

### 51. *The Thermal Isomerization of 1-Cyclopropyl-2-methylpropene.*

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The thermal decomposition of 1-cyclopropyl-2-methylpropene in a static system, between 350 and 390°, is first-order and probably unimolecular, and yields 3,3-dimethylcyclopentene, 5-methylhexa-1,4-diene, and *cis*- and *trans*-2-methylhexa-2,4-diene as products. The overall rate of reaction is independent of pressure from 2 to 17 mm. and is fitted by the Arrhenius equation

$$k_{\text{total}} = 10^{14.31} \exp(-53,800/RT) \text{ sec.}^{-1}.$$

The Arrhenius equations for the individual products are:

$$k \text{ (dimethylcyclopentene)} = 10^{14.00} \exp(-54,600/RT) \text{ sec.}^{-1}$$

$$k \text{ (5-methylhexa-1,4-diene)} = 10^{14.61} \exp(-56,650/RT) \text{ sec.}^{-1}$$

$$k \text{ (cis-2-methylhexa-2,4-diene)} = 10^{13.33} \exp(-53,000/RT) \text{ sec.}^{-1}$$

$$k \text{ (trans-2-methylhexa-2,4-diene)} = 10^{13.25} \exp(-52,100/RT) \text{ sec.}^{-1}.$$

Small amounts of unidentified cracking products were also formed.

AMONG the best known examples of unimolecular reactions are the isomerizations of cyclopropane<sup>1</sup> and alkylcyclopropanes<sup>2</sup> to olefins. These have been described in terms of a transition state involving an expanded-ring or biradical, or in terms of a complex where hydrogen migration is followed by, or occurs simultaneously with, carbon-carbon bond rupture.<sup>3</sup> *cis-trans*-Isomerizations of cyclopropanes can be described by either the expanded-ring or the biradical mechanism.<sup>4</sup> Recently, a third type of cyclopropane

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

<sup>2</sup> Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

<sup>3</sup> Smith, *J. Chem. Phys.*, 1958, **29**, 235; Benson, *ibid.*, 1961, **34**, 521; Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

<sup>4</sup> Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122; Frey and Marshall, *J.*, 1963, 5717.

isomerization has been investigated, namely, the isomerization of vinylcyclopropanes to cyclopentenes,<sup>5</sup> in which there is a considerable reduction in the energy of activation of the reaction owing to the contribution of allylic resonance energy in the transition state. The present work is a continuation of the study of the isomerization of substituted vinylcyclopropanes. For the compound investigated, 1-cyclopropyl-2-methylpropene, there is the possibility of a reduction in the contribution of allylic resonance owing to steric factors.

#### EXPERIMENTAL

The apparatus and procedure were essentially as described previously.<sup>6</sup>

*Materials.*—1-Cyclopropyl-2-methylpropene. Cyclopropanecarboxylic acid was converted into the acid chloride by treatment with thionyl chloride. Treatment with dimethylamine in ether gave the dimethylamide, which was reduced to the aldehyde with lithium diethoxyaluminium hydride.<sup>7</sup> The aldehyde reacted with isopropylmagnesium iodide to give 1-cyclopropyl-2-methylpropanol, and the alcohol (*ca.* 10 ml.) was dehydrated by heating with one drop of concentrated sulphuric acid, the 1-cyclopropyl-2-methylpropene being distilled off as it was formed; it was redistilled from sodium and subjected to preparative gas chromatography, and gas chromatography showed it to be 99.9% pure. The infrared and n.m.r. spectra were consistent with the expected structure.

3,3-Dimethylcyclopentene.<sup>8</sup> 2-Cyclobutylpropan-2-ol was prepared by the reaction of methylmagnesium iodide with methyl cyclobutanecarboxylate. Treatment with boiling 48% aqueous hydrobromic acid followed by aqueous potassium hydroxide, and steam-distillation, gave 2-iodo-1,1-dimethylcyclopentane, which was dehydrohalogenated by refluxing with alcoholic potassium hydroxide.

2,4-Dimethylpenta-1,3-diene.<sup>9</sup> This was obtained by reaction of methylmagnesium iodide with mesityl oxide, and was redistilled from sodium.

