NOTES

Some Reactions of Methoxy- and Ethoxydichloromethanesulfenyl Chlorides[1-3]

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Douglass and Osborne[4] have reported the formation of methoxydichloromethanesulfenyl chloride, CH_3OCCl_2SCl (I), when methyl methylxanthate or bis-(methoxythiocarbonyl) disulfide is chlorinated at the temperature of solid carbon dioxide.

$$CH_3OCSSCH_3 + 3Cl_2 \longrightarrow CH_3OCCl_2SCl\ (I) + CH_3SCl_3$$

In attempting to prepare derivatives of I it was observed that the reactions of this compound are not primarily those of a simple sulfenyl chloride, although the sulfenyl chloride relationship helps to explain some of the reactions which occur. Reduction of I with potassium iodide results in the formation of bis-(methoxythiocarbonyl)-disulfide, $(CH_3OCO)_2S_2$. Hydrolysis in aqueous sodium bicarbonate solution also yields the same disulfide, probably as a result of the combined hydrolysis of the chlorine atoms and subsequent disproportionation of the hypothetical methoxycarbonylsulfenic acid, $CH_3OCOSOH$, thus formed. The finding of sulfate ion in the reaction mixture supports this view although the failure to isolate any other products makes it impossible to designate the exact course of the reaction.

Anhydrous chlorine cleaves the molecule of I between the carbon and sulfur atoms with the formation of methyl trichloromethyl ether, a previously unreported compound.[5]

Aniline reacts vigorously with I forming diphenylurea, methyl chloride and sulfur. Ethyl alcohol also eliminates sulfur from I and forms ethyl carbonate and methyl chloride. The tendency for I to lose sulfur in these reactions resembles, in some respects, a similar characteristic of trichloromethanesulfenyl chloride.[6]

When methyl alcohol is added to ethoxydichloromethanesulfenyl chloride, $C_2H_5OCCl_2SCl$ (II), methyl chloride and ethyl methyl carbonate are formed. *n*-Butyl alcohol reacts with II to form butyl carbonate and ethyl chloride.

Experimental

Reaction of I with Potassium Iodide.—To 3.89 g. of potassium iodide dissolved in 200 ml. of water was added dropwise and with stirring 5 g. of I. Iodine was liberated immediately and the reaction appeared to be complete in 5 min. Saturated sodium thiosulfate solution was added to the reaction mixture until the iodine color disappeared. The oily product of the reaction was extracted with ether, the solution dried and the ether evaporated. The residual oil then was dissolved in condensed butane and the solution chilled to the temperature of solid carbon dioxide. A white crystalline solid melting at 36° separated. The yield was 1.6 g. or 64%.

Anal. Calcd. for $C_4H_6O_4S_2$: C, 26.36; H, 3.32; S, 35.19; mol. wt., 182.2. Found: C, 26.51; H, 3.57; S, 35.47; mol. wt., 184.

Hydrolysis of (I).—To 45 g. of I in 100 ml. of water was added solid sodium bicarbonate as long as there was evidence of reaction. After standing one hour, the reaction mixture was extracted with ether and the extract distilled. A fraction consisting of 11.7 g. of colorless oil, b.p. 113° (11 mm.), was obtained which began slowly to crystallize within a few hours. After standing two weeks the crystals were separated from the residual oil and melted at 36°. The melting point was unchanged on mixing with pure bis-(methoxycarbonyl) disulfide. The experiment was repeated and the aqueous solution from the reaction mixture was tested with barium chloride solution. A positive test for sulfate ion was obtained.

Bis-(methoxycarbonyl) disulfide also was obtained by the action of water on an acetone solution of I. In this case the yield was low and some high-boiling residue was obtained.

Reaction of I with Chlorine.—When 50 g. of I in 100 ml. of methylene chloride was treated for two hours at 0° with excess chlorine and subsequently fractionated, 27 g. (71%) of a colorless liquid was obtained. This product, believed to be methyl trichloromethyl ether, CH_3OCCl_3, had b.p. 109–110°, n^{20}_D 1.4536, d^{20}_4 1.4391.

Anal. Calcd. for $C_2H_3OCl_3$: Cl, 71.19; mol. wt., 149.4. Found: Cl, 71.27; mol. wt., 151.

Reaction of I with Aniline.—Aniline (232 g.) was added slowly to a solution of 91 g. of I in benzene. The mixture was stirred strongly and cooled in an ice-bath during the addition. When all the aniline had been added, the mixture was refluxed for two hours and the volatile products which did not condense in a water-cooled condenser were collected in a trap cooled by solid carbon dioxide. The solid products of the reaction were collected and washed with dilute hydrochloric acid to remove aniline hydrochloride. The residue, after washing with a mixture of benzene and ether and recrystallizing twice from alcohol, melted at 239°. A mixed melting point with pure diphenylurea was also 239°.

