The Intermolecular Dehydration Reaction of Benzhydrols in Dimethyl Sulfoxide

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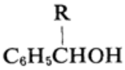
(Received February 29, 1964)

It has been shown[1] that the treatment of α-(bromomesityl)-benzyl alcohol (Ib) with polyphosphoric acid gives α-(bromomesityl)-benzyl ether (IIb). This mild reaction, which takes place when the mixture is warmed on a water bath for 15 minutes, constitutes the first example of the intermolecular dehydration of alcohol by means of polyphosphoric acid.



$C_6H_5\overset{\overset{R}{|}}{C}HOH$

I

$C_6H_5\overset{\overset{R}{|}}{C}HO\overset{\overset{R}{|}}{C}HC_6H_5$

II

a, R=phenyl
b, R=bromomesityl

The current interest in dimethyl sulfoxide as an efficient dehydrating agent, which gives olefins from aliphatic tertiary alcohols or secondary and tertiary benzylic alcohols[2] and substituted tetrahydrofurans from 1, 4-glycols,[3] has lead the present authors to reinvestigate the ether formation reaction of compound Ib in dimethyl sulfoxide.[4] The same reaction was also applied to benzhydrol (Ia) and 9-hydroxyfluorene.

Benzhydrol (0.010 mol.) was heated in dimethyl sulfoxide[5] (0.20 mol.) at 165~170°C for 8 hours under an atmosphere of nitrogen. The dilution of the reaction mixture with water, followed by the filtration and recrystallization of the crystalline product, afforded a 87.5% yield of bis(diphenylmethyl) ether (IIa) (m. p. 108~109°C; ν_{max}^{KBr} 1050, 737 and 698 cm^{-1}). The shorter reaction period employed apparently lowered the yield to 62.5% (4 hr.), whereas the longer heating did not affect the yield since 80% of IIa was obtained after 24 hr. α-(Bromomesityl)-benzyl alcohol (Ib) in the form of colorless prisms (m. p. 65~67°C) (Found: C, 62.77; H, 5.51. Calcd. for $C_{16}H_{17}OBr$: C, 62.96; H, 5.61%) was obtained in a 95% yield by the reduction of benzoylbromomesitylene[6] with a lithium aluminum hydride slurry in ether. It formed an acetate as colorless prisms (m. p. 99~100°C) (Found: C, 62.07; H, 5.21. Calcd. for $C_{18}H_{19}O_2Br$: C, 62.26; H, 5.51%). The treatment of Ib in dimethyl sulfoxide at 165~170°C for 16 hours, followed by the isolation procedure

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[1] M. Ōki and T. Sato, unpublished work, done in connection with their study of the sterically-hindered polyphenylethylenes. Cf. M. Ōki, This Bulletin, **26**, 161 (1953).

[2] V. J. Traynelis, W. L. Hergenrother, J. R. Livingston and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

[3] B. T. Gillis and P. E. Beck, ibid., **28**, 1388 (1963).

[4] After the completion of the present study, two reports along this line appeared: V. J. Traynelis, W. L. Hergenrother, H. T. Hanson and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964); V. J. Traynelis and W. L. Hergenrother, *J. Am. Chem. Soc.*, **86**, 298 (1964).

[5] Dimethyl sulfoxide was dried over potassium hydroxide and fractionally distilled through a Vigreux column under a current of nitrogen; b. p. 84~84.5°C/18 mmHg, n_D^{20} 1.4791.

[6] J. F. Hyde and R. Adams, *J. Am. Chem. Soc.*, **50**, 2503 (1928).

described above, afforded 20% of the crude ether as colorless prisms (m. p. 156∼158°C), the same compound as the product of dehydration reaction by polyphosphoric acid.[1] By a combination of fractional crystallization and chromatography on alumina it gave α-(bromomesityl)-benzyl ether (IIb) (m. p. 176∼177°C) (Found: C, 64.51; H, 5.51. Calcd. for $C_{32}H_{32}OBr_2$: C, 64.86; H, 5.44%), together with a low melting compound (m. p. 152∼154°C), probably the structural isomer.

As a related compound, 9-hydroxyfluorene was heated in dimethyl sulfoxide for 24 hours at 165∼170°C. It, however, gave 9-fluorenone as a major product (56%), with only a 14% yield of 9-fluorenyl ether. Benzyl alcohol has also been found to give an oxidation product on prolonged heating (20 hr.) in dimethyl sulfoxide at the same temperature; benzaldehyde was obtained in a 15.7% yield, characterized as 2, 4-dinitrophenylhydrazone, about 60% of the starting alcohol being recovered by distillation.

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