular migration of the alkyl group from the 5-position to a neighbouring carbon atom (via the 1,5-shift mechanism), since the reaction results in the elimination of the geminal substitution and the formation of 1,3-shift products has not been observed in any instance. In the concluding stage of the process equilibrium is established between isomers which differ by the positions of the endocyclic double bonds as a result of the 1,5-shift of hydrogen at a higher rate than the shift of the substituent.

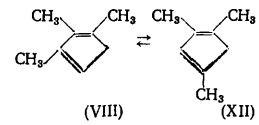
The thermal transformations of a series of 5,5-disubstituted cyclopentadienes, in which the 1,5-shift of the alkyl group should not lead to the elimination of geminal substitution, i.e. to cyclopentadienes with substituted 1- and 4-positions, have been investigated. It has been established[69–71] that 1,2,4,5,5-pentamethylcyclopentadiene (XIX) is converted at 400–500 °C (contact time ~8 s) into 1,2,3,4,5-pentamethylcyclopentadiene (XX) with 1,2,3,4,5-pentamethylcyclopentadiene (XXI) as the intermediate:



(XIX) (XXI) (XX)

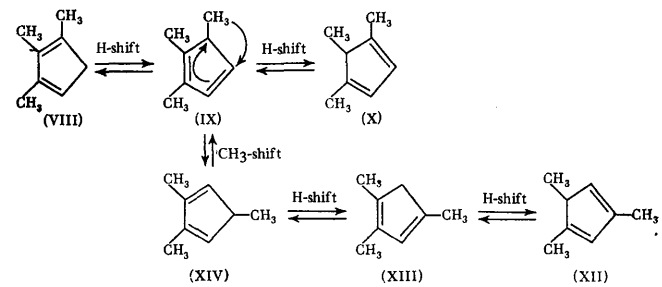
The formation of a *gem*-substituted diene (XXI) at intermediate stages shows that the reaction is a combination of two consecutive 1,5-shifts of the methyl group. The first, rate-limiting stage is the reversible isomerisation (XIX) ⇌ (XXI), which does not affect the geminal substitution; the second, irreversible stage (XXI) → (XX) leads to a thermodynamically stable diene, in which there is a possibility of a 1,5-shift of hydrogen. An analogous transformation at a somewhat lower temperature (330–460 °C) has been observed for 1,4,5,5-tetramethylcyclopentadiene[56,72].

In thermodynamically stable cyclopentadienes (with a free methylene group) reversible skeletal isomerisation, which leads to equilibrium mixtures of dienes differing in the nature of substitution, is observed at 400–500 °C (contact time ~8 s). An isomerisation of this type was observed for the first time in 1968 by Mironov and coworkers[73–75], who showed that at 400–500 °C 1,2,3- and 1,2,4-trimethylcyclopentadienes (VIII) and (XIII)¶ form an equilibrium mixture containing 55% of the "1,2,3-isomers" (VIII)–(X) and 45% of the "1,2,4-isomers" (XII)–(XIV):



(VIII) (XII)

The recorded rate of isomerisation (VIII) → (XII) is appreciably higher than that of the reverse reaction (XII) → (VIII), while the ratio of the concentrations of the groups of isomers [(VIII)–(X)] : [(XII)–(XIV)] in the state of equilibrium is 1.22 : 1. Hence it was concluded[73–75] that structures (VIII) and (XII) are not directly responsible for the transformation under discussion and that the intermediates are 5-substituted cyclopentadienes. Bearing in mind that the rate of reaction is satisfactorily correlated with the content of isomers (IX) and (XIV) in the corresponding initial equilibrium mixtures, the following scheme was considered as the reaction mechanism:



The initial stage of the process is migration of hydrogen leading to an unstable isomer containing the migrating substituent in the 5-position. The rate-limiting stage of the isomerisation is the reversible intramolecular 1,5-shift of the methyl group (IX) ⇌ (XIV). In the concluding stage of the reaction equilibrium with respect to the positions of the double bonds is established for an isomer with another type of substitution.

Under similar conditions, reversible skeletal isomerisation of 1,2- and 1,3-dimethyl-substituted[76] and also of 1,2- and 1,3-di-s-butyl-substituted cyclopentadienes[57] has been observed. In both cases equilibrium mixtures of isomers, differing in the relative positions of the substituents, were obtained. It was noted[57] that the rate of migration of the s-butyl group is higher than that of the methyl group.

1,2,3,4-Tetramethylcyclopentadiene, containing a [^{14}C]-labelled methyl group in the 1(4)-position, has been synthesised and its thermal transformations have been investigated[77]. It has been established that at 400–500 °C the label is uniformly distributed between the methyl groups in the 1(4)- and 2(3)-positions; the appearance of a labelled carbon atom in the ring was not noted. This result agrees well with the mechanism of the isomerisation of thermodynamically stable cyclopentadienes described above, in which the main stage is the reversible thermal intramolecular 1,5-shift of the alkyl group and it makes it possible to rule out unambiguously the

§ The thermal transformations of spiro[4,2]hepta-2,4-diene takes place in a different way, leading to a complex mixture of hydrocarbons containing 6-methylfulvene, allylcyclopentadienes, and 1,2-dimethylcyclopent-3-ene[63,68].

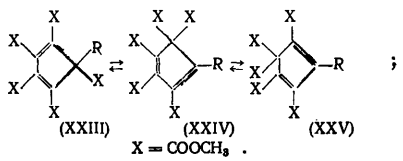
¶ More precisely the corresponding equilibrium mixtures of isomers with respect to positions of the double bonds in which the given dienes predominate.

alternative mechanism involving the rupture of the cyclopentadiene ring at the $C_{(1)}$–$C_{(5)}$ bond and subsequent recyclisation in the direction of CH_3 at $C_{(1)}$–$C_{(4)}$ (with transfer of the reaction centre and the shift of a hydrogen atom—cf. Section IV).

Thus in the series of substituted cyclopentadienes four types of migration of the alkyl group at 200–450 °C, leading to a change in the nature of the substitution, have been observed: (1) reversible thermal isomerisation of 5,5-disubstituted cyclopentadienes, which does not affect the geminal substitution; (2) irreversible thermal isomerisation of 5,5-disubstituted cyclopentadienes to dienes with a free methylene group; (3) irreversible thermal isomerisation of 5,5-disubstituted cyclopentadienes containing substituents in the 1- and 4-positions to dienes with a free methylene group, which constitutes a combination of the two types of isomerisation specified above; (4) reversible thermal isomerisation of cyclopentadienes with a free methylene group, which leads to the formation of equilibrium mixtures of dienes differing in the nature of the substitution.

The 1,5-shift of the alkyl group is independent of the type of substitution and constitutes a general feature of the series of cyclopentadienes. One must note that in each case the 1,5-shift of the alkyl substitutent is accompanied by the migration of the system of endocyclic double bonds, which indicates the similarity of the phenomena under discussion to the 1,5-shift of hydrogen. The transition state in reactions involving the 1,5-shift of an alkyl group is apparently also close to that described for the hydrogen shift. This is confirmed by the rigorously consecutive sequence of transformations and their stereospecificity.

The substitutents in the cyclopentadiene ring other than alkyl groups are also capable of migrating. Thus it has been observed[78–80] that the group $COOCH_3$ can migrate via the 1,5-shift mechanism, for example, in compounds (XXIII)–(XXV):



(XXIII) (XXIV) (XXV)

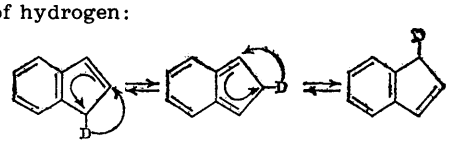
X = $COOCH_3$.

At 100–150 °C the transformation (XXIII) → (XXIV) takes place and at higher temperatures transformation (XXIV) → (XXV) occurs. The results of kinetic measurements for isomerisation of the type (XXIII) → (XXIV) are presented in Table 1. The reaction is of first order and the entropy of activation is typical for a 1,5-shift. It is striking that the migration of the methoxycarbonyl group takes place much more readily than that of an alkyl group but with much more difficulty than the 1,5-shift of hydrogen. It is noteworthy that the rate of isomerisation (XXIII) → (XXIV) depends significantly on the nature of the ring substituent (Table 1).

