SYNTHESIS OF SILICON-CONTAINING ESTERS OF PHOSPHORUS ACIDS AND STUDY OF THEIR THERMAL STABILITY.

3. THERMAL REARRANGEMENT OF TRIORGANOSILYLMETHYL ESTERS OF DIPHENYL PHOSPHORIC ACID

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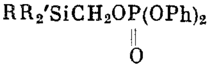
It has been shown previously that silico-neopentyl esters of pentavalent phosphorus oxyacids on heating undergo a peculiar rearrangement consisting in the transformation of a trimethylsilylmethyl group into dimethylethylsilyl. The rearrangement is quite general in character and takes place both with silico-neopentyl dichlorophosphates and with full silico-neopentyl esters of phosphorus acids under relatively mild conditions (175-200°C) [1].

A possible mechanism for the rearrangement of silico-neopentyl phosphates has been proposed, consisting in the thermal heterolysis of a C—OP bond and the migration of one of the CH_3 groups from the Si to a C atom carrying a positive charge with simultaneous nucleophilic attack on the Si atom by the anionic part of the molecule [2].

The present work is devoted to a study of the possible thermal migration of other radicals from the Si atom to the methylene C atom by a type of 1,2-shift.

For this study, a series of compounds was selected which have only one triorganosilylmethyl group which is prone to this type of rearrangement, namely diphenyl(triorganosilylmethyl) phosphates (Ia-e).

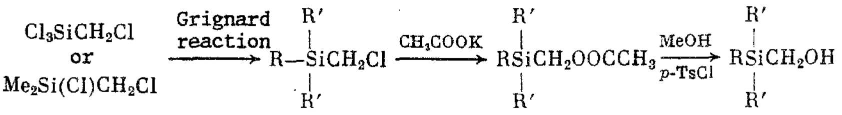


$$RR'_2SiCH_2O\underset{\underset{O}{\|}}{P}(OPh)_2$$

(Ia–e)

$R = R' = Me$ (a), $R = R' = Et$ (b), $R = R' = Pr$ (c), $R = R' = CF_3CH_2CH_2$ (d), $R = Ph$, $R' = Me$ (e).

The alcohol starting materials were prepared by the following route:



(IIa-e) (IIIa–e) (IVa–e)

using slight modifications of known methods.

Chloromethylsilanes (IIa, e) can be prepared by reaction of the corresponding chlorosilane with Grignard reagent by the customary method using ether as solvent [3, 4]. In the preparation of (IIb-d), the addition of an equimolar quantity of THF to the ether solution of the Grignard reagent leads to a marked increase in reaction rate and a considerable increase in yield. Thus, in the presence of THF the yields of (IIb) and (IIc) reach 84.2 and 77.5% respectively while without THF the yields are 62.5 [5] and 25% [3]. The formation of (IId) generally does not proceed at all without the addition of an equimolar quantity of THF to the solution of the mixed reagents.

Triorganosilylmethylacetates (IIIa-e) were prepared by reaction of the corresponding chloromethylsilanols (IIa-e) with AcOK. DMF was used as a solvent; in comparison with the AcOH generally used in reactions of this type, this made it possible to reduce the reaction temperature from 190° [6] to 145°C thus avoiding the necessity of carrying out the reaction under pressure and considerably increasing the yield. In general, (IIIe) can only be prepared in DMF; when the reaction of (IIe) with AcOK is carried out in AcOH at 190°C, the yield

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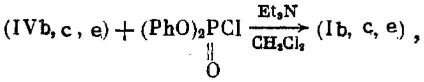
TABLE 1. Thermolysis of (Triorganosilylmethyl)diphenylphosphates (Ia-e) at 200°C

Starting material	Time, h	^{31}P NMR spectrum (δ, ppm)		Rearrangement %, from ^{31}P NMR
		starting material	rearranged product	
(Ia)	5	9,97	20,78	59,5 [2]
(Ib)	5	9,86	20,78	19,4
(Ic)	5	9,97	21,03	14,6
(Id)	5	9,82	20,54	70,0
(Ie)	1	10,54	20,75	100

of (IIIe) amounts to 1.5%. In such a case, the main product was the result of a rearrangement – benzyldimethylsilylacetate [4]. By the use of DMF, the yield of (IIIe) was increased to 90.4%.