The volatile product condensed in the cold trap was allowed to evaporate at room temperature and the vapor was bubbled successively through wash bottles containing potassium hydroxide solution, water and sulfuric acid. The purified gas boiled at −22° and had a mol. wt. of 51. It also formed a Grignard reagent which reacted with phenyl isocyanate to form acetanilide, identifying the low-boiling product as methyl chloride. The yield was 42%.

A yellow solid was obtained as an alcohol-insoluble residue after recrystallizing the diphenylurea. Upon recrystallization from carbon disulfide, the solid melted at 112–113°. A mixture of the solid with rhombic sulfur also melted at 112–113°.

Reaction of I with Ethanol.—When 92 g. of I was added slowly to 200 ml. of absolute alcohol an immediate reaction occurred, with formation of a finely divided yellowish precipitate. Heat was liberated and cooling with ice was necessary to maintain the temperature near 25°. After the addition of I was complete, the mixture was refluxed for two hours and all products not condensed by the water-cooled condenser were collected in a trap cooled by solid carbon dioxide.

The low boiling product from the cold trap was treated in the manner already described and proved to be methyl chloride; 21.9 g., 85% yield. The yellow precipitate was sulfur.

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(1) This work was supported by the Office of Naval Research under Contract Nonr 647(00) with the University of Maine.

(2) Presented at the 125th National Meeting of the American Chemical Society in Kansas City, Mo., March, 1954.

(3) Taken in part from the Master's Thesis of Frank Joseph Marascia.

(4) I. B. Douglass and C. E. Osborne, This Journal, **75**, 4582 (1953).

(5) Methyl trichloromethyl ether is mentioned as being formed by the chlorination of methyl ether, *C. A.*, **30**, 717 (1936), but examination of the original paper by H. S. Booth and P. E. Burchfield, This Journal, **57**, 2070 (1935), reveals that the authors made no claim as to the position of the chlorine atoms. The reported boiling point establishes that the compound was not methyl trichloromethyl ether.

(6) J. M. Connolly and G. M. Dyson, *J. Chem. Soc.*, 679 (1935); 827 (1937).

The main reaction mixture, after removal of precipitated sulfur, was washed with sodium bicarbonate solution and extracted with ether. Fractionation of the ether solution gave 56 g. of colorless liquid, with b.p. 126°, n^{20}_{D} 1.3852, d^{20}_{4} 0.978 and a molecular weight of 116. Ethyl carbonate is reported[7] to have b.p. 125.8°, n^{20}_{D} 1.3852, and d^{27}_{4} 0.9752 and has a calculated molecular weight of 118.13. The yield of ethyl carbonate was 93%.

Reaction of Ethoxydichloromethanesulfenyl Chloride with Alcohols.—Ethoxydichloromethanesulfenyl chloride, $\mathrm{C_2H_5OCCl_2SCl}$ (II), was treated with methanol in the manner described above. From the reaction mixture, a small yield of colorless liquid with b.p. 105–106°, n^{20}_{D} 1.3790, d^{27}_{4} 1.003 and molecular weight of 104 was isolated. An authentic sample of ethyl methyl carbonate was prepared from methanol and ethyl chlorocarbonate, using pyridine to accept the hydrogen chloride liberated, and the carefully purified product had b.p. 107° (760 mm.), d^{25}_{4} 1.0068, d^{20}_{4} 1.0132, d^{0}_{4} 1.0363, n^{25}_{D} 1.3762 and n^{20}_{D} 1.3780. The calculated molecular weight of ethyl methyl carbonate is 104.1. The yield of ethyl methyl carbonate, based on the quantity of II taken, was less than 10%.

The low-boiling product of the reaction had a boiling point below −20° and a molecular weight of 51.0 indicating that it was methyl chloride rather than the corresponding ethyl compound; the yield of methyl chloride was 72%.

Again following the same procedures, II was treated with *n*-butyl alcohol. From the main reaction mixture a liquid was isolated with b.p. 59° (4 mm.), n^{20}_{D} 1.4116, d^{20}_{4} 0.9237 and molecular weight of 174.5. Butyl carbonate is reported[7] to have b.p. 207.5° (740 mm.), n^{20}_{D} 1.4117, d^{20}_{4} 0.9238 and has a calculated molecular weight of 174.24.

The more volatile product of the reaction had a b.p. of 11.3° and a molecular weight of 64.6. Ethyl chloride is reported to have b.p. 13° and has a calculated molecular weight of 64.52.

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[7] P. N. Kogerman and J. Kranig, *Chem. Abs.*, **21**, 1729 (1927).

