constant between diacetone alcohol and mesityl oxide with changing hydronium ion concentration. The value was found to be 0.3 at 25°.

The heat of hydration of mesityl oxide is 7.5 ± 0.3 kcal. The heat of activation is 12.8 ± 0.15 kcal. for the hydration of mesityl oxide and 20.4 ± 0.3 kcal. for the dehydration of diacetone alcohol.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Cleavage of Ethers with Boron Bromide. I. Some Common Ethers

BY F. L. BENTON AND T. E. DILLON

Ether cleavage has been effected by the action of acid halides and anhydrides on ethers in the presence of metallic halides[1] as catalysts. Aluminum bromide[2] and boron chloride,[3] however, have been shown to cleave ethers even in the absence of acid halides and anhydrides. In each case it has been established[2,3,4] that the reaction takes place in the following steps: first the formation of a complex between the ether and metallic halide, and second the disproportionation of the complex resulting in cleavage of the ether.

The marked ability of boron halides to form complexes with ethers, and the ease with which etherates of boron chloride disproportionate led to the assumption that boron bromide might prove a very suitable reagent for cleaving ethers. In all cases boron bromide and the ether were allowed to react in a proportion of one mole of boron bromide to three moles of ether. Under those conditions our results indicate that the reaction proceeded according to the equation

$$\mathrm{R{-}O{-}R} + \mathrm{BBr_3} \longrightarrow \mathrm{(RO)_3B} + 3\mathrm{R{-}Br}$$

Hydrolysis of the orthoboric ester may be expressed by the equation

$$\mathrm{(RO)_3B} + 3\mathrm{H_2O} \longrightarrow 3\mathrm{R{-}OH} + \mathrm{H_3BO_3}$$

Ethers chosen for cleavage included simple alkyl ethers in which the alkyl groups were primary or secondary, and alkyl phenyl ethers in which the alkyl group was primary or secondary while in certain cases the phenyl group was substituted. Cleavage of simple alkyl ethers yielded an alcohol and alkyl bromide, while the alkyl phenyl ethers consistently yielded phenols corresponding to the phenyl group and alkyl bromides. The phenyl group, therefore, directs the course of the disproportionation of the boron bromide ether complex. The same effect was observed in the case of benzyl *n*-propyl ether, which yielded benzyl bromide and *n*-propyl alcohol instead of a mixture of products. The presence of substituent groups on the phenyl portion of the ether did not seem to affect the course of the cleavage, nor did any undesirable effects result when the reaction was carried out in an inert solvent. No disproportionation of the cleavage products or rearranged fragments was observed. That the method is applicable to the cleavage of sterically hindered methoxyls is indicated by the fact that mesityl methyl ether was cleaved without difficulty.

TABLE I

CLEAVAGE REACTIONS WITH BORON BROMIDE

	Products			
Ether	R-OH	Yield, %	R-Br	Yield, %
Diethyl	Et	61	Et	86
Diisopropyl	*i*-Pr	50	*i*-Pr	80
Di-*n*-butyl	*n*-Bu	62	*n*-Bu	77
*Iso*propyl phenyl	Ph	64	*i*-Pr	62
n-Butyl phenyl	Ph	75	*n*-Bu	76
2-Bromophenyl methyl	2-Br-Ph	81		
Mesityl methyl	Mesitol	87		
Benzyl-*n*-propyl	*n*-Pr	71	Ph-Me	75

Experimental

Reagents.—Boron bromide was prepared by the action of boron fluoride on anhydrous aluminum bromide according to the method of Gamble.[5] Diethyl, diisopropyl, di-*n*-butyl phenyl, and *o*-bromophenyl methyl ethers were products of the Eastman Kodak Co. Mesityl methyl ether was kindly furnished by Dr. G. F. Hennion, while isopropyl and benzyl *n*-propyl ethers were prepared by the Williamson synthesis.[6] With the exception of *o*-bromophenyl methyl ether all ethers were purified for use by

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[1] H. Meerwein and H. Maier-Hüser, *J. prakt. Chem.*, **134**, 51 (1932); H. W. Underwood, Jr., and G. C. Toone, THIS JOURNAL, **52**, 391 (1930); G. F. Hennion, H. D. Hinton and J. A. Nieuwland, *ibid.*, **55**, 2857 (1933); W. J. Monacelli and G. F. Hennion, *ibid.*, **63**, 1722 (1941); Ya. L. Gold'farb and L. M. Smorgonski, *J. Gen. Chem.* (U. S. S. R.), **8**, 156 (1938).

