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DIALKYL 3-ALKOXY-3-(TRIMETHYLSILOXY)-2-PROPENEPHOSPHONATE; A ONE STEP PREPARATION OF (DIALKOXYPHOSPHINYL)METHYL-SUBSTITUTED KETENE ALKYL TRIMETHYLSILYL ACETAL

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In the presence of chlorotrimethylsilane, trialkyl phosphite reacts smoothly with alkyl acrylates to give dialkyl 3-alkoxy-3-(trimethylsiloxy)-2-propenephosphonates in good yields.

Dialkyl 3-alkoxy-3-(trimethylsiloxy)-2-propenephosphonate (1) can be recognized as one of ketene silyl acetal derivatives, which have been known as new versatile reagents and utilized successfully in achieving a multitude of chemical transformation with acid chlorides,[1)] carbonyl compounds,[2)] Schiff base,[3)] heterocumulenes,[4)] and others.[5)] Such useful transformations can be also expected for this (dialkoxyphosphinyl)methyl-substituted ketene silyl acetal 1, which is an interesting intermediate for synthesis of new organophosphorus compounds and for Wittig-Horner olefin synthesis.

We now report on a new and convenient method for the preparation of 1 in good yields by means of the one step reaction of alkyl acrylate with trialkyl phosphite and chlorotrimethylsilane.

It has been shown that the reactions of the mixed reagent of tervalent phosphorus ester and chlorotrimethylsilane with α,β-unsaturated aldehydes or ketones give regioselectively 1,2- or 1,4-addition products of $X_2PO\text{-}SiMe_3$,[6)] while the reaction of triethyl phosphite with α,β-unsaturated ester in protic solvent proceeds smoothly to furnish β-(diethoxyphosphinyl)carboxylate.[7)]

In the presence of chlorotrimethylsilane, trialkyl phosphite reacts with alkyl acrylates to give the ketene silyl acetal 1 which is a new compound, as far as we know, and alkyl chloride.

To the equimolar mixture of triethyl phosphite (33.2 g, 0.20 mol) and chlorotrimethylsilane (21.7 g, 0.20 mol), methyl acrylate (8.6 g, 0.10 mol) was added within 20 min with careful protection of atmospheric moisture. The reaction mixture was heated to the refluxing temperature of chlorotrimethylsilane. After stirring for 1 h, the excess reagent was removed and the residue was subjected to distillation under reduced pressure. Diethyl 3-methoxy-3-(trimethylsiloxy)-2-propenephosphonate (1-a, 25 g, 85%) was obtained.[8] Bp 108-110 °C/5 Torr,* Anal. Found: C, 44.37; H, 8.60; P, 10.36%; M^+, 296. Calcd for $C_{11}H_{25}O_5PSi$: C, 44.56; H, 8.51; P, 10.46%; M^+, 296. IR(neat) 1740 cm^{-1} (ν C=C); ^1H NMR $\delta(DCCl_3)$ 0.20(9H, s, $SiCH_3$), 1.32(6H, t, J_{HH}=7.08 Hz, $CH_2C\underline{H}_3$), 2.52(2H, d-d, J_{PH}=19.6 Hz, J_{HH}=7.2 Hz, $PC\underline{H}_2$), 3.45(1H, d-t, J_{PH}=8.0 Hz, J_{HH}=7.2 Hz, CH=), 3.53(3H, s, OCH_3), 4.16(4H, d-q, J_{PH}=5.86 Hz, OCH_2); ^{13}C NMR $\delta(CDCl_3$-TMS-off-resonance) 0.67(q, $SiCH_3$), 15.59(q, $CH_2C\underline{H}_3$), 21.74(d-t, J_{PC}=144.0 Hz, PCH_2), 53.70(q, OCH_3), 60.57(t, OCH_2), 63.53(d-d, J_{PC}=9.8 Hz, -CH=), 157.4(d, J_{PC}=14.7 Hz, $=C{<}^{O-}_{O-}$).[9]

The yield of the product decreased to 54% when an equimolar amount of the mixed reagent with methyl acrylate was used. The product 1-a was assumed to be a pure iosmer from the data of NMR and GLC (5% of Silicone OV-17 Chromosorb W, 3 m X 3 mm, 180 °C), but its stereochemistry is not assigned. The ketene alkyl silyl acetal 1 is highly sensitive to atmospheric moisture and reacts vigorously with water to form alkyl 3-(dialkoxyphosphinyl)propanoate quantitatively. Other substituted α,β-unsaturated carboxylates,such as, methyl methacrylate, methyl cinnamate, methyl crotonate, and dimethyl maleate did not bring about the reaction under the same conditions. This limitation may reflect the greater sensitivity of this reagent to steric factors. Acrylic acid reacted exothermally with this mixed reagent to furnish trimethylsilyl 3-(diethoxyphosphinyl)propanoate in 96% yield, without cooling.[10] However, when this reaction was carried out with ice-cooling (0-2 °C), trimethylsilyl acrylate and diethyl phosphite were isolated as main products.

