2,5-Di-*tert*-butylphenylsilanetriol: synthesis and reactivity

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Stable 2,5-di-*tert*-butylphenylsilanetriol was prepared by a stepwise synthesis. This compound reacted with triethylenediamine and lanthanum silylamide to form a 1 : 1 molecular complex and highly thermally stable lanthanosilsesquioxane, respectively.

Key words: silanetriols, metallosiloxanes.

In recent years, attention of researchers to stable silanetriols markedly increased because they can be used to prepare cage metallosiloxanes, which are highly interesting due to their catalytic properties, thermal stability, and also unusual magnetic properties.[1]

One of the most important features of the chemistry of silanols is high acidity of the SiOH group. Therefore, silanols are prone to form strong hydrogen bonds with both one another and other organic compounds, which results in various associates and complexes ranging from simple dimers to complex three-dimensional networks.[2]

Finally, silanetriols are the closest analogs of silicic acid, which was found recently to take an active part (though indirectly) in the formation of bone tissue, because it binds aluminum, ruinous for this tissue (due to competition with calcium), into strong complexes.[3]

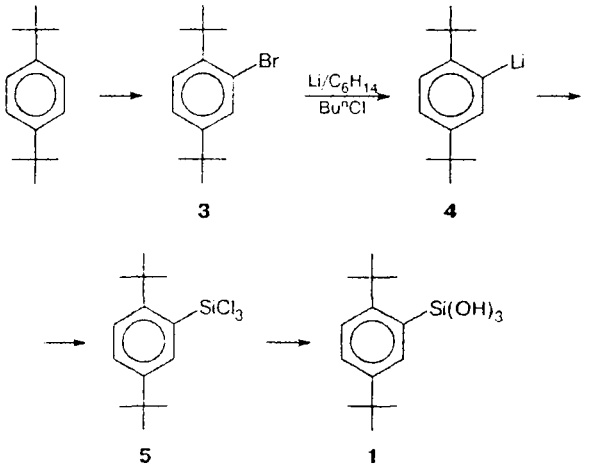
Up to now, several types of stable silanetriols are known,[1] namely, substituted aniline derivatives, $Ar(Me_3Si)NSi(OH)_3$, and alkylsilanetriols, $RSi(OH)_3$, where R is a branched organic radical or an organometallic fragment. Among aromatic derivatives in which the $Si(OH)_3$ group is bound directly to the aromatic ring, the simplest phenylsilanetriol has been reported[4]; however, this compound is unstable and rapidly condenses.

The subjects of our study were 2,5-di-*tert*-butylphenylsilanetriol (**1**) and 2,5-di-*tert*-butyl-1,4-bis(trihydroxysilyl)benzene (**2**). On the one hand, the silanetriol group in compound **1** is sterically sufficiently hindered to make this compound highly stable and, on the other hand, it should be highly reactive, because the second *ortho*-position of the benzene ring is nonsubstituted. Compound **2** contains two sterically hindered silanetriol groups in the *para*-positions of the aromatic ring; this may present interest regarding the synthesis of linear polymers containing built-in metallosilsesquioxane fragments.

Results and Discussion

Silanetriol **1** was synthesized from 1,4-di-*tert*-butylbenzene by a four-step procedure shown in Scheme 1.

Scheme 1



Bromo-2,5-di-*tert*-butylbenzene (**3**) was prepared by a procedure[5] that we have improved. Bromination of *p*-di-*tert*-butylbenzene* was carried out in the presence of $FeCl_3$ as a catalyst and NaX zeolite for absorption of the evolved HBr, whose excess concentration induces a side process, namely, elimination of the *tert*-butyl group. Thus, compound **3** was obtained in 75% yield. In addition, *m*-bromo-*tert*-butylbenzene (20%), easily separable by distillation, was formed as a by-product.

The exchange reaction of bromide **3** with Bu^nLi in ether to give 2,5-di-*tert*-butylphenyllithium (**4**) in 59% yield (an equilibrium mixture of the initial compound and the final product) has been reported.[5] However, when we attempted to reproduce this procedure, we observed even at −78 °C a different process, namely, cleavage of diethyl ether by the organolithium compound that formed, which gave EtOLi and 1,4-di-*tert*-

* Synthesis of bromo-2,5-di-*tert*-butylbenzene contaminated by 12% 3,4-dibromo-*tert*-butylbenzene, inseparable by distillation, has been reported.[5]

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butylbenzene. In a control experiment, Bu^nLi cleaves diethyl ether extremely slowly under these conditions.

