# The Preparation of Triorganosilyl Derivatives of Hydroquinone, Resorcinol, Bisphenol-A and Terephthalic Acid

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In the course of the preparation of phenylene- and phthalate-siloxy copolymers with $-C_6H_4O-Si-$ and $-O_2CC_6H_4CO_2Si-$, di-triorganosilyl derivatives of hydroquinone and resorcinol, *1,4(1,3)-di-triorganosiloxy benzene* ($R_3HQ$ and $R_3RC$), those of bisphenol-A (BPA), *2,2-bis-(4-triorganosiloxyphenyl)-propane* ($R_3BPA$), and terephthalic acid, *bis-triorganosilyl terephthalate* ($R_3TPA$) were isolated in pure states. $R_3HQ$ and $R_3RC$ were prepared from the reaction of triorganochlorosilane with the diphenols; $R_3BPA$, from the reaction of chlorosilane with BPA in the presence of aniline as a hydrogen chloride acceptor, or with the sodium salt of BPA in an inert solvent, and $R_3TPA$, from the reaction of chlorosilane with dipotassium terephthalate. $R_3TPA$ was found to be extremely sensitive towards solvolysis, while the phenolic silyl-ethers, the former three, were rather stable in both hydrolysis and alcoholysis.

## Experimental

**Triorganochlorosilanes.** — A pure sample of trimethylchlorosilane (b. p. 58°C) was obtained from the Shinetsu Chemical Industrial Co. Dimethylbutylchlorosilane (b.p. 139—140°C), dimethylphenylchlorosilane (b. p. 76—78°C/2 mmHg) and diphenylmethylchlorosilane (b. p. 145—146°C/2.5 mmHg) were prepared by the Grignard route.[1] Triphenylchlorosilane (m. p. 98—99°C) was isolated from high

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[1] T. Takiguchi and M. Abe, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 625 (1963).

boiling residue[2] of the direct synthesis of phenylchlorosilanes. All the compounds were further purified by conventional methods just before use.

**The Preparation of $R_3HQ$ and $R_3RC$.**—The general procedure will be described using 1,4-bis-trimethylsiloxy-benzene ($Me_3HQ$) as an example. A mixed sample of hydroquinone (33 g., 0.3 mol.) and trimethylchlorosilane (54 g., 0.5 mol.) was refluxed until the hydroquinone dissolved completely to give a clear yellow solution. The resultant solution was evaporated to remove the excess chlorosilan and then distilled under a vacuum. The distillate at 107—110°C/4 mmHg was a viscous liquid which solidified on standing. Recrystallization from ether gave 59 g. (77%) of pure $Me_3HQ$ (m. p. 48°C) (lit. m. p. 46°C,[3] 52°C,[4] 48.9—49.3°C[5]) ; b. p. 239°C (lit. b. p. 252°C,[6] 246°C[3]). The following disilyl ethers of the diphenols were obtained by a very similar procedure : $Me_3RC$, b. p. 235—236°C, 92—93°C/2 mmHg (lit. b. p. 239°C,[6] 243°C[4], 237—240°C,[7] 116°C/7 mmHg[3]) ; $n_D^{20}$ 1.4755 ; $d_4^{20}$ 0.947. $Me_2BuHQ$, b. p. 158—195°C/1.5 mmHg ; $n_D^{20}$ 1.4765 ; $d_4^{20}$ 0.925. $Me_2BuRC$, b. p. 161—162°C/3 mmHg ; $n_D^{20}$ 1.4798 ; $d_4^{20}$ 0.923. $Me_2PhHQ$, b. p. 137—139°C/0.5 mmHg ; $n_D^{20}$ 1.5720 ; $d_4^{20}$ 1.087. $MePh_2HQ$, b. p. 237—238°C/0.5 mmHg ; $n_D^{20}$ 1.5882 ; $d_4^{20}$ 1.113. $Ph_3HQ$, m. p. 225—226°C (lit. m. p. 215.8—216.0°C[5]). ($Ph_3HQ$ was prepared from the reaction in aniline.)

*$Me_3HQ(RC)$.* — Found : Si, 21.0 (21.7) ; mol. wt., 238 (244) (in benzene) ; $MR_D$,[8] — (75.35). Calcd. for $C_{12}H_{22}O_2Si_2$ : Si, 22.0% ; mol. wt., 254 ; $MR_D$, 74.38.

*$Me_2BuHQ(RC)$.*—Found : Si, 16.4 (16.0) ; mol. wt., 318 (326) ; $MR_D$, 104.7 (104.3). Calcd. for $C_{18}H_{34}O_2Si_2$ : Si, 16.6% ; mol. wt., 339 ; $MR_D$, 104.7.

*$Me_2PhHQ$.* — Found : Si, 14.5 ; mol. wt., 377, 373 ; $MR_D$, 111.4. Calcd. for $C_{22}H_{26}O_2Si_2$ : Si, 14.8% ; mol. wt., 379 ; $MR_D$, 112.7.

