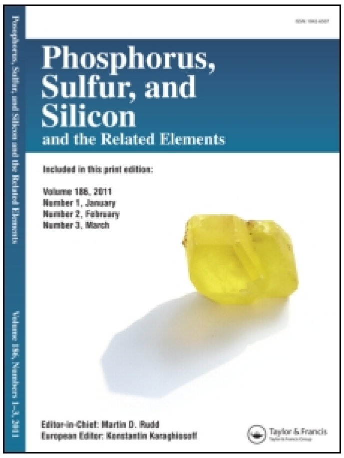

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New Chemistry of $ZP(RNCH_2CH_2)_3N$ Systems

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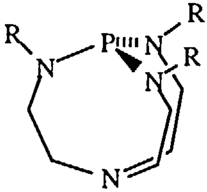
Compounds of the type $ZP(RNCH_2CH_2)_3N$ where Z = a lone pair are proving to be versatile reagents and catalysts for an ever increasing number of organic transformations. These properties stem from the extraordinary basicity and low nucleophilicity of the phosphorus atom when certain Z substituents induce the bridgehead nitrogen to transannulate (even partially) to the phosphorus. When Z = O, the phosphoryl oxygen also displays unusual basicity when transannulation is caused.

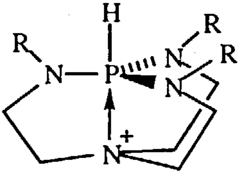
Keywords: nonionic base; catalysis; phosphorus; aminophosphine; azaphosphatrane

INTRODUCTION

Compounds of type **1** first reported from our laboratories[1] possess unusually high basicity and they protonate to give structures of type



	R	
1a	Me	**2a**
1b	*i*-Pr	**2b**



2. Thus **2a** has a pK_a in MeCN of 41[2] and **1b** has been shown to be somewhat more basic than **1a**.[3] The demonstrable partial flexibility toward transannulation appears to play an important role in the catalytic properties of compounds such as **1a** and **1b**.[4] Here we outline part of a still-growing list of useful organic transformations facilitated by **1a** (commercially available from Strem) or **1b**, acting as either a stoichiometric base or as a catalyst.

STOICHIOMETRIC REACTIONS

Although nonionic superbases of type **1** are 17 orders of magnitude more basic than DBU, deprotonation is often kinetically slow. Because MeCN ($pK_a = 25$[5]) is partially deprotonated by **1**,[3] we often take advantage of the strong nucleophilicity of the $^-CH_2CN$ anion which becomes the active deprotonation agent.[6]

Since we have already published on the stoichiometric use of **1a** in the synthesis of the separate enantiomers of a fluorescence agent **3**,[7] porphyrins,[8] olefins (via alkyl halide dehydrohalogenations),[9] and mono-alkylation of active methylene systems,[10] we center our attention here on some of the emerging applications.

Wittig Syntheses

Both **1a** and **1b** form ylides and although the acyclic analogue $P(NMe_2)_3$ also functions in this manner, E/Z ratios of alkenes formed upon reaction of ylides of **1a** with aldehydes are almost exclusively E. Compound **1a** also serves as an efficient base in facilitating Wittig and Wittig-Horner reactions.

Stille Syntheses

Here **1a** appears to be a reagent that reacts with the dba ligand [dba = (PhCHCH)C=O] thus creating a more naked palladium for catalysis. Yields are better or very competitive compared with reactions in which PPh_3, $P(2\text{-furyl})_3$ or PAs_3 are used as ligands.

CATALYTIC REACTIONS

Because of space limitations, we do not discuss here the advantageous catalytic use of **1a** in alcohol acylation with anhydrides, alcohol protective silylation, isocyanate trimerization[4] and α,β-unsaturated nitrile synthesis.

Transesterification

Compounds **1a** and **1b** catalyze the transesterification of carboxylic acid esters with high selectivity and in excellent yields at 25 °C. Substituents such as epoxides, carbamates, acetals and acetylenes are tolerated. N-protected peptide esters cleanly transesterify without significant racemization, making this methodology highly useful.

Deprotection of Acylated Alcohols

This important transformation was effected in virtually quantitative yields for primary, secondary and tertiary alcohols using **1a** as a catalyst in methanol at room temperature.

β-Nitroalkanol Synthesis

Compounds of the type $R_2C(OH)CH_2NO_2$ are important and versatile intermediates in the synthesis of nitroalkenes, 2-amino alcohols and α-nitro ketones. In the presence of $MgSO_4$ as a carbonyl activator, **1a** and **1b** catalyze the reaction of a wide range of aldehydes and ketones at room temperature to give the corresponding title products in excellent yields.

Michael Additions

α,β-Unsaturated ketones and esters readily react with MeOH, $NCCH_2CO_2Et$ or $MeNO_2$ to give the corresponding Michael Addition product in 88-98% yields. Dimers catalytically formed in 96-98% yield from $R^1R^2C{=}CCH_2CN$ in the presence of **1a** or **1b** are useful intermediates in copolymerization reactions.

β-Hydroxy Nitrile Synthesis

Aliphatic aldehydes and ketones react with MeCN to form the valuable intermediates $R^1R^2C(OH)CH_2CN$ under mild conditions in the presence of catalytic amounts of **1a** or **1b** using $MgSO_4$ as a carbonyl activator. Thus catalysts of type **1** are superior for this reaction despite the use of carbonyl substrates that are not easily enolized.

α,α-Dicyano-α,β-Olefin Synthesis

Aromatic aldehydes, ketones and secondary aldehydes react with malonitrile to give their corresponding $R^1R^2C=C(CN)_2$ derivatives in 98-99, 84-93 and in 98% yields, respectively, at room temperature in the presence of 5 mol % of **1a** or **2a**$[CH(CN)_2]$. Thus **1a** actually functions as a procatalyst and the $^-CH(CN)_2$ anion is the catalytic species.

During this lecture, additional examples of reactions catalyzed by **1a** and **1b** will be illustrated and reaction pathways will be proposed. Some unusual reactions of the title system wherein Z = O will also be discussed.

It is noteworthy that **1a** has been found by the Du Pont Company[12] and by the US Department of the Navy[12] to have interesting uses.

Acknowledgments

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