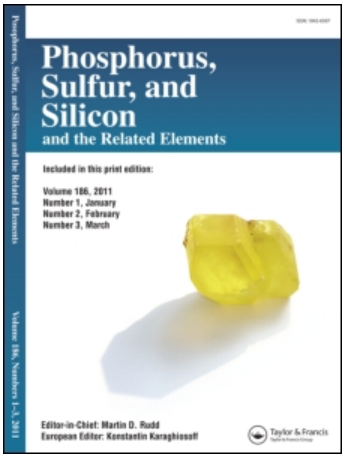

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND TRIBOCHEMICAL BEHAVIOUR OF SOME MONOTHIOPHOSPHORIC ACID DERIVATIVES

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To cite this Article Zinke, Horst and Schumacher, Rolf(1991) 'SYNTHESIS AND TRIBOCHEMICAL BEHAVIOUR OF SOME MONOTHIOPHOSPHORIC ACID DERIVATIVES', Phosphorus, Sulfur, and Silicon and the Related Elements, 63: 3, 315 — 322
To link to this Article: DOI: 10.1080/10426509108036835
URL: http://dx.doi.org/10.1080/10426509108036835

Phosphorus, Sulfur, and Silicon, 1991, Vol. 63, pp. 315–322
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SYNTHESIS AND TRIBOCHEMICAL BEHAVIOUR OF SOME MONOTHIOPHOSPHORIC ACID DERIVATIVES†

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(Received July 7, 1991; in final form July 17, 1991)

Diisopropylphosphite reacts with sulphur and ammonia to form ammonia monothiophosphoric acid-diisopropylester which, by subsequent reaction with different monochloroacetic acid esters, yields the corresponding monothiophosphoric-acid-O,O-diisopropyl-S-carboalkoximethylesters. These compounds show different wear- and friction-reducing properties in lubricating oils. The tribochemical activity at higher temperatures increases with the chain length of the carboxylic ester group. Auger electron spectroscopy (AES) of the worn metal surface shows that the wear reducing properties correspond with the phosphorus content in the metal surface produced by tribofragmentation of the monothiophosphates. A possible explanation of this effect is discussed.

Key words: Diisopropylphosphite; monothiophosphoric-acid-O,O-diisopropyl-S-carboalkoximethylesters; lubricating oils; Auger electron spectroscopy; wear; tribofragmentation.

INTRODUCTION

Phosphorus sulphur compounds, especially zinc dithiophosphates (ZDTP), are of great importance as friction- and wear-reducing additives in lubricants.

Although the ZDTPs provide good corrosion inhibition and antioxidant performance for the oils in addition to their antiwear properties, the zinc containing products have some important disadvantages, for example deposit formation on the valves of petrol engines.

As average temperatures and compression ratios in modern engines have increased there is a growing need for new ashless products with better thermal stability and friction- and wear-reducing properties at the higher temperatures.[1,2]

It is generally accepted that under boundary lubrication conditions additives form reaction layers on the metal surface resulting from tribofragmentation.[3] These reaction layers help to reduce the catastrophic wear which occurs by welding of two metal surfaces when the lubricating film breaks down. Although many investigations have been carried out to determine the composition of the reaction layers,

†Extended version of a poster presentation XI. International Conference on Phosphorus Chemistry, Tallinn USSR, July 3–7, 1989.

the detailed mechanism of these processes is still uncertain. Several elements are known to be active in the wear reducing process. Previous investigations with isogeometrical phosphorus compounds have shown that phosphorus in the surface layer provides particularly good antiwear and friction reducing performance.[4]

Since the friction- and wear-reducing behaviour of monothiophosphates is very similar to that of the dithiophosphates, it was of interest to synthesize monothiophosphoric acid esters with specific modified structures and to study their tribochemical activity.

RESULTS AND DISCUSSIONS

The monothiophosphates of the present investigation were synthesized starting from a carefully purified diisopropylphosphite (**1**) which was reacted with sulfur and ammonia in toluene to form the ammonia monothiophosphoric acid-O,O-diisopropylester (**2**). Further reaction with chloroacetic acid esters yields the corresponding monothiophosphates in good yields (Scheme).[5] The ^{31}P-chemical shift of approximately 23 ppm corresponds with the expected range for monothiophosphate esters and shows a slight downfield effect with increasing chain length (Table I).