On the basis of the data of Bladon et al.[81], it can be postulated that the phenyl group in cyclopentadienes migrates under less severe conditions than the methyl group: according to Bladon et al.[81], the reduction–dehydration of 3,4-diphenylcyclopent-3-en-1-one (with distillation of the reaction product at 250 °C) leads to the formation of 1,4-diphenylcyclopentadiene and not the 1,2-isomer, the former being evidently the product of the skeletal isomerisation of the 1,2-isomer formed initially via the mechanism described above. Thus in the cyclopentadiene series there is a possibility of both the 1,5-shift of hydrogen (20–80 °C) and the 1,5-shift of substituents (100–400 °C). The latter takes place under much more severe conditions and is accompanied by the 1,5-shift of hydrogen in the final and sometimes also the initial dienes.

III. INDENES

It was shown in 1964 [28] that heating of 1-deuteroindene (XXVI) at 200 °C leads to a uniform distribution of deuterium between the three non-aromatic carbon atoms in the absence of hydrogen exchange between the molecules. Hence, by analogy with cyclopentadienes[26], it was concluded[28] that in compounds of the indene series there is a possibility of a 1,5-shift of hydrogen:



(XXVI) (XXVII) (XXVIII)

Despite the fact that the reaction proceeds in the given instance via a stage involving the formation of the energetically unfavourable isoindene (XXVII), it always involves a 1,5-shift and not a 1,3-shift, in which the above stage is missing.

Table 1. Kinetic parameters of the 1,5-shift of the $COOCH_3$ group in 5-R-pentamethoxycarbonylcyclopentadienes (XXIII) → (XXIV)*.

R	t, °C	Solvent	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	Refs.
$N(CH_3)_2$	49–80	DCB**	21.7	−12.1	[80]
NHC_6H_5	49–80	DCB	21.2	−11.6	[80]
CN	85–129	DCB	24.0	−10.3	[80]
OCH_3	96–129	DCB	22.4	−15.0	[80]
C_6H_5	93–128	DCB	25.5	−10.6	[80]
CH_3COOCH_3	113–150	chlorobenzene	25.3	−9.7	[78]
	99–129	DCB	27.8	−4.8	[79]
$CH_3COOC_2H_5$	97–120	toluene	25.3	−10.9	[78]
	97–120	chloroform	25.2	−10.9	[79]
CH_3	104–144	DCB	26.9	−8.6	[79]
C_2H_5	99–129	DCB	29.3	−3.4	[79]
$CH(CH_3)_2$	99–129	DCB	30.6	+1.2	[79]
SCH_3	119–155	DCB	25.0	−13.4	[80]
Cl	150–190	DCB	27.3	−10.3	[79]

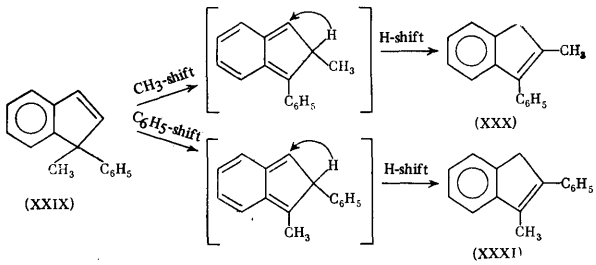
* The compounds are listed in order of decreasing rate of reaction.

**DCB = *o*-dichlorobenzene.

The isomerisation of indenes is known to be catalysed by bases, including amines[82,83]. However, a feature of such catalytic reactions, which has not so far been explained, is their stereoselectivity[84,85] and the virtual absence of hydrogen exchange[85].

The migration of a substituent in the indene series has been known for a relatively long time. In an early study Ziegler and Crössman (1929) observed[86] the irreversible isomerisation of 1,3,3-triphenylindene to 1,2,3-triphenylindene at 400 °C (the reaction mechanism was not discussed). At 450 °C thermodynamic equilibrium is established between the isomeric 1,3-, 1,2-, and 2,3-diphenylindenes[87]. Under the same conditions, the isomerisation of 1-methyl-1,3-diphenylindene to a mixture of 1-methyl-2,3-diphenyl- and 3-methyl-1,2-diphenyl-indenes has been observed[87]. The experimental data described can now be readily interpreted by a combination of consecutive 1,5-shifts of the substituent and hydrogen, by analogy with that described in the preceding Section. The 1,5-shift of substituents in indenes has

been observed directly in a study[88] devoted to the thermal transformations of 1-methyl-1-phenylindene (XXIX):

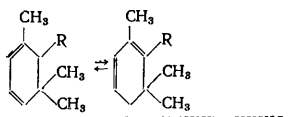


The ratio of isomers (XXX) and (XXXI) shows that the ability to migrate decreases in the sequence H ≫ C_6H_5 > CH_3, i.e. in the sequence mentioned above for cyclopentadienes. It has been reported[88] that the transformations (XXIX) → (XXX) and (XXIX) → (XXXI) are first-order reactions. Thus one must assume that the 1,5-shift reaction in the indene series has virtually the same features as for the cyclopentadienes.

IV. CYCLOHEXA-1,3-DIENES

1. The 1,5-Shift of Hydrogen

The interconversions of cyclohexa-1,3-dienes isomeric with respect to the position of the system of endocyclic double bonds were first observed in 1950 [89] in relation to the reversible isomerisation of 1,5,5,6- and 1,2,6,6-tetramethylcyclohexa-1,3-dienes (XXXII) and (XXXIII) at 350 °C, but the reaction mechanism was not investigated†:



(XXXII), (XXXIV) (XXXIII), (XXXV)

(XXXII), (XXXIII): R = CH_3

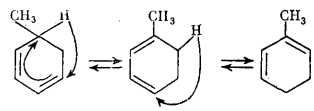
(XXXIV), (XXXV): R = H

The reversible isomerisation of 1,5,5- and 2,6,6-trimethylcyclohexa-1,3-dienes (XXXIV) and (XXV) at 300–400 °C was described[90] in 1956. It was suggested that the reaction proceeds via a "biallyl biradical" mechanism, which, in terms of modern terminology, involves ring rupture (with formation of a substituted hexatriene), the 1,7-shift of hydrogen in the resulting triene, and subsequent recyclisation (see below)#. In relation to the type of isomerisation considered, this mechanism aroused serious doubts, because it implied a change in the type of substitution during the reaction and the possibility of the degeneracy of the rearrangement to "automerisation" or a transformation without a change in the structure of the substance, for example, in the case of 5-methylcyclohexa-1,3-diene or 1,5,5-trimethylcyclohexa-1,3-diene (the isomerisation of the latter was observed in the same study[90]).

By analogy with the known behaviour of cyclopentadienes, it was later suggested[95] that the above reaction proceeds via the 1,5-shift of hydrogen and is completed by the attainment of thermodynamic equilibrium [(XXXIV) : (XXXV) ≅ 1 : 1]. An analogous hypothesis had been put forward in an earlier study[93].

In 1971 the migration of the system of double bonds in the cyclohexa-1,3-diene ring was investigated by the authors of this review[96,97]. All three possible isomeric methylcyclohexadienes with a high degree of purity were synthesised and their thermal transformations were investigated[96–98]. It was established[96,97] that the reversible isomerisation of 1-, 2-, and 5-methylcyclohexadienes (XXXVI), (XXXIII), and (XXXVIII) takes place at 300–420 °C and that each diene gives rise to the same equilibrium mixture: 57% (XXXVI), 30% (XXXVII), and 13% (XXXVIII)§.