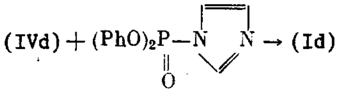
Triorganosilylmethyl alcohols (IVa-e) were prepared by methanolysis of the acetates (IIIa-e) in the presence of catalytic quantities of p-toluenesulfonylchloride which permitted a considerable reduction in the reaction time in comparison with the reaction using H_2SO_4 as catalyst [6].

The phosphate (Ia) has been prepared previously [2]. Phosphates (Ib, c, e) were prepared similarly by phosphorylation of alcohols (IVb, c, e) by diphenylchlorophosphate in CH_2Cl_2 in the presence of Et_3N



$$(\mathrm{IVb, c, e}) + (\mathrm{PhO})_2\underset{\underset{\mathrm{O}}{\|}}{\mathrm{P}}\mathrm{Cl} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{Et_3N}} (\mathrm{Ib, c, e}),$$

but on attempting to prepare phosphate (Id) by this method a quantitative yield of the corresponding chloromethylsilane (IId) was isolated as the sole product. Phosphorylation of alcohol (IVd) by diphenylphosphoric acid in the presence of dicyclohexylcarbodiimide gave a crystalline mixture of phosphate (Id) and carbodiimide conversion products which was difficult to separate. Phosphate (Id) was obtained as the sole product only by using diphenyl(imidazol-1-yl)phosphate as phosphorylating agent.

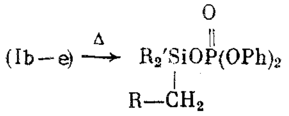


However, if the imidazolylphosphate introduced into the reaction mixture was not previously purified from imidazole hydrochloride, the sole product of the reaction was (IId), apparently as a result of decomposition of the phosphate formed by the imidazole hydrochloride. The reason for the formation of (IId) on phosphorylation of alcohol (IVd) by diphenylchlorophosphate is evidently the reaction of $Et_3N \cdot HCl$ with the phosphate (Id) which is formed and phosphate (Id) does in fact react with $Et_3N \cdot HCl$ to form (IId).

At the same time, phosphates (Ia-c) do not react with $Et_3N \cdot HCl$ under the same conditions. An analogous electron effect of three trifluoropropyl groups causing the C–O bond to rupture more readily also affects the reaction of alcohol (IVd) with Me_3SiCl in the presence of Et_3N. In this case, in contrast to alcohols (IVa-c) which form the corresponding silyl esters, TLC shows that only chloromethylsilane (IId) is formed. However, acylation of acetyl chloride is shown by TLC to take place for alcohols (IVa-c) and for alcohol (IVd) with the formation of acetates (IIIa-d) only. The different behavior of alcohol (IVd) to acylation and to phosphorylation is explained, apparently, by the different tendency to dealkylation of phosphates and acetates against a background of the negative inductive effect of the trifluoropropyl groups.

Thermolysis of chromatographically pure phosphates was carried out at 200°C. The percentage rearrangement was determined from the PMR and ^{31}P NMR spectra.

The thermal rearrangement of phosphate (Ia) has been described previously [2]. Rearrangement of phosphates (Ib-e) proceeds in a similar manner according to the NMR results, the corresponding silyl esters of diphenylphosphoric acid (Vb-e) being formed



$$(\mathrm{Ib-e}) \xrightarrow{\Delta} \underset{\displaystyle \mathrm{R{-}CH_2}}{\mathrm{R_2'Si}}\mathrm{O}\overset{\displaystyle \mathrm{O}}{\overset{\|}{\mathrm{P}}}\mathrm{(OPh)_2}$$

(Vb–e)

Thus, when phosphate (Ib) is heated at 200°C, there is a fall in the intensity of the signal of the methylene protons of OCH_2Si in the PMR spectrum and a corresponding increase in intensity and change in form of the alkyl proton signal in the 1.25-0.25 ppm region. A similar change in the PMR spectrum is observed in the thermolysis of phosphate (Ic).

