CCIII.—*The Action of Phosphoric Oxide on β-Anilinobutyracetal.*

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In previous communications (J., 1925, **127**, 1032; 1926, 955) a product was described which was obtained by the action of phosphoric oxide upon β-anilinobutyracetal and was at first believed to be 1 : 2-dihydroquinaldine. Later, however, it was shown that the base consisted largely of quinaldine, accompanied by some unidentified product.

On repeating the synthesis with larger amounts of substance it has been found that the crude condensation product on treatment with benzoyl chloride afforded benzanilide and a liquid residue consisting of practically pure quinaldine. The crude benzanilide melted at 161—163°, and after one recrystallisation at 167—168°. It is obvious, therefore, that no dihydro- or tetrahydro-quinaldine was present in the condensation product, otherwise it would have formed a corresponding benzoyl derivative which could have been readily identified.

The action of phosphoric oxide upon β-anilinobutyracetal yields, therefore, solely quinaldine accompanied by aniline formed as a by-product of hydrolysis.

Attempts were made to condense β-chlorobutyracetal with toluene-*p*-sulphonanilide in presence of sodium ethoxide or amyl-oxide in the hope of obtaining a more stable product; it was not, however, found possible to cause the substances to react.

EXPERIMENTAL.

β-*Anilinobutyracetal.*—The yield of this product is greatly improved by (1) continuous and vigorous stirring, (2) omission of all copper powder, (3) careful avoidance of all over-heating during the vacuum distillation of the residue, preferably indeed avoiding any distillation at all, as the anilinobutyracetal is unstable towards heat.

The best results obtained were these: β-Chlorobutyracetal (100 c.c.) was dissolved in dry amyl alcohol (200 c.c.) with the addition of well-dried potassium carbonate (100 g.) and sodium iodide (8 g.). After stirring for 20 minutes, aniline (52 c.c.) was added, and the mixture refluxed in an oil-bath for 22 hours with good stirring. After cooling, and filtration of the solid residue, the excess of amyl alcohol was removed under reduced pressure, and the residue fractionated at 25 mm., giving the following fractions: 100—120°, 15 c.c.; 120—160°, 28 c.c.; 160—190°, 50 c.c. (chiefly at 175—185°).

In another preparation the chief fraction measured 62 c.c.

Quinaldine.—62 C.c. of the crude β-anilinobutyracetal was added by degrees to pure dry benzene (200 c.c.) containing in suspension phosphoric oxide (60 g.). The mixture was left over-night at room temperature and was then heated under reflux on a water-bath for 9½ hours, cooled, and the benzene layer removed. After the addition of ice-water the residue was acidified with 10% hydrochloric acid (50 c.c.), and the residual benzene removed in a current of steam. The residue was made alkaline with sodium carbonate and again distilled in steam. The distillate was saturated with salt and extracted three times with a large amount of ether, which was then dried over sodium sulphate, the ether removed, and the residual pale yellow oil distilled at 17 mm. : to 120°, 3·8 c.c.; 120—145°, 6 c.c.; 145—165°, 10·5 c.c. (residue, 1—2 c.c. of yellow gum), the last fraction smelling strongly of quinaldine.

The three fractions were treated separately with a slight excess of benzoyl chloride in presence of aqueous sodium carbonate; a clean white crystalline benzoyl derivative separated in each case, melting at 161—163° in the crude state and at 167—168° after recrystallisation from methyl alcohol. It was identified by analysis and by mixed melting point as benzanilide.

The residual basic oils after removal of the benzanilide were combined, and distilled at atmospheric pressure, nearly all passing over at 240—250° and principally at 244—247°. The distillate was recognised by its odour and by the mixed melting point of the picrate as being pure quinaldine (m. p. of crude picrate 195—197°; after recrystallisation from alcohol, 196—197°; mixture, 196—198°).

No other bases than aniline or quinaldine could be detected except for the small amounts of high-boiling condensation products.

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