Thermal Unimolecular Isomerizations of Substituted Cyclobutenes

Part 2.—1,2-Dimethylcyclobutene

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The thermal isomerization of 1,2-dimethylcyclobutene has been studied from 149 to 197°C. In this range, 1,2-dimethylcyclobutene undergoes a " clean " isomerization to 2,3-dimethylbuta-1,3-diene. The reaction is homogeneous, first-order and unaffected by the presence of nitric oxide or propylene. The rate constants are accurately fitted by the Arrhenius equation

$$k = 10^{13.839} \exp(-36{,}036/RT) \text{ sec}^{-1},$$

and are independent of the pressure in the range 1-100 mm. The reaction is almost certainly a true unimolecular transformation.

The isomerizations of cyclobutene to butadiene [1] and 1-methylcyclobutene to isoprene [2] (part 1) are unimolecular transformations. This type of unimolecular isomerization may be general for many substituted cyclobutenes. In this paper another substituted cyclobutene is shown to undergo the expected isomerization. The investigation of a series of closely related unimolecular transformations is desirable, but in the studies of the reactions of cyclopropane [3] and alkylcyclopropanes [4] difficulties due to the multiple paths for isomerization for the substituted cyclopropanes makes detailed comparisons difficult. As a result it has still not been possible to determine unambiguously the exact nature of the transition state for these transformations.[5] The cyclobutenes may be a suitable series of compounds and it should be possible for the first time to investigate even relatively subtle effects of various substituents on the structure of the transition state in a unimolecular reaction.

EXPERIMENTAL

1,2-Dimethylcyclobutene was prepared by irradiation of a solution of 2,3-dimethylbuta-1,3-diene in isopentane. This method is essentially the same as that described by Crowley [6] except that a quartz sleeve was used in the irradiation. When *ca.* 60 % of the diene had been converted into the cyclobutene the photolysis was stopped. The bulk of the isopentane was removed by distillation, leaving a mixture of isopentane, 2,3-dimethylbuta-1,3-diene and 1,2-dimethylcyclobutene in the ratios of approximately 4 : 1 : 2. Pure dimethylcyclobutene was separated from this mixture by gas chromatography. Its n.m.r. spectrum in CCl_4 and b.p. agree well with the values given by Srinivasan.[7]

APPARATUS

A conventional high-vacuum " static " system was used. Stopcocks were replaced by glass-fluon diaphragm valves to minimize absorption problems. Two Pyrex reaction vessels were used, one a spherical bulb of *ca.* 150 ml, the other a cylindrical vessel of almost the same volume packed with Pyrex tubes, to give a surface to volume ratio almost 10 times larger than the unpacked vessel. The vessels were mounted vertically in a high-temperature oil thermostat. The temperature gradient over the vessel was less than 0·05°C and the mean temperature was constant to better than ±0·02°C. (There was always a short term cycling of

±0·07°C but no variation in the mean temperature was detected, and the cycling time was always considerably less than the time of the shortest run.) Temperatures were measured with a mercury-in-glass thermometer standardized against an N.P.L. calibrated thermometer. All temperatures should therefore be reproducible and accurate to better than ±0·1°C. By placing a diaphragm valve immediately outside the thermostat the dead space was reduced to a negligible value.

ANALYSIS

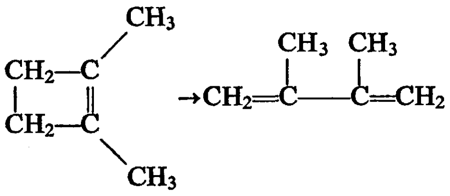
Gas chromatography was used to analyze reaction mixtures. This part of the apparatus consisted of an inlet system and variable sample volume, a 25 ft. × 0·17 in. int. diam. coiled copper column packed with 40–60 mesh Chromosorb containing 12% w/w of $\beta\beta'$-oxydipropionitrile and was maintained at 25°C. Hydrogen was the carrier gas and a Gow-Mac tungsten filament katharometer was used as the detector. Signals from the katharometer were recorded and integrated as described previously.[2] No greased stopcocks were used in any part of this system. All analyses were carried out in duplicate. With an inlet pressure of 10 lb/in.^{2} of hydrogen (outlet at atmospheric pressure) the dimethylcyclobutene was eluted in 10 min and the diene in 18 min.