On heating phosphate (Id) the PMR spectrum of the pyrolysate shows a reduction in the intensity of the methylene proton signals from the groups OCH_2Si and $CF_3CH_2C\underline{H}_2Si$ and the appearance of supplementary signals in the 0.80-0.90 and 1.33-1.53 ppm region which can in all probability be assigned respectively to the protons of $CF_3CH_2CH_2C\underline{H}_2Si$ and $CF_3CH_2C\underline{H}_2CH_2Si$ of the rearranged phosphate (IVd). Here, the reduction in the intensity of the signal from the methylene protons corresponds to the increase in intensity of the signal from the alkyl protons.

The ^{31}P NMR spectra of the pyrolysates of phosphates (Ib-d) show, besides the signals of the starting materials, signals lying in the region of the corresponding rearranged phosphates (Vb-d) (Table 1).

After only 1 h heating at 200°C, the PMR spectrum of phosphate (Ie) no longer shows proton signals from the starting material, only signals from the rearrangement product (Ve) are observed. The ^{31}P NMR spectrum likewise shows only signals from the rearrangement product.

Hydrolysis of phosphate (Ve) gives exclusively diphenylphosphoric acid and 1,3-dibenzyl-1,1,3,3-tetramethyldisiloxane (VIe)

$$(\mathrm{Ve}) \xrightarrow{H_2O} (PhO)_2P(O)OH + [(PhCH_2)Me_2Si]_2O$$

(VIe)

From the ^{31}P NMR results, we calculated the comparative extent of the rearrangements of phosphates (Ia-e) (Table 1).

The results obtained agree well with our proposed mechanism for the rearrangement. Introduction at the Si atom of a more bulky and more electron-accepting substituent (Et, Pr) reduces the rate of the rearrangement, apparently as a result of nucleophilic attack on the Si atom by oxygen of the phosphoryl group becoming more difficult. On the other hand, introduction of the more electron-accepting trifluoropropyl group increases the positive charge on the Si atom and, facilitating thereby the nucleophilic attack on this atom, increases the rate of the rearrangement.

Comparison of the rate of migration of the phenyl and methyl groups shows that the phenyl group considerably surpasses the methyl group in terms of migrating ability which is consistent with the behavior of these groups in already known 1,2-shift type rearrangements [7].

EXPERIMENTAL

PMR spectra of the compounds prepared were run on a Perkin-Elmer R-20 (60 MHz, HMDS external standard). ^{13}P NMR spectra were run on a Bruker HX-90 in impulse mode with noise suppression of the spin–spin interactions of the phosphorus nuclei with protons against 85% H_3PO_4 as internal standard.

All the reactions were carried out with pure, dry ("absolute") solvents. Yields and constants of the compounds prepared are set out in Table 2 and their PMR spectra in Table 3.

Triorganyl(chloromethyl)silanes (IIb-d). To a solution of Grignard reagent, prepared from 0.75 mole alkyl halide and 0.75 mole Mg in 150 ml ether, was added 150 ml THF followed by 0.22 mole $ClCH_2SiCl_3$, slowly with cooling in water. At the end of the vigorous stage of the reaction, the solution was heated at bp for 3.5 h and left overnight. The reaction mixture was decomposed with a solution of 10 ml HCl in 150 ml water and the organic portion washed with water, saturated $NaHCO_3$, and again with water. The ether extract was dried over $MgSO_4$. Distillation in vacuum yielded (IIb-d).

