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HYDROGEN MIGRATION IN CYCLOPENTADIENES

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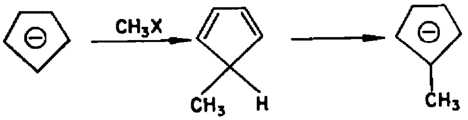
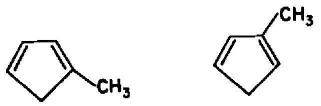
Abstract—A kinetic study of the rearrangement of 5-methylcyclopentadiene to 1-methylcyclopentadiene has been made, using NMR to monitor the reaction. In the absence of a strong base, the rearrangement took place through an intramolecular 1,2 hydrogen shift and showed the characteristics of a homogeneous reaction following the first order rate law. The activation energy and entropy were determined from the temperature dependence of the rate. Base did not catalyze this process, but, in the presence of a sufficiently strong base, an alternative process involving the intermediacy of the methylcyclopentadienide anion became an important route for isomerization. A study of the rearrangement of 1,5-dimethylcyclopentadiene was also made. Results from these experiments and other more approximate data serve as a basis for a discussion of the mechanism of the rearrangement.

In the studies[2] of the alkylation of the cyclopentadienide anion (I) considerable difficulty was experienced in isolating cyclopentadienes with one substituent at C-5 (e.g. II), the products expected from a simple reaction between sodium cyclopentadienide and, for example, methyl iodide; instead, rearranged products (e.g. IV and V) resulting from hydrogen migration were isolated. It became of considerable interest in the study of the nature of the alkylation reaction to determine whether the rearrangement involved loss of a proton to form an anion (e.g. III) which was then reprotonated, or whether an intramolecular hydrogen shift took place. Since it had already been demonstrated[3] that proton exchange between diene and anion can take place, the question at issue was whether it was necessary to postulate such a process in all cases, including those in which attempts had been made to keep the anion concentration to a minimum.



I II III



IV V

Coincidentally with this work, Mironov *et al.*[4] had also noted the lability of dienes such as II; they had succeeded in isolating II under carefully controlled conditions and, using Raman spectroscopy to monitor the course of the reaction, they made a

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[1] Holder of National Research Council (Canada) Scholarship (1963–1964).

[2] S. McLean and P. Haynes, *Tetrahedron* (21, 2313 (1965) *with this paper*).

[3] S. McLean and P. Haynes, *Canad. J. Chem.* 41, 1231 (1963).

[4] V. A. Mironov, E. V. Sobolev and A. N. Elizarova, *Tetrahedron* 19, 1939 (1963), and other papers reviewed there.

study of the rearrangement. Their results show that II rearranges to IV following first order kinetics, and the latter then rearranges to V. We have succeeded in isolating 5-methylcyclopentadiene[2] by a method similar to Mironov's, and, as we have pointed out in a preliminary communication,[5] we have confirmed his general observations and carried out a more extended study using a very simple NMR technique to monitor the reaction.

RESULTS

Rearrangement of 5-methylcyclopentadiene

The isomeric methylcyclopentadienes (II, IV, V) have distinctive NMR spectra,[2] and by observing the spectrum of II at the normal temperature of the probe, we were able to record its decay and replacement by the spectrum of IV, which was stable for a much longer period. Examination of the spectrum also established that the Diels–Alder dimerization of the dienes did not compete significantly with the rearrangement of II to IV, but it possibly became an important factor in the subsequent decay of IV.

For a quantitative kinetic study, the CH_3 signal (a doublet at 8·92 τ)[2] was the most distinctive feature of II and this was used to measure the progress of the rearrangement; because of the resolution and symmetry of the signal, its distance from the corresponding signal of the rearranged product, and the convenient rate of the reaction, it was possible to use the mean peak height of the doublet as a direct measure of the concentration of II. To correct for variations in instrument response with time, it was highly desirable to record peak heights in units based on the height of a standard peak produced by a reference compound; such a peak was normally present since, during the isolation of II,[2] the distillation from the reaction mixture carried over a small amount of diglyme (diethylene glycol dimethyl ether), the CH_3 signal of which was admirably suited for use as a reference. It was established that this contaminant did not affect the kinetics of the rearrangement, since variations in the concentration of diglyme down to vanishingly small values (by repeated vacuum distillation of the sample) did not change the rate of decay of II. It was possible to carry out the complementary study of the rate of growth of the CH_3 signal (a closely spaced doublet at 8·04 τ)[2] of IV. In this case, the proximity of the CH_3 signal (a closely spaced multiplet at about 8·05 τ)[2] of V made the technique somewhat more difficult and the results less reliable, but, as has been stated already, the appearance of the complete spectrum showed that IV was in fact the immediate product of rearrangement, and this was confirmed by vapour phase chromatography and by converting the components of a particularly rearranged sample to their N-phenylmaleimide adducts[2] and showing that the adduct of IV was the principal product.

The spontaneous decay of II followed the first order kinetic law accurately over the whole of the observable course of the reaction. In general, it was not possible to observe the commencement of the reaction since some rearrangement took place during introduction of the sample into the probe and adjustment of the instrument; in the best cases, however, the course of the reaction could be followed from a point where only a very small amount of rearrangement had taken place to a point where II could no longer be detected in the spectrum. Results are recorded in Table 1 as first order constants, k_1, for the statistically-corrected rate of hydrogen migration; these

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[5] S. McLean and P. Haynes, *Tetrahedron Letters* 2385 (1964).

