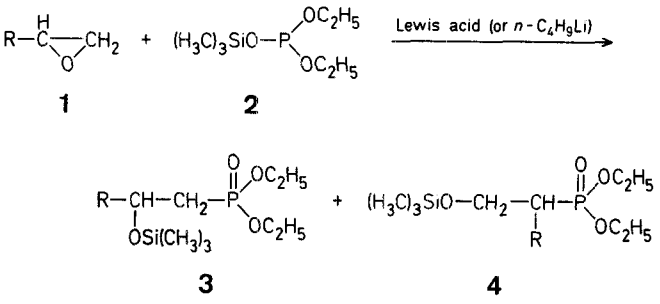

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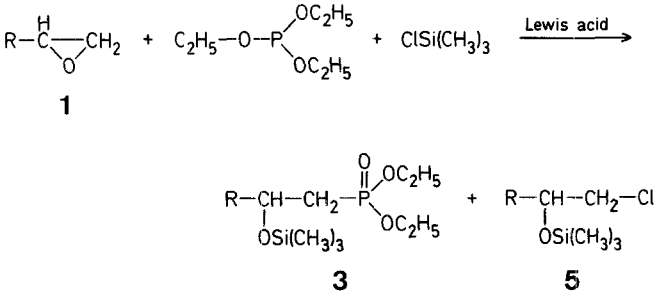
3 4

It is known that a mixture of trialkyl phosphite and chlorotrimethylsilane can be used in place of diethyl trimethylsilyl phosphite **(2)** in the addition reaction with α,β-unsaturated carboxylates[3], nitriles[4], and ketones[5]. Epoxides also react with this mixture to give diethyl 2-(trimethylsiloxy)-alkanephosphonates **(3)** but, in addition, a 2-chloroalkyl trimethylsilyl ether **(5)** is formed as a by-product. When the latter reaction is carried out in the absence of a catalyst under otherwise identical conditions, the 2-chloroalkyl trimethylsilyl ether **(5)** is obtained as the only product.



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3 5

Synthesis of Diethyl 2-(Trimethylsiloxy)-alkanephosphonates from Epoxides and Diethyl Trimethylsilyl Phosphite

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We report here the synthesis of diethyl 2-(trimethylsiloxy)-alkanephosphonates **(3)** by reaction of diethyl trimethylsilyl phosphite **(2)** with various epoxides **(1)** in the presence of Lewis acids or a base as catalysts.

The thermal uncatalyzed reactions of trialkyl phosphite with epoxides have already been described: ethylene and propylene oxides are quantitatively deoxygenated to the corresponding alkenes by triethyl phosphite at 150°C under pressure[1]. Triisopropyl phosphite reacts with ethylene oxide at 170°C for 5 h in an autoclave to give diisopropyl 2-isopropoxyethanephosphonate[2].

In the presence of zinc iodide, diethyl trimethylsilyl phosphite **(2)** reacts (50–60°C, 1 h) with propylene oxide **(1a)** to give diethyl 2-(trimethylsiloxy)-propanephosphonates **(3a)**. Other Lewis acids: zinc, iron(III), tin(II), and tin(IV) chlorides are also effective in this reaction. Epoxides **1a–e** undergo ring opening exclusively at the terminal C-atom to give primary phosphonates **(3)**. No selectivity is observed in the case of phenyloxirane **(1f)**: a 42/68 mixture of the regioisomers **3f** and **4f** is formed. When a base such as butyllithium is used as the catalyst the regioselectivity of the ring-opening reaction is almost 100%.

Diethyl 2-(Trimethylsiloxy)-alkanephosphonates (3):

Method A, from **1** and **2** in the Presence of Zinc Iodide; General Procedure: A mixture of the epoxide (**1**; 0.3 mol), diethyl trimethylsilyl phosphite (**2**; 21.0 g, 0.1 mol), and zinc iodide (0.3 g, 1 mmol) is stirred at 55–60°C for 1 h, cooled, and the unreacted material is evaporated under reduced pressure. The product **3** is isolated by distillation in vacuo. The purity of the product **3** is checked by G.L.C. (conditions: Silicone OV 17, 2% Uniport HP, 80/100, glass 2 m, 60→120°C.

Method B, from **1** and **2** in the Presence of Butyllithium; Special Procedure:

Diethyl 2-Trimethylsiloxy-2-phenylethanephosphonate **(3f)**: A solution of butyllithium (0.6 g, 1 mmol) in hexane (4 ml) is injected into a stirred mixture of styrene oxide (**1f**; 36 g, 0.3 mol) and diethyl trimethylsilyl phosphite (**2**; 21.0 g, 0.1 mol) at 0°C. Stirring at ambient temperature is continued for 12 h and the mixture then distilled under reduced pressure to give product **3f** containing 4% of the regioisomer **4f**; yield: 27.8 g (84%); b.p. 129–130°C/0.1 torr.

Method C, from **1**, Triethyl Phosphite, and Chlorotrimethylsilane; Special Procedure:

Diethyl 3-Chloro-2-(trimethylsiloxy)-propanephosphonate **(3c)**: Chlorotrimethylsilane (10.8 g, 0.1 mol) is added dropwise to a stirred mixture of epichlorohydrin (**1c**; 9.6 g, 0.3 mol), triethyl phosphite (16.6 g, 0.1 mol), and zinc iodide (3.2 g, 1 mmol) at room temperature. The mixture is gradually warmed at 55–70°C for 2 h, then fractionally distilled under reduced pressure to give a forerun of *1,3-dichloro-2-(trimethylsiloxy)-propane* [**5c**; yield: 3.6 g (18%); b.p. 70–73°C/11 torr (Ref.[6], b.p. 105–107°C/68 torr; ^{1}H-N.M.R. (CCl_4/TMS_{int}): $\delta = 0.15$ (s, 9H); 3.48 (d, 4H, $J = 5.0$ Hz); 3.97 ppm (quin, 1H, $J = 5.0$ Hz)] and *diethyl 3-chloro-2-(trimethylsiloxy)-propanephosphonate* **(3c)**; yield: 18.8 g (62%); b.p. 100–105°C/0.07 torr.