TABLE 2. (Triorganylsilylmethyl)diphenylphosphates (Ib-e), Triorganyl(chloromethyl)silanes (IIb-d), Triorganylsilylmethylacetates (IIIa-e), and Triorganylsilylmethanols (IVa-e)

Compound	Yield, %	Bp, °C (mm)	n_D^{20}	d_4^{20}	*MR* found	*MR* calculated	Found, % C	Found, % H	Found, % Si	Found, % F	Found, % P	Formula	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % F	Calculated, % P	Ref.
(Ib)	75,9	–	1,5082	1,0778	–	–	59,87	7,20	7,74	–	7,75	$C_{19}H_{27}O_4PSi$	60,29	7,19	7,42	–	8,18	
(Ic)	64,5	–	1,5070	1,0596	–	–	63,65	8,15	6,69	–	7,37	$C_{22}H_{33}O_4PSi$	63,82	7,91	6,68	–	7,37	
(Id)	62,0	mp 45°	–	–	–	–	45,28	4,12	4,63	28,71	5,33	$C_{22}H_{24}F_9O_4PSi$	45,36	4,15	4,82	29,35	5,31	
(Ie)	94,5	–	1,5502	1,1454	–	–	63,16	6,05	7,27	–	7,19	$C_{21}H_{24}O_4PSi$	63,30	5,82	7,05	–	7,77	
(IIb)	84,2	63–65(10)	1,4481	0,9141	–	–	–	–	–	–	–	–	–	–	–	–	–	[5]
(IIc)	77,5	95–98(10)	1,4425	0,8952	–	–	–	–	–	–	–	–	–	–	–	–	–	[3]
(IId)	60,8	76(1)	1,3850	1,3834	61,7	60,7	33,05	3,96	7,62	45,49	–	$C_{10}H_{14}ClF_9Si$	32,57	3,92	7,62	46,36	–	
(IIIa)	77,2	134–137	1,4072	–	–	–	–	–	–	–	–	–	–	–	–	–	–	[6]
(IIIb)	70,5	81–83(10)	1,4338	0,8931	–	–	–	–	–	–	–	–	–	–	–	–	–	[8]
(IIIc)	60,9	60(1)	1,4405	0,8991	67,6	69,1	62,19	11,47	11,92	–	–	$C_{12}H_{26}O_2Si$	62,55	11,37	12,18	–	–	
(IIId)	64,7	101–105(1)	1,3810	1,3286	68,5	69,3	36,93	4,53	7,14	43,79	–	$C_{12}H_{17}F_9O_2Si$	36,73	4,36	7,15	43,58	–	
(IIIe)	90,4	87–88(1)	1,5012	–	–	–	–	–	–	–	–	–	–	–	–	–	–	[9]
(IVa)	94,1	121–122	1,4183	–	–	–	–	–	–	–	–	–	–	–	–	–	–	[6]
(IVb)	86,4	83–85(17)	1,4470	0,8678	–	–	–	–	–	–	–	–	–	–	–	–	–	[8]
(IVc)	78,0	70–73(1)	1,4530	0,8611	59,0	59,6	63,74	12,59	15,72	–	–	$C_{10}H_{24}OSi$	63,75	12,84	14,91	–	–	
(IVd)	97,3	91, 92(1)	1,3808	1,3688	59,3	59,9	34,38	4,24	7,6	49,03	–	$C_{10}H_{15}F_9OSi$	34,29	4,31	8,0	48,81	–	
(IVe)	90,3	73–81(1)	1,5230	–	–	–	–	–	–	–	–	–	–	–	–	–	–	[9]

TABLE 3. PMR Spectra of $RR_2'SiCH_2X$: (Triorganylsilylmethyl)diphenylphosphates (Ib-e) [$X = OP(O)(OPh)_2$], Triorganyl(chloromethyl)silanes (IIb-d) (X = Cl), Triorganylsilylmethylacetates (IIIa-e) ($X = OC(O)CH_3$), and Triorganylsilylmethanols (IVa-e) (X = OH)*