TABLE 1. STATISTICALLY-CORRECTED RATE OF HYDROGEN MIGRATION FOR 5-METHYLCYCLOPENTADIENE

Reaction conditions		k_1 (sec^{-1} × 10^5)
neat	5°*	2·87
neat	10°*	4·96
neat	15°*	9·44
neat	20°*	16·6
neat	27°	36·5
neat Pt vessel	27°	37·3
neat	29°	50·8
20% in CCl_4	29°	48·6
10% in CCl_4	29°	49·1
neat† Me_3SiCl-treated tube	30°*	58·8
neat†	30°	62·0
neat	40°*	168

* used for Arrhenius plot
† diglyme absent

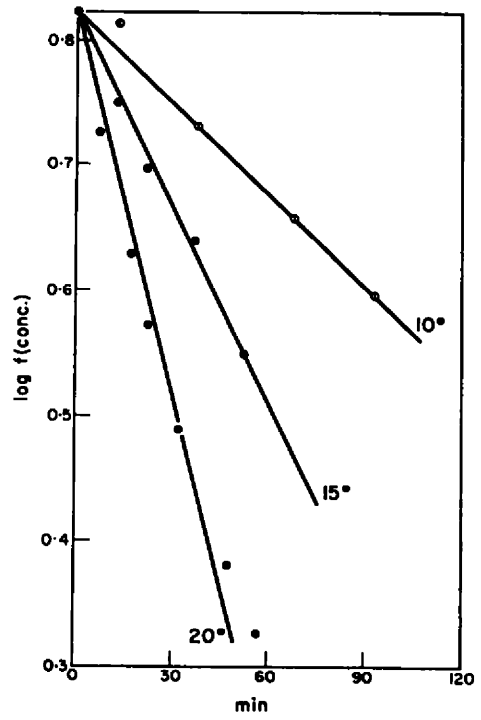

FIG. 1. Decay of 5-methylcyclopentadiene at three temperatures (°C).

are $\frac{1}{2}$ k_{obsd} (decay of II) since there are two equivalent routes from II to IV, and, in addition, the large value of the equilibrium constant for the reaction[8] allows the rate of the reverse process to be neglected. Rates were obtained at a series of temperatures from 5° to 40°, and Fig. 1 illustrates typical rate plots at three temperatures. Despite the rather short range of temperatures at which the rearrangement could be studied by the present technique, a good Arrhenius plot (Fig. 2) was obtained, which led to an activation energy (E_a) of 20·4 kcals mole^{-1} (standard deviation 0·3 kcals mole^{-1}) and an entropy of activation of −10 e.u. (assuming a true first order reaction). The reproducibility of the kinetic data was surprisingly good in view of some of the inherent shortcomings of the technique. Signal strength cannot normally be measured to a high degree of accuracy because of variations in instrument response, and the control of probe temperature is considerably less precise than would usually be demanded in a kinetic study, particularly one where only a restricted temperature range is accessible for investigation and the rate has a strong temperature dependence.

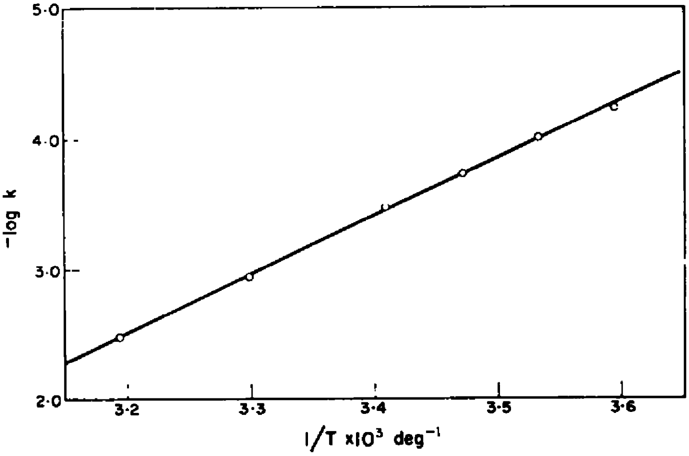

FIG. 2. Arrhenius plot of rearrangement of 5-methylcyclopentadiene.

Measurements were usually carried out using an undiluted sample, but in order to gain information on the kinetic order of the reaction, the effect of dilution of the sample with CCl_4 was investigated, and, as is shown in Table 1, the rate of decay of II remained unchanged at concentrations of sample between 10% and 100% in CCl_4 at a constant temperature. The rate of the rearrangement did not change when the glass sample tube normally employed was pre-treated with Me_3SiCl. As a further check, in one run the rearrangement was carried out in a platinum vessel and the sample removed only when a measurement was required, and again the rate was the same, within the rather larger experimental error, as that obtained by the normal technique at the same temperature. These latter experiments strongly indicate a homogeneous reaction with true first order characteristics.

