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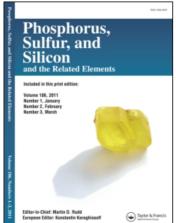
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Silylated phosphonic acids: Radical addition of diethylphosphoite to trimethylsilylethylene

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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 alcoholates¹⁻³ e.g.:

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:

$$(C_{2}H_{5}O)_{2}PH + nCH_{2} = CH - Si(CH_{3})_{3} \rightarrow 1 \qquad 2$$

$$(C_{2}H_{5}O)_{2}P - \left(CH_{2} - CH - \frac{1}{2}\right)_{n}H \qquad (2)$$

$$Si(CH_{3})_{3}$$

$$3/n$$

$$(AiBN = NC - C(CH_{3})_{2} - N = N - C(CH_{3})_{2} - CN)$$

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 ,	J_{PC_i}	δ _C ,	$J_{\mathrm{PC}_{i}}$		δ _C ,	J_{PC_i}
C,	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
\tilde{C}_{2}^{2}	24.292	•	24,253	•	4		_
Ċ,	15.109	•	15.002	•		_	_
Č.	- 2.154	•	-1.863	•	C_3	-2.902	•
C ₁ C ₂ C ₃ C ₄ C ₅ C ₆ C ₇ C ₈	- 2.568	•	- 2.353	*	- 3	_	_
Č.	60.916	6.9			C ₄	60.797	7.3
$\tilde{\mathbf{C}}'_{\bullet}$	60.733	6.9	_			_	_
Č,	16.135	5.5	-		C ₅	15.793	5.8
C_{10}	16.135	5.5	_		-,	201772	

25% solutions in CDCl₃. Reference: $\delta_{\rm C}({\rm CDCl_3}) = 76.900$ ppm. Data given in ppm $(\delta_{\rm C_i})$ and Hz $(J_{\rm PC_i})^{*}$. $J_{\rm PC_i}$ 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	$\frac{3}{\delta_{H}}$	4/2 δ _H	C_i	$\frac{3}{\delta_{H}}$
C ₁ C ₂ C ₃ C ₄ C ₅ C ₆ C ₇ /C ₈	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_{Δ}	4.005
C_{9}/C_{10}	1.32		C₄ C₅	1.245

25% solutions in CDCl₃. $\delta_{\rm H}({\rm TMS}) = 0.0$ ppm.

TABLE III Iterated data from [AB]₂X analysis of 90 MHz ¹H-NMR spectra of 3/1

$\nu_{A} = 61.2 \text{ Hz}$	
$\nu_{\rm R} = 142.0 \; {\rm Hz}$	
$J_{AA'} = -15.7 \text{ Hz}$	
$J_{BB'} = -15.0 \text{ Hz}$	
$J_{AB} = 4.3 \text{ Hz}$	
$J_{AB'} = 13.5 \text{ Hz}$	
$J_{Ax}^{CB} = 11.0 \text{ Hz}$	
$J_{\rm BY}^{\sim} = -17.4 \mathrm{Hz}$	

25% solution in dmso-d₆. $H_A = CH_2Si$; $H_B = P-CH_2$.

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

$$\begin{array}{c}
O \\
\parallel \\
(HO)_2P - \left(CH_2 - CH\right)_n H \\
\downarrow \\
Si(CH_3)_3
\end{array}$$
(3)

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

$$(CH_{3}CH_{2}O)_{2}P-CH_{2}-CH_{2}-Si(CH_{3})_{3}$$
5 4
9 7 O 1 2 3 4
$$CH_{3}-CH_{2}O \parallel CH_{2}-CH_{2}-CH_{2}$$

$$CH_{3}-CH_{2}O \parallel CH_{2}-CH_{2}-CH_{2}$$

$$Si(CH_{3})_{3} Si(CH_{3})_{3}$$
10 8 5 6

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) (C₂H₂O)₂P(O)H, 36.6 g (0.36 mol) CH₂=CHSi(CH₃)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⁺—CH₃—2C₂H₄; 2. 10.3 g (9%) 3/2, Bp. 94°C/0.1 Torr, MS: 338 (1%) M⁺, 73 (100%) (CH₃)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 H₂O were evaporated in vacuo. Quantitative yields of 4/1, colourless crystals from cyclohexane, m.p. 147°C, according to ref. 4) a monohydrate 4/1·1H₂O.

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

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