View Article Online / Journal Homepage / Table of Contents for this issue

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CXCI.—*The Action of Ammonia on the Glycide Aryl Ethers. Part II. Phenoxypropanolamines.*

By DAVID RUNCIMAN BOYD.

IN a previous communication (Boyd and Knowlton, Trans., 1909, **95**, 1802) an account was given of the bases obtained by the action of ammonia on *o*-tolyl glycide ether. From analogy to other cases, it was considered probable that in this reaction the amino-group becomes attached to the α-carbon atom of the *o*-tolyl glycide ether, giving a primary base of the formula

$$C_7H_7\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2.$$

This view has now been confirmed by the preparation of the same base from γ-chloro-β-hydroxy-α-*o*-tolyloxypropane,

$$C_7H_7\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2Cl,$$

and ammonia.

The action of ammonia on phenyl glycide ether has also been studied, and bases similar in character to those resulting from *o*-tolyl glycide ether have been obtained.

This reaction has also been investigated recently by Fourneau, who states (*J. Pharm. Chim.*, 1910, [vii], **1**, 99) that phenyl glycide ether and γ-chloro-β-hydroxy-α-phenoxypropane react with ammonia to produce a secondary base only, and who appears to regard such behaviour as typical of the aromatic and higher fatty halogen-hydrins. It is obvious, however, that the relative quantities of primary, secondary, and tertiary bases obtained in such a reaction as that under consideration must depend very largely on the conditions of the experiment. If, for instance, the glycide ether is dissolved in a considerable volume of a strong solution of ammonia in 50 per cent. alcohol, the principal product is the primary base.

EXPERIMENTAL.

β-*Amino*-β′-*phenoxy*iso*propyl Alcohol*, $C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NH_2$.

The *hydrochloride* of this base was prepared by the method already described in connexion with the corresponding *o*-tolyloxy-compound (*loc. cit.*). In one experiment, using 38 grams of phenyl glycide ether, 200 c.c. of concentrated aqueous ammonia, and 180 c.c. of alcohol, and keeping the mixture for some days at the ordinary temperature, about 30 grams of the hydrochloride were obtained. The salt resembles the corresponding *o*-tolyloxy-com-

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pound in having no definite melting point. It softens at 136°, but is not completely melted until about 228°. It dissolves very easily in cold water.

The free base separated in rosettes of small needles on adding sodium hydroxide to a concentrated aqueous solution of the hydrochloride. After washing with water and drying in a desiccator over potassium hydroxide, it melted at 97—98°:

0·1727 gave 0·4092 CO_2 and 0·1204 H_2O. C = 64·62; H = 7·81.
0·1982 „ 14·2 c.c. N_2 (moist) at 12° and 761 mm. N = 8·52.
$C_9H_{13}O_2N$ requires C = 64·62; H = 7·85; N = 8·38 per cent.

The base is easily soluble in water, giving a solution with a strongly alkaline reaction; it is less soluble in water containing sodium hydroxide.

The *platinichloride* melts and decomposes at 201°:

0·3066 gave 0·0804 Pt. Pt = 26·22.
$(C_9H_{13}O_2N)_2,H_2PtCl_6$ requires Pt = 26·21 per cent.

The *benzoate* crystallises from alcohol in prisms, which soften at 140°, and melt at 143°:

0·2560 gave 10·9 c.c. N_2 (moist) at 17° and 747 mm. N = 4·82.
$C_9H_{13}O_2N,C_7H_6O_2$ requires N = 4·84 per cent.

β-Amino-β′-phenoxy*iso*propyl alcohol can also be prepared by treating γ-chloro-β-hydroxy-α-phenoxypropane with a solution of ammonia in 50 per cent. alcohol. The method of procedure is practically the same as when the glycide ether is employed, except that after the alcohol and ammonia have been expelled, it is necessary to add some dilute hydrochloric acid in order to precipitate the hydrochloride of the secondary base, which otherwise would remain to some extent in solution along with the salt of the primary amine.

Dihydroxydiphenoxydipropylamine, $[C_6H_5\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2]_2NH$.

A secondary base, melting at 97—98°, and giving a hydrochloride melting at 175°, has been described by Fourneau (*loc. cit.*) as the product obtained by heating γ-chloro-β-hydroxy-α-phenoxypropane with aqueous ammonia.

The crude product obtained from phenyl glycide ether and ammonia, which melted about 97°, was washed twice with ether, and then treated with hydrochloric acid. After several crystallisations from dilute alcohol, the hydrochloride softened at 169°, and melted at 171—172°. (Found, Cl = 9·89. Calc., Cl = 10·03 per cent.) The salt is moderately soluble in cold water, but only very sparingly so in water containing hydrochloric acid.

The free base was obtained by adding sodium hydroxide to a

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solution of the hydrochloride in boiling dilute alcohol. After two crystallisations from alcohol, it melted almost completely at 101—102°, but fusion was not quite complete until 104°. Since the nitrogen estimation gave a result in satisfactory agreement with the figure required for a secondary base, it seems possible that the want of sharpness in the melting point may be due to the presence of both of the two possible stereoisomerides. (Found, N=4·46. Calc., N=4·42 per cent.)

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