174. *The Thermal Unimolecular* cis–trans-*Isomerization of 1-Ethyl-2-methylcyclopropane.*

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cis-2-Ethyl-2-methylcyclopropane undergoes a reversible *cis–trans*-isomerization which, in an " aged " reaction vessel, is first-order and homogeneous. The rate constants, which are independent of the pressure from 3 to 100 mm., have been determined at nine temperatures between 396 and 446°, and the Arrhenius parameters evaluated. Whence,

$$k(cis \longrightarrow trans) = 10^{15\cdot08}\exp(-58{,}870/\boldsymbol{R}T)\ \text{sec.}^{-1}.$$

Measurements of the equilibrium constants from 414° to 440° gave a least-squares value of 1·2 kcal./mole for the enthalpy change. Occurring simultaneously with the geometrical isomerization, there is a slower structural isomerization to give several C_6-olefins.

THE thermal isomerization of cyclopropane [1] to propene and of alkylcyclopropanes [2] to olefins are among the best-authenticated examples of unimolecular reactions. Recently, it has been shown that substituted cyclopropanes undergo reversible *cis–trans*-isomerizations which also appear to be truly unimolecular.[3] These geometrical isomerizations are faster than the corresponding structural transformations, and it has usually been possible to follow the kinetics of both reaction paths. The present Paper describes a continuation of this work with ethylmethylcyclopropane.

EXPERIMENTAL

cis-1-*Ethyl-2-methylcyclopropane*.—This was prepared by the action of methylene di-iodide and a zinc copper couple [4] on *cis*-pent-2-ene. After fractional distillation and preparative gas chromatography, the product was more than 99% pure (gas chromatography). All olefins used were commercially available or were synthesized by normal procedures.

Apparatus.—A conventional " static " vacuum system was used. Only greaseless stopcocks with Viton A diaphragms were employed, so that the usual troubles due to absorption of vapours were virtually eliminated. Isomerizations were carried out in a cylindrical Pyrex reaction vessel (about 200 ml.) fitted with a thermocouple well and with a dead-space of 0·2%. Temperatures were determined using a platinum/platinum–rhodium thermocouple. The furnace was tapped at four points for external shunts, and the temperature gradient over the entire length of the reaction vessel could be kept to ±0·2°. The furnace temperature was controlled by a Sunvic RT 3 R regulator and could be kept constant to better than ±0·25°.

Analysis.—Reaction products were analysed by gas chromatography using a coiled copper column (20 ft. × 0·17 in.) packed with 40—60 mesh Chromosorb P containing 20% w/w of di-2-cyanoethyl ether. Other details about the analytical system have been given previously.[5]

Procedure.—The ethylmethylcyclopropane was introduced into the reaction vessel from a gas pipette. At the end of the run the reaction mixture was frozen into a previously evacuated detachable bulb (100 ml.) cooled in liquid oxygen. The sample in the bulb was flash-evaporated, and transferred by Toepler pump to the analytical system. Between runs, the reaction vessel was evacuated below 10^{-4} mm.

RESULTS AND DISCUSSION

In the temperature range 396—446° *cis*-1-ethyl-2-methylcyclopropane undergoes a reversible first-order homogeneous reaction, to give the *trans*-isomer to the extent of

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[1] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563.

[2] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Flowers and Frey, *J.*, 1962, 1157; *Proc. Roy. Soc.*, 1961, *A*, **260**, 424.

[3] Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996; Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122; Frey and Marshall, *J.*, 1963, 5717.

[4] Shank and Shechter, *J. Org. Chem.*, 1959, **24**, 1825.

[5] Frey and Marshall, *J.*, 1962, 3052.

74·3—73·2% of the resulting equilibrium mixtures. Prior to kinetic runs, the reaction vessel was "aged" by heating samples of the cyclopropane for 1 hour at 440° until reproducible rate constants were obtained; this was rapidly achieved, and the process had to be repeated only if air was admitted to the vessel when it was hot.

A series of runs at various pressures from 3 to 100 mm. were carried out at 425·6° (Table 1). In each case the reaction time was 15 minutes. If k_1 and k_2 are the rates of the *cis*→*trans*- and *trans*→*cis* isomerizations, respectively, then, for runs starting with the pure *cis*-compound, $(k_1 + k_2) = (1/t) \ln [x_e/(x_e - x)]$, where x_e is the equilibrium concentration of the *trans*-isomer and x is its concentration after time t. In this pressure range the rate constant is clearly independent of pressure. In the remainder of the work a pressure of 5 mm. was always used.

