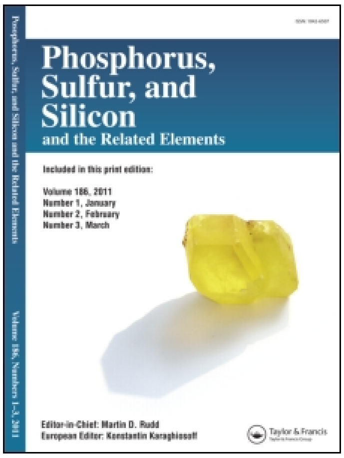

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CONVENIENT SYNTHESIS OF *S*-TRIMETHYLSILYL ESTERS OF DITHIO- AND TETRATHIOPHOSPHORIC ACIDS

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CONVENIENT SYNTHESIS OF *S*-TRIMETHYLSILYL ESTERS OF DITHIO- AND TETRATHIOPHOSPHORIC ACIDS

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S-Trimethylsilyl esters of dithio- and tetrathiophosphoric acids were obtained in the reaction of tetraphosphorus decasulfide with alkoxy- and alkylthiotrimethylsilanes, trimethylsilyl enol ethers and bis(trimethylsiloxy)alkylenes and phenylene.

Key words: *S*-Trimethylsilyl esters of dithio- and tetrathiophosphoric acids; tetraphosphorus decasulfide; alkoxy- and alkylthiotrimethylsilanes; trimethylsilyl enol ethers; bis(trimethylsiloxy)alkylenes.

INTRODUCTION

S-Trimethylsilyl dithiophosphates are important intermediates for the synthesizing useful organothiophosphorus compounds.[1] They are also efficient thiation reagents for ketones and isocyanates.[1] There are several methods for the preparation of *S*-trimethylsilyl dithiophosphates with dialkyl and 1,2-dioxyakylene or arylene substituents. They were obtained by the interaction of dithiophosphoric acids with 1,1,1,3,3,3-hexamethyldisilazane[2] or trimethylisocyanatosilane, or its thioanalogue, or trimethylsilyl enol ethers.[3] Reactions of ammonium dialkyl dithiophosphates with trimethylchlorosilane also result in *S*-trimethylsilyl dithiophosphates.[4] However, these techniques are multi-step procedures as the initial dithiophosphoric acids had been synthesized by treatment of organic hydroxy compounds with phosphorus sulfide (P_4S_{10}) with evolution of gaseous hydrogen sulfide.[5] The shortcomings of these syntheses also involve heating of the reaction mixture (60–70°C) and formation of by-products.

On the other hand, *S*-trimethylsilyl dithiophosphates with unsaturated substituents and dialkyl(trimethylsilyl)tetrathiophosphates remained unknown.

Tetraphosphorus decasulfide **1** is known to react with trimethyl(dialkylamino)silanes and bis(trimethylsilyl)sulfide to form *S*-trimethylsilyl *N*,*N*′-bis(dialkylamido)dithiophosphates and tris(trimethylsilyl)tetrathiophosphates respectively.[6] We have tried to extend these degradation reactions of **1** to other organosilicon compounds. In this article convenient and efficient methods are presented for the synthesis of *S*-trimethylsilyl esters of dithio- and tetrathiophosphoric acids directly from **1**.

