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A SERIES OF tert-BUTYLDIMETHYLSILOXANES OF INCREASING STERIC HINDRANCE

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SUMMARY

Reaction of bis(dimethylsilyl)acetamide with tert-butyldimethylsilanol gives 1-tert-butyl-1,1,3,3-tetramethyldisiloxane while reaction of trimethylchlorosilane with this silanol gives 1-tert-butyl-1,1,3,3,3-pentamethyldisiloxane. Similarly, reaction of tert-butyldimethylchlorosilane with tert-butyldimethylsilanol produces 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane and reaction of tert-butyldimethylchlorosilane with phthalocyaninosilanediol yields 1,5-di-tert-butyl-1,1,5,5-tetramethyl-3-phthalocyaninotrisiloxane. This latter compound is noteworthy because it is highly hindered.

INTRODUCTION

A number of years ago Sommer and Tyler reported the preparation of tert-butyldimethylchlorosilane.[1] Recently this compound has attracted considerable attention because, as Corey has shown,[2] it is a very effective blocking agent for hydroxyl groups in organic intermediates.

The silanol corresponding to this chlorosilane, tert-butyldimethylsilanol, also was reported by Sommer and Tyler,[1,3] but uses for it have not been found and it has attracted little attention. This compound is an interesting one nevertheless. It reacts with water very readily to form a hemihydrate (as does the corresponding carbinol, tert-butyldimethylcarbinol[4]), and more importantly no conditions which cause it to self condense in significant amounts to 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane are known.

This latter compound has, however, recently been reported as an unexpected product of the reaction of tert-butyldimethylsilylmethyltrifluoroacetamide with secondary amines in the presence of dimethylformamide and as a low yield product of the reaction of N-tert-butyldimethylsilylimidazole with tert-butyldimethylsilanol in base.[5] Unsymmetrical tert-butyldimethylsiloxanes have not been reported.

Recently an interest in tert-butyldimethylsiloxanes in this laboratory has led to a satisfactory preparation of the known symmetrical siloxane by a straightforward method. It has also led to the preparation of 1-tert-butyl-1,1,3,3-tetramethyldisiloxane, 1-tert-butyl-1,1,3,3,3-pentamethyldisiloxane, and 1,5-di-tert-butyl-1,1,5,5-tetramethyl-3-phthalocyaninotrisiloxane.

RESULTS AND DISCUSSION

The tert-butyltetramethyldisiloxane has been prepared by the reaction of bis(dimethylsilyl)acetamide with tert-butyldimethylsilanol and the tert-butylpentamethyldisiloxane by the reaction of trimethylchlorosilane with tert-butyldimethylsilanol in the presence of base. Because these compounds are relatively unhindered their preparability by standard routes is not surprising.

The known symmetrical disiloxane has been made by the reaction of tert-butyldimethylchlorosilane with tert-butyldimethylsilanol in the presence of base. The fact that it can be made easily in this way is not unexpected in view of the findings of Corey and Kutschinski with regard to the silylating ability of tert-butyldimethylchlorosilane toward alcohols.[2,5]

For the di-tert-butyltetramethylphthalocyaninotrisiloxane a route parallel to those utilized for the known symmetrical disiloxane and for tert-butylpentamethyldisiloxane has been used, e.g., the reaction of tert-butyldimethylchlorosilane with phthalocyaninosilanediol in the presence of base. That this compound can be made by this simple procedure is noteworthy because the compound is sterically very hindered (the hindrance is clearly great enough to very severely restrict rotation about the terminal $O\text{-}Si_R$ bonds).

On the basis of the work done it is apparent that many tert-butylmethylsiloxanes can be made and that, in general, they can be expected to be stable and easy to handle.

EXPERIMENTAL

Spectra

The nmr spectra were taken using a Varian HA-100 instrument operating in FT mode. Tetramethylsilane was used as an internal standard for the phthalocyaninosiloxane, while chloroform was used for the other compounds.

t-BuMe$_2$SiOSiMe$_2$H

A mixture of bis(dimethylsilyl)acetamide (0.7 ml, 3 mmol) *tert*-butyldimethylsilanol (1.0 ml, 6 mmol), and dry pyridine (25 ml) was refluxed with stirring and protection from atmospheric moisture for 3 hr. When cool the product was poured into 50 ml of water and the resulting mixture was extracted twice with 15 ml portions of hexane. The hexane extract was dried over $CaCl_2$, filtered, and stripped of hexane by distillation (final head temperature 85°C). This gave 0.7 g of a colorless liquid giving a gas chromatogram with peaks for the siloxane and silanol in a 95:5 ratio (theory 1.2 g of siloxane). Preparative gas chromatography of this liquid at 100°C on a 10% SE-30 Chromosorb W column gave the pure siloxane. NMR ($CDCl_3$): δ 0.02 (s, Si*Me*$_2$*t*-Bu), 0.15 (d, J = 2 Hz, Si*Me*$_2$H), 0.86 (s, SiMe$_2$*t*-*Bu*), and 4.69 ppm (m, SiMe$_2$*H*).

