LXII.—*On some Compounds of Phenols with Amido-bases.*

By GIBSON DYSON, Dalton Scholar of Owens College.

DALE and SCHORLEMMER, in their recent investigation on the action of aqueous and alcoholic ammonia upon aurin, discovered the remarkable fact that it is extremely difficult to separate the aurin from the amido-bases formed, by means of dilute acids. Hence they were led to conclude that the aurin combined with the amido-bases, and they were able to confirm this view by the preparation of pure rosaniline aurinate (*Chem. Soc. J.*, 1883, **1**, 185).

Aurin being a phenol and rosaniline an amido-base, it appeared probable that analogous compounds of the phenols with different amido-bases might be obtained. A mixture in molecular proportions of phenol and aniline was therefore heated to the boiling point for a considerable time, and then left to cool. After some time large thin plates crystallised out, and finally the whole solidified to a crystalline mass. This, on recrystallisation either from alcohol or from petroleum-naphtha, yielded beautiful glistening plates melting at $29\cdot5^{\circ}$ (*loc. cit.*). At the request of Professor Schorlemmer I undertook the further investigation of these bodies and other compounds of phenols with amido-bases. The following are the results I have so far obtained:—

I. *Aniline Phenate*, $C_6H_5NH_2.C_6H_5OH$.

Dale and Schorlemmer describe the preparation of this compound, which they obtained by heating together molecular proportions of aniline and phenol to the boiling point; but it is also formed in the cold on standing. The product was purified by recrystallisation, either from alcohol or from petroleum-naphtha, and is thus obtained in well-defined crystals, the best being deposited from the last-named solvent.

These crystals closely resemble pure naphthalene in appearance, and when pure melt at $30\cdot8^{\circ}$, and boil at 181° C. Dale and Schorlemmer

give the melting point 29.5° and the boiling point 184.5° , but their substance had been purified only by pressing.

Determination of the Aniline.—In order to determine the aniline in this compound directly, the following three methods were tried, but failed to give satisfactory results.

1. The aniline was precipitated as the double chloride of aniline and platinum by means of platinum tetrachloride. This method failed, in consequence of the reducing action of the phenol upon the double salt formed.

2. An excess of dilute hydrochloric acid was added to a weighed portion of the salt, and then the mixture was boiled until all the phenol had been expelled. The aniline hydrochloride left was next precipitated as the double salt by platinum tetrachloride, and the precipitate obtained was washed with a mixture of pure alcohol and ether. The results obtained, however, were considerably too low, this being probably due to the volatilisation of some of the aniline together with the phenol.

3. Varrentrapp and Will's method failed to give good results, since it was found impossible to prevent phenol or substances possessing a similar reducing action on the platinum double salt passing into the bulbs. The only method which promised to give accurate results was the determination of free nitrogen by Dumas' method, and subsequent experiments bearing out this promise, this method was adopted in the analysis of this compound, and also in similar determinations required in the course of the investigation.

The following analytical numbers were obtained :—

(a.) *Before recrystallisation, purified by Pressing only.*

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	1.01425 grams	61.0 c.c.	7.51
(2.)	1.2025 „	69.6 „	7.23
(3.)	0.9535 „	60.0 „	7.97

Mean of the three determinations = 7.57 per cent.

Calculated = 7.48 per cent.

(b.) *After repeated recrystallisation from Petroleum-naphtha
(boiling below 90°).*

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
	0.567 gram	34.4 c.c.	7.58

Found, 7.58 per cent. Calculated, 7.48 per cent.

The carbon and hydrogen, as obtained by combustion, were as follows:—

(1) substance, $0.213 - \text{CO}_2 : 0.601 - \text{H}_2\text{O} : 0.134$.

	Calculated	Found.
Carbon.....	77.0 per cent.	76.9 per cent.
Hydrogen	6.95 „	6.99 „

(2) substance, $0.21 - \text{CO}_2 : 0.5925 - \text{H}_2\text{O} : 0.1325$.

	Calculated.	Found.
Carbon.....	77.0 per cent.	76.9 per cent.
Hydrogen.....	6.95 „	7.01 „

II. *Toluidine Phenate*, $\text{C}_6\text{H}_4\text{CH}_3\text{NH}_2\cdot\text{C}_6\text{H}_5\text{OH}$.

This compound was obtained by fusing together molecular proportions of paratoluidine and phenol; on cooling the mixture solidified to a soft mass, which was freely soluble in hot light petroleum-naphtha (b. p. below 90°). This solution was left to cool, whereupon it deposited well-formed needle-shaped crystals of the pure phenate, melting at 31.1° , some of which were from 2 to 3 inches in length. The following analytical results were obtained:—

Nitrogen.