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TABLE I

Experimental, physical and analytical data of the products obtained

Initial cpd.	Prod.	Reaction conditions temp. (°C)/time (h)	Yield^a (%)	B.p. °C (mm Hg)	d_4^{20}	n_D^{20}	^{31}P NMR^f δ, ppm	Molecular formula	Analytical data Found/Calc. (%) C	H	P	S	Si	$[M+H]^+$ Found/Calc.
2a	**3a**	40–50/6.5	77	55–58 (0.02)^d		1.5287	93	$C_5H_{15}O_2PS_2Si$	25.96	6.91	13.69	27.58	12.25	231
									26.08	6.59	13.46	27.80	12.16	231
2b	**3b**	40/10	81	59–60 (0.02)^c		1.5141	89	$C_9H_{19}O_2PS_2Si$	32.17	7.20	12.41	25.01	10.82	
									32.55	7.44	12.00	24.78	10.84	
2c	**3c**	20/12	78	66–67 (0.03)	0.9902	1.4782	86	$C_9H_{23}O_2PS_2Si$	37.63	8.09	10.54	22.88	9.08	
									37.73	8.12	10.82	22.35	9.78	
6a	**5a**	40–50/10	80	110–117 (0.02)^b	1.0525	1.5090	89	$C_9H_{19}O_2PS_2Si$	37.94	6.48	10.66	22.51	10.19	283
									38.29	6.80	10.98	22.67	9.92	283
6b	**5b**	70–90/8	67	120–128 (0.02)^b	1.1606	1.5433	93	$C_9H_{15}O_2PS_2Si$	38.84	5.14	11.08	23.25	10.13	279
									38.84	5.45	11.14	23.00	10.06	279
6c	**5c**	40–50/9	85	140–160 (0.03)^b	1.0732	1.5500	60	$C_{15}H_{27}O_2PS_2Si$	49.51	7.67	8.43	17.82	7.43	363
									49.70	7.53	8.55	17.66	7.72	363
6d	**5d**	50–60/4	91^c			1.5622	59	$C_{13}H_{23}O_2PS_2Si$	46.78	6.58	9.20	19.36	8.22	
									46.69	6.95	9.27	19.14	8.37	
7a	**8a**	20/12	85	90–100 (0.02)^b	1.1067	1.5885	83	$C_7H_{19}PS_4Si$	28.84	6.74	10.62	43.89	9.58	291
									28.96	6.62	10.68	44.09	9.65	291
7b	**8b**	20/3	95	110–115 (0.02)^b	1.0628	1.5650	83	$C_9H_{23}PS_4Si$	33.38	7.64	9.60	40.03	8.66	319
									33.96	7.30	9.74	40.21	8.80	319
7c	**8c**	50/7	96	120–130 (0.02)^b	1.0377	1.5635	83	$C_{11}H_{27}PS_4Si$	38.32	7.71	8.80	37.28	8.26	
									38.14	7.88	8.95	36.95	8.08	
10a	**9a**	15–20/7	93^c		1.1856	1.5160	81	$C_6H_{15}O_2PS_2Si$	29.30	6.08	12.49	26.89	15.20	243
									29.75	6.25	12.79	26.41	15.56	243
10b	**9b**	20–25/10	84	110–115 (0.03)^b	1.0684	1.4966	99	$C_7H_{16}O_2PS_2Si$	33.19	6.58	12.47	25.27	10.69	
									32.93	6.34	12.14	25.08	10.97	
10c	**9c**	190–200/2	34	205–208^g			67.9^h	$C_9H_{13}O_2PS_2Si$	39.25	4.91	11.36	23.36	10.46	
									39.13	4.76	11.22	23.16	10.14	

[a] Yield of isolated product.

[b] Temperature of the spiral of the thermal element of the thin layer distillation apparatus.

[c] Yield of crude product.

[d] Lit.:[4] b.p. 44–46 (0.02).

[e] Lit.:[4] b.p. 55–56 (0.001).

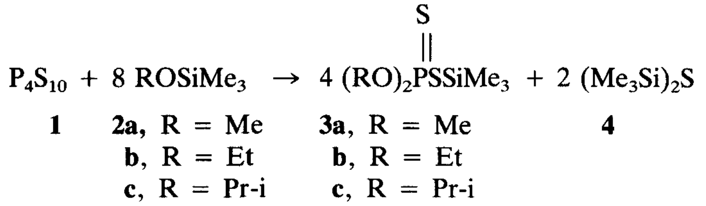
[f] Neat.

[g] M.p.

[h] In $PhNO_2$.

RESULTS AND DISCUSSION

We assumed that the use of the trimethylsilyl protecting group in protonodonating reagents such as alcohols, enols, thiols and diols may lead to *S*-trimethylsilyldithio- and tetrathiophosphates directly from **1** and thus avoid the formation of hydrogen sulfide. In fact we have found that **1** reacts with alkoxytrimethylsilanes **2a–c** at 20–50°C for 6.5–12 h with the formation of O,O-dialkyl-*S*-trimethylsilyl dithiophosphates **3a–c** and bis(trimethylsilyl)sulfide **4** (Equation 1, and Table I).



$$P_4S_{10} + 8\ ROSiMe_3 \rightarrow 4\ (RO)_2\overset{\overset{S}{\|}}{P}SSiMe_3 + 2\ (Me_3Si)_2S \qquad (1)$$

