The Preparation of Several Triphenylsiloxysilanes

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The reaction of an excess of sodium triphenylsilanolate with triorganochlorosilanes (trimethyl- and triphenylchlorosilane), diorganodichlorosilanes (dimethyl-, diphenyl-, methylphenyl- and vinylphenyldichlorosilane), organotrichlorosilanes (methyl-, phenyl- and vinyltrichlorosilane) and silicon tetrachloride gave the corresponding triphenylsiloxysilanes (hexaorganodisiloxanes, octaorganotrisiloxanes, organo-tris-triphenylsiloxysilanes and tetrakistriphenylsiloxysilane respectively).

The products obtained, including octaphenyltrisiloxane, 3 - vinylheptaphenyl - trisiloxane, 3-methylheptaphenyltrisiloxane, vinyl-tris-triphenylsiloxysilane and phenyl-tris-triphenylsiloxysilane, the new compounds were all crystalline substances of a high chemical stability; they were obtained in consistent yields of 63—67%. The siloxanes were all well defined and were characterized by means of their infrared absorption spectra.

Experimental

Sodium Triphenylsilanolate.—Sodium triphenylsilanolate neut. equiv. 294—297 was prepared according to the method of Hyde et al.[2]

Organolchlorosilanes.—Trimethylchlorosilane, b.p 58°C, dimethyldichlorosilane, b. p. 70—71°C, methyltrichlorosilane, b. p. 66—67°C phenyltrichlorosilane, b. p. 202—203°C, diphenyldichlorosilane, b. p. 130—133°C/2 mmHg and vinyltrichlorosilane, b. p. 90—92°C were obtained from the Shin-etsu Chemical Industrial Co. in commercial grades. All were further purified by distillation immediately before use. Triphenylchlorosilane, m. p. 97—98°C was isolated from a high boiling residue[3] of the direct synthesis of phenylchlorosilane. Vinylphenyldichlorosilane, b. p. 87—88°C/10 mmHg and methylphenyldichlorosilane, b. p. 197—199°C were synthesized by the Grignard process.[4] Reagent-grade silicon tetrachloride, b. p. 56—57°C was used after a single distillation.

Phenyl-tris-triphenylsiloxysilane.—A mixture of phenyltrichlorosilane (4 g., 0.0 2mol.), sodium triphenylsilanolate (30 g. 0.1 mol.) and a small portion of sodium ethylate in 300 ml. of toluene was heated to reflux. After this mixture had been refluxed for 15 hr., the jelly-like precipitate formed was centrifuged and the clear liquid was concentrated to about 50 ml., which in turn gave a white precipitate when added to a large excess of methanol. The precipitate was then recrystallized from 1, 4-dioxane to give 12 g. (67%) of elongated platelets, phenyl-tris-triphenylsiloxysilane, melting at 339—340°C (measured in molten *p*-diphenylbenzene as a medium), together with a small amount of hexaphenyldisiloxane.

Found: C, 76.7; H, 5.1; Si, 12.2; mol. wt., 895, 926 (in benzene). Calcd. for $C_{60}H_{50}O_3Si_4$: C, 77.4; H, 5.4; Si, 12.1%; mol. wt., 931.

Other Siloxanes.—The following siloxanes were obtained by substantially the same procedure: *Octaphenyltrisiloxane,* m. p. 153°C. Found: C, 77.7; H, 5.1; Si, 11.1; mol. wt., 720, 727. Calcd. for $C_{48}H_{40}O_2Si_3$: C, 78.8; H, 5.5; Si, 11.5%; mol. wt., 732.

3-Vinylheptaphenyltrisiloxane, m. p. 122—123°C.

Found: C, 77.0; H, 5.2; Si, 12.2; mol. wt., 659, 677. Calcd. for $C_{44}H_{38}O_2Si_3$: C, 77.4; H, 5.6; Si, 12.3%; mol. wt., 682.

3-Methylheptaphenyltrisiloxane, m. p. 119—120°C.

Found: C, 76.1; H, 5.4; Si, 12.5; mol. wt., 666, 663. Calcd. for $C_{43}H_{38}O_2Si_3$: C, 77.0; H, 5.7; Si, 12.5%; mol. wt., 670.

Vinyl-tris-triphenylsiloxysilane, m. p. 211—212°C.

Found: C, 75.8; H, 5.2; Si, 12.4; mol. wt., 894, 890. Calcd. for $C_{56}H_{48}O_3Si_4$: C, 76.4; H, 5.5; Si, 12.8%; mol. wt., 880.

Methyl-tris-triphenylsiloxysilane, m. p. 224°C (lit.[5] m. p. 224—225°C).

