322. *The Thermal Decomposition of Bicyclopropyl. Part I.*

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The thermal decomposition of bicyclopropyl in the temperature range 408—474°c has been investigated. In this temperature range, in an " aged " reaction vessel, bicyclopropyl undergoes a series of parallel first-order reactions to give cyclohexene, butadiene + ethylene, and four cyclopropylpropenes. The overall rate of decomposition is accurately fitted by the Arrhenius equation $k = 10^{15 \cdot 36} \exp(-60{,}710/\boldsymbol{R}T)$ sec.$^{-1}$. The decomposition to butadiene + ethylene is fitted by the equation $k = 10^{16 \cdot 8} \exp(-70{,}800/\boldsymbol{R}T)$ sec.$^{-1}$. The cyclopropylpropenes, formed initially, undergo isomerization to various C_6 dienes at rates comparable with those of the primary reactions, and this leads to complex mixtures which contain at least 17 products.

Thermal isomerization of cyclopropane and alkylcyclopropanes has received considerable attention in the last few years.[1,2] These compounds undergo unimolecular transformations, yielding olefins. Recently it has been shown that vinylcyclopropane undergoes a unimolecular isomerization, giving cyclopentene,[3] and spiropentane decomposes to methylenecyclobutane.[4] In these two cases rather extensive bond rearrangements occur; and the transition state must involve considerable bond distortion. It appears, however, that this path is preferred to that yielding olefins, which must involve, at some stage, the breaking of a carbon–hydrogen bond.

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[1] Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.

[2] Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277; Flowers and Frey, *J.*, 1959, 3953; *Proc. Roy. Soc.*, 1961, *A*, **260**, 424.

[3] Flowers and Frey, *J.*, 1961, 3547.

[4] Flowers and Frey, *J.*, 1961, 5550.

The thermal decomposition of bicyclopropyl has now been studied since it was possible that it might involve both types of isomerization. The path leading to olefins would be expected to yield as " first products " *cis*- and *trans*-propenyl-, isopropenyl-, and allylcyclopropane. The path analogous to that in the vinylcyclopropane–cyclopentene reaction might be expected to afford cyclohexene. As will be shown, both reactions occur, as well as others.

EXPERIMENTAL

An attempt was made to prepare 2,2,2′,2′-tetrachlorobicyclopropyl by the action of chloroform and potassium t-butoxide on butadiene. Even when an excess of these reagents was used the major product was 1,1-dichloro-2-vinylcyclopropane. Accordingly the dichloro-compound was itself treated with chloroform and potassium t-butoxide: 2,2,2′,2′-tetrachlorobicyclopropyl was then obtained in about 4% yield, nearly all the dichloro-compound being recovered unchanged. Thus the presence of the chlorine atoms (even though they are neither directly attached to, nor conjugated with, the double bond) leads to considerable deactivation towards attack by dichlorocarbene.

The tetrachlorobicyclopropyl was recrystallized from carbon tetrachloride and then reduced to bicyclopropyl by a two-fold excess of lithium and t-butyl alcohol in di-(2-methoxyethyl) ether. The reduction is slow but very efficient, and crude bicyclopropyl was obtained in 80% yield. Unsaturated impurities were removed by treatment with bromine at −78°, followed by washing with aqueous sodium carbonate water. High-boiling compounds were then removed by distillation through a Podbielniak column at low pressure. The bicyclopropyl was finally purified by gas chromatography, which yielded a product containing 0·05% of total impurity. The infrared spectrum of the product was identical with that reported for bicyclopropyl.[5]

cis- *and* trans-*Penta*-1,3-*diene*.—Pure samples of each isomer were obtained from a commercial sample of the mixed isomers by preparative gas chromatography.

The various cyclopropylpropenes required for identification were obtained by the reactions of methylene (prepared *in situ* by photolysis of keten) with the appropriate C_5 dienes. They were all separated from complex reaction mixtures by gas chromatography.