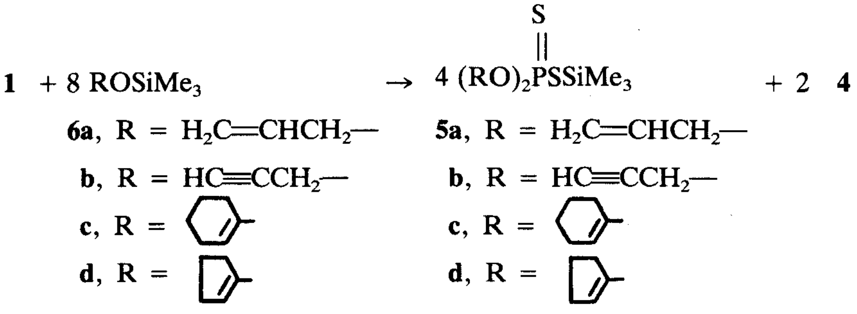
1 **2a**, R = Me; **b**, R = Et; **c**, R = Pr-i **3a**, R = Me; **b**, R = Et; **c**, R = Pr-i **4**

The structures of the products **3a–c** have been established by IR (Table II), ^{1}H NMR (Table III), ^{31}P NMR spectroscopy and by mass spectral data and microanalyses and by comparison of physical constants of the products (**3a,b**[4]) with literature data.

The dithiophosphates **3a–c** prepared with this method were not decomposed during distillation. Unlike this, *S*-trimethylsilyl *N,N'*-bis(dialkylamido)dithiophosphates decomposed during distillation to form bis(*N,N,N',N'*-tetraalkyldiamidothiophosphoryl)sulfide and **4**.[6]

It should be noted that this preparative method (Equation 1) is characterized by minimum steps, simple operation, mild conditions, high yields of products, no solvents and by-products.

We have tried to find the boundary of this method. Although unsaturated dithiophosphoric acids and their metallic salts were prepared[7–10] the corresponding *S*-silyl esters of unsaturated dithiophosphoric acid were not obtained. We assumed that these compounds may be prepared from trimethylsilyl enol ethers and **1**. Actually *S*-trimethylsilyl diallyl- and dipropargyldithiophosphates **5a,b** were synthesized in the reaction of trimethylallyloxysilane **6a** and trimethyl(2-propyneoxy)silane **6b** with **1** at 40–90°C for 8–9 h (Equation 2, Tables I–III).



(2)

Similarly trimethylsilyl cycloalkenylol ethers **6c,d** yield the corresponding *S*-trimethylsilyl esters of dithiophosphoric acid with cycloalkenyl substituents **5c,d** at

TABLE II

IR spectral data (cm^{-1}) of the products obtained

Prod.	CH_3^a as, s; CH_2^a as, s	$\delta[CH_3(Si)s]$	PO—C[a]	P—O—Si[a] as	$\rho[CH_3(Si)]$	P═S[a]	P—S[a], S—Si[a]
3a	2950, 2900, 2845	1258	1030		850	665	535, 496
3b	2990, 2970, 2945, 2910, 2875	1258	1025	968	855	663	546, 514
3c[c]	2975, 2960, 2930, 2897, 2870	1252	1050	968	848	654	546, 513
5a[d]	2965, 2880	1260	1020	930	860	685	
5b[e]	2965, 2930, 2900, 2875	1260	1020	950	855	680	560
5c[d]	2940, 2860, 2840	1258	1020		850	731	
5d[d]	2962, 2910, 2875, 2850	1258	1040	950	850	710	570
8a	2964, 2928, 2895, 2870	1252			846	680	546, 516
8b	2968, 2932, 2900, 2875	1255			855	668	548, 523
8c[c]	2960, 2930, 2900, 2874	1252			851	684	550, 525
9a	2975, 2908	1258	1060		850	693	
9b	2981, 2960, 2940, 2905	1258	1050	950	850	710	585, 537
9c[b,d]		1261			862,840	676	540, 525

[a] Valence vibrations.

[b] In vaseline oil.

[c] Deformation vibrations δ 1384, 1374–1370 cm^{-1} $(CH_3)_2C$ gem.

