[CONTRIBUTION FROM THE BEN MAY LABORATORY FOR CANCER RESEARCH AND THE DEPARTMENT OF BIOCHEMISTRY, UNIVERSITY OF CHICAGO]

Acid-catalyzed Decomposition of Chloro- and Fluoroformates[1,2]

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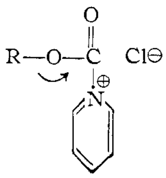
RECEIVED MAY 3, 1955

Studies with the chloro- and fluoroformate esters of ethyl, isopropyl, cyclopentyl and cyclohexyl alcohols show that the Lewis acid, boron trifluoride, is an effective catalyst for the decomposition of haloformates to form alkyl halides. The catalytic effect of boron trifluoride is particularly striking with secondary fluoroformates from which carbon dioxide is eliminated at room temperature or below.

It has long been known that on strong heating alkyl chloroformates eliminate carbon dioxide to produce the corresponding alkyl chlorides. In the presence of pyridine the reaction takes place at a lower temperature and appears to involve a different chemical mechanism, inasmuch as the stereochemical configuration of the halide produced is different from that formed in the absence of pyridine.[3] Recently it has been shown that alkyl fluoroformates undergo similar decomposition in the presence of pyridine to produce alkyl fluorides.[4]

The catalytic effect of pyridine on the decomposition of chloroformates is believed to result from its attack on the carbonyl carbon atom to form a pyridinium compound I in which the positive charge tends to labilize the ester bond toward displacement by a chloride ion.[3] In view of this hypothesis, it appeared likely that a similar labilizing of the alkyl–oxygen bond could be effected by an electron deficient compound, such as boron trifluoride, which would affix itself, not to the carbonyl carbon atom but to an adjacent center of electron density, either the oxygen atom as in II or the halogen atom as in III. Accordingly an investigation was carried out of the effect of boron trifluoride etherate on decomposition of the various alkyl chloro- and fluoroformates indicated in Table I.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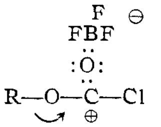
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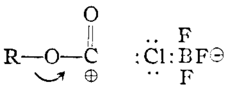
III

In the presence of small amounts of boron trifluoride etherate, the alkyl chloroformates investigated decompose smoothly at temperatures of 60 to 90° to produce the corresponding alkyl chlorides in high yield, except in the case of cyclopentyl chloroformate where the chloride is accompanied by a considerable amount of cyclopentene.

In the decomposition of alkyl fluoroformates the catalytic effect of boron trifluoride is especially striking. In the presence of small amounts of boron trifluoride etherate, carbon dioxide is eliminated from isopropyl and cyclohexyl fluoroformates at room temperature, whereas decomposition of cyclopentyl fluoroformate takes place even with the reaction mixture immersed in an ice-bath. The yield of ethyl and isopropyl fluorides was good; however, with the cyclic fluoroformates the alkyl fluoride was accompanied by some higher boiling, apparently dimeric, products.

TABLE I

BORON TRIFLUORIDE-CATALYZED DECOMPOSITION OF HALOFORMATES

R	Reactants Amount, g. ROCOX	BF_3-Et_2O	Reaction conditions Temp., °C.	Time, hr.	Yield, % CO_2	RX
Chloroformates						
Ethyl	10.0	14	90	46	64	62
Isopropyl	14.6	2	60	9	81	83
Cyclopentyl	14.9	3	75	3	86	31
Cyclohexyl	8.0	2	75	3	95	72
Fluoroformates						
Ethyl	6.2	2	50	4	84	86
Isopropyl	5.0	2	26	7	83	82
Cyclopentyl	10.0	2	0–5	4	85	39
Cyclohexyl	8.0	2	28	3	92	36

