Chemistry

E. A. CHERNYSHEV, E. F. BUGERENKO,

1963

SovietRxiv

Abstract

Full Text

Chemistry

E. A. CHERNYSHEV, E. F. BUGERENKO,
Corresponding Member of the Academy of Sciences of the USSR A. D. PETROV

SYNTHESIS OF SOME TRIETHYLSILYL-SUBSTITUTED ALKYLPHOSPHINIC ACIDS AND THEIR ESTERS

In the present work we have synthesized a series of esters of the general formula $(C_2H_5)_3Si(CH_2)_nPO(OC_2H_5)_2$, where $n = 1, 2, 3, 4$ (compounds I–IV, Table 1). Compounds I and III were obtained according to the scheme first proposed by Gilbert (^{1}), which is essentially a special case of the Arbuzov reaction:

$$(C_2H_5)_3Si(CH_2)_nCl + P(OC_2H_5)_3 \rightarrow (C_2H_5)_3Si(CH_2)_nPO(OC_2H_5)_2 + C_2H_5Cl,$$

$$n = 1, 3.$$

Compounds II and IV were synthesized according to the scheme proposed by Linville (^{2}), consisting in the radical addition of diethylphosphinic acid to an olefin containing a silicon atom in the molecule:

$$(C_2H_5)_3Si(CH_2)_nCH = CH_2 + (C_2H_5O)_2P(O)H \xrightarrow[140\text{–}150^\circ]{\text{tert.-}C_4H_9O)_2} (C_2H_5)_3Si(CH_2)_{n+2}PO(OC_2H_5)_2,$$

$$n = 0, 2.$$

The esters obtained were subjected to hydrolysis. Hydrolysis was carried out by heating a mixture of compounds I–IV with 38% HCl for 24 hr. The yields of the corresponding acids V–VIII were practically quantitative

Table 1

No.	Compound	B.p., °C (mm)	n_D^{20}	d_4^{20}	Found, % C	Found, % H	Found, % P + Si	Calculated, % C	Calculated, % H	Calculated, % P + Si
I	$(C_2H_5)_3SiCH_2PO(OC_2H_5)_2$	93–95 (2.5)	1.4475	0.9773	49.1 49.2	10.3 10.3	21.7 21.6	49.6	10.15	22.2
II	$(C_2H_5)_3Si(CH_2)_2PO(OC_2H_5)_2$	116–118 (2)	1.4493	0.9726	51.2 51.4	10.5 10.5	21.4 21.1	51.5	10.3	21.1
III	$(C_2H_5)_3Si(CH_2)_3PO(OC_2H_5)_2$	118–120 (1.5)	1.4498	0.9640	52.7 52.9	10.7 10.8	20.0 20.2	53.2	10.55	20.1
IV	$(C_2H_5)_3Si(CH_2)_2PO(OC_2H_5)_2$	142–143 (2)	1.4489	0.9722	54.5 54.7	10.6 10.5	19.0 19.3	54.6	10.7	19.2
V	$(C_2H_5)_3SiCH_2PO(OH)_2$	98.5–99.5*	—	—	40.0 40.2	9.08 9.13	27.9 28.0	40.0	9.05	28.1
VI	$(C_2H_5)_3Si(CH_2)_2PO(OH)_2$	112–113*	—	—	43.0 42.7	9.55 9.59	26.6 26.2	42.8	9.38	26.3
VII	$(C_2H_5)_3Si(CH_2)_3PO(OH)_2$	72.5–73*	—	—	45.4 45.6	9.83 9.92	24.9 24.6	45.4	9.66	24.8
VIII	$(C_2H_5)_3Si(CH_2)_4PO(OH)_2$	53–56*	—	—	47.2 47.6	10.0 10.2	23.2 22.9	47.6	9.93	23.4

* Melting point.

(96–98%). It seemed of interest to us to trace the dependence of the change in the ionization constants of these acids on the position of the triethylsilyl group relative to the phosphorus atom. For this purpose, potentiometric titration was carried out on the acids V–VIII obtained, as well as on $CH_3PO(OH)_2$ and $C_2H_5PO(OH)_2$, and the values of pK_1 and pK_2 were determined from the titration curves (see Table 2). Titration of $\sim 0.001\,N$ solutions of the acids in 50% ethanol

0.1 N NaOH was carried out at 20°. An LP-5 model was used as the pH meter, permitting determination of the pH value with an accuracy of $±$0.05. The mean values of pK_1 and pK_2 for n-$C_3H_7PO(OH)_2$ and n-$C_4H_9PO(OH)_2$ were calculated on the basis of the data given in (³).

From the data in Table 2 it is seen that replacement of a hydrogen atom in the methyl radical of methylphosphinic acid and at the β-carbon atom of ethylphosphinic acid by a triethylsilyl radical causes a decrease in the ionization constant of the indicated acids.

