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# A simple synthesis of octaphenylcyclotetra(siloxane)

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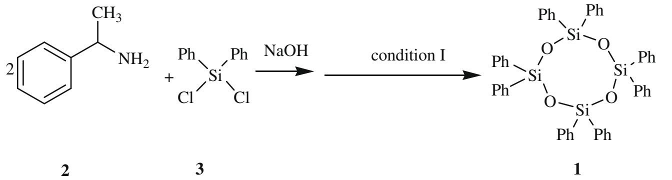
## ABSTRACT

An essential industrial monomer octaphenylcyclotetra(siloxane) or $(Ph_2SiO)_4$ was obtained by very simple procedures, The product was confirmed by NMR, IR, MS, elemental analysis, and X-ray crystallography.

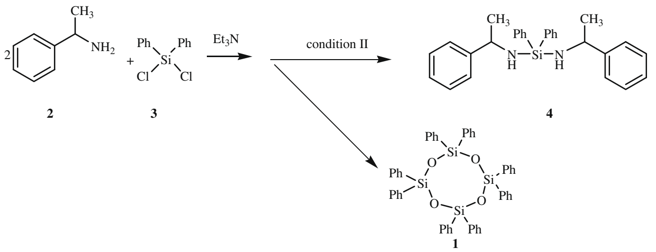
Octaphenylcyclotetra(siloxane), $(Ph_2SiO)_4$ is an important monomer for organosilicon polymers,[1,2] which have been used widely as thermal aging-resistant elastomers, thermostable material for capillary column,[3] silicone pressure sensitive adhesives and tapes, and for the preparation of heat-curable resins. It can also be used as a precursor for synthesizing phase transfer catalysts. According to previous reports, the synthesis of this compound has been complex, involving high temperatures.[4–7] Here we wish to report simple preparation of octaphenylcyclotetra(siloxane) (Fig. 1).

Reaction condition I:



Compound **1** was synthesized by reacting diphenyl-dichlorosilane with α-ethylphenylamine in toluene. Under anhydrous and anaerobic conditions, a 5 mL (23.8 mmol) of diphenyl-dichlorosilane in 15 mL of toluene was added to a refluxing solution of α-ethylphenylamine (6.1 mL or 47.6 mmol in 50 mL of toluene). The mixture was stirred and refluxed for 48 h, and then 10 mL of 50% sodium hydroxide solution was added. Products were collected by dichloromethane extraction (2 × 30 mL), and dried over anhydrous sodium sulfate. The mixture was evaporated under reduced pressure. The crude product was left standing overnight. White crystals (1.56 g) were formed and the yield was 33.1%. The crystals were subjected to characterization by NMR, IR, MS, elemental analysis, and X-ray crystallography. All results confirmed that the white crystal is octaphenylcyclotetra(siloxane).[8]

Reaction condition II:



Alternatively, toluene solution of diphenyl-dichlorosilane (23.8 mmol) was added slowly to a refluxing solution of α-ethylphenylamine (47.6 mmol) and $Et_3N$ (20 mL) in 50 mL of toluene. The mixture was refluxed for 48 h followed by dichloromethane extraction (2 × 30 mL). The crude mixture was dried over anhydrous sodium sulfate. The mixture was concentrated under reduced pressure and further purification was performed by silica gel (petroleum ether/dichloromethane 5:1 for the eluent). Compound **1** (2.23 g) was obtained and the yield was 47.3%.

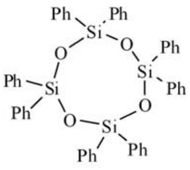


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**Figure 1.** The molecular structure of compound **1**.

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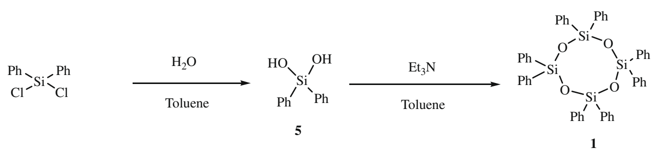
Reaction condition III:



In another approach, a solution of diphenyl-dichlorosilane (4.76 mmol) in 20 mL of water and 20 mL of toluene was added slowly into a flask. After 3 h, the product was extracted with dichloromethane and dried by rotary evaporation. Dihydroxy-diphenyl-silane (compound **5**) was obtained (0.83 g, yield, 80.7%).[9]

Compound **5** (3.84 mmol) was dissolved in 20 mL of toluene, and a 10 mL of triethylamine was added. After recrystallization in dichloromethane, a large amount of white crystals (compound **1**) was obtained (0.70 g, yield: 92.1%).