2-Methylhexa-2,4-diene.<sup>10</sup> This was prepared by dehydration of 5-methylhex-4-en-3-ol (from isopropylmagnesium iodide and crotonaldehyde) with concentrated sulphuric acid. The resulting mixture of *cis*- and *trans*-isomers was distilled from sodium.

5-Methylhexa-1,4-diene. This was prepared by the dehydration of 2-methylhex-5-en-2-ol (from allylacetone and methylmagnesium iodide) with concentrated sulphuric acid. (Attempts to prepare the diene by way of the xanthate of this alcohol were not successful.<sup>11</sup>) 5-Methylhexa-1,4-diene was fractionated from the mixture and distilled from sodium.

*Analysis.*—Reaction mixtures were analysed by gas chromatography (20 ft.  $\times$  0.17 in. i.d. coiled copper column, 40–60 mesh Chromosorb P containing 20% w/w dicyanoethyl ether, 43°, hydrogen flow gas, Gow-Mac tungsten-filament katharometer). Signals from the detector were fed by way of a variable attenuator to a Sunvic recorder fitted with a retransmitting slidewire, the signals from which were integrated by use of a low-inertia d.c. motor. Compounds could be trapped as they emerged from the column for secondary identification by infrared spectroscopy or mass spectrometry. Products were identified first by comparison of retention times with those of authentic samples, and then by trapping and comparison of spectra.

#### RESULTS

In an aged reaction vessel, 1-cyclopropyl-2-methylpropene isomerized to give, as major products, 3,3-dimethylcyclopentene, 5-methylhexa-1,4-diene, and *cis*- and *trans*-2-methylhexa-2,4-diene. The vessel was aged by heating a sample of the cyclopropane in it for 2 hr. at 370°, and care was taken never to allow air into the hot vessel after this treatment. A few minor products were formed; these appeared to arise entirely by thermal cracking of the primary (major) products. Despite a careful search, no 2,4-dimethylpenta-1,3-diene was detected.

<sup>5</sup> Flowers and Frey, *J.*, 1961, 3547; Wellington, *J. Phys. Chem.*, 1962, **66**, 1671.

<sup>6</sup> Elliott and Frey, *J.*, 1964, 900.

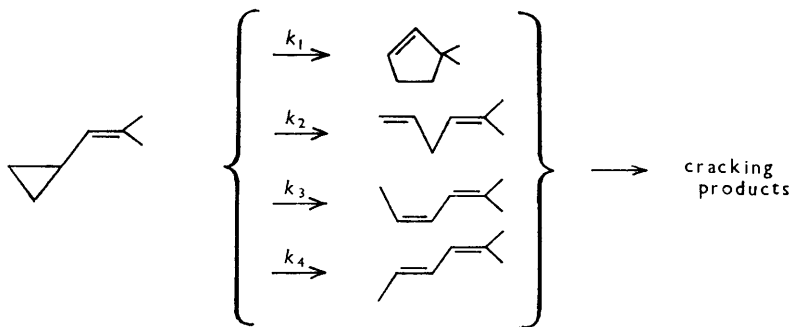
<sup>7</sup> Brown, *J. Amer. Chem. Soc.*, 1959, **81**, 502.

<sup>8</sup> Kizner, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 999; Kwart and Ford, *J. Org. Chem.*, 1959, **24**, 2060.

<sup>9</sup> Waterman and de Kok, *Rec. Trav. chim.*, 1933, **52**, 234.

<sup>10</sup> Stephens, *J. Amer. Chem. Soc.*, 1935, **57**, 1112.

<sup>11</sup> Robinson and Slater, *J.*, 1941, 380.



Preliminary runs were carried out to check the reproducibility of the system, and a series of runs was then performed at 366.8° at various pressures from 2 to 17 mm. The overall rate of isomerization was first-order and the rate constant independent of pressure in this range (Table 1).

TABLE 1.

Overall rate constants at various initial pressures at 366.8°.