A study of the compositions of mixtures of methylcyclohexa-1,3-dienes at various equilibration stages starting from the individual dienes (XXXVI)–(XXXVIII) showed[96] that the isomers are interconverted consecutively:



(XXXVIII) (XXXVI) (XXXVII)

The above sequence of transformations is typical for the 1,5-shift of hydrogen, which enabled the authors[96,97] to consider precisely this reaction mechanism. The following kinetic parameters of the isomerisation (XXXVIII) ⇌ (XXXVI) have been obtained[98] for the temperature range 230–250 °C: $\Delta H_1^{\neq} = 38.8$ kcal mol^{-1} and $\Delta S_1^{\neq} = -11.2$ e.u. for the reaction (XXXVIII) → (XXXVI) and $\Delta H_2^{\neq} = 38.5$ kcal mol^{-1} and $\Delta S_2^{\neq} = -14.5$ e.u. for the reaction (XXXVI) → (XXXVIII). In another study[106], where the isomerisation (XXXVIII) → (XXXVII) was regarded as an irreversible reaction, $\Delta G^{\neq} = 35.2$ kcal mol^{-1} and $\lg A = 11.2$ were obtained for the temperature range 300–360 °C. The high negative entropies of activation permitted the conclusion[98] that the reaction has a sigmatropic mechanism with a rigorously ordered transition state and the "biallyl biradical" mechanism could be ruled out[90,107], since if the latter operated the first and rate-limiting stage should have been ring opening with formation of acyclic trienes, to which positive values of $\Delta S^{\neq}$ would have corresponded.

It is striking that for significantly different rates of the reactions (XXXVIII) → (XXXVI) and (XXXVI) → (XXXVIII) (for example, the corresponding rate constants at 230 °C are 5.3×10^{-5} s^{-1} and 2×10^{-5} s^{-1}) the enthalpies of activation for the reactions are the same to within a high degree of accuracy. It has therefore been suggested[98] that the difference between the rates of the interconversions of cyclic dienes isomeric with respect to the position of the system of double bonds is determined almost entirely by the entropy factor.

Simultaneously with the above investigations[96,97] and independently of them, it has been shown[108] that mixtures of isomeric methylcyclohexa-1,3-dienes undergo a change in composition at 300–350 °C, i.e. the dienes isomerise under the experimental conditions. It has been suggested[108] that such isomerisation involves the 1,5-shift of hydrogen but no

† The formation in the synthesis of cyclohexa-1,3-dienes of isomers whose structures differ from that expected on the basis of the reaction mechanism has been observed[91–94].

The isomerisation of acyclic 3-*cis*-1,3,5-trienes to cyclohexa-1,3-dienes is one of the most thoroughly investigated electrocyclic reactions[99–104]; the process takes place quantitatively at 100–200 °C. The possibility of the reverse reaction under the conditions of the pyrolysis has been confirmed indirectly by data[105] for the conversion of cyclohexa-1,3-diene into 3-*trans*-hexa-1,3,5-triene (530 °C, yield 1%).

§ Under the given conditions, the isomerisation is not accompanied by the formation of appreciable amounts of side products; among side reactions, the aromatisation of methylcyclohexadienes via their thermal dehydrogenation[96] becomes appreciable only at 450 °C and above.

arguments in support of this have been adduced. It has also been suggested[108] that the process should lead to the establishment of thermodynamic equilibrium between the isomers, but this was not attained.

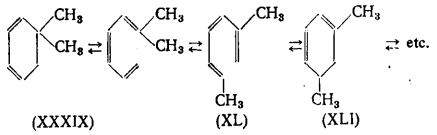
In subsequent studies[109–111] the 1,5-shift was widely used to account for the isomeric transformations of cyclohexa-1,3-dienes.

The information about the composition of the equilibrium mixtures of substituted cyclohexa-1,3-dienes is at present extremely limited, but the data available on this problem[94–96, 111] show that it is close to that of the equilibrium mixtures in the series of cyclopentadienes, which has been much more thoroughly investigated.

It is known that the isomeric transformations of cyclohexadienes can be catalysed by both acids[112] and bases[113], but in both cases the reaction mechanism is evidently different from the 1,5-shift of hydrogen.

2. The 1,5-Shift of the Substituent

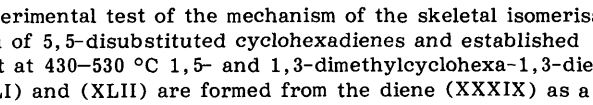
The migration of an alkyl group in the series of cyclohexa-1,3-dienes was first observed in 1956.[90,107] It was established[90] that 5,5-dimethylcyclohexa-1,3-diene (XXXIX) isomerises at 500 °C to 1,3-disubstituted cyclohexadienes, the process being accompanied by aromatisation (to the extent of ~25%; the aromatic fraction contained 33% of toluene and 67% of *m*-xylene). Analogous transformations are undergone by 1,5,5- and 2,6,6-trimethylcyclohexa-1,3-dienes (XXXIV) and (XXXV), forming 1,3,5-trimethyl-substituted cyclohexadienes, mesitylene, and *m*-xylene. The biallyl biradical mechanism has been proposed for the above skeletal isomerisation[90,107]:



(XXXIX) (XL) (XLI)

A characteristic feature of the process involving this mechanism should be a change in the type of substitution and the incorporation of the carbon atom of the side chain in the ring. It was believed that the ability of 5-ethylcyclohexa-1,3-diene (XLII) also to undergo skeletal isomerisation at 450–500 °C, leading to mixtures of 1,2- and 1,4-dimethyl-cyclohexa-1,3-dienes and the corresponding aromatic compounds, constitutes confirmation of this mechanism. It is noteworthy that the degree of conversion of the diene (XLII) into its skeletal isomer is extremely low (not more than 30% at 500 °C, including xylenes).

In 1971 the authors of this review[114,115] carried out an experimental test of the mechanism of the skeletal isomerisation of 5,5-disubstituted cyclohexadienes and established that at 430–530 °C 1,5- and 1,3-dimethylcyclohexa-1,3-dienes (XLI) and (XLII) are formed from the diene (XXXIX) as a result of the consecutive transformations (XXXIX) → (XLI) → (XLIII), corresponding to a mechanism involving the 1,5-shift of the methyl group:



(XXXIX) (XLI) (XLII) (XLIII)

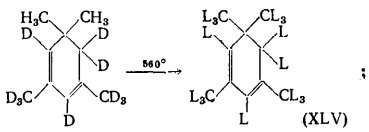
In the concluding stage of the reaction the diene (XLI) formed initially is converted as a result of the 1,5-shift of hydrogen (see above) into an equilibrium mixture of isomers, in which the diene (XLIII) predominates. The reaction is accompanied by aromatisation, toluene being formed from the initial diene (XXXIX) as a result of thermal demethylation and *m*-xylene being formed from the isomerisation products.

It has been noted[114] that the potential barrier to skeletal isomerisation in the series of cyclohexa-1,3-dienes exceeds only slightly the barrier to the hydrogen shift (in contrast to cyclopentadienes). Bearing in mind that, under the conditions of the hydrogen shift, ring opening is known not to occur (see above), presumably the skeletal isomerisation occurring under virtually the same conditions does not involve a ring opening–recyclisation mechanism[90,107] but proceeds via the 1,5-shift of the substituent.

In 1972 Spangler and Bolos[116] arrived independently at the same conclusions. As an additional argument against the ring rupture–recyclisation mechanism, they quoted the observation that the reaction products do not contain any acyclic derivatives of hexatriene. Furthermore, a special synthesis of the triene (XL) (in a mixture with the *trans,trans*-isomer), which might have been an intermediate in the ring dissociation–recyclisation process, was carried out and it was observed that during pyrolysis under identical conditions the diene (XXXIX) and the triene (XL) give rise to completely different mixtures of products[116].

Thus it was established that the irreversible 1,5-shift of the alkyl substituent takes place in 5,5-disubstituted cyclohexa-1,3-dienes in the temperature range 400–500 °C and leads to the elimination of geminal substitution, being completed by the 1,5-shift of hydrogen.

It has been observed[117] that the pyrolysis products of 1,3,5,5-tetramethylcyclohexa-1,3-diene (XLIV) with deuterium atoms in all the positions except for the two geminal methyl groups contain at 560 °C only 19% of the diene (XLV) (the rest consists of mesitylene and methylbenzenes). According to mass spectrometric data, in the absence of hydrogen exchange between the molecules the label is redistributed among the possible positions:



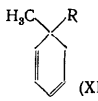
(XLIV) L = $^3/_8$H + $^5/_8$D. (XLV)

The above phenomenon was regarded[117] as proof of the ring dissociation–recyclisation mechanism for thermal transformations of the diene (XLIV). However, it is striking that the migration of the alkyl group in the cyclohexa-1,3-diene series takes place at an incomparably higher temperature than in the given experiment. We may note that the results of the above study[117] confirm unambiguously an intramolecular mechanism of the isomerisation of cyclohexadienes even under the very severe conditions used.

