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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 $\text{PhPCl}_2\text{-AlCl}_3$; 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 $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$ 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 $\text{PCl}_3/\text{AlCl}_3$ 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 $\text{NaOCD}_3\text{-CD}_3\text{OD}$ 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.

