The Pyrolysis of Halocyclopropanes at High Temperatures

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(Received December 14, 1970)

The pyrolysis reactions of dihalocyclopropanes and monohalocyclopropanes were carried out at 200—400°C. Bromo-substituted cyclopropanes were readily decomposed in this temperature range. In all cases, the pyrolysis products were ring-opened olefinic hydrocarbons. As for the monohalocyclopropanes, the reactions proceed in a stereospecific manner. The possible mechanism was discussed in terms of the requirements of the electrocyclic ring opening.

The slow solvolysis rates of cyclopropyl compounds have attracted much attention from organic chemists. The low reactivity of these compounds toward nucleophilic substitution has been attributed to the steric strain of the ring, which makes the intermediate cyclopropyl cation unstable.[1] Generally, the solvolysis, products are exclusively ring-opened allyl derivatives.

Examples of this type of transformation, the so-called cyclopropyl-allyl transformation, have been reported by many authors; the reaction presented in our next report, in which ring-opened products were obtained by the Friedel-Crafts reaction of halocyclopropanes, may also be included in this category.

The transformation requires the rotation of substituted groups on the cyclopropane ring. As a result, several steric courses may be considered with regard to the direction of rotation. According to the proposal of Woodward and Hoffmann,[2] the steric course of this process is determined by the symmetry of the highest occupied orbital of the ground state. They predicted

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1) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).

2) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

TABLE 1. PYROLYSIS OF DIHALOCYCLOPROPANES

Cyclopropane	Pyrolysis temperature (°C)	Total[a] pyrolysate (%)	Pyrolysis product	Yield (%)	Recovered[b] cyclopropane (%)
I-Cl	392	63	$CH_2=\overset{Cl}{\underset{}{C}}-\overset{CH_3}{\underset{}{C}}=CH_2$	24	31
I-Br	350	34	$CH_2=\overset{Br}{\underset{}{C}}-\overset{CH_3}{\underset{}{C}}=CH_2$	70	1
II	390—400	68		0	48
III	320—325	26	⬡	54	3
VI	390	43			12

a) The weight % of condensed hydrocarbons to the starting material.
b) The weight % of pyrolysis product to total pyrolysate.

that the direction of the ring opening of the cyclopropyl cation must be disrotatory. Some experimental evidence has been given by the solvolysis reactions of substituted cyclopropyl tosylates.[3,4]

In the present investigation, the pyrolysis reaction of halocyclopropanes was studied. Some differences with regard to the stereospecificity may be expected between the pyrolysis and cationic ring-opening reactions of cyclopropanes. Since the pyrolysis rates of halocylopropanes are quite fast at 200—400°C, this reaction is suitable for the investigation of the reactivity of chemically-inactive halocyclopropanes. The steric course of the pyrolysis reaction will be discussed on the basis of analyses of the pyrolysis products.
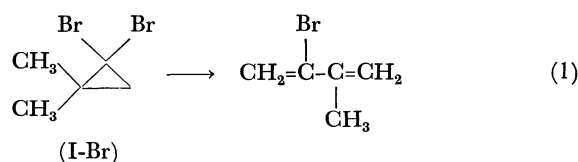
Results and Discussion

It is expected that dihalocyclopropanes are less reactive than the corresponding monohalocyclopropanes as a result of the introduction of electron-withdrawing halogen atoms. However, the thermal decompositions of some dichlorocyclopropanes have been reported recently,[5,6] and it has been recognized that, at temperatures higher than 400°C, even these chemically stable cyclopropanes can be decomposed.

In this work, the pyrolysis reactions of gem-dibromocyclopropanes were mainly investigated. The results for gem-dihalocyclopropanes are summarized in Table 1. The pyrolysis products which could not be isolated were identified by the use of a mass spectrometer directly connected to a gas chromatograph.

1,1-Dichloro-2,2-dimethylcyclopropane (I-Cl) was pyrolyzed at 390°C to give 2-chloro-3-methylbutadiene. This reaction has already been reported by Robinson.[5] Similarly, 1,1-dibromo-2,2-dimethylcyclopropane (I-Br) gave 2-bromo-3-methylbutadiene as a sole product at lower temperatures.

The formation of the butadiene derivative may be attributed to the above-described cyclopropyl-allyl

3) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, ibid., 87, 4006 (1965).

4) P. von R. Schleyer, G. W. VanDine, U. Schöllkopf, and J. Paust, ibid., 88, 2868 (1966).

5) G. C. Robinson, J. Org. Chem., 33, 607 (1968).

