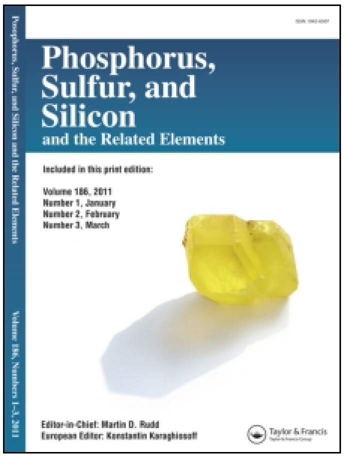

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Dioxyphosphoranes, an Emerging Class of Versatile Reagents for Organic Synthesis

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DIOXYPHOSPHORANES, AN EMERGING CLASS OF VERSATILE REAGENTS FOR ORGANIC SYNTHESIS

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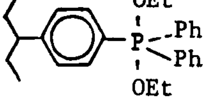
Abstract Several σ-dioxyphosphoranes have been prepared and their structural characterizations using NMR techniques support the trigonal bipyramidal conformer as the most stable for the acyclic phosphoranes. Their utility in smooth conversions of hydroxylated substrates [HO(CHR)$_n$XH, n=2-6; X=O,S,NH] to the corresponding X-heterocycles is documented.

INTRODUCTION

Popular preparative routes to reactive σ-heterophosphoranes involve "redox" reactions between alkyl, aryl, or aminophosphines (and phosphites) and compounds possessing labile heteroatom-heteroatom bonds (e.g., -O-O-, -O-S-, -S-S-, -S-N-, Cl-Cl, -N=N-, etc.) as well as carbon-halogen bonds.[1] Other σ-oxyphosphoranes are conveniently prepared by reaction of trivalent phosphorus compounds with o-quinones and α-diketones, the equivalent of a [4+2] cycloaddition reaction.[2] Collectively, these "organophosphorus reagents" have been effective in promoting mild synthetic transformations such as substitution and condensation reactions. The principal focus of this manuscript details the preparation and characterization of new dioxyphosphoranes (1-3) and emphasizes development of a versatile synthetic methodology.



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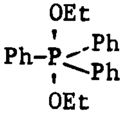

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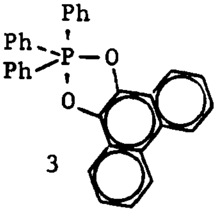

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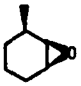
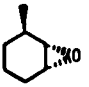
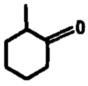
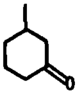
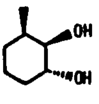
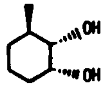
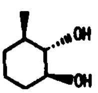
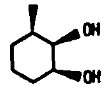
A. Diethoxydiphenylpolystyrylphosphorane (1). Polymeric dioxyphosphorane 1 is easily prepared by oxidative addition of diethyl peroxide to diphenylpolystyrylphosphine cross-linked with 2% divinylbenzene in anhydrous toluene under N_2.[3] The ^{31}P resonance for 1 (δ -55.3) is similar to that exhibited by diethoxytriphenylphosphorane (2) where the trigonal bipyramidal conformer having both ethoxy groups in the apical array is preferred.

Yields for conversion of diols to cyclic ethers with 1 are high and 1 is particularly useful in converting unhindered 1,2-, 1,4-, and 1,5-diols to epoxides (70-99%), tetrahydrofurans (95-99%) and tetrahydropyrans (85%), respectively.

The stereospecific conversion of meso-1,2-diphenylethane-1,2-diol to trans-stilbene oxide (99%) is in accord with the energetically favorable "3-exo-tet" cyclization with inversion of stereochemistry at the displacement terminus. Regioselective cyclodehydration of (S)-(+)-phenylethane-1,2-diol with 1 is evident from examination of the enantiomeric mixture of styrene oxides rich in the (S)-(+)-1,2-epoxyethane enantiomer (68%ee). This %ee translates into 85% retention of stereochemistry at C2 in the styrene oxide. By contrast, $Ph_3P(OEt)_2$ converts (S)-(+)-phenylethane-1,2-diol to racemized (±)-styrene oxide.[4]

B. Diethoxytriphenylphosphorane (2). We have examined the effect of methyl substitution on the regioselective phosphoranylation and cyclodehydration/oxidative rearrangement of trans/cis diastereomers of 3-methylcyclohexane-trans-1,2-diol and 3-methylcyclohexane cis-1,2-diol with 2.[5] The diastereoisomeric trans-1,2-diols undergo cyclodehydration with 2 to give a mixture of cis and trans-3-methylcyclohexene oxides. The ratio of epoxides appear dependent on the energetic constraints with the chain and twist boat transition states. On the other hand, the diastereomers of 3-methylcyclohexane-cis-1,2-diol react with 2 to afford stable 1,3,2-dioxaphospholanes (at 25 °C). These 1,3,2-dioxaphospholanes

TABLE 1. $Ph_3P(OEt)_2$ Promoted Cyclodehydration/Rearrangement of Diastereomeric Methyl Cyclohexane-1,2-diols.

DIOL			DIOL		
	78.8 %	21.2 %		70.4 %	29.6 %
	27.1	72.9		42.5	57.5

undergo oxidative rearrangement under thermolysis conditions to afford the isomeric 2- and 3-methylcyclohexanones via 1,2-hydride shifts (Table 1).

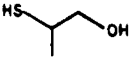
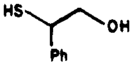
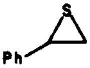
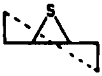
Cyclodehydration of optically active 2-substituted ß-aminoalcohols with 2 occurs with the expected retention of configuration at the amino carbon (C2). For example, enantiomerically homogeneous (S)-(+)-2-amino-1-propanol and (S)-(-)-2-amino-3-phenyl-1-ethanol, from borane reduction (BH_3, THF, 25°C, 24 h) of L-alanine and L-phenylalanine, respectively, undergo cyclodehydration (85%) with an equivalent of 2 to afford enantiomerically pure (S)-(+)-2-methylaziridine and (S)-(-)-2-benzylaziridine, respectively.[6]

C. 2,2,2-Triphenyl-4,5-(2',2"-biphenyleno)-1,3,2-dioxyphospholane (3). $Ph_3P(OEt)_2$ reacts with mercaptoalcohols to afford mainly ethylthioalcohols at ambient temperature. Here, the highly nucleophilic thiolate anion attacks ethoxytriphenylphosphonium ion in an Arbuzov fashion displacing Ph_3PO.

$$2 + HS(CH_2)_nOH \longrightarrow [Ph_3\overset{\oplus}{P}\text{-}OEt\ {}^{\ominus}S(CH_2)_nOH] \longrightarrow EtS(CH_2)_nOH$$

The use of dioxaphospholane 3, prepared from a [4+2] cycloaddition between triphenylphosphine and phenanthrenequinone, circumvents this problem and allows for smooth conversion of mercaptoalcohols to cyclic sulfides in good to excellent yields (Table 2).

TABLE 2. Cyclodehydration of Mercaptoalcohols with 3.

MERCAPTOALCOHOLS	SULFIDES	YIELD (%)
		98
		85
		98
		71
		80
		85
		84

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