Novel and Convenient Synthesis of Dioxaphospholes

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Synopsis. Treatment of 1,2-diketones **1a—d** with sodium in dry THF followed by addition of dry phenyl and ethyl phosphorodichloridate gave 2-phenoxy- and 2-hydroxy-4,5-diaryl-1,3,2-dioxaphosphole 2-oxides, respectively.

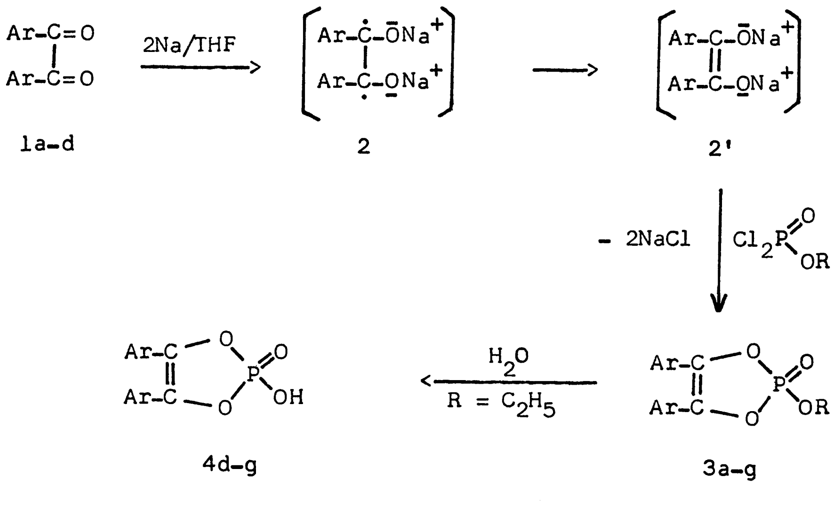
The preparation of some heterocyclic compounds containing nitrogen atoms and one four-coordinated phosphorus atom has been reported.[1] The synthesis of spiro-1,3,2-benzooxazaphospholes[2] from the reaction of 2-aminophenols with aryl phosphorodichloridates and 2,4,3-benzodiazaphosphepines[3] from the reaction of *o*-xylene-α,α'-diamines with dichlorophosphinyl carbamates have been described earlier. Five membered N,P and O,N,P-heterocyclic compounds have been obtained from benzil dianils and monoanils.[4] It has been observed that the reaction of phosphorothiodichloridate with benzil in presence of magnesium leads to the formation of 2,4,5-triphenyl-1,3,2-dioxaphosphole 2-sulfide.[5] We now wish to report a new and convenient one pot synthesis of 2-phenoxy- and 2-hydroxy-4,5-diaryl-1,3,2-dioxaphosphole 2-oxides from the dianions of 1,2-diketones. These dioxaphospholes could be used for the phosphorylation of alcohols.[6]

Results and Discussion

Treatment of 1,2-diketones **1a—d** with sodium in dry THF and subsequent addition of dry phenyl or ethyl phosphorodichloridate afforded 2-phenoxy-4,5-diaryl-1,3,2-dioxaphosphole 2-oxides **3a—c** and 2-hydroxy-4,5-diaryl-1,3,2-dioxaphosphole 2-oxides **4d—g** respectively. These products have been characterized by the satisfactory analytical and spectral data. It has been observed that using the reagents in 1:1 mole ratio, the yields of products **3** and **4** are reduced by 7 and 2%, respectively.

The formation of the products **3a—c** and **4d—g** from diketones **1a—d** is depicted in Scheme 1.

