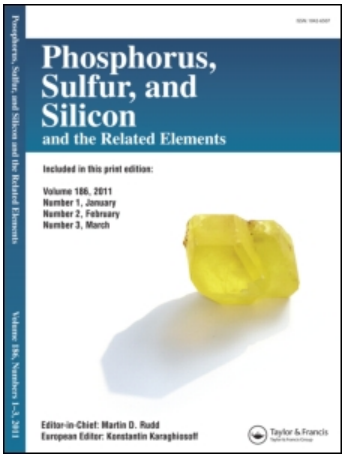

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NEW SYNTHETIC ROUTE TO DIALKYLPHOSPHINIC ACIDS

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NEW SYNTHETIC ROUTE TO DIALKYLPHOSPHINIC ACIDS

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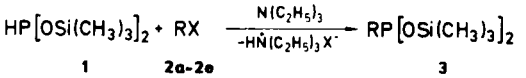
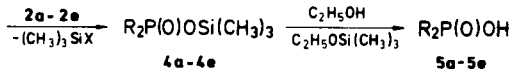
The dialkylphosphinic acids, **5a–5e**, can be obtained by reacting bis(trimethylsiloxy)phosphine with the highly reactive alkyl halides, **2a–2e**, in the presence of chlorotrimethylsilane and triethylamine, followed by ethanolysis of the resulting trimethylsilyl dialkylphosphinates, **4a–4e**.

Key words: Dialkylphosphinic acids; bis(trimethylsiloxy)phosphine, alkylation of; trimethylsilyl dialkylphosphinates, ethanolysis of; Arbuzov reaction.

Alkylation of dialkoxyphosphine with alkyl halides in the presence of triethylamine results in the formation of alkyldialkoxyphosphines.[1] Similar reaction of bis(trimethylsiloxy)phosphine (**1**) is, however, more complicated.[2] It is always accompanied by an Arbuzov type rearrangement of the primarily formed alkyl-bis(trimethylsiloxy)phosphines, **3**, leading to trimethylsily dialkylphosphinates, **4**. The ratio of **3** and **4** is to some extent dependent on the alkyl halide used.[2b] This paper describes the reaction of **1** with alkyl halides **2** to give the novel trimethylsilyl dialkylphosphinates, **4**, which are precursors to the dialkylphosphinic acids, **5**. It was found that when **1** reacts with two equivalents of a highly reactive alkyl halide, **2a–2e**, in the presence of one equivalent of trimethylchlorosilane and one equivalent of triethylamine in refluxing benzene the corresponding





2-5	R	2-5	R
a	CH_3OCCH_2 (O)	d	C_2H_5OC(O)$CH{=}C(OC_2H_5)CH_2$
b	$C_6H_5CH_2$		
c	H_B, H_A, H_C on $C{=}CCH_2$	e	H_B, H_A on $C{=}C(COC_2H_5)CH_2$

TABLE I

Trimethylsilyl dialkylphosphinates **4a–4e**

	Yield in %	Molecular Formula[a]	b.p. (°C)/torr	^{31}P-NMR ($C_6H_6/H_3PO_{4\ ext}$) δ(ppm)	^{1}H-NMR (CCl_4/TMS_{int}) δ(ppm)
4a	79	$C_9H_{19}O_6PSi$ (282.3)	110/0.6	26.0	0.2 (9H, s, CH_3Si); 3.40 (4H, d, $^2J_{PH}$ = 18 Hz, CH_2P); 4.05 (6H, s, CH_3O).
4b	64	$C_{17}H_{23}O_2PSi$ (318.4)	129/0.7	37.1	0.1 (9H, s, CH_3Si); 2.85 (4H, d, $^2J_{PH}$ = 17.0 Hz); 7.0–7.2 (10H arom.);
4c	59	$C_9H_{19}O_2PSi$ (218.3)	60–63/0.5	35.8	0.25 (9H, s, CH_3Si); 2.35 (4H, dd, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.25 Hz, CH_2P); 4.86–5.30 (4H, overlapped multiplets, $2H_A + 2H_B$); 5.35–6.10 (2H, m, H_c).
4d	36	$C_{19}H_{35}O_8PSi$ (450.5)	135/0.5	30.6	0.19 (9H, s, CH_3Si); 1.00 (6H, t, $^3J_{HH}$ = 7 Hz, CH_3CH_2OC); 1.03 (6H, $^3J_{HH}$ = 7.0 Hz, CH_3CH_2OOC); 3.20–3.85 (4H, m, $^2J_{PH}$ = 17.5 Hz, CH_2P); 3.43 (4H, q, $^3J_{HH}$ = 7 Hz, CH_3CH_2OC; 3.97 (4H, q, $^3J_{HH}$ = 7 Hz, CH_3CH_2OOC); 4.99 (2H, d, $^4J_{PH}$ = 3.5 Hz, HC = C).
4e	67	$C_{15}H_{27}O_6PSi$ (362.4)	140–142/0.2	35.2	0.15 (9H, s, $SiCH_3$); 1.05 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3CH_2); 2.95 (4H, d, $^2J_{PH}$ = 17.1, CH_2P); 4.10 (4H, q, $^3J_{HH}$ = 7 Hz, OCH_2CH_3); 5.87 (2H, dd, $^4J_{PH}$ = 5.5 Hz, $^2J_{HH}$ = 1.3 Hz, H_A); 6.33 (2H, dd, $^4J_{PH}$ = 5.5 Hz, $^2J_{HH}$ = 1.3 Hz, H_B).

a. Satisfactory microanalyses were obtained: C ± 0.35, H ± 0.20, P ± 30.