Table 2

Acid	pK_1	pK_2	Acid	pK_1	pK_2
$CH_3PO(OH)_2$	3.65	8.90	$(C_2H_5)_3SiCH_2PO(OH)_2$	4.40	9.60
$C_2H_5PO(OH)_2$	3.75	9.10	$(C_2H_5)_3Si(CH_2)_2PO(OH)_2$	3.90	9.45
n-$C_3H_7PO(OH)_2$	3.85	9.20	$(C_2H_5)_3Si(CH_2)_3PO(OH)_2$	3.85	9.40
n-$C_4H_9PO(OH)_2$	3.95	9.30	$(C_2H_5)_3Si(CH_2)_4PO(OH)_2$	3.90	9.35

It should be noted that in the first case the difference between the pK_1 values of the substituted and unsubstituted acids has the greatest magnitude (0.75); in the case of the substituted and unsubstituted ethylphosphinic acids this difference is already only 0.15. Since the steric factor of the substituent does not have a substantial influence on the ionization constants of substituted alkylphosphinic acids (³), the noted difference in the pK_1 values of methyl- and ethylphosphinic acids and their triethylsilyl derivatives should be attributed to the inductive effect of the $(C_2H_5)_3Si$ group.

It also follows from the data in Table 2 that the inductive effect of the triethylsilyl group is practically not manifested if the indicated group is located at the γ- or δ-carbon atoms of the alkyl chain of the alkylphosphinic acid.

It should be noted that analogous conclusions were made by American investigators for phosphorus-silicon-containing acids of somewhat different structure (⁴).

Experimental Part

The starting triethylchloromethylsilane, triethylvinylsilane, γ-chloropropyltriethylsilane, and γ-butenyltriethylsilane were obtained by the Grignard reaction and had the following properties: $(C_2H_5)_3SiCH_2Cl$, b.p. 59-61° (8 mm), n_D^{20} 1.4480, d_4^{20} 0.9097; $(C_2H_5)_3SiCH{=}CH_2$, b.p. 146-147° (760 mm), n_D^{20} 1.4347, d_4^{20} 0.7729, i.e., in agreement with (⁵); $(C_2H_5)_3SiCH_2CH_2CH_2Cl$, b.p. 87.5-88.5° (8 mm), n_D^{20} 1.4565, d_4^{20} 0.9089; $(C_2H_5)_3SiCH_2CH_2CH{=}CH_2$, b.p. 64-65° (8 mm), n_D^{20} 1.4439, d_4^{20} 0.7913, which practically coincides with the data given in (⁵). Methyl- and ethylphosphinic acids were obtained by hydrolysis of the corresponding acid chlorides and had melting points of 107.5° and 43-44°. According to the literature data (⁶), $CH_3PO(OH)_2$ has m.p. 105°, and $C_2H_5PO(OH)_2$, 44°.

Preparation of $(C_2H_5)_3SiCH_2PO(OC_2H_5)_2$ **(I).** In a two-necked flask equipped with a thermometer and a reflux condenser connected through a side arm to a Tishchenko bottle containing conc. H_2SO_4, were placed 28 g (0.17 mole) of triethylchloromethylsilane and 14 g (0.085 mole) of triethyl phosphite. The mixture was heated for 6.5 h within the temperature range 155–183°. Upon distillation, besides 13.8 g of triethylchloromethylsilane taken in excess, 11 g of a fraction boiling at 91–96° (2.5 mm), n_D^{20} 1.4478, was obtained; on redistillation this gave 10.5 g of compound I with b.p. 93–95° (2.5 mm), n_D^{20} 1.4475, d_4^{20} 0.9773. Yield 46.7%.

Preparation of $(C_2H_5)_3SiCH_2CH_2CH_2PO(OC_2H_5)_2$ **(III).** Into the apparatus described in the preceding example were placed 22.2 g (0.115 mole) of γ-chloropro-

vinyltriethylsilane and 19.1 g (0.115 mole) of triethyl phosphite. The mixture was heated for 16 h in the temperature range 168–210°. On distillation, 15.4 g of a fraction boiling at 115–120° (1.5 mm), n_D^{20} 1.4492, was obtained; on redistillation of this fraction, 14.8 g of compound III was isolated, b.p. 118–120° (1.5 mm), n_D^{20} 1.4498, d_4^{20} 0.9640. Yield 43%.

The method for obtaining $(C_2H_5)_3SiCH_2CH_2PO(OC_2H_5)_2$ was described by us in a previous paper ([7]).

