

PHOSPHONITRILIC CHLORIDE II - REACTION WITH ACID HALIDES

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Although the reaction of phosphonitrilic chloride (I)¹ with nucleophiles such as amines and alcohols is well documented², little work has been published regarding the reaction of I with compounds containing carboxyl groups. Sonabe³ and Bezman and Reed⁴ reported that salts of carboxylic acids react with I to yield nitriles, anhydrides and acid chlorides. Cagliotti et al⁵ have prepared amides and hydrazides by the reaction of carboxylic acid salts, I, and the corresponding amine or hydrazine. More recently, Graham and Marr⁶ reported the conversion of amides to nitriles using I.

During our investigation into the scope of the reaction of I with compounds containing carboxyl groups, we have discovered that the title compound reacts with both aliphatic and aromatic acid halides to produce nitriles in excellent yields (see Table I).

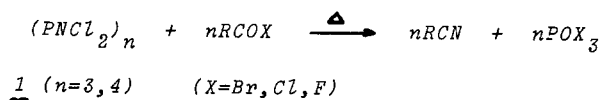


TABLE I

R=	Acid Halide ^a X=	Nitrile Yield(%) ^b	Reaction Time(hr) ^c	Initial Reaction Temp(°C)
phenyl	chloride	92	18	180
phenyl	bromide	95	16	196
phenyl	fluoride	49	16	165
p-chlorophenyl	chloride	83	12	195
p-methylphenyl	chloride	81	14	176
3-phenylcarbonyl chloride	chloride	88	24	190
3,5-dichlorophenyl	chloride	46	14	200
pentyl	chloride	95	9	160
ethyl	chloride	5	70	115
trichloromethyl	chloride	0	70	125

a. In all cases, an acid halide/(PNCℓ₂)₃ ratio of 3:1 was employed.

b. Melting points and boiling points were consistent with published data.

c. Reactants were heated continuously for the specified time.

This conversion of acid halides to nitriles is extremely facile forming easily distillable POX_3 as the only by-product and allows for the direct conversion of acid halides to nitriles under neutral conditions.

Although solvents such as chlorobenzene and dichlorobenzenes have been employed successfully in this reaction, ideally, the acid halides and P_4 are heated neat to a suitable temperature and by-product POX_3 collected continuously by distillation through a short vigreux column⁷. The nitrile is then obtained by direct distillation or crystallization from a suitable solvent system such as methanol/water or acetone/water which were found useful in this investigation. Using this technique, a 98% yield of 1,3-dicyanobenzene was obtained from isophthaloyl chloride within 4 hours at a constant reaction temperature of 240°C. The course of the reaction can be easily monitored using infrared or gas chromatographic techniques.

Unlike the reaction of P_4 with amides where the source of nitrilic nitrogen is the amide function⁶, the source of nitrogen in the reaction of P_4 with acid halides must be the phosphazene ring. This implies a much different mechanism than that proposed for the reaction of P_4 with amides⁶. It is hoped that studies now in progress will elucidate the mechanisms and define the scope of these reactions.

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REFERENCES

1. More properly 1,1,3,3,5,5-Hexachlorocyclophosphazatriene (P_4Cl_6) according to the nomenclature suggested by Shaw ((R.A. Shaw, B.W. Fitzsimmons and B.C. Smith, Chem. Rev., **62**, 247 (1962)). In this investigation, a mixture of phosphonitrilic chlorides was used consisting of ~75% P_4Cl_6 ($n=3$) and ~25% P_4Cl_8 ($n=4$).
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7. Using the method outlined in Table I, footnote c, the initial temperature decreased during the course of the reaction accompanied by a decrease in the reaction rate. Continuous distillation of by-product POX_3 as it is formed affords excellent yields in shorter reaction times at nearly constant reaction temperatures.