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DIFUNCTIONAL DERIVATIVES OF 1,3-DICHLOROTETRAMETHYLDISILOXANE

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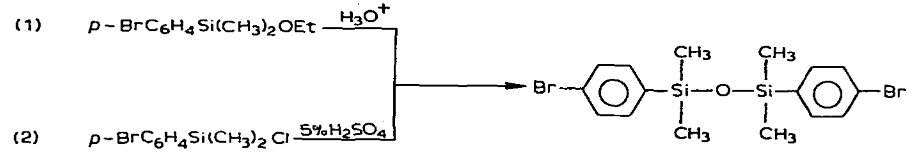
SUMMARY

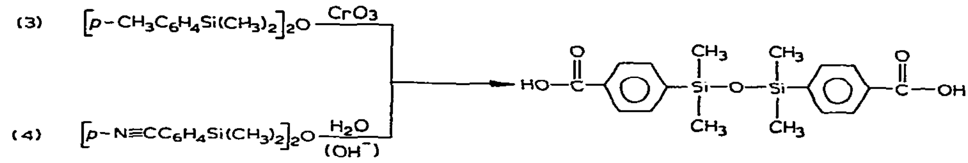
Difunctional compounds of the type $XR(CH_3)_2Si{-}O{-}Si(CH_3)_2RX$ (X = Br, OH, SH, and COOH) have been prepared by reaction of 1,3-dichlorotetramethyldisiloxane with the corresponding difunctional sodium or lithium reagents. The physical properties and analytical data of the new disiloxanes as well as their IR and PMR spectra are discussed.

INTRODUCTION

Only a limited number of 1,3-substituted symmetrical disiloxanes are known in which the carbon substituents contain functional groups suitable for further synthetic studies[1]. The use of 1,3-diethynyltetramethyldisiloxane in polymerization studies has been reported, however the synthesis and properties of this compound are not mentioned[2]. Typical condensation reactions described by Bazant[3] have been used to prepare 1,3-bis (*p*-bromophenyl)tetramethyldisiloxane, although the products obtained by these two methods do not have the same physical constants[4,5].



The 1,3-bis(*p*-carboxyphenyl)tetramethyldisiloxane was prepared via oxidation of 1,3-di-*p*-tolyltetramethyldisiloxane and base hydrolysis of 1,3-bis(*p*-cyanophenyl)tetramethyldisiloxane[4].



As an extension of our interest in organosilicon chemistry, the reactions of 1,3-dichlorotetramethyldisiloxane with difunctional lithium compounds were in-

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vestigated. A number of new symmetrical difunctional disiloxanes were prepared by this method. This procedure was also used to synthesize the above products.

RESULTS AND DISCUSSION

When siloxanes are treated with organolithium reagents, fission of the Si–O–Si linkage is known to occur[6]. Silicon halides, when treated with organolithium reagents, generally produce the corresponding organosilicon compound and lithium halide. Although cleavage of the Si–O–Si linkage has been observed at elevated temperatures using an excess of organolithium reagent, we have found at reduced temperatures that the disiloxane bond is stable in the presence of alkyl and aryl lithium reagents. A summary of the physical properties and analysis of the disiloxanes prepared is presented in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND ANALYSIS

Compound	Yield (%)	Phys. const.	Mol. wt. found (calcd.)	C(%) found (calcd.)	H (%) found (calcd.)
(I) $[HC{\equiv}CSi(CH_3)_2]_2O$	55	B.p. 122–128° (760 mm) n_D^{25} 1.4104	182 (182.4)	52.28 (52.68)	8.19 (7.74)
(II) $[CH_3C{\equiv}CSi(CH_3)_2]_2O$	74	B.p. 42–44° (0.75 mm)	210 (210.4)	57.30 (57.09)	9.14 (8.62)
(III) $[HO(CH_3)_2CC{\equiv}CSi(CH_3)_2]_2O$	70	M.p. 55–69	310 (298.5)	56.6 (56.3)	8.78 (8.78)
(IV) $[p\text{-}HOC_6H_4Si(CH_3)_2]_2O$	65	M.p. 86–87	328 (318.5)	60.40 (60.33)	6.82 (6.96)
(V) $[p\text{-}BrC_6H_4Si(CH_3)_2]_2O$	66	B.p. 142–147° (0.025 mm) n_D^{25} 1.5558	449 (444.3)	43.54 (43.25)	4.75 (4.54)
(VI) $[p\text{-}HSC_6H_4Si(CH_3)_2]_2O$	55	B.p. 158–159° (0.08 mm) n_D^{25} 1.5711	358 (350.7)	55.15 (54.80)	6.27 (6.32)
(VII) $[p\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$	75	M.p. 242–246°.	 (374.5)	57.92 (57.73)	6.02 (5.92)