[d] ν 3090–3080, 3055–3028 (:C—H[a]), 1645–1600 cm^{-1} (C═C[a]).

[e] ν 3299 (⋮C—H[a]), 2140 cm^{-1} (C≡C[a]).

TABLE III

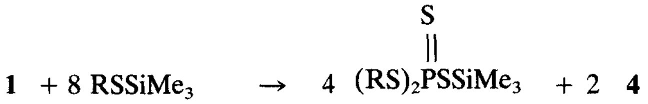
^{1}H NMR spectral data of the products obtained

Prod.	δ, ppm, J, Hz
3a	0.53 (s, 9H, $C\underline{H}_3Si$), 3.75 (d, $^3J_{P-H}$ 15.0) $C\underline{H}_3OP$).
3b	0.43 (s, 9H, $C\underline{H}_3Si$), 1.27 (t, 6H, $^3J_{H-H}$ 7.0, $C\underline{H}_3C$), 4.02 (dq, 4H, $^3J_{H-H}$ 7.0, $^3J_{P-H}$ 10.0, $C\underline{H}_2OP$).
3c	0.47 (s, 9H, $C\underline{H}_3Si$), 1.33 (d, 12H, $^3J_{H-H}$ 6.0, $C\underline{H}_3C$), 4.75 (dq, 2H, $^3J_{H-H}$ 6.0, $^3J_{P-H}$ 18.0, $C\underline{H}OP$).
5a	0.45 (s, 9H, $C\underline{H}_3Si$), 4.47 (dd, 4H, $^3J_{H-H}$ 5.5, $^3J_{P-H}$ 10.0, $C\underline{H}_2OP$), 4.97–5.38 (m, 2H, $C\underline{H}_2{=}CH{-}CH_2$), 5.39–6.07 (m, 1H, $C\underline{H}COP$).
5b	0.37 (s, 9H, $C\underline{H}_3Si$), 2.53 (t, 1H, $^4J_{H-H}$ 1.2, $C\underline{H}{\equiv}C{-}CH_2$), 4.60 (dd, $^4J_{H-H}$ 1.2, $^3J_{P-H}$ 11.0, $C\underline{H}_2OP$).
5c	0.32 (s, 9H, $C\underline{H}_3Si$), 1.23–2.44 (m, 16H, $C\underline{H}_2$ cycle), 5.88–6.12 (m, 2H, $C\underline{H}{=}COP$).
5d	0.32 (s, 9H, $C\underline{H}_3Si$), 1.50–2.97 (m, 12H, $C\underline{H}_2$ cycle), 5.67–5.90 (m, 2H, $C\underline{H}{=}C{-}OP$).
8a	0.54 (s, 9H, $C\underline{H}_3Si$), 1.35 (t, 6H, $^3J_{H-H}$ 7.5, $C\underline{H}_3C$), 2.92 (dq, 4H, $^3J_{H-H}$ 7.5, $^3J_{P-H}$ 17.0, $C\underline{H}_2SP$).
8b	0.80 (s, 9H, $C\underline{H}_3Si$), 1.27 (t, 6H, $^3J_{H-H}$ 6.5, $C\underline{H}_3C$), 1.70–2.25 (m, 4H, $^3J_{H-H}$ 6.5, $C\underline{H}_2CC$), 3.07 (dq, 4H, $^3J_{H-H}$ 6.5, $^3J_{P-H}$ 16.0, $C\underline{H}_2SP$).
8c	0.52 (s, 9H, $C\underline{H}_3Si$), 1.00 (d, 12H, $^3J_{H-H}$ 6.0, $C\underline{H}_3CC$), 1.72–2.22 (m, 2H, $C\underline{H}CS$), 2.76 (dd, 4H, $^3J_{P-H}$ 15.0, $C\underline{H}_2SP$).
9a$^+$	0.38 (s, 9H, $C\underline{H}_3Si$), 1.68–2.31 (m, CH_cH_aCOP), 3.84–5.61 (m, 4H, $CH_{BB'}H_{AA'}OP$).
9b$^+$	0.50 (s, 9H, $C\underline{H}_3Si$), 1.35–1.50 (m, 6H, $C\underline{H}_3COP$), 4.02–4.38 (m, 2H, $C\underline{H}OP$).
9c	0.17 (s, 9H, $C\underline{H}_3Si$), 6.96–7.07 (m, 4H, $C_6\underline{H}_5$).

