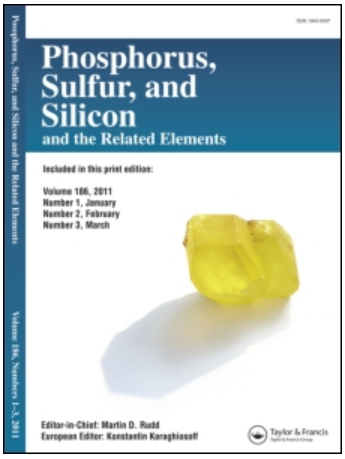

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SHORT COMMUNICATION
Silylated phosphonic acids: Radical addition of diethylphosphite to trimethylsilylethylene

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The addition of dialkylphosphites to polarized double bonds is difficult to achieve thermally, but proceeds smoothly with radical catalysis or preferrably with alkali alcoholates[1–3] e.g.:

$$(RO)_2\overset{O}{\overset{\|}{P}}H + CH_2{=}CH{-}O\overset{O}{\overset{\|}{C}}CH_3 \rightarrow (RO)_2\overset{O}{\overset{\|}{P}}{-}CH_2{-}CH_2{-}O\overset{O}{\overset{\|}{C}}CH_3. \quad (1)$$

1:1 adducts are formed having the activating substituent in β-position with respect to the phosphonic acid·ester group.

We found that the radical addition of diethylphosphite **1** to trimethylsilylethylene **2** proceeds in a more complex manner than expected from literature analogies.

Heating equimolar amounts of **1** and **2** in the presence of AiBN produced a mixture of oligosilylated alkane-phosphonic acid diethylesters:

$$\underset{\mathbf{1}}{(C_2H_5O)_2\overset{O}{\overset{\|}{P}}H} + n\underset{\mathbf{2}}{CH_2{=}CH{-}Si(CH_3)_3} \rightarrow$$

$$(C_2H_5O)_2\overset{O}{\overset{\|}{P}}{-}\left(CH_2{-}\underset{\displaystyle Si(CH_3)_3}{\underset{|}{CH}}{-}\!\!-\right)_n H \quad (2)$$

3 / *n*

(AiBN = NC—C(CH$_3$)$_2$—N=N—C(CH$_3$)$_2$—CN)

The more volatile numbers of this telomerization series **3 / *n*** were isolated in pure form by vacuum fractionation, to yield 2-trimethylsilylethane-phosphonic acid diethylester **3 / 1** (43%) and the hitherto unknown 2,4-bis-(trimethylsilyl)-butane-phosphonic acid diethylester **3 / 2** (9%).

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TABLE I

90.52 MHz ^{13}C-NMR-Data of compounds **3 / 2** and **4 / 2** and **3 / 1**

	3 / 2		**4 / 2**			**3 / 1**	
	δ_{C_i}	J_{PC_i}	δ_{C_i}	J_{PC_i}		δ_{C_i}	J_{PC_i}
C_1	24.782	137.3	24.345	141.5	C_1	19.187	141.0
C_2	22.400	8.3	22.171	5.5	C_2	7.497	8.7
C_3	24.292	•	24.253	•		—	—
C_4	15.109	•	15.002	•		—	—
C_5	−2.154	•	−1.863	•	C_3	−2.902	•
C_6	−2.568	•	−2.353	•		—	—
C_7	60.916	6.9	—	—	C_4	60.797	7.3
C_8	60.733	6.9	—	—		—	—
C_9	16.135	5.5	—	—	C_5	15.793	5.8
C_{10}	16.135	5.5	—	—			

25% solutions in $CDCl_3$.
Reference: $\delta_C(CDCl_3) = 76.900$ ppm. Data given in ppm (δ_{C_i}) and Hz (J_{PC_i})*). J_{PC_i} smaller than spectral half width.

TABLE II

360 MHz ^{1}H-NMR data of compounds **3 / 2**, **4 / 2** and **3 / 1**

H-atoms at Carbon C_i	**3 / 2** δ_H	**4 / 2** δ_H	C_i	**3 / 1** δ_H
C_1	1.73	1.77	C_1	1.608
C_2	1.10	1.12	C_2	0.761
C_3	1.58	1.69		
C_4	0.53	0.53		
C_5	0.05	0.05	C_3	0.015
C_6	0.01	0.01		
C_7/C_8	4.07	—	C_4	4.005
C_9/C_{10}	1.32	—	C_5	1.245

25% solutions in $CDCl_3$. $\delta_H(TMS) = 0.0$ ppm.