Anal. Calcd. for $C_8H_{22}OSi_2$: C, 49.93; H, 11.52. Found: C, 49.56; H, 11.38.

t-BuMe$_2$SiOSiMe$_3$

Trimethylchlorosilane (1.5 ml, 11 mmol) was added with stirring to a dry solution of tri-*n*-butylamine (3 ml) and dimethylformamide (15 ml). *tert*-Butyldimethylsilanol (1.0 ml, 6 mmol) was added after a minute and the mixture was refluxed with stirring and protection from atmospheric moisture for 3 hr. The product when cool was hydrolyzed with 60 ml of water and the resulting mixture was extracted twice with 15 ml portions of hexane. The extract was dried over $CaCl_2$, filtered, and concentrated by distilling off its volatile components (final head temperature 120°C). This gave 0.9 g of a colorless liquid giving a gas chromatogram with peaks for the siloxane and silanol in a 98:2 ratio (theory 1.3 g of siloxane). Chromatography of this liquid at 125°C gave the pure siloxane. NMR ($CDCl_3$): δ 0.03 (s, Si*Me*$_2$*t*-Bu), 0.09 (s, Si*Me*$_3$), and 0.88 ppm (s, SiMe$_2$*t*-*Bu*).

Anal. Calcd. for $C_9H_{24}OSi_2$: C, 52.87; H, 11.83; Si, 27.47. Found: C, 52.84; H, 11.89; Si, 27.20.

t-BuMe$_2$SiOSiMe$_2$*t*-Bu

A solution of imidazole (1.0 g) and pyridine (25 ml) was dried by distilling off about 5 ml of the solution and then cooled. *tert*-Butyldimethylchlorosilane (1.2 g, 8 mmol) and *tert*-butyldimethylsilanol (1.0 ml, 6 mmol) were added and the mixture was refluxed with stirring and protection from atmospheric moisture for 3 hr. When cool the product was hydrolyzed with 50 ml of water and extracted twice with 15 ml portions of hexane. The extract was dried over $CaCl_2$, filtered, and concentrated by distilling off its volatile components (final head temperature 120°C). The concentrate (1.9 g) gave a gas chromatogram with peaks for the siloxane and silanol in a ratio of 49:51 (theory 1.6 g of siloxane). Chromatography of this at 175°C gave the pure siloxane, a colorless liquid. NMR ($CDCl_3$): δ 0.01 (s, Me), and 0.87 ppm (s, *t*-Bu).

Anal. Calcd. for $C_{12}H_{30}OSi_2$: C, 58.46; H, 12.26; Si, 22.78. Found: C, 58.70; H, 12.05; Si, 22.64.

(t-BuMe$_2$SiO)$_2$SiPc

A mixture of *tert*-butyldimethylchlorosilane (1.0 g, 10 mmol), phthalocyaninosilanediol (prepared by Douglass' procedure[6]) (0.43 g, 0.74 mmol), dry tri-*n*-butylamine (15 ml), and distilled, dry, nitrogen-purged quinoline (30 ml) was refluxed with stirring and protection from atmospheric moisture for 1 hr. The product was cooled slowly and filtered. The solid, beautiful red-reflecting, blue-transmitting needles, was washed with water, acetone, and hexane, and dried (0.48 g, 84% yield). A portion was recrystallized from dry tetrahydronaphthalene, washed with hexane and acetone, and dried at 140°C in the air and 110°C under vacuum. This gave the siloxane as tiny red-reflecting, blue-transmitting crystals. NMR ($CDCl_3$): δ -2.98 (s, Me), -1.44 (s, *t*-Bu), 8.32 (m, 4,5 Pc), and 9.61 ppm (m, 3,6 Pc).

Anal. Calcd. for $C_{44}H_{46}N_8O_2Si_3$: C, 65.80; H, 5.77; Si, 10.49 . Found: C, 66.05; H, 5.51; Si, 10.19.

As expected, the solubility of this compound in organic solvents is low. The unusual positions of its methyl and *tert*-butyl protons compared with those of the other three compounds are due to the ring-current effects of the phthalocyanine ring.

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REFERENCES

1. L. H. Sommer and L. J. Tyler, J. Amer. Chem. Soc., 76, 1030 (1954).
2. E. J. Corey and A. Venkateswarlu, J. Amer. Chem. Soc., 94, 6190 (1972).
3. L. H. Sommer and F. J. Evans, J. Amer. Chem. Soc., 76, 1186 (1954).
4. H. A. Butlerow, Ann., 177, 176 (1875).
5. J. L. Kutschinski, Ph.D. Thesis, University of California, Davis, CA, 1974.
6. S. L. Douglass, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH, 1975.