

LIGAND EXCHANGE INVOLVING PHOSPHORANE INTERMEDIATES IN REACTIONS OF PHOSPHONIUM SALTS

DERIVED FROM TRIS-(DIMETHYLAMINO)PHOSPHINE

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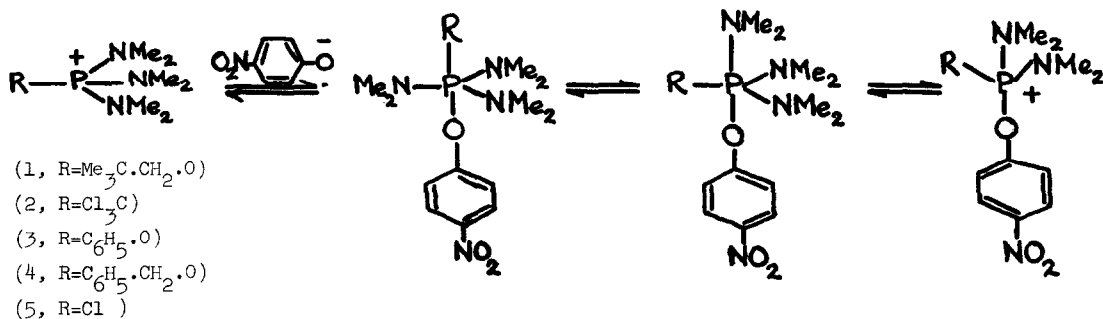
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In a recent investigation¹ we prepared alkyl-aryl ethers and thio-ethers by the interaction of potassium salts of phenols and thiophenols with alkoxy-tris(dimethylamino)phosphonium hexafluorophosphates in dimethylformamide (D.M.F.). We were surprised by the low yield (42%) of p-nitrophenyl-neo-pentyl ether. Other workers² have also reported reactions of a variety of nucleophiles with similar phosphonium salts in D.M.F.

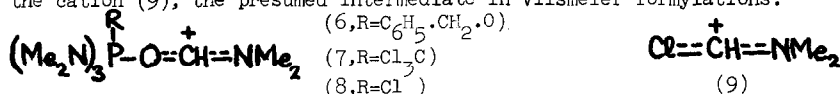
A re-investigation of the reaction of potassium p-nitrophenate with neo-pentyloxy-tris-(dimethylamino)phosphonium hexafluorophosphate (1) showed that another important product, p-nitro-N,N-dimethylaniline, was also formed, and was isolated in 29% yield. That the dimethylamino residue was derived from the phosphonium salt and not from the D.M.F. was established by the observation of the same products using tetrahydrofuran (T.H.F.) as the solvent. The absence of 4,4'-dinitrodiphenyl ether in these reactions is also significant. On the other hand we obtained p-nitro-N,N-dimethylaniline (23%) and 4,4'-dinitrodiphenyl ether (14%) in a reaction of potassium p-nitrophenate with trichloromethyl tris(dimethylamino)phosphonium hexafluorophosphate (2)³ in D.M.F. In this latter reaction we also detected chloroform and hexamethylphosphoramide by gas chromatography.

Clearly the p-nitrophenate anion not only displaces hexamethylphosphoramide from the phosphonium salt (1), but also attack on phosphorus must afford a relatively stable phosphorane. Loss of the dimethylamide anion then generates a new phosphonium salt which can then form the p-nitro-N,N-dimethylaniline by an S_NAr reaction. Ligand exchange by a direct displacement of the neo-pentyloxy anion or of the dimethylamide ion would be expected to lead to significant amounts of 4,4'-dinitrodiphenyl ether. This product was only observed in reactions of the phosphonium salt (2). A similar reaction involving ligand exchange was also observed in a reaction of potassium p-nitrophenate with phenoxy-tris(dimethylamino)phosphonium hexafluorophosphate (3). In this reaction p-nitro-N,N-dimethylaniline (15%) and 4-nitrodiphenyl ether (10%) were isolated.



Reactions of nucleophiles at phosphorus suggests that care should be taken to avoid the use of nucleophilic solvents such as dimethylsulphoxide⁴ and D.M.F. particularly when carrying out alkylations of weak nucleophiles. Thus in a reaction of the benzyloxy-salt (4) with *N*-methyl-aniline in D.M.F. we observed the formation of both *N*-benzyl-*N*-methylaniline and *N*-formyl-*N*-methylaniline. Other workers⁵ have shown that dealkylation of phosphonium salts such as (4) proceeds efficiently in solvents such as methylene chloride. We found that a reaction between *N*-methylaniline and the salt (4) in T.H.F. gave *N*-benzyl-*N*-methylaniline which was isolated in 79% yield. A reaction of *N*-methylaniline with the phosphonium salt (2) in D.M.F. gave *N*-formyl-*N*-methylaniline in 31% yield while using the chlorophosphonium salt (5)⁶ a quantitative yield of the formylated product was obtained. It is of interest to note that other workers have used D.M.F. in similar alkylation reactions of primary and secondary amines.⁷ In our hands the reaction of the salt (4) with aniline in D.M.F. affords a mixture of *N*-benzylaniline, *N*-formylaniline and *N*-benzyl-*N*-formylaniline.

The formylation reactions also implicate the intermediacy of phosphoranyl cations such as (6), (7), and (8), particularly since we have, thus far, not observed significant amounts of *C*-formylated products. For example the ready collapse of (8) would lead to hexamethylphosphoramide and the cation (9), the presumed intermediate in Vilsmeier formylations.



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