Regarding the mechanism, we proposed two possibilities. First, compound **4** maybe transiently formed and converted to **1**. This conversion might happen during the refluxing or after the addition of aq NaOH in reaction condition I or during the purification in condition II. The existence of compound **4** was indicated by its NMR data in moisture free reactions. Under the condition III, we also propose that the starting material is highly unstable in the presence of $H_2O$, and it may be quickly converted to compound **5** which is polymerized to form compound **1** in the presence of amine.

The structure of compound **1** was confirmed by X-ray diffraction (Fig. 2).

A colorless crystal of compound **1** with a dimension of $0.42 \times 0.40 \times 0.36$ mm was selected for the data collection on a BRUKER SMART diffractometer with graphite monochromated MoK$\alpha$ radiation ($\lambda = 0.7103$ Å). A total of 7088 reflections were collected in the range of $2.76° < \theta < 27.50°$ by using 'phi and omega' scan techniques at 293(2) K. $C_{48}H_{40}O_4Si_4$, $M = 793.16$, triclinic, $P\bar{1}$, $a = 10.7251(3)$ Å, $\alpha = 83.757°$, $b = 10.7595(4)$ Å, $\beta = 83.066(3)°$, $c = 19.1332(8)$ Å, $\gamma = 76.077°$, $V = 2120.08(14)$ Å$^3$, $Z = 2$, $D_{calc} = 1.243$ g/cm$^3$, the final $R$ factor was $R_1 = 0.0398$, 5180 for reflections with $I_0 > 2\sigma(I_0)$, $R\omega = 0.0831$ for all data. The structure was solved by full-matrix least-squares on $F^2$ using the SHELXTL Program.[10] The eight-membered ring is almost planar, the average of eight Si–O bond lengths was 1.6159 Å, and two types of Si–O–Si angles were found with mean values of 152.77° and 164.87°.

In summary, using simple procedures, we obtained the octaphenylcyclotetra (siloxane) in high yields. By comparing our results with those of the previous methods, this synthetic method was found to be simple and easy to operate. This enables the synthesis of octaphenylcyclotetra (siloxane) with much less cost for various applications.

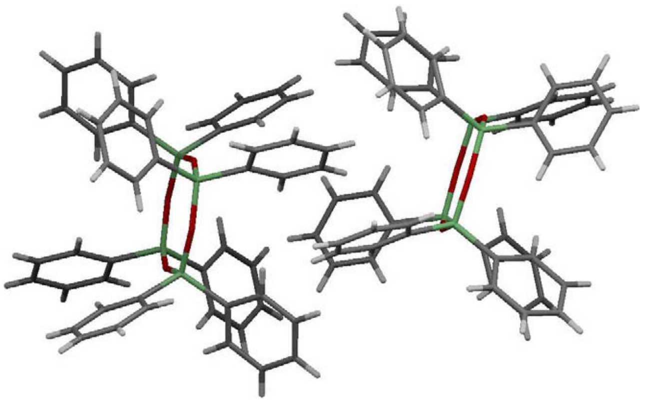


**Figure 2.** The crystal structure of compound **1**.

## Acknowledgments

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## Supplementary data

Supplementary data (X-ray and NMR) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.06.130.

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8. $^1$H NMR (500 MHz, $CDCl_3$) 7.19 (t, 4H, Ar–H), 7.35 (t, $J$ = 2.5 Hz, 2H, Ar–H), 7.48–7.49 (d, $J$ = 6.5 Hz, 4H, Ar–H). $^{13}$C NMR (125 MHz, $CDCl_3$) 127.70(×4), 130.11(×4), 134.46(×4). IR (KBr): 3440, 3070, 3049, 3024, 1591, 1487, 1429, 1187, 1119, 1103, 1028, 997, 741, 717, 698, 528, 510, 493 1/cm; HRMS(EI): $m/z$ (%): calcd for $C_{48}H_{40}Si_4O_4$: 792.2004; found: 792.1998. Elemental Anal. Calcd: C, 72.77; H, 5.08. Found: C, 72.37; H, 5.10.
9. $^1$H NMR (500 MHz, $CDCl_3$) 7.19 (d, $J$ = 7 Hz, 4H, Ar–H), 7.33–7.39 (m, 6H, Ar–H), 4.91(s, 2H).
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