# Thermal Reversible Isomerisation of 2-Ethyl-cis-penta-1,3-diene to 4-Methyl-trans-hexa-1,3-diene

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The reversible isomerisation of 2-ethyl-cis-penta-1,3-diene to 4-methyl-trans-hexa-1,3-diene is an example of the now well-authenticated 1.5-hydrogen migration reaction which occurs in a number of diene systems. The reaction is almost certainly unimolecular and the first-order rate constants, obtained in the temperature range 190-250° fit the Arrhenius equations,  $k_1 = 10^{10.77} \exp(-31.640/RT) \sec^{-1}$ ;  $k_{-1} = 10^{11.03} \exp(-34.530/RT) \sec^{-1}$ . Equilibrium constants have been determined by direct analysis in the range 230-340° and hence enthalpy and entropy differences between the isomers have been evaluated. The A factors of the isomerisations are discussed and compared with estimated values.

EXAMPLES of 1,5-hydrogen migrations are now well known for a number of aliphatic dienes<sup>1</sup> and also in many cyclic systems.<sup>2</sup> On the basis of orbital symmetry arguments such a process may occur in a concerted fashion with a ring transition complex in which the migrating hydrogen atom stays on the same face of the  $\pi$ -electron system, *i.e.*, a suprafacial process. Despite the large number of observations there is still relatively little precise kinetic information about these reactions, especially for the simple cases. Furthermore, recent work<sup>3</sup> has demonstrated that it is possible to estimate with remarkable precision the A factors for isomerisations which proceed through cyclic transition states. While in many cases there is excellent agreement between experimental and estimated values, this is not so for 1,5-hydrogen migrations in aliphatic dienes, where the estimated values are appreciably higher (and outside the combined quoted experimental and estimated error limits) than the experimental values. We have attempted to add to the available kinetic data on this type of reaction and to discover whether the observed discrepancies arise from experimental error or an incorrect description of the vibrational frequencies and rotational barriers of the activated complex.

### EXPERIMENTAL

2-Ethyl-cis-penta-1,3-diene.-Hex-4-en-3-ol was prepared by the action of ethylmagnesium bromide on freshly distilled crotonaldehyde and purified by fractional distillation  $(136-138^{\circ}/760 \text{ mm.})$ . A solution of the alcohol in acetone was oxidised to hex-4-en-3-one with chromic acid.<sup>4</sup> The ketone was extracted with ether, and the extract was washed with aqueous sodium hydrogen carbonate. The ketone was obtained by fractional distillation (b.p. 138-140°). Treatment of the hex-4-en-3-one with di-iodomethane and magnesium amalgam yielded 2-ethyl-trans-penta-1,3-diene

<sup>1</sup> J. Wolinsky, B. Chollar, and M. D. Baird, J. Amer. Chem. Soc., 1962, 84, 2775. <sup>2</sup> W. R. Roth, Chimia (Switz.), 1966, 20, 229; J. W. De Haan

and H. Kloosterziel, Rec. Trav. chim., 1968, 87, 228.

in only 5% yield. However the yield was improved to 30% by replacement of the di-iodomethane with dibromethane. A similar yield of the trans-diene was obtained by a Wittig reaction with the unsaturated ketone (methyltriphenylphosphonium bromide with phenyl-lithium). After a crude fractional distillation, pure 2-ethyl-transpenta-1,3-diene was obtained by preparative g.l.c. (17 ft.  $\times$  $\frac{3}{8}$  in. column) with 3,3'-oxydipropionitrile as the liquid phase. A 1% solution of the trans-diene in n-pentane containing 1% acetophenone was photolysed in a Pyrex vessel by means of a 500 w medium-pressure mercury lamp. A photo-stationary equilibrium mixture which contained 48% cis-diene and 52% trans-diene was obtained after irradiation for 1 hr. Distillation gave the n-pentane followed by the cis-trans mixture of dienes. The 2-ethylcis-penta-1,3-diene was obtained by preparative g.l.c. and shown to be 99% pure by analysis on a capillary column. The 1% impurity was subsequently found to be thermally stable at all the reaction temperatures used.

4-Methyl-trans-hexa-1,3-diene.—Small samples of this compound were obtained by the pyrolysis of 3-ethyl-3-methylcyclobutene. In order to obtain larger quantities several different syntheses were attempted. Despite many variations in experimental details we were unable to obtain more than trace amounts by the Wittig reaction of allyltriphenylphosphonium bromide on ethyl methyl ketone. Dehydration of 3-methylhex-5-en-3-ol with conc. sulphuric acid or toluene-p-sulphonic acid yielded a complex mixture of hydrocarbons. Analysis by use of a capillary column showed ten separate peaks, the largest of which represented ca. 30% of the mixture; six others each represented at least 5%. An alternative procedure of decomposing the oxalate of the alcohol gave the same complex mixture, though with slightly different relative intensities of the various peaks. Peaks with retention times which corresponded to 4-methylcis-hexa-1,3-diene and 4-methyl-trans-hexa-1,3-diene together accounted for ca. 20% of the total hydrocarbon products. The hydrocarbon mixture was separated into

<sup>3</sup> H. E. O'Neal and S. W. Benson, J. Phys. Chem., 1967, 71,

2903. <sup>4</sup> K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L.