In most of the kinetic runs we carried out the complementary study of the rate of appearance of IV by measuring the rate of growth of its CH_3 signal; this followed first order kinetics and gave the same slope as the decay of II up to about the half-life of II, but after that the plot began to diverge from a straight line. We had hoped to be able to get some measure of the rate of rearrangement of IV to V by observing their methyl signals, but it became clear that the resolution of the signals was not adequate. By observing other features in the spectrum, especially those arising from the methylene protons, we could see clearly that the rate constant for the appearance of V was considerably less than that for the appearance of IV; for example, in the time that II decayed from half its initial value (II and IV showed CH_3 signals of equal intensity) to zero, the increase in the methylene signal of V was immeasurably small.

Because of the difficulty in obtaining accurately functions of the concentration of IV and V, and bearing in mind that there were probably nine second order dimerizations involving II, IV and V competing at different rates with the rearrangement, we did not undertake the computational problem required to handle the kinetics of a three component system approaching equilibrium, but contented ourselves with using the very reasonable approximation required to compute the rate of rearrangement of II to IV, and the observation that the rate of rearrangement of IV to V must be smaller.

Interesting results were obtained when 5-methylcyclopentadiene was allowed to rearrange in the presence of a base. A very small amount of a strong base such as sodium cyclopentadienide in tetrahydrofuran accelerated the rearrangement enormously, making it much too fast to study kinetically by the present technique since the equilibrium mixture of II, IV and V was obtained by the time a satisfactory spectrum could be recorded. In contrast, a base such as aqueous NaOH had relatively little effect on the rate of rearrangement. We designed an experiment that would provide information on this latter point and at the same time show whether a hydrogen could be exchanged with the surrounding medium during the rearrangement. Solutions in diglyme of 5-methylcyclopentadiene (1·1 molar), D_2O (5·5 molar), and NaOD were allowed to rearrange. The concentration of NaOD was varied from zero to 0·15 molar (this was limited by the separation of the solution into two phases at higher concentrations) and for each of these solutions, the rate of rearrangement (at a fixed temperature) was determined by the usual technique, and the amount of deuterium incorporated after a standard interval (about 95% completion of the rearrangement) was determined from the mass spectrum[6] of the methylcyclopentadiene fraction isolated by VPC. The rearrangement followed first order kinetics in each case, and appeared to show a very slight increase in rate with increasing concentration of base, but the range of values obtained for k_{obsd} ($1·5 \times 10^{-3}$ to $1·9 \times 10^{-3}$ sec^{-1}) was so small that it was comparable with the experimental error. In the experiment carried out in the absence of alkali, the methylcyclopentadiene fraction showed no incorporation of deuterium (even after 24 hr, in this case); a slight incorporation (2·1%) occurred in the presence of 0·05 molar NaOH, and in the presence of 0·15 molar NaOH, 28·4% of the product had incorporated one deuterium atom and 3·0% had incorporated two. Addition of methanol had a dramatic effect, producing both marked acceleration of the rearrangement and considerable incorporation of deuterium. In this case, methanol was added to the solution containing 0·10 molar NaOH to make it 3·5 molar in MeOH; 5-methylcyclopentadiene had almost completely disappeared by the time a spectrum could be recorded and in the methylcyclopentadiene fraction (sampled after 15 min in this case, rather than at 25 min as in the others), 75% of the molecules had incorporated at least one deuterium, 26% had incorporated two deuterium atoms, and some had incorporated up to four.

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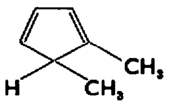
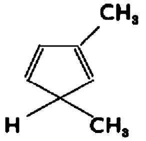
[6] We thank Mr. F. Meyer and Dr. A. G. Harrison of this Department for these measurements.

Rearrangement of 1,5- *and* 2,5-*dimethylcyclopentadiene*

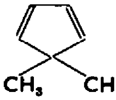
The reaction of sodium methylcyclopentadienide with methyl sulphate in diglyme at low temperatures followed by vacuum distillation produced a mixture of 1,5-(VI) (70·4%), 2,5-(VII) (20·4%), and 5,5-(VIII) (9·2%) dimethylcyclopentadienes, and a trace of diglyme.[2] It had already been shown[2] that a spontaneous rearrangement of VI, analogous to that of II, led eventually to a mixture of 1,2-(IX) and 2,3-(X) dimethylcyclopentadienes; in a similar way, VII led to 1,3-dimethylcyclopentadiene (XI), but VIII remained unchanged. The dienes were characterized by their NMR spectra, their VPC retention times, and their N-phenylmaleimide adducts.[2]



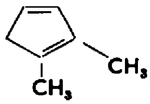
VI



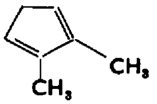
VII



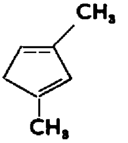
VIII



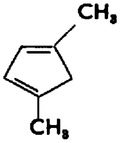
IX



X



XI



XII

A kinetic study of the rearrangement of VI was carried out by observing the decay of the C-5 methyl signal (a doublet at 8·95 τ; $J = 7{\cdot}8$ c/s) in a manner completely analogous to that used for II. Once again the first order law was followed over the accessible range; the results between 30° and 54° are recorded in Table 2 and the kinetic plots for typical runs at three temperatures are recorded in Fig. 3. Figure 4 shows the Arrhenius plot from which the values of $E_a = 23$ kcals mole^{-1} (standard deviation 1·5 kcals mole^{-1}) and entropy of activation of -4 e.u. were calculated. True first order characteristics were assumed, and since a 1,2 hydrogen migration in only one direction leads to a recognizable rearrangement, the k_{obsd} (decay of VI) was taken to measure the rate of hydrogen migration from C 5 to C-4 in VI.

