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SYNTHESIS OF BIS(3,3-DINITROBUTYL)POLYSILOXANES

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Summary

Phenyl groups were used as silicon-protecting groups in the synthesis of bis(3,3-dinitrobutyl)polysiloxanes. The addition of diphenylsilane to acrolein dimethyl acetal, followed by reactions with methyllithium and phosphorus tribromide gave bis(3-bromobutyl)diphenylsilane. Sodium nitrite displacement gave bis(3-nitrobutyl)diphenylsilane, and oxidative nitration gave bis(3,3-dinitrobutyl)diphenylsilane. Dephenylation with bromine and hydrolysis gave cyclic polysiloxanes.

We have reported [1] the synthesis of (3-fluoro-3,3-dinitropropyl)methylpolysiloxanes and of bis(3-fluoro-3,3-dinitropropyl)polysiloxanes by the stepwise introduction of nitro groups and fluorine atoms by displacement reactions, oxidative nitrations and fluorinations. A silicon-protecting group was needed that could survive these hydrolytic reaction conditions, yet could be transformed at the end of the reaction sequence into an easily hydrolyzable group. Phenyl groups were found to satisfy this requirement. Phenyl—silicon bonds were cleaved selectively by bromine without affecting the nitroalkyl—silicon bonds.

$$(C_6H_5)_2Si(CH_2CH_2CH_2Br)_2 \xrightarrow{NaNO_2} (C_6H_5)_2Si(CH_2CH_2CH_2NO_2)_2 \xrightarrow[NaNO_2, OH^-]{AgNO_3}$$

$$(C_6H_5)_2Si[CH_2CH_2CH(NO_2)_2]_2 \xrightarrow{FClO_3} (C_6H_5)_2Si[CH_2CH_2CF(NO_2)_2]_2 \xrightarrow{Br_2} \xrightarrow{H_2O}$$

$$—O\underset{|}{Si}[CH_2CH_2CF(NO_2)_2]_2 \text{ cyclic polysiloxanes}$$

The synthesis of an analogous series of compounds with internal *gem*-dinitro groups was undertaken in the present work. The starting material was obtained by a sequence of reactions beginning with the hydrosilylation of acrolein dimethyl acetal with diphenylsilane. The hydrosilylation of acrolein, as well as α, β-

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unsaturated ketones and esters, with triethylsilane has been reported to take place by 1,4-addition, yielding enol silyl ethers [2,3]. However, acrolein acetal and triethylsilane in the presence of chloroplatinic acid gave, after hydrolysis, 3-(triethylsilyl)propionaldehyde [2].

For the addition of diphenylsilane to allyl compounds [1], tris(triphenylphosphine)rhodium chloride [4] was found to be a more effective catalyst than chloroplatinic acid. Under these conditions, the bis-adduct of acrolein dimethyl acetal and diphenylsilane was obtained, and aqueous hydrolysis converted it to bis(3-oxopropyl)diphenylsilane. This aldehyde underwent such rapid self-condensation that it could not be analyzed. However, it reacted with methyllithium in ether to give bis(3-hydroxybutyl)diphenylsilane, a crystalline solid.

$$(C_6H_2)_2SiH_2 + CH_2{=}CHCH(OCH_3)_2 \longrightarrow (C_6H_5)_2Si[CH_2CH_2CH(OCH_3)_2]_2 \xrightarrow{H_2O}$$

$$(C_6H_5)_2Si(CH_2CH_2CHO)_2 \xrightarrow{CH_3Li} (C_6H_5)_2Si(CH_2CH_2CHCHCH_3)_2$$

The reaction of this alcohol with phosphorus tribromide in ether gave the corresponding dibromide. Bis(3-bromobutyl)diphenylsilane underwent displacement with sodium nitrite in dimethyl sulfoxide to yield bis(3-nitrobutyl)-diphenylsilane. Oxidative nitration [5] of the salt of this nitro compound with sodium nitrite and silver nitrate, in a mixed solvent consisting of water, methanol and ether, gave bis(3,3-dinitrobutyl)diphenylsilane.

$$(C_6H_5)_2Si(CH_2CH_2CHOHCH_3)_2 \xrightarrow{PBr_3} (C_6H_5)_2Si(CH_2CH_2CHBrCH_3)_2 \xrightarrow[DMSO]{NaNO_2}$$

$$(C_6H_5)_2Si[CH_2CH_2CH(NO_2)CH_3]_2 \xrightarrow[AgNO_3,\ NaNO_2]{OH^-} (C_6H_5)_2Si[CH_2CH_2C(NO_2)_2CH_3]_2$$

Dephenylation with bromine was similar to that of the analogous fluorodinitropropyl compound [1]. Only one phenyl group was removed readily in an inert solvent, but hydrolysis of the resulting bromosilane to the silanol facilitated removal of the second phenyl. A convenient one-pot procedure utilized glacial acetic acid as the solvent for the initial bromination, with water added to complete the bromination and hydrolysis. A cyclic polysiloxane with a molecular weight between trimer and tetramer was obtained, which melted at 240—250°C (dec.).

