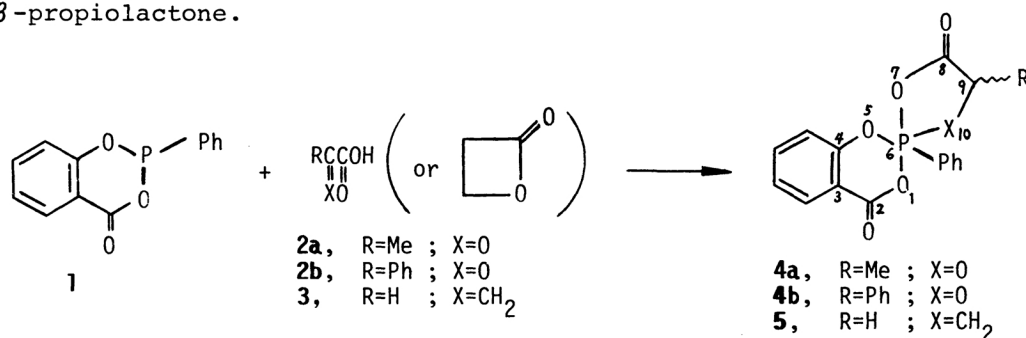


# NEW SYNTHESIS OF SPIRO DIACYLOXYPHOSPHORANES

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

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



2-Phenyl-4-oxo-5,6-benzo-1,3,2-dioxaphosphorinane (**1**) was for the first time prepared as follows. Phenylchlorophosphine (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  $\nu_{\text{max}}^{\text{Nujol}}$  (cm<sup>-1</sup>) 1760 (C=O); <sup>31</sup>P NMR (CHCl<sub>3</sub>)  $\delta$  159.4<sup>7)</sup>; Anal. Calcd for C<sub>13</sub>H<sub>9</sub>O<sub>3</sub>P : 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  $\nu_{\text{max}}^{\text{Nujol}}(\text{cm}^{-1})$  1755 (C=O) and no band for a P=O group;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.2-6.8 (m, 9H, aromatic protons) 4.95-4.45 (m, 1H, C(O)CH), 1.56 and 1.51 (two d<sup>8</sup>), 3H, CH<sub>3</sub>,  $J_{\text{H-H}}=6.8$  Hz);  $^{31}\text{P}$  NMR ( $\text{CHCl}_3$ )  $\delta$  -45.1 and -45.4<sup>7)</sup> with equal intensity by proton decoupling,<sup>8)</sup> a typical  $^{31}\text{P}$  NMR shift for acyloxyphosphoranes<sup>5)</sup>; Anal. Calcd for C<sub>16</sub>H<sub>13</sub>O<sub>6</sub>P: 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  $\nu_{\text{max}}^{\text{Nujol}}(\text{cm}^{-1})$  1750 (C=O) and no P=O band;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.3-6.9 (m, 14H, aromatic protons), 5.76 and 5.70 (two d<sup>8</sup>), 1H, C(O)CH,  $J_{\text{POCH}}=12.0$  and 17.2 Hz);  $^{31}\text{P}$  NMR ( $\text{CHCl}_3$ )  $\delta$  -42.8<sup>7)</sup> (without proton decoupling); Anal. Calcd for C<sub>21</sub>H<sub>15</sub>O<sub>6</sub>P: 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  $\beta$ -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  $\nu_{\text{max}}^{\text{Nujol}}(\text{cm}^{-1})$  1750 (C=O) and no P=O band;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.3-6.9 (m, 9H, aromatic protons), 3.62-2.18 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>);  $^{31}\text{P}$  NMR ( $\text{CHCl}_3$ )  $\delta$  -17.3<sup>7)</sup> (without proton decoupling); Anal. Calcd for C<sub>16</sub>H<sub>13</sub>O<sub>5</sub>P: 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.<sup>9-12)</sup> 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<sub>3</sub>PO<sub>4</sub> 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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