TABLE 2. RATE OF HYDROGEN MIGRATION (LEADING TO REARRANGEMENT) FOR 1,5-DIMETHYLCYCLOPENTADIENE

Temperature	k_1 (sec^{-1} × 10^5)
30°	5·5
32°	4·4
35°	9·6
38°	12·9
40°	21·0
42·5°	18·4
48°	42·6
50°	52·1
54°	73·4

All measurements were made with undiluted sample.

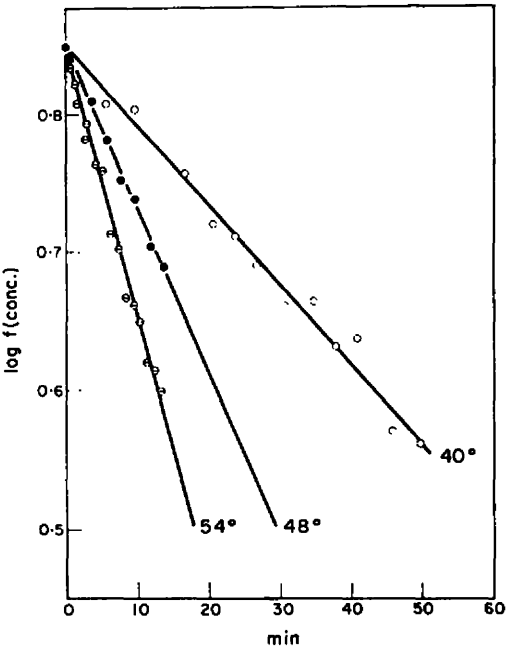


FIG. 3. Decay of 1,5-dimethylcyclopentadiene at three temperatures (°C).

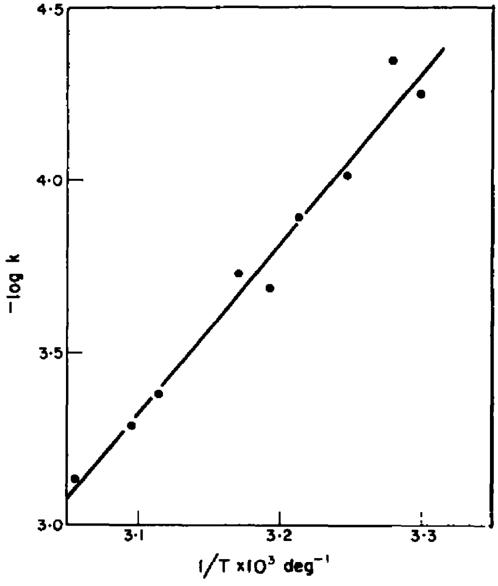
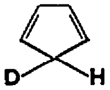


FIG. 4. Arrhenius plot of rearrangement of 1,5-dimethylcyclopentadiene.

It was experimentally more difficult to obtain accurate values for the decay of VI than for that of II since the sample always contained VII, which showed a C-5 methyl signal (a doublet at 8·93 τ; J = 7·8 c/s) almost superimposed on that of VI, and even a slight instability of the field during a kinetic run caused some overlap of the peaks and a consequent loss in accuracy in determining their individual areas. This difficulty prevented us from obtaining accurate values for the rate of decay of VII, the less abundant isomer at the start of the reaction, but it was clear that VII rearranged at a lower rate than VI, and comparison of the decay of the C-5 methyl signals of the two isomers showed that VI rearranged about 5 or 6 times more rapidly than VII, even though the rearrangement is statistically favoured in VII. Even if this rate could be obtained accurately for VII, there would be some difficulty in deriving individual rates of hydrogen migration from it, since the two possible migration termini are non-equivalent and the observed rate would be the sum of the rates of two distinct rearrangements; although we have demonstrated the presence of XI, the product of hydrogen shift from C-5 to C-4 in VII, in the mixture of rearrangement product, we have found no evidence for the formation of 1,4-dimethylcyclopentadiene (XII), the product of a C-5 to C-1 shift. Since the methyl signal shifts to a position near 8 τ after rearrangement of both VI and VII, and both already have other methyl groups which appear in this region, it has not been possible to study the complementary process, the rate of growth of the rearranged products, in this case.

Rearrangement of cyclopentadiene-5-d

It would be very instructive to be able to compare the rate of hydrogen migration in cyclopentadiene itself with the rates we have obtained for substituted cyclopentadienes. It seemed to us that this could be calculated from the rate at which cyclopentadiene-5-d (XIII) rearranged to the mixture having a statistical distribution of labelled isomers (a *hydrogen*-transfer process). The methylene protons of cyclopentadiene appear as a multiplet centred at 7·08 τ and the vinyl protons appear in a complex pattern near 3·5 τ.[7] The areas of the multiplets for pure cyclopentadiene-5-d should be vinyl:methylene = 4:1, and after randomization of the deuterium position these should become 2:1.



