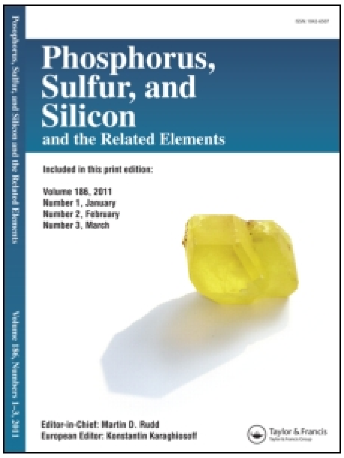

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Some uses of phospholes in general synthetic organophosphorus chemistry

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To cite this Article Mathey, F.(1983) 'Some uses of phospholes in general synthetic organophosphorus chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 18: 1, 101 — 104
To link to this Article: DOI: 10.1080/03086648308075977
URL: http://dx.doi.org/10.1080/03086648308075977

Phosphorus and Sulfur, 1983, Vol. 18 pp. 101-104
0308-664X/83/1801-0101/$18.50/0

SOME USES OF PHOSPHOLES IN GENERAL SYNTHETIC ORGANOPHOSPHORUS CHEMISTRY

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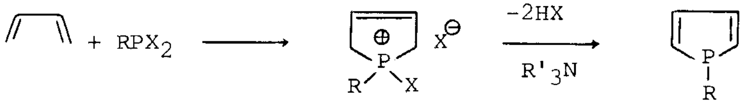
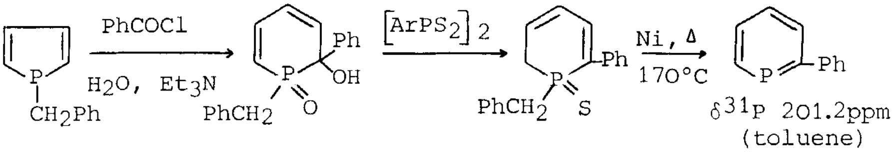
Abstract The uses of phospholes for building phosphorins, carbon-phosphorus saturated heterocycles and phosphinidene generators are described.

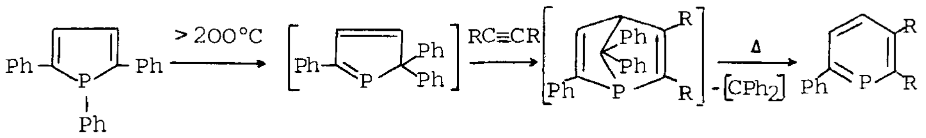
Phospholes are now readily available through dehydrohalogenation of diene $-RPX_2$ Mc Cormack cycloadducts by tertiary amines[1].



Thus, we have started to develop their uses in general synthetic organophosphorus chemistry. As a first example, we shall describe two routes converting phospholes into phosphorins. A good illustration of the first route is the synthesis of the previously unknown 2-phenylphosphorin[2].

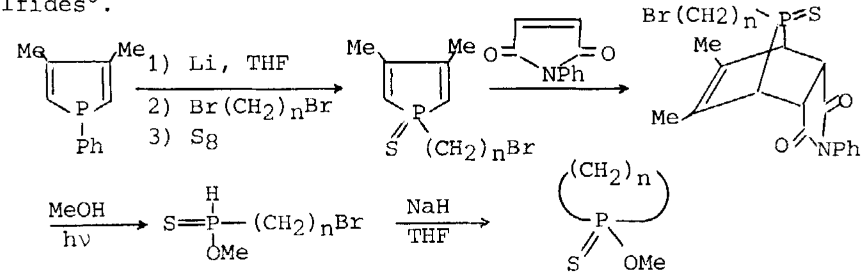


The overall yield is ca 23%. The ring expansion mechanism probably implies the hydrolysis of a transient 1-benzoyl-1-benzylphospholium salt. The same scheme has been also used for the synthesis of the first known 2,2'-pyridylphosphorin[3] and of some benzo-annelated phosphorins[4]. The second route relies upon the 1*H*- to 2*H*-phosphole conversion through phenyl [1,5] shifts at high temperature[5].



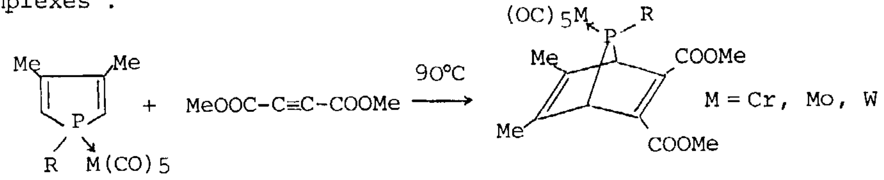
The transient 2H-phosphole reacts with acetylenic compounds to give 1-phosphanorbornadienes. At high temperature, when starting from 2,2,5-triphenyl-2H-phosphole, the 1-phosphanorbornadienes thus obtained spontaneously lose their diphenylcarbene bridge to give phosphorins. These two routes supplement nicely the phosphorin syntheses previously described by Ashe[6] and Märkl[7].