Compound	Solvent	δR	δR′	δCH_2X	δX
(Ib)	CCl_4+CDCl_3	0,25–1,25 m		3,92 d $J_{H-P}=6,1$	7,08–7,33 m
(Ic)	CCl_4	0,30–1,53m		3,88 d $J_{H-P}=5,8$	7,65 br.s
(Id)	$CDCl_3$	0,65–0,75 m ** 1,78–1,99 m ***		3,94 d $J_{H-P}=5,5$	6,95–7,30 m
(Ie)	CCl_4+CDCl_3	7,00–7,57 m	0,35 s	4,18 d $J_{H-P}=5,9$	7,00–7,57m
(IIb)	CCl_4	0,30–1,12 m		2,70 s	–
(IIc)	CCl_4	0,39–1,74m		2,75 s	–
(IId)	CCl_4	0,80–1,17m ** 1,66–2,50 m***		2,88s	–
(IIIa)	CCl_4	0,23 s		3,87 s	2,16 s
(IIIb)	CCl_4	0,20–0,30 m		3,79 s	1,79 s
(IIIc)	CCl_4	1,40–1,67 m		3,78 s	2,00 s
(IIId)	CCl_4	0,68–1,06 m ** 1,66–2,33 m***		3,82 s	2,00 s
(IIIe)	CCl_4	7,13 br.s	0,27 s	3,82 s	1,82s
(IVa)	CCl_4	0,33 s		3,45 s	–
(IVb)	CCl_4	0.30–1,20 m		3,36 s	–
(IVc)	CCl_4	0,40–1,67 m		3,35 s	–
(IVd)	CCl_4	0,85–0,94 m ** 1,98–2,23 m ***		3,55 s	–
(IVe)	CCl_4	7,36 br. s	0,22 s	3,35 s	–

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*δ, ppm, J, Hz.

**$CF_3CH_2CH_2$.

***$CF_3C\underline{H}_2CH_2$.

Triorganylsilylmethylacetates (IIIa-e). A mixture of 0.32 mole (IIa-e), 0.32 mole AcOK, and 160 ml DMF was kept for 2 h at 145°C. The organic layer was separated and the aqueous layer extracted with ether. The combined organic extracts were washed with water and dried over $MgSO_4$. Distilling off the solvent and redistilling in vacuum yielded methylacetates (IIIa-e).

Triorganylsilylmethanols (IVa-e). A mixture of 0.46 mole (IIIa-e), 0.0046 mole p-TsCl, and 60 ml methanol was heated 1 h at bp and the methanol–methyl acetate azeotrope distilled out at 58-60°C. Methanol (50 ml) was added and the solution left overnight. The methanol was distilled off and the residue distilled in vacuum to give silylmethanols (IVa-e).

(Triorganylsilylmethyl)diphenylphosphates (Ib, c, e). To a mixture of 0.10 mole (IVb, c, e) and 0.11 mole Et_3N in 100 ml CH_2Cl_2 was added, with cooling in water and stirring, 0.10 mole diphenylchlorophosphate in 50 ml CH_2Cl_2 and the mixture stirred for 1 h and left to stand for 2 days. The precipitated $Et_3N \cdot HCl$ was filtered off and washed with ether. The solvent was distilled off from the filtrate, pentane added, the precipitated solid filtered off, and the filtrate evaporated. The residue was passed through a layer of Al_2O_3 using pentane as eluent and the solvent removed from the eluate to give the phosphates (Ib, c, e).

Reaction of Tris(3,3,3-trifluoropropyl)silylmethanol (IVd) with Diphenylchlorophosphate. To a mixture of 12.08 g (0.035 mole) (IVd) and 5 g (0.05 mole) Et_3N in 40 ml CH_2Cl_2 was added, with stirring and cooling in water, 9.27 g (0.035 mole) diphenylchlorophosphate in 40 ml CH_2Cl_2. The mixture was stirred for 1 h and kept for 5 days until no more alcohol was detected by TLC. The CH_2Cl_2 was distilled off, 25 ml ether added, the upper ether layer separated, the ether evaporated and the residue passed through a layer of Al_2O_3 using hexane as eluent. Removal of the solvent and distillation in vacuum gave 12.3 g (~100%) (IId), bp 80°C/1 mm, n_D^{20} 1.3850.

