

## 187. The Thermal Unimolecular Isomerization of 1-Methyl-1-vinylcyclopropane.

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The thermal isomerization of 1-methyl-1-vinylcyclopropane has been investigated in the range 313—357°. Within this range, in an "aged" vessel, the reaction is homogeneous and first-order, and yields only 1-methylcyclopentene. The rate constants, which are independent of pressure from 2 to 30 mm., are accurately fitted by the Arrhenius equation

$$k = 10^{14.11} \exp(-49,350/RT) \text{ sec.}^{-1}.$$

The reaction is almost certainly truly unimolecular.

CYCLOPROPANES undergo three distinct types of isomerization reaction, all of which are believed to be unimolecular transformations. Alkylcyclopropanes undergo structural isomerizations to yield olefins,<sup>1</sup> and those which exist as *cis-trans*-isomers undergo reversible geometrical isomerizations.<sup>2,3</sup> Finally, vinylcyclopropanes undergo isomerization reactions to yield cyclopentenes.<sup>4,5</sup> The work described in this Paper is an extension of the investigation of this last type of reaction.

### EXPERIMENTAL

1-Methyl-1-vinylcyclopropane was prepared by the action of methylene di-iodide and a zinc-copper couple<sup>6</sup> on an excess of isoprene in dry ether. The distilled crude product contained 1-methyl-1-vinylcyclopropane and isopropenylcyclopropane in the ratio of approximately 3 : 1, together with about 5% of 1-methylbicyclopopyl. 1-Methyl-1-vinylcyclopropane was obtained more than 99.5% pure by preparative gas chromatography using dinonyl phthalate as the stationary phase. Its vapour pressure was determined at three temperatures between 0 and 15°, and extrapolation of the plot of  $\log p$  against  $1/T$  indicated a boiling point of about 56° (lit. b. p.s 54.5<sup>7</sup> and 71°<sup>8</sup>). The infrared spectrum was consistent with the expected structure.

The apparatus and procedure were essentially the same as described previously.<sup>9</sup>

Analysis was by gas chromatography using a copper column (12 ft.  $\times$  0.18 in.) filled with Chromosorb P containing 20% w/w of dinonyl phthalate and maintained at 35°. With a hydrogen flow of 50 ml./min. the retention times of 1-methyl-1-vinylcyclopropane and 1-methylcyclopentene were 12 and 20 min., respectively. The 1-methylcyclopentene was identified by comparison of its retention time and infrared spectrum with those of an authentic sample; a sample of the chromatographic "peak" was trapped and its spectrum recorded using a 5-ml. micro-gas-cell (5 cm. path length).

### RESULTS AND DISCUSSION

In the temperature range 313—357°, in an "aged" reaction vessel, 1-methyl-1-vinylcyclopropane isomerizes to 1-methylcyclopentene. Plots of the logarithm of per cent of undecomposed 1-methyl-1-vinylcyclopropane against time gave straight lines for decompositions varying from 5 to 60%. Rate constants (see Table) were determined from

Rate constants for the isomerization of 1-methyl-1-vinylcyclopropane.

Temp. (°C) .....	313.5	319.1	322.7	328.0	331.7	337.5	341.2	346.3	356.5
$10^4 k$ (sec. <sup>-1</sup> ) .....	0.540	0.774	1.03	1.46	1.99	2.90	3.55	5.03	9.28

<sup>1</sup> Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

<sup>2</sup> Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.

<sup>3</sup> Flowers and Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122.

<sup>4</sup> Flowers and Frey, *J.*, 1961, 3547.

<sup>5</sup> Frey and Marshall, *J.*, 1962, 3981.

<sup>6</sup> Simmons and Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 4256; Shank and Shechter, *J. Org. Chem.*, 1959, **24**, 1825.

<sup>7</sup> Nakhapetyan, Safonova, and Kazanskii, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1962, 902.

<sup>8</sup> Kishner and Klavordikov, *Chem. Zentr.*, 1911, **11**, 362.