The formation of the ketene alkyl silyl acetal 1 can be rationalized by a following scheme.[11]

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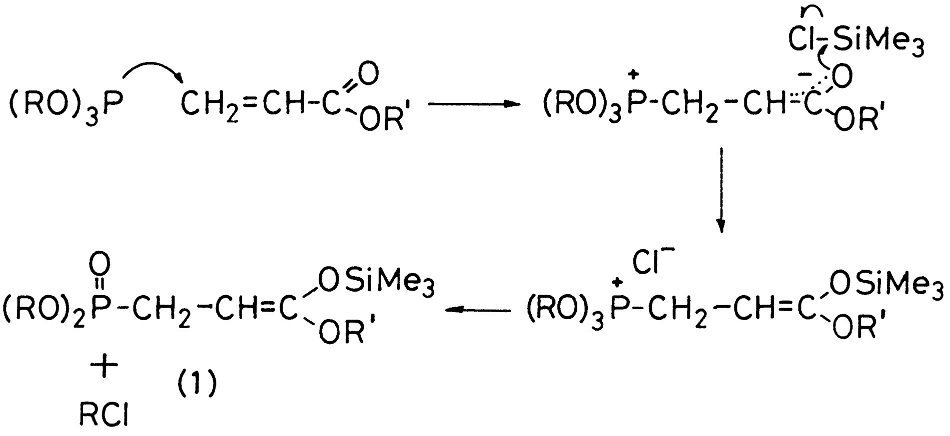
* Torr ≃ 133 Pa



Scheme

The results obtained on several alkyl acrylates are summarized in Table 1.

Table 1. The preparation of 3-(diethoxyphosphinyl)-substituted ketene alkyl trimethylsilyl acetals (1)

1	R	R'	Bp °C/ Torr	Yield (%)
a	C_2H_5	CH_3	115 - 117/5	58
b	C_2H_5	C_2H_5	98 - 105/1	86
c	C_2H_5	C_3H_7	108 - 110/1	79
d	C_2H_5	C_4H_9	126 - 128/3	75
e	i-C_3H_7	CH_3	99 - 101/1	62
f	C_2H_5	H	96 - 97/2	96[a]

[a] This product is trimethylsilyl 3-(diethoxyphosphinyl)propanoate.

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References

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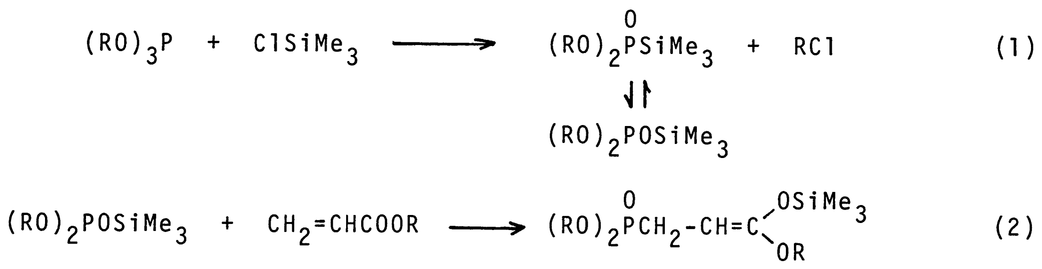
8) Substantial quantity of ethyl chloride was collected in a trap cooled with liquid nitrogen.

9) These spectra data are similar to these of related compounds [M.W. Rathke and D.F. Sullivan, Synthetic Commun., 3, 67 (1973); C. Aninsworth, F. Chen, and Y.N. Kuo, J. Organometallic Chem., 46, 59 (1972); Y. Kita, J. Haruta, J. Segawa, and Y. Tamura, Tetrahedron Lett., 1979, 4311; H. Herberhold, G.O. Wiedersatz, and C.G. Kreiter, Z. Naturforsch., B, 31, 35 (1976)]. However, the possibility of the formation of C-silylated product can not thoroughly be excluded on the basis of spectra data. A chemical evidence of high sensitivity to water supports the formation of O-silylated product.

10) In the presence of butyl bromide, acrylic acid reacts with triethyl phosphite to give butyl 3-(diethyoxyphosphinyl)propanoate [V.A. Kukhtin and G. Kamai, Zh. Obsch. Khim., 28, 1196 (1958): C.A., 52, 19909 (1958)].

11) An alternate path can be illustrated as follows.



$$(RO)_3P + ClSiMe_3 \longrightarrow (RO)_2\overset{O}{P}SiMe_3 + RCl \qquad (1)$$

$$\downarrow\uparrow$$

$$(RO)_2POSiMe_3$$

$$(RO)_2POSiMe_3 + CH_2{=}CHCOOR \longrightarrow (RO)_2\overset{O}{P}CH_2\text{-}CH{=}C\begin{matrix}\diagup OSiMe_3\\ \diagdown OR\end{matrix} \qquad (2)$$

In this scheme, the mixed silyl phosphite ester produced in situ by an Arbuzov rearrangement is an intermediate. However, upon heating an equimolar mixture of trialkyl phosphite and chlorotrimethylsilane for 7 h at 105 °C, there was no evidence (^{1}H NMR) of the formation of the silyl phosphite or any other reaction product.$^{6)}$

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