The Preparation of Several Tetrakis(triorganosiloxymethyl)methanes

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As regards the organosilyl or silylene derivatives of pentaerythritol (hereinafter called PET), very little has been said in the literature.[1-3]

In our investigations involving the reactions of PET with triorganochlorosilanes, some tetrakis-triorganosilyl derivatives of PET with the formula of $(R_3SiOCH_2)_4C$(hereafter R_3PET) were isolated in a pure form. They are tetrakis(trimethylsiloxymethyl)methane (Me_3PET), terakis(dimethylbutylsiloxymethyl)methane (Me_2BuPET), tetrakis-(dimethylphenylsiloxymethyl)methane (Me_2Ph-PET), tetrakis(diphenylbutylsiloxymethyl)methane (Ph_2BuPET), and tetrakis(triphenylsiloxymethyl)-methane (Ph_3PET), the last four being new compounds.

They were obtained from the reaction of PET either with the corresponding triorganochlorosilanes or with aminosilanes according to the following schemes.

$$(HOCH_2)_4C + 4R_3SiCl \rightarrow (R_3SiOCH_2)_4C + 4HCl$$

or

$$(HOCH_2)_4C + 4R_3SiNH_2 \rightarrow (R_3SiOCH_2)_4C + 4NH_3$$

The products were all soluble in toluene and dioxane, and were found to be quite stable towards hydrolysis in the absence of ionic catalysts.

Experimental

Triorganochlorosilanes. A pure sample of trimethylchlorosilane (bp 58°C) was obtained from the Shin-etsu Chemical Industrial Co. Dimethylbutylchlorosilane (bp 139—140°C), dimethylphenyl chlorosilane (bp 76—78°C/2 mmHg), and diphenylbutylchlorosilane (bp 129°C/1 mmHg) were prepared by the Grignard route.[4] Triphenylchlorosilane (mp 98—99°C) was isolated from a high-boiling residue[5] of the direct synthesis of phenylchlorosilanes. They were further purified by conventional methods immediately before use.

Triorganoaminosilanes. Hexamethyldisilazane (bp 121°C), dimethylbutylaminosilane (bp 128°C), dimethylphenylaminosilane (bp 142°C/3 mmHg), diphenylbutylaminosilane (bp 139°C/1.5 mmHg), and triphenylaminosilane (mp 60°C, bp 156°C/1.8 mmHg) were prepared from the reaction of dried gaseous ammonia with the corresponding chlorosilanes dissolved in ether; the yields were consistently 85—88%.

The Preparation of R_3PET. Typical procedures will be described in detail, using the preparations of Me_3PET and Ph_3PET as examples.

Me_3PET: When a mixture of trimethylchlorosilane (0.44 mol, 47.7 g) and PET (0.1 mol, 13.6 g) was gently refluxed, PET gradually dissolved with the evolution of hydrogen chloride, and the temperature rose to 120°C after 30 hr. The resultant substance was then fractionated and a fraction boiling at 105—115°C/1 mmHg was collected. The further purification of the product was effected by fractional vacuum distillation, giving pure Me_3PET, mp 27.5—28.5°C, bp 110°C/1 mmHg (lit.[2] bp 128—129°C/5 mmHg) in a yield of 77% (mean).

Found: Si, 26.4; C, 48.52; H, 10.54%; mol wt, 418 (determined cryoscopically in dioxane). Calcd for $C_{17}H_{44}O_4Si_4$: Si, 26.4; C, 48.06; H, 10.44%; mol wt, 425.

Several modifications of the above procedure, using some organic bases (aniline, *N*, *N*-dimethylaniline, pyridine, *etc.*) as a hydrogen-chloride acceptor and toluene as a reaction medium unfailingly gave identical products in similar yields.

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1) L. W. Breed, W. J. Haggerty, Jr. and J. Harvey, *J. Org. Chem.*, **25**, 1804 (1960).

2) M. M. Sprung and L. S. Nelson, *ibid.*, **20**, 1750 (1955).

3) B. N. Dolgov, G. Vinter, V. A. Komarov, N. P. Kharitonov and Y. I. Khudobin, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 2146; *Chem. Abstr.*, **60**, 9305c (1964).

4) T. Takiguchi and M. Abe, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **66**, 625 (1963).

5) T. Takiguchi and M. Abe, *ibid.*, **68**, 679 (1965).

Another effective method of preparing the product was by the reaction of PET with hexamethyldisilazane; here, there was a consistent yield of 83—86%.

Ph$_3$PET: When a mixed sample of triphenylaminosilane (0.44 mol, 123.4 g) and PET (0.03 mol, 4.1 g) was gently heated, a reaction occured with the evolution of ammonia. After the addition of PET (0.07 mol, 9.5 g) to the mixture, portion by portion, over a 1-hr period, the whole was further maintained at 160—170°C for 6 hr. After the resultant substance had stood, there was obtained a transparent viscous liquid from which a white crystalline mass, melting at 255—267°C, was obtained by the extraction of impurities with hexane. The recrystallization of the crude product from hexane-dioxane (1 : 1) gave 82 g (70%) of pure Ph$_3$PET, mp 285°C, as fine cubic crystals.

Found: Si, 9.6; C, 77.73; H, 5.15%; mol wt, 1165. Calcd for $C_{77}H_{68}O_4Si_4$: Si, 9.6; C, 79.07; H, 5.86%; mol wt, 1170.

