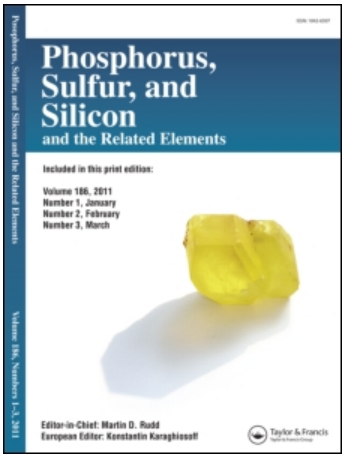

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Preparation, Reactions, and NMR Studies of 4-Methyl-4-Phospha-Tetracyclo [3.3.0.0^{2,8}.0^{3,8}] Octane 4-Oxide and Derivatives

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PREPARATION, REACTIONS, AND NMR STUDIES OF 4-METHYL-4-PHOSPHA-TETRACYCLO [3.3.0.0^{2,8}.0^{3,6}] OCTANE 4-OXIDE AND DERIVATIVES

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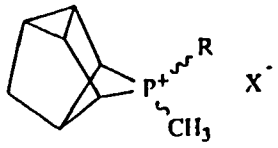
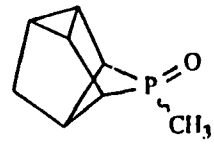
The title compound which we[1] and others[2] have previously synthesized has now been extensively investigated. The tetracyclic phosphonium chloride 1 was prepared by treatment of norbornadiene with CH_3PCl_2 at 65-80°C for one week. Treatment of 1 with $AlCl_3/CH_2Cl_2$ gave 2. Direct or "inverse" addition of water to 2 dictated the stereochemistry of the oxide 3. Stereoassignments of 3 were made based on lanthanide shift -- ^1H and ^{13}C nmr studies studies. Extensive 2-D nmr studies (HETCOR, COSY) and triple irradiation experiments enabled chemical shift and coupling constant assignments.

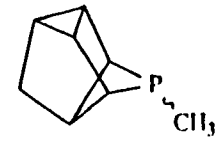
The stereochemistry of conversion of 3 to 4 can be controlled by selection of the reducing reagent. Various derivatives of 4 (sulfide, selenide and salts) were then prepared.

An extensive low-temperature ^{31}P nmr study was made by treatment of the salt 5 with CH_3Li at -70°C. The initial phosphorane (P^V) intermediate (^{31}P=-100 ppm) gave rise to several ring-opened species as the temperature was increased. Structures consistent with these results are proposed.

Detailed ^1H, ^{13}C, and ^{31}P nmr data as well as studies of ring opening reactions will be presented.







1 R=Cl, X=Cl
2 R=Cl, X=$AlCl_4$
5 R=CH_3, X=Br

3

4

1) S.E. Cremer et al., J.C.S. Chem. Commun., 374 (1974)
2) M. Green, J. Chem. Soc., 541 (1965)