Weight of substance taken.	Vol. of nitrogen obtained reduced to 0°C . and 760 mm.	Percentage of nitrogen.
(1.) 0.530 gram.	29.5 c.c.	6.94
(2.) 0.5235 „	29.5 „	7.04

Calculated, 6.99 per cent. of nitrogen.

Found, 6.99 per cent., mean of two determinations.

Carbon and Hydrogen.

Substance, $0.247 - \text{CO}_2 : 0.704 - \text{H}_2\text{O} : 0.173$.

	Calculated.	Found.
Carbon.....	77.61 per cent.	77.69 per cent.
Hydrogen	7.46 „	7.76 „

III. *Naphthylamine Phenate*, $\text{C}_{10}\text{H}_7\text{NH}_2\cdot\text{C}_6\text{H}_5\text{OH}$.

This body was obtained in a manner similar to that employed in the preparation of the aniline and toluidine phenates. By recrystallisation from light petroleum-naphtha (boiling below 90°) it is with difficulty obtained in well-formed needle-shaped crystals, possessing the characteristic smell of naphthylamine, and melting at 30.1° .

Nitrogen.

Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
1.587 grams	76.3 c.c.	6
Calculated, 5.9 of nitrogen. Found, 6 per cent. of nitrogen.		

Carbon and Hydrogen.

Substance, 0.253—CO₂ : 0.7515—H₂O : 0.145.

	Calculated.	Found.
Carbon.....	81.01 per cent.	81.01 per cent.
Hydrogen.....	6.32 „	6.36 „

IV. *Aniline β-Naphthate*, C₆H₅NH₂.C₁₀H₇OH.

When pure β-naphthol and aniline are heated together in the proportions required by the above formula, a fibrous mass is obtained resembling crude naphthol in appearance. It is but slightly soluble in cold, but more freely so in hot petroleum-naphtha, from which it is deposited on cooling in the form of a crystalline powder, melting at 82.4°.

Nitrogen.

	Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.)	1.099 grams	51.9 c.c.	5.9
(2.)	0.9745 „	45.5 „	5.83

Calculated, 5.9. Mean of two results, 5.86.

Carbon and Hydrogen.

(1) substance, 0.2035—CO₂ : 0.605—H₂O : 0.118.

	Calculated.	Found.
Carbon.....	81.01 per cent.	81.08 per cent.
Hydrogen	6.32 „	6.44 „

(2) substance, 0.221—CO₂ : 0.65925—H₂O : 0.1275.

	Calculated.	Found.
Carbon.....	81.01 per cent.	81.3 per cent.
Hydrogen	6.32 „	6.47 „

V. *Toluidine Naphthate*, C₆H₄.CH₃.NH₂.C₁₀H₇OH.

This compound was obtained in exactly the same manner as the aniline naphthate, which it closely resembles in appearance.

It is a crystalline solid, melting at $80\cdot8^{\circ}$.

Nitrogen.

Weight of substance taken.	Vol. of nitrogen obtained reduced to 0° C. and 760 mm.	Percentage of nitrogen.
(1.) 1.175	51.4 c.c.	5.46
(2.) 0.9295	43.9 „	5.89

Calculated = $5\cdot57$ per cent.

Mean of two determinations = $5\cdot67$ per cent.

Carbon and Hydrogen.

Substance, 0.1975 = CO_2 : $0\cdot5885$. H_2O : $0\cdot121$.

	Calculated.	Found.
Carbon	81.27 per cent.	81.31 per cent.
Hydrogen	6.77 „	6.8 „

VI. *Rosaniline Phenate*, $\text{C}_{20}\text{H}_{19}\text{N}_3\cdot\text{C}_6\text{H}_5\text{OH}$.

If a mixture of rosaniline base and phenol, in the proportions required by the above formula, be dissolved in alcohol, and the solution allowed to evaporate slowly, a purple residue is obtained, exhibiting all the characteristic properties of a rosaniline salt.

