# SECTION B Physical Organic Chemistry

# The Thermal Unimolecular Isomerisation of 2-Methylallyl Vinyl Ether

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The thermal isomerisation of 2-methylallyl vinyl ether has been investigated in the gas phase. In the range 423—461°  $\kappa$  the reactant isomerises by a first-order homogeneous process to yield only *trans*-hex-4-enal. The rate constants, which are independent of pressure in the range 6—100 mm., fit the Arrhenius equation  $k = 10^{11\cdot15} \exp(-29,100/RT) \sec^{-1}$ . The evidence suggests that the reaction is a true unimolecular isomerisation proceeding through a six-centre transition state.

THE isomerisations of allyl vinyl ethers to unsaturated aldehydes or ketones are simple examples of the Claisen rearrangement. Although this rearrangement has been extensively investigated for aromatic compounds, much less attention has been paid to the simpler ethers, and in these cases the rearrangement was mostly studied as a preparative source of the carbonyl compound. To date, the kinetics of the isomerisations have been followed almost entirely in solution. The only compounds of this type studied so far in the gas phase, by Murphy and his co-workers, are allyl vinyl ether <sup>1</sup> and allyl isopropenyl ether.<sup>2</sup> The work reported in this Paper is an extension of these latter studies to 2-methylallyl vinyl ether.

#### EXPERIMENTAL

2-Methylallyl Vinyl Ether.—This was made by a vinyl transetherification reaction.<sup>3</sup> 2-Ethoxyethyl vinyl ether was first prepared by refluxing a mixture of ethylhexyl vinyl ether and 2-ethoxyethanol in the presence of mercuric acetate and removing the 2-ethoxyethyl vinyl ether as an azeotrope (with the 2-ethoxyethanol) through an efficient fractionating column. The alcohol was removed by washing repeatedly with water, and the crude ether was dried and fractionally distilled. 2-Methylallyl vinyl ether was obtained by a similar procedure, using the 2-ethoxyethyl vinyl ether and 2-methylallyl alcohol with a mercuric acetate catalyst.

Apparatus.—The apparatus and techniques employed were basically similar to those described previously.<sup>4</sup> Decompositions were carried out in a spherical Pyrex reaction vessel (~150 ml.) immersed in a high-temperature oil thermostat. Analysis was by gas chromatography using an Aerograph model 600-C apparatus equipped with a flame ionisation detector and a gas sampling valve. A 10 ft.  $\times$  1/8 in. column packed with 60—80 mesh Chromosorb P containing 10% w/w of Carbowax 4000 was operated at 75°. Signals from the detector were fed to a recorder and automatically integrated using a Perkin-Elmer model 194 instrument. Toluene was used as an internal standard to obtain quantitative analytical data.

*Procedure.*—A calibration mixture was prepared by taking known pressures of toluene and the ether and mixing them

<sup>1</sup> F. W. Schuler and G. W. Murphy, J. Amer. Chem. Soc., 1950, 72, 3155.

<sup>2</sup> L. Stein and G. W. Murphy, J. Amer. Chem. Soc., 1952, 74, 1041.

after the addition of about 100 mm. of nitrogen in a gas pipette equipped with a magnetically operated paddle stirrer. After stirring for 48 hr., samples of these mixtures were analysed in the chromatograph. Further samples were then decomposed for various times and analysed. By comparison with the initial analyses, the percentage of undecomposed ether in each was estimated. Several runs were carried out with each mixture, and calibrations were checked frequently to compensate for possible non-linearity in the detector response with changes in sample size.<sup>5</sup>

### RESULTS

When heated, 2-methylallyl vinyl ether rearranged quantitatively to *trans*-hex-4-enal. The reaction vessel was aged by leaving a sample of the ether in it overnight at 188°. The reaction was first-order and runs were taken up to 70% completion. A series of runs were carried out at ten pressures from 6.0 to 98.7 mm., and the rates obtained were all equal within experimental error. Thereafter all runs employed between 10 and 15 mm. pressure of reactant. Nine series of runs were carried out in the range 423— 461°  $\kappa$ . At each temperature a plot of the logarithm of undecomposed ether against time was linear, and the rate constants were determined from these plots by the method of least-squares. The results obtained are shown in the Table. An Arrhenius plot of the data given in the Table

Rate constants for the isomerisation of 2-methylallyl vinyl ether

Temp. (°к)	423.3	426·2	<b>430·3</b>	<b>435</b> .0	<b>440-0</b>
$10^{4}k$ (sec1)	1.21	1.74	2.19	3.31	4.88
Temp. (°ĸ)	<b>446</b> .0	450.2	456-1	461.2	
$10^{4}k$ (sec. <sup>-1</sup> )	6.60	10.5	15.8	19.3	

gave a good straight line, but the deviation from this line of the point at the highest temperature was considerably greater than that of any other point, and it was not used in a least-squares calculation of the Arrhenius parameters. The calculation yielded the equation

$$k = 10^{11 \cdot 15} \exp(-29, 100/RT) \text{ sec.}^{-1}$$

The random statistical error (95% confidence limit) in the energy of activation was  $\pm 170$  cal.

<sup>3</sup> W. H. Watanabe and L. E. Conlon, J. Amer. Chem. Soc., 1957, 79, 2828.

- <sup>4</sup> H. M. Frey and R. F. Skinner, *Trans. Faraday Soc.*, 1965, **61**, 1918.
  - <sup>5</sup> C. S. Elliott and H. M. Frey, J. Chem. Soc., 1965, 4289.

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A series of runs was also carried out at  $455.9^{\circ}$  K in a cylindrical reaction vessel packed with glass tubes and having a surface-to-volume ratio 14 times greater than that with the unpacked vessel. The measured rate constant,  $15.9 \times 10^{-4}$  sec.<sup>-1</sup>, was within 5% of the value calculated from the Arrhenius equation, and indicates that there can be no appreciable heterogeneous component of the reaction.

Assuming a transmission coefficient of unity, the entropy of activation was calculated to be -10.2 cal. deg<sup>-1</sup> mole<sup>-1</sup>.

#### DISCUSSION

The Arrhenius parameters obtained in this work are similar to those obtained for the isomerisations of allyl vinyl ether  $[k = 10^{11\cdot70} \exp(-30,600/RT) \sec^{-1}]$  and allyl isopropenyl ether  $[k = 10^{11\cdot73} \exp(-29,300/RT)$ sec.<sup>-1</sup>] and make it very probable that the same transition state is involved in all three cases. The high negative values for the entropies of activation make a cyclic transition complex the most obvious choice. Both 4-membered and 6-membered rings can be envisaged as the complex involved in the isomerisations of the previously studied compounds. However, the 4-memberedring complex would lead to the formation of 3-methylpent-4-enal in the present case rather than the observed *trans*-hex-4-enal. This argues unambiguously for a 6-membered-ring complex. Also, the 6-membered-ring complex involves the loss of three internal rotations by the reactant whereas the 4-membered ring involves the loss of only two internal rotations. The former situation is more closely in accord with the observed entropies of activation.

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