XIII

Mironov[4] has described a preparation of XIII that consists of treating a Grignard derivative of cyclopentadiene with D_2O at a low temperature. We have attempted to isolate pure XIII following Mironov's method and several variants, but in every case the vinyl:methylene peak areas were in the ratio of about 3:1 by the time they could be measured and this changed to 2:1 within a few minutes at the normal probe temperature. This frustrated our efforts to get a reasonable measure of the rate of hydrogen migration, but it did seem that the rearrangement was rapid, and probably faster than the rearrangement of II under comparable conditions. However, Roth[8] has very recently reported rates of deuterium migration in pentadeuteriocyclopentadiene which

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[7] G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Amer. Chem. Soc.* **82**, 5846 (1960).

[8] W. R. Roth, *Tetrahedron Letters* 1009 (1964).

indicate that the rate of hydrogen migration in cyclopentadiene is lower than that in II, even allowing for a large isotope effect.

Equilibrium studies

In liquid ammonia containing a small amount of sodium methylcyclopentadienide, the equilibrium mixture of methylcyclopentadienes produced consisted of 1-(IV), 2-(V) and 5-(II) isomers in the ratio 0·80:1:0·02. Equilibrium values for IV:V between 0·82:1 and 0·86:1 were obtained by a similar equilibration in tetrahydrofuran, dimethoxyethane, and dimethylsulphoxide at room temperature, but the differences are probably within the experimental error. A value of approximately 0·74:1 was obtained in ether at −80°, but here the probable experimental error appeared too large to allow the temperature dependence to be deduced from these figures.

The methylation of sodium methylcyclopentadienide in liquid ammonia[2] almost certainly produced the equilibrium distribution of *vic*-dimethylcyclopentadienes, and analysis of the mixture showed the 1,2-(IX) and 2,3-(X) isomers in the ratio 1·35:1, and these were the only representatives of this set of isomers. 1,3-Dimethylcyclopentadiene (XI) was the only representative of the set of isomers with two methyl groups 1,3 related. Attempts to convert synthetic XI to an equilibrium mixture (the isolation of 1,4-dimethylcyclopentadiene (XII) was of particular interest) resulted in the recovery of XI only.

DISCUSSION

Substituted cyclopentadienes provide an interesting and valuable system for the study of rearrangements involving hydrogen migration, since rearrangement almost invariably leads to an isomer retaining the cyclic diene system; so, to a very good approximation, the contribution of this system to the total molecule remains constant, and any differences (in stability, rates of rearrangement, etc.) that can be detected between members of a series, particularly between isomers, can be wholly attributed to the influence of substituents in different environments.

Our initial object in undertaking a study of these rearrangements was to decide whether or not the hydrogen migration process always took place with the intervention of an anionic intermediate (I, III, etc). Although a mechanism involving separated ions could be presumed to be important in the presence of a base such as the cyclopentadienide ion since rapid intermolecular proton exchange had been observed when diene and anion were brought together,[3] all the evidence obtained by us or reported by others[4,8] pointed to the availability of a reaction pathway incorporating an intramolecular 1,2 hydrogen shift. Our present kinetic results lead to energies and entropies of activation not unreasonable for such a process, analyses of partially rearranged materials show that a sequence of 1,2 shifts occurs, and our failure to observe deuterium incorporation during rearrangements carried out in the presence of D_2O is evidence that separated ions were never formed during the rearrangement. When NaOD was also present, the rearrangement was probably accelerated very slightly and a small amount of deuterium was incorporated in the product.[9] Our interpretation of these results is that the intramolecular pathway predominates even in the presence of aqueous alkali and that the acceleration (if real) comes not from catalysis of this

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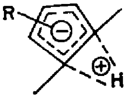
[9] Deuterium incorporation has been reported to occur in presence of a nitrogen base. *cf.* D. N. Kursanov and Z. N. Parnes, *Dokl. Akad. Nauk SSSR*. **109**, 315 (1956).

process but from the availability of the alternative pathway through the methylcyclopentadienide anion when sufficient base is present. In the presence of enough strong base such as the cyclopentadienide anion, the second pathway presumably becomes predominant. The rather surprising results, i.e. marked acceleration and incorporation, observed when the rearrangement was carried out in D_2O–NaOD–MeOH indicate that this medium is basic enough to allow the second pathway to become of considerable importance. Some slight evidence supporting this comes from the observation that, immediately after addition of the methanol, the solution became yellow, indicative of the formation of a cyclopentadienide anion (the colour is presumably caused by oxidation products of the anion). The precise rôle the methanol plays in the base-strengthening process is not obvious at present.[10]

Despite the evidence against the presence of an anionic intermediate on the reaction pathway in the absence of a strong base, it is intuitively attractive to suppose that, during the 1,2 shift, the hydrogen is proton-like and the ring assumes much of the character of a cyclopentadienide anion with concomitant π-electron stabilization; this implies a transition state of the form shown in XIV, similar to that postulated by Mironov.[4] In the course of our present study we have accumulated a number of kinetic and equilibrium data, some fairly accurate and some very approximate, relating to the effect of methyl substituents on the course of the hydrogen migration process.