Found: Si, 13.2; mol. wt., 844—853. Calcd. for $C_{55}H_{48}O_3Si_4$: Si, 13.0%; mol. wt., 868.

3, 3-Dimethylhexaphenyltrisiloxane, m. p. 147—149°C (lit.[5] m. p. 155—156°C).

Found: Si, 13.6; mol. wt., 610—617. Calcd. for $C_{38}H_{36}O_2Si_3$: Si, 13.9%; mol. wt., 608.

Tetrakis-triphenylsiloxysilane, m. p. 231—232°C (lit.[6] m. p. 235°C).

Found: Si, 12.2; mol. wt., 1117, 1127. Calcd. for $C_{72}H_{60}O_4Si_5$; Si, 12.4%; mol. wt., 1130.

1, 1, 1-Trimethyltriphenyldisiloxane, m. p. 49°C (lit. m. p. 48°C[2], 51°C[7]).

Found: Si, 15.6; mol. wt., 339. Calcd. for $C_{21}H_{24}OSi_2$: Si, 16.1%; mol. wt., 348.

Hexaphenyldisiloxane, m. p. 230—231°C (lit.[7] m. p. 226°C).

Found: Si, 9.7; mol. wt., 522—528. Calcd. for $C_{36}H_{30}OSi_2$: Si, 10.5%; mol. wt., 535.

X-ray powder patterns recorded by using Cu$K\alpha$ radiation filtered by Ni are given for purposes of their rapid identification.

$C_6H_5Si[OSi(C_6H_5)_3]_3$

d, kX 11.33 9.94 8.93 5.68 4.90 4.70 4.46 4.19 3.92 3.36 3.28

1) Present address: Dai-Nippon Ink Chemical Industrial Co., Itabashi, Tokyo.

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I/I_0	1.00	0.27	0.20	0.29	0.20	0.48	0.25	0.30	0.20	0.20	0.18
	$(C_6H_5)_2Si[OSi(C_6H_5)_3]_2$									
d, *kX*	10.91	9.31	7.83	5.40	5.04	4.72	4.51	4.35	4.27	4.04	3.90	3.20	2.96
I/I_0	0.43	0.86	0.51	0.50	0.50	1.00	0.95	0.70	0.91	0.54	0.53	0.29	0.29
	$CH_2{:}CH{\cdot}C_6H_5Si[OSi(C_6H_5)_3]_2$									
d, *kX*	9.41	7.50	7.25	5.54	5.37	5.10	4.93	4.70	4.51	4.23	3.83	3.59	3.45
I/I_0	1.00	0.31	0.34	0.25	0.22	0.24	0.28	0.39	0.44	0.50	0.20	0.26	0.19
	$CH_3{\cdot}C_6H_5Si[OSi(C_6H_5)_3]_2$									
d, *kX*	8.85	6.86	5.22	4.85	4.48	4.33	4.23	4.10	3.93	3.87	3.63	3.31	
I/I_0	0.84	0.36	0.51	0.61	1.00	0.45	0.46	0.27	0.24	0.24	0.27	0.23	
	$CH_2{:}CHSi[OSi(C_6H_5)_3]_3$									
d, *kX*	10.40	6.92	5.40	4.77	4.40	4.15							
I/I_0	0.63	0.23	0.23	0.91	1.00	0.47							
	$CH_3Si[OSi(C_6H_5)_3]_3$									
d, *kX*	9.94	9.31	4.77	4.33	4.10	3.27							
I/I_0	0.35	0.19	0.22	1.00	0.19	0.29							
	$(CH_3)_2Si[OSi(C_6H_5)_3]_2$									
d, *kX*	9.21	8.42	8.19	7.17	6.81	6.20	4.72	4.46	4.19	3.83			
I/I_0	0.15	0.26	0.33	0.30	0.20	0.55	0.83	1.00	0.17	0.14			
	$[(C_6H_5)_3SiO]_4Si$									
d, *kX*	19.64	9.94	4.96	4.75	4.40	3.79	3.29	3.25					
I/I_0	0.28	0.27	1.00	0.15	0.63	0.22	0.50	0.25					
	$(CH_3)_3SiOSi((C_6H_3)_3$									
d, *kX*	8.85	6.93	5.68	4.87	4.37	3.68	3.44	2.69					
I/I_0	0.35	0.26	0.22	1.00	0.31	0.51	0.27	0.20					
	$[(C_6H_5)_3Si]_2O$									
d, *kX*	9.94	8.51	7.76	7.57	6.92	5.47	4.96	4.75	4.60	4.46	4.21	3.79	3.29
I/I_0	0.19	0.19	0.25	0.23	0.22	0.19	1.00	0.33	0.33	0.51	0.32	0.33	0.18

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