I have not yet succeeded in obtaining this substance in the pure state, but an approximately pure compound may be obtained by employing the following method. A quantity of rosaniline is mixed with excess of phenol and heated. The product is dissolved in absolute alcohol, and the solution largely diluted with water, whereupon the rosaniline salt is partially precipitated, and completely so on standing, whilst the excess of phenol remains in solution. The precipitate is collected on a filter, redissolved in alcohol, and once more reprecipitated from this solution by excess of water, filtered off, and dried at a low temperature. The compound thus obtained is not chemically pure, as will be seen from the following analysis:—

Carbon and Hydrogen.

Substance, 0.16— CO_2 : $0\cdot46$ — H_2O : $0\cdot093$.

	Calculated.	Found.
Carbon	78.98 per cent.	78.4 per cent.
Hydrogen	6.32 „	6.26 „

The above discrepancies may be easily accounted for by the fact that the rosaniline base used in the experiments was not pure, as the commercial article contains in all probability an admixture of the para-compound.

When a solution of rosaniline phenate is treated with an alkali, a fine blue coloration is produced, which disappears on addition of an acid, but is restored on again making the solution alkaline. This remarkable reaction is probably due to the presence of some other compound in the rosaniline salt, and it will be interesting to ascertain whether this impurity would also be formed in the case of pure rosaniline being used in the preparation of the rosaniline phenate.

VII. *Xyloidine Naphthate.*

A mixture of isoxylidine and β -naphthol, in the proportions of their respective molecular weights, was heated until a uniform liquid was formed, which was then left to cool. The semi-solid magma thus obtained was exhausted with hot light petroleum, in which it is freely soluble, and the solution was left to crystallise. The analysis of the crystals obtained gave the following results:—

Carbon and Hydrogen.

Substance, $0.177 - \text{CO}_2 : 0.935 - \text{H}_2\text{O} : 0.0945$.

	Calculated.	Found.
Carbon.....	81.5 per cent.	82.42 per cent.
Hydrogen.....	7.169 „	5.9 „

From the above analysis it would appear that the treatment with the hot spirit had simply extracted the xyloidine from the substance, and in order to confirm this assumption, the substance was redissolved in hot petroleum-naphtha, and the crystals obtained on cooling were carefully dried and analysed.

Carbon and Hydrogen.

(1) substance, $0.1605 - \text{CO}_2 : 0.4885 - \text{H}_2\text{O} : 0.0795$.

	Calculated.	Found.
Carbon.....	81.5 per cent.	83.0 per cent.
Hydrogen	7.169 „	5.502 „

(2) substance, $0.238 - \text{CO}_2 : 0.725 - \text{H}_2\text{O} : 0.120$.

	Calculated.	Found.
Carbon.....	81.5 per cent.	83.06 per cent.
Hydrogen	7.169 „	5.58 „

Now as xyloidine contains 79.3 per cent. of carbon, and naphthol 83.3 per cent., we have $x + y = 100$.

$$79.3x + 83.3y = 83 \times 100$$

$$y = 92.5 \text{ per cent.} \quad y = \text{C}_{10}\text{H}_7\text{OH.}$$

Hence the substance was nearly pure naphthol.

I next tried to obtain the salt by heating β -naphthol with excess of isoxylidine, and leaving the mixture to cool and crystallise. The excess of xylidine was then removed by washing with cold light petroleum-naphtha, and the crystalline residue analysed.

Carbon and Hydrogen.

Substance, 0.2595 — CO_2 : 0.7787 — H_2O : 0.16.

	Calculated.	Found.
Carbon	81.5 per cent.	81.8 per cent.
Hydrogen	7.169 „	6.85 „

The above numbers again clearly show that the substance was either a mixture, or else a highly unstable compound.

VIII. *Rosaniline Aurinate*, $\text{C}_{20}\text{H}_{19}\text{N}_3\text{—C}_{19}\text{H}_{14}\text{O}_3$.

The preparation of this salt has already been referred to in the introduction to this paper. I have since succeeded in obtaining it in moderately large crystals possessing a fine beetle-green lustre. These crystals belong to the hexagonal system, and exhibit chiefly the form of a short prism and base ∞P . 0P .

IX. *Aniline Aurinate*, $\text{C}_6\text{H}_5\text{NH}_2\text{.C}_{19}\text{H}_{14}\text{O}_3$.

On dissolving molecular proportions of aniline and aurin in alcohol, and evaporating at a moderate temperature, a red crystalline residue is obtained, soluble in alcohol, imparting to it an orange colour.

It dyes silk in neutral solutions exactly the same shade as aurin. As the quantity of pure aurin at my disposal was very small, the further investigation of this compound had to be postponed.