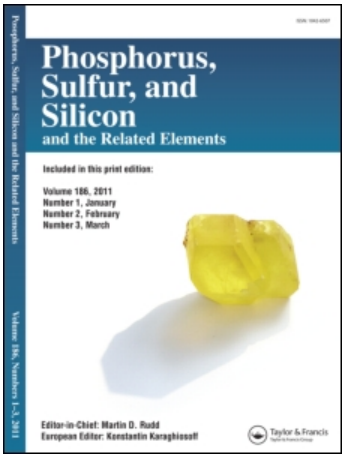

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THE SYNTHESIS OF 1,3,2-DIOXAPHOSPHOLENES. EVIDENCE FOR AN ARYLOXYPHOSPHINIDENE INTERMEDIATE

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THE SYNTHESIS OF 1,3,2-DIOXAPHOSPHOLENES. EVIDENCE FOR AN ARYLOXYPHOSPHINIDENE INTERMEDIATE

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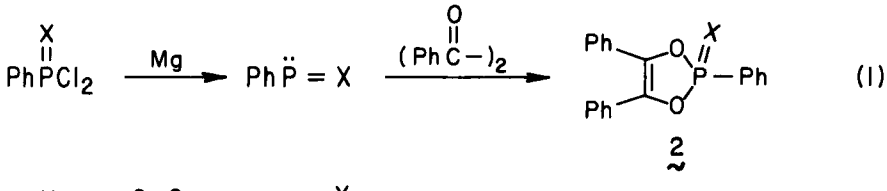
The reaction of 2,6-di-*t*-butyl-4-methylphenylphosphorodichloridite with α-diketones in the presence of magnesium metal affords modest yields of 1,3,2-dioxaphospholenes. This may be the first evidence for the existence of the monocoordinate aryloxyphosphinidene intermediate, ROP.

1,3,2-dioxaphospholenes
α-diketone
arylphosphorodichloridite
magnesium
aryloxyphosphinidine
heterocycle

Phosphinidenes[1] (**1a**), phosphinidene oxides[2] (**1b**), and phosphinidene sulfides[3,4] (**1c**) have been proposed as reactive species derived by the reaction of their corresponding dichlorides with magnesium or zinc metal (1). Furthermore, these intermediates have been inferred by the products of appropriate trapping experiments. Thus, when benzil, an α-diketone, was used as a trapping agent, **2** was obtained.[1–4]



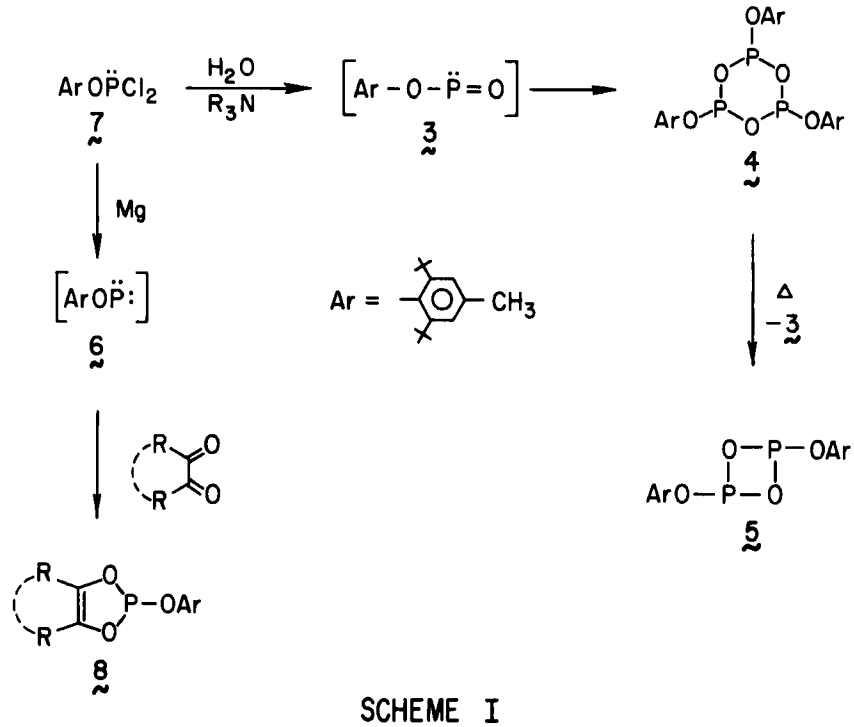
(1)

X = :, O, S

	X
1a	:
1b	O
1c	S

Recently, we[5] proposed the intermediacy of aryl phosphenites (**3**) in the synthesis of the P(III)-O heterocycle **4** and in the subsequent thermal degradation[6] of **4** to **5** (Scheme I). Quin *et al.*[7] have also reported the trapping of thiophosphenite esters (ROP=S).

