

782. *The Thermal Unimolecular Isomerization of Isopropenylcyclopropane.*

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Thermal isomerization of isopropenylcyclopropane between 332° and 386° in an "aged" vessel yields 1-methylcyclopentene in a first-order, homogeneous reaction. The rate constant is independent of the pressure down to 0.5 mm. and is fitted by the equation, $k = 10^{13.89} \exp(-50,900/RT)$ sec.⁻¹. The probable reaction mechanism for this isomerization and that of vinylcyclopropane is discussed and compared with that for cyclopropane.

DESPITE extensive investigation¹ of the thermal isomerization of cyclopropane and alkylcyclopropanes there is uncertainty about the reaction mechanism. Since the work of Chambers and Kistiakowsky,² the isomerization of cyclopropane has been discussed in terms of a hydrogen-migration mechanism, where movement of a hydrogen atom to a carbon atom to which it was not formerly bonded, is followed by carbon-carbon bond rupture, and an expanded-ring or trimethylene transition state³ is considered to be formed by initial extension or rupture of a carbon-carbon bond. The first mechanism is supported by Slater's calculations,⁴ the second by recent work on the *cis-trans*-isomerization of 1,2-dideuterocyclopropane.^{3a,5} Vinylcyclopropane has been shown⁶ to undergo an isomerization of a type distinct from that of the alkylcyclopropanes. The formation of the product, cyclopentene, does not require the breaking of a carbon hydrogen bond. In this paper the thermal isomerization of isopropenylcyclopropane has been investigated, to confirm that the second type of isomerization is not confined to the unsubstituted vinyl compound and to determine the Arrhenius parameters for the rearrangement. It is felt that consideration of these reactions may help to decide between the two possible transition states postulated for the isomerization of cyclopropane itself.

EXPERIMENTAL

Isopropenylcyclopropane.—2-Cyclopropylpropan-2-ol was prepared by treating cyclopropyl methyl ketone with methylmagnesium iodide by a method similar to that described by Volkenburgh *et al.*⁷ A drop of concentrated sulphuric acid was added to the alcohol (10 ml.) and the mixture gently heated. The product was slowly distilled from the mixture, through a packed column jacketed at 60° and was then distilled at reduced pressure at -10° through a Podbielniak column with a high reflux ratio. The final isopropenylcyclopropane was >99.5% pure.

The apparatus, procedure, and gas-chromatographic analysis of the reaction mixtures were similar to those used earlier.⁸ The chromatographic column was maintained at 33°, and a flow rate of carrier gas (hydrogen) of ~25 ml./min. was used, 1-methylcyclopentene and isopropenylcyclopropane being eluted in 19 and 30 min., respectively. The product was identified by trapping material corresponding to its chromatographic peak and recording the infrared spectrum; a micro-gas cell (path-length 5 cm., vol. ~5 ml.) and a Unicam S.P. 100 instrument were used.

¹ Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609; Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Flowers and Frey, *J.*, 1959, 3953; *Proc. Roy. Soc.*, 1961, *A*, **260**, 424.

² Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.

³ (a) Schlag, Rabinovitch, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; (b) Benson, *ibid.*, 1961, **34**, 521.

⁴ Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

⁵ Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.

⁶ Flowers and Frey, *J.*, 1961, 3547.

⁷ Volkenburgh, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 172.

⁸ Frey and Marshall, *J.*, 1962, 3052.

RESULTS AND DISCUSSION

In the range 332—386° isopropenylcyclopropane isomerizes to 1-methylcyclopentene, reaction obeying first-order kinetics up to high percentage conversions. The results of a typical series of runs are recorded in Table 1. The mean value of k , calculated by the method of least squares, is 2.77×10^{-4} sec.⁻¹.

Before kinetic runs were started the reaction vessel was "aged" by allowing some isopropenylcyclopropane to isomerize in it. Ageing was rapid and had to be repeated only if air was admitted to the hot reaction vessel. A series of runs at 365° and pressures from 21 to 0.5 mm. showed that in this range the rate constant is independent of the pressure (Table 2).

In detailed studies at 5 mm., at least 9 runs were performed at each of eight temperatures, the percentage decomposition varying from 5 to 60%. Plots of the logarithm of the amount undecomposed against time were linear; rate constants calculated for each temperature by the method of least squares are shown in Table 3. An Arrhenius plot

TABLE 1.

Isomerization of isopropenylcyclopropane at 364.5°.

Time (min.)	0	5	10	13	16	19	23	29
Undecomp. (%) ...	100	91.90	84.13	80.64	76.60	72.60	67.90	61.72
10 ⁴ k (sec. ⁻¹)	—	2.82	2.87	2.76	2.78	2.81	2.80	2.77
Time (min.)	32	36	40	44	48	49	50	60
Undecomp. (%) ...	58.67	55.16	51.57	47.84	45.06	44.14	43.76	37.22
10 ⁴ k (sec. ⁻¹)	2.78	2.75	2.76	2.79	2.77	2.78	2.76	2.75

TABLE 2.

Isomerization of isopropenylcyclopropane at 365°; all runs for 16 minutes.