XIV

It has been interesting to attempt to use these results along with those available in the literature, particularly from the reports of Mironov[4] and the very recent communication of Roth,[8] to test and, perhaps, improve this model. Even though the data are still inadequate to allow one even to approach a satisfactory account of the process, a few generalizations or trends have become clear enough for us to comment on them at this stage.

To begin with, our kinetic results are in accord with the gross features of the postulated scheme; the rearrangement has the characteristic of a spontaneous first order process, the values for activation energies, where available, show that the transition state receives a considerable amount of stabilization (throughout we will make the reasonable assumption that the transition states for all the isomerizations considered are very similar in character), and the small negative entropies of activation are predictable for a 1,2 shift. The situation appears to have a close analogy in the indene system.[8,11]

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[10] The rôle appears to be a particularly subtle one since it is difficult to see how the methanol can change the nature of the solvent sufficiently to promote the dissociation of 5-methylcyclopentadiene (II). It is true that some MeO^- is introduced into the equilibrium, but, since it arises from an equilibrium involving OH^-, it is hard to see why OH^- itself could not be directly in equilibrium with $MeC_5H_4^-$ unless the removal of the proton from II is kinetically unfavourably in presence of OH^-, but less so in presence of MeO^-. It can be noted that the pK_a of cyclopentadiene has been placed between those of H_2O and MeOH (cf. R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.* **84**, 2899 (1962)), and II is probably a stronger acid than cyclopentadiene.[8]

[11] G. Bergson and A. M. Weidler, *Acta Chem. Scand.* **17**, 862, 1798 (1963).

A general phenomenon that becomes apparent on examination of all the data is the trend towards lower rates of isomerization with increase in the number of methyl substituents. As will be discussed later, there may be particular pairs of compounds which are exceptional, but the trend is quite clear (*gem*-disubstituted compounds are obviously not included in this generalization). In the proposed model there is one feature that would be expected to contribute to this phenomenon in all cases, and that is the destabilization of the transition state by the inductive effect of methyl substituents, just as occurs with ground state cyclopentadienide anions.[3] Other effects may be expected to contribute to the final result in specific cases, but, if the simple model is valid, this destabilization of the transition state should be observed to depend in all cases on the degree of substitution.

A very striking feature that can be observed within any set of isomers is that the hydrogen migrates most rapidly from a carbon also carrying a methyl substituent. This is at first surprising since one would expect the inductive effect of the methyl group on the ground state of the molecule to cause a hydrogen to move less rapidly. Our equilibrium studies make it clear that a substituted cyclopentadiene with a methyl group at a double bond is considerably more stable than its isomer with a C-5 methyl substituent; for example, the free energy difference between 1-methylcyclopentadiene (IV) and its 5-methyl isomer (II) is between 2 and 2·5 kcals mole^{-1}. It may be expected that the difference is due to stabilization of the ground state of IV by the substituent,[12] and, using the simple reaction model, one seeks to explain the observation that II rearranges faster than IV on the basis of differences in ground state free energy. (Figure 5 shows relationships in a schematic fashion). Although it has not yet been possible to measure accurately the rate of rearrangement of IV, it does appear that the rate difference is larger than can be completely accounted for on this simple picture. Our failure to measure the rate of hydrogen migration in cyclopentadiene itself has left a serious gap in the data, but we felt that our evidence was compatible with a rate at least as large as that for 5-methylcyclopentadiene (II). However, Roth's values[8] for deuterium migration in cyclopentadiene contradict this, even allowing for a large isotope effect; this and our own observation that 1,5-dimethylcyclopentadiene (VI) appears to rearrange more rapidly than 1-methylcyclopentadiene (IV) serve as evidence that the 5-methyl group does not fit into the general pattern discussed above, and, in fact, accelerates the rearrangement rather than retards it. If these points can be confirmed quantitatively, they will require that the description of the transition state in the simple model be modified. The modification would probably involve placing the migrating hydrogen unsymmetrically between migration origin and migration terminus in the transition state for substituted cyclopentadienes. This is not unreasonable since a methyl substituent would be expected to distort the electron cloud of the quasi-cyclopentadienide system in the transition state; it also implies that

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[12] The approximation that the influence of a 5-methyl substituent on the ground state of the molecule is negligible (while a substituent at a double bond has an important effect) may prove to be a poor one since the ultraviolet spectra of cyclopentadienes carrying a 5-methyl substituent show a bathochromic shift with respect to their analogs without the 5-methyl substituent;[2,13] moreover, the electron-impact ionization potentials of methyl-substituted cyclopentadienes are independent of substituent distribution (but do vary with the number of substituents). cf. F. Meyer and A. G. Harrison, *Canad. J. Chem.* **42**, 2256 (1964).

[13] S. McLean and P. Haynes, *Tetrahedron* **21**, 2343 (1965).

the transition state resembles one of the ground states more than the other and consequently has a lower energy than the hypothetical symmetrical transition state. Thus, one anticipates that the transition state from cyclopentadiene itself is completely symmetrical, but that for the rearrangement of II to IV (or VI to IX) has much of the character of IV (or IX), while that for the rearrangement of IV to V should once again have the hydrogen more nearly symmetrically disposed between the two carbon atoms.

