

Fig. 1

hydrochloric acid in 6 per cent alcohol) from a normal resin ('AG 50X2'). Similarly, acid dyes have been separated on a superficial anion-exchange resin. For the convenient separation of colourless substances a continuous method of detection would be required. Ultra-violet absorption of the effluent might be measured in many cases, or the type of detector described by Stouffer *et al.*⁷ might be suitable if interference from the eluant could be avoided. It is possible to increase the capacity of the beads and use correspondingly larger quantities of the mixture to suit the sensitivity of the detector.

J. R. PARRISH

National Chemical Research Laboratory,
South African Council for Scientific
and Industrial Research,
Pretoria.

¹ Karr, C., Childers, E. E., Warner, W. C., and Estep, P. E., *Anal. Chem.*, **36**, 2105 (1964).

² Harlow, G. A., and Morman, D. H., *Anal. Chem.*, **36**, 2485 (1964).

³ Jentsch, D., Oesterhelt, G., Rödel, E., and Zimmermann, H. G., *Z. anal. Chem.*, **205**, 237 (1964).

⁴ Glueckauf, E., and Coates, J. I., *J. Chem. Soc.*, 1315 (1947).

⁵ Strelow, F. W. E., *Anal. Chem.*, **33**, 994 (1961); **32**, 1185 (1960).

⁶ Samuelson, O., *Ion Exchange Separations in Analytical Chemistry* (John Wiley and Sons, London, 1963). Ringbom, A., *Complexation in Analytical Chemistry* (Interscience, London, 1963).

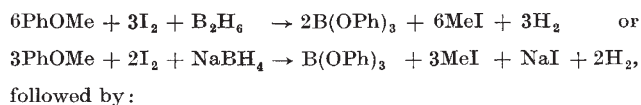
⁷ Stouffer, J. E., Kersten, T. E., and Kreuger, P. M., *Biochim. Biophys. Acta*, **93**, 191 (1964).

Low-temperature Cleavage of Ethers

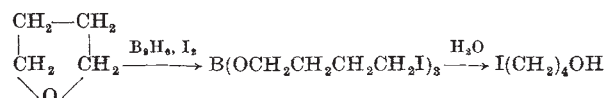
THE cleaving of an ether usually requires the use of a vigorous reagent such as an anhydrous mineral acid, an organic acid halide or anhydride, a Lewis acid, or an organometallic compound. Frequently heating for prolonged periods is necessary.

In examining the chemistry of boron, it has been found that, in conjunction with a halogen such as (by preference) iodine, boranes¹ and metal borohydrides² will destroy the

hydroxyl groups of alcohols, which are converted into organic halides. Although diborane on its own does not normally react with ethers near room temperature, except possibly to form a very loose addition compound, in the presence of free halogen a comparable reaction occurs with ethers¹. An oxygen-carbon link is ruptured, the oxygen attaching itself to the boron while the carbon links up with halogen. Thus anisole gives methyl iodide and triphenyl borate, from which phenol is immediately obtained on subsequent hydrolysis in the cold:



Attention is now directed to this reaction as a means of cleaving ethers under milder conditions than hitherto possible. By it, a rapid, smooth and complete cleavage can be effected, usually at room temperature or even below. The ether must be dry. The relative amount of diborane required is small, since one molecule cleaves six molecules of the ether. The reaction is moreover very widely applicable. The ether may be symmetric, unsymmetric, aliphatic, aromatic or cyclic. With cyclic ethers a boron ester is first produced which on subsequent hydrolysis yields the ω -iodo derivative of an alcohol as the ultimate product, for example:



In this way 4-iodobutan-1-ol, was prepared in more than 90 per cent yield from tetrahydrofuran. Its identity was confirmed by C, H and O analysis, both on the original product and on its *p*-nitrobenzoate derivative, which had an observed melting point of 104.5° C.

In general, the cleavage reaction is efficient and rapid, and proceeds quietly to completion within minutes at room temperature. Higher boranes are inclined to react more slowly than diborane. Metal borohydrides are comparable in reactivity to diborane, although sodium borohydride is less reactive than the lithium salt. Bromine and interhalogen compounds such as iodine chloride react more vigorously than iodine, but are in general less convenient. Large excesses of reagents are unnecessary and should be avoided.

The ready availability of metal borohydrides and hence diborane implies that this method could become a useful tool in degradative organic chemistry.

L. H. LONG

G. F. FREEGUARD*

Department of Chemistry,
University of Exeter.

* Present address: Department of Chemical Engineering, University of Nottingham.

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Unusual Role of Dimers in Thermal Polymerization of Chloroprene

THE dimerization products of chloroprene have been shown to consist principally of two substituted cyclohexenes and an eight-membered cyclic diene¹. Carothers *et al.*² have noted the presence of a distinct oligomeric fraction in the polymerization products of chloroprene, and more recently Klebanskii *et al.*³ have shown that this fraction contains both six- and eight-membered cyclic dimers. In previous kinetic studies of the thermal poly-