1090. *The Thermal Unimolecular Isomerization of* 1,2,3-*Trimethylcyclopropane.*

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The thermal isomerization of *cis*-1,2,3-trimethylcyclopropane between 395° and 452° has been studied. The compound undergoes reversible *cis–trans*-isomerization which, in an " aged " reaction vessel, was of the first order and homogeneous. Rates for the *cis*-compound were measured and the Arrhenius parameters evaluated: $k\ (cis \longrightarrow trans) = 10^{15\cdot78}\exp\ (-60{,}950/\boldsymbol{R}T)$ sec.$^{-1}$. Measurements of the equilibrium constants over part of the above temperature range gave a least-squares value for the enthalpy change of 2·30 kcal./mole. Occurring simultaneously with the geometrical isomerization, there is a slower structural isomerization to yield *cis*- and *trans*-3-methylpent-2-ene in about equal quantities.

THE thermal unimolecular isomerization of cyclopropane to propene has been known (and studied) for nearly thirty years. The recent discovery that 1,2-dideuteriocyclopropane undergoes thermal unimolecular geometrical isomerization which is faster than the structural isomerization[1] has reopened the question of the structure of the transition state for both of these rearrangements. An investigation[2] of the thermal decomposition of 1,2-dimethylcyclopropane showed that the geometrical isomerization is not restricted to the dideuterio-compound. With the dimethyl compound also, the geometrical was

[1] Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.

[2] Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.

considerably faster than the structural isomerization. This paper describes an extension of these studies to a trisubstituted cyclopropane, namely, 1,2,3-trimethylcyclopropane.

Experimental.—1,2,3-Trimethylcyclopropane was prepared from 3-methylpentane-2,4-diol by a method similar to that of Bartleson, Burk, and Lankelma.[3] The diol was brominated, to yield 2,4-dibromo-3-methylpentane, and ring closure was brought about by a modified form of Gustavson's reaction [4] with zinc dust in dioxan. The crude hydrocarbon mixture was separated by distillation, and olefins removed by treatment with bromine at −78°, followed by washing with ice-cold sodium carbonate solution and drying ($CaCl_2$). This mixture (which contained at least 8 hydrocarbons) was fractionally distilled in a Podbielniak column at −25°. Two fractions were collected, the first containing most of the *trans*-1,2,3-trimethylcyclopropane and the second containing most of the *cis*-isomer. Both fractions contained numerous impurities. Final purification was by gas chromatography.

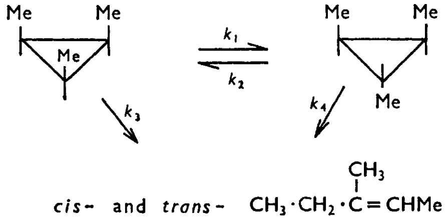
cis- and *trans*-3-Methylpent-2-ene were prepared by dehydration of 3-methylpentan-3-ol through the xanthate.[5] The reaction gave, in addition to these olefins, a small quantity of 2-ethylbut-1-ene.

The apparatus used and the procedure employed were essentially as described previously.[6]

Analysis was by gas chromatography. A 30 ft. × 0·17 in. coiled copper column packed with 40—60 mesh Chromosorb P containing 20% w/w of di-2-cyanoethyl ether was used for the kinetic runs. For the analysis of the mixtures obtained while investigating the variation of equilibrium constant with temperature, the 30 ft. column was extended by adding another copper column, 16 ft. × 0·17 in. packed with Chromosorb P containing 20% w/w of a saturated solution of silver nitrate in ethylene glycol. In all cases hydrogen was the flow gas, a Gow Mac tungsten-filament katharometer was used as detector, and signals from the detector were integrated electronically. Identification of the products of the thermal isomerization was by comparison of their retention times with those of known compounds.

Results and Discussion.—*cis*-1,2,3-Trimethylcyclopropane undergoes a reversible geometrical isomerization to produce an equilibrium mixture of the *cis*- and the *trans*-isomer, in the temperature range 395—452°. A parallel structural isomerization of both isomers occurs much more slowly, to give a mixture of *cis*- and *trans*-3-methylpent-2-ene. In runs carried to near completion increasing quantities of 2-ethylbut-1-ene were formed. The yield of this olefin, plotted as a function of the percentage reaction, gave a curve of zero initial slope and positive curvature. The olefin is, therefore, a secondary product formed from the 3-methylpent-2-ene. In addition, very small quantities of other olefins are formed.