The reaction of bromide **3** with Mg in THF gives the same result. When ether is replaced by a saturated hydrocarbon, the exchange of bromide with lithium does not occur. Lithium metal does not react with compound **3** in hexane. The situation is improved when the two methods are combined, namely, bromide **3** is made to react with a dispersion of lithium in the presence of tetramethylethylenediamine using *n*-butyl chloride (10 mol. %) for lithium activation. This procedure gives compound **4** contaminated by Bu^nLi in an amount equivalent to the amount of Bu^nCl used in the reaction. The resulting solution of compound **4** in hexane was used in the subsequent reaction with $SiCl_4$ without additional purification.

The replacement of lithium in compound **4** by a trichlorosilyl group occurs rather smoothly. The LiCl precipitate forms over a period of 2 h. Compound **5** was isolated by fractionation from the reaction mixture as a thick liquid, which solidified on cooling to give a finely crystalline material. The ^1H NMR spectrum of compound **5** indicates the presence of two nonequivalent *tert*-butyl groups and three nonequivalent protons in the aromatic ring.

Silanetriol **1** was synthesized under controlled conditions (0 °C) using strictly equivalent amounts of water and aniline. The reaction was carried out in THF rather than in ether, as has been reported earlier. Silanetriol **1** is readily soluble in polar solvents (THF, Et_2O, alcohols, acetone), sparingly soluble (on heating) in aromatic hydrocarbons (benzene, toluene) and chlorinated hydrocarbons ($CHCl_3$, CH_2Cl_2), readily crystallizes from the latter, and is insoluble in saturated hydrocarbons. The ^1H NMR spectrum of compound **1** is similar to the spectra of its precursors (brominated derivative **4** and trichlorosilane **5**) and exhibits signals for two nonequivalent *tert*-butyl groups and three nonequivalent protons of the aromatic ring. The protons of the silanol group ($-Si(OH)_3$) appear as a broad singlet at about δ 5.5—6.3. This broadening is obviously due to the intermolecular association. The IR spectrum exhibits absorption bands typical of *tert*-butyl groups (1255, 1195 cm^{-1}) and adjacent protons of the aromatic ring (820 cm^{-1}) as well as a broad band with a maximum at 3260 cm^{-1} due to the $Si(OH)_3$ group.

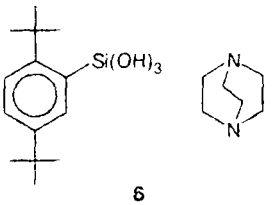
Silanetriol **1** has a high melting point (178 °C). After a sample of **1** has been kept for 1 min at 178 °C, the IR spectrum changes. The absorption band at 3260 cm^{-1} (SiOH) becomes even broader and its maximum shifts to 3400 cm^{-1}; a new broad intense band at 1030—1050 cm^{-1} appears, indicating the formation of a siloxane bond in the condensation products.

The retention times of silanols containing one (Ph_3SiOH), two ($Ph_2Si(OH)_2$), and three (compound **1**) hydroxy groups were determined by HPLC. The following values were found (Separon SGX, *n*-heptane—THF, 2.5 : 1, as the eluent): 5 min 40 s, 9 min 45 s, and 13 min 5 s, respectively. Compound **1** is retained longer than its analogs due to stronger interaction with the silica gel surface.

Since the acidity of the silanol group is rather high, silanols are able to form molecular associates and complexes due to strong hydrogen bonds. Most of the published data are examples of association of silanetriol molecules with one another.[1,2] Complexes with amines are less studied.

We studied the reaction of silanetriol **1** with amines. It was found that simple amines do not react with compound **1**. Thus after silanetriol **1** has been treated with triethylamine the amine can be completely removed *in vacuo*. In the case of more basic triethylenediamine (TED), fairly strong finely crystalline complex **6** is formed.

Elemental analysis of these crystals corresponds to a 1 : 1 adduct. The IR spectrum of this complex contains both the bands typical of silanetriol (1255, 1200 cm^{-1} (Bu^t); 1150, 1090, 1050, 920, 820 cm^{-1}) and those typical of TED (1300 (CN), 1050, 990, 760 cm^{-1}). The band at 3260 cm^{-1} observed in the spectrum of silanetriol becomes even broader (3500—2500 cm^{-1}), and new bands at 870, 840, and 740 cm^{-1} appear. In our opinion, these data attest to strong interaction of TED with silanetriol through hydrogen bonding; however, to establish the structure of complex **6** more exactly, additional studies are needed. Unfortunately, we were unable to grow crystals of **6** suitable for X-ray diffraction analysis.



