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LITHIATION OF N-ACETYLBENZYLAMINE

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In the reaction of lithiation of N-acetylbenzylamine with n-butyllithium, followed by treatment of the organolithium compound with benzaldehyde, we obtained, among other products, a compound $C_{16}H_{17}NO_2$,⊕ m.p. 103-104° (from benzene). The I R spectrum indicated the presence of the intact amide group (1640 cm^{-1}), while the P M R spectrum in $CDCl_3$, showed the presence of two monosubstituted benzene rings (δ=7.1 to 7.4 p.p.m., 10 H), one $\underline{CH}$-OH (δ=5.03 p.p.m., triplet J=6 cps, 1 H), and one $\underline{CH_2}$-CO (δ=2.52 p.p.m., doublet J=6 cps, 2 H). The structure of the compound could then be

$$Ph - CH_2 - NH - CO - CH_2 - CH(OH) - Ph$$

Consistent with this structure, the compound, on boiling with concentrated hydrochloric acid, lost a molecule of water to give another compound $C_{16}H_{15}NO$, m.p. 109-110° (from benzene-ether), whose I R spectrum showed the presence of a conjugated amide group (1608 and 1613 cm^{-1}). The U V

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

spectrum ($\lambda_{max}^{EtOH} = 275$ mμ, $\varepsilon = 21,000$) and the P M R spectrum in $CHCl_3$ ($\delta = 7.63$ and 6.50 p.p.m., doublets J=15.5 cps, 1 H each) then further indicated it to be <u>trans</u> N-benzylcinnamamide.

In the literature, there are three instances where the preparation of N-benzylcinnamamide has been described. However, none of the reported m.p.s agreed with the m.p. of our compound.

Dermer and King (1) have prepared N-benzylcinnamamide,⊕ m.p. 225-226° (from ββ' dichlorodiethyl ether), by heating a mixture of cinnamic acid (or its methyl ester), benzylamine and ammonium chloride, while Kushner and coworkers (2), who report m.p. 94-96.5°, have obtained it by treating cinnamoyl chloride with benzylamine in aqueous sodium hydroxide solution. Commenting on the difference in the m.p. of their synthetic specimen and that of Dermer and King, the latter group of authors then state that this may be due to <u>cis-trans</u> isomerism. In the third instance Knunyants and Gambaryan (3) have prepared N-benzylcinnamamide, m.p. 103-104°, by treatment of N-benzyl-2-Chloro-2-phenyl-propionamide, Ph - CH(Cl) - CH_2 - CO - NH - CH_2 - Ph, with potassium hydroxide.

In order to compare our compound with an authentic sample of N-benzylcinnamamide, we repeated the work of Dermer and King, and Kushner and coworkers. We now find that the

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⊕ Only Nitrogen values are reported for this compound by the authors.

compound obtained by the method of Kushner and coworkers, after crystallisation from ethyl alcohol, has m.p. 106-107° and does not depress the m.p. of our compound. The I R spectra are also identical.

However, the compound prepared by the method of Dermer and King,⊕ proved to be different. Actually this contained halogen and analysed for $C_{23}H_{25}Cl\,N_2O$. Chemically it reacted as an amine hydrochloride. (Eq.Wt.: Found=375, Calculated=380.94). On treatment with aqueous dilute sodium hydroxide, it liberated a base $C_{23}H_{24}N_2O$, m.p. 92-93° (from benzene-ether, Mol. Wt.: Found by Rast method = 337, Calculated = 344.44). The I R spectrum (1639 cm^{-1}) and P M R spectrum in CCl_4 (no other signals above δ=4.5 p.p.m. except those due to benzene protons) of the base showed the presence of only non-conjugated amide group, the P M R spectrum further revealing the presence of three monosubstituted benzene rings (δ=7 to 7.3 p.p.m., 15 H). A possible structure for the base could then be

$$Ph - CH_2 - NH - CH(Ph) - CH_2 - CO - NH - CH_2 - Ph$$

which is in agreement with further detailed analysis of the P M R signals as follows: $Ph - \underline{CH_2} - NH - CO$ (δ=4.17 p.p.m., doublet J=6 cps, 2 H); $-NH - \underline{CH}(Ph) - CH_2$ (δ=3.9 p.p.m., triplet J=6.5 cps, 1 H); $-NH - CH(Ph) - \underline{CH_2} - CO$ (δ=2.3 p.p.m., doublet J=6.5 cps further coupled slightly, 2 H);

⊕ It may be stated that in this preparation, we also obtained a small amount of N-benzylcinnamamide, m.p. 106-107° (from ethyl alcohol), identified by mixed m.p. and I R.

Ph - $\underline{CH_2}$ - NH - CH (δ=3.45 p.p.m., doublet J=2 cps, 2 H) and Ph - CH_2 - $\underline{NH}$ - CH (δ = 2.1 p.p.m., singlet which disappears on the addition of D_2O, 1 H).

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