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A CONVENIENT PREPARATION OF DIALKYL 3-(DIALKOXYPHOSPHINYL)-1-PROPENYL PHOSPHATE DERIVATIVES: ADDITION OF THE MIXED REAGENT TRIALKYL PHOSPHITE/ DIALKYL PHOSPHOROCHLORIDATE TO α,β-UNSATURATED ALDEHYDE

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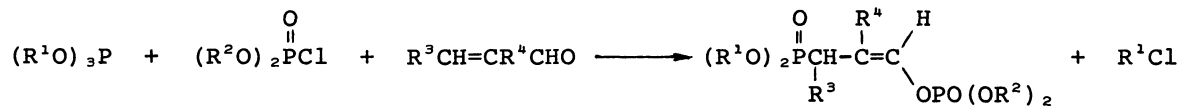
The mixed reagent trialkyl phosphite/dialkyl phosphorochloridate reacts readily with α,β-unsaturated aldehydes to give dialkyl 3-(dialkoxyphosphinyl)-1-propenyl phosphate derivatives.

Dialkyl 3-(dialkoxyphosphinyl)-1-propenyl phosphate derivatives 1 can be expected as an interesting bifunctional intermediate for organic synthesis. Recently, the reaction of enol phosphate with various nucleophiles has received much attention and it has been widely used as an intermediate for syntheses of alkyl- or alkenyl-substituted olefins,[1] vinylsilanes,[2] allylsilanes,[3] allenes,[4] and optically active secondary alcohols.[5] On the other hand, dialkyl allylphosphonate has been also utilized successfully in Wittig-Horner olefination[6] and stereoselective olefin synthesis by reductive C-P bond cleavage followed by α-alkylation.[7]

In this communication, the convenient synthesis of the enol phosphate 1, which can be converted to 3-substituted allylphosphonate or 1,4-disubstituted butadiene derivatives, by mean of the 1,4-addition of the mixed reagent, trialkyl phosphite 2/dialkyl phosphorochloridate 3, to α,β-unsaturated aldehyde 4 is reported. This mixed reagent reacts smoothly with several α,β-unsaturated aldehydes 4 in a manner similar to that described in the case of the mixed reagent trialkyl phosphite 2/chlorotrimethylsilane, which adds to α,β-unsaturated aldehyde 4 to give the phosphono-derivative of silyl enol ether.[8]



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The typical procedure is described: To an equimolar mixture of triethyl phosphite (3.3 g, 20 mmol) and diethyl phosphorochloridate (3.4 g, 20 mmol) in benzene (20 ml), 2-propenal (1.1 g, 20 mmol) was added with protection from atmospheric moisture within 20 min at room temperature. The reaction mixture was heated to the refluxing temperature. After stirring for 3 h, the solvent was removed and the residue was subjected to distillation under reduced pressure. Diethyl 3-(diethoxyphosphinyl)-1-propenyl phosphate (1c, 4.0 g, 61%) was obtained: Bp 120-122 °C/0.01 Torr; ^{1}H NMR δ($CDCl_3$/TMS) 1.33(6H, t, $^3J_{HH}$=7.0 Hz, CH_3 of R^1),

1.37(6H, t, $^3J_{HH}$=7.0 Hz CH_3 of R^2), 2.70(2H, ddd, $^3J_{HH}$=7.8, $^4J_{HH}$=0.7, $^2J_{PH}$=21.8 Hz, PCH_2), 4.09(4H, quintet, $^3J_{HH}$=$^3J_{PH}$=7.0 Hz, OCH_2 of R^1), 4.12(4H, quintet, $^3J_{HH}$=$^3J_{PH}$=7.0 Hz, OCH_2 of R^2), 4.95(1H, tdd, $^3J_{HH}$=7.8, $^3J_{HH}$=11.0, $^3J_{PH}$=2.2 Hz, CH_2CH=), 6.58(1H, tdd, $^3J_{HH}$=11.0, $^4J_{HH}$=0.7, $^3J_{PH}$=4.0 Hz, =CHO). ^{13}C NMR δ($CDCl_3$/TMS/^{1}H-decoupling) 16.38(s, CH_3), 22.44(d, $^1J_{CP}$=42.6 Hz, PCH_2), 61.98(d, $^2J_{CP}$=6.4 Hz, OCH_2 of R^1), 64.48(d, $^2J_{CP}$=5.7 Hz, OCH_2 of R^2), 104.3(t, $^2J_{CP^1}$=$^3J_{CP^2}$=12.0 Hz, CH_2CH=), 137.7(dd, $^2J_{CP}$=14.6, $^3J_{CP}$=4.8 Hz, =CHO). ^{31}P NMR δ($CDCl_3$/85% H_3PO_4)[9] -4.32(d, $^5J_{PP}$=1.9 Hz, $OPO(OEt)_2$), 26.63(d, $(EtO)_2P(O)CH_2$). Anal. Found: C; 39.85; H, 7.45; P, 18.93%; M^+ 330. Calcd for $C_{11}H_{24}O_7P_2$: C, 40.01; H, 7.32; P, 18.76%; M^+ 330.

The product 1c was shown to be pure by these NMR data and GLC analysis (5% of Silcone OV-17 Chromosorb W, 3 m X 3 mm, 100-250 °C), but the assigment of its olefin geometry could not be made. The adduct of the mixed reagent trialkyl phosphite/chlorotrimethylsilane to 2-propenal was assigned the Z-olefin geometry based on ^{1}H and ^{13}C NMR data and reaction mechanistic considerations.[8]

The present system afforded only the 1,4-addition product (by GLC analysis), while the trialkyl phosphite/chlorotrimethylsilane system afforded nearly a 1:1 mixture of 1,2- and 1,4-adducts in similar conditions.[8]

The results on several α,β-unsaturated aldehyde are listed in Table 1.

Table 1. The Preparation of Dialkyl 3-(Dialkoxyphosphinyl)-1-propenyl Phosphate 1

Product	R^1	R^2	R^3	R^4	Bp /°C (Torr)	Yield / %
1a	Me	Et	H	H	155-158 (0.1)	73
1b	Et	Me	H	H	153-155 (0.1)	72
1c	Et	Et	H	H	120-122 (0.01)	61
1d	Et	Et	H	Me	157-160 (0.1)	68
1e	Et	Me	H	Me	142-145 (0.05)	54
1f	Et	Et	Me	H	138-140 (0.03)	52
1g	Et	Et	Ph	H	155-160 (0.01)	26

Methyl vinyl ketone also reacted with this reagent under the same conditions, but any pure product could not be isolated. The extension of the study is now in progress.

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