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PREPARATION OF NITRILE FROM PRIMARY AMIDE (I)

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The recent report by Blum and Fisher (I) for preparing of nitriles from sec. and pri. amides prompted us to publish in a very preliminary form the results of our work along somewhat similar line, which is now in progress in our hands.

Confronted with the problem of converting a certain acid amide into the corrseponding nitrile under such a mild working condition as to make the known conventional methods unavailable, we truned our attention to the recent papers by Lee (2) and Hooz et al.(3), in which were described how to chlorinate acids and alcohols by means of PPh_3 and CCl_4 to produce the corresponding chlorides. Thus when this method is applied to acid amide, the latter would furnish the corresponding chloro-imide, which should give rise to nitrile with loss of HCl. As a preliminaly $C_6H_5CONH_2$ dissolved in THF was heated with a mixture of PPh_3 and CCl_4 in a certain excess. Under an appropriate working condition, which follows, C_6H_5CN was directly obtained in fairly a good yield (4).
The reaction probably proceeds as follows:

$$PhCONH_2 + PPh_3 + CCl_4 \longrightarrow PhC(Cl){=}NH + O{=}PPh_3 + CHCl_3$$

$$PhC(Cl){=}NH + PPh_3 \longrightarrow PhCN + PPh_3{\cdot}HCl$$

General procedure. A solution of benzamide (1.21 g, 0.01 mole) dissolved in THF (15 ml, dried over Na and distilled) was added to a mixture of PPh_3 (5.24 g, 0.02 mole, commercial product used without purification) and CCl_4 (15 ml, dried over $CaCl_2$ and distilled) with stirring; a slight evolution of heat was observed. The whole was then warmed at 45-55° to give a clear solution, from which colorless solid* began to separate after about 15 min. Warmed altogether for 2 hrs and cooled. A residue obtained after evaporation of filtered solution was distilled to give a colorless liquid of bp.$_{24}$ 65-70°, yield 0.68 g (83.5%), which was identified with authentic benzonitrile through IR spectral data: ν_{max}^{Film} 2280 cm^{-1} (CN).

As is shown in the accompanying table added tertiary base to remove HCl from chloroimide, the would-be intermediate, caused dark coloration of the reaction solution and ended in an inferior recovery of the product. Amoung a limitted numbers of solvent for benzamide THF gave the best result, which together with PPh$_3$ may probably be playing a certain role in removing HCl from chloroimide, isolation of which however was impossible.

Table. Conversion of benzamide into benzonitrile by PPh$_3$ and CCl$_4$.

Solvent	PPh$_3$ / Amide	Base (1 mole)	Temp. (°C)	Time (hr)	Yield (%)
THF	1.05	None	r.t.(ca.25)	20	31.4
THF	1.05	Et$_3$N	45 - 55	20	51.1
THF	1.05	Et$_3$N	r.t.(ca.25)	94	10.1
THF	1.05	None	45 - 55	20	82
THF	1.05	None	ref.(ca.70)	1.5	71
Pyridine	1.05	None	40	20	7.6
Dioxane	1.05	None	45 - 55	20	57.7

Work is now in progress to find scope and limitation of this novel method of nitrile preparation and the results will be the subject of our forthcoming publication.

References and Footnote

*) May be O=PPh$_3$ and / or PPh$_3$·HCl but not yet determined.

(1) J. Blum and A. Fisher, Tetrahedron Letters, No. 23, 1963 (1970).

(2) J. B. Lee, J. Am. Chem. Soc., 88, 3440 (1966).

(3) J. Hooz and S. S. H. Gilani, Can. J. Chem., 46, 86 (1968).

(4) cf. L. Horner et al. who utilized PPh$_3$Br$_2$ and tert. amine in benzene solution for the same purpose. L. Horner, H. Oediger and H. Hoffmann, Ann. d. Chem., 626, 26 (1959).