[2] P. Pfeiffer and E. Haack, *Ann.*, **460**, 156 (1928); P. Pfeiffer and W. Loewe, *J. prakt. Chem.*, **147**, 293 (1937).

[3] E. Wiberg and W. Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 22 (1931).

[4] E. Wiberg and W. Sütterlin, *ibid.*, **202**, 37 (1931).

[5] E. L. Gamble, P. Gilmont and F. J. Stiff, THIS JOURNAL, **62**, 1257 (1940).

[6] R. A. Smith, *ibid.*, **55**, 3718 (1933).

heating over sodium and subsequent distillation. The *o*-bromophenyl methyl ether was purified by distillation alone.

Apparatus.—The apparatus for cleavage consisted of a two-necked, 250-ml., round-bottom flask equipped with a reflux condenser and dropping funnel. Both the condenser and dropping funnel were protected from moisture by calcium chloride tubes.

General Cleavage Procedure.—A weighed quantity of ether[7] (usually 15 to 20 g.) was introduced into the reaction flask and cooled in an ice-bath. The calculated quantity of boron bromide was then slowly added through the dropping funnel. In all cases the boron bromide and ether were allowed to react in a ratio of one mole of boron bromide to three moles of ether. After addition of the boron bromide the reaction mixture was heated over a water-bath for forty minutes.

Recovery and Identification of Alkyl Bromides.—When the period of reflux was complete, the alkyl bromide was distilled directly from the reaction mixture, the distillate washed with a dilute solution of sodium bicarbonate, and dried over calcium chloride. A second distillation of the bromide usually yielded a constant boiling product. All alkyl bromides were identified by their boiling points and refractive indices.

Recovery and Identification of Alcohols.—After removal of the alkyl bromide by distillation the residue in the reaction flask was hydrolyzed with a minimum quantity of 10% aqueous sodium hydroxide and the resulting solution treated with an excess of anhydrous potassium carbonate to salt out the alcohol. The alcohol layer was then separated, dried over anhydrous magnesium sulfate, and distilled. All alcohols were identified by their boiling points, refractive indices, and the melting points of their 3,5-dinitrobenzoates.

Recovery and Identification of Phenols.—After removal of the alkyl bromide by distillation the residue remaining in the reaction flask was hydrolyzed with a minimum amount of 10% aqueous sodium hydroxide. The resulting solution was acidified with dilute hydrochloric acid, extracted with ether, and the ether layer separated and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the phenol further purified by distillation. Phenol was identified in all cases by its boiling point and the melting point of its derivative 2,4,6-tribromophenol.

Mesitol resulting from the cleavage of mesityl methyl ether was purified by sublimation. It was identified by its melting point and that of its derivative, 3,5-dinitromesitol.

o-Bromophenol was identified by its boiling point and the melting point of its derivative 2,4,6-tribromophenol. Its identity was further established by a Carius analysis for halogen.

Anal. Calcd. for C_6H_5OBr: Br, 46.19. Found: Br, 46.05.

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Summary

Several simple alkyl and mixed alkyl phenyl ethers were cleaved by boron bromide.

The products from cleavage of simple alkyl ethers were alcohols and alkyl bromides corresponding to the alkyl groups of the ethers. Cleavage of mixed alkyl phenyl ethers consistently yielded the phenol and an alkyl bromide.

The results indicate that no undesirable mixtures of products occur in the course of the cleavage and the boron bromide is a suitable reagent for cleaving the types of ethers investigated.

Further investigation of the action of boron bromide on ethers is in progress.

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[7] When 25 g. of low boiling petroleum ether was used as a reaction medium in the cleavage of di-*n*-butyl ether no undesirable effects were observed.