6) G. C. Robinson, ibid., 29, 3433 (1964).

$$CH_2=\overset{Br}{\underset{CH_3}{C}}-C=CH_2 \qquad (1)$$

(I-Br)

transformation, followed by the migration of the bromine atom, just as in the case of dichlorocyclopropanes. It must be noted that the ring opening is accompanied by the elimination of hydrogen bromide. As is well known, halogenated hydrocarbons easily decompose to olefins in the above temperature range, with the elimination of hydrogen halide. Therefore, dehydrohalogenation would seem to occur simultaneously with ring opening under the conditions studied in this work. This consideration is supported by the absence of ring-opened dibromides in the pyrolysis products.

The pyrolysis of 7,7-dibromonorcarane (III) gave cycloheptatriene as has been reported[6] for the high-temperature pyrolysis of 7,7-dichloronorcarane (II). However, the yield was relatively poor because of the carbonization of the starting material.

$$\underset{(III)}{} \xrightarrow[-2HBr]{} \qquad (2)$$
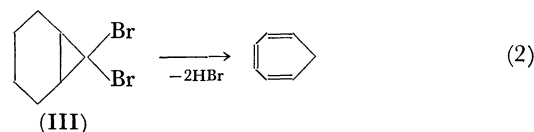
II did not decompose in the temperature range studied in this work. 1,1-Dibromo-2-phenylcyclopropane (IV) gave complex products at 350°C which could not be identified.

The pyrolysis of monohalocyclopropanes was carried out under the same conditions as were used for dihalocyclopropanes. As it was very difficult to separate completely cis- and trans-isomers of monohalocyclopropanes by distillation, mixtures of the two isomers were pyrolyzed.

Bromocyclopropane (V) was prepared by the bromination of cyclopropane carboxylic acid.[7] The other monohalocyclopropanes were prepared by the reduction of the corresponding dihalocyclopropanes with tri-n-butyltin hydride. The ratio of the cis isomer to the trans

7) J. S. Meek and D. T. Osuga, "Organic Syntheses," Vol. 43, p. 9 (1963).
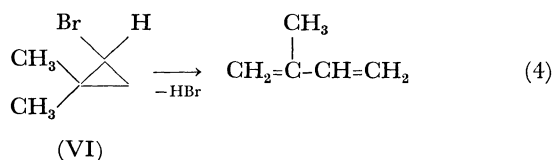
Table 2. Pyrolysis of monohalocyclopropanes

Cyclopropane	Pyrolysis temperature (°C)	Total pyrolysate (%)	Pyrolysis product	Yield (%)	Recovered cyclopropane (%)
V	303	61	$CH_2=CH-CH_2Br$	72	1
VI	300	34	CH_3	98	0
	210	49	$CH_2=\overset{\mid}{C}-CH=CH_2$	90	0
VII	355	43		61	6
	300	53	⬡	56	5
	253	41		40	8
VIII	300	37	C_2H_5	75	0
	250	34	$\overset{\mid}{CH}=CH-CH=CH_2$	66	0

one was determined by using a gas chromatograph and NMR as has been described by Seyferth.[8]

The pyrolysis of V gave allyl bromide as the main product. This bromide was identified by a comparison of its gas chromatograph with that of an authentic sample. The elimination of hydrogen bromide did not occur in this case.

$$\triangleright\text{-Br} \rightarrow CH_2=CH-CH_2Br \qquad (3)$$
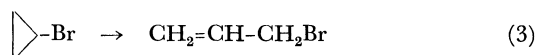
1-Bromo-2,2-dimethylcyclopropane (VI) was pyrolyzed almost completely at 300°C. None of the stereo-isomers exist for this cyclopropane. Carbonization was not observed, and the single product was identified as isoprene. Isoprene is probably formed by the dehydrohalogenation after the rearrangement of VI to 2-bromo-2-methylbutene-1. However, the rearranged bromide was not found in the pyrolysis product.

$$\begin{array}{c} \text{Br} \quad \text{H} \\ CH_3 \diagdown \diagup \diagdown \diagup \\ \qquad \qquad \diagup \diagdown \\ CH_3 \diagup \end{array} \xrightarrow[-HBr]{} \begin{array}{c} CH_3 \\ \mid \\ CH_2=C-CH=CH_2 \end{array} \qquad (4)$$

(VI)

A mixture of *exo*- and *endo*-7-bromonorcarane (VII) gave a hydrocarbon with a parent mass of 94. However, a considerable amount of the starting material was recovered. The hydrocarbon in the pyrolysate was separated by distillation and was identified as 1,3-cycloheptadiene by NMR and elemental analysis. On the other hand, the recovered starting material was

$$\begin{array}{c} \text{Br} \\ \diagup \diagup \\ \bigobot \diagdown \diagup \diagdown \\ \text{H} \end{array} \xrightarrow[-HBr]{} \bigcirc \qquad (5)$$