The reaction scheme for the preparation of these compounds can be described by two distinct steps representing, in general, the formation of the desired lithium reagent and subsequent exchange with 1,3-dichlorotetramethyldisiloxane.

$$RBr + n\text{-}C_4H_9Li \rightarrow n\text{-}C_4H_9Br + RLi$$

$$Cl(CH_3)_2Si\text{–}O\text{–}Si(CH_3)_2Cl + 2\,RLi \rightarrow R(CH_3)_2Si\text{–}O\text{–}Si(CH_3)_2R + 2\,LiCl$$

Reactions previously described [eqns. (1)–(4)] are not as useful as a general synthesis since starting materials are in some cases more difficult to obtain. The yields for starting materials of reactions (1)–(4) are: (1) 13%, (2) —, (3) 66%, (4) 24%. It is questionable whether the condensation reaction (2) yields the desired product since analytical results suggest the formation of $Si\text{–}O\text{–}SO_2\text{–}O\text{–}Si$ type linkage. On the other hand, 1,3-dichlorotetramethyldisiloxane can be obtained in almost quantitative yield as described by McCusker[7]. In addition to our studies in tetrahydrofuran, the desired intermediate lithium reagents have been characterized by a number of others in various solvents.

Physical and chemical properties

Molecular weights were determined in all cases by vapor pressure osmometry except for 1,3-diethynyltetramethyldisiloxane since its volatility was too great to obtain meaningful results by osmometry methods. The mass spectrum parent ions are reported for 1,3-diethynyltetramethyldisiloxane and 1,3-di-1-propynyltetramethyldisiloxane. Compound (III), 1,3-bis(3-hydroxy-3-methyl-1-butynyl)tetramethyldisiloxane, was found to autosublime in a closed vial at room temperature producing a mossy sublimate above the main portion of the compound, which was identical to the main compound. As indicated in the introduction, the Si–O–Si linkage has withstood oxidation of adjacent groups by CrO_3 and acid or base hydrolysis. In this study, compound (VII) was prepared in good yields from the bromide (V) using n-butyllithium with subsequent carboxylation and acid hydrolysis. The 1,3-bis(pentachlorophenyl)tetramethyldisiloxane has been metalated using n-butyllithium[8]. Organolead derivatives of some of the compounds described in this paper have also been prepared[9].

Spectral correlations

It is of interest to examine the infrared spectra of the difunctional analogs of 1,3-dichlorotetramethyldisiloxane in order to determine the more prominent group or skeletal absorptions for ease in identifying these and related compounds. Tabulation of their frequencies along with our assignments is given in Table 2.

