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CLEAVAGE OF ETHERS BY BORON TRIIODIDE

Thomas P. Povlock
Department of Science
State University College
Oneonta, New York 13820

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Ethers have been cleaved at room temperature by boron trichloride (1), boron tribromide (2), and diborane with iodine (3). Boron triiodide was found by this investigator to cleave aliphatic, cyclic, and mixed aliphatic aromatic ethers under similar reaction conditions. The reaction of one mole of an aliphatic or cyclic ether with one mole of boron triiodide produced the alkoxydiiodoborane (I) and the alkyl iodide. The alkoxydiiodoborane was unstable and decomposed to boron triiodide, boric oxide, and the alkyl iodide.

$$ROR + BI_3 \longrightarrow \underset{(I)}{ROBI_2} + RI$$

$$3\ \underset{(I)}{ROBI_2} \longrightarrow BI_3 + B_2O_3 + 3\ RI$$

The instability of the alkoxydiiodoborane is consistent with the trend that alkoxydifluoroboranes and alkoxydichloroboranes are stable but alkoxydibromoboranes decompose to give boron tribromide, boric oxide, and the alkyl bromide (4).

Table I lists the results of the reaction of the ethers with boron triiodide in a 1:1 mole ratio at room temperature. The ethers were added to the boron triiodide (5) at 0°C and the reaction mixture allowed to warm to room temperature and held at this temperature for two hours. The alkyl iodide was then distilled from the mixture under reduced pressure. The aliphatic and cyclic ethers reacted with boron triiodide and the alkoxydiiodoborane decomposed as described. Phenetole formed iodoethane and phenoxydiiodoborane which did not form iodobenzene under the reaction conditions. Phenol was isolated after aqueous hydrolysis of the reaction mixture. Phenyl ether was unreactive toward boron triiodide at these conditions.

TABLE I

Reaction of Ethers with Boron Triiodide (1:1 Mole Ratio)

Ethers	Iodide	Yield	Observed Values		Literature Values (6)	
		%	B.P. °C(mm)	n_D^{20}	B.P. °C(mm)	n_D^{20}
Ethyl ether	iodoethane	91	71	1.515	72	1.514
n-Propyl ether	1-iodopropane	88	101	1.505	102	1.505
Isopropyl ether	2-iodopropane	83	88	1.501	89	1.502
Tetrahydrofuran	1,4-diiodobutane	79	102(5)	1.617	125(15)	1.615
Phenetole	iodoethane	84	71	1.515	72	1.514
	phenol[a]	75	85(20)	-----	90(25)	-----
Phenyl ether	-----	--	-----	-----	----	-----

[a] Isolated after aqueous hydrolysis and characterized as the 2,4,6-tribromophenol, m.p. 94-95°. Literature value: m.p. 96°.

The reaction of two moles of ether with one mole of boron triiodide produced the dialkoxyiodoborane (II), which decomposed on distillation to the trialkoxyborane (III), boric oxide, and the alkyl iodide.

$$2\ ROR + BI_3 \longrightarrow \underset{(II)}{(RO)_2BI} + 2\ RI$$

$$3\ \underset{(II)}{(RO)_2BI} \longrightarrow \underset{(III)}{(RO)_3B} + B_2O_3 + 3\ RI$$

Ethyl and n-propyl ethers were reacted with boron triiodide under these conditions. Ethyl ether produced iodoethane and triethoxyborane, 35% yield, b. p. 52° (8 mm), literature value (7) b. p. 50-52° (8 mm). n-Propyl ether produced 1-iodopropane and tri-n-propoxyborane, 28% yield, b. p. 63-64° (8 mm), literature value (8) b.p. 68-69° (12 mm).

The reaction of three or more moles of ether per mol of boron triiodide yielded only the dialkoxyiodoborane even under prolonged reaction times. This is consistent with the stability of dialkoxychloroboranes toward ethers (9). Under similar reaction conditions boron tribromide reacts with ethers to produce the trialkoxyborane (2).

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