Thermal Isomerization of 3,6-Dimethyltricyclo[3.1.0.0^{2,4}]hexane

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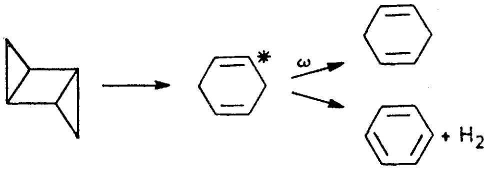
Thermal isomerization of the title compound yielded *trans*-3,6-dimethylcyclohexa-1,4-diene quantitatively in the gas phase by a first-order process. Rate constants determined between 156 and 204 °C yielded the Arrhenius equation:

$$\log k/\mathrm{s}^{-1} = 14.062 \pm 0.086 - (154\,300 \pm 740\ \mathrm{J\ mol}^{-1})/RT\ln 10$$

The evidence available suggests that the reaction is unimolecular and proceeds *via* a diradical. The relationship between this isomerization and those reported in the bicyclo[2.1.0]pentane system is discussed.

THE thermal isomerization of tricyclo[3.1.0.0^{2,4}]hexane to cyclohexa-1,4-diene is a unimolecular reaction whose Arrhenius parameters have been measured.[1] At low pressures, some further decomposition of the initially formed cyclohexadiene takes place, to benzene and hydrogen, due to a form of chemical activation [2] (Scheme 1). Application of RRKM theory to this system yielded a satisfactory agreement between the relative yields of cyclohexadiene and benzene and the pressure of the system. The present work was undertaken in an attempt to obtain more detailed information about the mechanism of this and related reactions.



SCHEME 1

EXPERIMENTAL

3,6-Dimethyl-*cis-transoid-cis*-tricyclo[3.1.0.0^{2,4}]hexane was prepared by dimerization of 3-methylcyclopropene.[3] It was purified by preparative g.l.c. on a 5.4 m × 4.4 mm column packed with 20% w/w bis-2-methoxyethyl adipate on Chromosorb P and dried over 4A molecular sieves. Analysis on several different chromatographic columns showed the purity of the sample to be $\geqslant$99.9%. Pure samples of *cis*- and *trans*-3,6-dimethylcyclohexa-1,4-diene were available from previous work.

The kinetic apparatus has been described previously.[4] Reaction mixtures were analysed by g.l.c. (Perkin-Elmer F11; gas sample valve; flame ionization detector; ball and disc integrator). Some analyses were carried out, purely for identification purposes, by using a chromatograph (Perkin-Elmer 452) equipped with a capillary column.

RESULTS

Preliminary pyrolyses were carried out at 253.4 °C. Analysis on several columns with the liquid phases Carbowax 20M, squalane, and bis-2-methoxyethyl adipate, showed only one product peak, which had the same retention time as either *cis*- or *trans*-3,6-dimethylcyclohexa-1,4-diene (which could not be resolved with these columns). Analysis with a 100 m × 0.25 mm capillary column coated with polypropylene glycol showed the product to be the *trans*-isomer, with less than 0.25% (the detection limit) of the *cis*-isomer.

A series of runs was carried out where the extent of reaction was determined by quantitative g.l.c. with the squalane column. The results fitted first-order behaviour even when the decomposition had proceeded to more than 80% completion. The first-order nature of the decomposition was confirmed by carrying out runs with initial reactant pressures in the range 0.5—8.0 Torr, when it was found that the rate constant was independent of initial reactant concentration.

Kinetic studies were carried out at nine temperatures in the range 156—204 °C. At each temperature 8—10 runs were analysed (usually in at least duplicate) and first-order rate constants were obtained by a least-squares analysis of the appropriate first-order plots. The values obtained in this way are given in the Table. A series of runs was carried out at 203.45 °C in a vessel filled with Pyrex tubes to give it a surfact-to-volume ratio 14 times that of the normal (unpacked) reaction vessel. The rate constant obtained in this series, 1.42 × 10^{-3} s^{-1}, compares well with the value (1.45 × 10^{-3} s^{-1}) obtained in the unpacked vessel and demonstrates that there is no appreciable surface reaction.

Rate constants for the isomerization of the dimethyltricyclohexane

T/°C	156.3	161.55	166.9	172.6	178.4
10^4k/s^{-1}	0.195	0.336	0.576	0.955	1.60
T/°C		183.95	190.3	197.6	203.45
10^4k/s^{-1}		2.63	4.66	8.72	14.50

The results in the Table gave an excellent Arrhenius line from which the parameters were calculated by least squares, whence:

$$\log k/\mathrm{s}^{-1} = 14.062 \pm 0.086 - (154\,300 \pm 740\ J\ \mathrm{mol}^{-1})/RT\ln 10$$

or

$$\log k/\mathrm{s}^{-1} = 14.062 \pm 0.086 - (36\,880 \pm 180\ \mathrm{cal\ mol}^{-1})/RT\ln 10$$

The quoted errors are standard deviations.

DISCUSSION

The evidence presented suggests that the reported isomerization takes place quantitatively and is a good example of a unimolecular process. The Arrhenius parameters for this isomerization and for that of the

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[1] J. E. Baldwin and J. Ollerenshaw, *Tetrahedron Letters*, 1972, 3757.

