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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 -RPX2 Mc Cormack cycloadducts by tertiary amines $^{\rm l}$.

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-phenylphosphorin².

The overall yield is <u>ca</u> 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'-pyridylphosphorin³ and of some benzo-annellated phosphorins⁴. The second route relies upon the 1H- to 2H-phosphole conversion through phenyl [1,5] shifts at high temperature⁵.

$$Ph \xrightarrow{Ph} Ph \xrightarrow{>200^{\circ}C} \left[Ph \xrightarrow{Ph} Ph\right] \xrightarrow{RC \equiv CR} \left[Ph \xrightarrow{Ph} R\right] \xrightarrow{A} \xrightarrow{Ph} Ph$$

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The transient $2\underline{H}$ -phosphole reacts with acetylenic compounds to give 1-phosphanorbornadienes. At high temperature, when starting from 2,2,5-triphenyl- $2\underline{H}$ -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 Ashe⁶ and Märkl⁷.

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 $7-(\omega-bromoalkyl)-7-phosphanorbornene$ 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-complexes⁹.

Me Me COOMe
$$M = Cr$$
, Mo, We R M(CO) 5

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.

$$(OC)_{5}M \star_{p}R$$

Me

 $COOMe$
 $A \to [RP \longrightarrow M(CO)_{5}] + Me$
 $COOMe$
 $COOMe$

The decomposition takes place around 150°C or, in the presence of CuCl as a catalyst, around 55°C. These transient phosphinidene com-

plexes 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 $R \longrightarrow P \longrightarrow M(CO)_5$ A = OH, OR, NH₂, NR₂...

The resulting complexes show an interesting synthetic potential. When A=NR₂, 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 phosphiranes¹¹.

$$[RP \longrightarrow M(CO)_5] + C = C < \frac{55 \circ C}{CuCl} > C - C < M(CO)_5$$

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

pholenes 11.

$$[RP \longrightarrow M(CO)_{5}] + // \sqrt{\frac{55^{\circ}C}{CuCl}} R^{P} M(CO)_{5}$$

$$R \longrightarrow M(CO)_{5}$$

On the contrary, α $\beta\text{-unsaturated}$ ketones give directly the 1,4-addition products $^{1\,1}.$

$$[RP \longrightarrow M(CO)_5] + \sqrt{\frac{55^{\circ}C}{CuCl}} \qquad P \searrow M(CO)_5$$

With enol ether, the resulting phosphirane is easily cleaved by water to give a rather extraordinary stable secondary α -phosphino-acetaldehyde 1 .

$$[RP \longrightarrow M(CO)_{5}] + \bigcirc OR' \qquad \underbrace{\begin{array}{c} 55 \circ C \\ CuCl \end{array}}_{R} \stackrel{P}{\longrightarrow} M(CO)_{5} \qquad \underbrace{\begin{array}{c} H \\ P \\ CH_{2}CHO \end{array}}_{CH_{2}CHO} \stackrel{H}{\longrightarrow} M(CO)_{5}$$

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

$$[RP \longrightarrow M(CO)_{5}] + R'C \equiv CR' \xrightarrow{150^{\circ}C} R' \xrightarrow{R'} C \longrightarrow R'$$

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 .

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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 $P \longrightarrow W(CO)_5$ complexes.

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