Apparatus.—The conventional " static " high-vacuum system used in this work has been described previously.[6]

Analysis.—Analysis was by gas chromatography and mass spectrometry. The gas chromatography apparatus had a 30 ft. × 0·18 in. coiled copper column containing di-(2-cyanoethyl) ether on 40—60 mesh Chromosorb. Hydrogen was the flow gas, and a Gow-Mac tungsten filament katharometer was the detector. The signals from the detector were fed, *via* a variable attenuator, to a 0—1 mv Sunvic recorder fitted with a retransmitting slidewire. Signals from this slidewire were used to drive a low-inertia integrating motor (Electro-Methods). The analytical precision was better than ±0·5%. Calibration mixtures were prepared in a specially designed vacuum-system which employed greaseless valves rather than conventional stopcocks, to avoid the troubles associated with the absorption of hydrocarbons in stopcock grease.

The mass spectrometer was an M.S. 3 instrument.

RESULTS

In the temperature range 405—480°c bicyclopropyl undergoes a series of parallel reactions which are all kinetically of the first order, as is the rate of disappearance of the bicyclopropyl. Many of the primary products undergo further reactions. Owing to the complexity of the system it will be convenient to state the probable reaction scheme before presenting the evidence for it.

In addition to the peak due to bicyclopropyl itself, the gas chromatograms of the reaction mixture contained 17 distinct peaks, so there were at least 17 products. To eliminate the danger of overlooking peaks due to compounds having considerably higher molecular weight than the majority of the products, the entire reaction mixture was analysed by mass spectrometry. This showed the absence of significant quantities of molecules containing more than six carbon atoms. The products shown in expressions (1)—(5) were tentatively identified in

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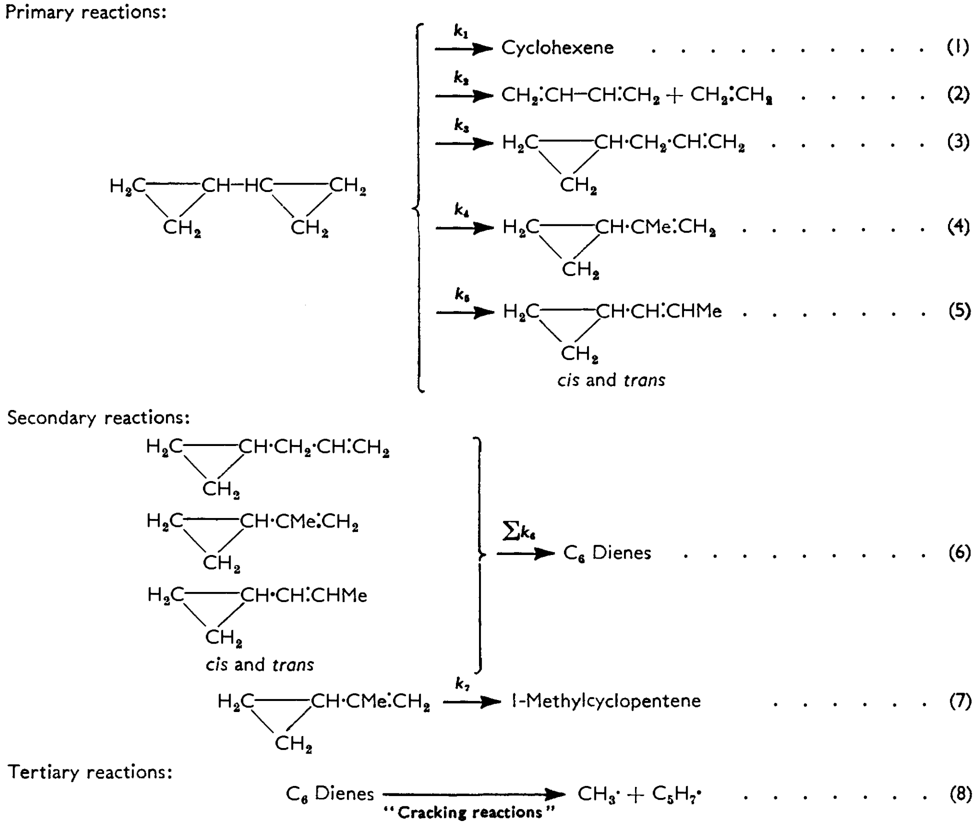
[5] Slabey, *J. Amer. Chem. Soc.*, 1952, **81**, 502.

