

805. The Thermal Unimolecular Isomerization of *trans*-1-Cyclopropylbut-1-ene.

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The isomerization of *trans*-1-cyclopropylbut-1-ene has been investigated from 332.7 to 373.3°. In this temperature range in an aged vessel the reaction is homogeneous and of first order. The product of the reaction is 3-ethylcyclopentene. The rate constants are independent of pressure from 2 to 25 mm. and yield the Arrhenius equation $k = 10^{13.79} \exp(-49,980/RT)$ sec.⁻¹. The reaction is almost certainly truly unimolecular.

CYCLOPROPANES are known to undergo three types of thermal unimolecular isomerization reaction. Of these, the geometric, *cis-trans*-isomerizations¹ and the structural rearrangements² to olefins have energies of activation between 60 and 65 kcal. Some unsaturated cyclopropanes rearrange to yield cyclopentenenes³⁻⁵ with energies of activation of around 50 kcal., the large difference in E_{act} being ascribed to the contribution of allylic delocalization energy to the diradical transition state. This present investigation is an extension of this work.

EXPERIMENTAL AND RESULTS

trans-4-Bromo-1-cyclopropylbut-1-ene was prepared⁶ by treating dicyclopropyl methanol with 60% hydrogen bromide at 0°. After extraction with methylene dichloride and washing with sodium hydrogen carbonate solution the extract was dried (MgSO₄). After removal of the methylene dichloride the bromo-compound was obtained by distillation under reduced pressure. The bromocyclopropylbutene was converted into its Grignard reagent in the usual manner and this was treated with dilute sulphuric acid to yield *trans*-1-cyclopropylbut-1-ene. The latter compound was finally purified by preparative gas chromatography. Analysis on three different chromatographic columns (silver nitrate in ethylene glycol, di-2-cyanoethyl ether, and dinonyl phthalate) showed the hydrocarbon to be at least 99.5% pure.

3-Ethylcyclopentene was prepared by the method of Crane, Boord, and Hense.⁷ The impure product was purified by steam distillation followed by fractionation and finally by preparative gas chromatography.

The apparatus and procedure were essentially the same as that described previously.⁸

Analysis was by gas chromatography with a 12-ft. coiled copper column (internal diam. 0.18 in.) filled with 40—60 mesh Chromosorb P containing 20% w/w dinonyl phthalate and operated at 50°. Hydrogen was the flow gas and a Gow-Mac katharometer the detector. Signals from the detector were integrated by using a low inertia D.C. motor. The product peak from the isomerization was found to have the same retention time as 3-ethylcyclopentene. For more positive identification the product peak was trapped out and its infrared spectrum determined by using a micro-cell. It was found to be identical with that of the ethylcyclopentene.

In the temperature range 332 to 374° in an "aged" reaction vessel, 1-cyclopropylbut-1-ene isomerizes to 3-ethylcyclopentene as the major product. Plots of the logarithm of undecomposed reactant against time gave straight lines for decompositions varying from 10 to 50%. At each of nine temperatures several decompositions for varying times were carried out, and the first-order rate constants determined by the method of least squares. The rate constants obtained in this manner are shown in the Table.

¹ 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.

² Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; Flowers and Frey, *J.*, 1962, 1157; Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Frey and Marshall, *J.*, 1962, 3052.

³ Flowers and Frey, *J.*, 1961, 3547.

⁴ Frey and Marshall, *J.*, 1962, 3981.

⁵ Ellis and Frey, *J.*, 1964, 959.

⁶ Hanak and Eggensperger, *Annalen*, 1963, **663**, 31; Julia, Julia, and Remy, *Compt. rend.*, 1959, **248**, 820.

⁷ Crane, Boord, and Hense, *J. Amer. Chem. Soc.*, 1945, **67**, 1237.

⁸ Ellis and Frey, *Trans. Faraday Soc.*, 1963, **59**, 2076.

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Rate constants for the isomerization of 1-cyclopropylbut-1-ene.

Temp.	332.7	342.7	347.6	354.0	359.9	365.3 *	367.0	371.4	373.3
10^4k (sec. ⁻¹)	0.591	1.11	1.56	2.32	3.45	4.83	5.22	6.65	7.37

* Refers to packed vessel.

One complete set of runs was carried out in a vessel packed with Pyrex tubes to increase its surface to volume ratio to a value ten times that of the unpacked vessel. The results obtained in this series (see the Table) were identical with those obtained with the unpacked vessel and fitted on the Arrhenius plot exactly. There is thus no appreciable heterogeneous component of the reaction.

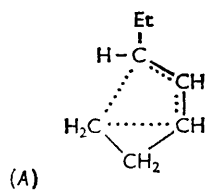
A series of runs was carried out at a fixed temperature and time but with varying initial pressures of reactant in the range 2—25 mm. In no case did the percentage reaction vary by more than the experimental analytical errors. Thus the rate constant is independent of pressure in this range.

A plot of the logarithm of the rate constants against the reciprocal of the absolute temperature gave a good straight line from which the Arrhenius parameters were evaluated by the method of least squares: $k = 10^{13.79} \exp(-49,980/RT)$ sec.⁻¹. Geometrical isomerization did not occur to any observable extent though it was looked for; the reaction product being analysed in two cases on three different chromatographic columns. At high temperatures and high percentage decomposition some very small chromatographic peaks were observed as well as the major product peak. Even at the highest temperature investigated these peaks were too small to affect the calculated rate constants. They are almost certainly products resulting from the isomerization of the reactant to various dienes. These processes have appreciably higher energies of activation than the isomerization to cyclopentenes.^{9,10}

DISCUSSION

The isomerization of the cyclopropylbutene to ethylcyclopentene is almost certainly a true unimolecular transformation. The reaction is of first order and homogeneous and no evidence of a chain reaction was obtained. The invariance of the rate constant in the pressure range studied is to be expected for a molecule of this complexity.

The Arrhenius parameters obtained for this isomerization are closely similar to those obtained for the isomerizations of the other vinylcyclopropanes so far studied. The low value of the energy of activation for these reactions compared with the values obtained for the *cis-trans*-isomerizations of cyclopropanes has been identified as mainly due to the contribution of allylic resonance energy in the transition state. Too close an identification



of the differences between these values and the actual resonance energy of the allyl radical should not, however, be made since it is probable that the two transition states are not identical. There is much evidence that the *cis-trans*-isomerizations proceed *via* a free trimethylene biradical. However the isomerizations to a cyclopentene almost certainly involve a concerted mechanism involving a transition complex (*A* for the present system). This cyclic transition state results in a smaller positive entropy of activation than one involving a free biradical, and this is reflected in the appreciably lower values for the “*A*” factors in the isomerizations leading to cyclopentenes as compared with those for the *cis-trans*-isomerizations. A further point of interest is that, provided the vinyl group is substituted in the *trans*-configuration, the substituting group will not hinder the formation of the transition complex. This will not be true for a *cis*-substituted vinyl compound or for a disubstituted compound. Such compounds should undergo isomerization with appreciably greater energies of activation. These predictions are being tested experimentally.

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⁹ Wellington, *J. Phys. Chem.*, 1962, **66**, 1671.¹⁰ Frey, *Trans. Faraday Soc.*, 1962, **58**, 516.