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Thermal Unimolecular Isomerization of Tricyclo[4,1,0,0^{1,3}]heptane

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The thermal isomerization of tricyclo [4,1,0,0^{1,3}] heptane to a mixture of 3-methylenehexa-1,5-diene and hepta-1,2,6-triene has been investigated in the gas phase in the temperature range 423-463 K. In an aged ' Pyrex reaction vessel, the isomerizations are homogeneous and first order, and the rate constants are independent of pressure down to 25 N m⁻². The rate constants for isomerization to 3-methylenehexa-1,5-diene fit the Arrhenius equation

 $k_3 = 10^{14.21} \pm 0.12 \exp(-148,800 \pm 1050 \text{ J mol}^{-1}/RT) \text{ s}^{-1}$

and those for the isomerization to hepta-1,2,6-triene fit the equation

 $k_1 = 10^{14.07} \pm 0.38 \exp(-155,800 \pm 2760 \text{ J mol}^{-1}/RT) \text{ s}^{-1}$

The results suggest both transformations are unimolecular and the possible transition states are discussed.

THE work reported here forms part of a continuing study on the thermal decomposition of strained-ring hydrocarbons. Many of these compounds undergo valencebond isomerizations, which are good examples of true unimolecular reactions. Among this class of compounds, very few quantitative kinetic studies have been carried out on those containing spiro-ring systems. The pyrolyses of spiropentane itself as well as a few derivatives have been reported.¹⁻³ We report here the results obtained from the pyrolysis of tricyclo[4,1,0,0^{1,3}] heptane, a system even more strained than spiropentane.

EXPERIMENTAL

Materials.—Tricyclo[4,1,0,0^{1,3}]heptane was prepared by treating 1,1-dibromo-2-but-3-enylcyclopropane with methyl-lithium at -78° as described previously.⁴ The tricyclic hydrocarbon was separated from the isomeric hepta-1,2,6-triene by fractional distillation through an annular Tefion spinning band column. Final purification was by preparative gas chromatography.

Apparatus.-The kinetic apparatus was essentially the same as one described previously.⁵ To eliminate adsorption problems the vacuum line and gas pipettes were wrapped with heating tape and maintained at 90 °C. Temperatures were measured with an N.P.L. calibrated platinum resistance thermometer.

Analysis was by gas chromatography using a Perkin-Elmer F11 instrument fitted with a gas-sampling valve. Signals from the flame detector were amplified and integrated. A good separation between reactant and products was obtained by use of a $3.7 \text{ m} \times 2.2 \text{ mm}$ (i.d.) column packed with 60/80 mesh Chromosorb W containing 15% w/w of di-isodecyl phthalate and operated at 60 °C. All analyses were carried out in triplicate. Products were identified by comparison of retention times on several columns, with authentic samples.

RESULTS

Previously it has been reported 4 that the pyrolysis at 250° of tricyclo[4,1,0,0^{1,3}]heptane (I) yields 3-methylenehexa-1,5-diene (II).

Preliminary experiments were carried out in a Pyrex reaction vessel which had been 'aged' by pyrolysis of the

¹ M. C. Flowers and H. M. Frey, J. Chem. Soc., 1961, 5550. ² P. J. Burkhardt, 'The Kinetics of the Thermal Decom-position of Spiropentane and Methylenecyclobutane, Ph.D. Thesis, University of Oregon, 1962.

reactant. As well as (II), we found hepta-1,2,6-triene (III) to be a product. The pyrolysis of the triene (III) yields the diene (II) but as the kinetics of this conversion have already been reported ⁶ it was possible to show that (II) arises directly from (I) as well as indirectly via (III) (see Scheme).



Plots of the logarithm of undecomposed (I) against time were linear, up to at least 80% conversion. The sum of the rate constants $(k_1 + k_3)$ was determined from these plots by least-squares methods. Experiments in which the initial reactant pressure was varied in the range 0.025-1.3 kN m⁻² gave the same value for $(k_1 + k_3)$ within experimental error. Thus the values of $(k_1 + k_2)$ are independent of pressure in this region, and it is also probable that the individual rate constants are pressure independent. Series of experiments were therefore carried out, with an initial reactant pressure of 130 N m⁻², at 14 temperatures.

