

XXX.—*On the Action of Carbon Oxydichloride (Phosgene Gas) upon Diethylnaphthylamine.*

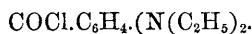
By BERNARD E. SMITH.

DIETHYLNAPHTHYLAMINE (25 grams) was dissolved in about twice its volume of carefully dried benzene, and phosgene gas passed into the solution to saturation. During the passage of the gas the contents of the flask became slightly warmed, and a white crystalline mass separated out. When fully saturated with phosgene gas, the contents of the flask were emptied out into an evaporating basin, and the benzene evaporated off over a water-bath; a black semi-solid mass remained behind. This was successively treated with boiling water and boiling dilute hydrochloric acid, the solution was filtered, and the residue washed to remove the last trace of hydrochloric acid. Both the aqueous and the hydrochloric acid solutions were found on examination to contain only diethylnaphthylamine hydrochloride.

The residue on the filter was next dissolved in alcohol. On allowing this solution to cool, and the alcohol to evaporate slowly in the air, a mass of crystals separated out, having a dirty brown colour, which, however, was easily removed by digesting with animal charcoal. By fractional distillation three distinct bodies were obtained, viz. :—

1. A colourless, transparent body, crystallising from alcohol in minute quadratic prisms, melting at 70°, and unattacked by dilute acids, or by boiling with caustic potash-solution.

Analysis yielded numbers agreeing nearly with the formula



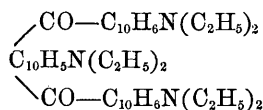
	Calculated.	Found.				
		I.	II.	III.	IV.	V.
C .....	68·830	68·31	68·20	—	—	—
H .....	6·110	6·28	6·76	—	—	—
N .....	5·364	—	—	5·66	5·72	—
Cl .....	13·570	—	—	—	—	13·82

2. A colourless crystalline body, crystallising from alcohol in transparent hexagonal prisms, melting at 225°, with decomposition, unattacked by dilute acids, or on boiling with caustic alkalis. It yields on analysis numbers corresponding with the formula of a body isomeric with that first described.

	Calculated.	Found.				
		I.	II.	III.	IV.	V.
C .....	68·83	68·98	69·11	—	—	—
H .....	6·11	6·42	6·76	—	—	—
N .....	5·36	—	—	5·43	5·67	—
Cl .....	13·57	—	—	—	—	13·73

3. A colourless crystalline body, crystallising from alcohol or glacial acetic acid in beautiful rhombs, which have a very high refractive power. This body was insoluble in water, and was not attacked by boiling with either dilute acids or alkalis.

Analysis yielded numbers corresponding with the following formula:—



	Calculated.	Found.				
		I.	II.	III.	IV.	
C .....	81·35	81·41	81·07	—	—	per cent.
H .....	7·24	7·53	7·39	—	—	„
N .....	6·47	—	—	6·77	6·30	„

The melting point of this body is 130°.

One molecular proportion of each of the bodies containing chlorine was enclosed in separate tubes, with a molecular proportion of diethylnaphthylamine, and heated for about five hours at 180—200°. After cooling the tubes were opened, when a quantity of gaseous hydrochloric acid escaped. Their contents were then removed and digested with dilute hydrochloric acid and water. Nothing entered into solution except a trace of diethylnaphthylamine hydrochloride. The residue, which in each case had a deep red colour, was then dissolved in alcohol. The solution thus obtained, after boiling for a short time with animal charcoal, was left at rest, in order that the substance might crystallise out. In both cases I obtained a body corresponding in every particular with the third body,  $\text{C}_{44}\text{H}_{47}\text{N}_3\text{O}_2$ , obtained by the action of phosgene gas upon diethylnaphthylamine at ordinary temperature.

Analysis of body obtained by the action of diethylnaphthylamine on the body containing chlorine, melting at 70°:—

0·1244 gram yielded C ....	81·11 per cent.
H ....	7·39           „
0·2073                                   N ....	6·60           „

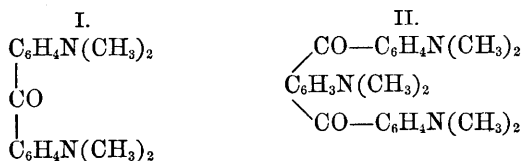
Analysis of body resulting from the action of diethylnaphthylamine upon the body containing chlorine, melting at 225°:—

0.2102 gram yielded C . . . .	81.40	per cent.
H . . . .	6.95	"
0.1953                                  N . . . .	6.78	"

Michler (*Ber.*, 9, 400) obtained by an analogous series of reactions, in which he substituted dimethylaniline for diethylnaphthylamine :

1. A compound to which he gave the formula  $\text{Cl} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{CH}_3)_2$ ; this body he found was easily decomposed on boiling with caustic alkalis, or even by prolonged boiling with water, thus differing essentially from either of the isomeric compounds containing chlorine obtained by me.

By heating a molecular proportion of this compound (*Ber.*, 9, 716) with a molecular proportion of dimethylaniline, he obtained two distinct bodies, to which he assigned the following formulæ:—



The second of these bodies is analogous to that obtained by me; but I have been unable, even after repeated trials, to obtain the slightest trace of a body analogous to the first, which Michler described as having high basic properties.

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