TABLE II

PHYSICAL CONSTANTS OF ALKYL HALIDES OBTAINED

	Mol. wt. Calcd.	Found	B.p., °C.	$n^{25}D$	Halogen, % Calcd.	Found
Chlorides						
Ethyl	64.5	64.2	11–12.5	....	...	...
Isopropyl	..	..	34–35	1.3740	45.15	45.19
Cyclopentyl	..	..	114–115.5	1.4439	33.90	33.83
Cyclohexyl	..	..	141–142	1.4528	29.89	29.96
Fluorides						
Ethyl	48.1	48.4	....	....	...	...
Isopropyl	62.1	62.2	....	....	...	...
Cyclopentyl	..	..	51–52 (300 mm.)	1.3919	21.56	21.59
Cyclohexyl	..	..	73–74 (300 mm.)	1.4145	18.62	18.65

From the foregoing results, it is evident that the Lewis acid, boron trifluoride, is an effective catalyst for haloformate decomposition. The stereochemical course of the reaction is being studied, and the findings will be reported in a subsequent paper.

Experimental

Materials.—Commercial ethyl chloroformate was redistilled before use. The other chloroformates were prepared by treating the alcohol with one equivalent each of phosgene and quinoline. Fluoroformates were prepared by the reaction of the chloroformates with anhydrous thallous fluoride as described previously.[4]

Decomposition Studies.—The decompositions of haloformates were carried out in a 50-ml. flask equipped with a Teflon-covered magnetic stirrer, a dropping funnel with ground glass attachment, an inlet for helium and a small

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[1] Presented before the Division of Organic Chemistry, 127th meeting of the American Chemical Society, Cincinnati, March, 1955.

[2] This investigation was supported in part by a grant from the American Cancer Society as recommended by the Committee on Growth of the National Research Council.

[3] G. W. Wheland, "Advanced Organic Chemistry," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1949, p. 287ff.

[4] S. Nakanishi, T. C. Myers and E. V. Jensen, THIS JOURNAL, **77**, 3099 (1955).

water-cooled reflux condenser, the outlet of which was connected to a graduated trap cooled in Dry Ice followed by a series of three tubes of soda lime and finally a glass tube dipping a few millimeters below the surface of a pool of mercury. The apparatus was dried carefully before use and swept out with a stream of dry helium (or other inert gas).

In experiments with ethyl and isopropyl haloformates, where the alkyl halides produced are volatile,[5] the boron trifluoride etherate was placed in the reaction flask, and a small amount of the haloformate was added. The stirred mixture was warmed if necessary until evolution of carbon dioxide commenced and then maintained at that temperature while the remainder of the haloformate was added gradually over the course of a few hours. When gas evolution had ceased, the system was swept out briefly with helium, and the soda lime tubes were weighed to determine the amount of carbon dioxide produced. The alkyl halide collected in the cold trap was redistilled into another cold receiver and its identity checked by a determination of its molecular weight by the vapor density method. None of the volatile alkyl halides obtained contained olefin, inasmuch as they did not reduce potassium permanganate in acetone solution.[6]

In experiments with cyclopentyl and cyclohexyl haloformates, in which the halide produced remained in contact with the catalyst during the entire reaction, considerable amounts of higher boiling material were formed. The production of this apparently dimeric product could be minimized by adding to the reaction mixture a paraffin hydrocarbon, such as *n*-pentane or *n*-hexane, in which boron trifluoride etherate is insoluble. The haloformate, which is soluble in the boron trifluoride etherate, was added slowly to the stirred mixture of hydrocarbon and catalyst held at the desired temperature.[7] As the carbon dioxide was evolved, the resulting alkyl halide, which is less soluble in the boron trifluoride etherate than is the haloformate, entered the hydrocarbon layer and was removed from further contact with the catalyst. When the reaction was complete, the carbon dioxide absorption tubes were weighed, and the hydrocarbon layer containing the product was separated, washed with water, dried over sodium sulfate and distilled. The products obtained from cyclohexyl haloformates appeared to be olefin free, but with cyclopentyl haloformates some cyclopentene invariably was formed.

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(5) In the decomposition of isopropyl chloroformate the reflux condenser was not cooled so that the isopropyl chloride was carried over to the cold trap by the carbon dioxide.

(6) In testing with potassium permanganate it is necessary that all traces of boron trifluoride etherate be absent, since a mixture of this substance and acetone reduces permanganate.

