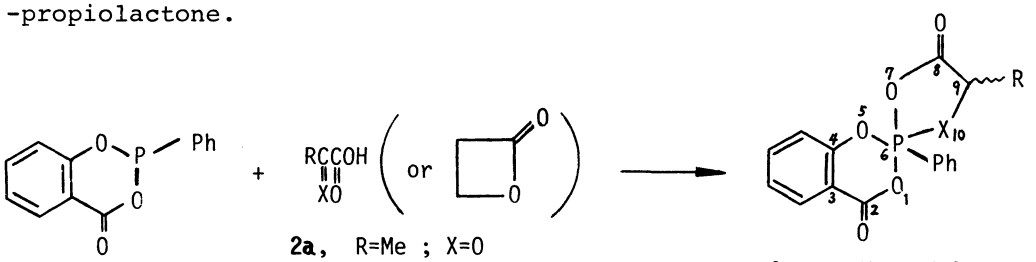
CHEMISTRY LETTERS, pp. 393-394, 1979. Published by the Chemical Society of Japan

NEW SYNTHESIS OF SPIRO DIACYLOXYPHOSPHORANES

Shiro KOBAYASHI, Takatoshi KOBAYASHI, and Takeo SAEGUSA
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Sakyo-ku, Kyoto 606

Spiro diacyloxyphosphoranes (**4**) and (**5**) were prepared by single-step reactions of a cyclic acyl phosphonite (**1**) with α-keto acids (**2**) and with acrylic acid (**3**) or β-propiolactone.

Chemistry of phosphoranes is quite a new research field of phosphorus compounds and this area is currently growing rapidly.[1-3] We have recently explored new synthetic methods to prepare cyclic acyloxyphosphoranes by reactions of a cyclic phosphonite or phosphite with acrylic acid[4] and with α-keto acids.[5] A related work has appeared, reporting a new bicylic acyloxyphosphorane prepared from an acrylic acid derivative and a phosphonite.[6] We report here new synthesis of spiro diacyloxyphosphoranes (**4**) and (**5**) by single-step reactions of a new cyclic acyl phosphonite (**1**) with α-keto acids (**2**) and with acrylic acid (**3**) or β-propiolactone.



1

2a, R=Me ; X=O
2b, R=Ph ; X=O
3, R=H ; X=CH_2

4a, R=Me ; X=O
4b, R=Ph ; X=O
5, R=H ; X=CH_2

2-Phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (**1**) was for the first time prepared as follows. Phenyldichlorophosphine (0.18 mol) in benzene (100 ml) was added at 0°C with stirring into a benzene solution (300 ml) containing salicylic acid (0.18 mol) and triethylamine (0.36 mol). After the addition the reaction system was warmed to room temperature and kept for 1 hr at the same temperature. The benzene layer was separated and concentrated by evaporation to yield a solid product, which was isolated by crystallization from chloroform to give 23.7 g of white crystals **1** (54% yield): mp 40.5°C, IR ν_{max}^{Nujol} (cm^{-1}) 1760 (C=O); ^{31}P NMR ($CHCl_3$) δ 159.4[7]; Anal. Calcd for $C_{13}H_9O_3P$: C, 63.94; H, 3.72; P, 12.68. Found : C, 63.85; H, 3.66; P, 12.58.

An equimolar mixture of **1** and pyruvic acid (**2a**) (3.0 mmol each) in diethyl ether was kept standing at 0°C for 10 hr under dry nitrogen. The mixture was further kept at -25°C for 10 days. Then, a crystalline solid which had

precipitated out was isolated by filtration, washed with a small amount of cold n-hexane, and dried in vacuo to give 0.64 g (62% yield) of the white crystals of 2,8-dioxo-3,4-benzo-6-phenyl-9-methyl-1,5,7,10-tetraoxa-6-phosphaspiro[5,4]decane (**4a**): mp 108-109 °C, IR $\nu_{max}^{Nujol}(cm^{-1})$ 1755 (C=O) and no band for a P=O group; ^{1}H NMR ($CDCl_3$) δ 8.2-6.8 (m, 9H , aromatic protons) 4.95-4.45 (m, 1H, C(O)CH), 1.56 and 1.51 (two d[8], 3H, CH_3, J_{H-H}=6.8 Hz); ^{31}P NMR ($CHCl_3$) δ -45.1 and -45.4[7] with equal intensity by proton decoupling,[8] a typical ^{31}P NMR shift for acyloxyphosphoranes[5]; Anal, Calcd for $C_{16}H_{13}O_6P$: C, 57.84; H, 3.94; P, 9.32. Found : C, 57.68; H, 4.16; P, 9.28.

In a similar manner the reaction of **1** with **2b** gave white crystals of **4b** (82% yield): mp 104-106 °C (from diethyl ether); IR $\nu_{max}^{Nujol}(cm^{-1})$ 1750 (C=O) and no P=O band; ^{1}H NMR ($CDCl_3$) δ 8.3-6.9 (m, 14H, aromatic protons), 5.76 and 5.70 (two d[8], 1H, C(O)CH, J_{POCH}=12.0 and 17.2 Hz); ^{31}P NMR ($CHCl_3$) δ -42.8[7] (without proton decoupling); Anal. Calcd for $C_{21}H_{15}O_6P$: C, 63.97; H, 3.83; P, 7.86. Found: C, 63.84; H, 4.06; P, 7.43.

The reaction of **1** with **3** or with β-propiolactone in diethyl ether at room temperature yielded white crystals of **5** (68% yield after 3 days), mp 126-128°C (from diethyl ether): IR $\nu_{max}^{Nujol}(cm^{-1})$ 1750 (C=O) and no P=O band; ^{1}H NMR ($CDCl_3$) δ 8.3-6.9 (m, 9H, aromatic protons), 3.62-2.18 (m, 4H, CH_2CH_2); ^{31}P NMR ($CHCl_3$) δ -17.3[7] (without proton decoupling); Anal. Calcd for $C_{16}H_{13}O_5P$: C, 60.77; H, 4.14; P, 9.79. Found: C, 60.84; H, 4.25; P, 9.67.

All spiro and bicyclic diacyloxyphosphoranes hitherto prepared contain two five-membered rings and preparations of these compounds normally require a few steps.[9-12] The present study provides a facile method to prepare spiro diacyloxyphosphoranes having five- and six-membered rings, which will permit a study of chemical reactivities and stereochemical problems of these new phosphoranes.

References and Notes

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7) The chemical shift is positive to the down-field and negative to the up-field from an external 80% H_3PO_4 standard.
8) **4** is present as stable two stereoisomers in solution at room temperature due to the chiral C-9 of the five-membered ring.
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(Received March 2, 1979)