According to Schiess and Dinkel[118], the rate of the thermal isomerisation of 5,5-diethylcyclohexa-1,3-diene is 8 times higher than for the dimethyl analogue. At 500 °C (1 s) the reaction is accompanied by a change in the type of substituent; as a result of this (as well as aromatisation), the mixture obtained contains not less than 30 components. The change in the type of substituent can be associated in this instance solely with the rupture of the ring and recyclisation. However, the problem of the nature of the given skeletal isomerisation at 300–400 °C, i.e. under what conditions it should occur if the comparative data of Schiess and Dinkel[118] concerning its rate are correct [cf. the above considerations for the diene (XXXIX)], remains open.

At 300–500 °C non-alkyl groups, for example, the formyl, acetyl, and methoxycarbonyl groups, are capable of migrating in the ring of cyclohexa-1,3-diene.[119] The reaction

results in a mixture of products corresponding to a mechanism involving the 1,5-shift of the substituent with a subsequent 1,5-shift of hydrogen and is accompanied by extensive aromatisation (particularly on prolonged heating). Kinetic measurements[106], the results of which are presented in Table 2, permitted the conclusion that the formyl group in the cyclohexadiene ring migrates at a higher rate than hydrogen, while the methoxycarbonyl and acetyl groups migrate at a lower rate (the rate of migration of the methyl groups is lower still). The pre-exponential factors obtained[106] correspond to a high negative entropy of activation for the reaction, characteristic of the 1,5-shift.



(XLVI)

R = $COOCH_3$(a), $COCH_3$(b), CHO (c), or C_6H_5 (d).

Table 2. Kinetic parameters of the thermal isomerisation of 5,5-disubstituted cyclohexa-1,3-dienes[106].

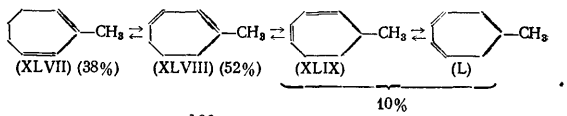
Compound	R	t, °C	$\Delta G^{\neq}$, kcal mol^{-1}	lg$A$
(XLVIa)	$COOCH_3$	270—304	40.8	11.8
(CLVIb)	$COCH_3$	200—240	35.9	12.1
(XLVIc)	CHO	150—200	31.0	11.5

The pyrolysis of 5-methyl-5-methoxycarbonyl- and 5-methyl-5-phenyl-cyclohexa-1,3-dienes (XLVI, a and d), containing a ^{13}C atom in the methyl group in the 5-position, has been investigated[118]. It was established[118] that the label in the methyl group of the diene (XLVIa) is retained to the extent of 85% at 300 °C (1 h in heptane) and 75% at 520 °C (1 s). On the other hand, in the pyrolysis products of compound (XLVId) at 550 °C (1 s) 96% of the label is concentrated in the main ring (disregarding the substituents) and only 4% in the methyl group. On the basis of foregoing, the authors[118] concluded that the migration of the substituents via the 1,5-shift mechanism takes place only when its rate is as high as for a hydrogen atom or a carbonyl group; otherwise the ring dissociation—recyclisation mechanism operates preferentially. However, the experimental data quoted by the authors[118] for the diene (XLVId) involve an evident error: in the statistical distribution of the label in the cyclohexadiene ring and in the methyl group as a result of repeated ring dissociation—recyclisation steps the content of the label in the methyl group cannot be less than ~14% (for a system comprising seven carbon atoms). Bearing in mind the above experimental error, one must suppose that above 500 °C some of the labelled carbon atoms of the methyl group enter the cyclohexadiene ring in the isomerisation process [at 530 °C this fraction is much smaller for the diene (XLVIa) than would be expected for a statistical distribution]. This agrees satisfactorily with the data described above[117].

Thus in 5,5-disubstituted cyclohexa-1,3-dienes different substituents, including alkyl substituents and those containing the carbonyl group, particularly the formyl substituent, should migrate via the 1,5-shift mechanism. Above 500 °C the reaction involves ring dissociation—recyclisation (with a 1,7-shift of hydrogen in the intermediate acyclic triene structure). It is reasonable to regard the latter process as a side reaction and not a parallel reaction, since the 1,5-shift of the substituent takes place already at 400 °C. The concluding stage of the process is in this instance the 1,5-shift of hydrogen in the resulting structures which do not contain geminal substituents.

V. CYCLOHEPTA-1,3-DIENES

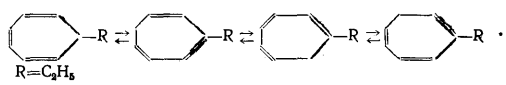
In 1970 Mironov and coworkers[120–123] described the synthesis and isomeric transformations of methyl- and monodeuterocyclohepta-1,3-dienes and established that at 120—160 °C in the liquid or gas phase 2-methylcyclohepta-1,3-diene (XLVII) undergoes reversible thermal isomerisation leading to the formation of an equilibrium mixture of the 1-, 2-, 5-, and 6-isomers (XLVIII), (XLVII), (XLIX), and (L). Here the initial product is the diene (XLVIII) and the reaction proceeds via a mechanism corresponding to the 1,5-shift of hydrogen:



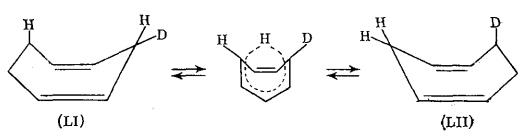
It has been established[122] that the reactions (XLVII) ⇌ (XLVIII) are of first order and have the following kinetic parameters: $\Delta H_1^{\neq} = 29.5$ kcal mol^{-1} and $\Delta S_2^{\neq} = -7.4$ e.u. for the reaction (XLVII) → (XLVIII) and $\Delta H_2^{\neq} = 28.6$ kcal mol^{-1} and $\Delta S_2^{\neq} = -9.9$ e.u. for the reaction (XLVIII) → (XLVII). Heating 2-deuterocyclohepta-1,3-diene at 140 °C leads[120,123] to a uniform distribution of deuterium between the possible positions in cycloheptadiene in the absence of hydrogen exchange between the molecules, which demonstrates an intramolecular reaction mechanism[123]. Thus it has been established unambiguously[120–123] that a reversible thermal intramolecular 1,5-shift of hydrogen takes place in the ring of cyclohepta-1,3-diene above 120 °C, leading to the establishment of thermodynamic equilibrium between the isomers with respect to the position of the system of endocyclic double bonds.

VI. CYCLOHEPTATRIENES

It has been established[124] that the pyrolysis of 7-ethylcycloheptatriene at 400 °C results in the formation of a mixture of all four possible isomers:



A 1,5-shift of hydrogen, accompanied by the migration of the system of two double bonds, has been suggested. This mechanism has been convincingly confirmed[125,126] and it has been shown that, on heating 7-deuterocyclohepta-1,3,5-triene (LI) at 100—140 °C, the deuterium is distributed between the four possible positions. This transformation takes place via an intramolecular mechanism (there is no hydrogen exchange between molecules) and the initial isomerisation product of the triene (LI) is the 3-deutero-isomer (LII). It has been suggested[125] that a non-planar symmetrical structure is formed in the transition state:



(LI) (LII)

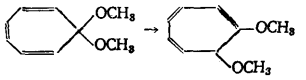
Subsequently the sequence of transformations of isomeric monosubstituted cycloheptatrienes (1,5-shift) was confirmed in a whole series of studies[127–137] dealing with the compositions of the equilibrium mixtures of cycloheptatrienes containing various substitutents [CH_3, C_6H_5, CN, OCH_3, SCH_3, $N(CH_3)_2$, p-$(CH_3)_2NC_6H_4$, COOH, or COOR]; a general tendency was demonstrated—the 7-isomers are energetically more favourable. It has been noted[129] that the presence of groups such as OCH_3 and particularly $N(CH_3)_2$ leads to a sharp increase of the rate of isomeric transformations. A thermal intramolecular 1,5-shift of hydrogen has also been observed in hexamethylcycloheptatrienes[138], in condensed systems containing the cycloheptatriene ring[139,140], in 1,4-di-(7-cycloheptatrienyl)benzene[141], and also in dihydrotropones[142].

