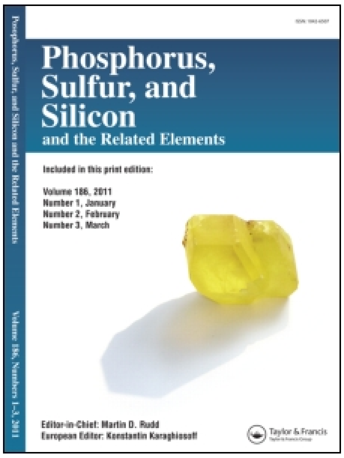

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Variations in properties of bridged phosphorus heterocycles

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VARIATIONS IN PROPERTIES OF BRIDGED PHOSPHORUS HETEROCYCLES

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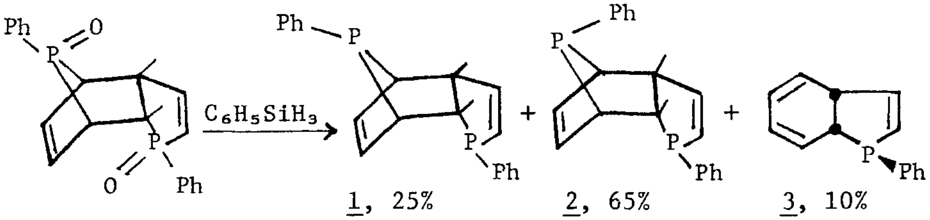
Abstract Highly strained cyclic phosphine oxides can give anomalous results (inversion, C-P cleavage) on deoxygenation with $HSiCl_3$ or $C_6H_5SiH_3$. Use of the pyridine complex of $HSiCl_3$ generally overcomes these difficulties, and a number of strained phosphines were prepared. Definite trends in ^{31}P NMR shifts among saturated and unsaturated structures have been observed. Phosphines in the 7-phosphanorbornene system are particularly prone to form P(V) cycloadducts, which then decompose by a reverse McCormack-type of reaction. The reactivity is so high that even dienes form adducts with these phosphines.

INTRODUCTION

When a phosphorus atom bridges a small ring, the C-P-C bond angle can be severely reduced from the values for unperturbed hybridization. Unsaturation may also be present in such systems and presents the possibility of orbital interactions. These effects are quite strong in the 7-phosphanorbornene system, and bring about quite unusual properties. Thus, in our earlier work[1], it was shown that phosphines in the syn-7-phosphanorbornene system, as found in phosphole dimers, have the most downfield ^{31}P NMR signals ever recorded for this class, and are isomerized to the anti isomers by direct interaction with alcohols or water. The oxides of phosphole dimers also have shifts at abnormally low field. Angle strain in these[2] and related[3] bridged compounds allows oxygen insertion into a C-P bond, in Baeyer-Villiger fashion, on reaction with peracids. The phosphole oxide dimers also give anomalous results[1a] on deoxygenation with silanes; with trichlorosilane or phenylsilane, the deoxygenation of phosphine oxides usually occurs with retention of configuration, but with the dimers inversion can predominate, and is also accompanied (or overwhelmed) by ejection of the bridging P grouping in a retrocycloaddition reaction, as in the example below (with $HSiCl_3$, only 3 was obtained).



We have studied the possibility of the appearance of some of these anomalies in other strained phosphorus heterocycles (Table I). During this study, a new reaction has been observed; dienes react directly with phosphines of the 7-phosphanorbornene system to give cycloadducts (unstable).

SILANE REDUCTIONS OF STRAINED PHOSPHINE OXIDES

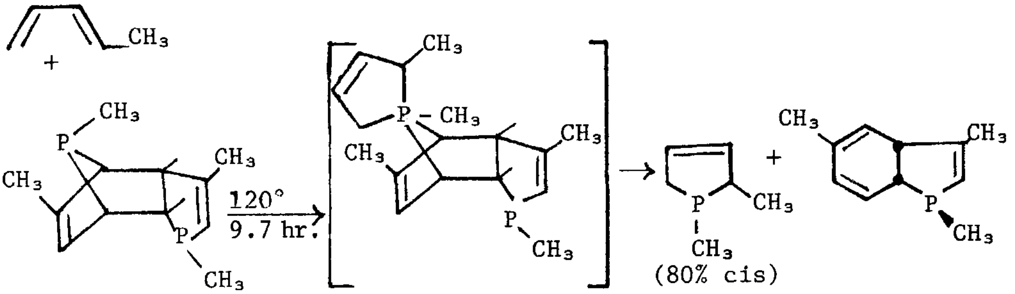
The difficulties with $HSiCl_3$ can be largely eliminated if it is used in the form of its pyridine complex, $HSiCl_3 \bullet 2C_5H_5N$. This allowed the production of diphosphines from the phosphole dimers (e.g. 1) in over 80% yield. The anomalous reduction with $HSiCl_3$ can be attributed to a diversion from the usual 4-center mechanism[4] to one involving a pentacoordinate intermediate that can undergo retrocycloaddition to give a diene unit and a P(III) fragment. The pyridine complex apparently functions by a mechanism that avoids the formation of P(V) intermediates. Experimental results from reductions with various phosphine oxides are summarized in Table I. Conclusions are: (1) in the phosphabicyclo[n.2.1]alkene system, only the [2.2.1] system reacts abnormally; with n = 3 or 4, ring strain is diminished and retention is observed, (2) saturated strained systems may also give anomalous results with $HSiCl_3$, including complete inversion (forming 5b from oxide 4), partial inversion (a mixture of syn, anti isomers from 8), or even degradation, as for 6, (3) when anomalies develop, they can be eliminated by use of $HSiCl_3 \bullet 2C_5H_5N$ except for the specially strained 4 where some inversion persists.

