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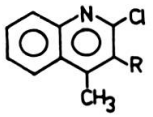
REDUCTION OF 2-CHLORO-3-ALKYL-4-METHYL QUINOLINES -PART III *

BY

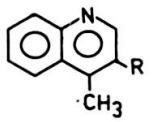
R. Sharma, R. K. Pande, Miss P. Jain and B. C. Joshi [1]

The present study of the reduction of 2-chloro-3,4-dimethyl (IA) and 2-chloro-3-ethyl-4-methyl (IB) quinolines with Sn and HCl is in continuation of earlier communications [1, 2]. Alongwith, the desired 3,4-dimethyl quinoline (IIA) and 3-ethyl-4-methyl quinoline (IIB) as major products, 2.2′-bis-3,4-dimethyl quinoline (IIIA) and 2,2′-bis-3-ethyl-4-methyl quinoline (IIIB) were also isolated as minor compounds.

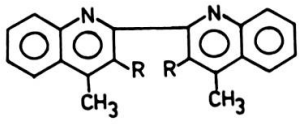
On the basis of elemental analysis, molecular formulae to IIIA and IIIB were suggested as $C_{22}H_{20}N_2$ and $C_{24}H_{24}N_2$ respectively.



IA – R = CH_3
IB – R = C_2H_5



IIA – R = CH_3
IIB – R = C_2H_5



IIIA – R = CH_3
IIIB – R = C_2H_5

Nmr spectra (in TFA using TMS as internal reference standard) for IIIA and IIIB were scanned. Eight aromatic protons of two carbocyclic rings were found to be present in the Nmr spectra of IIIA and IIIB (δ7.1-7.8-8.ArH). Nmr spectrum of IIIA revealed the presence of six protons each (δ2.1, S, *6*H; 2.4, S, *6*H) accounting for the presence of methyl groups at 3.3′ and 4,4′ positions. Nmr spectrum of IIIB revealed the presence of two ethyl groups at 3.3′ positions (δ0.9 tr, *6*H; 2.75 qr. *4*H) and for the methyl groups at 4,4′ positions (δ2.4, S, *6*H).

The absence of chlorine in IIIA and IIIB, the absence of protons at positions 2,2′-generally observed in the down-field due to the presence of nitrogen in the vicinity (c.a. δ8.2 in IIA and IIB) indicated the linkage of two quinoline moieties in IIIA and IIIB at 2,2′-positions resulting in the formation of bis molecules.

All these observations suggest the structures to IIIA as 2,2′-bis-3,4-dimethyl quinoline and to IIIB as 2,2′-bis-3-ethyl-4-methyl quinoline respectively.

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* Part I and II, see resp. ref. 1 and 2.

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EXPERIMENTAL

Melting points are uncorrected. Nmr spectra were recorded on Perkin Elmer R12B spectrometer in TFA (using TMS as IRS).

REDUCTION OF 2-CHLORO-3-ALKYL-4-METHYL QUINOLINES (IA AND IB) IA → IIA AND IIIA

2-Chloro-3,4-dimethyl-quinoline [3] (IA, 19.15 g., 0.1M) was reduced with conc. HCl (120 ml), H_2O (160 ml) and Sn (10 g) on the lines followed earlier [2-6]. After decomposition of the tin complex, with concentrated solution of NaOH the reaction mixture was extracted exhaustively with $CHCl_3$ and the $CHCl_3$ extract (dried over anhyd. Na_2SO_4) was concentrated to give a yellowish brown product.

TLC examination of this product, over silica gel 'G' plates using benzene, ethanol and ammonium hydroxide (7:2:1; solvent layer) as mobile phase, revealed the presence of two spots (Rf's 0.68 and 0.42). The product was chromatographed over neutral alumina column. The compound in pet. ether fraction was identified as 3,4-dimethyl quinoline (IIA, m.p. 72° [3]; Nmr, δ ppm 7.4-8.2 *5*.ArH; 2.3, S, *3*H; 2.6, S, *3*H) and in the fraction of methanol, benzene mixture (80:20), IIIa (m.p. 242°, Nmr, TFA δ ppm 7.1-7.8, *8*.ArH; δ2.1, S, *6*H, 2.4, S, *6*H) was isolated.

IB → IIB AND IIIB

On similar lines, 2-chloro-3-ethyl-4-methyl quinoline [3] (IB, 20.55 g., 0.1M) was reduced and 3-ethyl-4-methyl quinoline (IIB, m.p. 83° [3], Nmr δ ppm, 7.3-8.4, *5* ArH; 0.95, tr. *3*H; 2.8, qr. *2*H, 2.55 δ*3*H) and (IIIB, m.p. 265°, Nmr δ ppm 7.1-7.8; 8ArH; 0.9, tr, *6*H; 2.75, qr, 4H; 2,4, S, *6*H) were isolated.

Analysis (i) for $C_{22}H_{20}N_2$ (IIIA)
Calcd. C, 84.61; H, 6.41; N, 8.98%
M.W. 312
Found: C, 84.66; H, 6.46; N, 8.88%
M.W. (Rast method) 316

(ii) for $C_{24}H_{24}N_2$ (IIIB)
Calcd.: C, 84.70; H, 7.06; N, 8.24%
M.W. 340
Found: C, 84.75; H, 7.10; N, 8.18%
M.W. (Rast Method) - 336.

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