Some Observations on the Reactions of Cyclopropane with Hydrochloric Acid and of Bromocyclopropane with Hydrobromic Acid

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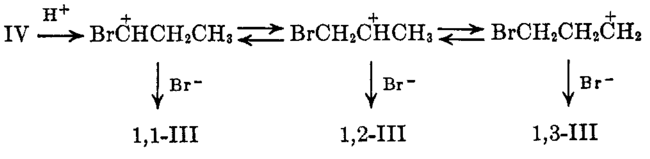
In a recent paper from this laboratory,[1] it was reported that the reaction between cyclopropane (I) and tritiated Lucas reagent ($ZnCl_2$–HCl-*t*) gave only 1-chloropropane (II-*t*) with no 2-chloropropane, and the *t* label was found in all three carbon positions of the 1-chloropropane. These results were interpreted as arising from equilibrating edge-protonated cyclopropane intermediates. In these experiments, II-*t* was swept out of the reaction mixture by an excess of I. This procedure also served to minimize the contact between II-*t* and the Lucas reagent, since Reutov and Shatkina[2] have reported that when 1-^{14}C-1-chloropropane (II-1-^{14}C) was treated with $ZnCl_2$–HCl, although no 2-chloropropane was formed, various extents of rearrangement to II-3-^{14}C were observed, depending on temperature and contact time; for example, at 50° for 100 hr, 7.5% rearrangement was noted. In an attempt to verify this reported 1,3-hydride shift, 1-*t*-1-chloropropane (II-1-*t*) and $ZnCl_2$–HCl were heated under reflux at 50 ±2° for 100 hr. The recovered II-1-*t* was uncontaminated by 2-chloropropane, as found by Reutov and Shatkina;[2] however, it also showed no rearrangement of the isotopic label. These results were confirmed when the treatment of II-1-*t* with $ZnCl_2$–HCl was carried out with shaking in a sealed tube at 50 ±2° for 100 hr. The present results, similar to those obtained in the earlier work on the deamination of 1-^{14}C-1-aminopropane,[3] again failed to confirm the 1,3-hydride shift reported by Reutov and Shatkina, and thus established that the isotope position rearrangements observed in the reaction between I and $ZnCl_2$–HCl-*t* did not involve complications arising from interactions between II-*t* and the Lucas reagent.

Since I has been protonated by H_2SO_4-*t* or D_2SO_4 of various concentrations without any catalyst,[4] it is of interest to ascertain if the $ZnCl_2$ is necessary in effecting the reaction between I and HCl. When I was passed through 12 *M* HCl-*t* and the material swept out by the excess I was studied as previously,[1] only II-*t*, uncontaminated by 2-chloropropane, was obtained. The yields of II-*t* and the distributions of the *t*-label are summarized in Table I. It is seen that there is no significant difference in the results obtained from the reactions of I with 12 *M* HCl, with or without the presence of $ZnCl_2$. When the reaction was effected in the presence of 5% $AlCl_3$, however, the product II-*t* was contaminated by 3–4% 2-chloropropane, and somewhat different *t*-distributions in the II-*t*, also shown in Table I, were observed. These differences are likely due, at least in part, to the effects of $AlCl_3$ on the initially formed II-*t*, since Karabatsos and coworkers[5] have reported that when D-labeled 1-bromopropane was treated with $AlBr_3$ both conversion to 2-bromopropane and scrambling of the D-label in the recovered 1-bromopropane were observed.

Deno and Lincoln[6] have reported that the bromination of I, catalyzed by a Lewis acid, resulted in the formation of 1,1-, 1,2- and 1,3-dibromopropanes (1,1-, 1,2-, and 1,3-III), as well as some 1,1,2-tribromopropane. The production of the three isomeric dibromopropanes was attributed to the involvement of protonated bromocyclopropane intermediates derived from reaction of Br^+ with I. In view of these findings of Deno and Lincoln, an investigation was made on the formation of dibromopropanes from the reaction between bromocyclopropane (IV) and HBr. The experiments were carried out by stirring IV with 68% HBr at room temperature for various lengths of time, and the products were analyzed by vpc. Two runs were also carried out in the presence of a catalytic amount of $AlCl_3$. The results are summarized in Table II. The vapor phase chromatograms also showed some additional small peaks, indicating the presence of small amounts of other products, the nature of which, however, was not investigated. The complexity of these unidentified materials was greater when the reaction was effected in the presence of $AlCl_3$, suggesting some interactions between $AlCl_3$ and IV and possibly also between $AlCl_3$ and the products 1,1-, 1,2-, and 1,3-III.

