29. *The Thermal Unimolecular Isomerization and Decomposition of* 1,1-*Diethylcyclopropane.*

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The thermal isomerization of 1,1-diethylcyclopropane in the temperature range 425—475° is a homogeneous, first order reaction. In agreement with earlier work, the isomerization yields 3-ethylpent-1-ene and 3-ethylpent-2-ene in approximately equal amounts. Simultaneously, however, a slower parallel reaction occurs to give 2-ethylbuta-1,3-diene and methane. A possible mechanism for this reaction, which is of a type not previously reported for a cyclopropane, is discussed. By using results obtained in the high-pressure region (4·5 mm.) at a number of temperatures, it can be shown that the individual rate constants fit the following Arrhenius equations:

k_1 (3-ethylpent-1-ene) = $10^{14\cdot95} \exp(-63{,}800/\boldsymbol{R}T)$ sec.$^{-1}$
k_2 (3-ethylpent-2-ene) = $10^{14\cdot84} \exp(-63{,}400/\boldsymbol{R}T)$ sec.$^{-1}$
k_3 (2-ethylbut-1,3-diene) = $10^{15\cdot44} \exp(-65{,}900/\boldsymbol{R}T)$ sec.$^{-1}$.

The olefins and the diene formed initially isomerize and decompose at a much slower rate than the cyclopropane, to give at least six additional products.

KINETIC studies of the structural isomerization of alkylcyclopropanes,[1] as well as of cyclopropane itself,[2] have been reported; these have, however, been restricted to compounds containing one or more methyl groups. The results of these investigations have shown that the reactions are true unimolecular transformations. The presence of the methyl groups has an important influence on the pressure at which " fall-off " of the first-order rate constant occurs. The field of study has now been extended to ethylcyclopropanes to determine the influence of a larger group on the path of the reaction. We report the results of an investigation of the pyrolysis of 1,1-diethylcyclopropane where, in addition to the normal rearrangement, a novel type of cyclopropane decomposition occurs.

EXPERIMENTAL

1,1-Dibromo-2,2-diethylcyclopropane was prepared by the addition of dibromocarbene to 2-ethylbut-1-ene by the method described by Skell and Garner.[3] The dibromo-compound was reduced to 1,1-diethylcyclopropane with sodium and aqueous methanol.[4] The crude product was partially purified by fractional distillation with a spinning-band column. Final purification was by gas chromatography, which produced 1,1-diethylcyclopropane containing less than 0·4% of total impurity. The infrared and n.m.r. spectra were as expected for a compound of its structure.

3-Ethylpent-1-ene was prepared by a contra-thermodynamic isomerization of commercially available 3-ethylpent-2-ene. Hydroboration of the latter was effected with sodium borohydride and boron trifluoride diethyl etherate in " Diglyme."[5] The 3-ethylpent-1-ene was displaced from the reaction mixture by the addition of an excess of oct-1-ene, followed by slow distillation through a packed fractionation column. A small sample of the 3-ethylpent-1-ene was purified by g.l.c., and its i.r. spectrum was found to be identical with the A.P.I. spectrum of this compound.

A sample of 2-ethylbuta-1,4-diene was given to us by the V.E.B. Leuna-Werke Walter Ulbricht, Germany.

The apparatus, procedure, and method of analysis were essentially the same as those used in

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[1] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Flowers and Frey, *J.*, 1962, 1157; *Proc. Roy. Soc.*, 1961, *A*, **260**, 424.

[2] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 463.

[3] Skell and Garner, *J. Amer. Chem. Soc.*, 1956, **78**, 3409.

[4] Doering and Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.

[5] Brown and Subba Roa, *J. Amer. Chem. Soc.*, 1959, **81**, 6428.

previous work.[6] Katharometer signals were fed to a Speedomax type G recorder used in conjugation with a Perkin-Elmer model 194 integrator.

RESULTS AND DISCUSSION

The thermal decomposition of 1,1-diethylcyclopropane in the temperature range 425—475° is kinetically of first order. At 454°, the rate constant is independent of pressure between 16 and 1·0 mm., and has fallen by 5% of this value at a pressure of 0·2 mm. The reaction was studied in detail at a pressure of 4·5 mm. at eight temperatures. At each temperature, the products from 8 or 9 runs were analysed, and the decomposition was found to vary from 6·5 to 32%. At all temperatures, plots of the logarithms of the percentages of undecomposed diethylcyclopropane against time were linear over the range studied. The overall rate constants were calculated by the method of least squares from the slope of these plots and are given in the Table.

Thermal isomerization of 1,1-diethylcyclopropane.

Temp. (°c)	425·0	429·3	437·1	445·0	453·3	461·6	469·9	475·1
k (verall) × 10^5 ...	2·58	3·57	5·84	9·63	15·5	26·6	43·1	58·6
$k_1 \times 10^5$	0·979	1·22	2·15	3·43	5·51	9·71	14·3	22·1
$k_2 \times 10^5$	0·941	1·33	2·19	3·56	5·92	9·65	15·8	20·3
$k_3 \times 10^5$	0·606	0·946	1·56	2·38	3·92	7·04	11·9	15·7

The Arrhenius plot from these values gave a straight line from which the frequency factor and energy of activation for the overall reaction were calculated, again by the method of least squares. The overall rate constant is given by the equation

$$k\ (\text{overall}) = 10^{15\cdot74} \exp\left(-64{,}900/\boldsymbol{R}T\right)\ \text{sec.}^{-1}.$$

All the results were obtained with a reaction vessel that had been "aged" for a long enough time to give reproducible kinetic results. The absence of any appreciable heterogeneous component of the reaction was shown by the analysis of the products of some runs made at 452° in a reaction vessel packed with glass tubes, which gave it a surface : volume ratio 11 times greater than that of the normal vessel. After a correction for temperature difference, the rate constant was found to be 2% greater in the packed than in the unpacked vessel.

