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LITHIATION OF N, N-DIMETHYL-β-PHENYLETHYLAMINE

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In a recent communication, Hauser and coworkers (1) have reported that in the lithiation of N,N-dimethyl-β-phenylethylamine, when the metalation mixture was treated with benzophenone, no compound corresponding to the entry of lithium in the aromatic ring was obtained. In connection with another work, we had also done this lithiation, where we treated the metalation mixture with benzaldehyde. Working up in the usual way, the basic fraction of the reaction mixture, on distillation in vacuo gave unreacted starting compound, leaving a residue which on chromatography (alumina - 10% chloroform in benzene) gave a compound* $C_{17}H_{21}ON$, m.p. 92°(from hexane or ether). The I.R. spectrum of the compound showed the presence of one mono-substituted and one ortho disubstituted benzene rings (709, 772, 782 cm^{-1}). The N.M.R. spectrum in $CDCl_3$ besides confirming the presence of nine aromatic protons (δ= 7.3 p.p.m.,

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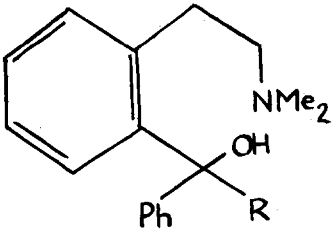
* Satisfactory microanalytical results have been obtained for all the compounds reported in this communication.

multiplet, 9H), also revealed the intact $-N(CH_3)_2$ group (δ= 2.2 p.p.m., singlet, 6H), $Ph-\underline{CH_2}-\underline{CH_2}-N$ group (δ= 2.4 to 2.9 p.p.m., complex multiplet, 4H), one -OH group (δ= 4.6 p.p.m., singlet, 1H, disappears on addition of D_2O) and one $\underline{CH}OH$ (δ= 5.99 p.p.m., singlet, 1H.). The spectral data is then consistent with the structure I which corresponds to ortho lithiation in the benzene ring.



I R = H

II R = Ph

At this stage, our attention was drawn to the communication (1) of Hauser and coworkers and we repeated the lithiation, this time using benzophenone. Decomposing the reaction mixture with water, the ethereal solution on treatment with dilute hydrochloric acid, gave a white precipitate which, with aqueous sodium carbonate solution, furnished a compound $C_{23}H_{25}ON$, m.p. 156-158° (from hexane -absolute ethanol). The I.R. spectrum of the compound was markedly similar to that of I, and that of its methiodide (m.p. 259-260°, from methyl alcohol-ether) clearly indicated the presence of a hydroxyl group (3400 cm^{-1}). However, the

N.M.R. spectrum in $CDCl_3$ had some interesting features. Thus in the high field region there were two singlets at $\delta = 2.12$ p.p.m. (6H) and $\delta = 2.55$ p.p.m. (4H). The former was attributed to the $-N(CH_3)_2$ group, while the latter to $Ph-CH_2-CH_2-NMe_2$, in which the methylene group protons appeared (accidentally) equivalent. In accord with this interpretation, the N.M.R. spectrum of the compound in pyridine, had a different signal pattern in the high field region. Thus, while the $-N(CH_3)_2$ appeared as a singlet at $\delta = 2.02$ p.p.m. (6H), the $Ph-\underline{CH_2}-\underline{CH_2}-N$ now appeared, as in the N.M.R. spectrum of compound I, as a complex multiplet at $\delta = 2.25$ to 3.0 p.p.m. (4H). The spectral data is then in aggreement with structure II for the compound, once again indicating ortho substitution in the benzene ring.

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References :

(1) R.L.Vaulx, F.N.Jones and C.R.Hauser, J.Org.Chem., **30**, 58 (1965).