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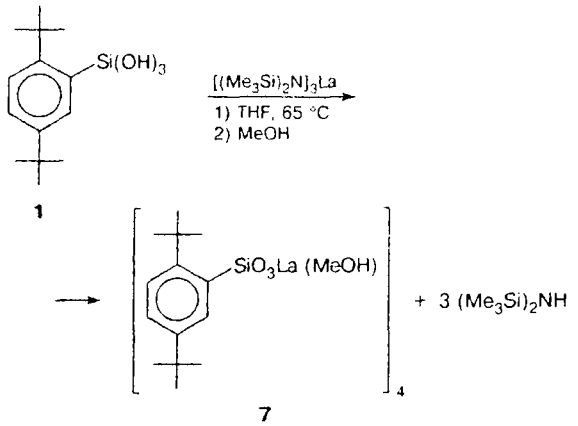
We studied the interaction of silanetriol **1** with lanthanum tris[bis(trimethylsilyl)amide]. The reaction was carried out in THF at 65 °C at an 1 : 3 ratio of the reactants. The residue obtained after removal of the solvent was a glassy material readily soluble in saturated hydrocarbons (recall that the initial silanetriol is insoluble in them). GLC analysis of volatile fractions codistilled with the solvent showed the presence of hexamethyldisilazane. The glassy reaction product proved to be stable against hydrolysis or alcoholysis both in the solid state and in solution. The addition of methanol to a toluene solution of the product gave a white finely crystalline powder; this compound, readily soluble in many organic solvents including saturated hydrocarbons, was identified as lanthanosilsesquioxane (**7**) (Scheme 2).

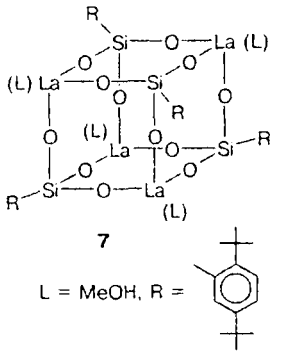
The IR spectrum of compound **7** has a pattern typical of metallosilsesquioxanes.[6] It contains an intense band at 1020 cm^{-1} (shoulders at 950 and 1070 cm^{-1}), corresponding to vibrations of the SiOLa fragment. In addition, the spectrum displays bands due to vibrations of the *tert*-butyl group (1255 cm^{-1}), aromatic ring protons (830 cm^{-1}), and a very broad (diffuse) band (3600—2500 cm^{-1}), which can be assigned to associated hydroxy groups.

The ^1H NMR spectrum of the resulting compound is fairly interesting. Unlike the spectra of **1**, **4**, and **5**, which contain two singlets for nonequivalent *tert*-butyl

Scheme 2



groups, the spectrum of lanthanosilsesquioxane **7** was found to exhibit three signals for three nonequivalent methyl groups with relative intensities of 3 : 2 : 1. The most intense signal (δ 1.23) belongs evidently to the *tert*-butyl group located in the *meta*-position with respect to the $Si(OLa)_3$ substituent. The signal for the second *tert*-butyl group, which occupies the *ortho*-position, is split into two components (δ 1.20 and 0.85) in a ratio of 2 : 1; this implies hindrance to the rotation of this fragment caused by the presence of the rigid $Si(OLa)_3$ cage so that the methyl groups become nonequivalent.



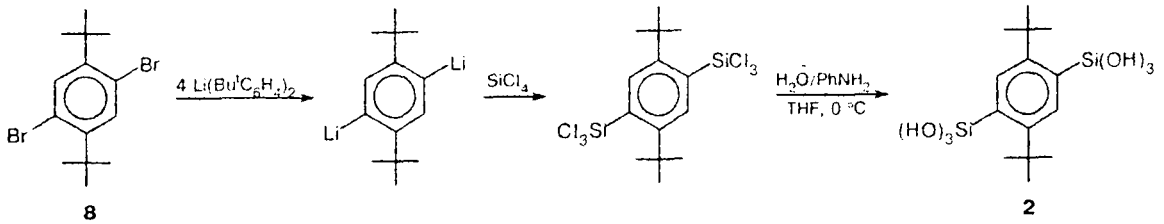
The molecular weight of the compound obtained, measured by cryoscopy in benzene, was ~1900 Da (the calculated weight of the tetramer corresponding to formula **7** is 1744 Da). Based on the ^1H NMR and IR data, cryoscopic measurements, and elemental analysis, the structure shown below can be ascribed to complex **7** synthesized.

