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The Preparation of Tri-*t*-butoxysiloxy-substituted 1,3,5-Triazines

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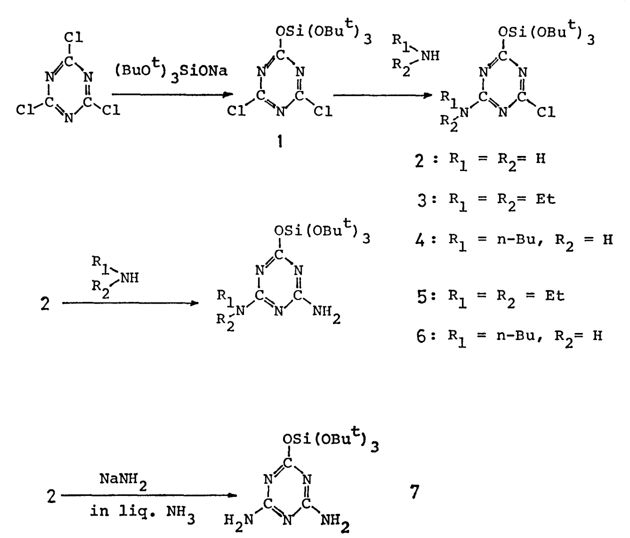
Synopsis. The title derivatives were prepared to obtain 1,3,5-triazines with a better solubility than chloro- and amino-1,3,5-triazine, which are not very soluble in common organic solvents.

Several reports have been published on the preparation and reaction of 1,3,5-triazines substituted with trimethylsilyl groups.[1–6] These silicon-containing derivatives are prepared by the reaction of cyanurate, ammeline, and melamine with hexamethyldisilazane, which are purified by distillation *in vacuo*. This implies that the substitution with trimethylsilyl group affords a high volatility and/or a good solubility to the starting materials by prevention of interactions among molecules. However, these derivatives are sensitive to hydrolysis.

In this work, therefore, the chloro- and amino-substituted 1,3,5-triazines with tri-*t*-butoxysiloxy group were prepared. Our hope was that derivatives with a good solubility in organic solvents together with hydrolytic stability may be obtained by the prevention of interactions among molecules through introducing this group into the 1,3,5-triazine ring. Earlier results showed that condensations of functional groups such as amino and hydroxyl group are effectively protected.[7]

The experimental results showed that the reaction of cyanuric chloride with sodium tri-*t*-butoxysilanolate gave the compound **1**, but further replacement of the chlorine atom of **1** by this group did not take place. Compound **1** was allowed to react with ammonia, diethylamine and butylamine to give the derivatives **2**,**3**, and **4**, respectively. The reaction of **2** with ammonia did not occur under the conditions. Amines such as diethylamine and butylamine, however, were reacted with **2** to form the products **5** and **6**, which indicates that a low reactivity of the last chlorine atom is not due to the steric factor of tri-*t*-butoxysiloxy group but to the low electrophilicity of the carbon of carbon–chlorine bond. An attempt to isolate **7** from the reaction product of **2** with sodium amide in liquid ammonia was not successful, but it was obtained as the hydrochloride.



All these compounds were very soluble in organic solvents such as methanol, ethanol, acetone, ether, tetrahydrofuran, chloroform, and benzene and were stable to hydrolysis; most of **2** was recovered without hydrolysis after it was heated at 50 °C for about thirty minutes in a mixed solvent of water and dioxane. The hydrochloride of **7** was also soluble in methanol, ethanol, and acetone. These results indicate that introduction of tri-*t*-butoxysiloxy group affords an appreciable solubility and hydrolytic stability to the derivatives.

Experimental

Materials. All the melting points and boiling points were uncorrected. The solvents and reagents were dehydrated and purified by distillation or recrystallization. Tri-*t*-butoxysilanol was prepared by the method already mentioned.[7] Sodium tri-*t*-butoxysilanolate was prepared by the reaction of tri-*t*-butoxysilanol and sodium in benzene and was used without isolation.

*2,4-Dichloro-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**1**). Sodium silanolate prepared by the reaction of tri-*t*-butoxysilanol (14.0 g) with sodium (1.1 g) in benzene (80 ml) was reacted with cyanuric chloride (9.2 g) in benzene (100 ml) under reflux for 3 h to give **1**, 12.9 g (62.8%); bp 139 °C—/2 Torr†; IR 1533, 1501, 1475, 1393, 1377, 1085, 1038, 855, 818 cm^{-1}. Found: C, 43.59; H, 10.07; N, 6.81; Si, 6.52%. Calcd for $C_{15}H_{17}N_3Cl_2O_4Si$: C, 43.69; H, 10.19; N, 6.60; Si, 6.81 %.

