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REDUCTION OF 2-CHLORO-4-METHYLQUINOLINE

BY

D. KISHORE, Asha SURANA and Bhuwan C. JOSHI

ABSTRACT

From the reduction of 2-chloro-4-methylquinoline (1) three compounds (2~4) were obtained, besides 4-methylquinoline. The structures were assigned on the basis of elemental analysis and spectral studies.

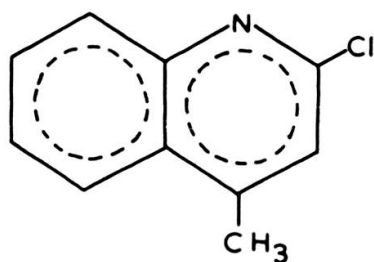
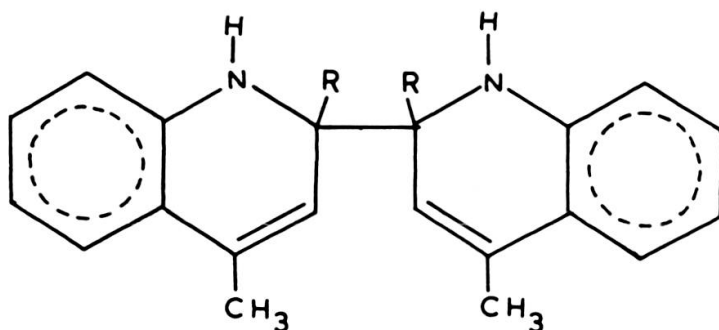
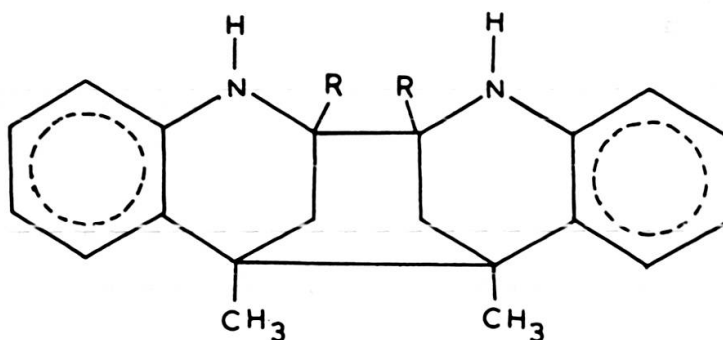
DISCUSSION

The reduction of 2-chloro-4-methylquinoline ¹ with Sn and HCl indicated the presence of six compounds on TLC examination and three products (2~4) besides 4-methyl-quinoline (major product) could only be separated in small amounts.

NMR spectral studies of 2 (C₂₀H₁₈N₂Cl₂) revealed the presence of a singlet for 6H at δ 2.55 and a singlet for 2H at δ 6.15, accounting for the presence of two methyl groups and two olefinic protons. The aromatic protons had the chemical shift in the range of δ 7.1 ~ 7.8 for 8H and for 2H attached to nitrogen at δ 10.2. However, 3 (C₂₀H₂₀N₂) showed the presence of a singlet for 6H of two methyl groups at δ 2.5 for two olefinic protons (as doublet) at δ 6.70 and for eight aromatic protons at δ 7.1 ~ 7.8, for 2H attached to nitrogen at δ 9.5 and for 2H as N-CH at δ 3.05 (doublet). The NMR spectra would confirm the structures as (2-2'-bis-(2-chloro-4-methyl-1H-1,2-dihydro-quinolyl) for 2 and 2,2'-bis-(4-methyl-1H-1,2-dihydro-quinolyl) for 3. Further it could be supported from the fact that protons at nitrogen in 2 shifted to the lower field as against one in 3 along with the presence of N-CH proton in 3 and its absence in 2 thus confirming that 2 and 2' positions in 2 were occupied by chlorine. The possibility of 2 as 3 HCl was also ruled out as chlorine was not in ionic form.