Compound **7** possesses high thermal stability. The coordinating solvent (MeOH) is removed at 200 °C *in vacuo*. Further heating of the sample to 400 °C in an evacuated tube causes no visible or spectral changes. Decomposition starts at ~410 °C. Compound **7** is hydrolytically fairly stable. It sluggishly reacts with water; only on heating with HCl, are $LaCl_3$ and the products of condensation of silanetriol formed.

We also attempted to prepare 2,5-di-*tert*-butyl-1,4-bis(trihydroxysilyl)benzene (**2**). To the best of our knowledge, no attempts to synthesize compounds containing two $Si(OH)_3$ groups in one aromatic ring had been undertaken. We expected to obtain compound **2** similarly to **1**, using dibromo-1,4-di-*tert*-butyl-2,5-benzene (**8**) as the initial compound. Several approaches to polylithioarenes can be found in the literature. The one used most often, namely, the reaction of bromoarenes with Bu^nLi, did not lead to the desired result; in hexane, this reaction did not occur, while in ether, a complex mixture of condensation products was obtained. A procedure for the synthesis of benzene polylithium derivatives by the replacement of bromine atoms in the corresponding bromides by lithium using lithio-4,4′-di-*tert*-butylbiphenyl (a radical ion salt) in THF at −78 °C has been reported.[7] Under these conditions, the researchers attained the highest yield of 1,3,5-trilithiobenzene. Using this method, we made 2,5-dibromo-1,4-di-*tert*-butylbenzene react with 4 equivalents of lithio-4,4′-di-*tert*-butylbiphenyl and then carried out the one-pot transformations shown in Scheme 3.

The final reaction mixture contained the required product **2** and a large amount of 4,4′-di-*tert*-butylbiphenyl formed in the first step. It was possible to separate bis(silanetriol) from 4,4′-di-*tert*-butylbiphenyl by taking advantage of the fact that silanetriols are readily soluble in methanol, whereas the latter compound is not. Three recrystallizations from methanol gave a small amount of crude silanetriol **2**, whose IR spectrum exhibited absorption bands characteristic of the $Si(OH)_3$ group (a broad band at 3400 cm^{-1}) and the Bu^t group (1255, 1200 cm^{-1}) and also a band at 1100 cm^{-1} (Si—Ph, OH deformation band) and a band at about 800—900 cm^{-1} (aromatic ring protons). We

Scheme 3



were unable to isolate compound **2** in a pure state and to characterize it more extensively.

Experimental

GLC analysis of reaction mixtures was carried out using a Tsvet-530 gas chromatograph (a 0.3×200 cm stainless-steel column packed with Chromaton N-AW-DMCS with 5% SE-30 silicone, katharometer as the detector, helium as the carrier gas). IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer. ^{1}H NMR spectra were run on a Tesla BS-487-C instrument (80 MHz) in $CDCl_3$ using $CHCl_3$ as the internal standard.

The solvents were purified by standard procedures.[8] THF was refluxed over sodium and distilled from sodium with addition of benzophenone. Hexane was distilled from P_2O_5. Ether was kept over P_2O_5 and distilled from sodium in the presence of benzophenone.

Bromo-2,5-di-*tert*-butylbenzene (3). A solution of di-*tert*-butylbenzene[9] (30 g, 0.16 mol) in a minimum amount of EtBr (~15 mL) was placed in a 500-mL three-neck flask equipped with a stirrer and a dropping funnel, and 0.3 g of anhydrous $FeCl_3$ and 20 g of NaX molecular sieves were added. Bromine (8.2 mL, 0.16 mol) was added with vigorous stirring (20 °C). The mixture was stirred for 1 h, separated from the molecular sieves, washed with water, and dried with Na_2SO_4. The solvent was removed and the residue was distilled *in vacuo*. Yield 31.1 g (75%), b.p. 110 °C (0.1 Torr); n_D^{17} 1.5333; d_4^{20} 1.1741. Found: mol. weight 71.20. Calculated: mol. weight 70.68. IR (thin film), ν/cm^{-1}: 1255 s (Bu^t); 1200 s (Bu^t); 850 m, 820 m (1,2,5-Ar). ^{1}H ($CDCl_3$), δ: 1.26 and 1.49 (both s, 9 H); 7.21 (dd, 1 H, ^3J = 8.7 Hz, ^4J = 2.2 Hz); 7.34 (d, 1 H, J = 8.7 Hz); 7.55 (d, 1 H, ^4J = 2.2 Hz).