(VII)
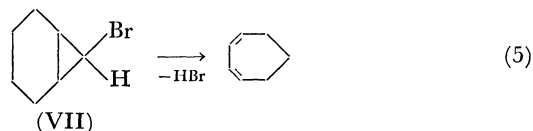
found by gas-chromatographic analysis to be an almost pure *exo* isomer of VII. It is evident that the *endo* isomer was completely decomposed to 1,3-cycloheptadiene, while the *exo*-isomer was quite stable in the temperature range studied in this work.
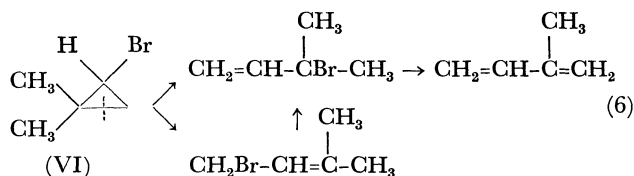
A mixture of *cis*- and *trans*-1-bromo-2-propylcyclopropane (VIII) was pyrolyzed to give two major products with a parent mass of 82. The product formed in the higher yield may be *trans*-1,3-hexadiene, as the results

8) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28**, 703 (1963).

of the NMR analysis indicate. The other product is probably *cis*-1,3-hexadiene, but no unambiguous assignment for the two isomers formed in this reactions was possible because of the presence of other components.

Monohalocyclopropanes with a phenyl group, *i.e.*, 1-bromo-2-phenylcyclopropane and 1-bromo-2-methyl-2-phenylcyclopropane, were also investigated. However, the products were complex and could not be identified.

The pyrolysis conditions for monohalocyclopropanes are summarized in Table 2.

In view of the pyrolysis product of V, it is rather surprising that the only product of the pyrolysis of VI was isoprene, which may be formed by the dehydrobromination of 3-bromo-3-methylbutene-1. Another possible bromide, 1-bromo-3-methylbutene-2, probably rearranges to 3-bromo-3-methylbutene-1 to form the same product.

$$\begin{array}{c} \text{H} \quad \text{Br} \\ CH_3 \diagdown \diagup \diagdown \diagup \\ \qquad \diagup \diagdown \\ CH_3 \diagup \end{array} \diagup^{\nearrow} \begin{array}{c} CH_3 \\ \mid \\ CH_2=CH-CBr-CH_3 \rightarrow CH_2=CH-\overset{\mid}{C}=CH_2 \\ \\ \uparrow \begin{array}{c} CH_3 \\ \mid \end{array} \\ CH_2Br-CH=C-CH_3 \end{array} \quad (6)$$

(VI)

The lack of the reactivity of *exo*-norcaranyl compounds toward solvolysis reaction was attributed to its incapability of forming an intermediate allylic carbonium ion by the outward rotation of groups trans to the leaving group, as is shown in Fig. 1.[3]
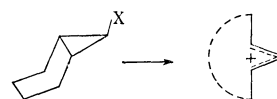
Fig. 1

Analogous considerations can possibly explain the great difference in the pyrolysis rates of *exo*- and *endo*-7-bromonorcarane. As is shown in Fig. 2, if the electrons of the C_2–C_3 bond move to the back face of the C_1–Br bond, as has been described by DePuy[3], the bromine atom would migrate to the C_2 or C_3 position along the lower side of the plane formed by the three-membered ring. On the other hand, if the electrons of the C_2–C_3 bond move to the same side of the bromine atom with respect to the cyclopropane ring, the bromine atom must go across the plane of cyclopropane to migrate to the C_2 or C_3 position.
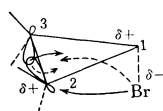
Fig. 2

In conclusion, in the pyrolytic rearrangement of halocyclopropanes, the direction of the rotation of the groups on the cyclopropane ring also obeys the rule proposed by DePuy,[3] i.e., the groups trans to the halogen atom rotate outward, while the groups cis to the halogen atom rotate inward. As for the exo isomer VII, the groups trans to the bromine atom are ristricted by the cyclohexane ring. Therefore, the outward rotation of these groups is impossible.

Experimental

gem-Dihalocyclopropanes.   Dihalocarbenes generated from haloform and potassium t-butoxide were added to the corresponding olefins, and finally purified by distillation.[9] The dihalocyclopropanes investigated in this work were 1,1-dichloro-2,2-dimethylcyclopropane (I-Cl) (bp 120—121°C), 1,1-dibromo-2,2-dimethylcyclopropane (I-Br) (bp 62—64°C/21 mmHg), 7,7-dichloronorcarane (II) (bp 78—79°C/15 mmHg), 7,7-dibromonorcarane (III) (bp 104°C/3 mmHg), and 1,1-dibromo-2-phenylcyclopropane (VI) (bp 110—112°C/4 mmHg).