In NMR spectrum of 4 (C₂₀H₂₀N₂Cl₂) the signal for two methyl groups was observed as singlet at δ 1.3 (at comparatively much higher field). There were only

eight aromatic protons at δ 7.1 ~ 7.8. There were indications of 4H at δ 1.52 ~ 2.10 indicating the presence of two methylene groups. There was no signal for the olefinic proton at δ 6.4 ~ 6.7. Mass spectra of **4** gave the m/e peaks at 288, 144 and base peak at 143. On the basis of these spectral evidences, the structure to **4** was assigned as 'tricyclo (5,3,1,1^{2,6})-3,10-diaza-1,2-dichloro-6,7-dimethyl-4,5 : 8,9-dibenzodecane.

**1****2**, R = Cl**3**, R = H**4**, R = Cl**5**, R = H

Formation of **2**, **3** and **4** along with the lepidine indicated that the reduction at first stage could involve the condensation of 2-chlorolepidine molecule at position 2 resulting in the formation of **2** which on further reduction would either cyclise at position 4 and 4' resulting in the formation of **4**^{2,3} or the chlorine atom would be replaced with hydrogen.

The reduction of **1** through **3** should also yield **5** but it could not be isolated.

Table

| No. | Molecular formula | Chemical Shifts (δ) of protons | | | | | |
|----------------------------------|--|---|--------------|------------------|------------------|----------------------------|----------------------------|
| | | Aromatic protons | -NH protons | =CH protons | -N-C-H protons | -CH ₂ - protons | -C-CH ₃ protons |
| <u>2</u> (CDCl ₃) | C ₂₀ H ₁₈ N ₂ Cl ₂ | 7.1-7.8 (8H) | 10.2 (2H) | 6.15 (s) (2H) | — | — | 2.55 (s) (6H) |
| <u>3</u> (CDCl ₃) | C ₂₀ H ₂₀ N ₂ | 7.1-7.8 (8H) | 9.5 (2H) | 6.7 (d) (2H) | 3.05 (d) (2H) | — | 2.50 (s) (6H) |
| <u>4</u> (TFA) | C ₂₀ H ₂₀ N ₂ Cl ₂ | 7.1-7.8 (8H) | 8.8 (2H) | — | — | 1.5-2.1 (4H) | 1.30 (s) (6H) |

EXPERIMENTAL

Melting points are uncorrected. Microanalyses were done at Central Drug Research Institute, Lucknow. NMR spectra are from NIH, Bethesda, Md. U.S.A. or CDRI and are recorded in CDCl₃ (of 2 and 3) and in T.F.A. (of 4) on a Varian A-60D model using TMS as internal reference standard. Mass spectrum of 4 was also from NIH.

REDUCTION OF 2-CHLORO-4-METHYLQUINOLINE

2-Chloro-4-methylquinoline (17.8 g, 0.1 M) was reduced with conc. HCl (120 ml), H₂O (160 ml) and Sn (16 g) on the lines followed earlier¹. After decomposition of the complex the reaction mixture was extracted with chloroform. The chloroform extracts were dried over anhydrous Na₂SO₄ and concentrated to give a white product, insoluble in ether. Compounds 2 (mp 238°) and 3 (mp 227°) were separated from this white product on repeated crystallisation with acetone.

Ether soluble portion afforded the crude product which was distilled under reduced pressure [(0.5 mm) 80-85°]. At first a solid sublimed followed with the lepidine. The solid (4) was crystallised from acetone.

ANALYSIS

for $C_{20}H_{18}N_2Cl_2$ (2)

Calcd.: C, 67.22; H, 5.04; N, 7.84 %

Found: C, 67.48; H, 5.16; N, 7.56 %

for $C_{20}H_{20}N_2$ (3)

Calcd.: C, 83.33; H, 6.94; N, 9.71 %

Found: C, 83.46; H, 6.72; N, 9.88 %

for $C_{20}H_{20}N_2Cl_2$ (4) 246° C

Calcd.: C, 66.85; H, 5.57; N, 7.69 %

Found: C, 66.33; H, 5.76; N, 7.30 %

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