$^+$The mixture of cis and trans isomers.

40–60°C for 4–9 h (Equation 2, Tables I–III). However these reactions (Equation 2) proceed at higher temperature (40–90°C) and **5d** decomposed when distillation was attempted.

Tris(trimethylsilyl) tetrathiophosphate was described.[6] In spite of the existance of metal and ammonium dialkyl tetrathiophosphates[11–13] the corresponding *S*-silyl esters of dialkyl tetrathiophosphoric acid remained unknown. We have found that the interaction of alkylthiotrimethylsilanes **7a–c** with **1** gives dialkyl(trimethylsilyl)tetrathiophosphates **8a–c** and **4** at 20–50°C for 3–12 h (Equation 3, Tables I–III).



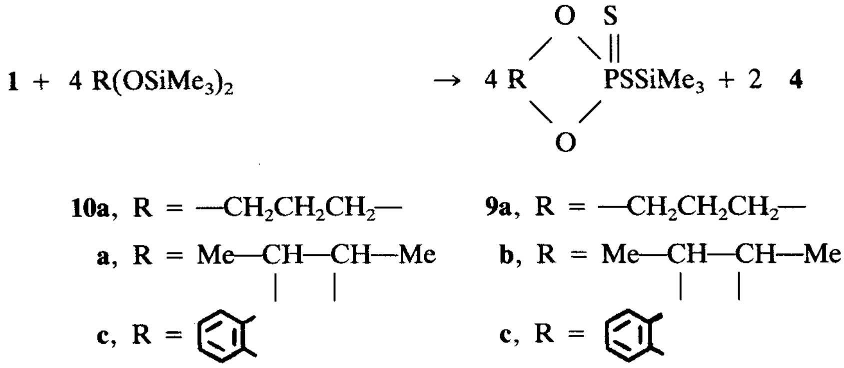
$$\mathbf{1} + 8\,RSSiMe_3 \rightarrow 4\,(RS)_2\overset{\overset{\displaystyle S}{\|}}{P}SSiMe_3 + 2\,\mathbf{4} \qquad (3)$$

7a, R = Et
b, R = Pr
c, R = Bu-i

8a, R = Et
b, R = Pr
c, R = Bu-i

Tetrathiophosphates **8a–c** are stable compounds and were isolated from the reaction mixture by distillation pure (thin layer distillation). It is noteworthy that the reaction of **1** with **7a** proceeds more readily than that with **2b**.

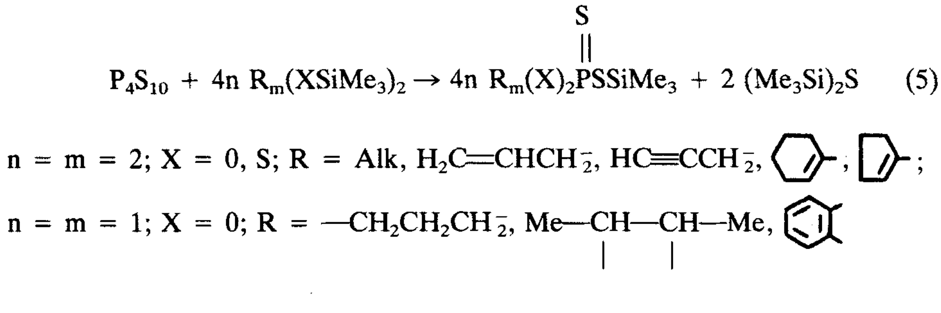
Our approach enabled us to obtain *S*-trimethylsilyl derivatives of cyclic dithiophosphoric acid with 1,2-dioxyalkylene and arylene substituents **9a–c** with the help of the ring-closure reaction of **1** with bis(trimethylsiloxy)alkylenes **10a,b** and phenylene **10c** (Equation 4, Tables I–III).



(4)

It is remarkable that the reactivity of benzene **10c** (reaction conditions: 190–200°C, 2 h) is lower than that of alkylene derivatives **10a,b** (15–25°C, 7–10 h) and the yield of **9c** is not high (34%) (Table I). Ester **9a** is thermally unstable and decomposes on distillation. The stability of the cyclic products **9** is increased when sterically hindered substituents at the phosphorus atom are introduced (**9b** is more stable than **9a**). Esters **9** decompose when stored for a long time in sealed tubes at room temperature.