This synthesis involves the initial formation of diradical dianion **2**, by the electron teansfer from sodium to diketones, which on radical coupling would give the dianion **2′**;[7] the latter attacks phenyl or ethyl phosphorodichloridate with elimination of chloride ions (detected by the formation of silver chloride with aq. silver nitrate) to give rise to 2-phenoxy- and 2-ethoxy-4,5-diaryl dioxaphole 2-oxides, respectively. In cases of **3d—g**, the 2-ethoxy derivatives, initially formed, are hydrolyzed to 2-



Dioxaphosphole	Ar	R	Yield/%
3a	*p*-CH_3-C_6H_4	C_6H_5	41
3b	*p*-CH_3O-C_6H_4	C_6H_5	30
3c	*p*-Cl-C_6H_4	C_6H_5	36
4d	*p*-CH_3-C_6H_4	C_2H_5	36
4e	*p*-CH_3O-C_6H_4	C_2H_5	45
4f	*p*-Cl-C_6H_4	C_2H_5	44
4g	C_6H_5	C_2H_5	62

Scheme 1.

hydroxy compounds **4d**—**g** during the work up. A similar hydrolysis of 2-methoxy-4,5-dimethyl-1,3,2-dioxaphosphole 2-oxide at 0 °C has been reported earlier.[8] Although products **3a**—**c** were stable to alkaline solution for 3 h but were hydrolyzed in 7 h to the corresponding hydroxy derivatives **4a**—**c**.

Experimental

Measurement. All melting points were uncorrected. The IR spectra were recorded in Nujol mull on a Perkin-Elmer 720 spectrophotometer. The ^{1}H NMR spectra were obtained on a JEOL JNM-FX-90Q NMR spectrometer using $CDCl_3$ as a solvent. The chemical shifts are given in δ, with tetramethylsilane (TMS) as the internal standard. Mass spectra were determined on a CEC 110 double-focussing mass spectrometer, Purdue University, W. Lafayette, U. S. A. Elemental analyses were carried out using Coleman carbon-hydrogen analyzer.

Materials. 4,4′-Dimethylbenzil, 4,4′-dimethoxybenzil, 4,4′-dichlorobenzil, benzil, and phenyl and ethyl phosphorodichloridate were obtained from EGA Chemicals, West Germany. The sodium metal and other solvents were commercially obtained.

Preparation of 4,5-Diaryl-2-phenoxy-1,3,2-dioxaphosphole 2-Oxides 3a—c. Freshly cut sodium pieces (1.0 g, 0.044 g atom) were slowly added to dry THF (65 ml) with stirring under a nitrogen atmosphere and a solution of 1,2-diketone (1.4 g) in dry THF (10 ml) was added dropwise; stirring at reflux temperature was continued for 7 h and the contents were allowed to cool. Unreacted sodium pieces were removed. Dry phenyl phosphorodichloridate (2 ml) was slowly added and the mixture was heated to reflux. The solvent was evaporated under reduced pressure and the residual material was treated with 50 ml of ether. The ethereal suspension was washed 2—3 times with water and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residual material was crystallized from ethanol to afford the products.

Preparation of 4,5-Diaryl-2-hydroxy-1,3,2-dioxaphosphole 2-Oxides 4d—g. In place of phenyl phosphorodichloridate in the above procedure, dry ethyl phosphorodichloridate (2 ml) was slowly added. The products were crystallized from pet. ether.

4,5-Bis(4-methylphenyl)-2-phenoxy-1,3,2-dioxaphosphole 2-Oxide (3a). A yield of 41% was obtained, mp 170—171 °C; IR (Nujol) 1620 (C=C), 1290 (P=O),[9] and 1190 (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40 (s, 6H, two CH_3) and 7.00—8.10 (m, 13H, aromatic H); MS *m/z* 378 (M$^+$, 2%) and 119 (100).

Found: C, 69.59; H, 5.16%. Calcd for $C_{22}H_{19}O_4P$: C, 69.84; H, 5.06%.

4,5-Bis(4-methoxyphenyl)-2-phenoxy-1,3,2-dioxaphosphole 2-Oxide (3b). A yield of 30% was obtained, mp 181—182 °C; IR (Nujol) 1610 (C=C), 1260 (P=O),[9] and 1170 (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.00 (s, 6H, two OCH_3) and 6.75—8.20 (m, 13H, aromatic H); MS *m/z* 410 (M$^+$, 5%) and 135 (100).