The most prominent absorption of the disiloxane is the asymmetric Si–O–Si stretching vibration found between 1210–1100 cm^{-1} as a broad and intense band. It is known that the frequency of this vibration will vary depending on the mass and inductive effects of the groups attached to silicon[10]. The above observation for 1,3-diethynyltetramethyldisiloxane is marginal as compared to compounds (II), (V), (VI), and (VII). It is interesting to note that the shift of the Si–O–Si asymmetric vibrations of (III), 1,3-bis(3-hydroxy-3-methyl-1-butynyl)tetramethyldisiloxane and (IV), 1,3-bis(*p*-hydroxyphenyl)tetramethyldisiloxane are of the order of 25–35 cm^{-1}. Both compounds are capable of hydrogen bonding intermolecularly and with the oxygen of the Si–O–Si linkage. Comparison of the spectra of 2-methyl-3-butyne-2-ol and *p*-bromophenol *vs.* the corresponding siloxanes shows a shift in the OH vibration to a lower frequency in the order of 70–100 cm^{-1} as might be expected for intermolecular hydrogen bonding. Such a shift in frequency is not observed for the corresponding acid. It should be noted that the Si–O–Si asymmetric absorption for bis(*p*-bromophenyl)tetramethyldisiloxane was obtained from the band width at 1/2 peak height due to the superposition of the phenyl bromide absorption at almost maximum intensity.

Besides the characteristic C–H asymmetric stretching vibration of the CH_3 in the 2965 cm^{-1} region, three very intense vibrations typical of the symmetrical tetramethyldisiloxanes studied here are of value in their identification. The invariant symmetric deformation and the two absorptions of the methyl rocking and stretching modes of the $Si–CH_3$ are found around 1260 cm^{-1} and 840–800 cm^{-1}, respectively. Typical of the acetylenes is the Si–C≡ stretching vibration in the 700 cm^{-1} region[11]. The functional group frequencies not listed in Table 2 are: (I) ≡C–H, 3295 cm^{-1}; (III) OH, 3295 cm^{-1}; (IV) OH, 3310 cm^{-1}; (V) C_6H_4Br, 1070 cm^{-1}; (VI) SH, 2565 cm^{-1}; (VII) C=O, 1695 cm^{-1}.

TABLE 2

SPECTRAL DATA

Compound	IR (cm^{-1})							PMR (Hz)[a]
	CH_3 as str	C≡C str	Si-CH_3 sym def	Si-C_6H_5	Si-O-Si str	Si-CH_3 str, rock	Si-C≡ str	
(I) $[HC{\equiv}CSi(CH_3)_2]_2O$	2975	2045	1263		1070	846, 808	690	[HC≡] 144.9 [CH_3Si] 15.2
(II) $[CH_3C{\equiv}CSi(CH_3)_2]_2O$	2970	2195	1260		1061	838, 801	678	[CH_3C≡] 108.4 [CH_3Si] 9.6
(III) $[HO(CH_3)_2CC{\equiv}CSi(CH_3)_2]_2O$	2985	2180	1260		1090	840, 810 788	670	[$(CH_3)_2$C] 90.6 [CH_3Si] 15.0
(IV) $[p\text{-}HOC_6H_4Si(CH_3)_2]_2O$	2968		1260	1120	1102	844, 827, 800, 788[b]		[C_6H_4] 419.5 [CH_3Si] 15.0
(V) $[p\text{-}BrC_6H_4Si(CH_3)_2]_2O$	2960		1258	1114	1065	832, 792[b]		[C_6H_4] 428.0 [CH_3Si] 3.6
(VI) $[p\text{-}HSC_6H_4Si(CH_3)_2]_2O$	2960		1257	1128	1065	835, 794[b]		[C_6H_4] 433.4 [CH_3Si] 18.4
(VII) $[p\text{-}HOOCC_6H_4Si(CH_3)_2]_2O$	2960		1258	1101	1065	838, 800[b]		[C_6H_4] 451.4 [CH_3Si] −1.0

[a] TMS standard, 60 MHz. [b] Para substitution absorption is not differentiated from these values in frequency assignments.

EXPERIMENTAL

The molecular weights were determined from their parent ion Mass Spectra for compounds (I) and (II) using a CEC Model 21-110B Mass Spectrometer. All other molecular weights were determined with a Mechrolab Vapor Pressure Osmometer, Model 301A, in benzene. Spectral data were obtained using a Beckman IR-12 spectrophotometer and a Varian Model A-60 PMR spectrometer. Uncorrected melting points were determined using a Thomas Hoover melting point apparatus.

