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SYNTHESES OF FIVE-MEMBERED HETEROCYCLES CONTAINING BOTH RING AND SIDE-CHAIN PHOSPHORUS ATOMS

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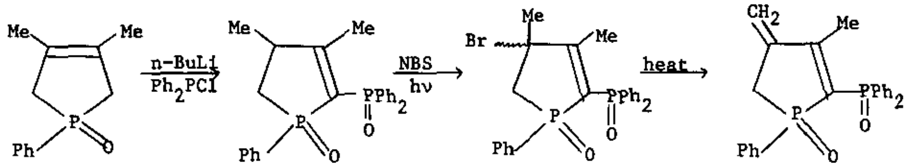
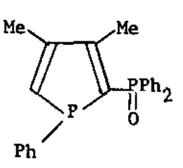
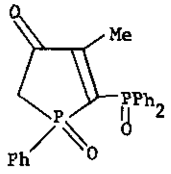
A preliminary investigation of synthetic approaches to 2-diphenylphosphino-substituted 2-phospholene and phosphole derivatives has been carried out. These are of interest for electronic reasons (possible aromatic character of phospholes), NMR spectroscopic reasons (e.g. P-P and P-C coupling), and as precursors for both organophosphorus synthetic studies and inorganic coordination studies. The basic synthetic sequence follows the route I→II→III→IV. The synthesis of compound II is stereospecific and only one stereoisomer is obtained whereas both possible stereoisomers of III are obtained. The reaction III→IV gives exclusively exocyclic dehydrobromination. Even reduction ($HSiCl_3$) of the ring P=O bond of IV leaves the exocyclic methylene group intact whereas significant aromatic character in the isomeric phosphole system V would be expected to lead to isomerization. Compound IV is of limited stability in that even in the solid state under refrigeration in the dark it oxidizes slowly (ca. 6 weeks) to give the ketone VI. This appears to be a free-radical catalyzed oxidation (analogous to the oxidation of styrene to benzaldehyde) since treatment of IV with trace amounts of AIBN in benzene at 60° exposed to air leads to rapid oxidation of IV to give VI and both possible stereoisomers of the epoxide VII. Both isomers of VII may also be obtained from IV by oxidation with *m*-chloroperbenzoic acid. The results of AIBN catalyzed oxidations of related systems containing a methylene group exocyclic to the heterocyclic ring (e.g. VIII) will be reported as will the behaviour of the ketone VI towards various reducing agents and the phosphorus and carbon NMR spectroscopic properties of all new compounds discussed.



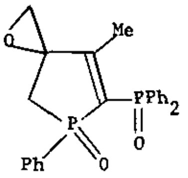
I II III IV



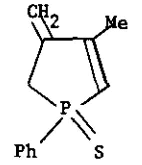
V



VI



VII



VIII