It is easy to show that for the reaction scheme suggested equation (1) could be applied. At each experimental

$$\frac{k_1}{k_2 - (k_1 + k_3)} \cdot \frac{[(I) + (II) + (III)]}{[(III)]} = \left\{ \frac{[(I)]}{[(I) + (II) + (III)]} - e^{-k_3 t} \right\}^{-1} \quad (1)$$

temperature values of k_2 were calculated from the rate equation of Frey and Lister.⁶ Plots of [(I) + (II) +(III)]/[(III)] against the R.H.S. of equation (1) yielded good straight lines from which values of $k_1/[k_2 - (k_1 + k_3)]$ were obtained at the 14 temperatures. It was thus possible to obtain the individual values of k_1 and k_2 , which are listed in the Table.

- ³ J. C. Gilbert, Tetrahedron, 1969, 25, 1459.

- J. Skattebøl, J. Org. Chem., 19966, 31, 2789.
 R. J. Ellis and H. M. Frey, J. Chem. Soc., 1964, 5578.
 H. M. Frey and D. H. Lister, J. Chem. Soc. (A), 1967, 26.

Arrhenius plots of the data in the table yielded the following equations,

 $\begin{array}{l} k_{3} = 10^{14 \cdot 21 \pm 0 \cdot 12} \exp \left(-148,800 \pm 1050 \text{ J mol}^{-1}/RT \right) \text{ s}^{-1} \\ k_{1} = 10^{14 \cdot 07 \pm 0 \cdot 33} \exp \left(-155,800 \pm 2760 \text{ J mol}^{-1}/RT \right) \text{ s}^{-1} \end{array}$

where the error limits are standard deviations.

A series of runs was carried out in a packed reaction vessel with a surface : volume ratio 10 times that of the unpacked vessel. At 440.5 K in this packed vessel $(k_1 + k_3)$ was found to be $4 \cdot 11 \times 10^{-4} \text{ s}^{-1}$ which is exactly the value calculated from the unpacked vessel data. (The individual values for k_1 and k_3 were also the same within experimental error as those calculated from the Arrhenius equations.)

Rate constants for the isomerization of tricyclo[4,1,0,0^{1,3}]heptane

Temp. K	423.7	$425 \cdot 1$	427.7	429.3	429.5
$10^{4}k_{3}$ s ⁻¹	0.713	0.861	1.07	1.28	1.24
10 ⁵ Å ₁ s ⁻¹	0.822	0.944	1.03	1.24	1.12
Temp. K	$432 \cdot 5$	440·0	443 ·9	451.1	$455 \cdot 2$
$10^4 \bar{k_3} \mathrm{s}^{-1}$	J·84	3.49	5.08	9.71	14.1
10 ⁵ k ₁ s ⁻¹	1.61	3.71	5.97	10.8	16.3
Temp. K	458·8	460 ·9	$462 \cdot 4$	463-1	
$10^4 k_3 \text{ s}^{-1}$	19.6	21.7	24.6	$25 \cdot 4$	
$10^{5} k_{1}^{\circ} s^{-1}$	23.6	24.7	28.4	$29 \cdot 4$	

There can thus be no appreciable heterogeneous component of the reaction.

DISCUSSION

The structural isomerization of spiropentane to methylenecyclobutane and also the *cis-trans* isomerization of 1,2-dideuteriospiropentane both probably involve biradical intermediates. The geometric isomerization is considerably more facile than the structural isomerization. For the former process an energy of activation of 215.5 ± 4 kJ mol⁻¹ has been reported ³ whereas for the structural isomerization the two reported values are 16 and 25 kJ mol⁻¹ higher. For the *cis-trans* isomerization, arguments can be presented for the intermediate formation of biradical (IV) or (V), with, in



our opinion, the probability that (IV) rather than (V) is involved. The isomerization to methylenecyclobutane must involve the opening of the second ring, with a further 'energy cost.' In the pyrolysis of spiropentane to methylenecyclobutane some allene and ethylene is also formed. While this pathway is a minor one at high



pressures (ca. 1 kN m^{-2}), at low pressures it becomes the preferred mode of decomposition. The pyrolysis of methylenecyclobutane itself yields allene and ethylene. Finally if the methylene hydrogen atoms in methylene-

