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# THE REACTION OF DICHLOROMETHYLENE WITH 2,3-DIMETHYLINDOLE AND 1,2,3,4-TETRAHYDROCARBAZOLE

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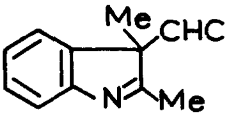
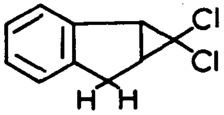
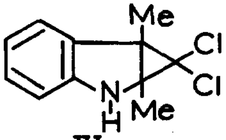
THE reaction of 2,3-dimethylindole in the presence of ethanolic sodium ethoxide and chloroform was first investigated by Plancher and Carrasco[1] who obtained a single basic product which they formulated as I by analogy with results obtained by similar treatment of *ortho*- and *para*-cresol and 1,2,3,4-tetrahydrocarbazole. However, Parham and coworkers[2] later observed that indene, in the presence of potassium t-butoxide under non-polar conditions gives, in 65-70% yield, a product of structure II, this product being readily converted to 2-chloronaphthalene by heating in a polar solvent, conversion being slower in a non-polar solvent or in the solid phase. This observation led Wynberg[3] to suggest III as an alternative for Plancher and Carrasco's base. Experimental evidence is now presented supporting structure I.


I


II


III

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[1] G. Plancher and O. Carrasco, *Atti Accad. Nazl. Lincei* [5], **13**, I, 573 (1904); *Chem. Zentr.* II, 341 (1904).

[2] W.E. Parham, H.E. Reiff and R. Swartzentruber, *J. Amer. Chem. Soc.* **78**, 1437 (1956).

[3] H. Wynberg, *Chem. Rev.* [2], **60**, 169 (1960).

It has been found that treatment of 2,3-dimethylindole[4] with ethanolic sodium ethoxide and chloroform, as already described,[1] gave 66% of the unchanged indole and a basic product which consisted of two bases, separated by fractional crystallization of their picrates from ethanol.

The least soluble picrate was obtained as bright-yellow prisms, m.p. 211-212° (sintering from 188°), in 7% yield (from 2,3-dimethylindole), (Found: C, 48.9; H, 3.4; N, 13.4 Calc. for $C_{17}H_{13}ClN_4O_7$: C, 48.6; H, 3.1; N, 13.3%) from which the free base, 3-chloro-2,4-dimethylquinoline, IV, was obtained as white prisms from 60-80 pet. ether, m.p. 73-74° (Found: C, 69.0; H, 5.1; N, 7.6. Calc. for $C_{11}H_{10}ClN$: C, 69.1; H, 5.2; N, 7.3%), $\lambda_{max}$ 214, 232, 237, 273, 287, 294, 310, 318 324 mμ (ε 35,800, 42,800, 86,300, 4000, 3500, 2700, 3500, 2200, 4300 respectively in ethanol). Although Plancher and Carrasco initially[1] obtained only I from the above reaction, they subsequently[5] isolated both I and IV, the quinoline being obtained via the picrate, m.p. 210°, as white shining needles, m.p. 75°.

The more soluble picrate gave orange-yellow plates from ethanol, m.p. 163-164° (sintering from 141°) (lit.[5] 164-165°), in 12% yield (from 2,3-dimethylindole), (Found: C, 44.6; H, 2.7; N, 12.1. Calc. for $C_{17}H_{14}Cl_2N_4O_7$: C, 44.7; H, 3.0; N, 12.25%) from which the free base, I, was obtained as white prisms from 60-80 pet. ether, m.p. 74-75° (lit.[1] 73-74°) (Found: C, 58.9; H, 5.0; N, 6.2. Calc. for $C_{11}H_{11}Cl_2N$: C, 58.7; H, 4.9; N, 6.0%). $\lambda_{max}$ 263 mμ (ε 4700 in ethanol). $\lambda_{max}$ 231-232, 287-288 mμ (ε 7000, 4500 respectively in ethanolic hydrochloric acid). $\nu_{max}$ 1619 (w) $cm^{-1}$ (in nujol) (conjugated C = N[6]). No strong band around 1000 $cm^{-1}$ (cyclopropane[7]), or