Pressure (mm.) ...	21	13.5	9.5	6.5	3.5	2.5	2.5	1.5	1.0	0.5
Undecomp. (%) ...	75.89	76.11	75.91	76.05	75.89	75.67	75.46	75.76	75.94	75.64
10 ⁴ k (sec. ⁻¹)	2.87	2.84	2.87	2.85	2.87	2.90	2.93	2.89	2.87	2.91

TABLE 3.

Rate constants for decomposition of isopropenylcyclopropane at various temperatures.

Temp.	332.2°	337.2°	345.8°	356.9°	364.5°	371.1°	381.6°	386.4°
10 ⁵ k (sec. ⁻¹)	3.32	4.53	8.34	17.0	27.7	42.4	80.1	107

gave a good straight line. Calculation of the A factor and the energy of activation by the method of least squares gives: $k_{\infty} = 10^{13.89} \exp(-50,900/RT)$ sec.⁻¹. Calculation of the standard deviations of the Arrhenius parameters by the normal statistical procedures shows that random errors are negligible. The probable error in the energy of activation is estimated as ± 600 cal. and results largely from uncertainties in the temperatures.

To verify that the isomerization was entirely homogeneous, runs were carried out at 355.5° in a reaction vessel filled with glass tubing of 8 mm. diameter (surface : volume ratio 11 times greater than for the unpacked vessel). The mean value of the rate constant then obtained was 1.7% less than that for the unpacked vessel. Since the two vessels had slightly different geometries no significance can be attached to this fractionally lower value, and there can be no appreciable heterogeneous component of the isomerization.

Methylcyclopentene is a powerful inhibitor of radical reactions, and since the linear nature of the first-order plots indicates no reduction of the rate constant of the isomerization due to build-up of methylcyclopentene in the system, there can be no radical-chain

component of the reaction. Thus all the evidence indicates that the isomerization is a true unimolecular reaction.

The Arrhenius constants for the isomerization of vinylcyclopropane to cyclopentene [$k = 10^{13.5} \exp(-49,600/RT)$ sec.⁻¹] are very similar to those for the isomerization of isopropenylcyclopropane to methylcyclopentene. If the energies of activation are assumed to be equal (which is probably just possible within the combined experimental errors), then the A factors of the two reactions will be virtually identical. The formation of cyclopentenes from these cyclopropanes can most easily be understood in terms of the formation of the biradical $\cdot\overset{1}{\text{C}}\text{H}_2\cdot\overset{2}{\text{C}}\text{H}_2\cdot\overset{3}{\text{C}}\text{H}\cdot\overset{4}{\text{C}}\text{R}\cdot\overset{5}{\text{C}}\text{H}_2 \longleftrightarrow \cdot\text{C}\text{H}_2\cdot\text{C}\text{H}_2\cdot\text{C}\text{H}\cdot\text{C}\text{R}\cdot\text{C}\text{H}_2\cdot$ (R = H or Me). Ring closure at positions 1—3 regenerates the cyclopropane; at positions 1—5 it affords cyclopentene. *cis-trans*-Isomerization of 1,2-dideuterocyclopropane very probably proceeds through an intermediate biradical $\cdot\text{C}\text{H}_2\cdot\text{C}\text{H}_2\cdot\text{C}\text{H}_2\cdot$, though whether this is a "free" biradical, or whether there is a remaining interaction between C-1 and C-3 is probably not susceptible to direct experimental test (indeed it is doubtful whether trimethylene can be completely "free"). The difference between the energy of activation for this process and that resulting in the cyclopentane biradical should be that of the delocalization energy of the latter. This has been calculated⁹ in the case of allyl itself to be 17—18 kcal. mole⁻¹. For the geometrical isomerization of dideuterocyclopropane $E_A = 64$ kcal. mole⁻¹; hence the experimental difference in energy of activation between the two processes is ~14 kcal. mole⁻¹, close to the value expected for the suggested mechanism. The 3—4 kcal. mole⁻¹ difference between theory and experiment may be due to the requirement that the "transition-state configuration" of the cyclopentene biradical leading to the formation of a cyclopentene is somewhat distorted from the "free-biradical" configuration. Such a slightly strained transition state would also be consistent with the fact that the A factors for the reactions leading to cyclopentenes are considerably smaller than for the geometrical isomerization of the deuterocyclopropane (even after allowance for the small difference expected from differences in path degeneracy).

If the suggested biradical mechanism is valid then two predictions are possible: (i) a vinylcyclopropane with another substituent in the cyclopropane ring should undergo *cis-trans*-isomerization with an energy of activation approximately 17 kcal. mole⁻¹ less than for dideuterocyclopropane; (ii) a compound such as propenylcyclopropane should show *cis-trans*-isomerization about the double bond with a "relatively low" energy of activation. Both these predictions are being checked experimentally.

It is highly probable that the geometrical and the structural isomerization of cyclopropane occur by similar mechanisms. Hence the support given by the work reported in this paper for the biradical mechanism for the geometrical isomerization of 1,2-dideuterocyclopropane also supports a similar mechanism for the isomerization to propene.

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⁹ Franklin and Field, *J. Amer. Chem. Soc.*, 1953, **75**, 2819.