Thus a general scheme can be conceived on the basis of the results of the following reactions of **1** with alkoxytrimethylsilanes, trimethylallyloxysilane, trimethyl(2-propynoxy)silane, trimethylsilyl cycloalkenylol ethers, alkylthiotrimethylsilanes and bis(trimethylsiloxy)alkylenes and phenylene (Equation 5).



$$P_4S_{10} + 4n\,R_m(XSiMe_3)_2 \rightarrow 4n\,R_m(X)_2\overset{S}{\overset{\|}{P}}SSiMe_3 + 2\,(Me_3Si)_2S \quad (5)$$

The mechanism of the degradation of **1** with silylamines has been discussed by Roesky and Remmers[6] when the nucleophilic nitrogen atom attacks the phosphorus atom of **1**. Perhaps the mechanisms of formation of **3**, **5**, **8** and **9** are similar to those suggested by Roesky and Remmers.[6]

In all cases the reactions (Equations 1–4) were accompanied by the formation of **4**, which is easily given off from the reaction mixture. It may be utilized by treating it with **1** or 2,4-bis(4-phenyl)-2,4-dithioxo-1,3,2λ^5,4λ^5-dithiadiphosphetane to yield organosilylthiophosphorus compounds,[6] which are useful as intermediates in organophosphorus synthesis.

The toxicity measurements of products obtained were performed and the minimal toxicity dose (in vitro) was 15.6 for **6a**, 15.6 for **8a**, 7.8 for **8b** and 500 mkg/mL for **8c**.

EXPERIMENTAL

The initial compounds **2**, **6**, **7** and **10** were prepared according to Reference 14. ^{31}P NMR spectra were recorded with a Bruker WM 250 (101.3 MHz) and a non-serial NMR KGU-4 (10.2 MHz) spectrometer, reference external H_3PO_4 (85%). ^1H NMR spectra were run on a Varian T-60 (60 MHz) spectrometer in CCl_4 with C_6H_6 as an internal reference and on a Bruker WM 250 (250 MHz) spectrometer in CD_3CN. IR spectra were obtained in KBr with a UR-20 and Specord M 80 infrared spectrophotometer. Mass spectra (electron impact, 70 eV; chemical ionization, 100 eV) were determined on a M 80 B Hitachi chromato mass spectrometer.

Dipropyl-S-trimethylsilyl tetrathiophosphate **8b**; *Typical Procedure.* **1** (20.4 g, 46 mmol) is added portionwise to a stirred **7b** (54.6 g, 368 mmol) at 20°C under an argon atmosphere and stirring is continued for 3 h at 20°C. The mixture is evaporated at reduced pressure (10 and 0.03 mm Hg) at 40°C. **8b** (55.6 g, 95%) is isolated from the residue by means of thin layer distillation (see Tables I–III). **4** is distilled from the reaction mixture; the yield is 7.9 g (98%); b.p. 159°C (733 mm Hg); n_D^{20} 1.4591 (Lit.[13] b.p. 162.5–163.5°C (750 mm Hg); n_D^{20} 1.4598).

The products **3a–c**, **5a–d**, **8a** and **8c** are obtained similarly. Products **3a–c** are in addition purified by distillation after the isolation by means of thin layer distillation. Products **9a,b** are prepared by the reaction of **1** with **10a,b** in the molar ratio 1:4 and isolated similarly. Products **5d** and **9a** are not purified by the following distillation.

2-Trimethylsilylthio-2-thio-4,5-benzene-1,3,2-dioxaphospholane **9c**. The mixture of **1** (10.0 g, 22.5 mmol) and **10c** (23.0 g, 90.4 mmol) is stirred for 2 h at 190–200°C under an argon atmosphere. The precipitate is filtered, washed with anhydrous hexane and dried at reduced pressure (0.02 mm Hg) at 40°C. Yield of **9c**: 8.5 g (34%) (see Tables I–III).

"The toxicity measurements of the products obtained were performed and the minimal toxicity dose (in vitro) was: 15.6 for **6a**, 15.6 for **8a**, 7.8 for **8b** and 500 mkg/mL for **8c**.

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