FORSTER AND WITHERS:

XXXI.—Vaubel's Supposed Phenyldi-imine.

By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

WHILE investigating the reduction of diazoaminobenzene with zinc dust in alkali, Vaubel (*Ber.*, 1900, **33**, 1711) obtained a liquid boiling at 162—164°, appearing to have the composition $C_6H_6N_2$, and regarded by him as phenyldi-imine, C_6H_5 ·N:NH.

Our attention was attracted to this substance by two factors, namely, the improbability of its surviving the method of preparation, and the importance of studying such a type supposing it to be capable of existence. We accordingly attempted to prepare phenyldi-imine by Vaubel's process, which consists in slowly distilling the alcohol from a solution of diazoaminobenzene in alcoholic alkali to which zinc dust has been added, and then passing a current of steam through the residual liquid after acidification.

It is not clear from the meagre details furnished by Vaubel whether acidification was practised on the alkaline liquid alone or on the solid matter suspended in it; we therefore separated the solid in the earlier experiments, but finding that the liquid alone did not give oil when acidified and distilled in steam, we conclude that Vaubel allowed the solid to remain suspended in the alkaline liquid to which dilute sulphuric acid was then added. On following this course, we also obtained a yellow oil which, after being shaken with alkali to remove phenol, was divisible by distillation under 13 mm. pressure into two fractions, boiling at 67—70° and 74—75° respectively, the latter being pure aniline. The more volatile, pale yellow fraction, which should have been phenyldi-imine, was analysed several times because the empirical formula indicated, namely, $C_{18}H_{17}N_7$, was difficult to reconcile with any probable individual.

Qualitative examination of the substance, however, revealed the

properties of both aniline and phenylazoimide, and we believe, therefore, that the liquid obtained in the manner described is a constant boiling mixture of those two compounds in the proportion $2C_6H_5 \cdot N_3 + C_6H_5 \cdot NH_2$. This conclusion is confirmed by the fact that on distilling a mixture of phenylazoimide with excess of aniline under the above-mentioned pressure, the lower fraction was a liquid agreeing in every detail, qualitative and quantitative, with the supposed phenyldi-imine which we obtained from diazoaminobenzene.

The fact that Vaubel's product has the composition $C_6H_6N_2$ is explained by the circumstance that, having been distilled under atmospheric pressure, its composition would be different from that of a product fractionated under 13 mm., and it is significant that an equimolecular mixture, $C_6H_5\cdot N_3 + C_6H_5\cdot NH_2$, would have the same percentage composition as phenyldi-imine.

Certain points in Vaubel's description of phenyldi-imine are in agreement with our hypothesis that his material is a mixture of phenylazoimide and aniline. According to his statement, it does not form salts with dilute alkalis, it is dissolved only in part by hydrochloric acid, and with sulphuric acid yields "eine eigenthümliche, weissliche, klebrige Verbindung, die sich aber bald wieder in Oel und Säure scheidet," and which doubtless consists of aniline sulphate impregnated with phenylazoimide. Furthermore, the boiling point of phenyldi-imine under atmospheric pressure was stated to be 162-164°, and the only recorded boiling point of phenylazoimide at such a high pressure is 161-162°/754 mm. Moreover, the distillation of phenyldi-imine was accompanied by extensive decomposition and the production of a white solid, the composition of which was not determined; it is highly significant that when phenylazoimide is allowed to mix with aniline at 150°, a colourless, solid base, C₁₂H₁₂N₂, is produced, accompanied by liberation of nitrogen (Wolff, Annalen, 1912, 394, 59).

It remains to explain how this mixture is produced in the circumstances of Vaubel's experiment. Recalling the fact, already mentioned, that the solid was not removed from the alkaline liquid before acidification, it will be recognised that the supposed phenyldiimine arose from the action of dilute sulphuric acid on a mixture of zinc dust and diazoaminobenzene. Supposing the acid to resolve the latter into aniline and diazonium salt, a portion of which becomes reduced to phenylhydrazine, this base, in action with diazonium salt, would yield a further quantity of aniline accompanied by phenylazoimide. It might be supposed that on distillation in steam, phenylazoimide would pass over alone, but we find that a faintly acid solution of aniline sulphate will yield a considerable proportion of the base when a current of steam is passed continuously through the liquid. The variety of the changes involved in this explanation will readily account for the low yield recorded by Vaubel and confirmed by our own experiments.

EXPERIMENTAL.

Twenty-five grams of diazoaminobenzene, freshly prepared, were dissolved in 100 c.c. of alcohol, and heated with 50 c.c. of 20 per cent. aqueous sodium hydroxide and 20 grams of zinc dust during two hours, in the course of which time there distilled over 125 c.c. of liquid containing aniline and phenylhydrazine. The pale yellow oil remaining in the flask became solid on cooling, and consisted of pure diazoaminobenzene, as stated by Vaubel; this was filtered, and the alkaline filtrate, after extraction with ether, did not give an oil when acidified and distilled in steam. In subsequent experiments, therefore, the zinc and diazoaminobenzene were not removed before sulphuric acid was added, and in these circumstances a pale yellow oil slowly distilled in the steam.

The product accumulated from 225 grams of diazoaminobenzene was dissolved in ether and extracted with sodium hydroxide, from which phenol alone was recovered; on evaporating the ether after drying with sodium sulphate about 15 grams of oil remained, divided by fractional distillation under 13 mm. pressure into 4 grams boiling at $67-70^{\circ}$ and 10 grams boiling at $74-75^{\circ}$, the latter consisting of pure aniline. The more volatile portion, which had a distinct odour of phenylazoimide, was redistilled, boiling at $64--65^{\circ}/13$ mm.:

0.1385 gave 0.3300 CO₂ and 0.0623 H₂O. C=64.98; H=5.03. 0.1162 ,, 29.0 c.c. N₂ at 15° and 756 mm. N=29.08. $2C_6H_5 \cdot N_3 + C_6H_5 \cdot NH_2$ requires C=65.22; H=5.17; N=29.61 per cent.

When shaken with dilute hydrochloric acid a portion dissolved, and the solution, when freed from oil by ether, gave with hypochlorite the colour characteristic of aniline, which was also indicated by diazotisation and coupling; the ethereal extract deposited phenylazoimide on evaporation, this effervescing strongly with concentrated sulphuric acid or a solution of stannous chloride in hydrochloric acid. The original substance also gave the intense colour with hypochlorite, and when reduced with stannous chloride gave aniline and nitrogen, unaccompanied by phenylhydrazine, which should be formed if phenyldi-imine were present. With concentrated sulphuric acid vigorous liberation of gas took place: αδ-derivatives of adipic and β-methyladipic acids. 269

0.3003 gave with 75 per cent. H_2SO_4 43.4 c.c. N_2 at 20.5° and 764 mm. N=16.50.

 $2C_6H_5 \cdot N_3 + C_6H_5 \cdot NH_2$ requires 2/3 azidic N=16.92 per cent.

For comparison with this material an artificial mixture of phenylazoimide with considerable excess of aniline was distilled under 13 mm. pressure, yielding an early fraction boiling at $62-65^{\circ}$; this was redistilled and analysed, the percentages of nitrogen and twothirds the azidic nitrogen being in close agreement with the above, from which it did not differ by any qualitative test.

ROYAL COLLEGE OF SCIENCE, LONDON. South Kensington, S.W.