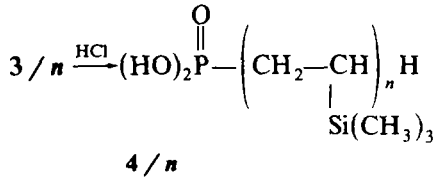
TABLE III

Iterated data from $[AB]_2X$ analysis of 90 MHz ^{1}H-NMR spectra of **3 / 1**

$\nu_A = 61.2$ Hz
$\nu_B = 142.0$ Hz
$J_{AA'} = -15.7$ Hz
$J_{BB'} = -15.0$ Hz
$J_{AB} = 4.3$ Hz
$J_{AB'} = 13.5$ Hz
$J_{AX} = 11.0$ Hz
$J_{BX} = -17.4$ Hz

25% solution in dmso-d_6. $H_A = CH_2Si$; $H_B = P—CH_2$.

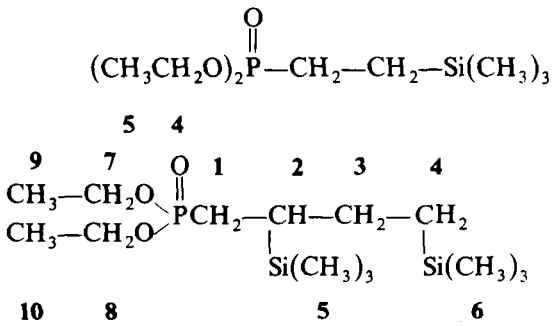
Acidolysis of these esters **3 / *n*** with concentrated hydrochloric acid yielded the corresponding phosphonic acids in almost quantitative yield:



4 / *n*

(3)

Molecular structures of **3 / 1**, **3 / 2**, **4 / 1** and **4 / 2** were established by NMR-techniques. ^{1}H- and ^{13}C-NMR-data are given in tables I–III using the following spin notations.



EXPERIMENTAL

2-Trimethylsilylethane phosphonic acid diethylester **3 / 1** *and 2,4-Bis-(trimethylsilyl)-butane phosphonic acid diethylester* **3 / 2**. 50.0 g (0.36 mol) $(C_2H_5O)_2P(O)H$, 36.6 g (0.36 mol) $CH_2{=}CHSi(CH_3)_3$ and 3.0 g (0.018 mol) AiBN were heated together for 24 h/120°C in a 200 ml laboratory autoclave under autogeneous pressure. Fractionated destillation using a 30-cm-Vigreux column yielded:

1. 33.1 g (43%) **3 / 1**, Bp. 70°C/1 Torr, n_D^{20} = 1,4329, MS: 238 (4%) M^+, 167 (100%) $M^+{-}CH_3{-}2C_2H_4$;
2. 10.3 g (9%) **3 / 2**, Bp. 94°C/0.1 Torr, MS: 338 (1%) M^+, 73 (100%) $(CH_3)_3Si^+$; colourless liquids, NMR data given in Tables I–III.

2-Trimethylsilylethane phosphonic acid **4 / 1** *and 2,4-Bis-(trimethylsilyl)-butane phosphonic acid* **4 / 2**. **3 / 1** and **3 / 2** resp. were heated together with a ten-fold amount of concentrated hydrochloric acid for 24 h under reflux. Surplus HCl and H_2O were evaporated in vacuo. Quantitative yields of **4 / 1**, colourless crystals from cyclohexane, m.p. 147°C, according to ref.[4] a monohydrate **4 / 1** · $1H_2O$.

4 / 2 a very viscous, colourless oil, was identified by NMR data given in Tables I and II.

REFERENCES

1. K. H. Worms and M. Schmidt-Dunker, *Organophosphorus Compounds* Vol. 7, John Wiley and Sons, New York, 1976, p. 28ff.
2. R. L. McConnell and H. W. Coover, Jr., *J. Amer. Chem. Soc.*, **79**, 1961 (1957).
3. B. Ackerman, T. A. Jordan and D. Swern, *J. Amer. Chem. Soc.*, **78**, 6025 (1956).
4. G. H. Barnes and M. P. David, *J. Chem. Soc.*, **1960**, 1191.