Insertion Reactions of P–N Compounds with Isocyanates

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INSERTION reactions of the kind

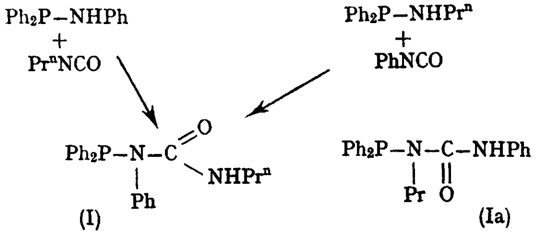
$$MX + A{=}B \rightarrow M\text{–}ABX$$

where M is a metal or metalloid, and X is an electronegative species such as N, O, S, Hal, *etc.*, have been widely investigated in recent years.[1]

We find that isocyanates give different products with tervalent P–N compounds depending on the structures of the reactants. In general, derivatives of secondary amines react endothermically to give mainly the isocyanate dimer or trimer together with some polymer, although an insertion product has been isolated from the reaction of bis(dimethylamino)phenylphosphine and phenyl isocyanate.[2]

Mukaiyama[3] has reported a ready de-oxygenation of isocyanates by the cyclic phosphoramidite, 2-phenyl-3-methyl-1,3,2-oxazaphospholidine, a reaction which again involves the preferential interaction of the oxygen and phosphorus atoms.

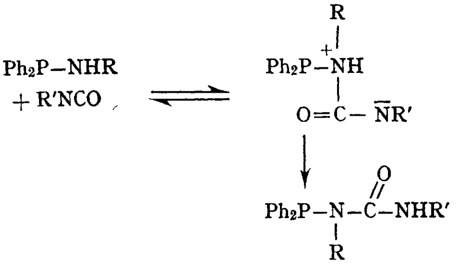
The reactions of tervalent phosphorus derivatives of primary amines with isocyanates are exothermic and no polymer is formed. Moreover the same product (I) is isolated from the reactions of phenyl isocyanate with *N*-n-propyldiphenylphosphinous amide and of n-propyl isocyanate with *N*-phenyldiphenylphosphinous amide.



(I) (Ia)

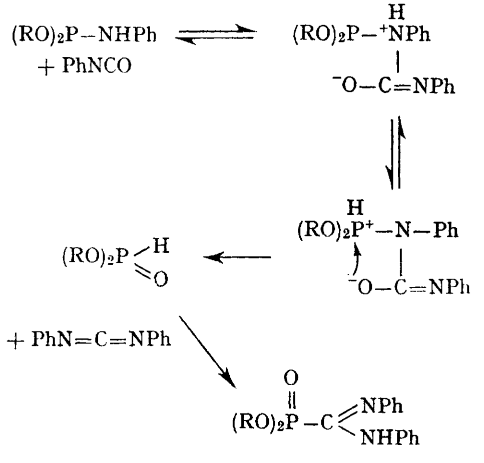
The structure (I) was indicated by n.m.r. studies although the isomer (Ia) cannot be definitely ruled out. Similar results were obtained for the compounds with Me in the place of the Prⁿ group.

It is clear that the hydrogen atom of the primary amino-compound greatly accelerates these reactions, which may be initially N–H insertions of the kind:



This product may rearrange to the thermodynamically stable isomer by a cyclic process similar to the mechanism we have suggested for various P–N insertion reactions.[4]

Phosphoramidites however react in a different way. Thus diethyl *N*-phenylphosphoramidite reacts with phenyl isocyanate to give diethyl-*NN*-diphenylamidinophosphonate (II) in 78% yield. This is probably formed by the interaction of the oxygen atom of the zwitterionic intermediate with the electrophilic phosphorus atom as follows:



(II)

This process involves proton transfer to phosphorus, the reaction then becoming of the conventional Staudinger–Wittig type.

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[2] R. H. Cragg and M. F. Lappert, *J. Chem. Soc.* (*A*), 1966, 82.
[3] T. Mukaiyama and Y. Yokota, *Bull. Chem. Soc. Japan*, 1965, **38**, 858.
[4] R. F. Hudson and R. J. G. Searle, *Chimia* (*Switz.*), 1966, **20**, 117.