2,5-Di-*tert*-butylphenyllithium (4). Anhydrous hexane (100 mL) was poured in a 500-mL three-neck flask equipped with a stirrer, the flask was purged with argon, and bromo-2,5-di-*tert*-butylbenzene (**3**) (30 g, 0.11 mol), a dispersion of Li (4.62 g, 0.66 g-at), tetramethylethylenediamine (1.28 g, 0.01 mol), and Bu^{n}Cl (4.5 g) were added. The reaction mixture was refluxed for 5 h (GLC monitoring). The resulting solution was filtered to remove the remaining lithium. The yield of the lithium derivative **4** (determined by acid—base titration) was 80%.

Trichloro(2,5-di-*tert*-butylphenyl)silane (5). Hexane (100 mL) and $SiCl_4$ (8.5 g, 0.05 mol) were placed in a 500-mL three-neck flask equipped with a stirrer. A 1 *M* solution of 2,5-di-*tert*-butylphenyllithium (**4**) (51 mL, 0.05 mol) was added dropwise with intense stirring. During the reaction, a voluminous precipitate of LiCl was formed. The mixture was stirred for 2 h and filtered, and the solvent was evaporated. Vacuum distillation gave 11.5 g (70%) of product **5**, b.p. 115 °C (0.05 Torr), which solidified to give a crystalline material. Found (by titration) (%): Cl, 31.2. Calculated (%): Cl, 32.5. IR (Vaseline oil), ν/cm^{-1}: 1255 s (Bu^t); 1195 m (Bu^t); 1150 s, 1100 s, 890 s, 870 m (1,2,5-Ar); 575 vs ($SiCl_3$). ^{1}H NMR ($CDCl_3$), δ: 1.32 and 1.52 (both s, 9 H); 7.48 (dd, 1 H, ^3J = 8.5 Hz, ^4J = 2.0 Hz); 7.53 (d, 1 H, ^3J = 8.5 Hz); 8.28 (d, 1 H, ^4J = 2.0 Hz).

2,5-Di-*tert*-butylphenylsilanetriol (1). A solution of trichloro(2,5-di-*tert*-butylphenyl)silane (**5**) (10.28 g, 0.032 mol) in THF was slowly added dropwise to a mixture of H_2O (2.0 g) and aniline (10.41 g, 0.111 mol) in THF at 0 °C. During the hydrolysis, a precipitate of aniline hydrochloride was formed. The precipitate was filtered off and the solvent was removed *in vacuo*. The residue was crystallized from CH_2Cl_2 to give 2,5-di-*tert*-butylphenylsilanetriol as a finely crystalline (thin needles) powder, m.p. 178 °C. Yield 6.5 g (76%). ^{1}H NMR ($CDCl_3$), δ: 1.13 and 1.36 (both s, 9 H); 5.50—6.30 (s, 3 H); 7.30 (dd, 1 H, ^3J = 7.5 Hz, ^4J = 2.0 Hz); 7.36 (d, 1 H, J = 7.5 Hz); 8.01 (d, 1 H, ^4J = 2.0 Hz). IR (Vaseline oil), ν/cm^{-1}: 3260 s, 1255 m (Bu^t); 1200 m (Bu^t); 1150 m, 1090 s, 1050 w, 920 m, 820 m.