[Tris(3,3,3-trifluoropropyl)silylmethyl]diphenylphosphate (Id). To a solution of 6.4 g (0.094 mole) imidazole in 35 ml THF was added 13.3 g (0.049 mole) diphenylchlorophosphate in 20 ml THF and heated at bp for 1.5 h. The precipitate was filtered off and washed with 10 ml THF. To the filtrate, which contained the imidazole phosphate, was added, with cooling in water and stirring, 16.4 g (0.049 mole) (IVd) in 15 ml THF. The mixture stirred for 1h, left to stand for 2 days, the solvent distilled off, the residue filtered and the solid washed with ether. The solvent was evaporated from the filtrate and the residue passed through a layer of silica gel using hexane—ether as eluent. Distilling off the solvent gave 17.56 g phosphate (Id).

Thermolysis of (Triorganylsilylmethyl)diphenylphosphates (Ia-d). A sample of 2.0 g (Ia-d) was heated for 5 h at 200°C in a glass vessel with a reflux condenser equipped with a calcium chloride tube. The progress of the reaction and the extent of the decomposition were monitored by PMR and ^{31}P NMR spectroscopy (Table 1).

Thermolysis of (Phenyldimethylsilylmethyl)diphenylphosphate (Ie). A sample of 19.95 g (0.05 mole) (Ie) was heated in a flask equipped with a reflux condenser with a calcium chloride tube for 1 h at 200°C. Distillation of the pyrolysate in vacuum yielded 13.2 g (65.0%) (Ve), bp 167-168°C/1 mm, n_D^{20} 1.5459. Found, %: P 7.6, Si 6.9. $C_{21}H_{23}O_4PSi$. Calculated, %: P 7.8; Si 7.3. PMR spectrum (CCl_4, δ, ppm): 0.13 s (CH_3), 2.20 s ($PhCH_2$), 7.11 br.s (C_6H_5).

Hydrolysis of (Benzyldimethylsilyl)diphenylphosphate (Ve). To a solution of 3.1 g (0.008 mole) (Ve) in 50 ml ether was added 50 ml water and the mixture stirred for 1 h. The ether layer was separated, the aqueous layer extracted with ether and the combined ether extracts washed with a solution of 0.1 g KOH in 30 ml water, dried over $MgSO_4$ and filtered through a layer of Al_2O_3. Removal of the solvent and distillation in vacuum yielded 0.8 g (63.7%) 1,3-dibenzyl-1,1,3,3-tetramethyldisiloxane (VIe), bp 145.5°C/0.5 mm, n_D^{20} 1.5188, d_4^{20} 0.9810, cf. [10]. PMR spectrum (CCl_4, δ, ppm): 0.10 s (CH_3), 2.00 s (CH_2), 7.04 br.s (C_6H_5). The aqueous extract was acidified with HCl, extracted with ether, and dried over $MgSO_4$. After removal of the solvent there was obtained 0.4 g (21.1%) diphenylphosphoric acid, mp 57°C. After recrystallization from a mixture of hexane and CCl_4, mp 70°C. The sample mixed with authentic diphenylphosphoric acid had mp 69-70°C (cf. [11]).

CONCLUSIONS

1. A method has been developed for the preparation of a series of triorganosilylmethyl esters of diphenylphosphoric acid.

2. All the triorganosilylmethyl esters of diphenylphosphoric acid which were examined undergo thermal rearrangement involving the migration of a radical from the Si atom to the methylene C atom according to a 1,2-shift. The influence of the type of radical at the Si atom on the rate of the rearrangement has been studied.

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