In contrast to the bromination of I, which gave 1,3-III as the main product,[6] the reaction between IV and HBr gave mostly 1,1- and 1,2-III, with 1,3-III only as a minor product.[7] These results can be explained either by reactions involving classical carbonium ions (Scheme I[8]) or *via* short-lived nonisomerizing protonated bromocyclopropanes (Scheme II). A similar conclusion was reached by Deno and coworkers,[4c] who explained the sole formation of $CH_3CHClCH_2CH_2D$

SCHEME I



$$\begin{array}{ccccc} IV \xrightarrow{H^+} Br\overset{+}{C}HCH_2CH_3 & \rightleftarrows & BrCH_2\overset{+}{C}HCH_3 & \rightleftarrows & BrCH_2CH_2\overset{+}{C}H_2 \\ \downarrow Br^- & & \downarrow Br^- & & \downarrow Br^- \\ 1,1\text{-III} & & 1,2\text{-III} & & 1,3\text{-III} \end{array}$$

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(1) C. C. Lee, W.K.-Y. Chwang, and K.-M. Wan, *J. Amer. Chem. Soc.*, **90**, 3778 (1968).

(2) O. A. Reutov and T. N. Shatkina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 180 (1963); O. A. Reutov, *Pure Appl. Chem.*, **7**, 203 (1963).

(3) C. C. Lee and J. E. Kruger, *J. Amer. Chem. Soc.*, **87**, 3986 (1965).

(4) (a) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964); (b) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968); (c) N. C. Deno, D. La Vietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968).

(5) G. J. Karabatsos, J. L. Fry, and S. Meyerson, *Tetrahedron Lett.*, 3735 (1965).

(6) N. C. Deno and D. N. Lincoln, *J. Amer. Chem. Soc.*, **88**, 5357 (1966).

(7) Professor N. C. Deno, acting as a referee, has stated that some of the 1,3-III reported in ref 6 may have arisen from light-catalyzed free-radical addition of Br_2 to I. By operating entirely in the dark at 15°, the introduction of I into Br_2 containing 1% Fe powder was found to give 38% 1,1-III, 6% 1,2-III, 50% 1,3-III, and 6% 1,1,2-tribromopropane. Some work on the reaction between IV and HBr has also been done by Deno and Lincoln. When IV was stirred at 25° with a solution of one part 48% aqueous HBr and three parts $ZnBr_2$, after 2 weeks there was 70% unreacted IV, 23% 1,1-III, and 7% 1,2-III. Taking into consideration the difference in reaction conditions, Professor Deno regards their results as in substantial agreement with those obtained in the present work.

(8) It may be pointed out that direct protonation of IV could also give rise to the primary cations $CH_3CHBrCH_2^+$ and $BrCH_2CH_2CH_2^+$, which could react with Br^- to give 1,2-III and 1,3-III, respectively. However, by analogy with the protonation of methylcyclopropane,[4c] only the direct formation of $Br\overset{+}{C}HCH_2CH_3$ is shown in Scheme I.

TABLE I

ACTIVITY DISTRIBUTIONS IN THE 1-CHLOROPROPANE FROM REACTION OF CYCLOPROPANE WITH HCl-*t*

	c-C_3H_6 + $ZnCl_2$ − HCl-t^a				c-C_3H_6 + HCl-t				c-C_3H_6 + $AlCl_3$ − HCl-t			
		t-Distribution, %				*t*-Distribution, %				*t*-Distribution, %		
Run	Yield,[b] g	C-1	C-2	C-3	Yield,[b] g	C-1	C-2	C-3	Yield,[b] g	C-1	C-2	C-3
1	4.6	38.6	16.6	44.7	3.4[c]	37.7	18.2	44.1	3.5[c]	33.3	21.4	45.3
2	4.8	37.2	19.7	43.1	5.7	37.7	15.6	46.7	5.9	33.8	22.8	43.4
3	5.8	37.7	18.8	43.5	4.8	38.3	17.1	44.6				

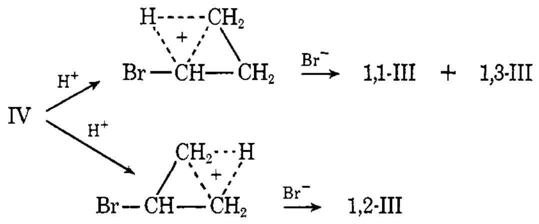
[a] From ref 1. [b] Estimated by isotope dilution calculations. [c] The c-C_3H_6 was bubbled through the reaction mixture for 16 hr; in the other experiments, the bubbling time was 24 hr.

TABLE II

DATA FROM REACTIONS BETWEEN BROMOCYCLOPROPANE (IV) AND HBR WITH OR WITHOUT THE PRESENCE OF $AlCl_3$

	Reaction time, hr	Recovered IV, %	Dibromopropane obtained, %		
			1,1-	1,2-	1,3-
No $AlCl_3$	1	95.8	0.8	1.1	...
	2	86.7	2.9	3.7	Trace
	6	71.6	9.0	10.4	3.5
	24	53.4	21.5	14.5	6.5
$AlCl_3$	2	69.6	6.6	8.1	Trace
	12	64.3	12.9	15.3	0.5

SCHEME II



from the addition of DCl to methylcyclopropane as the result of the addition of D^+ to methylcyclopropane to give the 2-butyl cation directly or *via* a short-lived nonisomerizing protonated methylcyclopropane.

