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SILYL PHOSPHITES. III.
REACTION OF TRIS(TRIMETHYLSILYL) PHOSPHITE WITH DIKETONES

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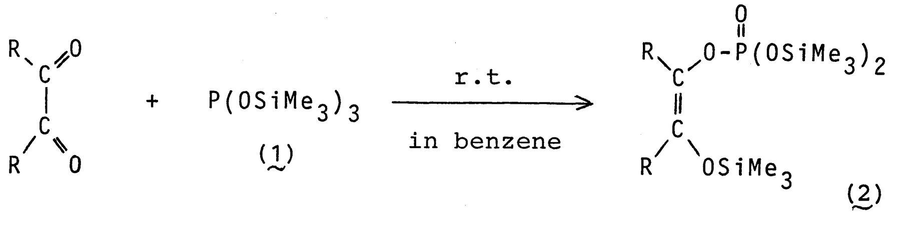
The silylated enediol- and quinol-phosphates were obtained in high yields by the reactions of α-diketones or p-quinones with tris(trimethylsilyl) phosphite.

The reactions of tervalent phosphorus compounds with diketones such as α-diketones, o-quinones, or p-quinones provide a variety of interesting products, which have been investigated in considerable detail in recent years. One of the interesting products, cyclic oxyphosphoranes, prepared from the reactions of α-diketones or o-quinones with trialkyl phosphites, have been widely studied by Ramirez.[1)] On the other hand, it has been found recently that silyl phosphites are very useful tervalent phosphorus compounds for the synthesis of S-aryl phosphorothioates,[2)] alkylphosphonates, and enol-phosphates[3)] since the silyl group can be removed easily by simple addition of water without using any acid or alkali.

In this communication, we wish to report a convenient method for the synthesis of silylated enediol-phosphates and quinol-phosphates, which have been interested in biological chemistry.

First, the synthesis of silylated enediol-phosphates was studied.



2a: $R=CH_3$, 2b: $R=C_4H_9$, 2c: $R=C_6H_5$

The following experiment provides the detail of a typical procedure for the synthesis of the enediol-phosphate derivatives: Tris(trimethylsilyl) phosphite (1) (10.32 g, 34.6 mmol)[1)] was added dropwise to a solution of biacetyl (2.29 g, 26.7 mmol) in dry benzene (10 ml) at room temperature and then the mixture was allowed to stand at room temperature for 30 min. After removal of the solvent, an addition compound was obtained in almost quantitative yield by distillation. This compound was no oxyphosphorane derivative as reported in the case of trialkyl phosphites,[1)] but it was confirmed as a silylated enediol-phosphate (2a) by ^{1}H NMR, ^{31}P NMR, IR spectra (see Fig. 1 and Table 1), and elemental analysis.

