XXV.—*An Isomeride of Amarine.*

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ACCORDING to Laurent (*Annalen*, 1844, **52**, 356), benzoylazotide, on distillation, yields a mixture of "amarone" and lophine, and we have shown (Trans., 1897, **71**, 528) that amarone is tetraphenylazine; a further examination of the products of distillation has shown that a third base, $C_{21}H_{18}N_2$, is also present; this melts at 198°, and when subjected to dry distillation yields lophine, $C_{21}H_{16}N_2$. Like amarine, with which it is isomeric, it forms salts with one equivalent of acid, and yields a mono-silver derivative, which, on heating, decomposes, with formation of lophine; the silver derivative combines directly with ethylic iodide, hence the base contains an imido-group.

The new base differs from amarine in that it has a much higher melting point; moreover, its chromate does not undergo oxidation when boiled with glacial acetic acid, whereas that of amarine chromate, under similar conditions, yields lophine.

Neither is this base identical with the iso-amarine (melting at 175°) described by Feist and Arnstein (*Ber.*, 1895, **28**, 3177), nor with the isomeride of amarine (melting at 259°) mentioned by O. Fischer (*Annalen*, 1888, **245**, 288) as having been prepared by Lorenz Kohler.

The isolation of the base and the preparation of some of its derivatives are described below.

Isolation of the New Base.

1. *From the Products of Distillation of Benzoylazotide.*—The higher distillation products of benzoylazotide, or preferably the residue which is left in the retort when that compound is heated to about 215°, were treated with excess of warm, dilute hydrochloric acid, which dissolved the base and some resinous matter, leaving the tetraphenylazine and lophine undissolved; the base was then precipitated with ammonia, and purified from resinous matter by suspending it in a large quantity of water, adding hydrochloric acid in quantity insufficient to dissolve the whole of the base, and heating the solution by passing in steam; the base was then reprecipitated by ammonia. By repeating this process several times, the resinous matter, which is insoluble in pure water, is gradually removed, as it remains adhering to the walls of the vessel.

2. *From Mother Liquors.*—The alcoholic mother liquors obtained in the preparation of benzoylazotide from benzaldehyde and ammonium cyanide (Trans., 1897 **71**, 529), especially when excess of the aldehyde

was employed, were also found to contain the new base; the volatile substances were removed from these liquors by heating with steam, and the dried and powdered residue was extracted with small quantities of alcohol and ether. A crystalline substance melting at 267° was left behind, which, on analysis, proved to be lophine, whilst the new base was extracted by dilute hydrochloric acid from the residue left on evaporating the alcoholic ethereal solution.

It was subsequently found that the most convenient method for extracting the base from the benzoylazotide mother liquors consisted in acidifying with hydrochloric acid, diluting, and distilling with steam; the hydrochloride of the base was thus obtained in solution, whilst the resin, benzoylazotide, and the hydrochloride of lophine remained undissolved. The last-named salt was isolated in octahedral crystals, in one experiment, by crystallisation from chloroform; but generally the residue was subjected to dry distillation at 200—215°, and the residue left in the distillation flask worked up in accordance with the method first given for the isolation of the base. Most of the base used for the experiments recorded in this paper was prepared by the method just described.

In all cases, the hydrochloride was precipitated by ammonia, and the base recrystallised from alcohol, when it was obtained in colourless needles which are soluble in benzene and chloroform, and melt at 198° without decomposing. The alcoholic solution does not become luminous in the dark after treatment with caustic potash (distinction from lophine).

0·1778 gave 0·5500 CO_2 and 0·0990 H_2O. C = 84·36; H = 6·13.
0·1885 „ 15·3 c.c. moist nitrogen at 10·5° and 760·1 mm. N = 9·70.
$C_{21}H_{18}N_2$ requires C = 84·56; H = 6·04; N = 9·40 per cent.

The Hydrochloride, $C_{21}H_{18}N_2,HCl + H_2O$.—A solution of the base in warm, dilute hydrochloric acid, decanted from the amorphous salt which separated on standing, was evaporated in a vacuum over sulphuric acid, when the crystalline salt slowly separated. It has an alkaline reaction, is exceedingly soluble in alcohol and chloroform, very slightly in ether or benzene, and insoluble in carbon bisulphide. It melts at 135—140° in a capillary tube, and, on cooling, solidifies to a transparent glass. The crystals were dried at 100° until their weight was constant.

0·209 gave 0·0854 AgCl. Cl = 10·05.
$C_{21}H_{18}N_2,HCl + H_2O$ requires Cl = 10·07.

