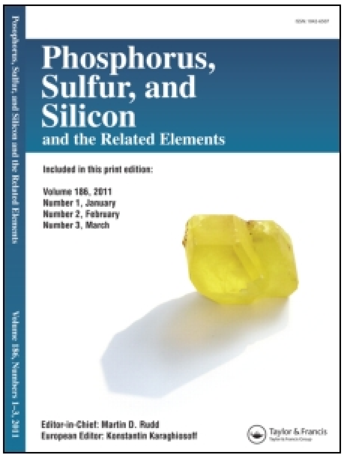

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REACTION OF BIS(TRIMETHYLSILOXY)PHOSPHINE WITH α-HALO CARBONYL COMPOUNDS. A NEW ROUTE TO SUBSTITUTED 0,0-DIVINYL-0-TRIMETHYLSILYL PHOSPHATES

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Substituted 0,0-divinyl-0-trimethylsilyl phosphates **4** have been obtained in satisfactory yields by reacting bis(trimethylsiloxy)phosphine (**1**) with α-halo carbonyl compounds **2** in the presence of chlorotrimethylsilane and triethylamine.

Key words: Substituted 0,0-divinyl-0-trimethylsilyl phosphates; substituted 0-vinyl-0-trimethylsilyl-1-(trimethylsiloxy)alkylphosphonates; bis(trimethylsiloxy)phosphine; derivatives of 3-halo-2-oxoalkanoic acids; Perkow reaction.

Physiological activities of enol phosphates have made these compounds important synthetic goals[1] and have stimulated the development of various biochemical[1a,2] and chemical investigations.[3] Unexpectedly, the synthesis and properties of the related dienol phosphates have been studied only to a limited extent.[2c,4] In this paper a novel approach to the substituted 0,0-divinyl-0-trimethylsilyl phosphates **4** based on the reaction of bis(trimethylsiloxy)phosphine (**1**) with α-halo carbonyl compounts **2** is described. It has been previously reported that **1** reacts with chloroactone to give a phosphonite and 0-(1-methylvinyl) 0-trimethylsilyl phosphite.[5] So it might be expected that in the presence of silylating reagent the reaction of **1** with an excess of **2** should lead to vinyl phosphites **3** which in turn by the action of **2** would be converted to **4** by classical Perkow rearrangement (Scheme). Indeed, it was found that **1** reacts with two equivalents of **2** in refluxing benzene in the presence of one equivalent of triethylamine and one equivalent of chlorotrimethylsilane to yield in general the desired dienol phosphates **4** slightly contaminated with enol phosphonates **5** (Scheme, Table I).[6] The structures and the ratios of **4** and **5** have been established from NMR spectra of the crude products (Table I).

In the cases of α-halo carbonyl compounds such as bromal (**2a**), ethyl DL-3-bromo-2-oxopentanoate (**2b**), ethyl DL-chloro-(4-chlorophenyl)pyruvate (**2c**) and 2,4-dichlorophenacyl bromide (**2d**) the yield of phosphonates **5a**–**5d** does not exceed ~10% and the dienol phosphates **4a**–**4d** could be easily separated by simple distillation. When chloral (**2f**) and 1,3-dichloroacetone (**2e**) were used as the starting materials the enol phosphonates **5e** and **5f** were formed as main products (Table I). The ratio of **4e**/**5e** and **4f**/**5f** was found to be dependent to

TABLE I

Composition and some spectral features of **4** and **5** in the crude product from the reaction of **1** with two equivalent of **2** in refluxing benzene in the presence of one equivalent of chlorotrimethylsilane and one equivalent of triethylamine

Starting α-halo carbonyl compounds	^{31}P-NMR(neat), δ(ppm) **4**[a]	**5**	Molar ratio of **4**:**5**
2a	−20.4	–	100:0
2b	−19.7, −20.0; −20.4; (1:3:1)[b]	1.7; 1.4; 1.1; 0.7 (3:3:2:5)[b,c]	88:12
2c	−20.0; −20.7; −21.7 (1:3:3)[b]	2.5; 0.5; −3.3; −5.2 (1:2:2:1)[b,c]	92:8
2d	−22.0	—	100:0
2e	−22.5	4.8[e]	33:67 (50:50)[d]
2f	−19.5[f]	1.3; 2.3 (1:1)[b,e,g]	4:96 (16:74)[d]

[a] ^{1}H-NMR spectra of the isolated **4a**–**4e** are given in Table II.