TABLE 1.

Isomerization of *cis*-1-ethyl-2-methylcyclopropane at 425·6°.

Pressure (mm.)	100	27·5	22	16	15	11	7	5	3·2
% of *trans*-isomer ...	31·49	31·49	31·16	31·06	31·47	31·19	31·10	31·50	31·30
$10^4(k_1 + k_2)$ (sec.$^{-1}$)	6·280	6·280	6·298	6·302	6·285	6·296	6·300	6·278	6·292

As well as the *cis–trans*-isomerization, a series of simultaneous structural isomerization reactions occur in the present system. By analogy with other cyclopropane rearrangements no less than nine products are to be expected from the ethylmethylcyclopropane.

$$\text{C}_6\text{-Olefins} \xleftarrow{\Sigma k_3} cis\text{-Isomer} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} trans\text{-Isomer} \xrightarrow{\Sigma k_4} \text{C}_6\text{-Olefins}$$

The olefin peaks on gas chromatograms were all very small, indicating that Σk_3 and Σk_4 were small compared with k_1 and k_2. Olefins positively identified were *cis*- and *trans*-hex-2-ene, 2-ethylbut-2-ene, and 2-methylpent-1-ene. No attempts were made to identify other olefins since the peaks were too small to be measured quantitatively and were not completely resolved.

To determine the values of k_1 and k_2, the values of the equilibrium constants had to be determined at various temperatures. These were measured directly by allowing the *cis*-cyclopropane to isomerize for increasing lengths of time until no further change occurred in the *cis* : *trans* ratio. Some values were checked by heating pre-mixed *cis*- and *trans*-ethylmethylcyclopropane. If Σk_3 is not equal to Σk_4 the values determined in this fashion are not the true equilibrium values. However, since Σk_3 and Σk_4 are small compared with k_1 and k_2, the errors introduced by their neglect are less than the experimental errors of the determinations. Equilibrium constants were determined at five temperatures (Table 2). A plot of the logarithm of the equilibrium constant against $1/T$ was linear, and a least-squares analysis of the data gave a value of 1·2 kcal./mole for the enthalpy change for the reaction.

TABLE 2.

Equilibrium constants for the *cis*- and *trans*-isomerization.

Temperature (°c)	414·1	419·7	425·6	432·3	440·0
Equilibrium constant	2·831	2·817	2·788	2·774	2·745

Plots of log (equilibrium value of *trans*-cyclopropane minus measured value) against time were linear for runs carried out at nine different temperatures. At each temperature, values of $k_1 + k_2$ were determined from these plots by the least-squares method. Combination of these values with values for the equilibrium constants at the appropriate temperatures allowed the values of k_1 in Table 3 to be calculated, since $K = k_1/k_2$. From

TABLE 3.

Rare constants for the isomerization of *cis*-1-ethyl-2-methylcyclopropane.

Temp. (°c)	396·7	402·0	407·8	414·1	419·7	425·6	432·3	440·0	446·5
$10^4 k_1$ (sec.$^{-1}$)	0·7523	1·013	1·524	2·242	3·227	4·619	6·903	10·88	15·59

these results the Arrhenius parameters were calculated by least-squares, whence, $k_1 = 10^{15\cdot08} \exp(-58{,}870/\boldsymbol{R}T)$ sec.$^{-1}$. Temperature fluctuations are probably the limiting factor on the accuracy with which the energy of activation has been determined, and introduce a maximum uncertainty of ±500 cal.

A series of runs were carried out in a packed reaction vessel in which the surface : volume ratio was 8·2 times that in the normal vessel. Rate constants obtained in both vessels were identical within experimental error; hence, there can be no appreciable heterogeneous component of the reaction.

One series of runs at 436·4° was carried out starting with the *trans*-isomer; this was prepared by heating the *cis*-isomer and freezing out the *trans*-component after chromatographic separation. Within experimental error the calculated value for k_1 determined in this manner fell exactly on the Arrhenius plot.

That the *cis–trans*-isomerization is a true unimolecular transformation is further supported by the similarity of the kinetic features and parameters of this reaction to those for 1,2-dimethyl- and 1,2,3-trimethyl-cyclopropane.

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