Pressure (mm.) .....	2	2.5	3.5	4	5	7.5	11	17
$10^5 k$ (sec. <sup>-1</sup> ) .....	8.69	8.69	8.60	8.69	8.69	8.77	8.77	8.77

All subsequent runs were carried out with pressures between 3.5 and 6 mm. Isomerizations were studied in detail at eight temperatures between 350 and 390°. Ten or more runs were carried out at each temperature, and the reaction was followed from 5 to 30% decomposition. At each temperature plots of the logarithm of the 1-cyclopropyl-2-methylpropene undecomposed against time were linear, indicating the overall reaction to be first-order. Further, the ratio  $t_{1/4} : t_{1/8}$  was in close agreement with that expected for a first-order reaction. The absence of curvature in the first-order plots is evidence for the absence of any radical-chain component of the reaction, since the products (especially the dimethylcyclopentene) would be powerful radical-chain inhibitors. In addition, even a minor radical path for the reaction, which would not produce appreciable curvature, was ruled out by mass-spectrometric analysis of the entire reaction mixture, since no compound with a molecular weight greater than that of the parent compound was detected. A radical path would be expected to produce such compounds by addition reactions.

In each analysis five major and four minor peaks were integrated. The major products were heated in turn in the reaction vessel, and although they gave rise to the observed minor peaks it was not possible to get an accurate assessment of what fraction of each minor peak was due to the secondary decomposition of each major peak. That the minor peaks all arose by secondary reactions was shown by plotting their yields against the total percentage decomposition of the cyclopropane; all the minor products yielded graphs showing positive curvature and zero initial slope. Although the yield of secondary products at 30% overall decomposition was always less than 2%, neglect of them could have a significant effect on the individual yields of the primary products. Accordingly, a quarter of the total secondary products were arbitrarily added to each of the major products in all the remaining calculations.

TABLE 2.

Overall rate of isomerization of 1-cyclopropyl-2-methylpropene at various temperatures.

Temp. (°K) .....	623.15	629.3	634.5	639.8	644.1	652.4	657.85	663.2
$10^5 k$ (sec. <sup>-1</sup> ) .....	2.691	4.176	5.765	8.103	11.49	19.32	27.44	36.96

The overall rate of isomerization (Table 2) at each temperature was found by the method of least-squares. The plot of  $\log k$  against the reciprocal of the absolute temperature was linear, and from it the Arrhenius parameters were evaluated by least-squares, whence

$$k = 10^{14.31} \exp(-53,800/RT) \text{ sec.}^{-1}.$$

The random statistical error (95% confidence) was negligible, and probably the largest single

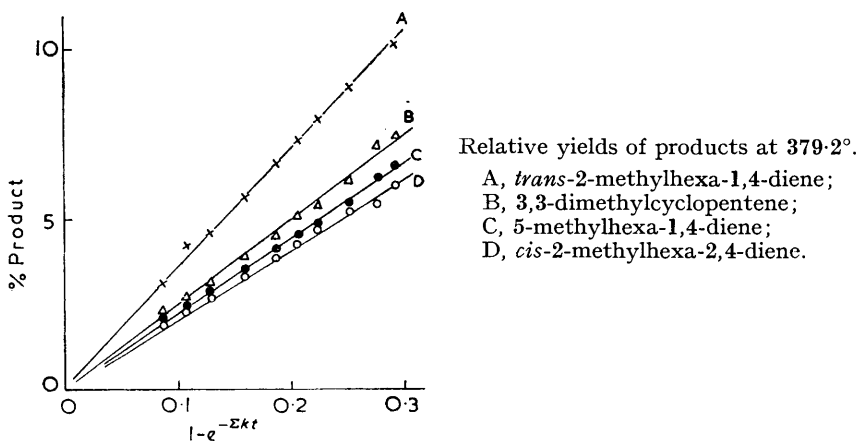
source of error is due to fluctuations in the temperature of the furnace. This could give rise to a maximum uncertainty of  $\pm 600$  cal. in the value for the energy of activation.

A series of runs was carried out at  $375.2^\circ$  in a vessel packed with glass tubing, having a surface to volume ratio ten times that of the ordinary vessel. The measured rate constant,  $1.547 \times 10^{-4}$  sec. $^{-1}$ , was 4% higher than that calculated from the Arrhenius equation, and indicates that there can be no appreciable heterogeneous component of the reaction.

