

The Cleavage of Ethers, and the Dehydration of Alcohols, by Boron Trifluoride

By E. F. MOONEY and M. A. QASEEM

(The Chemistry Department, The University, Birmingham)

WHILE it is generally recognized that boron trichloride complexes of ethers are unstable and readily disproportionate (Scheme 1) to give the alkyl chloride and the alkylchloroborinate,¹ the corresponding complexes with boron trifluoride were thought to be stable. The stability of the latter complexes has been attributed to the low polarisability of the B-F bond arising from the extensive

$p_{\pi}-p_{\pi}$ bonding between the fluorine and boron atoms; this similarity accounts for the poor acceptor power of boron trifluoride.

In our study of donor properties of Lewis bases,² we have reinvestigated the complexes of ethers with boron trifluoride. However, in a number of cases, we observed cleavage of the ethers, even at -80° , and only the cleavage products could be isolated.

TABLE.

Products obtained by the reaction of boron trifluoride with some ethers and alcohols at -80°

									Products*
n-Propyl isopropyl ether	n-PrOH, BF ₃ (90.9) + polypropene
Di-isopropyl ether†	H ₂ O, BF ₃ (94.7) + polypropene
s-Butyl ethyl ether	EtOH, BF ₃ (97.9) + polybutene
t-Butyl ethyl ether	EtOH, BF ₃ (93.0) + polybutene
Isopropyl alcohol	H ₂ O, BF ₃ (93.7) + polypropene
t-Butyl alcohol	H ₂ O, BF ₃ (94.1) + polybutene

* The values in parenthesis are the % yields based upon Scheme 2. The identities of the isolated boron trifluoride adducts were confirmed by comparison of the ¹H, ¹⁹F, and ¹¹B resonance spectra (recorded on Perkin-Elmer R. 10 spectrometers at 60.0, 56.4, and 12.83 Mc./sec., respectively) with the authentic compounds prepared by standard procedures. The polyolefins were identified from the i.r. spectra.

† See text.

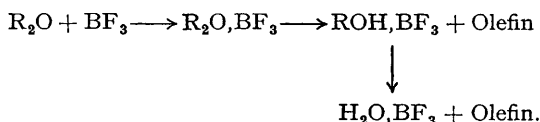


SCHEME 1

Since the ether-boron trifluoride complexes were first described³ only one example of the decomposition of the complex has been reported. It was recorded⁴ that di-isopropyl ether-boron trifluoride decomposed on heating at 50°. It was assumed, by analogy with the boron trichloride system, that the products were alkyl fluoride and alkyl difluoroborate; there was, however, no evidence to substantiate this.

In the present investigation it has been found that isopropyl, s-butyl, and t-butyl ethers afforded the alcohol-boron trifluoride complex and the polyolefin (Table). However, in the case of di-isopropyl ether, the solid boron trifluoride complex was isolated but this rapidly decomposed, at room

temperature, to afford not the alcohol-boron trifluoride but the water-boron trifluoride complex. It is suggested that the isopropyl alcohol-boron trifluoride complex is first formed (Scheme 2) and undergoes dehydration to afford water-boron trifluoride and polyolefin. This view is supported as it has now been observed that both isopropyl alcohol and t-butyl alcohol are dehydrated by boron trifluoride at -80° to give water-boron trifluoride and the corresponding polyolefin.



SCHEME 2

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³ V. Gasselien, *Bull. Soc. chim. France*, 1892, **7**, 17; *Ann. Chim. Phys.*, 1894, **3**, 5.

⁴ H. C. Brown and R. M. Adams, *J. Amer. Chem. Soc.*, 1942, **64**, 2557.