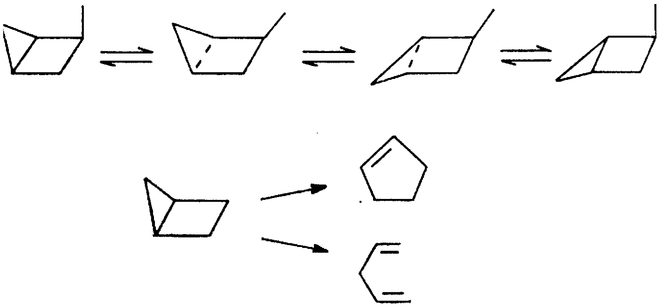
[2] M. C. Flowers, H. M. Frey, and H. Hopf, *J.C.S. Chem. Comm.*, 1972, 1284.

[3] A. J. Schipperijn and J. Lukas, *Tetrahedron Letters*, 1972, 231.

[4] H. M. Frey, R. G. Hopkins, and N. S. Isaacs, *J.C.S. Perkin II*, 1972, 2082.

unsubstituted tricyclohexane are similar; in fact, the rate constants are within a factor of 2 of one another. Thus the methyl substitution has little effect on the rate of the reaction. This is in line with the results for the isomerizations and decompositions of many hydrocarbon ring systems such as cyclopropanes, cyclobutenes, and cyclobutanes.

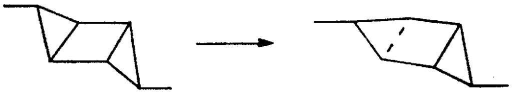
The isomerization of *cis*-2-methylbicyclo[2.1.0]pentane to the *trans*-isomer (Scheme 2) has been studied by Chesick,[5] who obtained the Arrhenius parameters for the reaction. The energy of activation (162 kJ mol^{-1}) is low and the mechanism of the reaction has been analysed in terms of a diradical intermediate [formed by fission of the C(1)–C(4) bond] by Benson.[6] To account for the value of the energy of activation a barrier to recyclization of the cyclopropane ring of about 37 kJ mol^{-1} is required. Inversion of the ring system by C(1)–C(5) or C(4)–C(5) bond fission, unlikely on thermochemical grounds, has been ruled out by experimental work with *exo,exo*-2,3-dideuterio-*exo*-5-benzyloxybicyclo[2.1.0]pentane. For the unsubstituted bicyclo[2.1.0]pentane, thermal isomerization yields cyclopentene and, by a higher energy pathway, penta-1,4-diene (Scheme 2). This latter pathway[7] has an energy of activation of 219 kJ mol^{-1}. If this pathway also involves the intermediate diradical, then the subsequent transition state involving rupture of the C(2)–C(3) bond has a barrier 93 kJ mol^{-1} above that of the diradical.



SCHEME 2

If the first stage in the thermal isomerization of the dimethyltricyclohexane is analogous to that occurring in the bicyclopentanes, it must involve rupture of the C(1)–C(5) [or C(2)–C(4)] bond. The facts that no isomerization to another dimethyltricyclohexane occurs and that only the *trans*-dimethylcyclohexadiene is formed are further strong evidence that in molecules of this structure there is no initial rupture of the C(1)–C(6) bond [equivalent to the C(1)–C(5) bond in the bicyclopentanes]. Previous to the present work, the exact configuration, *viz. exo,exo*, *exo,endo*, or *endo,endo*, of the methyl groups in the tricyclohexane was unknown. As only the *trans*-dimethylcyclohexadiene was observed, only the *exo,exo* and *endo,endo* isomers are possible. Steric factors strongly suggest that the compound is in fact *exo,exo*-3,6-dimethyl-*cis,transoid,cis*-tricyclo-[3.1.0.0^{2,4}]hexane.

The second stage in the reaction would involve the fission of the C(2)–C(4) bond. In the case of the bicyclo[2.1.0]pentane isomerization to penta-1,4-diene, the energy of this transition state is well above that of the diradical and indeed much higher than that of the transition state leading to recyclisation or yielding cyclopentene (by hydrogen migration). The difficulty is that the observed energy of activation of 154.3 kJ mol^{-1} observed in the present work is *less* than that reported for even the *cis-trans* isomerization of the 2-methylbicyclopentane. Thus, even if the second stage had zero energy (as it might because of the large assistance that the release of ring strain in the second cyclopropane ring could produce), there would still be an apparent inconsistency. This could be more apparent than real. The release in ring strain in going from (1) to (2) could well be 10 kJ mol^{-1} greater than the corresponding release in going from bicyclo[2.1.0]pentane to the diradical. This would be consistent with the suggestion that the strain energy of the tricyclohexane system is higher than simple estimates based on 'strain additivity' yield.[2] If this is so, then a two-stage mechanism involving a diradical intermediate is possible, with the second stage having an energy of activation of less than perhaps 35 kJ mol^{-1}. Alternatively, the entire reaction may be a one-step concerted process. The present work does not allow an obvious choice between the two possibilities; however, since the latter process is forbidden by orbital symmetry arguments, we prefer the diradical mechanism.



(1) (2)

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[5] J. P. Chesick, *J. Amer. Chem. Soc.*, 1962, **84**, 3250.

[6] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 87.

[7] C. Steel, R. Zand, P. Hurwitz, and S. G. Cohen, *J. Amer. Chem. Soc.*, 1964, **86**, 679.