SYNTHESIS OF N,N-DISUBSTITUTED AMINOACETOPHENONES

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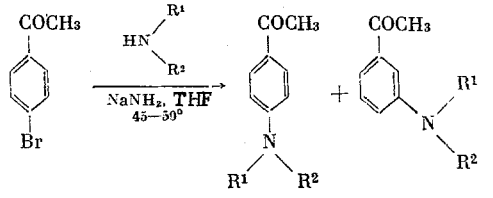
It has been shown that [1] p-bromophenylacetylene, like alkylated halobenzenes [2], reacts with secondary amines in the presence of sodamide to give aminophenylacetylenes. This paper examines the possibility of preparing N,N-dialkylaminoacetophenones by this reaction. These compounds would be useful as starting materials for the synthesis of the corresponding acetylenes [3], and of other compounds such as N,N-dialkylaminostyrenes which are used in the preparation of polymers [4].

For this purpose, p-bromoacetophenone (I) was reacted with several secondary amines



(I) (II)—(V) (VI)—(IX)

$R^1—R^2 = CH_2CH_2OCH_2CH_2$ (II), (VI); $R^1—R^2 = -(-CH_2-)_5-$ (III), (VII);

$R^1 = R^2 = C_2H_5$ (IV), (VIII); $R^1 = R^2 = C_4H_9$ (V), (IX)

Replacement of the acetylene group by acetyl accelerates the reaction considerably, since it is complete within 2-3 h as compared with the 30-35 h required in the case of p-bromophenylacetylene. The yields of products are 60-70%, since concurrent aldolone and crotonic condensations of the ketone take place. The ratio of the isomers varies, the m-isomers predominating (see Table 1).

The purity of the products after fractional distillation through a column was established by GLC, and their structures were established from their elemental analyses and spectra.

EXPERIMENTAL METHOD

GLC analyses were carried out on a 'Vyrikhrom' chromatograph with a flame-ionization detector. Column 2 m × 3 mm, 5% XE-60 on Chromatone, carrier gas nitrogen, 180-185°. Melting points were determined on a Kofler block.

TABLE 1. Preparative Conditions, Yields and Isomer Ratios for N,N-Dialkylaminoacetophenones

Amines*	Time, h	Reaction product	Yield, %	Isomer ratio, %	Amines*	Time, h	Reaction product	Yield, %	Isomer ratio, %
O⟨⟩NH	2	(VI) (II)	70	65† 35‡	$(C_2H_5)_2NH$	3	(VIII) (IV)	63	63† 37‡
⟨⟩NH	3	(VII) (III)	68	66† 34‡	$(C_4H_9)_2NH$	3	(IX) (V)	60	59† 41‡

*Starting material, p-bromoacetophenone.

† The IR spectra of the m-isomers exhibited bands at 785 and 690 cm^{-1} (1,3-disubstituted benzene ring).

‡ The IR spectra of the p-isomers exhibited bands at 820-830 cm^{-1} (p-substituted benzene ring), and the NMR spectra exhibited two doublets at 6.79 and 7.75 ppm (protons in the p-substituted benzene ring).

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Condensation of (I) with Secondary Amines. To sodamide (obtained from 20 g of Na and 500 ml of liquid ammonia) in 200 ml of THF was added 0.4 mole of the amine. The mixture was heated for 30 min at 35-40°, then a solution of 39.8 g (0.2 mole) of (I) was added with vigorous stirring. The reaction was followed by GLC, until all the (I) had disappeared. When the reaction was complete, the mixture was decomposed with water and extracted with THF. The combined extracts were passed through a thin layer of Al_2O_3 (grade II activity), the solvent removed, and the residue distilled in vacuo.

p-Morpholinoacetophenone (II), mp 96° (from ether). Found: C 70.01; H 7.14; N 7.00%.

m-Morpholinoacetophenone (VI), bp 133° (0.5) mm; n_D^{20} 1, 5816. Found: C 69.94; H 7.31; N 7.01%. $C_{12}H_{15}O_2$. Calculated: C 70.23; H 7.37; N 6.82%.

p-Piperidinoacetophenone (III), mp 89° (from heptane). Found: C 77.07; H 8.45; N 6.80%.

m-Piperidinoacetophenone (VII), bp 124-125.5° (0.5 mm); n_D^{20} 1.5774. Found: C 76.79; H 8.44; N 6.76. $C_{13}H_{17}NO$. Calculated: C 76.80; H 8.43; N 6.88%.

p-Diethylaminoacetophenone, (IV) mp 45-46° (from heptane). Found: C 75.20; H 9.05; N 7.54%.

m-Diethylaminoacetophenone, (VIII) bp 114.5-115° (1 mm); n_D^{20} 1.5622. Found: C 75.22; H 8.96; N 7.27%. $C_{12}H_{17}NO$. Calculated: C 75.34; H 8.96; N 7.32%.

p-Dibutylaminoacetophenone (V), bp 156° (0.5 mm); n_D^{20} 1.5666. Found: C 77.53; H 10.12; N 5.94%.

m-Dibutylaminoacetophenone (IX), bp 137-138° (0.5 mm); n_D^{20} 1.5365. Found: C 77.58; H 9.98; N 5.94%. $C_{16}H_{25}NO$. Calculated: C 77.68; H 10.19; N 5.66%.

CONCLUSIONS

Reaction of p-bromoacetophenone with secondary amines affords mixtures of N,N-disubstituted p- and m-aminoacetophenones, with a predominance of the m-isomers.

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