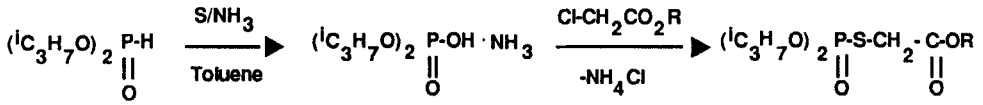
The thermal stability of the monothiophosphates was investigated by thermogravimetric analysis (TGA)[6] (Table II).

Tribochemical Activity

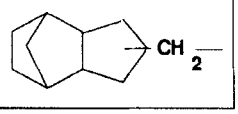
The tribofragmentation of the synthesized monothiophosphates were investigated by the SRV friction wear tester.[7] Figure 1 shows its principal function.

The test specimens of the SRV-ball-on-plate test device used are made of 100 steel Cr6, 58–60 HRC.

While the ball is oscillating it is pressed against the plate with a load of 200 N. All measurements were made at additive concentrations which are based on the same P-level of 0.174% in a poly-α-olefin (PAO). Tests were carried out at different temperatures over the range of 40–150°C. During the test period of 2 hrs. the



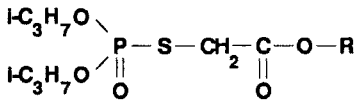
1 2 3a – 3d

	a	b	c	d
R	i-C_4H_9-	n-C_6H_{13}-	$C_{13/15}H_{27/31}$-	

SCHEME

TABLE I

Physical properties of monothiophosphoric acid-O,O-diisopropyl-S-carboalkoxi-methylesters **3**



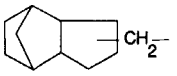
No.	R	Yield (%)	Refr. index n_{20}^{D}	^{1}H-NMR ($CDCl_3$) PSCH$_2$	(J_{PSCH})	OCH_2	OCH	31-P-NMR ($CDCl_3$)
3a	i-C_4H_9–	92.4	1.4553	3.63	(J14 Hz)	3.94	4.79	22.8
3b	n-C_6H_{13}–	95.5	1.4580	3.5	(J15 Hz)	4.14	4.78	22.8
3c	$C_{13/15}H_{27/31}$–	98.6	1.4600	3.54	(J14 Hz)	4.17	4.82	23.1
3d		92.1	1.4961	3.63	(J14 Hz)	3.91	4.79	23.3

TABLE II

Thermogravimetric analysis of monothiophosphates **3**.
Apparatus: METTLER-TA 3000.
Heating rate: 5°C/min Sample: 10 mg (AL pans) Airflow: 150 ml/min.

Comp. No,	Temperature * T_A [°C]	T_M [°C]	% Residue at 330 °C
3a	108	188	9
3b	132	205	12
3c	186	211	15
3d	182	207	24

*T_A : Beginning of decomposition (weight loss 10^{-3} g/sec)
T_M : Maximum of decomposition

coefficent of friction μ was measured continuously. At the conclusion the cross-section of the wear scar on the plate was determined[8] (Table III).

High/low figures mean high/low cross-section areas which correspond to high/low material loss by the friction process on the metal surface.[3]

To investigate the analytical composition of the metal surface in the friction zone the plates of the tests with compounds **3b** and **3d** were determined by AES (Table IV).

The concentration of phosphorus and sulphur is shown in a depth profile from 0 to 18 nm. A typical curve is given in Figure 2. For compound **3b** surface analysis was also made on the test plate *outside* the wear scar.