The kinetic parameters of the thermal 1,5-shift of hydrogen in a series of cycloheptatrienes are presented in Table 3; a study was made of the transformation of the 7-isomer into the 3-isomer, which was regarded as irreversible. It has been noted[127,128] that the nature of the solvent does not affect the rate of isomerisation. In all the instances investigated the isomerisation was a first-order reaction. The extremely high negative entropy of activation for the reaction confirms the symmetry of the structure of the transition state. Thus it has been shown convincingly that a 1,5-shift of hydrogen takes place in cycloheptatrienes and involves only two of the three double bonds in the ring. The fairly close kinetic parameters of the isomerisation of methylcycloheptadienes and methylcycloheptatrienes constitute an additional confirmation of this fact.

Table 3. Kinetic parameters of the 1,5-shift of hydrogen in the series of cycloheptatrienes (7-isomer → 3-isomer).

Compound	$\Delta H^{\neq}$, kcal mol^{-1}	$\Delta S^{\neq}$, e.u.	Refs.
7-Deuterocycloheptatriene	31	−10	[125]
7-Methylcycloheptatriene	33.3	−4.9	[136]
7-Phenylcycloheptatriene	27.6	−11.6	[127]
7-Methoxycycloheptatriene	25.7	−15	[137]
7-(4-Dimethylaminophenyl)-cycloheptatriene	27.6	−9.3	[130]
1,4-Di(7-cycloheptatrienyl)benzene	29.8	−3.9	[141]

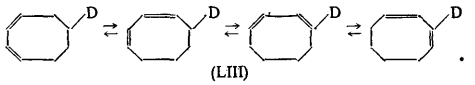
It has been established[143,144] that oxygen-containing substituents can migrate in cycloheptatrienes at 80–150 °C, for example:



This transformation has been observed[145] also in the ethylene ketal of cyclohepta-2,4,6-trien-1-one ($\Delta H^{\neq}$ = 23.2 kcal mol^{-1} and $\Delta S^{\neq}$ = −23 e.u.). The rate of migration of the methoxy-group in 7,7-disubstituted cycloheptatrienes exceeds, according to Hoffmann et al.[144], the rate of migration of hydrogen. The migration of the methoxy-group from the 7-position of the cycloheptatriene ring in trienes without geminal substituents has also been observed[144]. The combination of the shifts of a substitutent and hydrogen leads to the formation of extremely complex mixtures of compounds. According to some data[143–145], the migration of the alkoxy-group involves the 1,7-shift mechanism, i.e. all three double bonds of the cycloheptatriene ring participate in the transformation, which indicates a sharp difference between this reaction and the shift of substituents in related systems.

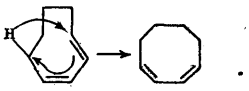
VII. CYCLO-OCTA-1,3-DIENES

In the study of the thermal transformations of 5-deutero-cyclo-octa-1,3-diene (LIII) in 1966 it was established[146] that the system of double bonds in the ring of cyclo-octa-1,3-diene migrates at 130–150 °C, which leads to the attainment of thermodynamic equilibrium between the isomers:



(LIII)

It has been shown[146] that the reaction is not accompanied by hydrogen exchange and that the sequence of the interconversions of the isomers corresponds to the scheme presented above. It has been noted that the reaction proceeds at comparable rates in the liquid and gas phases. The study of the kinetics of the isomerisation of the diene (LIII) in the temperature range 125–150 °C yielded $\Delta H^{\neq}$ = 29.3 kcal mol^{-1} and $\Delta S^{\neq}$ = −10 e.u. From the foregoing, it was concluded[146] that the reversible thermal intramolecular 1,5-shift of hydrogen takes place in cyclo-octa-1,3-dienes. In subsequent studies[147] of the quenching of the fluorescence of naphthalene under the influence of *cis,trans*-octa-1,3-diene (LIV) it was established that the observed phenomenon is due to the transformation of the diene (LIV) into its *cis,cis*-isomer (LV):

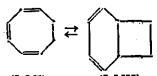


(LIV) (LV)

The authors[147] suggest that the isomerisation (LIV) → (LV) proceeds via the 1,5-shift of hydrogen ($\Delta G^{\neq}$ = 33 kcal mol^{-1}).

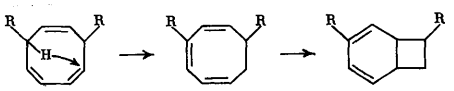
VIII. CYCLO-OCTATRIENES

The study of the migration of the system of double bonds in cyclo-octatrienes is complicated by the fact that the 1,3,5-isomer (LVI) readily undergoes the electrocyclisation reaction: as a result of the reversible reaction at 80–100 °C, equilibrium is established between the triene (LVI) (85%) and its valence tautomer—bicyclo[4,2,0]octa-2,4-diene (LVII) (15%):[148,149]



(LVI) (LVII)

The thermal isomerisation of 5,8-di(α-cyanoisopropyl)-cyclo-octa-1,3,6-triene (LVIII) to the corresponding bicyclic compound (LIX) in boiling xylene (20 h) or benzene (75 h) has been observed[150]:



(LVIII) (LX) (LIX)

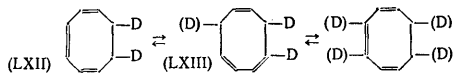
R = —C(CH$_3$)$_2$(C≡N)

The thermal isomerisation of the initial 1,3,6-triene (LVIII) to the 1,3,5-triene (LX) was regarded[150] as the intermediate stage of the reaction¶. By analogy with the isomerisation of

¶ The isolation of the homogeneous diene (LIX) from the reaction products is evidently associated with the loss of the isomer (LX) in the crystallisation process.

cycloheptatrienes described above, it was assumed that the reaction proceeds via the 1,5-hydrogen shift mechanism. The examination of a model of the initial compound led the authors[150] to the conclusion that the distance between the migrating H atom (at $C_{(5)}$) and the corresponding $C_{(1)}=C_{(2)}$ double bond is only 1.5 Å.

The reversible thermal isomerisation of cyclo-octa-1,3,6-triene (LXI) and cyclo-octa-1,3,5-triene (LVI) at 100–130 °C, leading to the formation of their equilibrium mixture containing slight (0.5–1%), but susceptible to determination amounts of the triene, (LXI), was described almost simultaneously[151]. The kinetic process parameters have been obtained (first reaction order, $\Delta H^{\neq} = 27.3$ kcal mol^{-1}, $\Delta S^{\neq} = -8$ e.u.[151], $\Delta G^{\neq} = 28.9$ kcal mol^{-1}, and $\lg A = 11.74$ [152]); it was shown[151] that the reaction proceeds at comparable rates in the liquid and gas phases. The 1,5-shift of hydrogen was considered as the reaction mechanism. This mechanism was subsequently confirmed by elegant experiments[152,153]. Thus the isomerisation of 7,8-dideuterocyclo-octatriene (LXII) [152] via the 1,5-hydrogen shift mechanism should lead to a redistribution of deuterium only between the 7(8)- and 3(4)-positions, while a redistribution of deuterium between all possible positions should correspond to the 1,3-shift of hydrogen. It has been established[152] that isomerisation results in the attainment of thermodynamic equilibrium between the trienes (LXII) and (LXIII) (isomer ratio 43.7 : 1 at 225 °C). The redistribution of deuterium takes place already at 180 °C, but even at 270 °C the label is located solely in the 3(4)- and 7(8)-positions:

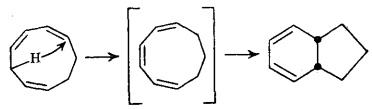


Analogous conclusions were reached in a study[153] of the thermal transformations of 5,8-dideuterocyclo-octa-1,3,6-triene as a result of the isomerisation of which the distribution of the label in the 1,3,5-triene formed also corresponds to 1,5-shift of hydrogen. The absence of hydrogen exchange between the molecules in both cases[152,153] confirms the intramolecular reaction mechanism. It has been established[152,153] that a high primary kinetic isotope effect ($k_H/k_D = 5.0$) corresponds to the isomerisation of cyclo-octatrienes with a slight secondary isotope effect (1.02–0.2). Thus the double bonds in cyclo-octatriene migrate via the 1,5-hydrogen shift mechanism.

