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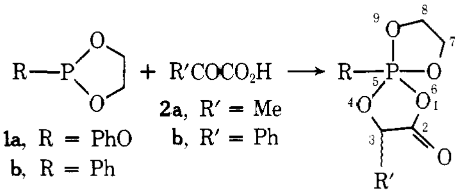
A New Route to Pentacovalent Cyclic Acyloxyphosphoranes

Sir:

The chemistry of pentacovalent oxyphosphoranes is currently one of the most active research fields.[1] These phosphorus compounds are closely related to reactions of the biologically important phosphate esters. For example, a pentacovalent cyclic acyloxyphosphorane has been implicated as an intermediate in the hydrolysis of phosphoenolpyruvate.[2] It becomes important, therefore, to prepare well-defined species of cyclic acyloxyphosphoranes and to examine their chemical reactivities. The present paper discloses a new synthetic method and the isolation of pentacovalent cyclic acyloxyphosphoranes, **3a–3d**, which are pentaoxy- and tetraoxyphosphorane derivatives. The reaction (eq 1) involves a hydrogen-transfer process of α-keto acids (**2**).



1a, R = PhO
b, R = Ph

2a, R' = Me
b, R' = Ph

3a, R = PhO; R' = Me
b, R = PhO; R' = Ph
c, R = Ph; R' = Me
d, R = Ph; R' = Ph

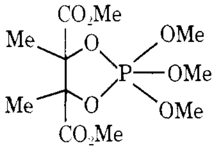
Into 20 ml of diethyl ether containing 3 mmol of 2-phenoxy-1,3,2-dioxaphospholane (**1a**) was added 3 mmol of pyruvic acid (**2a**) at 0 °C under nitrogen, and then the mixture was allowed to react at room temperature for 15 h. The mixture was further kept at −20 °C for 2 weeks in order to crystallize the product. The crystalline material was separated after washing with a small amount of diethyl ether and dried in vacuo to give 0.25 g (31% yield) of the product: mp 87 °C (from diethyl ether, hygroscopic); ir (KBr) 1745 (ν (C═O)), 1220 (ν(P—O—Ph)), 1035 (ν (P—O—CH$_2$)) cm^{-1} and no band at 1300-1250 cm^{-1} due to ν(P═O); ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ1.57 and 1.62 (two d, 3H, CH$_3$, J_{HCCH} = 7 Hz),[3] 3.5-4.5 (m, 4 H, OCH$_2$CH$_2$O), 4.5-4.8 (m, 1 H, OCOCHO), 6.7-7.5 (m, 5 H, C$_6$H$_5$O). Anal. Calcd for $C_{11}H_{13}O_6P$: P, 11.38. Found: P, 10.91. All the above data support the structure of 2-oxo-3-methyl-5-phenoxy-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (**3a**).

The ^{31}P NMR gave additional support for the structure of **3a**: ^{31}P NMR (DMF, H$_3$PO$_4$ external) +39.7 and 36.5 ppm (relative intensity, 2.3:1.0).[3] The chemical shift of ^{31}P NMR is quite reasonable for the pentaoxyphosphorane structure having spiro ring system **3a**.[1a,4]

Similarly, the reaction of **1a** with phenylglyoxylic acid **2b** in a diethyl ether-hexane (5:3) mixture gave hygroscopic, white crystals of **3b** in an isolated yield of 25%: mp 60-62 °C (hygroscopic); ir 1750 (ν(C═O)), 1210 (ν(C—O—Ph)), 1027 (ν(P—O—CH$_2$)) cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.62-4.62 (m, 4 H), 5.78-5.84 (two d, 1 H, J_{POCH} = 12 Hz and 16 Hz),[3] 6.66-7.82 (m, 10 H); ^{31}P NMR (CH$_3$CN) a broad signal at +39.1 ppm.[1a] Anal. Calcd for $C_{16}H_{15}O_6P$: P, 9.27. Found: P, 8.84.

Reactions of 2-phenyl-1,3,2-dioxaphospholane (**1b**) with **2a** and **2b** also took place to produce **3c** and **3d**, respectively, in high isolated yields. The reaction of **1b** with **2a** (3 mmol each) in 15 ml of diethyl ether at room temperature yielded white crystalline product of **3c** (85% after 3 days): mp 56–58 °C (hygroscopic); ir (KBr) 1735 (ν(C═O)), 1035 (ν(P—O—CH$_2$)) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.47 and 1.62 (two d, 3 H, J_{HCCH} = 7 Hz),[3] 3.50-4.60 (m, 4 H), 4.72 (m, 1 H), 7.28-8.18 (m, 5 H); ^{31}P NMR (CH$_3$CN) +22.2 ppm.[1a] Anal. Calcd for $C_{11}H_{13}O_5P$: C, 51.57; H, 5.11; P, 12.09. Found: C, 51.78; H, 5.30; P, 11.31. The reaction of **1b** with **2b** occurred readily to give white crystals of **3d** (isolated in a 92% yield after 3 h at room temperature): mp 103–105 °C (ir (KBr) 1750 (ν(C═O)), 1040 (ν(P—O—CH$_2$)) cm^{-1}; ^{1}H NMR (CD$_3$CN) δ 3.53-4.60 (m, 4 H), 5.60 and 5.75 (two d, 1 H, J_{POCH} = 15 and 9 Hz),[3] 6.71–8.10 (m, 10 H); ^{31}P NMR (DMF) a broad signal at +22.0 ppm. Anal. Calcd for $C_{16}H_{15}O_5P$: C, 60.38; H, 4.75; P, 9.73. Found: C, 60.63; H, 4.92; P, 9.54.

