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Diastereoselective Synthesis of Phosphines and Phosphoranes using Fluorinated Acetylacetones

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A two step formal insertion of 1,1,1,5,5,5-hexafluoro- (1) and 1,1,1-trifluoropentane-2,4-dione (2) into the P-H bonds of phosphane gave the primary α -hydroxyphosphanes, precursors for 2-phospha-6-oxa-9-oxabicyclo[3.3.1]-nonane and 2,4,8-trioxa-6-phospha-adamantane, both formed diastereospecifically. The molecular structures of the two latter compounds were established by single-crystal X-ray structure analysis. Compound 1 reacted diastereospecifically with phosphonous acid dichlorides, RPCl_2 ($\text{R} = \text{Me}, \text{Et}, i\text{Pr}, t\text{Bu}, \text{Me}_3\text{SiCH}_2, \text{PhCH}_2, \text{Ph}$) to give in a concerted mechanism thermally stable tricyclic $\lambda^5\sigma^5\text{P}$ phosphoranes containing two five- and one six-membered ring. In one case hydrolysis gave 3,5-dihydroxy-2-oxo-1,2 $\lambda^5\sigma^4$ -oxaphospholane, whereas methanol added to the double bond in the six-membered ring furnishing two isomeric phosphoranes. When 2 was reacted with RPCl_2 ($\text{R} = \text{Et}, \text{Me}_3\text{SiCH}_2, \text{PhCH}_2, \text{Ph}$), diastereomerically pure regioisomeric phosphoranes were obtained. The solid state molecular structures of three $\lambda^5\sigma^5\text{P}$ species exhibited two oxygen atoms in the axial position of a slightly distorted trigonal-bipyramidal geometry at phosphorus.