Experimental Section

1-*t*-1-Chloropropane (II-1-*t*).—A mixture of 10.7 g (50 mmol) of 1-*t*-1-propyl tosylate and 11.0 g (100 mmol) of $CaCl_2$ in 75 ml of ethylene glycol was placed in a flask fitted for distillation. The flask was heated at 70–75° for 3 hr while a slow stream of nitrogen was passed over the reaction mixture to sweep out the product. The 1-*t*-1-chloropropane so obtained (in about 75% yield) was passed through anhydrous $CaCl_2$ and collected in a receiver cooled in Dry Ice-acetone.

Treatment of 1-*t*-1-Chloropropane (II-1-*t*) with $ZnCl_2$–HCl.—A mixture of 8.0 g (102 mmol) of II-1-*t*, 20.4 g (150 mmol) of $ZnCl_2$, and 12.5 ml (150 mmol) of 12 *M* HCl in a 50-ml flask was heated under reflux at 50 ± 2° for 100 hr. An efficient condenser was employed and the top of the condenser was loosely stoppered to minimize the loss of chloride. After the period of gentle refluxing was completed, about 2.0 g of II-1-*t* was recovered. Analysis by vpc showed the absence of 2-chloropropane. In a number of experiments starting with II-1-*t* of specific activities varying from about 200,000 to 1,200,000 cpm per mmol, the recovered II-1-*t* was converted to 1-*t*-1-propanol, which on oxidation gave inactive propanoic acid,[1] showing no rearrangement of the *t*-label to C-2 and C-3. The same results were obtained when the mixture of II-1-*t* and $ZnCl_2$–HCl in a sealed tube was placed in a hydrogenation bomb and then shaken and heated at 50 ±2° for 100 hr.

Reaction between Cyclopropane (I) and HCl.—I was bubbled through 25 ml of 12 *M* HCl-*t* at room temperature for 24 hr, and the product obtained was worked up and degraded as described previously.[1] Vpc analysis of the 1-chloropropane so obtained showed the absence of any 2-chloropropane. When the reaction was carried out in the presence of $AlCl_3$, 5.0 g of anhydrous $AlCl_3$ per 100 g of 12 *M* HCl was employed. Since the solubility of $AlCl_3$ in 12 *M* HCl was low, the suspension was stirred by a magnetic stirrer during the passage of I through the mixture. Vpc analysis of the product by an 8 ft × 0.25 in. stainless steel column packed with 25% FFAP on 60–80 mesh Chromosorb W showed that the 1-chloropropane contained about 3–4% 2-chloropropane.

Reaction between Bromocyclopropane (IV) and HBr.—The HBr solution was prepared by bubbling gaseous HBr into distilled water cooled at about 0° until a saturated solution was obtained. Titration showed the HBr concentration as 68%. The same batch of HBr solution was used in all the experiments.

A mixture of 2.42 g (20 mmol) of IV and 10 ml of 68% HBr, without or with the presence of 1.5 mmol of $AlCl_3$, was placed in a 50-ml flask fitted with a reflux condenser and was stirred at room tmperature for the desired length of time. Water was then added and the resulting material was extracted with ether. The extract was washed with water uutil free of acid, dried over anhydrous $MgSO_4$, and analyzed by vpc for IV, 1,1-III, 1,2-III, and 1,3-III by the FFAP column described above. All identifications and calibrations were based on chromatographically pure samples of IV, 1,1-III, 1,2-III, and 1,3-III. 1,1-III was prepared by the method of Stevens and coworkers,[9] while the other authentic samples were purchased commercially.

Registry No.—I, 75-19-4; hydrochloric acid, 7647-01-0; IV, 4333-56-6; hydrobromic acid, 10035-10-6.

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Alkylation of Naphthalene with Alkenes

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Whitmore and James[2] reported the formation of 2-*t*-butylnaphthalene plus uncharacterized higher alkylation products in the aluminum chloride catalyzed reaction of naphthalene with isobutylene. Other reports of the alkylation of naphthalene with olefins, alcohols, or alkyl halides also indicate preferential formation of the 2 isomer.[3,4] This preference for the 2 isomer has been argued on steric grounds in the case of bulky olefin-catalyst complexes and on the basis of rearrangement of the kinetically favored 1 isomer.

This communication reports work undertaken to investigate the alkylation of naphthalene with olefins under nonisomerizing conditions and thereby to deter-

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[2] F. C. Whitmore and W. H. James, *J. Amer. Chem. Soc.*, **65**, 2088 (1943).

[3] "Friedel-Crafts and Related Reactions," Vol. II, G. Olah, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, Chapter XIV.

[4] H. E. Nursten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).