The overall rate of the isomerizations has been shown to be first-order, and it seemed probable that each individual reaction path was also first-order. For such a series of parallel first-order reactions it is easy to show that

$$x_i = (100k_i/\Sigma k)(1 - e^{-\Sigma kt}),$$

where  $x_i$  is the percentage of product  $i$ ,  $k_i$  the rate constant for this particular reaction path, and  $\Sigma k$  the sum of the rate constants for all the paths, *i.e.*, for the overall rate of isomerization. By plotting  $x_i$  against  $(1 - e^{-\Sigma kt})$  the value of  $k_i$  can be obtained from the slope. Graphs such as these gave straight lines, and a typical set is shown in the Figure. From these graphs at each



of seven temperatures the values of  $k_1$ ,  $k_2$ ,  $k_3$ , and  $k_4$  (Table 3) were determined by least-squares. The Arrhenius parameters were evaluated by least-squares for each of the four paths. The statistical deviations (95% confidence) were about 120 cal. in each case. The Arrhenius equations obtained in this fashion were:

$$k_1(3,3\text{-dimethylcyclopentene}) = 10^{14.00} \exp(-54,600/RT) \text{ sec.}^{-1};$$

$$k_2(5\text{-methylhexa-1,4-diene}) = 10^{14.61} \exp(-56,650/RT) \text{ sec.}^{-1};$$

$$k_3(\textit{cis}\text{-2-methylhexa-2,4-diene}) = 10^{13.33} \exp(-53,000/RT) \text{ sec.}^{-1};$$

$$k_4(\textit{trans}\text{-2-methylhexa-2,4-diene}) = 10^{13.25} \exp(-52,100/RT) \text{ sec.}^{-1}.$$

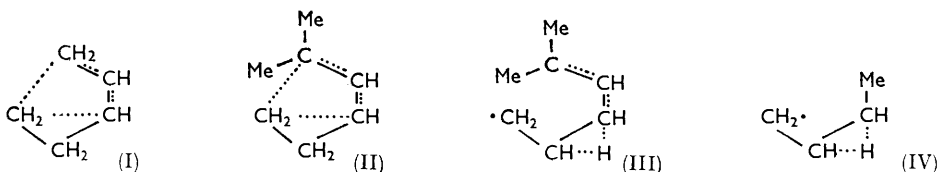
TABLE 3.

Values for individual rate constants at various temperatures.

Temp. ( $^\circ\text{K}$ )	$10^6 k$ (sec. $^{-1}$ )			
	$k_1$	$k_2$	$k_3$	$k_4$
623.15	6.480	5.420	5.176	9.530
629.3	10.72	8.646	8.307	14.22
634.5	15.12	12.27	11.51	20.05
639.8	20.89	16.42	15.99	27.01
644.1	28.95	24.37	22.42	39.27
657.85	67.98	60.37	53.25	95.12
663.2	96.79	86.49	67.41	111.5

## DISCUSSION

The above results show that the isomerizations of 1-cyclopropyl-2-methylpropene are homogeneous, first-order, and non-chain in nature. Taken in conjunction with previous results with similar systems, this is good evidence that the isomerizations are all unimolecular reactions. The absence of fall-off in the value of the rate constant over the range studied is also expected for a molecule of this complexity. The isomerizations of vinylcyclopropane,<sup>5</sup> isopropenylcyclopropane,<sup>12</sup> 1-methyl-1-vinylcyclopropane,<sup>13</sup> and *trans*-1-cyclopropylbut-1-ene<sup>14</sup> to the various cyclopentenes all occur with energies of activation close to 50 kcal. Here the isomerization to the cyclopentene occurs to the virtual exclusion of the "normal" type of cyclopropane isomerization, which in these cases would yield various dienes. In the present work the energy of activation for the reaction leading to a cyclopentene is some 4.5 kcal. greater and the various possible reactions occur with similar rates. Thus, at 370.9° the ratios  $k_1 : k_2 : k_3 : k_4$  are 1.28 : 1.08 : 1 : 1.74. The transition state for the isomerization of vinylcyclopropane to cyclopentene can be pictured as (I).