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t-Alkyl Borates

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Considerable confusion exists concerning *t*-alkyl borates even though the picture on other borate esters is quite clear. The latter are prepared by reaction of hydroxyl compounds with boric oxide or with lower alkyl borates.[1–5]

$$6\mathrm{ROH} + \mathrm{B_2O_3} \rightleftarrows 2(\mathrm{RO})_3\mathrm{B} + 3\mathrm{H_2O}$$
$$3\mathrm{ROH} + (\mathrm{R'O})_3\mathrm{B} \rightleftarrows (\mathrm{RO})_3\mathrm{B} + 3\mathrm{R'OH}$$

The reactions are driven to completion by continuous removal of the water or lower alcohol formed. There is general agreement on the applicability of these methods to *n*-alkyl, *sec*-alkyl and aromatic borates, but the results with *t*-alkyl borates are conflicting.

Some investigators report that *t*-alkyl borates cannot be made by the alcoholysis of boric acid[4,5] or of *n*-alkyl borates.[5] Others report that they can be made by both methods but are too unstable to isolate.[3,6] Nevertheless distillable *t*-butyl borate has been obtained[7] by refluxing *t*-butyl alcohol, boric acid and benzene under an efficient fractional distillation column in order to continuously remove the water formed; other *t*-alkyl borates have been prepared similarly.[8]

We can confirm this recently reported synthesis because we had obtained the same *t*-butyl borate from the alternate synthesis involving alcoholysis of ethyl borate. *t*-Butyl borate was prepared readily in good yield by reaction of *t*-butyl alcohol, ethyl borate and a catalytic amount of sodium under conditions providing for continuous ethanol removal by efficient fractional distillation. Even though equimolar amounts of the starting materials were used, none of the intermediate ethyl *t*-butyl borates was found. The products were ethanol, unreacted ethyl borate and *t*-butyl borate, which was obtained in 45% yield. These results contrast markedly with those obtained upon alcoholysis of ethyl orthosilicate under analogous conditions; there *t*-butyltriethyl silicate was the major product.[9]

When the synthesis of *t*-butyl borate by the alcoholysis of boric acid appeared, we repeated it and obtained results comparable to those reported.[7] This method of preparation is more convenient than the ethyl borate alcoholysis. The latter is complicated by the proximity of the boiling points of ethyl and *t*-butyl alcohols and also by the availability of ethyl borate only as its ethanol azeotrope containing 30% borate.

t-Butyl borate appeared somewhat more hydrolytically stable than *n*- and *sec*-alkyl borates; however the compound hydrolyzed on exposure to atmospheric moisture. Moreover it was about 50% hydrolyzed on standing with distilled water for 24 hours, and it was 100% hydrolyzed on standing with 0.1 *N* HCl for 24 hours.[10] Alkyl borates are apparently more susceptible to hydrolysis than are the corresponding alkyl silicates.[11,12] This difference cannot be rationalized on the basis of electronegativity, inasmuch as boron is more electronegative than silicon. A more attractive explanation is found in the open sextet of the boron atom, which offers a coördination site for the unshared electron pair of the attacking water molecule.

Experimental

A reaction mixture consisting of 952 g. (6.5 moles) of ethyl borate, 518 g. (7.0 moles) of commercial *t*-butyl alcohol and

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[1] W. J. Bannister, U. S. Patent 1,668,797, May 8, 1928; *C. A.*, **22**, 2172 (1928). See also J. R. Johnson and S. W. Tompkins, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 106.

[2] A. Dupire, *Compt. rend.*, **202**, 2086 (1936).

[3] H. Wuyts and A. Duquesne, *Bull. soc. chim. Belg.*, **48**, 77 (1939); *C. A.*, **33**, 7274 (1939).

[4] A. Scattergood, W. H. Miller and J. Gammon, Jr., THIS JOURNAL, **67**, 2150 (1945).

[5] L. H. Thomas, *J. Chem. Soc.*, 820 (1946)

[6] J. R. Anderson, K. G. O'Brien and F. H. Reuter, *J. Applied Chem.*, **2**, 241 (1952).

[7] S. B. Lippincott, U. S. Patent 2,642,453 (June 16, 1953).

[8] There was an earlier report that *t*-butyl borate had been obtained as an ordinary distillable liquid by reaction of *t*-butyl alcohol with boron triacetate—L. Kahovec, *Z. physik. Chem.*, **43B**, 109 (1939). Other workers[6] could not repeat this synthesis and neither could we.

[9] P. D. George and J. R. Ladd, THIS JOURNAL, **75**, 987 (1953).

[10] These results confirm the report[7] that *t*-butyl orthoborate is hydrolyzed easily. In reference 4 it is stated that diisopropylcarbinyl borate defied all attempts at hydrolysis even in alkaline solution at 100°; nevertheless in the same article there is reported for this compound a quantitative boron analysis made by titrating the boric acid liberated upon hydrolysis with standard sodium hydroxide solution in the presence of mannitol.

[11] C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).

[12] R. Aelion, A. Loebel and F. Eirich, THIS JOURNAL, **72**, 5705 (1950).