An attempt to synthesize 1,4-di-*tert*-butyl-2,5-bis(trihydroxysilyl)benzene (2). 2,5-Dibromo-1,4-di-*tert*-butylbenzene[10] (**8**) (0.55 g, 1.59 mmol) was placed in a tube and evacuated, and THF (10 mL) was frozen into it. A solution of lithio-4,4′-di-*tert*-butylbiphenyl[11] (1.74 g, 6.36 mmol) in 15 mL of THF was added *in vacuo* to the resulting solution cooled to −78 °C. During the reaction, lithium bromide precipitated and the solution acquired a red-brown color. The THF was removed *in vacuo* at −10 °C and replaced by hexane. $SiCl_4$ (0.54 g, 3.18 mmol) was frozen *in vacuo* into the reaction mixture. A voluminous precipitate of LiCl was formed. The solution was separated from the precipitate and the hexane was removed *in vacuo*. The resulting 1,4-di-*tert*-butyl-2,5-bis(trichlorosilyl)benzene was hydrolyzed without isolation from the reaction mixture. The solution of 1,4-di-*tert*-butyl-2,5-bis(trichlorosilyl)benzene was added with intense stirring to a mixture of water (0.17 g, 9.54 mmol) and aniline (0.89 g, 9.54 mmol) in diethyl ether. During the hydrolysis, aniline hydrochloride precipitated. The solution was decanted from the precipitate and the solvent was removed *in vacuo*. To purify product **2** from 4,4′-di-*tert*-butylbiphenyl, the product was repeatedly recrystallized from MeOH. This gave 0.055 g (10%) of a product containing, according to IR spectroscopy, compound **2** contaminated with 4,4′-di-*tert*-butylbiphenyl. IR (Vaseline oil), ν/cm^{-1}: 3400 (SiOH); 1580, 1260 (Bu^t); 1100, 1010, 880, 860, 820 (CH arom.).

Synthesis of adduct (6) of 2,5-di-*tert*-butylphenylsilanetriol (1) with triethylenediamine. Triethylenediamine (0.21 g, 1.86 mmol) in 7 mL of ether was added to a solution of compound **1** (0.5 g, 1.86 mmol) in 7 mL of anhydrous ether, and the mixture was allowed to stand for 1 h. After 5 min, precipitation of crystals from the solution started. The yield of adduct **6** was 0.7 g (~100%). Found (%): C, 63.36; H, 8.85; Si, 7.11. $C_{20}H_{36}N_2O_3Si$. Calculated (%): C, 63.11; H, 9.53; Si, 7.38. IR, ν/cm^{-1}: 3500—2500 (O—H—N); 1255 m (Bu^t); 1200 m (Bu^t); 1150 m, 1090 s, 1050 s, 990 m, 920 s, 870 m, 840 m, 820 m, 760 s, 740 s.

Synthesis of lanthanosilsesquioxane (7). $[(Me_3Si)_2N]_3La$[12] (0.62 g, 1 mmol) in THF was added to a solution of compound **1** (0.27 g, 1 mmol) in 5 mL of THF. The mixture was heated for 30 min at 65 °C, and the solvent and hexamethyldisilazane were removed *in vacuo*. The residue was a solid glassy material soluble in aromatic and saturated hydrocarbons, chlorohydrocarbons, and ethers but insoluble in methanol. The product was recrystallized from PhMe—MeOH or CH_2Cl_2—MeOH mixture to give 0.37 g (85%) of product **7**. Found (%): C, 42.07; H, 5.98; La, 30.95. $C_{15}H_{25}O_4SiLa$. Calculated (%): C, 41.29; H, 5.77; La, 31.83. IR (CCl_4), ν/cm^{-1}: 3500—2500 (OH); 1255 m (Bu^t); 1120 m, 1070 m, 1020 vs (SiOLa); 830 m (CH arom.); 720 s. ^{1}H NMR, δ: 0.85 (s, 3 H, Me); 1.20 (s, 6 H, Me_3C); 1.23 (s, 9 H, Me_3C); 3.2 (s, 3 H); 7.0—8.0 (m, 3 H). Molecular weight. Found: 1900 (cryoscopy in benzene). Calculated: 1744.

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References

1. R. Murugavel, V. Chandrasekhar, and H. W. Roesky, *Acc. Chem. Res.*, 1996, **29**, 183.
2. P. D. Lickiss, *Adv. Inorg. Chem.*, 1995, **42**, 147.
3. J. D. Birchall, *Chem. Soc. Rev.*, 1995, **24**, 351.
4. K. A. Andrianov, *Metody elementoorganicheskoi khim. Kremnii [Methods of Organoelement Chemistry. Silicon]*, Nauka, Moscow, 1968, 218 pp. (in Russian).
5. J. Thies, *Ann. Chim. (France)*, 1954, **9**, 51.
6. A. Voigt, R. Murugavel, U. Ritter, and H. W. Roesky, *J. Organomet. Chem.*, 1996, **521**, 279.
7. N. Rot and F. Bickelhaupt, *Organometallics*, 1997, **16**, 5027.
8. Ch. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*. VCH, Weinheim, 1988.
9. L. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Wiley-Interscience, New York, 1966.
10. H. Kofod, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 1951, **7**, 1790.
11. B. Wakefield, *Organolithium Methods*, Academic Press, London, 1988.
12. D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021.

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