^{31}P NMR SHIFT EFFECTS

The norbornene framework is now known to cause deshielding of many nuclei when present at the 7-position, an effect attributed to interaction of the sigma orbital at this position with the π-bond[5]. The very large deshielding of one ^{31}P nucleus in the phosphole dimers (e.g., 1 δ + 114.2 and +15.7; 2 δ +48.5 and +11.4) may be explained on this basis. The pronounced difference (generally 60-70 ppm) between syn and anti isomers is now tentatively attributed to shielding that is superimposed on the anti isomer. This is thought to arise from a second orbital interaction, repulsion between the lone pair and the π-bond as found for 7-azanorbornenes[6]. These orbital interactions might be expected to be influenced by changing the rigidity and shape of the bicyclic framework, and when the saturated bridge is lengthened by one carbon as in 11-13, and then by another to give 15-17, pronounced and progressive upfield shifts occur. The syn, anti difference is maintained only in 11-13. Among saturated compounds, chemical shifts tend to be on the downfield side of the range set by acyclic tertiary phosphines (-62 to +60), but are not abnormal.

CYCLOADDITIONS WITH PHOSPHINES

The phosphole dimers reacted immediately with phenanthraquinone at 30°, giving a cycloadduct specifically at the bridging P. The half-life of the adducts from syn isomers was only a few minutes, but ^{31}P NMR spectra could be obtained before their decomposition by retrocycloaddition. For example, the adduct from 1,3-dimethylphosphole dimer had δ +25.0 and +17.0 (J_{PP}=24.4). The adducts from anti isomers are less crowded and have longer half-lives (several hours). The strained phosphabicyclo[3.2.1]octene derivatives 11 and 13 also formed adducts rapidly, but these showed little tendency to decompose at 30°. The great reactivity at the bridging phosphorus, attributed to the strain relief involved in achieving the P(V) state with the opportunity for a smaller bond angle (90°, apical-equatorial) was observed in another, unprecedented reaction. The P-methyl dimers reacted with dienes at 120° to give exclusively the products of retrocycloaddition of a P(V) adduct, as in the example below.



In the absence of the diene, no decomposition of this dimer occurred. The less strained phosphines 11, 13, and 18 did not react with dienes under these conditions.

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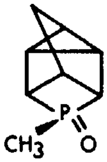
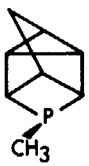
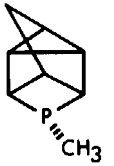
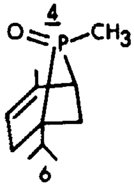
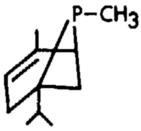
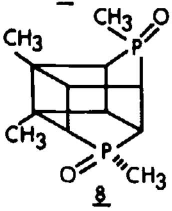
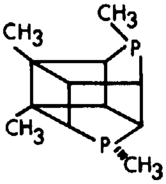
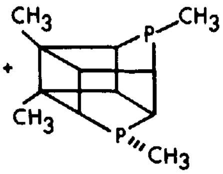
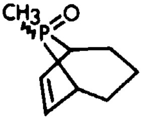
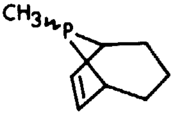
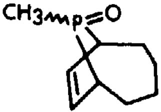
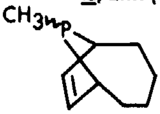
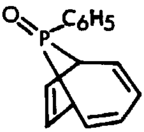
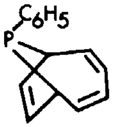
Table 1. Silane reduction of strained phosphine oxides.

Oxide	Reduction with $HSiCl_3$[a]	Reduction with $HSiCl_3 \cdot 2C_5H_5N$[a,b]	$\delta^{31}P$
 4	 +  5a (nil) 5b (100%)	5a + 5b, 2:1	5a, +47.4 5b, +39.5
 6	(complex mixture)	 7 only	7, +25.5
 8	 +  9a (50%) 9b (50%)	9a only	9a, −3.4 9b, −15.1, −17.2 ($^3J_{PP} \sim 0$)
 10, syn (32%) 12, anti (68%)	 11, syn (31%) 13, anti (69%)	11 (32%), 13 (68%)	11, +49.7 13, −18.2
 14, syn (80%) 16, anti (20%)	 15, syn (80%) 17, anti (20%)	15 (80%), 17 (20%)	15, −8.2 17, −8.2
 18	 19	19	19, −79

[a] 3-5 equivalents, refluxing benzene, 1-2 hr. [b] with excess pyridine.