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REDUCTION OF 2-CHLORO-4-METHYLQUINOLINE

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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.

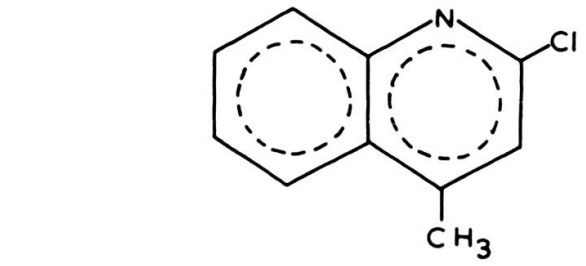
DISCUSSION

The reduction of 2-chloro-4-methylquinoline [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* ($C_{20}H_{18}N_2Cl_2$) 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 $\sim$ 7.8 for 8H and for 2H attached to nitrogen at δ 10.2. However, *3* ($C_{20}H_{20}N_2$) 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 $\sim$ 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* ($C_{20}H_{20}N_2Cl_2$) 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.



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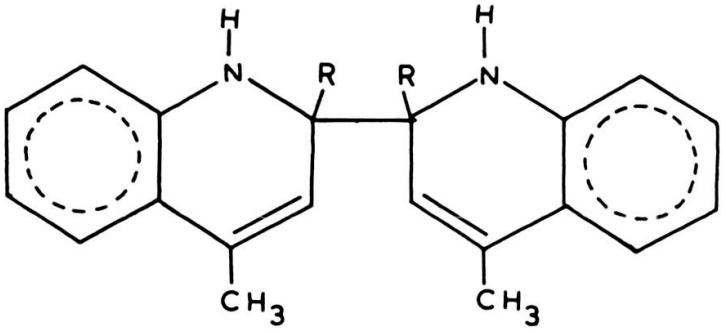
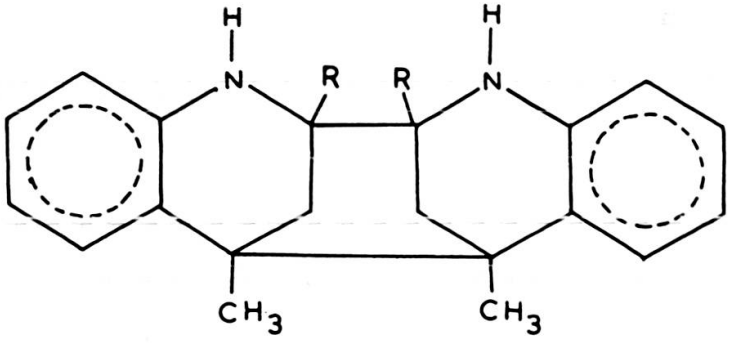


2, R = Cl

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
2 ($CDCl_3$)	$C_{20}H_{18}N_2Cl_2$	7·1–7·8 (8H)	10·2 (2H)	6·15 (s) (2H)	–	–	2·55 (s) (6H)
3 ($CDCl_3$)	$C_{20}H_{20}N_2$	7·1–7·8 (8H)	9·5 (2H)	6·7 (d) (2H)	3·05 (d) (2H)	–	2·50 (s) (6H)
4 (TFA)	$C_{20}H_{20}N_2Cl_2$	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 $CDCl_3$ (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_2O (160 ml) and Sn (16 g) on the lines followed earlier [1]. After decomposition of the complex the reaction mixture was extracted with chloroform. The chloroform extracts were dried over anhydrous Na_2SO_4 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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