[b] Molar ratio of distareoisomers.

[c] In this case the individual spectral lines can correspond to more than one diastereoisomer.

[d] The reaction has been carried out in acetonitrile as a solvent.

[e] ^{1}H-NMR spectra of the isolated **5e**–**5f** are given in the experimental part.

[f] Undecoupled ^{31}P-NMR spectrum exhibits the triplet signal with $^3J_{PH} = 5.5$ Hz.

[g] Undecoupled ^{31}P-NMR spectrum exhibits the signals having doublet of doublet structure with J values identical with those observed in the corresponding ^{1}H-NMR spectrum; $^2J_{PH} = 9.1$ Hz; $^3J_{PH} = 6.5$ Hz for each of the diastereoisomer.

2, 3, 4, 5	**a**	**b**	**c**	**d**	**e**	**f**
R^1	H	$COOC_2H_5$	$COOC_2H_5$	2,4-$Cl_2C_6H_3$	CH_2Cl	H
R^2	Br	C_2H_5	4-ClC_6H_4	H	H	Cl
R^3	Br	H	H	H	H	Cl
X	Br	Br	Cl	Br	Cl	Cl

some extent on the reaction condition, particularly on the solvent used. When benzene was replaced by acetonitrile the proportion of **4e**/**5e** and **4f**/**5f** increased (Table I). Simple distillation of the crude mixture of **4f** and **5f** allowed to islolate pure **5f**, however, separation of the mixture containing **4e** and **5e** into individual components required fractional distillation. Yields, physical constants and spectroscopic data of isolated substituted divinyl phosphates **4a**–**4e** are compiled in the Table II.

