# XLIX.—*A Study of the Aliphatic Ethers.*

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MANY aromatic and tertiary aliphatic ethers are attacked by sodium–potassium alloy at the ordinary temperature, the course of

$$ROR' + 2K = ROK + R'K \text{ or } RK + R'OK.$$

the reaction depending on the nature of the radicals R and R'. The alcohol formed in each case was identified, and information was thus obtained concerning the relative strengths of the bonds between the radicals and the oxygen atom of the ether (Ziegler and Thielmann, *Ber.*, 1923, **56**, 1740; Schorigin, *ibid.*, p. 176).

The lower members of the saturated aliphatic ethers are not attacked by the alkali metals singly at the ordinary temperature, and it has now been found that even the liquid alloy has no action on them under pressure at higher temperatures. It thus appears that in ethers the bonds between the simple alkyl radicals and the oxygen atom are stronger than the corresponding bonds holding heavier radicals containing more highly branched chains.

## EXPERIMENTAL.

Ethers were prepared containing the radicals *n*-propyl and *iso*-butyl, *n*-butyl, *iso*propyl, ethyl, or methyl; *n*-butyl and *iso*butyl, *iso*propyl, ethyl or methyl; *iso*propyl and ethyl or methyl; and *iso*butyl and ethyl or methyl. As the method of Senderens (*Compt. rend.*, 1924, **179**, 1015) gave in each case a mixture of three ethers, which could not be separated, the mixed ethers were prepared by the method described below, which, however, failed to produce *iso*propyl *iso*butyl ether. The *iso*-alcohol was always used with the *n*-iodide, since *iso*-iodides readily decompose in these reactions.

n-*Propyl* iso*Butyl Ether*.—To a solution of sodium (12·5 g.) in *iso*butyl alcohol (137 g.) at 10°, *n*-propyl iodide (85 g.) was added in small portions during 1 hour with occasional shaking. After 12 hours, the liquid was heated at 100° for an hour, cooled, filtered from sodium iodide, distilled, and dissolved in an equal volume of dilute sulphuric acid (1 : 6). Any alkyl iodide separating was removed and water was added until no more ether separated. [This method of separation was used for all the ethers, which are insoluble in sulphuric acid of this dilution (see Senderens, *loc. cit.*), but dissolve in it in the presence of a large quantity of the alcohol and are precipitated on addition of water.] The ether was washed with half its volume of water, dried, kept for 24 hours over sodium–potassium alloy, and distilled, the fraction, b. p. 106°/720 mm., being collected

(yield, 67·2%). Sodium or potassium alone is not a trustworthy agent for removing the last traces of alcohol and alkyl iodide unless the ether is kept over it for several weeks; the alloy, however, completely removes them in 24 hours (Found: C, 71·9; H, 13·9; *M*, from vapour density, 115. $C_7H_{16}O$ requires C, 72·4; H, 13·8%; *M*, 116). n-*Propyl* iso*butyl ether* has $d^{15°}$ 0·7549, and $n_{5461}^{24·9°}$ 1·3852. (Through the kind offices of Prof. Lapworth the refractive indices of this and the following ether were taken in the Manchester University Chemical Laboratories by Dr. F. Fairbrother, to whom I wish to express my gratitude.) When boiled with concentrated hydriodic acid it yields *n*-propyl iodide, b. p. 99—100°/748 mm., and *iso*butyl iodide, b. p. 117—118°/765 mm., in small quantity.

iso*Propyl* n-*Butyl Ether*.—In a similar way, from 12·5 g. of sodium in 150 g. of *iso*propyl alcohol and the equivalent amount of *n*-butyl iodide, a product was obtained, most of which boiled below 112° but about one-sixth above this temperature. The fraction collected (yield, 72·4%) had b. p. 108°/738 mm., $d^{15°}$ 0·7594, and $n_{5461}^{24·9°}$ 1·3889 (Found: C, 71·9; H, 14·1; *M*, from vapour density, 118. $C_7H_{16}O$ requires C, 72·4; H, 13·8%; *M*, 116). Boiled with concentrated hydriodic acid, it gave *n*-butyl iodide, b. p. 130°/756 mm., and a very small quantity of *iso*propyl iodide, b. p. 83—86°/756 mm.

*Behaviour of the Ethers with Sodium–Potassium Alloy*.—Each of the above thirteen ethers (3 g.) was heated with 12—15 g. of the liquid alloy, in a sealed tube filled with nitrogen, at 190—200° for 24—100 hours; at higher temperatures charring occurred. An extremely small quantity of solid was formed in four cases. The ethereal liquid was decanted from the alloy, shaken with dilute acetic acid, and extracted three times with 25 c.c. of water to dissolve any alcohol present. The aqueous solution, after being acidified, responded to none of the usual tests for alcohols or their esters, this indicating that the ethers had not reacted with the alloy in the manner described by Ziegler and Thielmann.

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