J. Chem. Soc. (A), 1969

TABLE 2

Rate constants as a function of temperature

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Гетр	190·2°	195·5°	200·3°	210.7°	$215 \cdot 1^{\circ}$
$10^{4}k_{1}$ (sec. <sup>-1</sup> )	0.7049	1.036	1.462	3.011	3.996
$10^{5}k_{-1}$ (sec1)	0.5594	0.8513	1.240	2.728	3.721
Гетр	221.2	230.8	240.4	$245 \cdot 1$	250.0
$10^{4}k_{1}$ (sec. <sup>-1</sup> )	6.000	11.03	20.38	26.99	35.54
$10^{5}k_{-1}$ (sec. <sup>-1</sup> )	5.797	11.27	21.98	29.84	40.37

to-volume ratio ten times greater than the unpacked vessel) yielded the same rate constants as those with the unpacked vessel. However it was necessary to 'age' the vessel with reactant before reproducible results could be obtained. In the 'clean' packed vessel the rates  $k_1$  and  $k_{-1}$  were approximately the same as those obtained in the aged vessel, but other reactions occurred to give four other products. When the reaction vessel was partially aged values of  $k_1$  and  $k_{-1}$  were essentially identical with those obtained with the fully aged vessel; the only difference lay in the continued formation of small quantities of these other compounds. It thus seems likely that even in the clean vessel there is no appreciable heterogeneous reaction to correspond to the homogeneous isomerisation under observation, but that a quite different surface-catalysed reaction can occur. The ageing process was complete after only one run in the unpacked reaction vessel.

The data in Table 2 fit the Arrhenius equations:

 $k_1 = 10^{10.77 \pm 0.03} \exp(-31,640 \pm 75/RT) \text{ sec.}^{-1}$  $k_{-1} = 10^{11.03 \pm 0.03} \exp(-34,530 \pm 74/RT) \text{ sec.}^{-1}$ 

The errors quoted are standard deviations.

#### DISCUSSION

The results obtained support previous ideas that the 1,5-hydrogen migration which occurs is a concerted unimolecular isomerisation. Orbital symmetry arguments indicate that in this process the hydrogen moves in such a way that it is always associated with the same face of the  $\pi$ -electron system, *i.e.*, a suprafacial rearrangement.

The reported A factors for the 1,5-hydrogen migrations of alicyclic diene fall in the range 10<sup>11.2</sup>-10<sup>10.8</sup>. While values appreciably lower than 'normal' are to be expected, these values are appreciably less than those obtained on the basis of the estimates of O'Neal and Benson.<sup>3</sup> The transition complex suggested by these authors is a loose ' semi-cyclic ' structure which may be depicted as (III); on the basis of this model the calcu-



lated entropy loss in the present case is 7.1 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, as compared with the experimental value of 10.5 cal. deg.<sup>-1</sup> mole<sup>-1</sup>. The discrepancy of 3.4 cal. deg.<sup>-1</sup> mole<sup>-1</sup> in this case is about the same as for the isomerisation of cis-hexa-1,3-diene to cis, trans-hexa-2,4-diene.<sup>6</sup> A slightly smaller, but still very significant, difference is similarly obtained between estimated and experimental values for the isomerisation of 2-methyl-

four fractions by preparative g.l.c. The fraction which contained the required diene was then re-chromatographed and a sample of 4-methyl-trans-hexa-1,5-diene was obtained (99.5% purity).

Apparatus.—The apparatus and general procedure have been described previously.<sup>5</sup> Reaction mixtures were analysed by g.l.c. with a Perkin-Elmer 452 chromatograph equipped with a capillary column (100 m.; polypropylene glycol) and a flame ionisation detector. Signals from the detector were fed to a high-speed electronic integrator (Perkin-Elmer D2). Reaction mixtures from kinetic runs were analysed in duplicate, and those from equilibrium studies in at least triplicate.

#### RESULTS

In the temperature range 190-250°, 2-ethyl-cis-penta-1,3-diene undergoes a reversible isomerisation to yield an equilibrium mixture with 4-methyl-trans-hexa-1,3-diene.



In this temperature range, after the first run, no other compounds were detected. In equilibrium studies the temperature range was extended to 340°. At the highest temperature some other products were detected but in total they accounted for <0.1% of the mixture. Equilibrium compositions were determined in the range 229.8-339.8°. In most cases equilibrium was approached from 4-methyltrans-hexa-1,3-diene but at two temperatures equilibrium was also approached from the ethylpentadiene. The results are given in Table 1.

