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# 6 A SERIES OF tert-BUTYLDIMETHYLSILOXANES OF INCREASING STERIC HINDRANCE.

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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 has been found to give 1-tert-butyl-1,1,3,3-tetramethyldisiloxane while reaction of bis(trimethylsilyl)-acetamide or trimethylchlorosilane with this silanol has been found to give 1-tert-butyl-1,1,3,3,3-pentamethyldisiloxane. Similarly, reaction of tert-butyldimethylchlorosilane with this silanol has been found to produce 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane and reaction of tert-butyldimethylchlorosilane with phthalocyaninosilanediol has been found to produce 1,5-tert-butyl-1,1,5,5-tetramethyl-3-phthalocyaninotrisiloxane. This last siloxane is noteworthy because it is highly hindered.

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## INTRODUCTION

A number of years ago Sommer and Tyler reported 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, was also reported by Sommer and Tyler, but uses for it have not been found and it has attracted

little attention.[1,2] 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 significantly, it does not self-condense on being heated to fairly high temperatures.

The symmetrical siloxane of this series, 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane, has not been reported although Sommer and Tyler attempted to prepare it from the silanol (i.e., tert-butyldimethylsilanol) with the aid of sulfuric acid and with the aid of iodine. These workers did imply, however, that while hindered this compound could well be synthesizeable.

Unsymmetrical siloxanes of this series also have not been reported, apparently.

Recently an interest in siloxanes of this general type in this laboratory has led to work on some of them. This has yielded a series of tert-butyldimethylsiloxanes having differing amounts of steric hindrance.

## RESULTS AND DISCUSSION

Two of these siloxanes are 1-tert-butyl-1,1,3,3-tetramethyldisiloxane and 1-tert-butyl-1,1,3,3,3-pentamethyldisiloxane. The first of these has been prepared by the reaction of bis(dimethylsilyl)acetamide with tert-butyldimethylsilanol. The second has been prepared by the reaction of bis(trimethylsilyl)acetamide with the silanol and also by the reaction of trimethylchlorosilane with the silanol. Since these compounds are relatively unhindered, the fact that they can be made is not surprising. Further, the fact that they can be made by the routes used is likewise not surprising because these are of standard types.

Another of these siloxanes is the already mentioned 1,3-di-tert-butyl-1,1,3,3-tetramethyldisiloxane. This has been

prepared by the reaction of tert-butyldimethylchlorosilane with tert-butyldimethylsilanol. In keeping with its preparability, as already mentioned, is the viewpoint implied by Sommer and Tyler.

Still another is 1,5-tert-butyl-1,1,5,5-tetramethyl-3-phthalocyaninotrisiloxane. This compound has been prepared by the reaction of tert-butyldimethylchlorosilane with phthalocyaninosilanediol. It is of interest because it is so highly hindered. Without doubt rotation about its terminal O-Si bonds is severely limited. The route used to prepare it is noteworthy only in that it is simple and straightforward.

From this it is clear that many tert-butylmethylsiloxanes can be made. Further, it is clear that in general they will be stable and easy to handle.

## EXPERIMENTAL

### Spectra

The nmr spectra were taken with the aid of a Varian HA-100 instrument operating in FT mode. Tetramethylsilane was used as an internal standard for the phthalocyaninosiloxane. Chloroform was used as an internal standard for the remaining compounds.

### t-$BuMe_2SiOSiMe_2H$

A mixture of bis(dimethylsilyl)acetamide (0.7 ml), tert-butyldimethylsilanol (1.0 ml), and dry pyridine (20 ml) was refluxed with stirring and protection from atmospheric moisture for 3 hr. The product was distilled and nearly all of the 108-115°C fraction was set aside for 3 weeks (during this time it separated into two fractions). It was then mixed with water (20 ml) and the resultant was extracted once with hexane (15 ml). After being dried ($CaCl_2$) and filtered, the hexane layer

was distilled to a head temperature of 120°C. The liquid remaining (∿ 0.7 ml) was retained and a portion of it was chromatographed at 100°C on a 10% SE-30 Chromosorb W column. The major component, which was a colorless liquid and constituted about 75% of the total, was the siloxane. NMR ($CDCl_3$): δ 0.02 (s, $SiMe_2$t-Bu), 0.15 (d, $SiMe_2H$), 0.86 (s, $SiMe_2$t-Bu), and 4.69 ppm (m, $SiMe_2H$).

t-$BuMe_2SiOSiMe_3$

Trimethylchlorosilane (1.5 ml) was added with stirring to a dry solution of tri-n-butylamine (3 ml) and dimethylformamide (15 ml). tert-Butyldimethylsilanol (1.0 ml) 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 mixed with water (20 ml) and extracted once with hexane (15 ml). After being dried ($CaCl_2$) and filtered, the hexane layer was distilled. The 130-135°C fraction (∿ 1 ml) was retained and a portion of it was chromatographed at 125°C as above. The major component, about 65% of the total, was the siloxane. It was a colorless liquid. NMR ($CDCl_3$): δ 0.03 (s, $SiMe_2$t-Bu), 0.09 (s, $SiMe_3$), 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.

The siloxane was also prepared by reacting bis(trimethylsilyl)acetamide with tert-butyldimethylsilanol in refluxing pyridine.

t-$BuMe_2OSiMe_2$t-Bu

A solution of imidazole (1 g) and pyridine (25 ml) was dried by distilling off a small amount of it (∿ 5 ml) and cooled. tert-Butyldimethylchlorosilane (1.2 g) and tert-butyldimethylsilanol (1.0 ml) were added and the mixture was

refluxed with stirring and protection from atmospheric moisture for 3 hr. and cooled. The product was mixed with water (20 ml) and the resultant was extracted once with hexane (15 ml). After being dried ($CaCl_2$) the hexane layer was filtered and distilled to a head temperature of 148°C. The liquid remaining (∿ 0.4 ml) was retained and a portion of it was chromatographed at 175°C. The major component, a colorless fairly mobile liquid constituting about 85% of the total, proved to be the siloxane. 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.

The siloxane was also synthesized both by refluxing the chlorosilane in wet pyridine and by refluxing it in pyridine exposed to moist air.

$(t\text{-}BuMe_2SiO)_2SiPc$

A mixture of tert-butyldimethylchlorosilane (1.0 g), phthalocyaninosilanediol (prepared by Douglass' procedure[5]) (0.43 g), 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 resultant 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). A portion of it 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.

The solubility of this compound in common organic solvents is very low.

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REFERENCES

1. L. H. Sommer and L. J. Tyler, J. Am. Chem. Soc., 76, 1030 (1954).
2. E. J. Corey and A. Venkateswarlu, J. Am. Chem. Soc., 94, 6190 (1972).
3. L. H. Sommer and F. J. Evans, J. Am. Chem. Soc., 76, 1186 (1954).
4. H. A. Butlerow, Ann., 177, 176 (1875).
5. S. L. Douglass, Ph.D. Thesis, Case Western Reserve Univ., Cleveland, O., 1975.

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