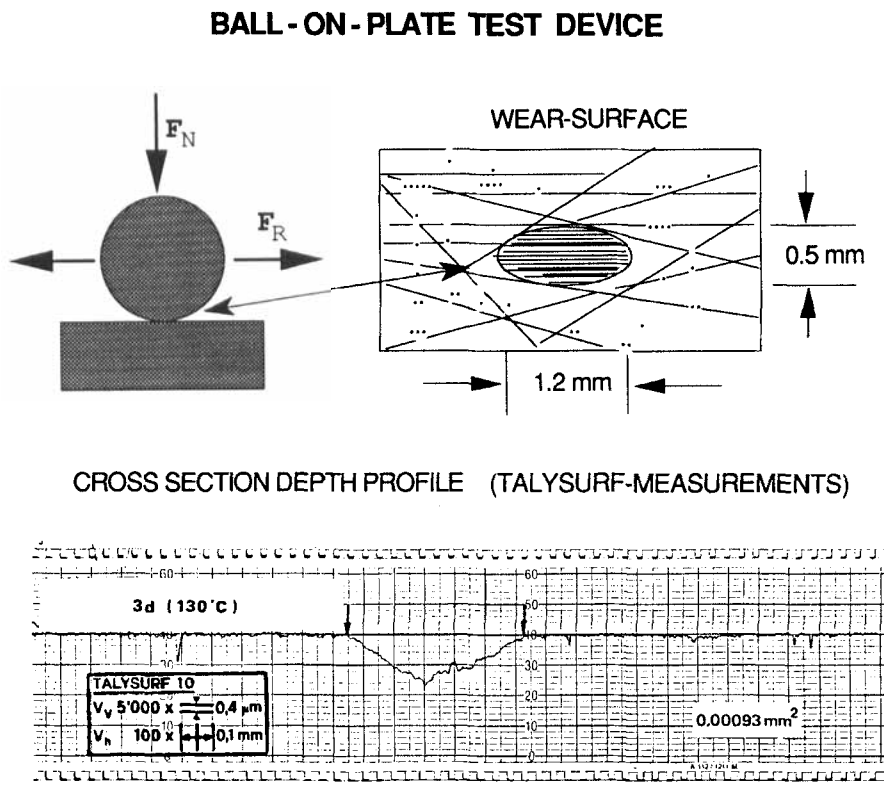


FIGURE 1 SRV friction and wear tester (principal function); test conditions: load F_N 200 N, frequency 50 Hz, amplitude 1.2 mm.

TABLE III

Tribofragmentation of monothiophosphoric acid-O,O-diisopropyl-S-carboalkoxi-methylesters **3**

Compound	Additive * Conc. %	Wear [mm² x 10^{-4}] at Temperature [°C] 40°	80°	100°	120°	150°
Base Oil **	—	6.2	7.8	25	57.8	57.0
3a	1.758	5.6	13.6	25.2	59.6	63.6
3b	1.915	4.8	9.8	13.2	53.2	139.0
3c	2.507	3.8	5.2	9.4	32.8	25.0
3d	2.274	4.4	10.2	15.0	10.2	15.0

* 0.174 % Phosphorus (0.0563 mMol/g)

** Poly- α- olefin (PAO) [Viscosity: 113.9 cSt (40°C): 14.2 cSt (100°C)]
Sulphur-content: 1.5 ppm

TABLE IV
Fragmentation of monothiophosphates **3** and surface analysis by AES

No.	Temperature (°C)	Composition of the reaction layer *			
		$\%P_{th}$	$\%P_{trib}$	$\%S_{th}$	$\%S_{trib}$
3b	40	0.81	4.5	0.4	1.0
	80	1.24	3.6	0.3	0.8
	100	0.65	4.0	0.8	1.5
	120	0.65	0.22	0.5	0.9
	150	10.0	0.22	0.9	0.1
3d	40		2.8		1.5
	80		4.2		2.1
	100		6.1		1.2
	120		4.1		0.4
	150		4.2		7.1

* P, S-content at 4.3 nm
th = thermal fragmentation trib = tribochemical fragmentation

Figure 3 shows the AES-phosphorus content of tests with compounds **3b** and **3d** *inside* and *outside* (**3b**) the wear scar at different temperatures.

Discussion

A comparison of the thermogravimetric analyses (Table II) of the monothiophosphates with the wear-reducing properties (Table III) shows that the temperature range for good antiwear performance depends significantly on the thermal stability of these compounds. These findings confirm previous results.[9]

In the range up to 100°C both compounds **3b** and **3d** were active as friction and wear reducers. With increasing temperature **3b** loses activity and is inactive at 120–150°C, while **3d** is still active in this temperature range. A possible explanation for this behaviour is the lower thermal stability of the compound **3d**. The temperture at which decomposition (weight loss) starts is 30°C lower for **3b** than for **3d**.

The different thermal stabilities of compounds **3b** and **3d** results in a higher additive depletion of **3b** in the friction zone caused by general thermal decomposition reactions on hot metal surfaces. AES analysis confirms that the activity can be correlated with the phosphorus incorporation into the reaction layer of the friction zone (Table IV). It is emphasized that a significant difference has been detected on the phosphorus incorporation *inside* the wear scar (tribofragmentation) and *outside* the wear scar (thermal fragmentation) as seen in Figure 3. Compound **3b** loses its activity at 120–150°C corresponding to a phosphorus decrease in the wear scar from 4–0% (depth 4.3 nm). Compound **3d** is still active in the same temperature range at a constant phosphorus level of approximately 4%.