This involves a concerted mechanism where the rupture of the cyclopropane ring and the formation of the new carbon-carbon bond occur simultaneously. If the *cis-trans*-isomerization of cyclopropanes occurs through a biradical transition state, then the difference between the energies of activation for the two types of isomerization cannot be ascribed simply to the contribution of allylic resonance energy in the unsaturated cyclopropanes. This would be true only if the two complexes had similar configurations. The essentially different paths for the two reactions is further reflected in their appreciably different frequency factors. The same transition state as pictured for vinylcyclopropane would be equally applicable to all those cyclopropanes already mentioned which isomerize with  $E_{act} \sim 50$  kcal. The compound investigated in the present work differs in one important respect from those previously investigated. If a similar transition state is involved, then it could be represented as (II). In this case the presence of the methyl groups interferes with the formation of the ring complex. Some rotation about the appropriate carbon-carbon bonds is necessary so that the methyl groups are slightly out of the plane of the ring. (In the product they are, of course, in a plane at right angles to that of the cyclopentene ring.) Any rotation of this kind must reduce the allylic resonance energy available for reducing the energy of activation of this reaction path. This is apparent in the value of  $E_{act}$  of 54.6 kcal. By the same argument we should expect a *trans*-substituted vinylcyclopropane to follow a "high" energy path for isomerization to a cyclopentene.

The isomerizations to the various dienes may be considered as either proceeding through a biradical transition state followed by hydrogen migration, or involving a complex in which the two processes are concerted. Thus, the formation of 5-methylhexa-1,4-diene, assuming a concerted mechanism, would be represented as involving the transition complex (III). In this complex the geometrical requirements of the unsaturated group attached to the cyclopropane in no way affect the rest of the molecule. Essentially the same transition state can be used for the formation of but-1-ene from methylcyclopropane (neglecting of course the allylic contribution), *i.e.*, (IV), and in fact both reactions have closely similar frequency factors. The formation of *cis*- and *trans*-2-methylhexa-2,4-diene

<sup>12</sup> Frey and Marshall, *J.*, 1962, 3981.

<sup>13</sup> Ellis and Frey, *J.*, 1964, 954.

<sup>14</sup> Ellis and Frey, *J.*, 1960, 4188.

would involve transition states formally analogous to those in the formation of *cis*- and *trans*-but-2-ene from methylcyclopropane, and comparison of the relevant energies of activation will yield the allylic resonance energy contribution to the transition state. Taking the values for  $E_{\text{act}}$  in this work for the *cis*- and *trans*-compounds to be  $52.1 \pm 0.6$  and  $53.0 \pm 0.6$ , respectively, and comparing them with the values of  $61.9 \pm 0.6$  and  $64.4 \pm 0.6$  for *cis*- and *trans*-but-2-ene,<sup>15</sup> we obtain  $9.8 \pm 1.2$  and  $11.4 \pm 1.2$  for the allylic resonance energy contribution. These values are equal within the rather large experimental errors, and a mean value of  $10.6 \pm 2$  kcal. may be taken as the resonance contribution. This value is in reasonable agreement with the value of  $12 \pm 1$  kcal. recently suggested<sup>16</sup> for the resonance energy of methallyl, but is considerably smaller than the theoretical estimates for allylic resonance energy.<sup>17</sup> In this respect it is interesting that the difference between the energy of activation for the decomposition of isopropenylcyclobutane<sup>18</sup> to isoprene and ethylene, and that of methylcyclobutane<sup>19</sup> to propene and ethylene, is  $10.2 \pm 1.2$  kcal. This again we would identify with the allylic resonance energy contribution to these formally similar transition states.

Finally, the absence of 2,4-dimethylpenta-1,3-diene in the reaction products is understandable in terms of the transition states that have been discussed. The formation of this compound would require a biradical (or partial biradical) in which there was no allylic stabilization, and hence such a reaction must proceed by a much higher energy path.

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<sup>15</sup> Setser and Rabinovitch, *J. Amer. Chem. Soc.*, 1964, **86**, 564.

<sup>16</sup> Benson, Bose, and Nangia, *J. Amer. Chem. Soc.*, 1963, **85**, 1388.

<sup>17</sup> Franklin and Field, *J. Amer. Chem. Soc.*, 1953, **75**, 2819.

<sup>18</sup> Ellis and Frey, *Trans. Faraday Soc.*, 1963, **59**, 2076.

<sup>19</sup> Das and Walters, *Z. phys. Chem.*, 1958, **15**, 22.

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