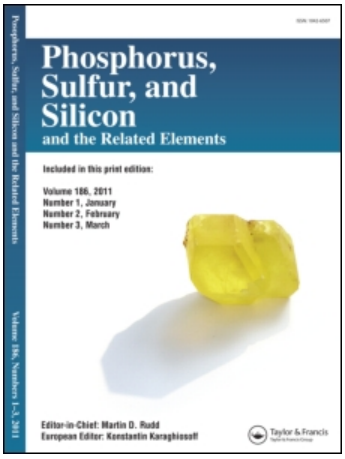

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Synthesis and Stereochemical Studies of Derivatives of 1,4-Dimethyl-2-phosphabicyclo[2.2.1]heptane

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Synthesis and Stereochemical Studies of Derivatives of 1,4-Dimethyl-2-phosphabicyclo[2.2.1]heptane

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1,4-Dimethyl-2-phenyl-2-phosphabicyclo[2.2.1]heptane 2-oxide 1 was prepared by the reaction of 2,5-dimethyl-1,5-hexadiene with $PhPCl_2$-$AlCl_3$; stereoassignments of the exo and endo isomers were established by ^{13}C NMR spectroscopy (using lanthanide shift reagents) and by x-ray crystal structures. The isomers of 1 were separately reduced (phenylsilane) to give the phosphine derivative; in turn the phosphines were thermally equilibrated at 190°C to give a predominance (70%) of the exo-phenyl isomer.

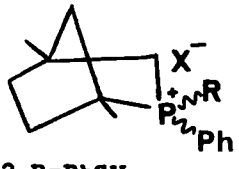
The phosphines were converted to the salts 2-4 for stereochemical investigation. For example, aqueous, alkaline hydrolysis of the benzylphenylphosphonium salt 2 gave 1 with retention of configuration. The isomeric methylphenylphosphonium salts 3 equilibrated under basic conditions prior to oxide formation. Reaction of 1 with $(CH_3)_3O^+ BF_4^-$ gave the salt 4 with retention. Hydrolysis of either isomer of 4 with ^{18}O enriched water gave 1 with retention, but without ^{18}O incorporation; thus, C-O bond cleavage occurred. Hydrolysis of the endo-methoxy salt 4 with $Na^{18}OH$ gave retention of configuration with complete ^{18}O incorporation; the exo-methoxy isomer gave partial ^{18}O incorporation (30-60%) with retention of configuration.

In addition to 1, the acid chloride 5 was prepared by treatment of the 1,5-hexadiene with $PCl_3/AlCl_3$ to give an 85:15 isomer mixture (exo-Cl : endo-Cl). Stereoassignments were based on ^{13}C nmr (lanthanide shift reagent) data. Reaction of 5 with PhLi gave 1 with retention. Reaction of 5 with alkoxides gave the phosphinate esters with retention. The methyl phosphinate ester was treated with $NaOCD_3$-CD_3OD to give the phosphinic acid (no prior CD_3O- exchange). Compound 6 was prepared in two steps from 5; reaction with PhLi gave the phenyl-phosphine with inversion.

^{13}C nmr data of 18 derivatives of the title compound have been recorded; x-ray crystal structures of 1 and 2 will be shown.

1 R=Ph

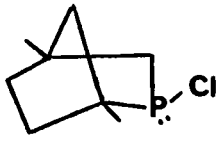
5 R=Cl



2 R=$PhCH_2$

3 R=Me

4 R=MeO



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