EXPERIMENTAL

A Bruker AC 200P Spectrometer was used for recording the ^{31}P-NMR spectra at 32.28 MHz (Reference 85% H_3PO_4) and the ^{1}H-NMR spectra (Reference $(CH_3)_4Si$). Chemical shifts are reported in ppm with

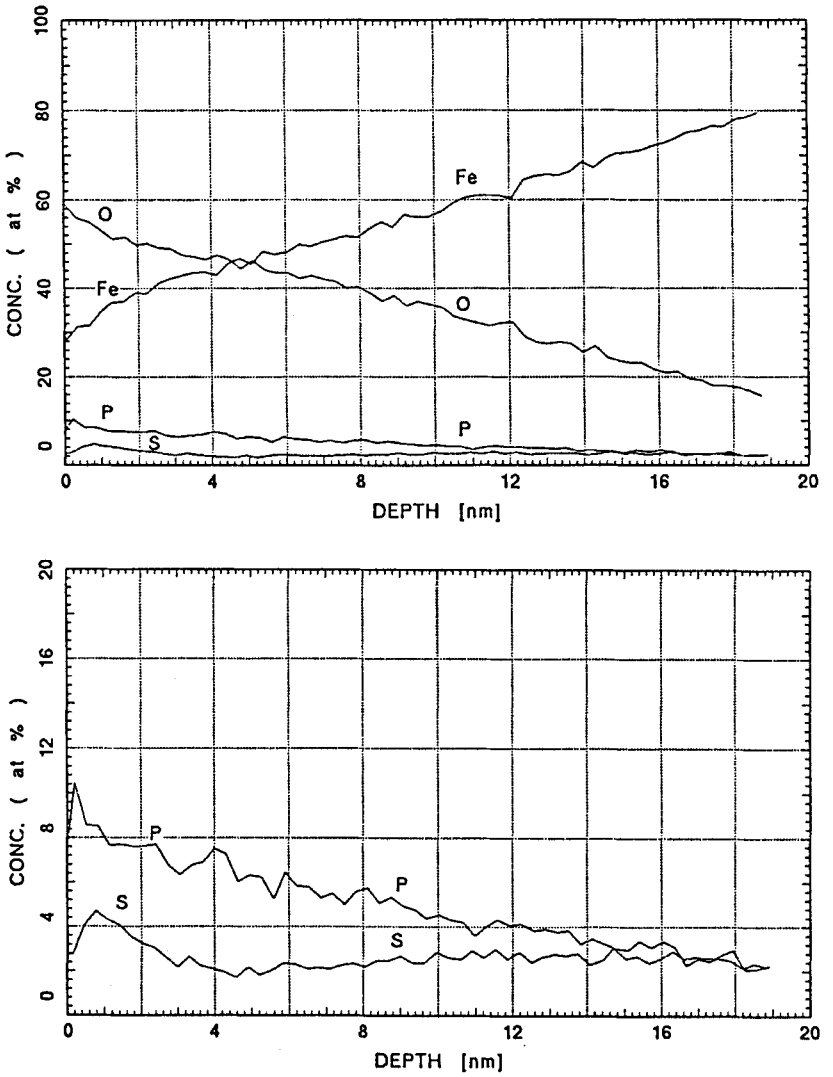


FIGURE 2 Auger Electron Spectroscopy; phosphorus and sulphur content depth profile.

negative values upfield and positive values downfield of the standard. For the thermogravimetric analysis a Mettler TA 3000 instrument, equipped with a Mettler TC 10 processor, was used.[10]

1. *Ammonium thiophosphoric acid-O,O-diisopropylester*, **2**. To 581.7 g (3.50 mol) of diisopropylphosphite dissolved in 1.2 l of i-propanol 112.21 g (3.50 mol) of sulphur is added. Into the vigorously stirred suspension subsequently ammonia was injected from a steel cylinder. The temperature increased and is kept below 30°C by cooling. After 3 hrs. stirring sulphur has dissolved and the ammonia injection is stopped. The colourless solution is stirred for another hour at 40°C, cooled to room temperature and after treating with fuller's earth it is filtered. From the i-propanol solution after standing some hours **2** partially crystallizes and is separated by filtration. The filtrate is evaporated on a rotavapor and the crystallized product is isolated by filtration. This procedure is repeated twice.

By collecting the fractions 740.0 g (98.2%) of **2** are obtained, colourless crystals, m.p. 172–173°C (Lit.[11] 156–157°C).