Thus, the pentaoxy cyclic acyloxyphosphoranes, **3a** and **3b**, have been isolated for the first time as crystalline species. The isolated yields were higher with tetraoxyacyloxyphosphoranes, **3c** and **3d**, than with pentaoxy derivatives, **3a** and **3b**.[5] The present reaction (eq 1) involves the oxidation of **1** from trivalent to pentavalent and the reduction of **2** to an α-oxy acid derivative accompanying a hydrogen-transfer step. As to the reaction of eq 1, the following reaction should be cited. Trimethyl phosphate and 2 mol of methyl pyruvate (not pyruvic acid) reacted to give pentaoxyphosphorane **4**,[6] which is not a cyclic acyloxyphosphorane.



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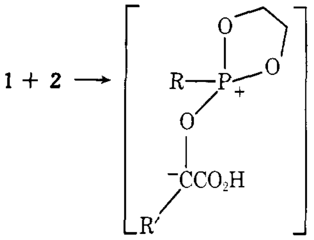
The formation of **3** from **1** and **2** probably involves an intermediate phosphonium carbanion **5**, which undergoes a hydrogen-transfer intra- and/or intermolecularly to yield a zwitterion **6**. Then, the cyclization of **6** leads to the product **3**.



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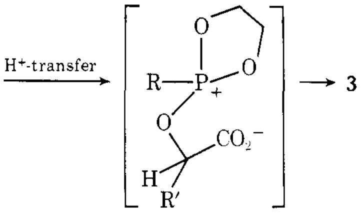
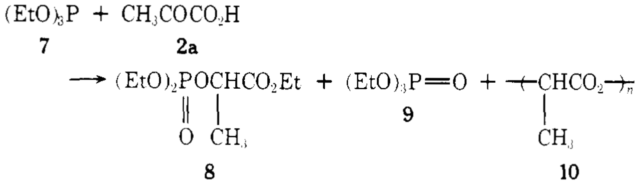


6

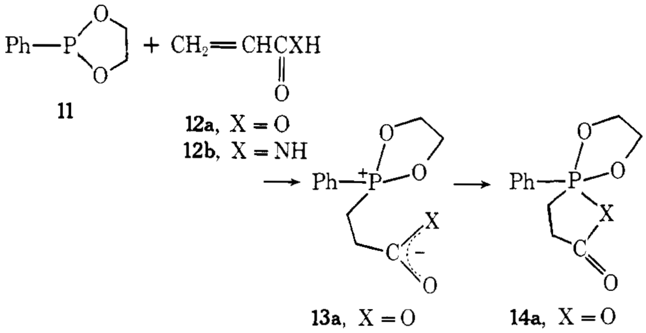
The presence of the dioxaphosphorane ring in **1** markedly facilitates the ring closure of **6** to give a spiro compound **3**. The reaction of an acyclic phosphite **7** with **2a** however, gave **8** (22% yield), **9**[7] (64% yield), and presumably polymer **10**. No spirooxyphosphorane corresponding to **3** was obtained.



$$\underset{\mathbf{7}}{(\mathrm{EtO})_3\mathrm{P}} + \underset{\mathbf{2a}}{\mathrm{CH_3COCO_2H}} \longrightarrow \underset{\mathbf{8}}{(\mathrm{EtO})_2\underset{\mathrm{O}}{\underset{\|}{\mathrm{P}}}\mathrm{O}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCO_2Et}} + \underset{\mathbf{9}}{(\mathrm{EtO})_3\mathrm{P{=}O}} + \underset{\mathbf{10}}{\left[\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCO_2}\right]_n}$$

A five-membered cyclic pentaoxyacylphosphorane, which has been considered as a biologically important transient species,[2] has now become available. Acyloxyphosphoranes, **3a-3d**, are a new class of mixed anhydrides. They can be taken as ortho esters of cyclic acyl phosphate, a high-energy compound in biological metabolism.[8] The nature of the anhydride bond POC =O is of high energy,[8b] and therefore, acyloxyphosphoranes such as **3a-d** have a potential for the synthetic application.[1e]

In reference to the synthesis of the above phosphorane compounds, the reactions of 2-phenyl-1,3,2-dioxaphospholane **11** with acrylic acid **12a** and with acrylamide **12b** are to be mentioned here. Pentacovalent acyloxy- (**14a**) and amidophosphoranes (**14b**) are produced via zwitterions **13a** and **13b**, respectively.[9]



11

12a, X = O
12b, X = NH

13a, X = O
13b, X = NH

14a, X = O
14b, X = NH

Acknowledgment. The authors are indebted to Dr. Y. Chokki, Takeda Pharmaceutical Co., Osaka, Japan, for the ^{31}P NMR spectra.