Preliminary runs at 428° with various pressures of *cis*-1,2,3-trimethylcyclopropane showed that the rate constants for the geometrical isomerization were independent of pressure from 12·5 to 3·5 mm., and had fallen by only 2% from this " high pressure limit " at 0·5 mm. The reaction was studied in detail at 2·5 mm., at which pressure the rate constant was within 1% of the high-pressure limit. At each temperature at least 10 runs were analysed, in which the percentage of the *trans*-isomer formed varied from 4% to



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[3] Bartleson, Burk, and Lankelma, *J. Amer. Chem. Soc.*, 1946, **68**, 2513.
[4] Gustavson, *J. prakt. Chem.*, 1887, **36**, 300.
[5] *Org. Reactions*, **12**, p. 57.
[6] Frey and Marshall, *J.*, 1962, 3052.

66%. As frequently with other hydrocarbon isomerizations, it was necessary to age the reaction vessel before reproducible rate constants were obtained.

The values of the equilibrium constant for the *cis*- and *trans*-trimethylcyclopropanes are required at each temperature investigated so that the individual values of k_1 and k_2 can be calculated. These constants were determined by heating samples of the *cis*-isomer for increasing lengths of time until successive analyses differed by less than 0·2%. Times were chosen so that if equilibrium had not been reached the variation in these values would have been greater than this amount. The ratio *cis* : *trans*-isomer (K') is not equal to the true equilibrium constant K but is related to it by the equation

$$K = K'[1 + (k_3 - k_4)/k_1(1 + K')].$$

However, since both k_3 and k_4 are small compared with k_1 and k_2 the difference between K and the experimentally determined ratio will be very small. A plot of the logarithm of this ratio against the reciprocal of the absolute temperature gave a good straight line from which ΔH for the *cis–trans*-isomerization was calculated as 2·3 kcal./mole. It is to be noted that an error of 0·7% in the experimental value found for the content of *trans*-isomer, which would result in a value of the ratio *cis* : *trans* well off the log ratio–$1/T$ plot, produces a 2·8% error in the calculated value of k_1.

The calculated values for k_1, obtained for the eight temperatures studied are shown in the Table. An Arrhenius plot of these values gave an excellent straight line from which the energy of activation and frequency factor were calculated by the method of least squares, whence $k_1 = 10^{15 \cdot 78} \exp(-60{,}950/\boldsymbol{R}T)$ sec.$^{-1}$. The statistical probable error is negligible (15 cal./mole), but an estimated uncertainty in the energy of activation of about ±600 cal./mole arises mainly from possible variations in the temperature of the reaction vessel.

Rate constants for the *cis–trans*-isomerization of *cis*-1,2,3-trimethylcyclopropane.

Temp.	451·7°	443·7°	435·6°	427·5°	420·6°	411·8°	404·6°	395·1°
$10^4 k_1$ (sec.$^{-1}$)	24·5	15·4	9·54	5·80	3·69	2·08	1·29	0·69

A series of runs was carried out in a reaction vessel packed with glass tubes which had a surface : volume ratio 11 times greater than that of the unpacked vessel. The rate constant obtained in the packed was 3% lower than that in the unpacked vessel. Since the two vessels had slightly different external geometries and were not placed in identical positions in the furnace this difference in rate constant is insignificant, and it can be concluded that there can be no appreciable heterogeneous component of the reaction.

The Arrhenius equation relating to the *cis–trans*-isomerization of 1,2-dimethylcyclopropane, $k = 10^{15 \cdot 25} \exp(-59{,}420/\boldsymbol{R}T)$ sec.$^{-1}$, yields rates virtually the same as those obtained in this work, in the temperature range studied. The differences in the energies of activation and frequency factors in the two studies are covered by the combined experimental errors of the two determinations and cannot, therefore, be considered significant. The difference in the enthalpy of formation between *cis*- and *trans*-1,2-dimethylcyclopropane of 1·07 kcal./mole may be ascribed to the difference in repulsion between the methyl groups in the *cis*- and the *trans*-orientation. Twice this value is to be expected for *cis*- and *trans*-1,2,3-trimethylcyclopropane, in agreement with the experimental value of 2·3 kcal./mole found in this work.

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