[6] Flowers and Frey, *J.*, 1962, 1157.

the mixture by comparison of retention times with those of pure samples. Later, pure samples of these compounds were added to the reaction mixture immediately before analysis; the initial assignments were confirmed by this procedure, there being no sign of asymmetric peaks.

Most of the remaining peaks on the chromatograms were shown to be due to compounds C_6H_{10} (*i.e.*, C_6 dienes) by individual " trapping " and mass spectrometry. Three products were formed in quantities too small to allow even this sensitive method of detection to be employed. In most cases pure isomers of the various C_6 dienes are not available, or have not been prepared in high purity, so further identification has not been attempted at this stage. In a few instances it was possible to be reasonably certain of the presence of particular dienes, *e.g.*, 2-methylpenta-1,4-diene, as well as to show the absence of others, *e.g.*, diallyl.



As well as the C_6 dienes and the compounds occurring in expressions (1)—(5) small quantities of ethane and propene were formed. Also, one of the products shown by its peak in mass spectrometry to have the formula C_6H_{10} had the same retention time as 1-methylcyclopentene and this may be its constitution.

In determining the percentage decomposition of bicyclopropyl it was assumed that the integrated peak area ascribed to a C_6 diene or to a cyclopropylpropene was directly proportional to its molar fraction in the mixture, *i.e.*, that these products have the same calibration factor as bicyclopropyl. Preliminary experiments with many hydrocarbon isomers in the analytical system employed in this work showed that for hydrocarbons of the same molecular weight the calibration factors were identical within 2%. Calibration factors for ethylene and butadiene were determined experimentally by analysing mixtures of known composition.

The rate of decomposition of the bicyclopropyl was found to be accurately of the first order even when the reaction proceeded to 80% completion. The precision with which complex mixtures may be analysed by quantitative gas chromatography is illustrated in Fig. 1. The rate constants for the decomposition of bicyclopropyl, computed by the method of least squares, are:

Temp.	408·5°	428·2°	453·3°	474·0°
10^4k (sec.$^{-1}$)	0·793	$2{\cdot}72_5$	$12{\cdot}1_7$	$40{\cdot}4_7$

These results are fitted by the Arrhenius equation $k = 10^{15\cdot36} \exp(-60{,}710/\boldsymbol{R}T)$ (sec.$^{-1}$) with a probable error of less than 20 cal. While it is not suggested that the energy of activation has been established with this precision (temperature uncertainties probably result in an error of ±500 cal.) the small probable error reflects the very high reproducibility of the results.

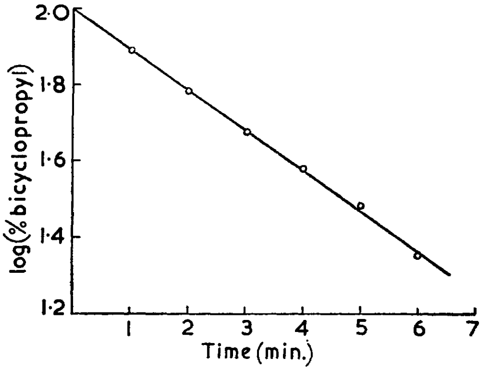


FIG. 1. First-order plot for decomposition of bicyclopropyl at 474·0°.

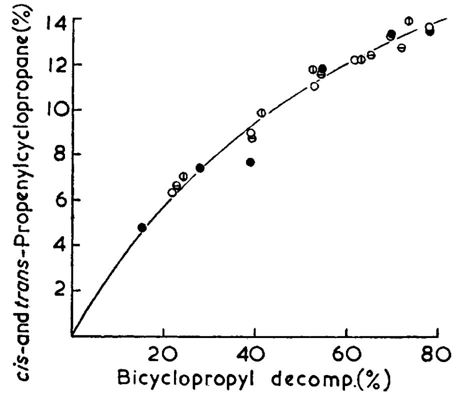


FIG. 2. Formation of *cis*- and *trans*-propenylcyclopropane as a function of the total percentage decomposition.