PROCEDURE

This was essentially identical to that employed previously [1]

RESULTS

In the range 149·6-197°C, 1,2-dimethylcyclobutene was found to undergo a " clean " first order-isomerization to 2,3-dimethylbuta-1,3-diene,



No other products were detected by gas chromatography. Isomerizations were investigated at 11 temperatures in the above range. Several runs were carried out at each temperature, the duration of the runs varying from 1 to 15 h at the lowest temperature, and up to 12 min at the highest temperature. No change was found for the computed rate constants even for runs carried to over 80 % completion, which is additional evidence for the absence of side reactions. Table 1 shows the results obtained at 170·7°C.

TABLE 1.—THERMAL ISOMERIZATION AT 170·7°C

time (sec)	1200	1800	2730	3605	3780	4200
% dimethylcyclobutene remaining	86·2	80·01	70·79	63·54	61·93	59·12
10^4k, sec^{-1} (calc.)	1·238	1·239	1·265	1·258	1·267	1·253
time (sec)	4500	4890	6120	7200	9000	
% dimethylcyclobutene remaining	56·86	54·40	46·51	40·96	32·56	
10^4k, sec^{-1} (calc.)	1·255	1·245	1·250	1·240	1·247	

The rate constants obtained for the various temperatures are shown in table 2, the pressure of the dimethylcyclobutene being 3·0 mm.

TABLE 2.—RATE CONSTANTS FOR THE ISOMERIZATION OF 1,2-DIMETHYLCYCLOBUTENE

temp., °C.	149·65	159·3	163·1	168·3	170·7	
10^4k (sec^{-1})	0·1620	0·4349	0·6069	0·9905	1·246	
temp., °C.	173·3	179·0	182·23	187·5	193·3	196·96
10^4k (sec^{-1})	1·581	2·585	3·500	5·576	8·906	12·25

Runs carried out at 170·7°C with dimethylcyclobutene in the presence of either 10 % of nitric oxide or 10 % of propylene showed that the rate of isomerization was unaffected. The mean values of the rate constants were within 1 % of the mean value shown in table 1.

It was found that the rate constant of isomerization of 1,2-dimethylcyclobutene was independent of pressure in the range 1-100 mm at 170·7°C, as is shown in table 3.

TABLE 3.—EFFECT OF PRESSURE ON RATE CONSTANT AT 170·7°C

pressure, mm	1·0	1·5	2·1	3·0	6·0	12·2	21·0	45·0	99·4
10^4k, sec^{-1}	1·290	1·240	1·242	1·246	1·264	1·255	1·261	1·243	1·260

The first few runs carried out in the packed reaction vessel at 170·7°C gave irreproducible values. However, after leaving 15 mm of the cyclobutene in the vessel overnight reproducible values were obtained. The rate constant for isomerization in the "aged" packed reaction vessel ($1{\cdot}250\times10^{-4}$ sec^{-1}) was the same as in the unpacked vessel.

An Arrhenius plot of the rate constants shown in table 2 gave an excellent straight line, and the frequency factor and energy of activation were calculated by the method of least squares, whence $k = 10^{13{\cdot}839}\exp(-36{,}036/RT)$ sec^{-1}. The standard deviation of the energy of activation was only ±3 cal which indicates the high degree of reproducibility of the data. Consequently any errors in the value of E are " non-random " and their estimation becomes very uncertain.

DISCUSSION

The isomerization of 1,2-dimethylcyclobutene is kinetically first order, homogeneous and unaffected by radical inhibitors, i.e., it is a true unimolecular transformation. (Since cyclobutene and 1-methylcyclobutene undergo analogous isomerizations under similar conditions and with the same kinetic characteristics the evidence for the unimolecular nature of the reaction becomes even stronger.) The absence of pressure effect on the rate constant in the range investigated is to be expected for a molecule of this complexity. Methylcyclobutene was found [2] to isomerize to isoprene approximately 4½ times more slowly than the corresponding reaction of cyclobutene at 150°C. This was rationalized in terms of the electron donating properties of the methyl group leading to an increase in bond length of the carbon double bond causing a corresponding reduction in the strain in the C3—C4 bond, and hence an increase in energy of activation of the reaction. The present work shows that the rate of isomerization of the dimethylcyclobutene at 150°C is slower still, being approximately one third of the value of that for methylcyclobutene. Comparison of the two Arrhenius equations shows that the further reduction is entirely due to a further increase in the energy of activation of the reaction. This is clearly consistent with the previously suggested effect of the methyl group.

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