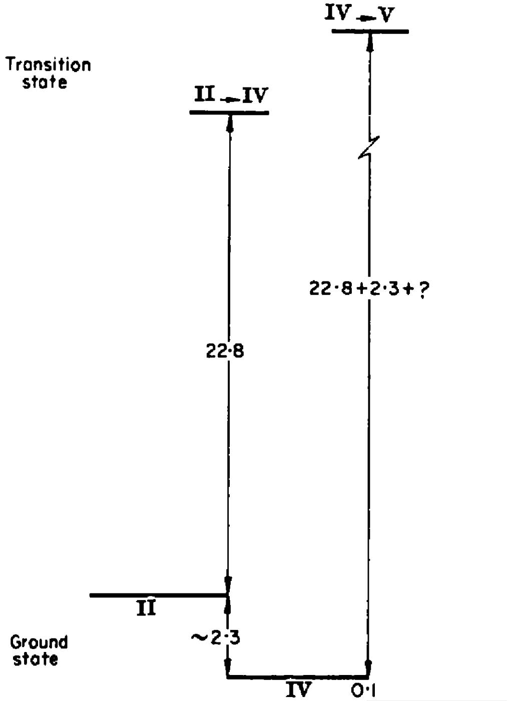

Fig. 5. Schematic representation of free energy relationships for hydrogen migration in methylcyclopentadienes.

The nature of the interaction of a methyl substituent with a double bond system has aroused a considerable amount of discussion recently. Although we are unable to make a useful comment on this directly, we note a feature that, although involving only small differences in stability, persists through our work and can also be observed in Mironov's results[4]: in a set of methyl-substituted cyclopentadienes where isomerization can place a methyl group at either C-1 or C-2 the 2-methyl isomer is the more stable. The difference is very small, but it is surprising to find it at all since hyperconjugation should favour the 1-methyl isomer (in cases[14] where true conjugation can occur, i.e. with —COOR, Ph, etc. as substituents, this is certainly true); as has been noted previously, both isomers are, however, more stable than the 5-methyl compound, as can be expected. As examples, we note that the equilibrium ratio of V to IV is 1·20:1 (and does not seem to have an appreciable temperature dependence), that of

[14] N. L. Drake and J. R. Adams, *J. Amer. Chem. Soc.* **61**, 1326 (1939); R. Riemschneider and R. Nehrin, *Monatsh.* **91**, 829 (1960); D. Peters, *J. Chem. Soc.* 1761 (1959); J. A. Berson and E. M. Evleth, *Chem. & Ind.* 1362 (1961); but see G. V. Boyd and L. M. Jackman, *J. Chem. Soc.* 548 (1963).

IX to X is 1·35:1 (statistical distribution would give 2:1), and 1,4-dimethylcyclopentadiene (XII) has not yet been found, the 1,3-isomer (XI) invariably being the only isomer isolated. The latter point has been particularly perplexing to us since we would have expected the intramolecular rearrangement of VII to lead to XII preferentially. Incidentally, this difference in stability may contribute to the lower rate of rearrangement of 1,3-dimethylcyclopentadiene (VII) compared with that of its 1,2 isomer (VI), but it cannot be completely responsible and this is further evidence that the transition state of the simple reaction model must be modified.

In summary, cyclopentadienes can rearrange by a series of intramolecular 1,2 hydrogen shifts; the general features of the process can be described by a reaction pathway which passes through a transition state such as XIV, but there is evidence that the detailed structure of this species is modified by the nature and distribution of substituents. We have made suggestions concerning the nature of the modifications required, but we recognize that they are still speculative since the data available, at present, are very incomplete, and, where comparison was possible, the differences (in rates, activation energies, etc.) were often rather small and their significance was consequently difficult to assess.

EXPERIMENTAL

Materials. The preparation of the required 5-substituted cyclopentadienes (containing a small amount of diglyme) has already been described.[8] A diglyme-free sample of II was prepared by redistillation of the sample at 0° under red. press.

Cyclopentadiene-5-d was prepared by slowly adding sodium cyclopentadienide (0·1 mole) in 100 ml diglyme at $-10°$ to a stirred solution of D_2O (4·5 g; 0·225 mole) in 100 ml diglyme at the same temp. After 10 min the product was distilled at $-10°$ under red. press. The distillate (3·1 g; 47%) showed a vinyl:methylene proton ratio of 3:1 in the NMR.

Samples were collected and stored over dry ice until the commencement of each kinetic run.

NMR *spectra* were obtained on a Varian A-60 spectrometer; a variable-temp probe (V-6057; calibration specification $\pm 3°$ but considered to be operationally reliable to $\pm 1°$) was employed for studies of temp dependence, and the temp was checked from the spectrum of a standard sample of MeOH or ethylene glycol. Ordinary glass sample tubes were used unless otherwise indicated.

Kinetic methods. Samples were rapidly inserted in the probe, and, after 2 min (to allow the sample to reach thermal equilibrium), the appropriate part of the spectrum was repeatedly recorded at the time interval suitable for the rate of the reaction studied. In all but the slowest reactions, observations were made through at least two half-lives, and, where possible, were continued to completion of the observable rearrangement.

