

NOVEL SYNTHESIS OF NITRILES FROM AMIDES BY REACTION WITH  
PHOSPHOROUS TRIS(DIETHYLAMIDE)

Touru SODEYAMA\*, Mitsuo KODOMARI\*\*, and Kunio ITABASHI\*

\* Department of Industrial Chemistry, Faculty of Science  
and Engineering, Nihon University, Chiyoda-Ku, Tokyo

\*\* Shibaura Institute of Technology, Minato-Ku, Tokyo

Benzamide was allowed to react with phosphorous tris(diethyl-  
amide)  $P(\text{NEt}_2)_3$  under reflux in THF, and benzonitrile was obtained  
in good yield. Under the same condition, acetamide, nicotinamide,  
and thiobenzamide also reacted with  $P(\text{NEt}_2)_3$  to give the correspond-  
ing nitriles respectively. Similar reaction with triethyl phosphite  
did not occur.

Recently it was reported that the reaction of N-haloamide with triethyl  
phosphite gave a corresponding nitrile.<sup>1)</sup> It has also been known that amide  
is converted by the treatment with triphenylphosphine and tetrachloromethane  
into nitrile via chlorimide which was dehydrochlorinated by another triphenyl-  
phosphine.<sup>2)</sup> Several reports on the synthesis of nitriles by dehydration of  
amides have been presented,<sup>3)</sup> but it has not been known that amide is directly  
dehydrated to yield nitrile from the reaction with only trivalent phosphorus  
compound. In the present paper, we wish to report the novel synthesis of  
nitriles from the reaction of amides such as benzamide, acetamide and so on  
with  $P(\text{NEt}_2)_3$ .

The general procedure is as follows. A solution of  $P(\text{NEt}_2)_3$  ( 4.94 g,  
0.02 mol ) in THF ( 20 ml ) was added to a solution of benzamide ( 2.42 g,  
0.02 mol ) in THF ( 30 ml ) which was placed in a 100 ml-flask equipped with  
a reflux condenser, and the mixture was heated under reflux for 3 hr. The THF  
in the mixture was evaporated and the residue was distilled to give benzonitrile  
( 1.68 g, 89.6 % ), bp  $126\sim 128^\circ\text{C}/10$  mmHg, which was identified by comparison  
of its bp and IR spectrum with an authentic sample.

The result shows that amide reacts with  $P(\text{NEt}_2)_3$  in the 1 : 1 molar ratio.  
Diethylamine was also formed in almost the same molar amount with that of  
nitrile. The reaction was completed within 1 hour. From these results, the  
reaction is considered to proceed as follows.

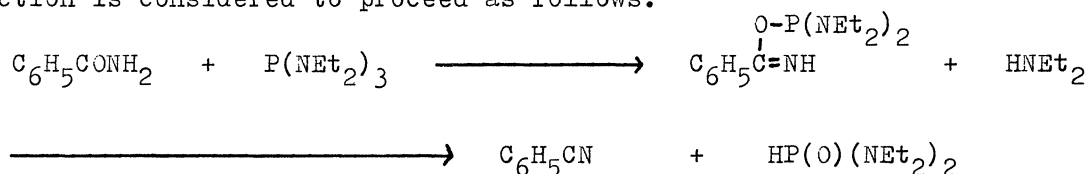


Table 1. Conversion of Amides into Nitriles by  $P(\text{NEt}_2)_3$  at  $70\sim 80^\circ\text{C}$ 

amide	mol ratio of $P(\text{NEt}_2)_3$ to amide	solvent	reaction time ( hr )	yield of nitrile ( % )
$\text{C}_6\text{H}_5\text{CONH}_2$	0.5	THF	3	32.6
$\text{C}_6\text{H}_5\text{CONH}_2$	1	THF	3	89.6
$\text{C}_6\text{H}_5\text{CONH}_2$	1	THF	1	82.4
$\text{C}_6\text{H}_5\text{CONH}_2$	2	THF	3	81.2
$\text{C}_6\text{H}_5\text{CONH}_2$	1	Benzene	3	70.0
$\text{C}_6\text{H}_5\text{CONH}_2$	1	Dioxane	3	23.0
$\text{CH}_3\text{CONH}_2$	1	THF	3	98.5
$\text{C}_5\text{H}_4\text{NCONH}_2^*$	1	THF	3	70.5
$\text{C}_6\text{H}_5\text{CSNH}_2$	1	Benzene	3	90.4

\* Nicotinamide

The influence of solvents was investigated, and the yield of nitrile decreased in the following order ( see Table 1 );

THF > Benzene > Dioxane

When triethyl phosphite was used, similar reaction did not occur and amide was almost recovered. In the case of acetamide and nicotinamide, the corresponding nitriles were obtained respectively. Thiobenzamide reacted with  $P(\text{NEt}_2)_3$  easily more than benzamide and was converted into the nitrile quantitatively.

#### REFERENCES

- 1) J.M.Desmarchelier and T.R.Fukuto, *J.Org.Chem.*, 37, 4218 (1972).
- 2) E.Yamato and S.Sugasawa, *Tetrahedron Lett.*, 4383 (1970).
- 3) D.J.Cram, *J.Amer.Chem.Soc.*, 83, 2354 (1961).  
S.E.Ellzey, *J.Org.Chem.*, 32, 846 (1967).

( Received April 11, 1973 )