## TABLE 1

Equilib	rium const	tants as a	function	of temper	rature
Temp.	229·8°	240·4°	240·6°	250∙0°	251.9°
K (II/I)	9·693	9·288	9·302	8∙794	8.814
Temp.	261·5	$271 \cdot 2 \\ 7 \cdot 929$	281·0	290·3	299·8
K (II/I)	8·390		7·444	7·187	6·979
Temp.	309·6	317·1	330·0	339∙8	
K (II/I)	6·527	6·430	6·174	5∙806	

A van't Hoff plot of these results gave a good straight line which fitted the equation log  $K = 631 \cdot 5/T - 0 \cdot 2623$ . This yields an enthalpy difference, H(II) - H(I) = $-2.89 \pm 0.06$  kcal. mole<sup>-1</sup> and an entropy difference,  $S(II) - S(I) = -1.20 \pm 0.11$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>.

Rate studies were carried out at ten temperatures in the range 190-250°. At each temperature the composition (originally pure 2-ethyl-cis-penta-1,3-diene) was determined Values of  $(k_1 + k_{-1})$  were obtained at ten or more times. from a least-squares analysis of the plots of log([(II)]equil. - [(II)]) vs. time; values of [(II)]<sub>equil.</sub> were obtained from the van't Hoff equation. The rate constants are given in Table 2.

For most of the runs an initial reactant pressure of 2 torr was used. A series of runs with reactant pressures from 0.08 to 20 torr, and also with added nitrogen up to 160 torr, showed that the rate constants were independent of pressure. Runs carried out with a packed reaction vessel (surface-

<sup>5</sup> H. M. Frey and R. K. Solly, Trans. Faraday Soc., 1968, 64, 1858.
<sup>6</sup> H. M. Frey and B. M. Pope, J. Chem. Soc. (A), 1966, 1701.

penta-1,3-diene.<sup>7</sup> It appears unlikely that all the experimental determinations of A factors can be incorrect to this extent and we prefer to believe that the activated complex has a much tighter structure than the model used for the estimates. A limit can probably be set on the magnitude of the entropy decrease to be expected for this isomerisation by equating the entropy of the activated complex with that of the related cyclopentadiene. In the case of the isomerisation of 2-methylpenta-1,3-diene this would set a minimum value on the A factor of about  $10^{10\cdot8}$ , which is not inconsistent with the experimental value of  $10^{11\cdot2}$ . The minimum value is, however, disturbingly close to some of the other experimental values.

The enthalpy difference of -2.89 kcal. mole<sup>-1</sup> between reactant and product in the present work is at first sight remarkably high. A similar large difference  $(-3.4 \text{ kcal. mole}^{-1})$  had previously been reported for the isomers 2-methylpenta-1,3-diene and 4-methylpenta-1,3-diene. We believe that both these differences are due to the same effect. The most stable diene conformation should be that with the double bonds in the trans configuration and the four carbon atoms planar. Because of steric interactions, this is not possible for the less stable isomers, and the two  $\pi$ -systems will be twisted from a linear (planar) configuration. Thus some of the delocalisation energy of the butadiene system will be lost. Since this is not the case for the more stable isomers, relatively large enthalpy differences are obtained. This factor also accounts for the observed relatively large entropy differences. Thus the decrease in delocalisation energy must also decrease the barrier to torsional vibrations about the single bond linking the

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double bonds, and hence result in relatively higher entropies for the less stable isomers. Perhaps these effects can be best demonstrated by comparison of  $\Delta H = -2.89$  kcal. mole<sup>-1</sup> and  $\Delta S = -1.2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>, obtained in the present study, with the calculated values of -0.35 kcal. mole<sup>-1</sup> and 0.3 cal. deg.<sup>-1</sup> mole<sup>-1</sup>, respectively, obtained from group additivity tables. In these tables no allowance is made for the effect which we believe to be responsible for the differences in the compounds used here.

The errors quoted in the Arrhenius parameters are standard deviations computed by normal statistical procedures. In general, the magnitude of these deviations indicates only the reproducibility of the data. In the present situation the procedure employed to obtain  $k_{-1}$  results in a correlation of errors between  $k_1$  and  $k_{-1}$ . Since  $k_1$  is much greater than  $k_{-1}$ , the errors in  $k_{-1}$  will essentially be due to the errors in K. However the values of K have been obtained from the van't Hoff plot, which has the same dependence on temperature as has the Arrhenius equation. Thus errors in the Arrhenius parameters do not reflect the reproducibility of  $k_{-1}$  (though they do reflect the reproducibility of  $k_1$ ) and the true reliability of the parameters for  $k_{-1}$ may be as much as a power of ten worse than those quoted. However, treatment of the results in the manner employed will still give the ' best ' values for the Arrhenius parameters.

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