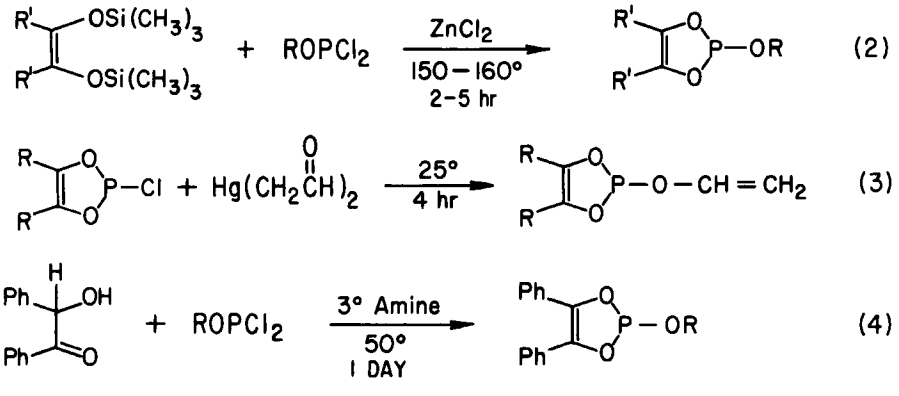
To our knowledge, however, alkoxy- or aryloxyphosphinidenes (**6**) have never been proposed or trapped in any reactions. Thus, if **6** could be generated by the reaction of the corresponding dichloridite[8] (**7**) with magnesium and then trapped



SCHEME I

by α-diketones as described for **1**a–c, then this method could be useful for the synthesis of 1,3,2-dioxaphospholenes **8** (Scheme I).

There is a paucity of literature on the synthesis and properties of P(III) 1,3,2-dioxaphospholenes. Lutsenko and co-workers[9] have prepared dioxaphospholenes by the method shown in (2) and by a multistep synthesis,[10] the last step of which is shown in (3). Mukhametov *et al.*[11] have used the scheme shown in (4). Overall yield in reactions (2)–(4) are typically 20–50%.



We report here the reaction of **7**[12] with α-diketones in the presence of magnesium to form P(III)-1,3,2-dioxaphospholenes **8** (Scheme I). The results are shown in Table I. The yields were comparable to those in (2)–(4). However, the reaction with aliphatic α-diketones, e.g., 2,3-butanedione, (±) camphoquinone,

and 3-methyl-1,2-cyclopentanedione, and with acenaphthenequinone, were unsuccessful. Compounds with electron donating substituents on benzil gave higher yields of **8**. Thus, this synthetic procedure is a relatively simple route to the 1,3,2-dioxaphospholenes (**8**).

EXPERIMENTAL

Melting points were obtained on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed at Huffman Labs, Wheatridge, CO. All field desorption mass spectra (FD/MS) were obtained on a Finnigan MAT 311A mass spectrometer. All ^1H NMR spectra were obtained on a Bruker WH-200 instrument and the chemical shifts are reported in ppm from internal TMS. The proton decoupled ^{31}P spectra were obtained on a Bruker HX90E/SXP spectrometer at 36.44 MHz. Chemical shifts were measured downfield relative to an external capillary of 85% aqueous H_3PO_4.

General Synthetic Procedure

7[12] (0.31 mol) in tetrahydrofuran (THF) (50 mL) was added dropwise to a stirred solution of the α-diketone (0.031 mol) in THF (125 mL) containing magnesium metal (0.062 mol, 40–80 mesh), all under a nitrogen atmosphere at ambient temperature. After 2 hr, the mixture was filtered and the solvent was evaporated to yield a yellow-to-brown glass.

Work-up and Isolation

8a. The crude glass was extraced with acetonitrile and a solid removed by filtration. The filtrate was evaporated to dryness and the resulting glass was extracted with hexane. After filtration, the filtrate was evaporated to a glass. This glass was column chromatographed on 25 g of Woelm silica gel (70–230 mesh) using 50/50 chloroform/hexane on a 4.5 cm ID column. TLC on silica gel plates was used to monitor the separation. An oil, which slowly crystallized, was obtained. This solid was then slurried in hexane and a white solid product, mp 127–130°C, was obtained by filtration for an 11% yield.