As a second example, we shall describe a new approach to the synthesis of saturated carbon-phosphorus heterocycles. Its key step is the photolytic cleavage of 7-(ω-bromoalkyl)-7-phosphanorbornene sulfides[8].

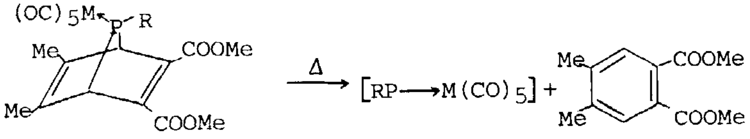


In this way, we have prepared five-, six-, and seven-membered rings.

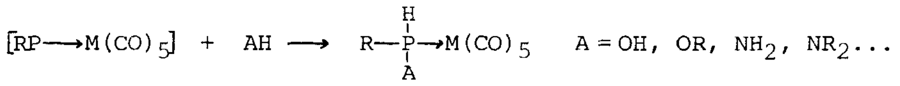
But the most recent and striking application of phospholes in organophosphorus chemistry is their use as building blocks for the synthesis of phosphinidene (P^I) generators. The reaction of 3,4-dimethylphosphole P-M(CO)5 complexes (M=Cr, Mo, W) with dimethyl acetylenedicarboxylate gives the corresponding 7-phosphanorbornadiene P-complexes[9].



The same reaction does not work with phosphole oxides, sulfides or P-Fe(CO)4 complexes : a loss of the phosphorus bridge is observed in each case. These 7-phosphanorbornadiene P-complexes are useful generators for transient terminal phosphinidene complexes.

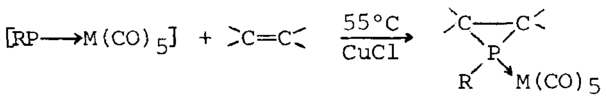


The decomposition takes place around 150°C or, in the presence of CuCl as a catalyst, around 55°C. These transient phosphinidene complexes react cleanly and easily with numerous organic functions. Compounds having a reactive hydrogen such as water, alcohols, amines... give the corresponding secondary phosphane complexes[10].

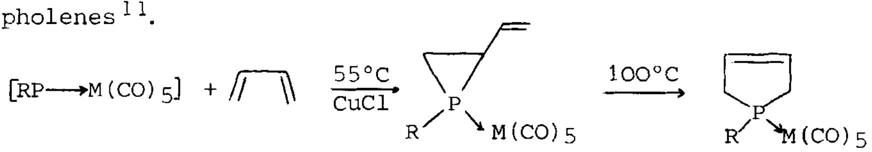


$$[RP\longrightarrow M(CO)_5] + AH \longrightarrow R{-}\overset{H}{\underset{A}{P}}{\rightarrow}M(CO)_5 \qquad A = OH,\ OR,\ NH_2,\ NR_2...$$

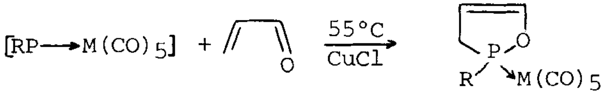
The resulting complexes show an interesting synthetic potential. When A=NR_2, their reaction with HX affords the first known stable complexes of secondary halogenophosphines $[RP(H)X]M(CO)_5$. At 55°C in the presence of CuCl, olefins react to give phosphiranes[11].



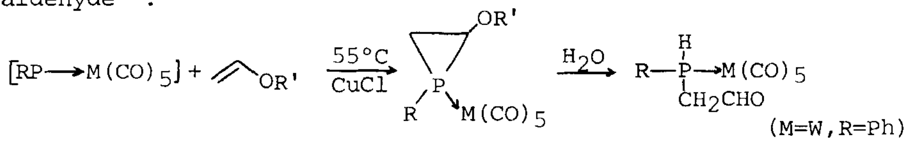
Under the same experimental conditions, conjugated dienes give vinylphosphiranes which rearrange around 100°C to the corresponding phospholenes[11].



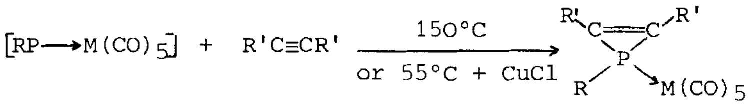
On the contrary, α β-unsaturated ketones give directly the 1,4-addition products[11].



With enol ether, the resulting phosphirane is easily cleaved by water to give a rather extraordinary stable secondary α-phosphinoacetaldehyde[11].



The reaction with acetylenic compounds lead to brandnew phosphirene complexes[12].



These complexes contain the first authenticated phosphirene rings. X-ray crystal structure analysis indicates a CPC internal angle of 42.8° for one of these complexes. Since this discovery, another approach to the phosphirene structure has been described in the literature[13].

Terminal phosphinidene complexes show obviously a much cleaner and wider reactivity than phosphinidene themselves[14]. In order to fully develop their synthetic potential in organophosphorus chemistry, we are currently devising a mild decomplexation method for recovering free phosphines from their P⟶W(CO)$_5$ complexes.

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