

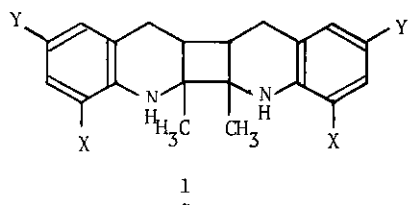
BIMOLECULAR PRODUCTS FROM THE REDUCTION OF QUINOLINES WITH ZINC AND
HYDROCHLORIC ACID

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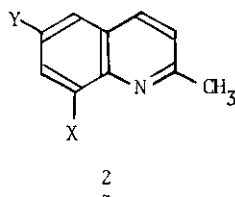
Comparison of the ^{13}C nuclear magnetic resonance spectra of the bimolecular products 4a-4c obtained on reduction of 2-methylquinoline, 2,4-dimethylquinoline, and 6-bromo-2-methylquinoline, respectively, with zinc and hydrochloric acid with the spectra of the corresponding products from 8-methoxy-2-methylquinoline and 6-chloro-2-methylquinoline shows that the latter have the analogous bridged ring structures 4d and 4e, respectively, and not fused cyclobutanoid structures of type 1.

Structures 1a and 1b have been assigned recently to the products obtained on reduction of 8-methoxy-2-methylquinoline (2a)¹ and 6-chloro-2-methylquinoline (2b),² respectively, with zinc and hydrochloric acid. The assignments were based on ^{13}C and ^1H n.m.r. and mass spectroscopic data and are analogous to structures first proposed by Meisenheimer³ for products obtained in similar fashion from 2-methylquinoline (3a) and several other quinoline derivatives.⁴



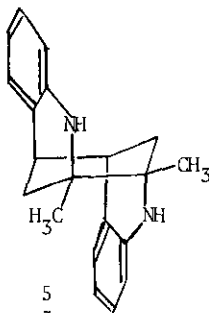
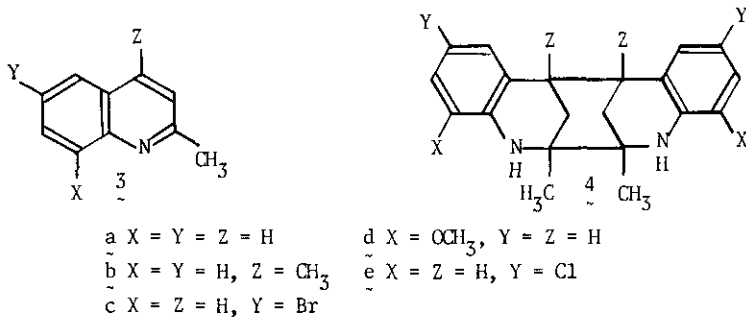
a X = OCH_3 , Y = H

b X = H, Y = Cl



However, earlier work in our Laboratories led us to revise Meisenheimer's original structural assignment for the reduction product from 3a and to assign structures 4a and 4b to this and the reduction product from 2,4-dimethylquinoline (3b), respectively.⁵ This revision was based on ^1H n.m.r. spectroscopic and pK_b data for these products and was subsequently confirmed by a

single crystal X-ray analysis of the dibromo derivative 4c, which was obtained both by reduction of 6-bromo-2-methylquinoline (3c) and by bromination of the reduction product from 3a.⁶ This analysis also established the stereochemistry of 4a to be that shown in 5, as provisionally assigned previously⁵ and corroborated by dipole moment measurements.⁷



It appeared to us unlikely that the reactions of 2a and 2b with zinc and hydrochloric acid would take a different course from those of 3a-c, and we have undertaken an examination of the ¹³C n.m.r. spectra of compounds 4a-c since the ¹³C n.m.r. spectra of the reduction products from 2a and 2b had been invoked as evidence in favor of assignment of structures 1a and 1b to these products.^{1,2} These spectra are tabulated in the Table together with the spectra of the reduction products from 2a and 2b. The relationship among these spectra leaves no doubt that all of these compounds have analogous structures and thus that the reduction products from 2a and 2b must have structures 4d and 4e, respectively. It may further be noted that the argument¹ that the ¹J_{CH} coupling constant value of 133.8 Hz for the carbon signal assigned to C.3 in structure 1a (C.4 in 4d) corresponds to observed values for cyclobutane derivatives is unconvincing in that ¹J_{CH} for the signal assigned to C.4 in 1a (C.3 in 4d) has the similar value of 131.4 Hz. As in the case of the reduction products from 3a and 3b,⁵ the ¹H n.m.r. spectra of the products from 1a and 1b are in better accord with structures of type 4 than of type 1. The mass spectra of the reduction products of 2a and 2b^{1,2} are readily reinterpreted in terms of structures 4d and 4e since they are dominated by initial fragmentation to give monomeric species.

TABLE. ^{13}C nuclear magnetic resonance spectra of compounds 4a-4e^a

Carbon	4a	4b	4c	4d	4e ^b
8a	145.4	145.3	145.0	135.1	143.8
7	128.4*	128.6*	130.4*	107.8	128.1*
5	127.1*	126.9*	129.5*	120.8	127.1*
4a	125.1	126.2	126.4	125.2	126.3
6	115.9	115.2	105.9	114.6	120.5
8	112.2	112.3	113.7	144.7	113.4
2	57.5	57.0	57.5	57.3	57.6
4	43.0	42.3	42.7	42.8	42.7
3	29.9	40.6	29.5	30.1	29.7
CH ₃ (2)	22.7	22.4	22.3	22.7	22.6
CH ₃ (4)	-	21.0	-	-	-
OCH ₃	-	-	-	55.4	-

^aSpectra were recorded of solutions in CDCl_3 , except for compound 4c, whose spectrum was recorded in $\text{DMSO}-d_6/\text{CDCl}_3$. The multiplicities of signals in single frequency off-resonance decoupled spectra are in accord with the assignments. Assignments for pairs of signals marked with asterisks may be interchanged. ^bRef. 2.

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