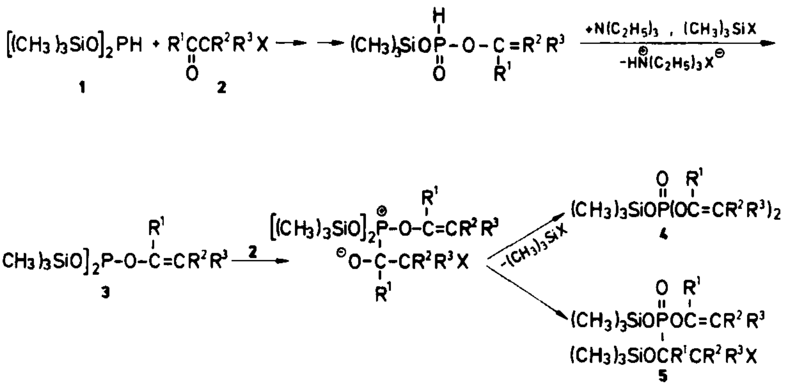


TABLE II

Substituted 0,0-divinyl 0-trimethylsilyl phosphates **4a–4e**

Yield (%)	b.p. (°C)/torr	Molecular formula[a]	IR: (ν cm^{-1}) (C=C)	^{31}P-NMR (neat/H_3PO_{4ext}) δ (ppm)	^{1}H-NMR (solvent/TMS_{int})[b] δ (ppm)
84.3	125/0.4	$C_7H_{11}Br_4O_4PSi$ (537.9)	1632	−20.4	(CD_2Cl_2) 0.33 (s, 9H, $Si(CH_3)_3$); 7.25 (d, 2H, $^3J_{PH} = 5.5$ Hz, C=CH).
85.2	135–140/0.5	$C_{17}H_{31}O_8PSi$ (422.5)	1662	−19.7; −20.0; −20.4 (1:3:1)[c]	(C_6D_6) 0.29, 0.31, 0.34 (3s, 9H, $Si(CH_3)_3$); [0.87 (t, $^3J_{HH} = 7$ Hz) + 0.90 (t, $^3J_{HH} = 7$ Hz), 6H, $C\underline{H}_3CH_2C{=}C$], 1.01 (t, 6H, $^3J_{HH} = 7$ Hz, $C\underline{H}_3CH_2O$); 2.05–2.70 (overlapped multiplets, 4H, $CH_3C\underline{H}_2C{=}C$); 4.04 (q, 4H, $^3J_{HH} = 7$ Hz, $CH_3C\underline{H}_2O$); 6.12–6.51 (overlapped multiplets, $^3J_{HH} = 7$ Hz, $^4J_{PH} \simeq 2.5$ Hz, C=CH).
70.2	170/0.5	$C_{25}H_{29}Cl_2O_8PSi$ (587.4)	1650	−20.0; −20.7; −21.7 (1:3:3)[c]	(CCl_4) 0.20 (s, 9H, $Si(CH_3)_3$; [1.25 (t, $^3J_{HH} = 7$ Hz) + 1.25 (t, $^3J_{HH} = 7$ Hz) + 1.28 (t, 7 Hz), 6H, $C\underline{H}_3CH_2O$]; 4.0–4.5 (overlapped q, $^3J_{HH} = 7$ Hz, $CH_3C\underline{H}_2O$); [6.95 (d, $^4J_{PH} = 2.7$ 7.00 (d, $^4J_{PH} \simeq 2$ Hz) + 7.07 (s), 2H, C=CH]; 7.1–7.9 (m, 8H arom).
63.2	161/0.3	$C_{19}H_{19}Cl_4O_4PSi$ (512.2)	1648	−22.0	(C_6D_6) 0.15 (s, 9H, $Si(CH_3)_3$); 4.87 (m, 2H, $^2J_{HH} = 2.35$, $^4J_{PH} = 2.65$, $C{=}CH_z$); 5.53 (m, 2H $^2J_{HH} = 2.35$, $^4J_{PH} = 2.65$, $C{=}CH_E$); 6.64–7.25 (m, 6H arom.).
25.2	90/0.4	$C_9H_7Cl_2O_4PSi$ (319.2)	1654	−22.5	(C_6D_5) 0.19 (s, 9H, $Si(CH_3)_3$); 3.82 (Br.s, 4H, CH_2); 4.70 (m, 2H, $^4J_{PH} \simeq {}^2J_{HH} \simeq 2.2$ Hz; $^4J_{HH}$ $C{=}CH_Z$); 5.20 (t, 2H, $^4J_{PH} = {}^2J_{HH} = 2.2$ Hz,

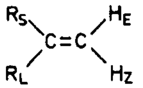
tisfactory microanalyses obtained: C ± 0.40, H ± 0.25, P ± 0.30.

enzene was also used as an internal standard to obtain the chemical shift of the trimethylsilyl groups.

e ratio of diastereoisomers.

EXPERIMENTAL

All operations were carried out in carefully dried apparatus under argon atmosphere, and anhydrous solvent were used. ^{1}H-NMR spectra were measured at 90 MHz with a Bruker HFX 90 spectrometer. The scheme applied for the assignment of ^{1}H-NMR signals of the vinyl moiety is as follows:



where R$_S$ and R$_L$ have a typical meaning.

^{31}P-NMR spectra were measured at 24.3 MHz with a Jeol JNMR-C-60 HL spectrometer using a Heteronuclear Spin Decoupler, JNM-SD-HC. IR spectra were recorded for liquid films on a IR-225 (Perkin-Elmer) spectrophotometer. 2,4-Dichlorophenacyl bromide (**2d**) was obtained by the action of bromine in carbon tetrachloride on 2,4-dichloroacetophenone.[7] Crude ethyl DL-2-hydroxypentanoate, prepared according to the procedure of Mendel and Coops[8] for methyl DL-2-hydroxystearate, was oxidatively brominated with bromine in carbon tetrachloride to give ethyl DL-3-bromo-2-oxopentanoate (**2b**); yield 64%; b.p. 98–99/12 torr; $n_D^{18} = 1.4607$; IR (cm^{-1}): 1715, 1730 (C=O); ^{1}H-NMR (CCl$_4$): 1.09 (t, 3H, $^3J_{HH} = 7$ Hz, CHCH$_2$C$\underline{H}_3$); 1.4 (t, 3H, $^3J_{HH} = 7$ Hz, OCH$_2$C$\underline{H}_3$); 1.8–2.5 (m, 2H, CHC$\underline{H}_2$CH$_3$); 4.4 (q, 2H, $^3J_{HH} = 7$ Hz, OC$\underline{H}_2$CH$_3$); 5.0 (dd, 1H, $^3J_{HH} = 8$ Hz, $^3J_{HH} = 6$ Hz, C$\underline{H}$CH$_2$CH$_3$).

