

TETRAHEDRON REPORT NUMBER 186

ORGANOTHIOPHOSPHORUS REAGENTS IN ORGANIC
SYNTHESISR. A. CHERKASOV, G. A. KUTYREV and A. N. PUDOVIK*
Kazan State University, Kazan, U.S.S.R.

(Received in UK 9 May 1984)

CONTENTS

1. Phosphorus Thioacids and their Derivatives	2568
1.1. O,S-Interchange reactions	2568
1.2. Reactions with compounds containing multiple carbon-nitrogen bonds	2572
1.3. Other synthetic uses of phosphorus thioacid derivatives	2578
2. Combined Reagent—Triphenylphosphine—thiocyanogen	2582
3. Lawesson's Reagent (LR)	2588
3.1. Reactions with carbonyl compounds	2589
3.1.1. Ketones	2589
3.1.2. Esters of carboxylic and thiocarboxylic acids	2592
3.1.3. Amides of carboxylic acids	2594
3.1.4. Hydrazides of carboxylic acids	2598
3.2. Synthesis of sulfur-containing heterocyclic compounds	2601
3.3. Synthesis of phosphorus- and sulfur-containing heterocycles	2608
3.4. Reactions with compounds containing element-oxygen bonds	2618

Organophosphorus compounds are widely used in organic synthesis.¹ The use of phosphorus ylides—Wittig reagents—for the synthesis of unsaturated systems is well known.^{1,2} Various derivatives of pentacoordinated phosphorus have served as valuable initial substances in the molecular design of bioorganic structures.^{3,4} One can hardly overestimate the importance of phosphine,⁵ phosphoryl,⁶ and phosphacyclane⁷ metal complexes in the development of the chemistry of organometallic compounds and metal-complex catalysis. Great progress has been made in the application of combined reagents—tertiary phosphine, di- or polyfunctional organic compounds—for the functionalization of organic substrates.^{8,9}

Inorganic phosphorus compounds have found an extensive application in synthetic organic chemistry for the purposes of halogenation, thionation and in other preparative problems.^{10,11} The most frequently used thionating agent, mainly for carbonyl-containing substrates, is phosphorus pentasulfide, P₄S₁₀.¹²

In recent years a new area of intensive development has appeared in the application of organophosphorus compounds in organic synthesis. This involves the use of organothiophosphorus reagents which not only introduce a sulfur atom into organic substances but also permit other synthetic operations. As a rule, such processes are characterized by a high regio- and, sometimes, also stereoselectivity, and almost in all cases by exceptional efficiency: the yields of required products are usually from satisfactory to quantitative.

In the present review an attempt has for the first time been made at summarizing and systematizing the methods of using in organic synthesis the new thionating and functionalizing reagents: (i) derivatives of phosphorus thio- and dithioacids, (ii) triphenylphosphine-thiocyanogen (TPPT) combined reagent and (iii) *p*-methoxyphenylthiophosphine sulfide dimer (Lawesson's reagent—LR).

The driving force of many of these reactions involving organothiophosphorus reagents is the formation of stronger P=O and P—O bonds instead of labile P=S and P—S bonds.¹³ An important contribution to the reaction energetics is made by the transformation of intermediate 4-membered heterocycles or intermediate phosphorane structures into more stable 6-membered cyclic or acyclic