Found: C, 64.66; H, 4.73%. Calcd for $C_{22}H_{19}O_6P$: C, 64.39; H, 4.67%.

4,5-Bis(4-chlorophenyl)-2-phenoxy-1,3,2-dioxaphosphole 2-Oxide (3c). A yield of 36% was obtained, mp 215—217 °C; IR (Nujol) 1600 (C=C), 1295 (P=O),[9] and 1200 (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.50—8.00 (m, aromatic H); MS *m/z* 418 (M$^+$, 7%) and 139 (100).

Found: C, 57.40; H, 3.40%. Calcd for $C_{20}H_{13}O_4Cl_2P$: C, 57.28; H, 3.12%.

4,5-Bis(4-methylphenyl)-2-hydroxy-1,3,2-dioxaphosphole 2-Oxide (4d). A yield of 36% was obtained, mp 198—200 °C; IR (Nujol) 2680—2540 (w, acid, P-OH),[9] 1610 (C=C), 1285 (P=O),[9] and 1190, (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.23 (s, 6H, two CH_3), 6.63 (br, s, 1H, hydroxyl H, which is exchangeable on D_2O shake), and 7.06—8.35 (m, 8H, aromatic H).

Found: C, 63.37; H, 4.98%. Calcd for $C_{16}H_{15}O_4P$: C, 63.58; H, 5.00%.

4,5-Bis(4-methoxyphenyl)-2-hydroxy-1,3,2-dioxaphosphole 2-Oxide (4e). A yield of 45% was obtained, mp 177—179 °C; IR (Nujol) 2660—2550 (w, acid, P-OH), 1610 (C=C), 1270 (P=O),[9] and 1190 (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.40 (s, 6H, two OCH_3), 7.10—8.10 (m, 8H, aromatic H), and 11.10 (br, s, 1H, hydroxyl H, which is exchangeable on D_2O shake).

Found: C, 57.67; H, 4.79%. Calcd for $C_{16}H_{15}O_6P$: C, 57.48; H, 4.52%.

4,5-Bis(4-chlorophenyl)-2-hydroxy-1,3,2-dioxaphosphole 2-Oxide (4f). A yield of 44% was obtained, mp 224—225 °C; IR (Nujol) 2730—2660 (w, acid, P-OH), 1615 (C=C), 1290 (P=O),[9] and 1185 (P-O-C) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.25 (br, s, 1H, hydroxyl H, which is exchangeable on D_2O shake) and 7.20—8.15 (m, 8H, aromatic H).

Found: C, 48.68; H, 2.72%. Calcd for $C_{14}H_9O_4PCl_2$: C, 48.97; H, 2.62%.

4,5-Diphenyl-2-hydroxy-1,3,2-dioxaphosphole 2-Oxide (4g). A yield of 62% was obtained, mp 116—118 °C; IR (Nujol) 2680—2550 (w, acid, P-OH),[9] 1600 (C=C), 1280 (P=O),[9] and 1180 (P-O-C)[9] cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.20—8.35 (m, 10H, aromatic H) and 11.05 (br, s, 1H, hydroxyl H, which is exchangeable on D_2O shake).

Found: C, 61.09; H, 3.80%. Calcd for $C_{14}H_{11}O_4P$: C, 61.32; H, 4.04%.

Hydrolysis of 4,5-Bis(4-methylphenyl)-2-phenoxy-1,3,2-dioxaphosphole 2-Oxide (3a). A dilute solution containing 0.50 g of **3a** in 50 ml of ether was treated with 10 ml of a 20% solution of sodium hydroxide at room temperature for 7 h with vigorous shaking. The reaction mixture was extracted with ether and dried over anhydrous sodium sulfate. The solvent was removed on a rotary evaporator and the residual material was crystallized from pet. ether to give 0.29 g (57%) of the product, mp 197—99 °C and mmp 196—199 °C.

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