The salt was not changed by heating with concentrated hydrochloric acid in a sealed tube for 6 hours at 100°.

Platinochloride, $(C_{21}H_{18}N_2)_2,H_2PtCl_6$.—This was prepared by pouring an aqueous solution of the hydrochloride into a solution of platinic chloride, the latter being in excess, and the precipitate crystallised from rectified spirit. The orange-coloured crystals thus obtained begin to lose weight on heating to 220—230°, and fuse with further decomposition at 230—240°. The platinochloride is sparingly soluble in hot water, and rather more soluble in boiling alcohol.

0·2246 gave 0·0434 Pt. Pt = 19·33.
0·3741 „ 0·0726 Pt. Pt = 19·40.
$(C_{21}H_{18}N_2)_2,H_2PtCl_6$ requires Pt = 19·30 per cent.

Nitrate, $C_{21}H_{18}N_2,HNO_3 + H_2O$.—The base was dissolved in dilute nitric acid on the water-bath, and the crystalline crust which formed on the bottom of the vessel, on standing, was redissolved in water; the white crystals which separated from the neutral solution thus obtained had an alkaline reaction, and after drying in a vacuum over sulphuric acid, melted in a capillary tube at about 165°.

0·2040 gave 0·4992 CO_2 and 0·1058 H_2O. C = 66·73; H = 5·76.
0·1807 „ 17·4 c.c. moist nitrogen at 15° and 755 mm. N = 11·2.
$C_{21}H_{18}N_2,HNO_3 + H_2O$ requires C = 66·46; H = 5·57; N = 11·08 per cent.

Chromate.—A solution of the hydrochloride, precipitated by potassium chromate, gave a yellow precipitate which separated from hot glacial acetic acid in well-defined, yellow crystals. The salt was not altered by heating it with glacial acetic acid for 3 hours at 150° in a sealed tube.

Silver Derivative, $C_{21}H_{17}N_2Ag$.—Freshly prepared silver oxide was dissolved in a dilute alcoholic solution of ammonia, and a solution of the base in rectified spirit poured in in a thin stream, agitating meanwhile. The almost white compound which at once separated was dried at 100°; after being well washed on the filter with alcohol, the light grey powder thus obtained consisted of exceedingly minute, transparent crystals melting and decomposing at 210°. It dissolves in minute quantity in boiling absolute alcohol, but is insoluble in ether, benzene, and light petroleum. When heated with ethylic iodide in a sealed tube at 100°, it dissolves, forming a clear solution.

0·1953 gave 0·4466 CO_2 and 0·0756 H_2O. C = 62·36; H = 4·30.
0·2503 „ 15 c.c. moist nitrogen at 21° and 764·3 mm. N = 6·83.
0·2041 „ 0·0540 Ag. Ag = 26·45.
$C_{21}H_{17}N_2Ag$ requires C = 62·22; H = 4·20; N = 6·91; Ag = 26·67 per cent.

Although the relative proportions of base and of ammoniacal silver solution were varied in different experiments, nothing but the mono-silver derivative could be obtained; when excess of silver was employed, the yield was practically quantitative.

Conversion of the Silver Derivative into Lophine.—On heating this silver compound to fusion, lophine was formed, but no hydrogen or other gas was evolved. Two grams were heated in a paraffin bath to 210° ; the transparent, yellow melt, which contained particles of silver in suspension, solidified to a hard mass on cooling ; the portion extracted by hot benzene, after being crystallised from alcohol, deposited fine needles sparingly soluble in alcohol, and melting at 267° without decomposition. The alcoholic solution, on adding caustic potash, became luminous in the dark when shaken with air. These properties indicate that the crystals consisted of lophine.

Destructive Distillation of the Base.

On heating the base under diminished pressure, decomposition occurred below 360°, ammonia being evolved and a small quantity of liquid distilling over, the last portions of which solidified on cooling ; the residue left in the distillation flask and the solid distillate were dissolved in boiling spirit, from which lophine crystallised out in fine needles ; the later crystallisations, which also contained lophine, were digested with warm dilute hydrochloric acid, which dissolved the unaltered base. On recrystallising the insoluble portion from alcohol, more lophine was obtained, and also a small quantity of a colourless substance which separated in thin plates and melted at about 120° ; as it volatilised below the melting point of lophine, it was easily separated from the latter by heating the mixed crystals in an air-bath. The crystals of lower melting and boiling point have not been further investigated.

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