*$MePh_2HQ$.* — Found : Si, 10.7 ; mol. wt., 491 ; $MR_D$, 152.2. Calcd. for $C_{32}H_{30}O_2Si_2$ : Si, 11.2% ; mol. wt., 503 ; $MR_D$, 150.9.

*$Ph_3HQ$.*—Found : Si, 8.2 ; mol. wt., 633 (1,4-dioxane). Calcd. for $C_{42}H_{34}O_2Si_2$ : Si, 8.9% ; mol. wt., 627.

$R_3HQ$ was fairly stable in hydrolysis ; e. g., $Me_3HQ$ recovered unchanged even after 2 hr.' boiling with distilled water. $R_3RC$ was less stable than $R_3HQ$. However, both were hydrolyzed gradually by prolonged heating with 1/20 N sulfuric acid, yielding the diphenols and the corresponding disiloxanes. The produts were also characterized by their infrared absorption spectra.[9] X-Ray powder patterns for crystalline ethers are given below :

$Me_3HQ$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $d, kX$ : | 11.05 | 5.57 | 5.31 | 4.93 | 4.42 | 3.90 | 3.71 |
| | 3.47 | 3.04 | | | | | |
| $I/I_0$ : | 1.00 | 0.39 | 0.29 | 0.14 | 0.24 | 0.29 | 0.26 |
| | 0.14 | 0.13 | | | | | |

$Ph_3HQ$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $d, kX$ : | 12.26 | 8.51 | 7.76 | 6.92 | 6.15 | 4.70 | 4.53 |
| | 4.37 | 4.17 | 4.02 | 3.59 | 3.48 | 3.39 | |
| $I/I_0$ : | 0.19 | 0.45 | 0.36 | 0.28 | 0.93 | 1.00 | 0.48 |
| | 0.98 | 0.63 | 0.36 | 0.26 | 0.24 | 0.25 | |

**The Preparation of $R_3BPA$.**—A typical procedure will be detailed for 2,2-bis-(4-dimethylphenylsiloxyphenyl)-propane ($Me_2PhBPA$). A mixture of BPA (46 g., 0.2 mol.) and dimethylphenylchlorosilane (85 g., 0.5 mol.) was refluxed for 5 hr. After it had then been cooled to room temperature, a solution of aniline (37 g., 0.4 mol.) in 300 ml. of ether was vigorously stirred into the mixture, after which the mixture was refluxed for an additional 2 hr. The resultant solution was filtered to remove aniline hydrochloride and concentrated to a clear viscous liquid, from which crude $Me_2PhBPA$ boiling at 266—285°C (1.5 mmHg) was obtained by distillation. The redistillation of the fraction gave 74 g. (74%) of pure $M_2PhBPA$ ; b. p. 286—287°C/1.5 mmHg, $n_D^{20}$ 1.5746, $d_4^{20}$ 1.117.

It was found that the use of aniline as a hydrogen chloride acceptor was essential for the successful preparation ; otherwise, the reaction was not completed, it was always accompanied by the formation of considerable amounts of mono-silyl ether, and the yield of bis-silyl ether was less than 40%.

In another preparation, an ethereal solution of dimethylphenylchlorosilane (85 g., 0.5 mol.) was added to a stirred slurry of sodium salt of BPA (54 g., 0.2 mol.) in ether. After it has been stirred for 2 hr. under refluxing, the mixture was filtered to remove sodium chloride ; then the filtrate was evaporated to give an oily viscous liquid, which gave 66 g. (66%) of $Me_2PhBPA$ by fractionation under a vacuum. The following were obtained analogously in a consistent yield of 65—70%. $Me_3BPA$, b. p. 179—180°C/1.5 mmHg, $n_D^{20}$ 1.5178, $d_D^{20}$ 0.981 ; $Me_2BuBPA$, b. p. 211—214°C/1.5 mmHg, $n_D^{20}$ 1.5102, $d_4^{20}$ 0.976 ; and $MePh_2BPA$, b. p. 297—300°C/0.5 mmHg, $n_D^{20}$ 1.5777, $d_4^{20}$ 1.084.

Triphenylchlorosilane was found to be much less reactive to BPA than the other chlorosilanes. Therefore, a reaction in a high boilng solvent (toluene, xylene, etc.) using aluminum chloride as a catalyst was necessary ; otherwise, the yield of bis-silyl-ether always remained below 20%. $Ph_3BPA$ was a fine crystalline substance melting at 151—152°C ; it was obtained in a 47% (mean) yield by preparation in xylene. It was readily soluble in benzene, toluene and xylene, and insoluble in hexane, acetone, ethanol and methanol.