*2-Amino-4-chloro-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**2**). The reaction of **1** (30.0 g) in benzene (300 ml) with dry ammonia gas at 5—10 °C for 2 h gave **2**; 23.3 g (recrystallized from hexane 73.3%); mp 105 °C; IR: 3350, 3225, 1608, 1557, 1517, 1393, 1370, 1082, 1030, 820 cm^{-1}. Found: C, 45.42; H, 7.35; N, 13.79; Si, 7.13%. Calcd for $C_{15}H_{19}N_4ClO_4Si$: C, 45.85; H, 7.44; N, 14.26; Si, 7.15%.

Compound **2** was also obtained by introducing ammonia into the reaction mixture of sodium tri-*t*-butoxysilanolate with cyanuric chloride without isolation of **1** (44% yield).

*2-Chloro-4-diethylamino-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**3**) *and 2-Chloro-4-butylamino-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**4**). To the reaction mixture of tri-*t*-butoxysilanol (28.0 g) with sodium (2.3 g) in benzene (150 ml), followed by addition of cyanuric chloride (18.4 g) in benzene (200 ml), diethylamine or butylamine (15.0 g) in benzene (100 ml) was added. Recrystallization of a residue from the reaction mixtures with hexane gave the compounds: **3**, 21.5 g (47.8%); mp 58.0—58.5 °C; IR 1595, 1514, 1430, 1405, 1378, 1080, 1060, 810 cm^{-1}; NMR (CCl_4): δ 1.2 (t, 6H), 1.35 (s, 27H), 3.62 (q, 4H); MS: *m*/*e* 448 (M^+). Compound **4**, 28.3 g (63%); mp 94.3—94.5 °C; IR 1585, 1550, 1405, 1380, 1080, 1055, 1030, 813 cm^{-1}; NMR (CCl_4): δ 0.95 (m, 7H),

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† 1 Torr≈133.322 Pa.

1.35 (s, 27H), 3.50 (q, 2H), 8.08 (t, 1H); MS: *m/e* 448 (M^+). Found for **3**: C, 51.36; H, 8.64; N, 12.16%. Found for **4**: C, 50.30; H, 8.45; N, 12.57%. Calcd for $C_{19}H_{27}N_4ClO_4Si$; C, 50.82; H, 8.30; N, 12.48%.

*2-Amino-4-diethylamino-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**5**) *and 2-amino-4-butylamino-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**6**). Compound **2** (5.0 g) in benzene (100 ml) was reacted with diethyamine or butylamine (2.0 g) in benzene (50 ml) under reflux for 2 h. Removal of the solvent and subsequent recrystallization of a residue with ether (**5**) or petroleum ether (**6**) gave the compounds: **5**, 5.9 g (56.8%); mp 89.0—90.0 °C; IR: 3390, 3220, 3070, 1640, 1540, 1520, 1404, 1380, 1045, 1028, 830 cm^{-1}; NMR (CCl_4): δ 1.14 (t, 6H), 1.34 (s, 27H), 3.53 (q, 4H); MS: *m/e* 429 (M^+). Compound **6**, 2.3 g (44.5%); mp 110.0 °C (decomp); IR: 3510, 3050, 3000, 1646, 1547, 1503, 1403, 1378, 1050, 1025, 830 cm^{-1}; MS: *m/e* 429 (M^+). Found for **5**: C, 53.17, H, 9.39; N, 16.30%. Found for **6**: C, 53.28; H, 9.42; N, 16.18%. Calcd for $C_{19}H_{38}N_4O_4Si$: C, 53.12; H, 9.15; N, 16.30%.

*2,4-Diamino-6-(tri-*t*-butoxysiloxy)-1,3,5-triazine* (**7**). Into a flask containing dry liquid ammonia (about 100 ml) trapped under cooling with Dry Ice–acetone was added with stirring first a catalytic amount of iron (III) nitrate hydrate (0.05 g) and then 0.55 g of sodium divided into several pieces over several times. After the completion of disappearance of a blue color, 10.1 g of **2** was added, and the mixture was stirred for 2 h. The ammonia was evaporated while the reaction mixture was allowed to rise to room temperature after addition of hexane. The mixture was refluxed, and the solid was filtered by hot filtration. After drying in vacuo and dissolving into methanol, it was reacted with a dilute hydrochloric acid solution. The precipitate was filtered, washed with water, and dried. It was recrystallized with methanol to give crystals (2.7 g, 30% yield) of the hydrochloride of **7**. Mp 178 °C (decomp); IR: 3160, 3080, 2985, 1710, 1590, 1430, 1396, 1379, 1080, 843 cm^{-1}; NMR ($(CD_3)_2SO$): δ 1.25 (s, 28H), 8.70 (s, 4H). Found for hydrochloride of **7**: C, 44.38; H, 7.41; N, 17.07; Si, 6.87%. Calcd for $C_{15}H_{32}N_5O_4ClSi$: C, 43.93; H, 7.86; N, 17.08; Si, 6.85%.

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