It has been reported that the isomerisation of cyclo-octa-1,3-triene to the 1,3,5-isomer (mixed with its bicyclic valence tautomer) takes place in t-butyl alcohol in the presence of potassium t-butoxide (2 h, 90 °C) [148,149,154] or under the influence of an alcoholic solution of potassium hydroxide (4 h, 90–100 °C).[149] However, comparison with the thermal isomerisation conditions does not permit an unambiguous claim that in this case the process is vigorously catalysed by bases.

IX. CYCLONONATRIENES

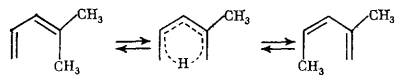
The thermal isomerisation of *cis,cis,cis*-cyclonona-1,3,6-triene to bicyclo[4,3,0]nona-2,4-diene at 200 °C was observed in 1963:[155]



The 1,5-shift of hydrogen was regarded as a hypothetical intermediate stage in the reaction[155].

X. ACYCLIC DIENES

The reversible thermal isomerisation of 4-methylpenta-1,3-diene (LXIV) to *cis*-2-methylpenta-1,3-diene (LXV) in the vapour phase at 350–450 °C (contact time ~1 s) has been described[156]:



It was concluded[156] that the transformation takes place via the 1,5-shift of hydrogen and the migration of two double bonds; a planar six-membered cyclic system was considered as the transition state in the reaction. *trans*-Dienes, incapable of forming a cyclic transition state (for example, *trans*-2-methylpenta-1,3-diene and *trans*-2,5-dimethylhexa-1,3-diene), are thermally stable. According to Wolinsky et al.[156], the (LXIV) + (LXV) equilibrium mixture contains ~80% of the diene (LXIV). Subsequently these results were reproduced[157] and it was shown that at 200 °C the equilibrium mixture contains 93% of compound (LXIV) and at 400 °C its content is 81%.

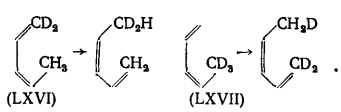
The kinetic data obtained for isomerisations of this type are presented in Table 4. In all the instances investigated the reaction is of first order and has an activation entropy characteristic of the 1,5-shift.

Table 4. Kinetic parameters of the 1,5-shift of hydrogen in the series of acyclic dienes (200–250 °C).

Compound	Reaction product	$\Delta G^{\neq}$, kcal mol^{-1}	$\lg A$	Refs.
2-Methyl-*cis*-penta-1,3-diene	4-methylpenta-1,3-diene	32.8	11.24*	[157]
2-Ethyl-*cis*-penta-1,3-diene	4-methyl-*trans*-hexa-1,3-diene	31.6	10.77	[159]
4-Methyl-*trans*-hexa-1,3-diene	2-ethyl-*cis*-penta-1,3-diene	34.5	11.03	[159]
cis-Hexa-1,3-diene	*cis, trans*-hexa-2,4-diene	32.5	10.80**	[160]
2,3-Dimethyl-*cis*-penta-1,3-diene	3,4-dimethylpenta-1,3-diene	33.8	11.13	[161]
3,4-Dimethylpenta-1,3-diene	1,3-dimethyl-*cis*-penta-1,3-diene	33.3	10.97	[161]

*$\Delta S^{\neq} \cong -8$ e.u.
**$\Delta S^{\neq} \cong -12$ e.u.

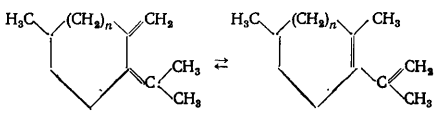
The thermal transformations of 1,1-dideutero- and 5,5,5-trideutero-*cis*-penta-1,3-dienes (LXVI) and (LXVII) have been investigated[158]:



The above reactions are not accompanied by hydrogen exchange between the molecules (intermolecular mechanism) and are not base-catalysed. Comparison of the results of kinetic measurements for the isomerisation of the diene (LXVI) ($\Delta H^{\neq} = 35.4$ kcal mol^{-1}, $\Delta S^{\neq} = -7.1$ e.u., migration of hydrogen) and the diene (LXVII) (migration of deuterium in the same system) led to $k_H/k_D = 12.2$, which agrees well with a cyclic highly symmetrical transition state.

Thus a typical 1,5-shift of hydrogen can occur in acyclic *cis*-diene systems with a chain length corresponding to more than 5 carbon atoms. We may note that the rate of isomerisation is close to that of cycloheptadienes.

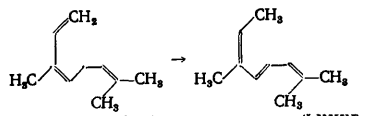
Isomerisation of a similar type also takes place in dienes with two exocyclic double bonds; for example, the reversible transformations (LXVIII)⇌(LXIX) and (LXX)⇌(LXXI) have been observed[156]:



(LXVIII), (LXX) (LXIX), (LXXI)

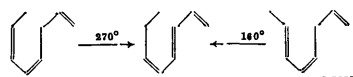
(LXVIII), (LXIX): $n = 0$ in equilibrium with ~80% (LXIX)
(LXX), (LXXI): $n = 1$ in equilibrium with ~90% (LXXI).

Two double bonds can migrate via the 1,5-shift mechanism in acyclic polyene systems; for example, the isomerisation of natural ocimene [3,7-dimethylocta-1,3,6-triene (LXXII)] to allo-ocimene [2,6-dimethylocta-2,4,6-triene (LXXIII)], which takes place at 160–190 °C, can be readily explained from these standpoints[162–164]:



(LXXII) (LXXIII)

It has been reported[165] that two double bonds in 6-*cis*,4-*cis*- and 6-*trans*,4-*cis*-octa-1,4,6-trienes (LXXIV) migrate with formation of octa-1,3,5-triene (LXXIV):

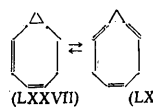


(LXXIV) (LXXVI) (LXXV)

The triene (LXXV) isomerises much more readily than its geometrical isomer (LXXIV) (at 160 °C instead of 270 °C) and the centres involved in the reaction are therefore distributed more readily in a single plane.

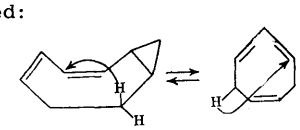
XI. HOMODIENYL SYSTEMS

Isomerisation of a similar type can occur in cyclic systems where one of the double bonds is replaced by a three-membered ring (homodienyl systems). It has been observed[151] that at 150–180 °C bicyclo[6,1,0]nona-2,4-diene (LXXVII) is converted into cyclonona-1,4,7-triene (LXXVIII):

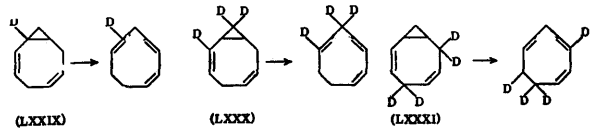


(LXXVII) (LXXVIII)

It has been established that this reaction is reversible; the equilibrium mixture contains 8–9% of compound (LXXVII). The 1,5-shift of hydrogen was considered as the reaction mechanism and the conformational proximity of the migration centres was noted:

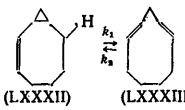


The isomerisation of bicyclo[6,1,0]nona-2,5-diene takes place similarly and the direction of the reaction (the 1,5-shift of hydrogen) has been convincingly confirmed by the study of the position of deuterium in the products of the thermal transformations of the three labelled compounds (LXXIX), (LXXX), and (LXXXI):[166]



(LXXIX) (LXXX) (LXXXI)