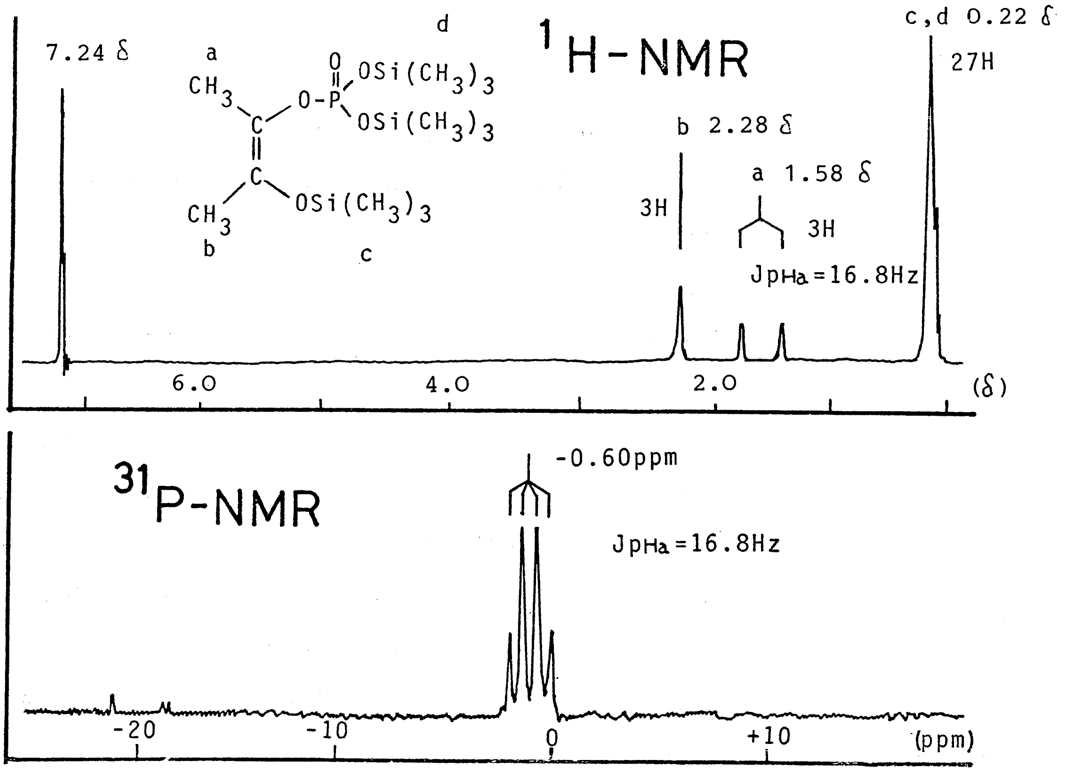


Fig. 1 Spectra of ^{1}H and ^{31}P NMR of the 1:1 Adduct from biacetyl and 1.

^{1}H NMR of the adduct, at 60 Mc/sec in benzene. Chemical shifts are given relative to TMS in the δ scale, where the line for TMS is assigned the value of 0.

^{31}P NMR spectrum of the adduct, at 40.5 Mc/sec in benzene. Chemical shifts are given in p.p.m. relative to 85% H_3PO_4 (0 ppm). Ph_3P is used as external reference (+5.6 ppm).

Similarly, the silylated enediol-phosphates were obtained in high yields from the reaction of bibutyryl or benzil with 1. The results are listed in Table 1.

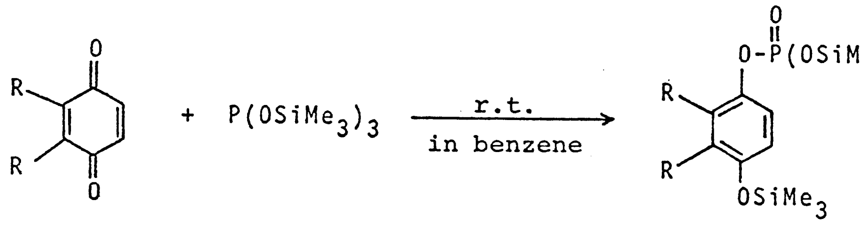
Table 1. Synthesis of Silylated Enediol-phosphates

α-Diketone	Yield (%)	B.p. °C (mmHg)	IR $\nu_{C=C}$ (cm^{-1})	^{1}H NMR (δ ppm)	J_{PH}(Hz)	^{31}P NMR* (δP ppm)	J_{PH}(Hz)
biacetyl	quant.	110(0.8)	1712	$1.58\left(\mathrm{CH_3{-}}\underset{\mathrm{O{-}P}}{\mathrm{C}}\mathrm{{=}C{-}}\right)$	16.8	-0.6	16.8
bibutyryl	71	126(0.6)	1708	$2.67\left(\mathrm{{-}CH_2{-}}\underset{\mathrm{O{-}P}}{\mathrm{C}}\mathrm{{=}C{-}}\right)$	7.8	-1.2	7.8
benzil	94	183-185(0.3)	1705 1745	—	—	+24.4	—

* Ph_3P as external reference; Solvent: benzene.

Next, the synthesis of quinol-phosphate derivatives by the reactions of p-quinones with 1 was examined.

p-Benzoquinone (1.08 g, 10 mmol) was treated with 1 (2.98 g, 10 mmol) in dry benzene (20 ml) at room temperature for 30 min. The yellow color disappeared, indicating the formation of the adduct. After removal of the solvent, the adduct, bis-trimethylsilyl (4-trimethylsilyloxyphenyl) phosphate (3a), was obtained in 86% yield by distillation.



(3)

3a: R=H, 3b. R-R = $(CH_2)_4$

In a similar manner, naphthoquinone was allowed to react with 1 to afford the corresponding quinol-phosphate derivative (3b) in 92% yield. The structures of 3a and 3b were supported by ^{31}P NMR (see Table 2) and elemental analysis.

Table 2. Synthesis of Silylated Quinol-phosphates

Quinone	$P(OSiMe_3)_3$ (equiv.)	Yield (%)	B.p. °C (mmHg)	^{31}P NMR* (δP ppm)
benzoquinone	1.1	86	140(0.3)	+23.1
naphthoquinone	1.4	92	173-175(0.4)	+21.8

* Ph_3P as external reference; Solvent: benzene.

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