TABLE II

Dialkylphosphinic acids **5a–5e**

	Yield in %	Molecular Formula[a]	IR (film)[b] $\nu(cm^{-1})$	^{31}P-NMR ($CHCl_3/H_3PO_{4\ ext}$) δ(ppm)	^{1}H-NMR ($CDCl_3/TMS_{int}$) δ(ppm)
5a	85	$C_6H_{11}O_6P$ (210.1)	1725 (C=O)	31.5	3.15 (4H, d, $^2J_{PH}$ = 17.5 Hz, CH_2P); 3.70 (6H, s, CH_3O); 8.1 (1H, br, s, OH).
5b	92	m.p. 192–194°C Lit.[7] 190–192°C			2.85 (4H, d, $^2J_{HH}$ = 16.5 Hz, CH_2P); 7.2–7.3 (10 H arom.); 8.0 (1H, br, s, OH).
5c	90	$C_6H_{11}O_2P$ (146.1) Lit.[8]	1635 (C=C)	47.5	2.60 (4H, m, $2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.0 Hz, $^4J_{H_AH} \simeq {}^4J_{H_BH} \simeq$ 1 Hz, CH_2P); 5.21, 5.24, 5.82 (6H, ABC system[c], $^3J_{H_AH_C}$ = 17.5 Hz, $^2J_{H_AH_B}$ = 2 Hz, $^4J_{PH_A} = {}^4J_{PH_B}$ = 4.25 Hz, $^4J_{H_AH} \simeq {}^4J_{H_BH} \simeq$ 1 Hz, $^3J_{H_BH_C}$ = 9.25 Hz, $^3J_{H_CH}$ = 7.0 Hz, $^3J_{PH_C}$ = 5.25 Hz, $2H_A + 2H_B + 2H_C$); 12.3 (1H, s, OH).
5d	89	$C_{16}H_{27}O_8P$ (378.3)	1620 (C=C) 1720 (C=O)	44.5	1.25 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_3CH_2OC); 1.35 (6H, t, $^3J_{HH}$ = 7.0 Hz, CH_2OOC); 3.25–3.6 (4H, m, $^2J_{PH}$ = 17.6 Hz, CH_2P); 3.8 (4H, q, $^3J_{HH}$ = 7 Hz, CH_3CH_2OC); 4.0 (4H, q, $^3J_{HH}$ = 7 Hz, CH_3CH_2OOC); 5.0 (d, 2H, $^4J_{PH}$ = 2.6 Hz, HC = C); 8.9 (1H, s, OH).
5e	95	$C_{12}H_{19}O_6P$ (290.1)	1625 (C=C) 1720 (C=O)	48.5	1.3 (6H, t, $^3J_{HH}$ = 7 Hz, CH_3CH_2); 2.93 (4H, d, $^2J_{PH}$ = 17.1 Hz, CH_2P); 4.22 (4H, q, $^3J_{HH}$ = 7 Hz, OCH_2CH_3); 5.89 (2H, dd, $^4J_{PH}$ = 5.5 Hz, $^2J_{HH} \simeq$ 1.0 Hz, H_A); 6.37 (2H, dd, $^4J_{PH}$ = 5.5 Hz, $^2J_{HH} \simeq$ 1.0 Hz, H_B); 8.0 (1 H, br, s, OH).

a. Satisfactory microanalyses were obtained: C ± 0.40, H ± 0.25, P ± 0.30.

b. All compounds show bands characteristic for a dialkylphosphinic acid moiety P (:O) OH[9]: weak broad bands between 2725–2525, 2350–2080 and 1740–1600 cm^{-1} (Specord 71 IR C. Zeiss spectrophotometer).

c. An ABX approximation was applied.

phosphinates, **4a–4e**, are formed in good yields. Compounds **4a–4e** could be easily purified by distillation. The physical constants and spectroscopic data are listed in Table I. The reaction of **1** with **2a–2e**, performed in the absence of chlorotrimethylsilane, gives lower yields of the respective phosphinates, **4a–4e**, and their purity is lower. Dialkylphosphinic acids, **5a–5e**, were easily prepared in a pure state from the phosphinates, **4a–4e**, by refluxing in ethanol (c.f. Table II). The synthetic procedure is limited to highly active alkyl halides. Unsatisfactory results were obtained with methyl iodide, butyl bromide, and hexyl bromide.

EXPERIMENTAL

^{1}H-NMR- and ^{31}P-NMR spectra were recorded at 80 MHz on a Tesla BS 487C spectrometer and at 36, 43 MHz on a Bruker HFX 90 spectrometer, respectively. Alkyl halides, besides those which are commercially available, **2d** and **2e**, were prepared using described procedures.[3–6]

Trimethylsilyl Dialkylphosphinates, **4a–4e**, *General Procedure.* To a 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) is added the appropriate alkyl halide, **2a–2e** (28.8 mmol). The resulting mixture is stirred at 30°C for 30 min and then refluxed for 1 h. The precipitate is filtered off, the filtrate evaporated and the residue distilled in vacuo to give pure **4a–4e**.

Dialkylphosphinic Acids, **5a–5e**; *General Procedure.* A solution of the appropriate phosphinate, **4a–4e**, (10 mmol) in ethanol (20 ml) is refluxed for 5 min. The solvent is then evaporated, leaving the pure acids, **5a–5e**, as oils, with the exception of **5b**: mp. 192–194°C (recrystallized from benzene). The dialkylphosphinic acids, **5a–5e**, are contaminated with alkyl-phosphinic acids if all operations are not carried out with complete exclusion of oxygen. The contaminated acids, **5a–5e**, can be purified by dissolving in water and extraction with chloroform.

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