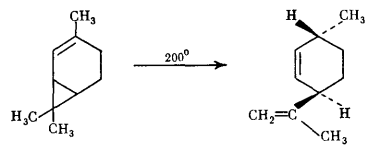
A similar reaction has been observed[146] in relation to bicyclo[6,1,0]non-2-ene (LXXXII) at 150–170 °C:



(LXXXII) (LXXXIII)

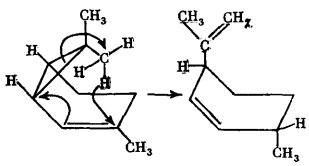
The equilibrium constant $K = k_1/k_2 = 82.3$. $\Delta H_1^{\neq} = 31.4$ kcal mol^{-1} and $\Delta S_1^{\neq} = -6$ e.u. have been obtained for the reaction (LXXXII) → (LXXXIII), which differs insignificantly from data for the 1,5-shift of hydrogen in the corresponding diene system. The rate constants for the isomerisation (LXXXII) → (LXXXIII) in the liquid and gas phases have similar values. The same isomerisation occurs[167] in *exo*-9-hydroxymethylbicyclo[6,1,0]non-2-ene at 240–340 °C, leading to the 3-hydroxymethylnona-1,4-diene. The 1,5-shift of hydrogen has also been observed in the bicyclo[5,1,0]oct-2-ene system (LXXXIV) at 180–300 °C, cyclo-octa-1,4-diene (LXXXV) being formed as a result of the reversible reaction[168]. The equilibrium constant $K = 36$; kinetic measurements led to $\Delta G^{\neq} = 38.6$ kcal mol^{-1} and $\lg A = 13.17$. It is noteworthy that a common feature of the 1,5-shift in homodienyl systems is the opening of the three-membered ring with formation of dienes containing isolated (1,4) double bonds†.

An interesting example of isomerisation in homodienyl systems with a six-membered main ring is provided by the transformations of 3,7,7-trimethylbicyclo[4,1,0]hept-2-ene (LXXXVI) (Δ^4-carene) and its derivatives into non-conjugated dienes [isolimonene (XXXVII)], which are rigorously stereospecific[174,175]:



(LXXXVI) (LXXXVII)
($a_D^{20} = +92.7°$) ($a_D^{20} = +119.5°$)

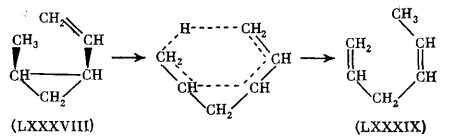
The kinetic parameters obtained for this reaction[174] are typical for the 1,5-shift of hydrogen: $\Delta H^{\neq} = 27.2$ kcal mol^{-1} and $\Delta S^{\neq} = -17.2$ e.u. The isomerisation of (+)-3-hydroxymethyl-Δ^4-carene is just as stereospecific[176]. Transformations of this type also evidently involve a transannular 1,5-shift of hydrogen, in which the hydrogen atom of the *endo*-methyl group in the 7-position, conformationally close to that of the second migration centre, is involved:



† In homodienyl systems with a smaller main ring (C_6 and smaller) the opening of the three-membered ring proceeds via a mechanism differing from the 1,5-shift[109,169–173].

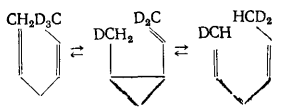
The absence of the 1,5-shift in homodienyl systems with a six-membered main ring but without an *endo*-substituent in the three-membered ring is probably due precisely to conformational factors or, in other words, to the remoteness of the hydrogen atom in the 5-position from the corresponding p-π-orbital of the double bond (in the 3-position).

In methylvinylcyclopropane systems the mechanism of the thermal transformations also depends on their configuration. Thus it has been established[177,178] that at temperatures above 160 °C *cis*-1-methyl-2-vinylcyclopropane (LXXXVIII) isomerises quantitatively to *cis*-hexa-1,4-diene (LXXXIX); under these conditions, *trans*-1-methyl-2-vinylcyclopropane is thermally stable:



(LXXXVIII) (LXXXIX)

The kinetic parameters of the reaction (LXXXVIII) → (LXXXIX) ($\Delta G^{\neq} = 31.2$ kcal mol^{-1} and $\lg A = 11.03$ according to the data of Ellis and Frey[177] and $\Delta H^{\neq} = 30.2$ kcal mol^{-1} and $\Delta S^{\neq} = -11$ e.u. according to the data of Roth and Konig[179]) are satisfactorily consistent with the 1,5-hydrogen shift mechanism. This mechanism was subsequently convincingly confirmed[179] by a study of the thermal isomerisation of 6,6,6-trideutero-*cis*-hexa-1,4-diene (XV):

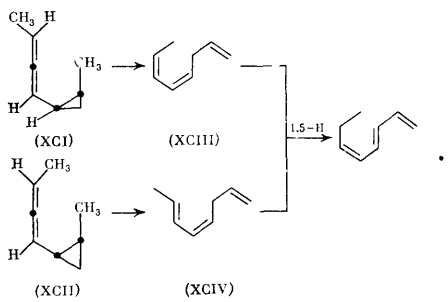


(XC)

The redistribution of deuterium between the terminal C atoms of the system can be accounted for in this instance solely by a reversible intramolecular 1,5-shift of hydrogen.

Thus the necessary and sufficient condition for the 1,5-shift of hydrogen in conjugated homodienyl systems is the coplanarity of the five C atoms which are potential participants in the reaction and the spatial proximity of the terminal C atoms in this system.

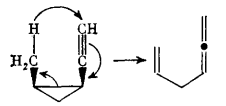
The 1,5-homodienyl shift of hydrogen has been observed recently[165] in compounds where the double bond is part of the allene system. One of the diastereoisomers of the substituted cyclopropylallene (XCI) readily isomerises in the form of a 5% solution in benzene at 125 °C to *cis*-octa-1,3,5-triene (XCIII), while the isomerisation of the other diastereoisomer (XCII) to the triene (XCVI) takes place at 160 °C at a much lower rate[165]:



(XCI) (XCIII)

(XCII) (XCIV)

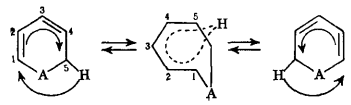
The only instance of the 1,5-shift in a system containing a triple bond is the thermal isomerisation of *cis*-2-ethynyl-1-methylcyclopropane above 350 °C; the initial product is hexa-1,2,5-triene[180]:



XII. GENERAL AND CHARACTERISTIC FEATURES OF THE REACTION AND ITS MECHANISM

The experimental data examined above show that the 1,5-shift of hydrogen or a substituent is an extremely common phenomenon in organic chemistry. This reaction is evidently characteristic of any *cis*-1,3-diene or polyene system including cyclic, acyclic, and homodienyl systems.

In general the 1,5-shift involves the displacement of a system of two double bonds to a neighbouring carbon atom (at the 5-position) and the migration of hydrogen (or a substituent) from this atom to the $C_{(1)}$ atom of the initial diene system:



(XCV)

Only the 1,3-diene system exhibits the ability to migrate, since it is well known that cyclohexa-1,4-diene[181] and cyclohepta-1,4-diene[182] do not undergo thermal isomerisation. In 1,4-dienes with C_9 and larger rings the 1,5-shift of hydrogen leads to the closure of a three-membered ring (to a slight extent as a reversible reaction). 1,4-Homodienyl systems are also thermally stable up to 500 °C, which has been established in relation to bicyclo[4,1,0]hept-3-ene[172] and 3,7,7-trimethylbicyclo[4,1,0]hept-3-ene.[175,183]

The migrating system of double bonds must have the *cis*-configuration, since the *trans*-dienes in the acyclic series (see above) as well as cyclic dienes with a fixed transoid system of double bonds do not enter into the reaction under consideration[74,96].

It has been established reliably for each of the cases discussed above that the thermal isomerisation proceeds precisely as the 1,5-shift and not the 1,3-shift, involving the migration of one of the double bonds; the latter would have led to a sequence of interconversions of isomers which has been reliably ruled out by experimental data.