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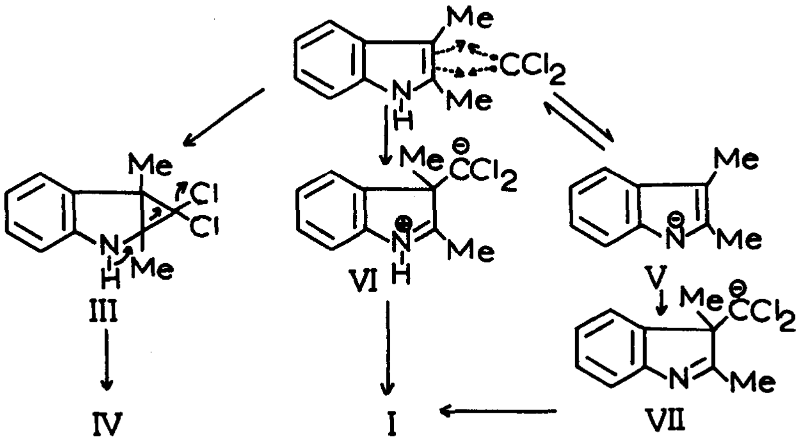
[4] J.T. Fitzpatrick and R.D. Hiser, J. Org. Chem. 22, 1703 (1957).

[5] G. Plancher and O. Carrasco, Atti Accad. Nazl. Lincei [5], 14, I 162 (1905); Chem. Zentr. I, 1155 (1905).

[6] a, J. Kebrle, H. Schmid, P. Waser and P. Karrer, Helv. Chim. Acta 36, 102 (1953);
b, B. Witkop and J.B. Patrick, J. Amer. Chem. Soc. 73, 2188 (1951).

[7] L.J. Bellamy, The Infra-red Spectra of Complex Molecules p. 29. Methuen, London; John Wiley, New York (1958).

any band above 3100 $cm^{-1}$ (N-H). These spectral properties are closely similar to those of 2,3,3-trimethylindolenine (prepared in 69% yield by refluxing equi-molar quantities of phenylhydrazine and methyl isopropyl ketone in monoethylene glycol[4] and purified via the picrate[8]), $\lambda_{max}$ 259 m$\mu$ ($\varepsilon$ 6000 in ethanol).[6a] $\lambda_{max}$ 230-231, 277-278 m$\mu$ ($\varepsilon$ 6350, 5200 respectively in ethanolic hydrochloric acid). $\nu_{max}$ 1614 (m) $cm^{-1}$ (liquid film) (conjugated C = N). They thus confirm structure I as opposed to III, which would have shown no C = N absorption but absorption due to a cyclopropane ring and an N-H group in the infra-red, and whose ultra-violet spectrum would have been that not of an indolenine but of an indoline, changed on acidification to benzenoid absorption.[9] Although I has previously[5] been converted to IV by heating with ethanolic sodium ethoxide in a sealed tube at 100° for 5 hr, attempted conversion of I into IV by heating with 10%



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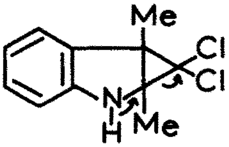
[8] G. Plancher, *Ber. Dtsch. Chem. Ges.* **31**, 1488 (1898).

[9] H.F. Hodson and G.F. Smith, *J. Chem. Soc.* 1877 (1957).

ethanolic sodium ethoxide for 2 hr at 60-65° followed by 1/4 hr refluxing, conditions similar to those employed in their simultaneous formation from 2,3-dimethylindole, failed, no sodium chloride being precipitated during this treatment and I being recovered as the picrate in 89% yield. It is therefore unlikely that I is an intermediate in the formation of IV, but more likely that both bases are formed by different simultaneous mechanistic pathways as shown on page 141.

Dichloromethylene, formed by the action of base on chloroform,[10] can react with 2,3-dimethylindole as shown to give a 1,1-dichlorocyclopropane,[11] III, which, owing to the strain in the 5,3-ring system, rapidly looses chloride ion, suffers ring scission and looses a proton to yield IV.[3,11] Alternatively, electrophilic attack by the dichloromethylene at the 3-position of the indole and/or indole anion, V (formed by the action of ethoxide on the indole) nucleus can give VI and VII respectively, which by proton transfer or abstraction from the reaction medium can lead to I. VI might also be formed from III as shown in VIII. The formation of IV via III is analogous to the formation of II and subsequently 2-chloronaphthalene from indene.[2] However, the formation of a compound from indene analogous to I does not occur owing to the absence of the nitrogen atom in the indene nucleus, the presence of which renders feasible the electrophilic attack of



VIII

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[10] J. Hine and J.M. van der Veen, J. Org. Chem. 26, 1406 (1961), see ref.2 therein.