The ratio (mean ht. of the peaks of the 5-methyl doublet): (height of the diglyme CH_3, signal at 6·78 τ) was used as a function of the concentration of the 5-methyl species. For diglyme-free 5-methyl-cyclopentadiene (II), the ratio (sum of the heights of the peaks of the 5-methyl doublet)/(sum of the heights of the peaks of the 5-methyl doublet and the 1-methyl signal of the product IV) was used. Rate constants were determined from the slope of a plot of the logarithm of the function of concentration against time by use of the standard least squares treatment.[15] Good straight lines were obtained; typical rate plots are shown in Figs 1 and 3 and the rate constants obtained are shown in Tables 1 and 2, along with a summary of the reaction and the conditions employed. Activation energies and entropies were computed from Arrhenius plots (shown in Figs 2 and 4) of log k against 1/T by use of a standard method.[16]

Dilution experiments were carried out by mixing 5-methylcyclopentadiene with the required amount of CCl_4 immediately prior to the run. The runs were carried out in the quick succession at the natural temperature of the probe and compared with an undiluted sample run at the same time.

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[15] H. D. Young, *Statistical Treatment of Experimental Data* p. 145. McGraw-Hill, Toronto (1962).

[16] W. J. Youden, *Statistical Methods for Chemists* Chap. 5. J. Wiley, New York (1961).

Surface effects were studied (a) by pretreating a sample tube with a solution of Me_3SiCl in hexane, adding 5-methylcyclopentadiene, and then carrying out the kinetic run in the manner just described; (b) by allowing the 5-methylcyclopentadiene to rearrange in a platinum vessel at constant temp, and withdrawing aliquots of sample at intervals and recording the NMR spectrum.

The rearrangement of the cyclopentadiene-5-d sample was studied in a similar way by recording the ratio of vinyl to methylene protons as a function of time. The ratio changed rapidly, but the results were not deemed satisfactory for use in a determination of rate constants.

Hydrogen-deuterium exchange experiments

A solution of 5-methylcyclopentadiene (II; 1·1 molar) and D_2O (5·5 molar) in diglyme was prepared. Similar solutions containing, in addition, NaOD (0·05, 0·10 and 0·15 molar) were prepared from standardized solutions of NaOH in D_2O. Methanol (to produce a 3·5 molar solution) was added to the solution containing 0·10 molar NaOD. NMR spectra were repeatedly recorded in the usual way immediately after the solutions had been prepared and the rate of decay of II was determined by the technique described above for rearrangements carried out in the absence of diglyme. These runs were made in quick succession at the natural temp of the probe (estimated to be 33° from the rate of decay of untreated II). The values (in $sec^{-1} \times 10^5$) for k_{obsd} were: in absence of NaOD, 1·6; in 0·05 molar NaOD, 1·5; in 0·15 molar NaOD, 1·9. Samples of the mixture were separated by VPC[2] 25 min after the commencement of the rearrangement, and the methylcyclopentadiene fraction was collected and analyzed on the mass spectrometer.[6] In the absence of NaOD $< 0·5\%$ deuterium was incorporated (and no change was observed after 24 hr contact); with 0·05 molar NaOD the analysis showed C_6H_8 97·9%, C_6H_7D 2·1%; with 0·15 molar NaOD the analysis showed C_6H_8 68·6%, C_6H_7D 28·4%, $C_6H_6D_2$ 3·0%. The sample containing MeOH rearranged at a rate too fast to measure. After 15 min, the methylcyclopentadiene fraction consisted of C_6H_8 25·5%, C_6H_7D 38·8%, $C_6H_6D_2$ 26·0%, $C_6H_5D_3$ 8·4%, $C_6H_4D_4$ 1·3%.

Equilibrium studies

Methylcyclopentadienes. The mixture of methylcyclopentadienes (16·0 g; 0·2 mole) obtained by cracking the dimer[4] was stirred 1·5 hr with a solution of sodium methylcyclopentadienide (0·1 mole) in liquid ammonia. The organic layer, analyzed by VPC, contained 1- and 2-methylcyclopentadiene in the ratio VII:VIII = 0·80:1, and about 1% of 5-methylcyclopentadiene (IX).

The mixture of methylcyclopentadienes was also allowed to equilibrate in solutions of sodium methylcyclopentadienide (about 0·3 equiv.) in dimethoxyethane, tetrahydrofuran, and dimethyl sulphoxide at room temp. forl·5 hr. Each solution was analyzed by VPC and in every case the ratio VII:VIII = 0·82 (±0·02):1 was found; the small amounts of IX were not usually detectable because of the dilution in these cases. A similar run was carried out in ether at −80° and the sodium cyclopentadienide was removed at the end of the equilibration period by addition of CO_2. Analysis of the solution by VPC showed VII:VIII = 0·74:1.

1,3-*Dimethylcyclopentadiene* was allowed to equilibrate in tetrahydrofuran in presence of a small amount of sodium sand. VPC analysis after 10 hr showed only starting material in the dimethylcyclopentadiene fraction.

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Note added in proof

The discussion of sigmatropic reactions by Woodward and Hoffmann[17] allows this rearrangement to be seen in a new perspective. However, it should be noted that their generalizations covering sigmatropic reactions serve as selection rules and do not define the reaction mechanism; in particular, they do not define the character of the migrating hydrogen and they are not incompatible with the description given in the present discussion.

[17] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 2511 (1965).