X-Ray powder diffraction data of $Ph_3BPA$ :

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $d, kX$ : | 8.93 | 7.48 | 6.86 | 6.42 | 5.83 | 5.28 | 5.19 |
| | 4.80 | 4.60 | 4.51 | 4.33 | 3.87 | 3.68 | |
| $I/I_0$ : | 0.47 | 0.25 | 0.43 | 0.23 | 0.48 | 0.38 | 0.37 |
| | 0.31 | 0.55 | 0.73 | 1.00 | 0.22 | 0.38 | |

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[2] T. Takiguchi and M. Abe, ibid., **68**, 679 (1965).

[3] M. G Voronkov and Z. I. Shabarova, *Zhur. Obshchei Khim.*, **30**, 1955 (1960).

[4] F. A. Heinlein and J. Krämer, *Chem. Ber.*, **92**, 2585 (1959).

[5] G. Illuminati and F. Tarli, *Ric. Sci., Rend. Sez.*, **A3**, 329 (1963).

[6] M. Jacovic, *Z. anorg. u. allgem. Chem.*, **288**, 324 (1956).

[7] S. H. Langer, S. Connell and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

[8] E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2445 (1946); R. O. Sauer, ibid., **68**, 954 (1946).

[9] T. Takiguchi, M. Abe and H. Kobuna, Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

*$Me_2PhBPA$*.—Found: Si, 11.0; mol. wt., 506 (benzene); $MR_D$, 147.0. Calcd. for $C_{31}H_{36}O_2Si_2$: Si, 11.3%; mol. wt., 497; $MR_D$, 146.9.

*$Me_3BPA$*.—Found: Si, 14.7; mol. wt., 366; $MR_D$, 115.2. Calcd. for $C_{21}H_{32}O_2Si_2$: Si, 15.1%; mol. wt., 373; $MR_D$, 112.0.

*$Me_2BuBPA$*.—Found: Si, 11.9; mol. wt., 455; $MR_D$, 140.1. Calcd. for $C_{27}H_{44}O_2Si_2$: Si, 12.3%; mol. wt., 457; $MR_D$, 139.8.

*$MePh_2BPA$*.—Found: Si, 8.83; mol. wt., 617; $MR_D$, 191.3. Calcd. for $C_{41}H_{40}O_2Si_2$: Si, 9.1%; mol. wt., 621; $MR_D$, 188.5.

*$Ph_3BPA$*.—Found: Si, 7.1; mol. wt., 750. Calcd. for $C_{51}H_{44}O_2Si_2$: Si, 7.5%; mol. wt., 745.

The identifications of these bis-silyl ethers were further established by their hydrolytic cleavage. The hydrolysis of $Me_2BuBPA$ (22.8 g., 0.05 mol.) with 1/20 N sulfuric acid by refluxing it for 10 hr. afforded BPA (10.0 g., 0.044 mol.) and 1,3-dibutyltetramethyldisiloxane (b. p. 207—208°C; 11.3 g., 0.046 mol.). Infrared absorption data[9] were also recorded.

Throughout the infrared absorption spectra of all silyl ethers ($R_3BPA$, $R_3HQ$ and $R_3RC$), a very strong and characteristic absorption band in the 910—925 $cm^{-1}$ region was found to exist. Its assignment still remains uncertain; however, it is very probably due to the existence of phenylene- or phenyl-silyl ether bonding ($-C_6H_4-O-Si-$ or $C_6H_5-O-Si-$) in these compounds. An entire absence of the band in BPA, diphenols and in phenol, and its appearance in the silyl derivatives of BPA, in diphenols and in all phenoxysilanes[10] seems to support this assignment strongly.

**Bis-triphenylsilyl Terephthalate.**—In a manner similar to that employed for $R_3TPA$ ($R_3=Me_3$, $Me_2Bu$, $Me_2Ph$ and $MePh_2$) in the preceding paper,[11] bis-triphenylsilyl terephthalate ($Ph_3TPA$) was obtained in 67% yield from the reaction of dipotassium terephthalate with triphenylchlorosilane in boiling toluene.

$Ph_3TPA$ was a fine acicular crystal melting at 242—243°C, hardly soluble in ordinary solvents at room temperature, and fairly soluble in boiling toluene, xylene, dioxane and chlorobenzene.

Found: Si, 7.7; mol. wt., 688, 692 (Rast method). Calcd. for $C_{44}H_{34}O_4Si_2$: Si, 8.2%; mol. wt., 683.

X-Ray powder diffraction data of $Ph_3TPA$:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $d, kX$: | 8.93 | 7.83 | 7.31 | 7.28 | 5.79 | 5.13 | 5.10 |
| | 4.75 | 4.57 | 4.15 | 4.02 | | | |
| $I/I_0$: | 0.28 | 0.18 | 0.13 | 0.11 | 0.12 | 0.62 | 0.19 |
| | 0.39 | 1.00 | 0.34 | 0.21 | | | |

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[10] T. Takiguchi, M. Abe and M. Niwano *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), in press.

[11] M. Abe, ibid., in press.