Anal.	$C_7H_{11}O_3Br$	calc.	C 37.68	H 4.97 (%)
	(223.0)	found	37.50	4.72 (%)

Ethyl DL-chloro-(4-chlorophenyl)pyruvate was prepared in 70% yield from the reaction of 4-chlorobenzaldehyde with ethyl dichloroacetate in the manner given for chlorophenylpyruvate.[9] The chloro ester showed b.p. 117–120/0.4 torr; $n_D^{20} = 1.5335$. IR (cm^{-1}): 1720 (C=O); ^{1}H-NMR(CDCl$_3$): 1.26 (t, 3H, $^3J_{HH} = 7$ Hz, CH$_3$); 4.3 (q, 2H, $^3J_{HH} = 7$ Hz, CH$_2$); 6.12 (s, CHCl); 7.32 (m, 4H arom.).

Anal.	$C_{11}H_{10}O_3Cl_2$	calc.	C 50.59	H 3.86 (%)
	(261.1)	found	50.72	3.95 (%)

Reaction of bis(trimethylsiloxy)phosphine (**1**) with α-halo carbonyl compounds **2a**–**2f**; General Procedure:

To a stirred solution of bis(trimethylsiloxy)phosphine (**1**; 3 g, 14.4 mmol), chlorotrimethylsilane (1.55 g, 14.4 mmol) and triethylamine (1.47 g, 14.4 mmol) in benzene (35 ml) was added dropwise appropriate α-halo carbonyl compounds **2a**–**2f** at 50°C. The resulting mixture was stirred at 50–55°C for 30 min and then refluxed for 1 h. After the mixture had been cooled to room temperature, dry ether (20 ml) was added and the resultant mixture cooled to 5°C. The precipitated triethylamine hydrochloride was filtered off and the filtrate evaporated. Simple distillation of the residue from **2a**–**2d** and **2f** gave **4a**–**4d** and **5f** (yield 71.5%), respectively. The residue from the starting **2e** was subjected to fractional distillation to affort **4e** and **5e** (yield: 23.7%). Yields, physical and spectroscopic data for **4a**–**4e** are recorded in Table II. The enol phosphonates **5e** and **5f** showed, **5e**: b.p. 120°/0.4 torr; IR: 1654 cm^{-1}(C=C); ^{31}P-NMR (neat): 4.8 ppm; ^{1}H-NMR (CDCl$_3$): 0.15 (s, 9H, COSi(CH$_3$)$_3$); 0.20 (s, 9H, POSi(CH$_3$)$_3$); $\delta_A = \delta_{A'} = 3.74$, $\sigma_B = \delta_{B'} = 3.90$[m(ABX + A'B'X', where X = X' = P), 4H, $^2J_{H_AH_B} = {}^2J_{H_{A'}H_{B'}} = 11.7$ Hz, $^3J_{PH_A} \simeq {}^3J_{PH_{A'}} \simeq 14.5$ Hz, $^3J_{PH_B} \simeq {}^3J_{PH_{B'}} = 8.5$ Hz, 2 × ClCH$_2$CP]; 3.81 (br.s, 2H, ClCH$_2$C=C); 4.62 (m, 1H, $^2J_{HH} = {}^4J_{PH} = 2.1$ Hz, $^4J_{HH} < 1$ Hz, C=CH$_Z$); 5.08 (t, 1H, $^2J_{HH} = {}^4J_{PH} = 2.1$ Hz, C=CH$_E$).

Anal.	$C_{12}H_{26}Cl_3PSi_2$	calc.	C 33.68	H 6.12	P 7.28 (%)
	(427.8)	found	33.50	6.21	7.12 (%)

5f: b.p. 112/0.5 torr; IR: 1642 cm^{-1}(C=C), ^{31}P-NMR(neat): $\delta = 1.3$ and 2.3 ppm (1:1); ^{1}H-NMR (CDCl$_3$): 0.23 (s, 9H, COSi(CH$_3$)$_3$); 0.31 (s, 9H, POSi(CH$_3$)$_3$); 4.49 (d, 1H, $^2J_{PH} = 9.1$ Hz, PCH); 7.06 (d, 1H, $^3J_{PH} = 6.5$ Hz).

Anal.	$C_{10}H_{20}Cl_5O_4PSi_2$	calc.	C 25.62	H 4.30	P 6.62 (%)
	(468.7)	found	25.41	4.18	6.52 (%)

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