Monohalocyclopropanes.   These cyclopropanes were prepared by the reduction of the corresponding gem-dihalocyclopropanes with tri-n-butyltin hydride.[8] The monohalocyclopropanes thus obtained were mixture of cis and trans isomers. The clear separation of these isomers by distillation could not be achieved. The ratios of the cis isomer to the trans one were determined by gas chromatography with the aid of the NMR spectra, as has been reporyed bt Seyferth.[8]

1-Bromo-2,2-dimethylcyclopropane (VI)

bp 50—52°C/130 mmHg, lit,[8] 107—108°C.

7-Bromonorcarane (VII)

bp 86—96°C/28 mmHg, lit,[8] 94—109°C/24—27 mmHg. cis/trans : 2.8.

1-Bromo-2-propylcyclopropane (VIII)

bp 52—54°C/33 mmHg, cis/trans : 2.0.

1-Bromo-2-phenylcyclopropane

bp 93—102°C/3 mmHg, lit,[8] 48—50°C/0.15 mmHg.

1-Bromo-2-methyl-2-phenylcyclopropane

bp 80—83°C/4 mmHg.

The accurate determination of the cis-to-trans ratios for the last two cyclopropanes were not possible because of their decompositions in the column of the gas chromatograph.

Bromocyclopropane (V) was prepared by the bromination of cyclopropane carboxylic acid[7] (bp 67—68.5°C, lit, 69°C).

Pyrolysis Apparatus.   The pyrolysis reactions were carried out in a vertical electric furnace equipped with a calcium oxide column. From the top of the furnace, halocyclopropanes were introduced, drop by drop, with nitrogen as the carrier gas. The hydrogen halide evolved in the couse of the reaction was absorbed by calcium oxide. The gaseous pyrolysis products were condensed in a dry ice - methanol bath. The trapped pyrolysates were dried and distilled or were directly analyzed by gas chromatography. The pyrolysis temperature was 200—400°C.

Identification of Pyrolysis Products.   2-Chloro-3-methylbutadiene had a bp of 89—95°C (lit,[5] 91—101°C).

Found: C, 58.37; H, 7.05; Cl, 34.57%.   Calcd for C_5H_7Cl: C, 58.55; H, 6.88; Cl, 34.73%.

2-Bromo-3-methylbutadiene had a bp of 36—37°C/35 mmHg, (lit,[10] 35°C/40 mmHg).

Found: C, 40.23; H, 4.79; Br, 54.88%.   Calcd for C_5H_7Br: C, 40.85; H, 4.80; Br, 54.35%.

Cycloheptatriene had a bp of 53.5—55°C/97 mmHg, (lit,[6] 61°C/125 mmHg).

Found: C, 90.91; H, 8.37%.   Calcd for C_7H_8: C, 91.25; H, 8.75%.

NMR signals (in carbon tetrachloride): $\tau=3.5$, 3.7, 4.7 (olefinic protons), $\tau=7.83$ (methylene protons, triplet).

The allyl bromide was identified by comparing the retention time of its gas chromatograph with that of an authentic sample.

Found: C, 30.04; H, 4.07; Br, 65.79%.   Calcd for C_3H_5Br: C, 29.78; H, 4.17; Br, 66.05%.

The isoprene was also identified by gas chromatography using an authentic sample.

Found: C, 88.35; H, 11.85%.   Calcd for C_5H_8: C, 88.16; H, 11.84%; mol wt (parent mass), 68.

1,3-Cycloheptadiene had a bp of 119—121°C (lit,[11] 121.5°C).

Found: C, 89.24; H, 10.90%.   Calcd for C_7H_{10}: C, 89.29; H, 10.71%; mol wt (parent mass), 94.

NMR signals (in carbon tetrachloride): $\tau=4.33$ (olefinic protons), $\tau=7.69$, 8.10 (methylene protons).

The pyrolysis product of VIII was distilled to give a fraction of 67.5—73°C. The gas chromatograph of this fraction showed two major components, both of which have a parent mass of 82. The NMR signals indicate that the product formed in a higher yield may be trans-1,3-hexadiene.

Found: C, 86.79; 13.06%.   Calcd for C_6H_{10}: C, 87.73; H, 12.27%.

NMR signals: $\tau=8.7$ (methylene protons), $\tau=9.0$ (methyl protons, triplet). The signals for the olefinic protons were complex and could not be assigned.

9) W. von E. Doering and A. K. Hoffmann, J. Amer. Chem. Soc., 76, 6162 (1954).

10) A. A. Petrov, Zh. Obshch. Khim., 13, 748 (1948).

11) J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, J. Amer. Chem. Soc., 61, 1868 (1939).