In polyene chains or rings only two double bonds participate in the reaction, i.e. the thermal isomerisation involves the 1,5- and not the 1,7-shift. The migration of the alkoxy-group in the series of cycloheptatrienes (the 1,7-shift) is one of the few exceptions known at the present time.

Reactions proceeding via a stage involving the elimination of a proton, particularly in the series of cyclopenta-, cyclohexa-, and cyclohepta-dienes capable of forming the corresponding anions, can formally lead to the same final results as the 1,5-shift of hydogen (i.e. to the establishment of thermodynamic equilibrium between the isomers). However, in relation to such reactions the 1,5-shift has the following clear-cut distinctive features:

(1) The absence of hydrogen exchange in the isomerisation process (intramolecular mechanism).

(2) Comparable rates of reaction in the liquid and gas phases.

(3) A high (in absolute magnitude) negative entropy of activation ($\Delta S^{\neq} = -8$ – -12 e.u.).

(4) A high primary kinetic isotope effect $k_H/k_D \geq 6$ (for the migration of hydrogen).

(5) Stereospecificity of the reaction.

The above features of the isomerisation of diene and polyene systems make it possible to classify it unambiguously as the 1,5-shift.

The rate of isomerisation decreases in the sequence cyclopentadiene–cyclohepta-1,3-diene–cyclohexa-1,3-diene ($C_5 > C_7 \gg C_6$); comparison with the acidity sequence of hydrocarbons ($C_5 > C_6 \cong C_7$) shows that there is no charge separation in the transition state. This conclusion has also been confirmed by the weak dependence of the rate of reaction on the nature of the solvent and by the comparable rates of reaction in the liquid and gas phases. Thus the 1,5-shift is a process proceeding as a "reaction without a mechanism".

The transition state of the reaction is cyclic, rigorously ordered, and highly symmetrical, the migrating hydrogen atom being approximately equidistant from the migration centres (the 1- and 5-positions). This has been confirmed by the high negative entropies of activation for the reaction and the high primary kinetic isotope effect. This transition state corresponds to a synchronous shift of hydrogen and the double bonds. In the transition state the five carbon atoms participating in the reaction form a planar or almost planar system of the type of (XCV). A mechanism of this type is referred to as sigmatropic, since it is based on the migration of a σ-bonded hydrogen atom, which interacts in the transition state with the two ends of a 4π-electron system. The total number of electrons in the system constitutes a sextet, i.e. the most stable (according to the Hückel rule) system is formed. As a result of the reaction the π orbital of the carbon atom in the 1-position is converted into the sp^3-hybrid orbital of the new C–H bond, while the sp^3-orbital of the $C_{(5)}$–H bond is converted into the π orbital of the diene (polyene) system. A similar mechanism has been discussed in a number of studies[184–187] and has been confirmed by quantum-mechanical calculations[188].

From the standpoint of the conservation of orbital symmetry, considered in detail, for example, by Woodward and Hoffmann[187] and Gilchrist and Storr[189], the fact that the isomerisation of diene and polyene systems takes place as the 1,5-shift has been explained on the basis of selection rules. This mode of reaction is of the suprafacial type[187,189], i.e. the *s* orbital of hydrogen overlaps a lobe of the *p* orbital of carbon in the 1-position located on the same side of the plane; this overlap makes the given process allowed for the thermal reaction. In the same systems the 1,3- and 1,7-shifts should proceed via an antarafacial pathway with participation of the *p* orbital on the opposite side of the plane of the system. In the 1,3-shift such overlap requires a considerable angular strain in the molecule and it does not therefore occur under the conditions of the thermal reaction. For the 1,7-shift, the antarafacial pathway in the thermal reaction is in principle possible, but in this case the potential barrier to the reaction is much higher than for the 1,5-shift.

The velocity of the 1,5-shift of hydrogen in different systems varies within fairly broad limits. The reaction takes place most readily in cyclopentadienes ($\Delta G^{\neq} \cong 20$ kcal mol^{-1}) and with the greatest difficulty in cyclohexadienes ($\Delta G^{\neq} \cong 39$ kcal mol^{-1}); for cycloheptadienes as well as dienes and trienes with large rings, $\Delta G^{\neq} = 29$–31 kcal mol^{-1}. Presumably the above differences are associated with the distance between the $C_{(1)}$ and $C_{(5)}$ migration centres; in other words, the ease of isomerisation is determined by the conformational proximity of the $C_{(5)}$–H bond and the π orbital of the $C_{(1)}$ atom. Cyclopentadiene is known to have a planar conformation[190–192], the cyclohexa-1,3-diene molecule is almost planar[193], while the cyclohepta-1,3-diene[194] and cyclo-octa-1,3-diene molecules[50,195–197] are non-planar and have a large dihedral angle; for higher cyclodienes, a non-planar configuration is apparently also typical. An approximate estimate of the distances between the migration centres (the 1- and 5-positions) in cyclopenta-, cyclohexa-, and cyclohepta-dienes in the given conformations shows that, in terms of this distance, the cyclic dienes can be arranged in the sequence $C_5 < C_7–C_9 \ll C_6$, which is satisfactorily correlated with the sequence based on decreasing rates of isomerisation.

The 1,5-shift of substituents in all the cases investigated takes place under more severe conditions than the 1,5-shift of hydrogen; the greater the ease of migration of hydrogen in the given system, the greater the difference between the rates of migration of hydrogen and substituents. Evidently the shift of substituents takes place fundamentally via the same pathway as the shift of hydrogen. The lower rate of migration of alkyl groups is apparently due to the fact that the ability of the *s* orbital of hydrogen to form a "bridge"[189] bond in the transition state is greater than that of the sp^3-hybrid orbital of the alkyl group. The more pronounced *s* character of the sp^2-hybrid orbital in the phenyl group can account for the greater rate of its migration compared with that of the alkyl group.

In all cases the 1,5-shift of hydrogen is completed by the establishment of thermodynamic equilibrium between the isomers with respect to the position of the system of endocyclic double bonds. The composition of the equilibrium mixture is determined by the operation of thermodynamic factors alone. Two limiting cases are possible in principle: (1) if the difference between the free energies of the isomers is close to zero, their concentrations in the equilibrium mixture are practically equal; examples of such mixtures are provided by deutero-derivatives of dienes and polyenes; (2) if one of the isomers is much more favoured by energy factors ($\Delta\Delta G > 1.5$ kcal mole^{-1}), than its concentration in the equilibrium mixture is close to 100%; examples of such systems are provided by 1,2,3- and 1,2,4-trimethylcyclopentadienes (see above).

Comparison of the compositions of the equilibrium mixtures in different series revealed general features; (a) a lower stability of isomers containing a substituent in the methylene groups; (b) comparable thermodynamic stabilities of isomers differing in the position of an alkyl group attached to the system of double bonds; (c) the fact that isomers containing a substituent which lengthens the conjugation chain inthe 1-position are preferred. These features should apparently hold for the substituted *cis*-dienes which have not yet been investigated.

For cyclic diene systems, the main contribution to the difference between the free energies of the isomers comes from the entropy factor. Hence one may conclude that the composition of the equilibrium mixtures of cyclic dienes and polyenes should vary insignificantly within wide temperature limits, since the temperature dependent term in the equation defining the equilibrium constant is either small or close to zero. The temperature dependence of the composition of the equilibrium mixtures has been hardly investigated, but comparison of the ratios of the isomeric 1,2,3,4-, 1,2,3,5-, and 1,2,4,5-tetramethylcyclopentadienes at 20 °C (79 : 10 : 11)[21,77] and 500 °C (79 : 5 : 16)[77] confirms this hypothesis.

Systems in which there is a possibility of a 1,5-shift of hydrogen or a substituent are naturally not exhausted by those listed above. Presumably transformations of this type will be discovered in the immediate future for other representatives of the class of *cis*-diene and polyene structures, including homodienyl structures. In particular, the 1,5-shift of substituents, especially functional groups, has been virtually uninvestigated for systems with more than seven carbon atoms in the ring.

In conclusion one should note that the possibility of a 1,5-shift, particularly the 1,5-shift of hydrogen, should be taken into account in the study of any chemical reactions of dienes and polyenes.

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