^{31}P-NMR($CDCl_3$) 55.4 ppm

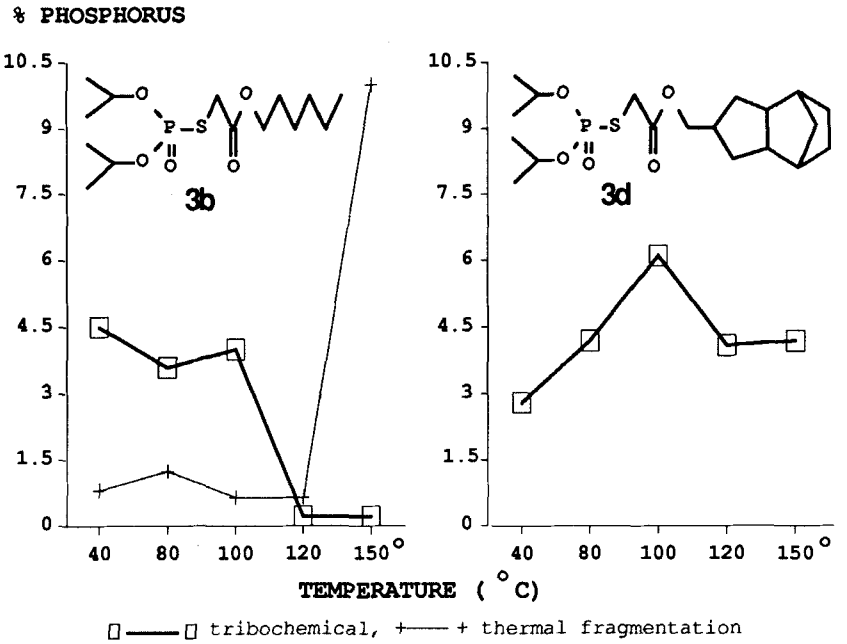


FIGURE 3 Fragmentation of monothiophosphate **3b** and **3d**; phosphorus content of the reaction layer at 4.3 nm.

2. *Monothiophosphoric acid-O,O-diisopropyl-S-carbobutoxi-methylester*, **3a**. To 107.65 g (0.50 mol) of **2** dissolved in 400 ml of i-propanol 78.44 g (0.50 mol) of chloroacetic acid isobutylester is added. The stirred stolution is heated to reflux temperature (87°C) while ammonium chloride is precipitating (start at ca. 50°C). After 10 hrs. stirring at reflux temperature the mixture is cooled to room temperature and filtered off. The ammonium chloride is washed with i-propanol and dried (26.63 g, 99.6%). From the filtrate and the washings i-propanol is removed on a rotavapor. The residue is dissolved twice in 125 ml of toluene and evaporated on the rotavapor. The obtained colourless liquid is dissolved in 500 ml of toluene and washed three times with 200 ml of a saturated solution of sodium hydrogen carbonate in water. After washing with 200 ml of water the toluene solution is dried with sodium sulphate and the solvent is removed on a rotavapor. To remove the rest of the toluene the product is kept for 2 hrs. at 60°C/0.1 mbar under a low stream of nitrogen.

Yield: 144.3 g (92.4%) of **3a**, colourless liquid, $n_D^{20} = 1.4553$.
$C_{12}H_{25}O_5PS$ (312.37) calc.: C 46.14, H 8.07, P 9.92, S 10.26%.
found: C 46.14, H 8.07, P 9.85, S 10.11%.
^{1}H-NMR ($CLCl_3$) δ = 0.95 (*d*, J_{HCCH} 7.5, CH_3 6 H); 1.36 (*t*, J_{POCCH} 5, CH_3, 12 H); 1.97 (*m*, CH, 1 H); 3.63 (*d*, J_{PSCH} 14, SCH_2, 2 H); 3.94 (*d*, J_{HCCH} 7.5, CH_2, 2 H); 4.79 (*m*, OCH, 2 H) [ppm].
^{31}P-NMR ($CDCl_3$) 22.8 ppm.

3. *Monothiophosphoric acid-O,O-diisopropyl-S-carbohexoxi-methylester*, **3b**. 75.36 g (0.35 mol) of **2** dissolved in 600 ml of toluene is treated with 62.55 g (0.35 mol) of chloroacetic acid n-hexylester for 12 h at 90°C. The ammonium chloride precipitated is filtered off and the filtrate washed with 150 ml of a saturated solution of sodium hydrogen carbonate in water. After a second washing with 150 ml of dist. water the organic phase is dried with sodium sulphate. The solvent is distilled off on a rotavapor. By treatment with a low stream of nitrogen at 60°C/0.07 mbar for 2 hrs. the residues of toluene are removed.