The pyrolysis of the diethylcyclopropane produced three major products. Two of these were identified as 3-ethylpent-1-ene and 3-ethylpent-2-ene, by comparison of their retention times on the chromatographic column with those of authentic samples. These are the only expected products from a "normal" cyclopropane isomerization. The third compound, which constituted about 20% of the total reaction product, had the longest retention time. The mass spectrum of a sample of this compound, which was isolated chromatographically from the reaction mixture, showed it to be a six-carbon hydrocarbon with a molecular weight of 82. Its cracking pattern indicated that it was probably a diene, and its infrared spectrum suggested a conjugated diene. Comparison of the relative retention time of this compound with those listed by Hively for a 2·5-metre column containing di-(2-cyanoethyl) ether suggested that it might be 2-ethylbuta-1,3-diene. Final confirmation that the compound was in fact this diene was obtained when a pure sample of 2-ethylbutadiene became available; the retention time, mass spectrum, and infrared spectrum of the unknown and the authentic sample were identical.

A linear relationship was found between the percentage of any of the major products and the total percentage decomposition of the diethylcyclopropane. This is to be expected if they are all primary products formed by first-order reactions. Although the analytical results for the six minor products were rather imprecise, similar plots showed considerable positive curvature; this is to be expected if they arise by secondary decomposition of the primary products. More positive information was provided by the analysis of mixtures

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[6] Frey and Marshall, *J.*, 1962, 3052.

obtained by heating pure samples of 3-ethylpent-1-ene, 3-ethylpent-2-ene, and 2-ethylbutadiene at 453°. Their decomposition produced all the minor products in approximately the correct proportions. In addition, 3-ethylpent-2-ene gave a compound with the same retention time as the 3-ethylbutadiene, but at a rate that would account for only about 15% of that obtained from the diethylcyclopropane; this is further evidence that the diene results principally from a primary reaction.

The rate constant k_1 for one of a series of n parallel first-order reactions is related to x, the % of product resulting from this reaction in time t, by the expression

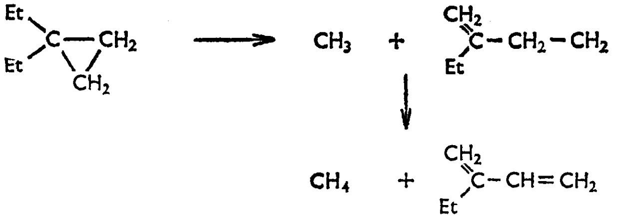
$$x/100 = k_i\left[1 - \exp\left(-t\sum_{i=0}^{n} k_i\right)\right] \Big/ \sum_{i=1}^{n} k_i$$

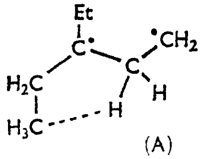
where $\sum_{i=1}^{n} k_i$ is the rate constant for the overall reaction. The rate constants for the three primary reactions were calculated from the slope of the plots of $x/100$ against $\exp\left(-t\sum_{i=1}^{n} k_i\right)$, after applying a correction to x for the decomposition to secondary products. The values of k_1, k_2, and k_3 are given in the Table. From the Arrhenius plots of these rate constants the following equations were obtained:

$$k_1 \text{ (3-ethylpent-1-ene)} = 10^{14.95} \exp(-63{,}800/\boldsymbol{R}T) \text{ sec.}^{-1};$$
$$k_2 \text{ (3-ethylpent-2-ene)} = 10^{14.84} \exp(-63{,}400/\boldsymbol{R}T) \text{ sec.}^{-1};$$
$$k_3 \text{ (2-methylbuta-1,3-diene)} = 10^{15.44} \exp(-65{,}900/\boldsymbol{R}T) \text{ sec.}^{-1}.$$

The decomposition of the 1,1-diethylcyclopropane to 2-ethylbuta-1,3-diene produces, in addition, one molecule of methane. It was not possible to determine the yield of this compound with precision, owing to its extremely short retention time. However, within the rather large experimental errors of the determination, the amount of methane formed was equivalent to the diene produced.

The formation of 3-ethylpent-1-ene and 3-ethylpent-2-ene in approximately equal amounts is to be expected from the results of similar work on the thermal isomerization of 1,1-dimethylcyclopropane. These reactions can be explained in terms of a biradical intermediate or, alternatively, of an expanded-ring transition state, with the migration of the hydrogen atom occurring either after, or simultaneously with, this bond-breaking or bond-lengthening process. The formation of a diene and methane is a new type of reaction for a substituted cyclopropane; it is probably general for ethyl cyclopropanes. Chesick [7] has observed the formation of butadiene in the thermal decomposition of ethylcyclopropane itself. The two reasonable reaction mechanisms for the formation of the diene and methane are a molecular one and one involving the methyl radical. The path of the latter may be





(A)

However, any path involving methyl radicals would be expected to yield numerous products by abstraction and addition to the ethylpentenes; such compounds were not in fact observed in the present work. We, therefore, favour a molecular process involving the formation of ethylbutadiene and methane in one step. A possible transition state for such a reaction may be (*A*). This envisages the rupture of the cyclopropane ring to give a diradical, followed by the migration of a hydrogen atom and the breaking of a further

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[7] Chesick, personal communication.

carbon–carbon bond, and would be expected to lead to an appreciably higher energy of activation than the conventional cyclopropane isomerization reaction (though some energy is "recovered," owing to the ~4 kcal. resonance energy of the diene). The high "*A*" factor for this reaction is surprising for a transition state involving a five-membered ring, and would indicate a complex where the ring is so enlarged that partially hindered or free rotation is possible.

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