8b. The crude glass was extracted with methanol and a tan solid removed by filtration. This solid was column chromotographed as for **8a** to afford a white solid, mp 135–138°C, in 30% yield. ^{31}P $\{^1H\}$ NMR ($CDCl_3$) 132.1 ppm.

8c. The crude glass was extracted with hexane and a solid removed by filtration. The filtrate was evaporated to give a glass which was then extracted with methanol. The resulting solid was column chromatographed as for **8a** to afford a glass which was crystallized by strirring it in methanol to give a 43% yield of a white solid, mp 124–129°C.

8d. The crude glass was extraced with methanol and the resulting solid was column chromatographed as with **8a** to afford a 60% yield of a white solid, mp 147–152°C.

8e. The crude glass was extracted with acetonitrile and a solid removed by filtration. The filtrate was evaporated to a glass. This glass was column chromotographed as with **8a** to give a glass. This glass was stirred in acetonitrile to afford white product (19% yield), mp 167–169°C (lit.[13] bp 199–200°/2 mm). ^{31}P {H} NMR ($CDCl_3$) 140.5 ppm

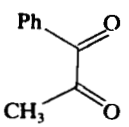
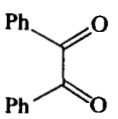
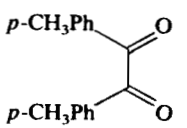
8f. The crude glass was extracted with methanol and the resulting tan solid was column chromotographed as with **8a**. There was obtained a 37% yield of a light yellow product, mp 224–233°C. ^{31}P $\{^1H\}$ NMR ($CDCl_3$) 142.6 ppm.

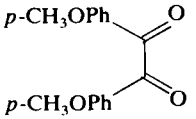
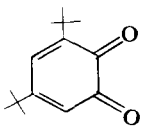
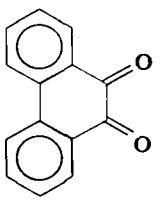
ACKNOWLEDGEMENTS

I thank Mr. Perry Matheny for carrying out the synthetic portion of this work.

TABLE I

Physical data for compounds **8a-f** prepared from **7** with α-diketones

Product 8	Diketone	Elemental analysis F/C	%	Found/Calc'd C	H	P	^{1}H NMR ($CDCl_3$)[a]	FD/MS (m/e)
a		C:	72.34	7.84	7.77	1.48 (s, 18 H); 2.29 (s, 3 H); 2.37 (s, 3 H); 7.12 (s, 2 H); 7.20–7.61 (m, 5 H)		398
		F:	72.40	7.77	7.71			
b		C:	75.63	7.22	6.72	1.43 (s, 18 H); 2.30 (s, 3 H); 7.13 (s, 2 H); 7.59–7.64 (m, 4 H); 7.31–7.35 (m, 6 H)		460
		F:	75.40	7.24	6.81			
c		C:	76.20	7.63	6.34	1.48 (s, 18 H); 2.29 (s, 3 H); 2.36 (s, 6 H); 7.12 (s, 2 H); 7.14 (d, J = 8, 4 H); 7.49 (d, J = 8, 4 H)		488
		F:	75.94	7.60	6.51			

d		C: F:	71.52 71.16	7.16 7.13	5.95 6.11	1.48 (s, 18 H); 2.29 (s, 3 H); 3.82 (s, 6 H); 6.67 (d, J = 8.8, 4 H); 7.12 (s, 2 H); 7.52 (d, J = 8.8, 4 H)	520
e		C: F:	74.01 74.06	9.21 9.25	6.58 6.79	1.33 (s, 9 H); 1.47 (s, 9 H); 1.48 (s, 18 H); 2.30 (s, 3 H); 7.04 (d, J = 1, 1 H); 7.07 (d, J = 1, 1 H); 7.13 (s, 2 H)	470
f		C: F:	75.96 75.77	6.81 6.85	6.75 6.93	1.52 (s, 18 H); 2.30 (s, 3 H); 7.14 (s, 2 H); 7.65 (p, J = 8, 4 H); 8.18 (d, J = 8, 2 H); 8.69 (d, J = 8, 2H)	458

[a] Coupling constants (J) are in Hz.

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8. **7** was available in our labs from previous work.[5,6] The hindering *t*-butyl groups allow for a high purity and yield of **7** while stabilizing **7** against hydrolysis. The *t*-butyl groups may contribute to the formation of **6**. No reactions with unhindered analogs of **7** were attempted.
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