Yield: 113.8 g (95.5%) of **3b**, colourless liquid, $n_D^{20} = 1.4580$.
$C_{14}H_{29}O_5PS$ (340.4) calc.: C 49.40, H 8.59, P 9.10, S 9.42%.
found: C 49.37, H 8.43, P 9.12, S 9.49%.
^{1}H-NMR ($CDCl_3$) δ = 0.88 (*t*, CH_3, 3 H); 1.25–1.43 (*m*, CH_3, CH_2, 18 H); 1.65 (quin., CH_2, 2 H); 3.5 (*d*, J_{PSCH} 15, SCH_2, 2 H); 4.14 (*t*, J_{HCCH} 7.5, OCH_2, 2 H); 4.78 (*m*, OCH, 2 H) ppm.
^{31}P-NMR ($CDCl_3$) 22.5 ppm.

4. *Monothiophosphoric acid-O,O-diisopropyl-S-carbo-tridecyl-/pentadecycloxi-methylester,* **3c**. As described for **3a** 71.05 g (0.33 mol) of **2** dissolved in 600 ml of i-propanol is treated with 94.14 g (0.33 mol) of chloroacetic acid tridecyl-/pentadecylester[a] under reflux conditions. Solvent removing and purification is done as described for **3a**.

Yield: 132.3 g (98.6%) of **3c**, colourless liquid, n_D^{20} = 1.4600.
$C_{21}H_{43}O_5PS/C_{23}H_{47}O_5PS$ (447.0) calc.: C 58.02, H 9.96, P 6.93, S 7.18%.
found: C 58.4, H 9.9, P 6.9, S 7.0%.
^{1}H-NMR($CDCl_3$) δ = 0.79–1.70 (*m*, CH_3, CH_2, 38 H); 3.54 (*d*, J_{PSCH} 14, SCH_2, 2 H); 4.17 (*t*, OCH_2, 2 H); 4.82 (*m*, OCH, 2 H) [ppm].
^{31}P-NMR ($CDCl_3$) 23.1 ppm.

5. *Monothiophosphoric acid-O,O-diisopropyl-S-carbo-tricyclo[4,3,3,0^{1,6}]*decylmethoxi-methylester, **3d**. 34.88 g (0.162 mol) of **2** and 39.33 g (0.162 mol) of monochloroacetic acid tricyclo[4,3,3,0^{1,6}]decylmethylester[b] dissolved in 300 ml of i-propanol is reacted and purified as described for **3**.

Yield: 58.6 g (90.5%) of **3d**, colourless liquid, n_D^{20} = 1.4961.
$C_{19}H_{33}O_5PS$ (404.51) calc.: C 56.42, H 8.22, P 7.66, S 7.93%.
found: C 56.6, H 8.1, P 7.6, S 7.8%.
^{1}H-NMR ($CDCl_3$) δ = 1.2–1.88 (*m*, cycl. CH, CH_2, 22H); 1.98–2.18 (*m*, cycl. CH, CH_2, 3 H); 2.39 (*m*, cycl. CH_2, 2 H); 3.63 (*d*, J_{PSCH} 14, SCH_2, 2 H); 3.88–4.08 (*d*, OCH_2, 2 H); 4.79 (*m*, OCH, 2 H) [ppm].
^{31}P-NMR ($CDCl_3$) 23.3 ppm.

a) The ester mixture is made by esterification of monochloroacetic acid with the technical grade alcohol mixture ®ACROPOL-35 from Exxon containing 70% of tridecanol and 30% of pentadecanol.
b) Monochloroacetic acid tricyclo[4,3,3,0^{1,6}]decyl-methylester is prepared by esterification of monochloroacetic acid with tricyclo[4,3,3,0^{1,6}]decyl-methanol (TCD-M alcohol from Farbwerke Hoechst).

$C_{13}H_{19}ClO_2$ (242.75) calc.: C 64.32, H 7.89, Cl 14.60%.
found: C 64.5, H 7.8, Cl 14.6%.
Yield: 94.2%, colorless liquid, n_D^{20} = 1.5048.

ACKNOWLEDGEMENT

The authors wish to thank the Management of Ciba-Geigy for the permission to publish these results. They would also like to thank Prof. Dr. D. Landolt and PD. Dr. H. J. Mathieu, Ecole Poly-technique Fédérale de Lausanne (EPFL), Switzerland, for the AES surface analysis, Dr. H. Bayha for the NMR spectra and H. P. Gutknecht and F. J. Schmoll for experimental assistance.

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