Ph$_3$PET was readily soluble in dioxane, soluble in hot toluene, soluble only with difficulty in boiling benzene, and insoluble in ether, hexane, and ethanol. This was also found highly resistant to hydrolysis and was recovered quite unchanged after prolonged boiling with water.

The preparation of this compound from a direct reaction between PET and triphenylchlorosilane was also attempted; however, this attempt failed because of the presumably lower reactivity of triphenylchlorosilane. The yield of the tetrakis-derivatives always remained below 20%, even when an organic base was used as a hydrogen-chloride acceptor, the majority of the by-product being partially triphenylsilyl-substituted PET with hydroxyl groups.

Other Tetrakis-derivatives. Me$_2$BuPET (bp 155°C/1 mmHg), Me$_2$PhPET (bp 224°C/0.1 mmHg), and Ph$_2$BuPET (mp 76°C, bp 332°C/0.1 mmHg) were prepared by procedures similar to those used for Me$_3$PET or Ph$_3$PET. Throughout all the preparations, reactions with aminosilanes proved to be more advantageous than those with chlorosilanes, both in the marked simplicity of the procedure and in the higher yield of tetrakisderivatives.

Me$_2$BuPET Found: Si, 18.5; C, 58.95; H, 12.61%; mol wt, 575. Calcd for $C_{29}H_{68}O_4Si_4$: Si, 18.9; C, 58.73; H, 11.56%; mol wt, 593.

Me$_2$PhPET Found: Si, 16.5; C, 65.89; H, 7.97%; mol wt, 665. Calcd for $C_{37}H_{52}O_4Si_4$: Si, 16.7; C, 66.02; H, 7.97%; mol wt, 673.

Ph$_2$BuPET Found: Si, 10.2; C, 75.78; H, 7.96%; mol wt, 1075. Calcd for $C_{69}H_{84}O_4Si_4$: Si, 10.3, C, 76.05; H, 7.77%; mol wt, 1090.

The products thus obtained were all readily soluble in dioxane and were soluble in acetone, toluene and boiling benzene. The compounds with methyl groups were soluble in hot hexane and ethanol. They were all fairly resistant to solvolysis in the absence of an ionic catalyst. However, the addition of a few drops of acid or alkali to the boiling ethanolic solution readily decomposed it to the original PET and the ocrresponding hexaorganodisiloxanes.

IR Absorption Spectra and X-Ray Powder Patterns. All the products were well defined and were characterized by their IR spectra. The X-ray powder diffraction data were also recorded for crystalline products by using Cu*K*α radiation filtered by Ni.

IR Spectra

Me$_3$PET 745(m) 840(vs) 870(vs) 906(s) 1070(vs) 1170(m) 1260(vs) 1305(w) 1460(w) 1475(w) 2870(w) 2920(m) 2965(s)

Me$_2$BuPET 745(m) 785(s) 840(vs) 883(s) 905(m) 963(w) 998(w) 1023(m) 1073(vs) 1171(m) 1192(m) 1257(vs) 1340(w) 1375(w) 1466(m) 2875(s) 2925(vs) 2965(vs)

Me$_2$PhPET 670(s) 740(s) 785(vs) 840(vs) 905(m) 996(m) 1065(vs) 1120(vs) 1170(m) 1193(m) 1263(vs) 1305(w) 1320(w) 1407(w) 1427(s) 1460(w) 1470(m) 1487(w) 1593(m) 2895(m) 2935(s) 2980(vs) 3035(m) 3095(m)

Ph$_2$BuPET 700(vs) 735(vs) 783(w) 819(vs) 835(m) 853(w) 873(w) 961(w) 995(m) 1028(s) 1058(vs) 1116(vs) 1171(m) 1190(m) 1268(w) 1305(w) 1340(w) 1376(w) 1425(vs) 1458(m) 1485(w) 1566(w) 1589(m) 2880(s) 2935(vs) 2995(s) 3065(m) 3095(m)

Ph$_3$PET 700(vs) 740(vs) 815(vs) 838(s) 852(m) 920(w) 974(w) 996(m) 1028(s) 1066(vs) 1116(vs) 1156(w) 1190(m) 1268(w) 1308(w) 1328(w) 1380(w) 1425(vs) 1468(w) 1485(m) 1566(w) 1589(m) 2885(m) 2935(m) 3030(s) 3065(vs) 3090(vs)

X-Ray Powder Diffraction Data

Me$_3$PET d,*k*X: 9.51 8.35 8.19 8.04 7.44 6.71 5.95 5.22 5.04 4.44 4.08 3.72
I/I_0: 0.43 0.35 0.51 0.49 0.19 0.33 0.45 0.47 1.00 0.69 0.35 0.18

Ph$_2$BuPET d,*k*X: 15.11 13.59 11.05 10.05 7.50 6.76 5.01 4.90 4.65 4.55 4.48 4.04
I/I_0: 0.11 1.00 0.16 0.13 0.16 1.00 0.28 0.12 0.23 0.16 0.23 0.11

Ph$_3$PET d,*k*X: 13.19 10.65 8.76 7.56 7.31 6.71 6.61 5.01 4.70 4.44 4.19 3.93
I/I_0: 0.17 0.35 0.49 0.33 0.24 0.44 0.45 0.55 0.42 1.00 0.44 0.65

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