The authors thank Shin-Etsu Chemical Industry Ltd. for a gift of chlorotrimethylsilane.

Table. Diethyl 2-(Trimethylsiloxy)-alkanephosphonates **(3)** prepared

3	R	Method	Yield [%]	b.p. [°C/torr]	Molecular Formula[a,b]	^{1}H-N.M.R. ($DCCl_3$/TMS_{int}) δ [ppm]
a	CH_3	A	71	71–74°/ 0.1	$C_{10}H_{25}O_4PSi$ (268.4)	0.13 (s, 9H); 1.28 (d, 3H, J=7.0 Hz); 1.32 (t, 6H, J=7.0 Hz); 1.88 (ddd, 1H, J=15.1, 6.8, 18.1 Hz); 2.08 (ddd, 1H, J=15.1, 5.9, 18.6 Hz); 3.92–4.35 (m, 5H)
b	C_2H_5	A	67	85–90°/ 0.06	$C_{11}H_{27}O_4PSi$ (282.4)	0.14 (s, 9H); 0.90 (t, 3H, J=7.0 Hz); 1.33 (t, 6H, J=7.0 Hz); 1.61 (dq, 2H, J=7.0, 8.0 Hz); 2.96 (dd, 2H, J=6.1, 19.4 Hz); 4.09 (dq, 4H, J=7.0, 7.1 Hz); 3.8–4.6 (m, 1H)
c	Cl—CH_2—	C	68	100–105°/ 0.07	$C_{10}H_{24}ClO_4PSi$ (302.8)	0.18 (s, 9H); 1.34 (t, 6H, J=6.8 Hz); 2.02 (ddd, 1H, J=23.0, 15.4, 6.2 Hz); 2.20 (ddd, 1H, J=23.0, 15.4, 6.2 Hz); 3.52 (dd, 1H, J=5.37, 8.0 Hz); 3.61 (dd, 1H, J=5.37, 8.0 Hz); 4.14 (quin, 4H, J=6.8 Hz); 4.1–4.2 (m, 1H)
d	Br—CH_2—	A	62	135–138°/ 0.04	$C_{10}H_{24}BrO_4PSi$ (347.3)	0.18 (s, 9H); 1.34 (t, 6H, J=7.0 Hz); 2.03 (ddd, 1H, J=6.1, 16.0, 24.0 Hz); 2.20 (ddd, 1H, J=6.1, 16.0, 24.0 Hz); 3.35–3.57 (m, 2H); 4.0–4.4 (m, 1H); 4.10 (quin, 4H, J=7.0 Hz)
e	n-C_4H_9—O—CH_2—	A	77	150–153°/ 0.08	$C_{14}H_{33}O_5PSi$ (340.5)	0.15 (s, 9H); 0.91 (t, 3H, J=7.6 Hz); 1.32 (t, 6H, J=7.1 Hz); 1.3–1.7 (m, 4H); 1.93 (ddd, 1H, J=6.0, 9.0, 24.0 Hz); 2.11 (ddd, 1H, J=6.0, 9.0, 24.0 Hz); 3.37–3.50 (m, 4H); 4.08 (qd, 4H, J=7.1, 7.0 Hz); 3.96–4.36 (m, 1H)
f	C_6H_5	B	84	129–130°/ 0.1	$C_{15}H_{27}O_4PSi$ (330.5)	0.18 (s, 9H); 1.37 (t, 3H, J=7.1 Hz); 1.44 (t, 3H, J=7.1 Hz); 2.23 (ddd, 1H, J=15.1, 5.2, 17.5 Hz); 2.50 (ddd, 1H, J=15.1, 7.9, 16.5 Hz); 4.10 (dq, 2H, J=7.1, 7.6 Hz); 4.21 (dq, 2H, J=7.1, 7.3 Hz); 5.25 (ddd, 1H, J=5.1, 7.9, 8.0 Hz); 7.36–7.60 (m, 5H)

[a] Satisfactory microanalyses were obtained: C, ±0.27; H, ±0.21; P, ±0.28.

[b] The positional isomers **4** were not detected in the products, except for **3f** which contained 4% **4f**.

Received: May 5, 1983

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[1] N. P. Neureiter, F. G. Bordwell, *J. Am. Chem. Soc.* **81**, 578 (1959).

[2] C. B. Scott, *U.S. Patent* 2793225 (1957), Union Oil Co.; *C. A.* **51**, 16515 (1957).

[3] Y. Okamoto, H. Sakurai, *Synthesis* **1982**, 497.

[4] M. Nakano, Y. Okamoto, H. Sakurai, *Synthesis* **1982**, 915.

[5] K. M. Hurst, J. M. Takacs, *J. Am. Chem. Soc.* **100**, 3467 (1978).

[6] M. S. Malinovskii, M. K. Romantsevich, *Zh. Obshch. Khim.* **27**, 1680 (1957); *C. A.* **52**, 3669 (1958).