[11] P.S. Skell and S.R. Sandler, J. Amer. Chem. Soc. 80, 2024 (1958).

dichloromethylene on the indole nucleus, as does the oxygen anion in similar attack on the phenoxide anion.[10]

Treatment of 1,2,3,4-tetrahydrocarbazole[12] under similar conditions to those described above gave a 68% recovery of the starting product and only one basic product, as previously described,[13] obtained in 14% yield as white prisms from methanol, m.p. 160-162$^{\circ}$ (sintering from 148$^{\circ}$) (lit.[13] 158-159$^{\circ}$) (Found: C, 61.9; H, 4.75; N, 5.5. Calc. for $C_{13}H_{13}Cl_2N$: C, 61.7; H, 5.1; N, 5.5%). The picrate crystallized from ethanol as yellow prisms, m.p. 179-180$^{\circ}$ (sintering from 150$^{\circ}$) (Found: C, 47.5; H, 3.3; N, 11.5. $C_{19}H_{16}Cl_2N_4O_7$ requires C, 47.3; H, 3.3; N, 11.6%). It has been reported[13] that reduction of the above base with phosphorus/hydriodic acid gives 1,2,3,4,10,11-hexahydro-11-methylcarbazole hydriodide which was taken as support for structure IX for the base. This has now been confirmed spectroscopically, the base having $\lambda_{max}$ 264 m$\mu$ ($\epsilon$ 5500 in ethanol), $\lambda_{max}$ 233, 287-288 m$\mu$ ($\epsilon$ 7400, 5300 respectively in ethanolic hydrochloric acid) [*cf.* 1,2,3,4-tetrahydro-11-methylcarbazolenine, $\lambda_{max}$ 255 m$\mu$ ($\epsilon$ 7030 in ethanol), $\lambda_{max}$ 231, 275 m$\mu$ ($\epsilon$ 8000, 6300 respectively in ethanolic hydrochloric acid].[14] $\nu_{max}$ 1618 (m) cm$^{-1}$ (in nujol) (conjugated C = N); no band above 3100 cm$^{-1}$ (N-H). The absence of indoline or quinoline bases in the total reaction product was shown by ultra-violet spectroscopic examination of the mother-liquors from the crystallization of IX. In this case the formation of the quinoline corresponding to IV is probably suppressed by the steric effect of ring C of the 1,2,3,4-tetrahydrocarbazole, which could either prevent the formation of the 1,1-dichlorocyclopropane intermediate or, alternatively, may prevent the subsequent ring expansion, preferential formation of IX occurring by the alternative cleavage of the cyclopropane

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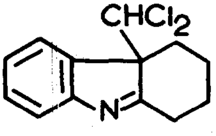
[12] C.U. Rogers and B.B. Carson, *Org. Synth.* **30**, 90 (1950)

[13] C.U. Zaretti and Levi, *Gazz. Chim. Ital.* **24**, II, 115 (1894).

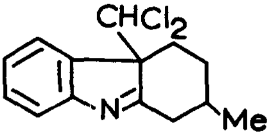
[14] G.F. Smith and J.T. Wróbel, *J. Chem. Soc.* 792 (1960).

ring (cf. VIII).

By analogy, the above structural proof of IX can be taken as verification, up till now lacking,[3] of the structure of the basic product from the reaction of 1,2,3,4-tetrahydro-2-methylcarbazole[15] in the presence of ethanolic sodium ethoxide and chloroform[16] as X.



IX



X

This work was carried out during the tenure of an Imperial Chemical Industries Postdoctoral Research Fellowship.

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[15] W. Borsche, Liebigs Ann. 359, 49 (1908). B.M. Barclay and N. Campbell, J. Chem. Soc. 530 (1945). In these papers the orientation of the 1,2,3,4-tetrahydro-2-methylcarbazole which had been used in ref. 16 and which was prepared by Fischer cyclization of meta-methylcyclohexanone phenylhydrazone was established as opposed to the possible 4-methyl isomer.

[16] G. Plancher and O. Carrasco, Atti Accad. Nazl. Lincei [5], 13, I, 632 (1904); Chem. Zentr. II, 342 (1904).