Preparation of $(C_2H_5)_3SiCH_2CH_2CH_2CH_2PO(OC_2H_5)_2$ **(IV).** Into a round-bottomed flask equipped with a reflux condenser with a calcium chloride tube, a stirrer, and a thermometer were placed 25.5 g (0.15 mole) of γ-butenyltriethylsilane, 41.5 g (0.3 mole) of $(C_2H_5O)_2P(O)H$, and 0.5 ml of tert-$C_4H_9O_2$.

The mixture was stirred for 3 h at 135–145°. Then a further 0.5 ml of peroxide was added, and stirring was continued for another 3 h at 140–150°. On distillation, 20.5 g of $(C_2H_5O)_2P(O)H$ and 33 g of a fraction boiling at 131–141° (2.5 mm), n_D^{20} 1.4480, were obtained; on redistillation of this fraction, 29 g of compound IV was isolated, b.p. 142–143° (2 mm), n_D^{20} 1.4489, d_4^{20} 0.9722. Yield 63%.

Hydrolysis of ethyl esters I-IV. 10–15 g of compound I-IV and 50 ml of 38% HCl were placed in a round-bottomed flask with a reflux condenser and boiled for 24 h. The needle-shaped crystals that precipitated after cooling were separated in the usual manner, washed with distilled water until the residual HCl was completely removed, and then dried to constant weight in a vacuum desiccator. The yields of acids were practically quantitative (96–98%). Acids V, VI, VII were recrystallized from petroleum ether. Acid VII could not be recrystallized, since it is readily soluble in all organic solvents. Therefore, in this case the following procedure was used: the crystals were placed in a Büchner funnel, washed with a small amount of petroleum ether, and then thoroughly dried in a vacuum desiccator.

IR spectra* of the esters obtained (recorded on an ISP-51) ($\Delta\nu$ in cm^{-1}):

$(C_2H_5)_3SiCH_2PO(OC_2H_5)_2$ 150(3), 249(2), 300(3), 567(10), 586(2), 649(1sh), 732(0sh), 761(1sh), 803(0sh), 979(3sh), 1009(1sh), 1028(1sh), 1104(3sh), 1145(0), 1163(0), 1194(1sh), 1235(4), 1248(2), 1291(3), 1373(1), 1415(3), 1460(8sh), 2877(10), 2898(7), 2935(5), 2956(2), 2981(3).

$(C_2H_5)_3SiCH_2CH_2PO(OC_2H_5)_2$ 150(2), 243(0), 301(0), 569(10sh), 584(2), 709(2sh), 734(0), 755(1sh), 784(0sh), 806(1sh), 977(3), 1008(0sh), 1030(1sh), 1064(0), 1103(4sh), 1171(0sh), 1238(6 o. sh), 1297(1sh), 1416(7sh), 1442(1), 1463(8sh), 2880(10sh), 2905(4), 2937(3), 2958(2), 2984(3).

$(C_2H_5)_3SiCH_2CH_2CH_2PO(OC_2H_5)_2$ 150(4), 299(2), 522(0), 544(0), 570(10), 584(2), 637(0), 699(0), 719(0), 830(0), 977(3sh), 1020(1sh), 1042(0), 1104(6sh), 1170(2), 1233(4sh), 1302(1sh), 1416(7sh), 1460(9 o. sh), 2879(10), 2911(5), 2937(3), 2960(1), 2981(2sh).

$(C_2H_5)_3SiCH_2CH_2CH_2CH_2PO(OC_2H_5)_2$ 150(2), 168(0), 300(1), 568(10), 587(2), 628(0), 656(0), 699(1sh), 759(1sh), 976(2sh), 1018(1sh), 1053(0sh), 1101(5sh), 1139(1), 1166(2sh), 1230(1 o. sh), 1259(0), 1303(3 o. sh), 1358(1), 1412(7sh), 1460(10 o. sh), 2877(10sh), 2909(6), 2935(7), 2954(1), 2981(3).

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

Received
2 XI 1962

REFERENCES

1. A. R. Gilbert, Am. pat. 2768193 (1956); Chem. Abstr., **51**, 5816 (1957).
2. R. G. Linville, Am. pat. 2843615 (1958); Chem. Abstr., **53**, 1147 (1959).
3. M. I. Kabachnik, DAN, **110**, No. 3, 393 (1956).
4. G. H. Barnes, M. P. David, J. Org. Chem., **25**, 1191 (1960).
5. V. F. Mironov, N. A. Ponomarenko, Izv. AN SSSR, OKhN, 1955, 183.
6. A. W. Hofmann, Ber., **5**, 104 (1872).
7. E. F. Bugerenko, E. A. Chernyshev, A. D. Petrov, DAN, **143**, No. 4, 840 (1962).

* Recorded by I. D. Kravtsova, to whom the authors express their deep gratitude.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.