New Synthesis of Pentacovalent Phosphorus Compounds of Cyclic Acyloxy- and Amido-phosphoranes

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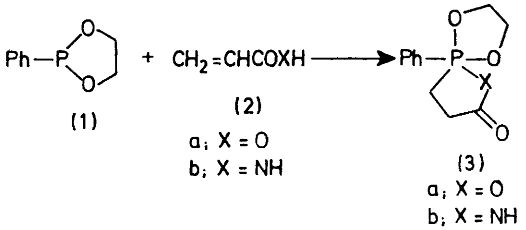
Summary The reactions of 2-phenyl-1,3,2-dioxaphospholan (**1**) with acrylic acid (**2a**) and with acrylamide (**2b**) afford the pentacovalent cyclic acyloxy (**3a**) and amido-phosphoranes (**3b**), respectively.

Much attention has recently been paid to pentacovalent phosphorus compounds because of both the stereochemistry and the chemical reactivity associated with the biologically important phosphate esters.[1,2] We report a versatile, novel method for preparation of pentacovalent cyclic phosphoranes. The cyclic acyloxy- (**3a**) and amido-phosphoranes (**3b**) were obtained in good yields by the single-step reactions of 2-phenyl-1,3,2-dioxaphospholan (**1**) with acrylic acid (**2a**) and with acrylamide (**2b**), respectively. In both cases a hydrogen-transfer process is involved.

The reaction of (**1**) and (**2a**) in diethyl ether at 25 °C for 15 h yielded needle-like crystals of (**3a**)† (92%), m.p. 80 °C (from chlorobenzene, hygroscopic); ν_{max} (KBr) 1735 (C=O) and 1025 (P–O–C) cm^{-1}; δ (^{1}H) (CD_3CN), 2·0—3·2 (m, 4H), 3·4—4·5 (m, 4H), and 7·4—8·1 (m, 5H); ^{31}P n.m.r. ($HCONMe_2$) +2·9 p.p.m. (relative to H_3PO_4 external standard).[1a] Furthermore, preliminary *X*-ray results show that (**3a**) adopts a trigonal bipyramidal phosphorane structure.‡

The reaction of (**1**) with (**2b**) in acetonitrile at 50 °C gave white crystals of (**3b**)† (71% yield after 25 h), m.p. 158 °C (from MeCN, hygroscopic); ν_{max} (KBr) 3400 and 3175 (NH), 1680 and 1640 (C=O), and 1065 (P–O–C) cm^{-1}; δ (^{1}H) (CD_3NO_2) 1·7—3·0 (m, 4H), 3·4—4·2 (m, 4H), and 7·3—8·0 (m, 5H); ^{31}P n.m.r. ($HCONMe_2$) + 23·4 p.p.m.



To our knowledge, (**3a**) and (**3b**) are the first reported examples of crystalline pentacovalent cyclic acyloxy- and amido-phosphoranes. A five-membered cyclic acyloxyphosphorane has been implicated as an intermediate in the hydrolysis of phosphoenolpyruvate esters.[2] The 5-oxo-1,2-azaphospholidine ring system, as in (**3b**), was hitherto unknown.

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† Satisfactory elemental analyses were obtained.

‡ Detailed *X*-ray crystallographic results will be published elsewhere, in collaboration with Professor Y. Higuchi of Osaka City University.

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