<sup>9</sup> Ellis and Frey, *Trans. Faraday Soc.*, in the press.

these results by the method of least-squares, at each of nine temperatures. An Arrhenius plot of the rate constants gave a good straight line, and the Arrhenius parameters were evaluated by the method of least-squares, whence,  $k = 10^{14.11} \exp(-49,350/RT)$  sec.<sup>-1</sup>. Random errors in the determination of the energy of activation were completely negligible (thus the 95% confidence limits calculated by normal statistical procedures show the value of  $E$  to have an associated error of only  $\pm 10$  cal.). Errors due to uncertainties in temperature lead to a maximum error in  $E$  of  $\pm 500$  cal.

A series of runs was carried out at 356.3° in a vessel packed with glass tubes giving a surface: volume ratio approximately ten times greater than that in the normal vessel. The rate constant obtained in this series,  $9.33 \times 10^{-4}$  sec.<sup>-1</sup>, fits on the Arrhenius plot exactly, and indicates that there can be no appreciable heterogeneous component of the reaction.

Since the first-order plots were linear even when runs were carried to high percentages of decomposition, it is improbable that the isomerization has a radical-chain component. The presence of such a component would lead to curvature of the plot owing to the accumulation of radical inhibitor (the methylcyclopentene) as the reaction proceeded.

Finally, a series of isomerizations was carried out with initial pressures of the cyclopropane varying from 2 to 30 mm. The rate constants so obtained were all the same within experimental error.

From the experimental evidence it is probable that the isomerization is truly unimolecular. The energies of activation and  $A$ -factors for the isomerizations of vinylcyclopropane, isopropenylcyclopropane, and 1-methyl-1-vinylcyclopropane are closely similar; this is to be expected if the reactions proceed by way of essentially identical transition states. We have already identified<sup>5</sup> the difference between the energy of activation of these processes and those for the *cis-trans*-isomerization of alkylcyclopropanes with the contribution due to allylic resonance energy. The *cis-trans*-isomerization of 1,2-dideuterocyclopropane has an energy of activation approximately 1 kcal./mole less than that for the isomerization to propene. The energy of activation for the isomerization of 1,1-dimethylcyclopropane to 3-methylbut-1-ene and 2-methylbut-2-ene is 63.6 kcal./mole. We may therefore estimate the energy of activation for the reaction leading to the formation of the substituted biradical in this latter case as 62.6 kcal./mole. Comparison of this value with the energy of activation of 49.4 kcal./mole found in the present work yields a value of 13.2 for the contribution due to allylic resonance. Recently Benson *et al.*<sup>10</sup> suggested a value for allylic resonance in the methylallyl radical of  $12 \pm 1$  kcal./mole. If this figure is accepted, complete delocalization of the electron must take place in the transition state which leads to cyclopentenes. We consider that this is not realistic, and that the value suggested by Benson *et al.* is a serious underestimate of the resonance energy of this radical. Theoretical estimates<sup>11</sup> have suggested values of 17—18 kcal./mole, and some experimental results indicate values as high as 22 kcal./mole. The difference between the 13 kcal./mole found in this work for the contribution due to allylic resonance and the value of 17 kcal./mole for the total delocalization energy in the radical is no doubt due to the steric requirements of the transition state which prevent the complete delocalization of the electron. In this respect it should be noted that the contribution of the cyclopropane strain energy to the reduction of the energy of activation for these reactions, while large (*ca.* 19 kcal./mole), is still considerably less than the total value of nearly 28 kcal./mole associated with the three-membered ring.<sup>12</sup>

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<sup>10</sup> Benson, Bose, and Nangia, *J. Amer. Chem. Soc.*, 1963, **85**, 1388.

<sup>11</sup> Franklin and Field, *J. Amer. Chem. Soc.*, 1953, **75**, 2819.

<sup>12</sup> Knowlton and Rossini, *J. Res. Nat. Bur. Standards*, 1949, **43**, 113.