Experimental

NMR and IR spectra were recorded with a Varian T-60 spectrometer and a Perkin—Elmer 700 spectrometer, respectively. Molecular weights were determined with a Mechrolab 301A vapor osmometer.

Bis(3-hydroxybutyl)diphenylsilane. A solution of 18.4 g (0.1 mol) of diphenylsilane, 22 g (0.215 mol) of acrolein dimethyl acetal and 0.01 g of tris(triphenylphosphine)rhodium chloride in 25 ml of benzene was refluxed for 4 h. An additional 0.01 g of catalyst was added and the solution was refluxed for 2 h. The solvent was removed under vacuum and the residue was added to a mixture of 100 ml of water, 20 ml of ethanol, 0.5 ml of concentrated hydrochloric acid and 0.2 g of potassium iodide. Ethanol and methanol were distilled off slowly until the head temperature reached 80°C. The mixture was cooled and the product was extracted with three 50 ml portions of ether. The organic layer was dried and distilled to remove solvent. The aldehyde, which polymerized on standing, was dissolved immediately in 50 ml of ether and the solution was added dropwise to 150 ml of 1.5 *M* methyllithium in ether. The mixture was refluxed for 15 min, cooled and acidified with 10% hydrochloric acid. The ether layer was separated, washed with 50 ml of water, dried and distilled to remove the ether. Bis(3-hydroxybutyl)diphenylsilane (27%, m.p. 91—92°C) was isolated by crystallization from carbon tetrachloride and Skelly F (petr. ether). IR (KBr): 3300, 2900—3000, 1430, 1120 and 705 cm^{-1}: NMR ($CDCl_3$): δ 7.40 (broad s, 10 H, C_6H_5) 3.72 (sextet, 2 H, $\underline{CH}OH$), 2.17 (s, 2 H, OH) and 1.0—1.8 ppm (m, 14 H, $\underline{CH_3}CHOH\underline{CH_2CH_2}$).

Anal. Found: C, 73.19; H, 8.73. $C_{20}H_{28}O_2Si$ calcd.: C, 73.12; H, 8.59%.

Bis(3-bromobutyl)diphenylsilane. A solution of 9.0 g (0.0275 mol) of bis(3-hydroxylbutyl)diphenylsilane and 8.6 g (0.032 mol) of phosphorus tribromide in 30 ml of ether was stirred at ambient temperature for 90 h. The solution was added to 100 ml of ice-water and the product was extracted with three 30 ml portions of carbon tetrachloride. The combined organic layers were washed with water, dried and evaporated. The product was purified by column chromatography (silica gel and carbon tetrachloride) followed by crystallization from Skelly F, to give 6.5 g (48%) bis(3-bromopropyl)diphenylsilane (m.p. 61—62°C). IR (film): 2900—3000, 1425, 1225, 1190, 1120, 740 and 710; NMR ($CDCl_3$): δ 7.5 (broad s, 10 H, C_6H_5), 4.2 (sextet, 2 H, CHBr), 2.0 (m, 4 H, $\underline{CH_2}CH_2Si$) 1.85 (d, $J = 7$ Hz, 6 H, CH_3) and 1.4 ppm (m, 4 H, CH_2Si).

Anal. Found: C, 52.88; H, 5.77. $C_{20}H_{26}SiBr_2$ calcd.: C, 52.87; H, 5.77%.

