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LETTERS
TO THE EDITOR

Reaction of 2-Phenyl-1,3,2-benzodioxaphosphinan-4-one with Diethyl Benzylidenemalonate

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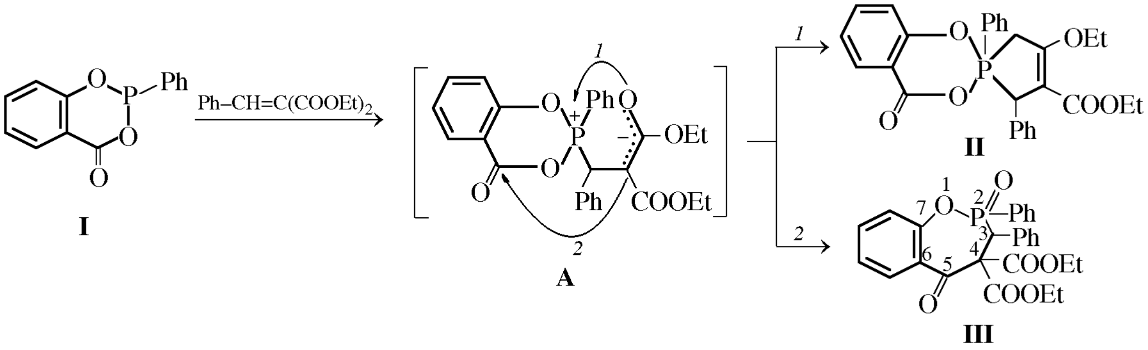
Reactions of 2-substituted 1,3,2-benzodioxaphosphinan-4-ones **I** (salicyl phosphites) with carbonyl compounds activated by electron-acceptor substituents, as well as with Schiff bases, provide a convenient route to seven-membered phosphorus-containing heterocycles: 1,3,2- and 1,4,2-dioxa- or 1,3,2- and 1,4,2-oxazaphosphepines [1–3]. In these reactions compounds **I** can act as both nucleophile and electrophile, and the process is characterized by high regio- and stereoselectivity.

Phosphorus(III) compounds are known to readily react with ylidene derivatives of β-dicarbonyl compounds having activated C=C bonds, yielding the corresponding phosphoranes [4]. We are the first to report that ylidene derivatives of diethyl malonate are capable of being inserted into the dioxaphosphinane ring of **I**. Diethyl benzylidenemalonate readily reacts with phenylphosphonite **I** along two pathways, yielding five- and four-coordinate phosphorus derivatives **II** (δ_P –22.6 ppm) and **III** (δ_P 38.4 and 38.1 ppm), respectively. Heating of the reaction mixture for a short time leads to disappearance of the phosphorane signal. In keeping with the δ_P value, compound **II** is likely to contain two P–C bonds and one five-membered ring. Oxaphosphepine **III** is formed with high stereoselectivity: the intensity ratio of the signals with δ_P 38.4 and 38.1 ppm is 3 : 1. Its structure was unambiguously determined by ^{1}H and ^{13}C NMR spectroscopy.

Presumably, the reaction scheme involves nucleophilic attack by the phosphorus on the β-carbon atom of diethyl benzylidenemalonate to produce dipolar ion A. The latter is stabilized either via attack by the oxygen atom on the phosphorus with reversible formation of phosphorane **II** (pathway *1*) or through nucleophilic substitution at the carbonyl carbon atom (pathway *2*) to give a new phosphorus-containing ring, 1,2-benzoxaphosphepine **III**.



This reaction is the first example of participation of compounds with a double C=C bond in dioxaphosphinane ring expansion.

Diethyl 2,5-dioxo-2,3-diphenyl-1,2λ^5-benzoxaphosphepine-4,4-dicarboxylate (III) was obtained by heating a mixture of 5 g of phosphonite **I** and 5.02 g of diethyl benzylidenemalonate in 10 ml of methylene chloride for 2 h at 40°C. The product was isolated by precipitation (the reaction mixture was poured into ether). Yield 70%, mp 166°C. IR spectrum, ν, cm^{-1}: 1690 (C=O), 1740 and 1770 (COO), 1290 (P=O). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.47 d (3-H, $^{2}J_{\mathrm{P,CH}}$ = 27.5), 4.29 m and 4.14 m ($\mathrm{OCH}_A\mathrm{H}_B$, ABX_3 system, $^{3}J_{BX}$ = 7.0, $^{3}J_{AX}$ = 7.0, $^{3}J_{AB}$ = 10.8), 3.79 m and 3.84 m ($\mathrm{OCH}_A\mathrm{H}_B$, ABX_3 system, $^{3}J_{AX}$ = 7.1, $^{3}J_{\mathrm{BX}}$ = 7.1, $^{3}J_{\mathrm{AB}}$ = 10.7), 1.50 t and 0.74 t (CH_3, X_3 part of the ABX_3 system, $^{3}J_{A(B)X}$ = 7.0, $^{3}J_{(A)BX}$ = 7.1). ^{13}C NMR spectrum, δ_{C}, ppm (*J*, Hz): 50.84 d.d.t (C^3, $^{1}J_{\mathrm{CP}}$ = 84.2, $^{1}J_{\mathrm{CH}}$ = 126.9, $^{3}J_{\mathrm{CH}}$ = 4.4), 74.58 d.d (C^4, $^{2}J_{\mathrm{CP}}$ = 1.8, $^{2}J_{\mathrm{CH}}$ = 5.4), 188.05 d.d.d (C^5, $^{3}J_{\mathrm{CP}}$ = 0.96, $^{3}J_{\mathrm{CH}}$ = 5.8–5.9, $^{3}J_{\mathrm{CH}}$ = 4.6–4.8), 126.41 m (C^6, $^{3}J_{\mathrm{CP}}$ = 1.54), 148.74 d.d.d.d.d (C^7, $^{2}J_{\mathrm{CP}}$ = 8.1, $^{3}J_{\mathrm{CH}}$ = 9.7–9.8, $^{2}J_{\mathrm{CH}}$ = 4.0, $^{4}J_{\mathrm{CH}}$ = 1.76), 165.80 d.t.d (COO, $^{3}J_{\mathrm{CP}}$ = 14.1, $^{3}J_{\mathrm{CH}}$ = 3.5, $^{3}J_{\mathrm{CH}}$ = 2.5), 165.79 m (COO, $^{3}J_{\mathrm{CP}}$ = 6.6, $^{3}J_{\mathrm{CH}}$ = 3.5), 62.71 t.q and 62.17 t.q (OCH_2, $^{1}J_{\mathrm{CH}}$ = 148.8, $^{3}J_{\mathrm{CH}}$ = 4.5), 13.59 q.t and 13.06 q.t (CH_3, $^{1}J_{\mathrm{CH}}$ = 127.5, $^{3}J_{\mathrm{CH}}$ = 2.6). Found, %: C 65.48; H 4.94; P 6.10. $\mathrm{C}_{27}\mathrm{H}_{25}\mathrm{O}_7\mathrm{P}$. Calculated, %: C 65.85; H 5.08; P 6.30.

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