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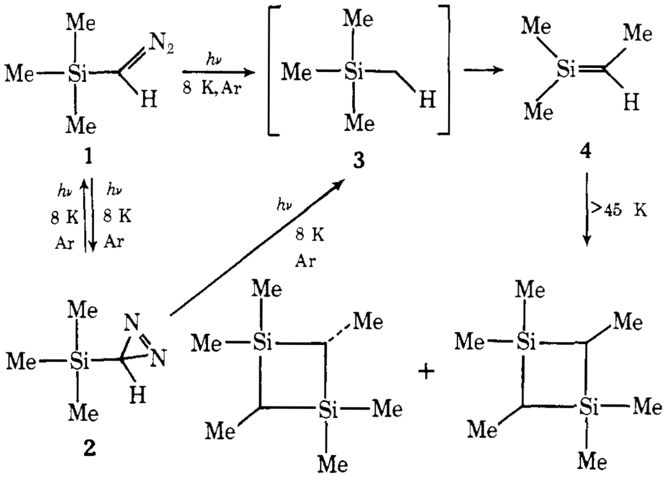
1,1,2-Trimethylsilaethylene

Sir:

A variety of presumptive evidence based on chemical trapping suggests that it is possible to generate reactive intermediates containing a formal silicon-carbon double bond.[1] In spite of intense interest in silicon-carbon double bonds, only one report of an attempt to observe such a species spectroscopically is available.[2,3] We wish to describe the first physical and chemical characterization of a silicon-carbon double bond, 1,1,2-trimethylsilaethylene.

Trimethylsilyldiazomethane[5] provides an attractive precursor for photochemical generation of 1,1,2-trimethylsilaethylene. During the course of our experiments, Kreeger and Shechter[6] described the room temperature photochemistry and the thermolysis of trimethylsilyldiazomethane and provided evidence for the generation of 1,1,2-trimethylsilaethylene as a transient intermediate.

Irradiation of trimethylsilyldiazomethane (**1**) matrix isolated in argon at 8 K produces a photostationary state involving a new species, trimethylsilyldiazirine (**2**). Trimethylsilyldiazirine is also formed on irradiation in a variety of solvents at room temperature (δ −0.03 (s, 9 H), δ −0.53 (s, 1 H), $CDCl_3$; $\lambda_{max}^{2MeTHF, 77K}$ 340, 332, 324, 317, and 309 nm, Figure 1). Trimethylsilyldiazirine can be isolated and is reasonably stable at room temperature. Continued irradiation of the photostationary mixture produced from either **1** or **2** matrix isolated in argon gives 1,1,2-trimethylsilaethylene (**4**) via the carbene (**3**).[10] The infrared spectrum of 1,1,2-trimethylsilaethylene



1 **3** **4** **2** **5a** **5b**

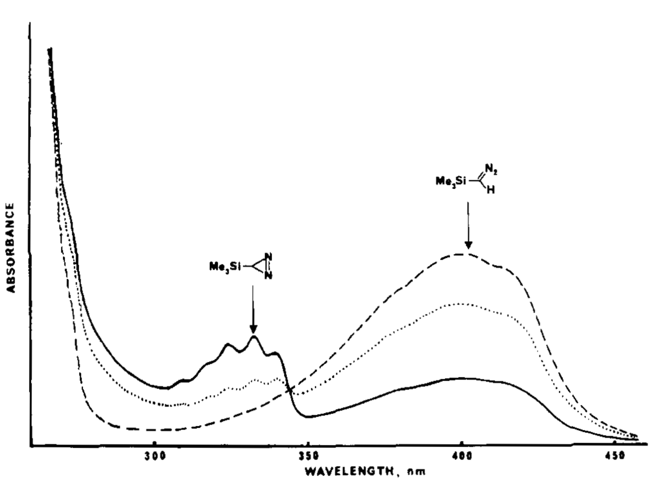


Figure 1. Ultraviolet spectrum of trimethylsilydiazomethane (**1**) in 3-methylpentane at 77 K: before irradiation (- - -), after 50 min of irradiation (· · ·), and after 190 min of irradiation (λ >355 nm) (—).