(7) In the case of cyclopentyl fluoroformate, the reaction was initiated at room temperature, and the mixture was then cooled in an ice-bath whereupon smooth reaction continued.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Mechanisms of Elimination Reactions. XV. The Reaction of Phenyllithium with *cis*- and *trans*-β-Bromostyrene[1]

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RECEIVED MARCH 30, 1955

Both isomers of β-bromostyrene are converted by phenyllithium in ether to phenylacetylene, the *trans* isomer reacting about twice as rapidly as the *cis* isomer. Reaction-rate studies, with *n*-butyl ether as solvent, show that the reaction is first order in phenyllithium, rather than second order in phenyllithium, as has been claimed with chlorostyrene. Under these conditions, the *trans* isomer is about six times as reactive as the *cis* isomer. The results are rationalized in terms of an α-elimination mechanism. Decomposition of the sodium salt of *trans*-cinnamic acid dichloride in water has been shown to give a mixture of isomers of β-chlorostyrene, the *cis* isomer being formed in predominant amount.

It has been reported[2] that the rate of the reaction between β-chlorostyrene and phenyllithium (equation 1) in ether is first order in the halide and second

$$\mathrm{PhCH{=}CHX} + 2\mathrm{PhLi} \longrightarrow \mathrm{PhC{\equiv}CLi} + 2\mathrm{C_6H_6} + \mathrm{LiX} \quad (1)$$

order in phenyllithium. The order of the reaction was attributed to the dimeric nature of phenyllithium in ether solution,[3] and a mechanism was suggested involving simultaneous lithium–hydrogen exchange at both the α- and β-carbon atoms of β-chlorostyrene, followed by elimination of lithium chloride. The order of the reaction was derived from the observation that second-order rate constants drifted downward from 0.54 to 0.17 l./mole/min. at 0° over the range 14–84% reacted, whereas the same data calculated in a third-order equation (first order in styryl chloride and second order in phenyllithium) gave fairly reproducible rate constants. No other tests of order, such as variations of initial concentrations, appear to have been reported. These observations have been confirmed by Grummitt and Lucier.[4]

On the other hand, it had been shown[5] that the reactions of phenyllithium and of methyllithium with *n*- and *t*-butyl chlorides in *n*-butyl ether were first order in the halide and first order in the organolithium compound, regardless of whether substitution (coupling) or elimination occurred. In addition, the question of the *cis–trans* nature of the chlorostyrene used by Wittig and Harborth remained, no statement having been made regarding the stereochemical purity of the materials or the relative reactivities of each isomer.

The preparation of chlorostyrene followed that of Biltz[6] and involved the decomposition of sodium *erythro*-α,β-dichloro-β-phenylpropionate (salt of *trans*-cinnamic acid dichloride) in water, a medium in which the salt of the corresponding dibromo acid is known to lead to mixtures of β-bromostyrene[7-11] containing principally the *trans* isomer. We have now repeated the preparation of β-chlorostyrene by

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(1) Previous paper in series: E. Grunwald and S. J. Cristol, THIS JOURNAL, **77**, 2891 (1955).

(2) G. Wittig and G. Harborth, *Ber.*, **77B**, 315 (1944).

(3) G. Wittig, *Angew. Chem.*, **62**, 231 (1950).

(4) O. Grummitt and J. J. Lucier, Abstracts of Papers, the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952, p. 49K.

(5) S. J. Cristol, J. W. Ragsdale and J. S. Meek, THIS JOURNAL, **73**, 810 (1951).

(6) H. Biltz, *Ann.*, **296**, 263 (1897). See G. Wittig and H. Witt, *Ber.*, **74**, 1474 (1941).

(7) K. v. Auwers, *ibid.*, **45**, 2781 (1912).

(8) C. Dufraisse, *Compt. rend.*, **171**, 960 (1920); *Ann. chim.*, [9] **17**, 198 (1922).

(9) A. T. Dann, A. Howard and W. Davies, *J. Chem. Soc.*, 605 (1928).

(10) E. Grovenstein and D. E. Lee, THIS JOURNAL, **75**, 2639 (1953).

(11) S. J. Cristol and W. P. Norris, *ibid.*, **75**, 2645 (1953).