⦶ 408·5°. ● 428·2°. ⊖ 453·3°. ○ 474·0°.

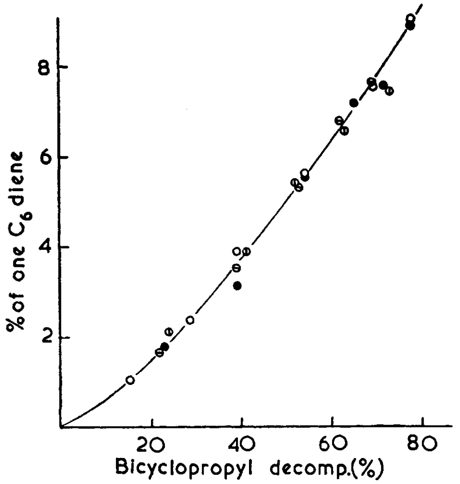


FIG. 3. Formation of a C_6 diene as a function of the total percentage decomposition.

⦶ 408·5°. ○ 428·2°. ● 453·3°. ⊖ 474·0°.

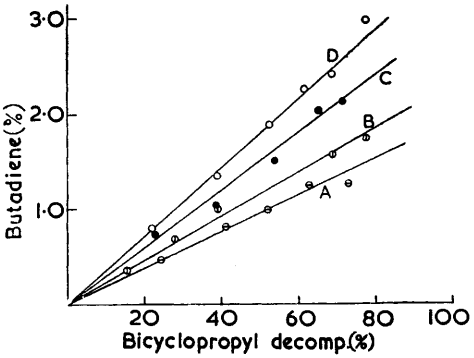


FIG. 4. Formation of butadiene as a function of the total % decomposition.

A (⊖), 408·3°. B (⦶), 428·2°. C (●), 453·3°. D (○), 474·0°.

To determine which products were formed directly from bicyclopropyl and which resulted from secondary reactions, the yields of the various compounds were plotted against the total percentage decomposition of bicyclopropyl. Primary products which do not undergo further reactions yield a linear plot; primary products which undergo further reactions yield a curve with a positive initial slope and a negative curvature. Secondary products yield a curve with an initial slope of zero and a positive curvature. Figs. 2—4 illustrate the method. In this way it was shown that the products in expressions (1) and (2) were primary and underwent no further decomposition, while those in (3), (4), and (5) were primary products which underwent secondary reactions. All the C_6 dienes were secondary products.

As shown in Fig. 2 the yields of *cis-* and *trans*-propenylcyclopropane [and of the C_6 dienes (see Fig. 3)] fall on the same curve for runs at the various temperatures. This implies that the energy of activation for the isomerization of the cyclopropylpropenes must be fairly close to that for bicyclopropyl itself. Fig. 4 shows this not to be the case for the reaction leading to butadiene; relatively more butadiene is formed as the temperature is raised: the reaction leading to butadiene has a higher energy of activation than the overall decomposition of bicyclopropyl. The Arrhenius equation for the decompositon of bicyclopropyl to butadiene + ethylene is $k = 10^{16 \cdot 8} \exp(-70{,}800/\boldsymbol{R}T)$ (sec.$^{-1}$), the precision being considerably less than for the overall decomposition because of the relatively small yields of butadiene.

Two difficulties prevented determination of the Arrhenius parameters for the isomerization of the bicyclopropyl to cyclohexene. The first was analytical, being caused by the proximity of the cyclohexene and bicyclopropyl peaks on the chromatograms. At low percentage decompositions (when the bicyclopropyl peak was relatively large) there was considerable overlap, which made the determination of the yield of cyclohexene inaccurate. The second difficulty was the secondary production of small quantities either of cyclohexene or of a C_6 diene of the same retention time at high percentage decompositions. It appears, however, that the reaction postulated in expression (1) has an energy of activation somewhat lower than that for the overall decomposition, and a frequency factor which is considerably smaller.

Expression (7) which is suggested as a possible reaction by analogy with the isomerization of vinylcyclopropane to cyclopentene is not definitely established by the present work. The peak on the chromatogram which has the same retention time as 1-methylcyclopentene is too small to permit unambiguous identification by secondary methods. It is expected that work in progress with pure isopropenylcyclopropane will settle this point.