Bis(3-nitrobutyl)diphenylsilane. A solution of 6.0 g (13.0 mmol) of bis(3-bromobutyl)diphenylsilane and 12.0 g (174 mmol) of sodium nitrite in 30 ml of dimethyl sulfoxide was stirred for 3 h at 25°C. The solution was added to 250 ml of water and was extracted with three 25 ml portions of carbon tetrachloride. The combined organic layers were washed with water, dried and distilled to remove solvent. Column chromatography and crystallization from carbon tetrachloride and Skelly F, yielded 1.5 g (29%) of bis(3-nitrobutyl)diphenylsilane (m.p. 84—85°C). IR (KBr): 2900, 1530, 1430, 1320, 1180, 1110 and 700 cm^{-1}; NMR ($CDCl_3$): δ 7.3 (broad s, 10 H C_6H_5), 4.5 (sextet, 2 H, $CHNO_2$), 1.4 (m, 4 H, $\underline{CH_2}CH_2Si$), 1.5 (d, J 7 Hz, 6 H, CH_3) and 1.1 ppm (m, 4 H, CH_2Si).

Anal. Found: C, 61.93; H, 6.58; N, 7.39. $C_{20}H_{26}N_2O_4Si$ calcd.: C, 62.15: H, 6.78; N, 7.25%.

Bis(3,3-dinitrobutyl)diphenylsilane. Bis(3-nitrobutyl)diphenylsilane (1.2 g, 3.1 mmol) was dissolved, with stirring at 70°C, in a mixture of 5 ml of methanol, 13 ml of water and 6.2 mmol of potassium hydroxide. The solution was cooled to room temperature and 2.2 g (6.2 mmol) of sodium nitrite was added. The resulting solution was added quickly to a vigorously stirred mixture of 2.2 g (13 mmol) of silver nitrate, 15 ml of water and 20 ml of ether. After 5 min an additional 25 ml of ether was added and the mixture was stirred for 2 h. Saturated sodium chloride solution (10 ml) was added and the mixture was filtered. The precipitate was washed with ether, and the combined ether layers were dried and solvent was evaporated. Column chromatography (silica gel, methylene chloride) and crystallization (carbon tetrachloride, Skelly F) gave 0.90 g (61%) of bis(3,3-dinitrobutyl)diphenylsilane (m.p. 70—71°C). IR (film): 3000, 2900, 1550, 1420, 1380, 1320, 1190, 1110, 1020, 845, 785 and 700 cm^{-1}; NMR ($CDCl_3$): δ 7.37 (broad s, 10 H, C_6H_5), 2.4 (m, 4 H, $\underline{CH_2}CH_2Si$), 2.07 (s, 6 H, CH_3) and 1.1 ppm (m, 4 H, CH_2Si).

Anal. Found: C, 50.71; H, 5.15; N, 11.96. $C_{20}H_{24}N_4O_8Si$ calcd.: C, 50.41; H, 5.09; N, 11.76%.

Bis(3,3-dinitrobutyl)cyclopolysiloxanes. A solution of 3.0 g (6.3 mmol) of bis(3,3-dinitrobutyl)diphenylsilane and 1 ml (18 mmol) of bromine in 20 ml of glacial acetic acid was refluxed for 30 min. Water (100 ml) was added and the mixture was refluxed for 10 min. The solution was cooled to room temperature and 20 ml of methylene chloride was added. A fine white precipitate was filtered and the methylene chloride layer dried, and one drop of triethylamine was added. After 24 h, additional precipitate was isolated by filtration to give a total of 1.5 g (70%) of a mixture of cyclic bis(3,3-dinitrobutyl)polysiloxanes, (m.p. (dec) 240—250°C). IR (KBr): 2900, 1545, 1320, 1200, 1090 and 1010 cm^{-1}; NMR (D_3CCOCD_3): δ 2.7 (m, 4 H, $\underline{CH_2}CH_2Si$), 2.20 (s, 6 H, CH_3) and 1.0 ppm (m, 4 H, CH_2Si); molecular weight (vapor phase osmometer, 2-butanone), 1210 ± 5% (trimer 1014, tetramer 1352).

Anal. Found: C, 28.06; H, 4.03; N, 16.21. $C_8H_{14}N_4O_9Si$ calcd.: C, 28.40; H, 4.17; N, 16.56%.

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References

1 K. Baum, D.A. Lerdal and J.S. Horn, J. Org. Chem., 43 (1978) 203.
2 S.I. Sadykj-Zade and A.D. Petrov, J. Gen. Chem. U.S.S.R., 29 (1959) 3159.
3 A.D. Petrov and S.I. Sadykj-Zade, Bull. Soc. Chim. Fr., (1959) 1932.
4 A.J. Chalk, J. Organometal. Chem., 21 (1970) 207.
5 R.B. Kaplan and H. Schechter, J. Amer. Chem. Soc., 83 (1961) 3535.