⁷ W. von E. Doering and J. C. Gilbert, Tetrahedron Suppl., 1969, 7, 397.

cyclobutane are replaced by deuterium then reaction (2) occurs far more readily than the cleavage to allene and ethylene. Quantitative data on these changes led Doering and Gilbert ⁷ to suggest a detailed mechanism, which with a very minor modification in some of the calculated enthalpies and the addition of the quantitative data on the *cis-trans* isomerization of 1,2-dideuteriospiropentane, we show in the Figure. (It should be



Enthalpy, 'reaction co-ordinate' diagram for the spiropentanemethylenecyclobutane system. To convert to kJ mol⁻¹ the values of $\Delta H^{\circ}_{\rm F}$ shown should be multiplied by 4-184

noted that values for ΔG°_{298} will be quite similar to those for ΔH°_{298} except in the case of allene + ethylene. In this case the large entropy increase will ensure that these species would be present in highest concentration if the system came to thermodynamic equilibrium under all normal experimental conditions.)

Here we may take the decomposition pathways to be exact analogues of the spiropentane to allene +ethylene reaction. Thus the first stage in the reaction might be expected to proceed by either biradical (VI) or (VII) [which are the analogues of (IV) and (V)] followed



by the formation of (VIII). While biradical (VII) will be less stable than (VI) by virtue of the free electron on the cyclopropyl centre this is probably more than

balanced by the small strain energy of the six-membered ring compared with the five-membered ring in (VI). Thus we expect (VII) to be a lower energy species than (VI). The transformations of (VI) and (VII) to (VIII) are analogous to the isomerization of the cyclopropylcarbinyl radical and the cyclopropyl radical to the butenyl and allyl radicals respectively. The former rearrangement is considerably more facile than the latter so it may well be that the favoured path to (VIII) is via (VI) rather than (VII). Even if we assume that (VIII) can rearrange directly by a lowenergy path to either of the observed products, rather than via the formation of the analogue of methylenecyclobutane, the overall reaction parameters will be largely determined by the energy barrier to be overcome in forming (VIII), and this must be at least that required to form (VI) or (VII). In the case of spiropentane itself this requires $ca. 215 \text{ kJ mol}^{-1}$. For biradical (VII) the energy required will be of the order of 215 kJ mol⁻¹ less the additional strain energy of the tricycloheptane compared with spiropentane. To fit the observed Arrhenius parameters this mechanism would require this additional strain energy to be at least 66 kJ mol⁻¹. The five-membered ring in the tricycloheptane would contribute *ca*. 21 kJ mol⁻¹ just by virtue of its presence but there will be additional strain due to its distorted nature. It appears to us improbable that there is a minimum of 45 kJ mol⁻¹ of additional strain, and if this is correct, then a biradical mechanism of the type proposed for the spiropentane system does not apply to the decomposition of tricyclo[4,1,0,0^{1,3}]heptane. (Direct evidence on this possibility must await a heat of formation value for the tricycloheptane.)

If a biradical mechanism is not involved then the low value of the observed energies of activation can only be rationalised on the basis of a concerted mechanism. Two possibilities arise naturally. Either the observed products are formed directly, or they may involve the intermediate formation of 2-methylenebicyclo[2,2,0]hexane. The direct formation of the observed products or the isomerization to 2-methylenebicyclo[2,2,0]hexane are both allowed processes on the basis of the conservation or orbital symmetry. The decomposition of the 2-methylenebicyclo[2,2,0]hexane would not be symmetry allowed but its decomposition is likely to be very fast by a biradical pathway. We have no experimental evidence to favour one of these alternatives over the other. Further, while the observed 'A' factors and energies of activation are consistent with a concerted reaction they do not produce unambiguous evidence for such a pathway.

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