In addition to the products postulated in expressions (1)—(7) small yields of " cracking products " were present. Of these, the most important was ethane. While the absolute yield of ethane was always small, its relative yield increased rapidly with percentage decomposition and it is believed that it arises from the decomposition of some of the C_6 dienes.

A number of products which were thought to be likely were shown to be absent, including allene, cyclopropane, acetylene, and methylenecyclopropane.

DISCUSSION

The Arrhenius parameters for the overall rate of decomposition of bicyclopropyl are very close to the values observed for the alkylcyclopropanes.[2] As about 80% of the primary decompositions are isomerizations yielding the various cyclopropylpropenes, this is not unexpected, since the transition state must be similar in all these cases. In the particular case of bicyclopropyl compared with methylcyclopropane, there is a further degeneracy of two in the reaction path, due to the symmetry of the molecule, which probably accounts for the higher value of the *A* factor.

In the past the isomerization of cyclopropane has been discussed in terms of two possible reaction mechanisms, both suggested in the original paper on the cyclopropane isomerization, by Chambers and Kistiakowsky.[7] One involves the intermediate formation of a trimethylene biradical. The other considers a transition state where the movement of a hydrogen atom is rate-determining. The latter mechanism gained considerable support from Slater's theoretical calculations.[8] Recently experimental evidence has tended to favour the former mechanism,[9] though the results do not allow a distinction to be made between an " expanded ring " transition state, with free or slightly hindered internal rotation, and one involving a free trimethylene biradical. The work reported in this paper does not permit a choice to be made between these two mechanisms. It is, however, interesting that, since neither allene nor cyclopropane is present in the reaction

[7] Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399.

[8] Slater, *Proc. Roy. Soc.*, 1953, *A*, **218**, 224.

[9] Schlag and Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.

mixture, there is no movement of hydrogen atoms from $C_{(1)}$ to $C_{(1')}$, or *vice versa*, in the reacting bicyclopropyl molecule.

The decomposition of bicyclopropyl to butadiene and ethylene has an energy of activation approximately 10 kcal. mole^{-1} higher than the isomerizations. It probably occurs *via* a transition state involving very considerable distortion of the bicyclopropyl molecule. It may be pictured as a movement of $C_{(2)}$ or $C_{(3)}$ towards $C_{(1')}$ (or $C_{(2')}$ or $C_{(3')}$ towards $C_{(1)}$) with the simultaneous elimination of $C_{(2')}$–$C_{(3')}$ as ethylene. That the reaction may involve intermediate formation of cyclobutene (which would immediately yield butadiene at the reaction temperature) cannot be definitely ruled out. However, the very high *A* factor suggests direct formation of butadiene. This reaction accounts for about 3% of the primary decomposition of the bicyclopropyl.

The isomerization of bicyclopropyl to cyclohexene is one of the most interesting features of this work: unlike the reactions leading to cyclopropylpropenes, it does not involve fission of carbon–hydrogen bonds. The transition state probably involves the close proximity of $C_{(2)}$ and $C_{(2')}$, or $C_{(2)}$ and $C_{(3')}$, or the two other equivalent configurations. There is thus a degeneracy of four in the reaction path. The experimental evidence suggests that the *A* factor for this isomerization is smaller than for the reaction leading to the cyclopropylpropenes. This is to be expected with the mechanism involving as it does a somewhat rigid transition state (cf. vinylcyclopropane to cyclopentene).

The reactions of the cyclopropylpropenes to give C_6 dienes have energies of activation closely equal to one another and are approximately the same as the overall value for the decomposition of bicyclopropyl itself; but the complexity of the reaction mixture prevented separation of the various secondary products.

The formation of various cracking products probably proceeds by a radical path. The presence of a large number of compounds in the reacting mixture which may act as chain inhibitors ensures that these radical reactions must involve very short chains. This is consistent with the very low yields of such cracking products, and also with the fact that a major cracking product appears to be ethane, presumably formed by the dimerization of methyl radicals.

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