XXI.—*Condensation Products from Benzylamine and several Benzenoïd Aldehydes.*

By Arthur T. Mason, Ph.D., F.I.C., and Goodlatte R. Winder, Ph.D., F.I.C.

The products described below, and prepared from benzaldehyde, orthohydroxybenzaldehyde, parahydroxybenzaldehyde, and benzylamine, are similar in their properties and methods of formation to those obtained from the primary fatty and benzenoïd amines. They are well defined compounds, which are easily reconverted into their generators by mineral acids.

Benzylamine and Benzaldehyde. Benzylidenebenzylamine,

$$C_6H_5\cdot CH_2\cdot N{:}CH\cdot C_6H_5.$$

—Pure benzaldehyde, prepared from the bisulphite compound easily interacts with benzylamine in cold ethereal solution. When dissolved in ether in molecular proportion, the solution became warm and opalescent after a few moments, and the eliminated water gradually separated in the form of drops. The mixture was heated for a short time on the water bath to complete the action, and, after a while, the ethereal solution was decanted through a filter. The filtrate was then dried with calcium chloride, the ether distilled off, and the residual oil rectified under diminished pressure (10—20 mm.), when the greater part distilled at 200—202° (bath 235—240°) as a colourless liquid. A freshly distilled sample was submitted to analysis.

0·1248 gave 0·3938 CO_2 and 0·0762 H_2O. C = 86·05; H = 6·77.

$C_{14}H_{13}N$ requires C = 86·15; H = 6·66 per cent.

The product is insoluble in water, but miscible in all proportions with alcohol, ether, benzene, toluene, and light petroleum. On

warming with dilute mineral acids, a strong smell of benzaldehyde is noticed.

In the above account of the preparation of the compound, it was expressly stated that benzaldehyde from the bisulphite compound was used. When the commercial product was employed, a crystalline precipitate was formed on warming the ethereal solution; this was collected, and, after being washed with ether, in which it is but sparingly soluble in the cold, was obtained in beautiful, white, glistening plates. It was dried at 100° and analysed.

0·1240 gave 0·3368 CO_2 and 0·0760 H_2O. C = 74·07; H = 6·81.
0·1419 „ 0·3856 „ „ 0·0857 „ C = 74·11; H = 7·08.
0·1440 „ 9·1 c.c. moist nitrogen at 15° and 730 mm. N = 7·08.
$C_{24}H_{26}N_2O_3$ requires C = 78·85; H = 6·66; N = 7·17 per cent.

It is a very stable substance, boiling at a very high temperature, apparently without decomposition. It dissolves easily in dilute hydrochloric acid on warming, and is not reprecipitated on cooling.

Benzylamine and Orthohydroxybenzaldehyde. Orthohydroxybenzylidenebenzylamine, $C_6H_5{\cdot}CH_2{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$.—5 grams (1 mol.) of benzylamine and 6 grams (1 mol.) of the aldehyde were brought together in a flask. On the addition of the first few drops of amine, heat was developed, the mixture became yellow, and the water formed gradually collected into small drops. After warming on the water bath for a short time, the contents of the flask were extracted with ether, and the water removed by means of a separating funnel; the ethereal solution was then dried with calcium chloride, and the ether distilled off. The pale yellow oil which remained solidified to a crystalline mass on standing; this, when crystallised from a small quantity of ether, gave small, bright yellow crystals melting at 29°. They were dried in a vacuum over sulphuric acid and analysed.

0·1701 gave 0·496 CO_2 and 0·0938 H_2O. C = 79·52; H = 6·12.
0·1438 „ 8·9 c.c. moist nitrogen at 17·5° and 716 mm. N = 6·73.
$C_{14}H_{13}NO$ requires C = 79·62; H = 6·16; N = 6·63 per cent.

The substance is insoluble in water, but very easily soluble in ether, alcohol, benzene, and toluene in the cold, giving intense yellow solutions; in light petroleum, it is easily soluble with a pale yellow colour. On treatment with cold dilute hydrochloric acid, the compound becomes oily, and, after warming, smells strongly of orthohydroxybenzaldehyde.

Benzylamine and Parahydroxybenzaldehyde. Parahydroxybenzylidenebenzylamine, $C_6H_5{\cdot}CH_2{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$.—A mixture of 3 grams (1 mol.) of amine and 3·45 grams (1 mol.) of aldehyde was heated for half an hour on an asbestos plate; water was formed, and the product solidified to a pale yellow, crystalline mass; this was shaken

well with ether, and the white, crystalline residue dissolved in hot alcohol. On standing, semi-transparent prisms separated melting at 205—206°. They were dried at 100° and analysed.

0·1638 gave 0·4784 CO_2 and 0·0926 H_2O. C = 79·65; H = 6·28.
0·1408 „ 8·6 c.c. moist nitrogen at 18° and 715 mm. N = 6·63.
$C_{14}H_{13}NO$ requires C = 79·62; H = 6·16; N = 6·63 per cent.

The compound is easily soluble in hot alcohol, but only sparingly in cold; it is insoluble in water, ether, benzene, toluene, and light petroleum. Like the products already described, it is easily reconverted into its constituents by dilute mineral acids.

Zurich University.