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# REDUCTION OF 2-CHLORO-4-METHYLQUINOLINE

BY

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## 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.

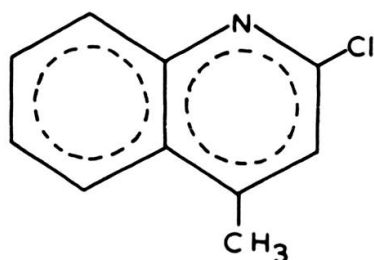
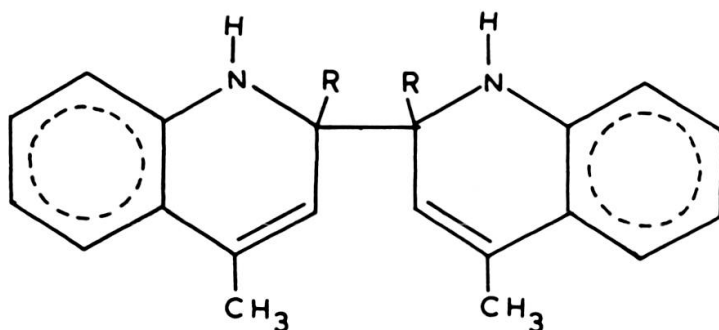
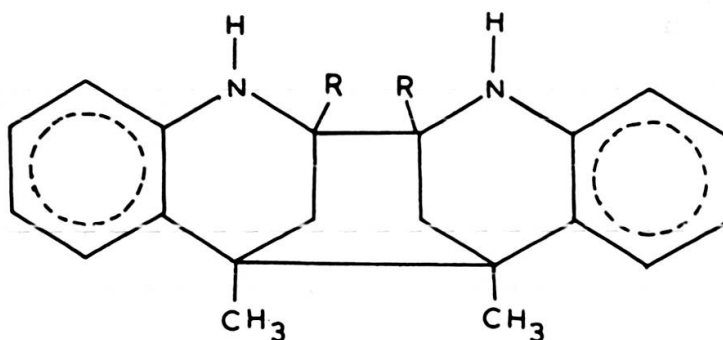
## DISCUSSION

The reduction of 2-chloro-4-methylquinoline<sup>1</sup> 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 (C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>Cl<sub>2</sub>) revealed the presence of a singlet for 6H at  $\delta$  2.55 and a singlet for 2H at  $\delta$  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  $\delta$  7.1 ~ 7.8 for 8H and for 2H attached to nitrogen at  $\delta$  10.2. However, 3 (C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>) showed the presence of a singlet for 6H of two methyl groups at  $\delta$  2.5 for two olefinic protons (as doublet) at  $\delta$  6.70 and for eight aromatic protons at  $\delta$  7.1 ~ 7.8, for 2H attached to nitrogen at  $\delta$  9.5 and for 2H as N-CH at  $\delta$  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 (C<sub>20</sub>H<sub>20</sub>N<sub>2</sub>Cl<sub>2</sub>) the signal for two methyl groups was observed as singlet at  $\delta$  1.3 (at comparatively much higher field). There were only

eight aromatic protons at  $\delta$  7.1 ~ 7.8. There were indications of 4H at  $\delta$  1.52 ~ 2.10 indicating the presence of two methylene groups. There was no signal for the olefinic proton at  $\delta$  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<sup>2,6</sup>)-3,10-diaza-1,2-dichloro-6,7-dimethyl-4,5 : 8,9-dibenzodecane.

12, R = Cl3, R = H4, R = Cl5, 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**<sup>2,3</sup> 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 ( $\delta$ ) of protons					
		Aromatic protons	-NH protons	=CH protons	-N-C-H protons	-CH <sub>2</sub> - protons	-C-CH <sub>3</sub> protons
<u>2</u> (CDCl <sub>3</sub> )	C <sub>20</sub> H <sub>18</sub> N <sub>2</sub> Cl <sub>2</sub>	7.1-7.8 (8H)	10.2 (2H)	6.15 (s) (2H)	-	-	2.55 (s) (6H)
<u>3</u> (CDCl <sub>3</sub> )	C <sub>20</sub> H <sub>20</sub> N <sub>2</sub>	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 <sub>20</sub> H <sub>20</sub> N <sub>2</sub> Cl <sub>2</sub>	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 CDCl<sub>3</sub> (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), H<sub>2</sub>O (160 ml) and Sn (16 g) on the lines followed earlier<sup>1</sup>. After decomposition of the complex the reaction mixture was extracted with chloroform. The chloroform extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> 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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