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## An Abnormal Product in the Chichibabin Reaction of Quinoline

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Sir:

The Chichibabin reaction (1,2,3) of quinoline (I) in dimethylaniline (1) with sodium amide gave a mixture of 2-aminoquinoline (II) and unexpected 2-amino-3,4-dihydroquinoline (III). Quinoline (I) was added dropwise to a stirred suspension of sodium amide in dimethylaniline at 120°. After the addition, the mixture was heated at 120-130° for 3 hours. After cooling, the reaction mixture was decomposed with water and extracted with ether. Removal of the solvent gave a crude oil, from which the excess of dimethylaniline was removed by distillation *in vacuo* to give a viscous substance. This residue afforded a colourless powder on being triturated with a small amount of ether. Recrystallization from benzene gave 3.3 g. (24.3%) of III as colourless prisms, m.p. 135-136°;  $\lambda$  max  $m\mu$  (log  $\epsilon$ ): 252 (4.07) and 267 (4.13) in EtOH. The n.m.r. spectrum of the compound (III) in  $CDCl_3$  solution shows a  $-CH_2CH_2-$  band at 7.0 - 7.8  $\tau$  (4H) (multiplet) and the peak attributable to the amino hydrogens was shown at 4.5  $\tau$  (2H) (broad singlet).

*Anal.* Calcd. for  $C_9H_{10}N_2$ : C, 73.94; H, 6.90; N, 19.16. Found: C, 74.35; H, 6.49; N, 19.03.

The picrate formed yellow crystals (from EtOH), m.p. 247° (decomp.).

*Anal.* Calcd. for  $C_9H_{10}N_2 \cdot C_6H_3N_3O_7$ : C, 48.00; H, 3.49; N, 18.66. Found: C, 48.21; H, 3.44; N, 18.72.

The above filtrate, from which crystals of III were filtered off, was concentrated and then distilled *in vacuo* to give a substance, which sublimed at b.p. 250° (0.5 mm.). Recrystallization from water gave 1.0 g. (7.5%) of 2-aminoquinoline (II) as colourless scales, m.p. 128° (4), from the point of IR spectrum and mixed melting point test. The picrate of II formed yellow crystals, m.p. 255-256°.

Hydrolysis of the above compound (III) with water gave 3,4-dihydrocarbostryl (IV) as colourless prisms (from ethanol), m.p. 163°, whose infrared spectrum showed a strong band for the C=O stretching vibration at  $1680\text{ cm}^{-1}$ . This compound also showed no depression of melting point on admixture with the authentic sample (5).

*Anal.* Calcd. for  $C_9H_9NO$ : C, 73.45; H, 6.16; N, 9.52. Found: C, 73.92; H, 6.30; N, 9.74.

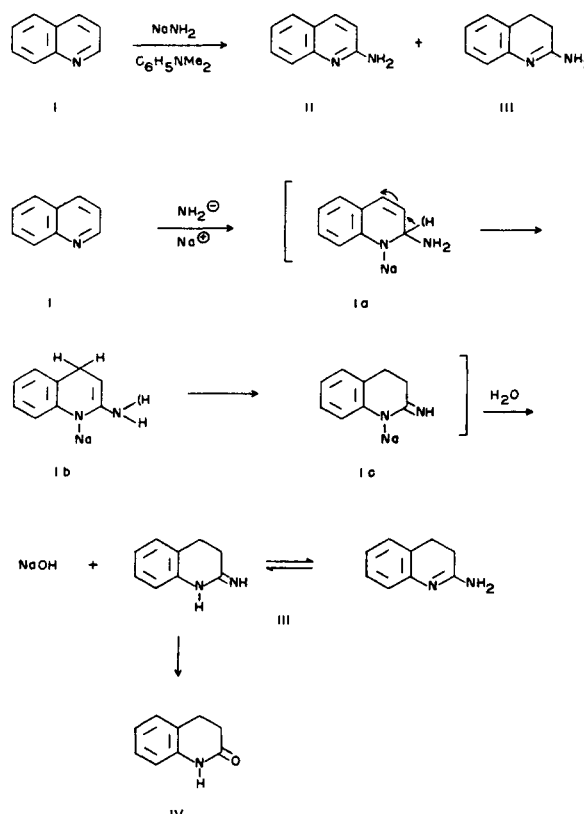
Perhaps the simplest mechanism to explain the formation of III would involve addition of sodium amide ( $Na^+$  and  $NH_2^-$ ) to I and formation of Ib by rearrangement of double bond *via* Ia to yield (Ic), which was converted into III and then IV by hydrolysis with water.

While the other solvent, for instance, benzene and toluene, were used instead of dimethylaniline, the Chichibabin reaction did not give the abnormal product (III), but only 2-aminoquinoline (II). This fact reveals

that the role of dimethylaniline as reaction solvent would be very important. Perhaps the proton at position 2 of the quinoline intermediate (Ia) would be removed with activation at the *para* position due to the resonance of dimethylaniline. The attempted abnormal Chichibabin reaction of pyridine and isoquinoline in dimethylaniline failed, thus the expected 3,4-dihydro-derivative was not obtained. Further work is under way.

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