All reactions were initiated under anhydrous conditions in a three-neck flask fitted with an argon inlet and exit, thermometer, dropping funnel or powder funnel, and mechanical stirrer. Tetrahydrofuran, freshly distilled from lithium aluminum hydride, was used as the solvent medium for all reactions. The starting material, 1,3-dichlorotetramethyldisiloxane, was prepared from boron trichloride and the cyclic, trimer, tetramer mixtures of methyl siloxane as described by McCusker and Ostdick[7]. All other reagents were commercially available.

Preparation of 1,3-*diethynyltetramethyldisiloxane (I)*

A solution of 1,3-dichlorotetramethyldisiloxane (51.4 g, 0.25 mole) in 1.5 liter of tetrahydrofuran was cooled to −10°. To the above solution, powdered sodium acetylide (25.6 g, 0.53 mole) was added over a 1 h period. The reaction mixture was allowed to warm to 5° and stirred until a pH test was neutral. The mixture was filtered under argon using a medium glass frit. The filtrate was concentrated under vacuum (1 mm) to 50 ml and rapidly distilled under vacuum. Fractional distillation of the above distillate yielded 25.6 g (55.4%) of product boiling at 122–128° (760 mm).

Preparation of 1,3-*di*-1-*propynyltetramethyldisiloxane (II)*

To a stirred suspension of 1-propynyllithium (10 g, 0.217 mole) in 400 ml of tetrahydrofuran at −70°, 1,3-dichlorotetramethyldisiloxane (20 g, 0.098 mole) was added over a half hour period. Allowed to warm to room temperature, the reaction mixture was stirred for 2 h and its pH tested neutral. The reaction mixture was then washed with a saturated ammonium chloride solution and the combined organic and ether extracts dried over sodium sulfate. The organic layer was evaporated under vacuum and the remaining residue (20 g) was distilled yielding 15.2 g of product (74%) boiling at 42–44° (0.75 mm).

Typical procedure using n-butyllithium

1,3-*Bis*(3-*hydroxy*-3-*methyl*-1-*butynyl*)*tetramethyldisiloxane (III)*. To 900 ml of tetrahydrofuran cooled to −70°, to which 500 ml (0.75 mole) of n-butyllithium (1.5 *N* in hexane) had been added, 27.3 g (0.325 mole) of 2-methyl-3-butyne-2-ol was added dropwise. The above mixture was stirred for 1 h at −70°, allowed to warm to room temperature and cooled to −70° again. A solution of 1,3-dichlorotetramethyldisiloxane (33.0 g, 0.162 mole) in 50 ml of tetrahydrofuran was added dropwise to the reaction mixture. The contents were then allowed to warm to 0° and washed with water saturated with ammonium chloride. The combined organic layer and ether washings were dried over sodium sulfate, filtered, and evaporated under vacuum to a yellow oil. Vacuum distillation of the crude oil gave 34.7 g (70%) of clear colorless liquid boiling at 95–100° (0.06 mm) which crystallized overnight. Further recrystallization of this waxy product from undecane yielded the compound with a melting range of 55–69°.

1,3-*Bis(p-hydroxyphenyl)tetramethyldisiloxane (IV)*. As above, *p*-bromophenol (56.3 g, 0.325 mole) in one liter of tetrahydrofuran was added dropwise to 500 ml (0.75 mole) of n-butyllithium at −70°. The maximum temperature allowed was 0° during which time a thick white gel formed. To the reaction mixture at −70° 1,3-dichlorotetramethyldisiloxane (20.1 g, 0.10 mole) was added dropwise. Since the exchange produces only 60–70% of the lithium lithiophenoxide, only 60% of the required halide was used[1 2]. The reaction mixture was allowed to warm to −10° with additional stirring for 1 h. The clear solution at 0° was hydrolyzed using a saturated ammonium chloride solution. Evaporation of the combined organic and ether washings under high vacuum yielded a yellow solid product. The crude product was treated with activated charcoal in ether, yielding 20.7 g (65.8%) product which was recrystallized from hot ligroin.

1,3-*Bis(p-bromophenyl)tetramethyldisiloxane (V)*. In a similar manner, n-butyllithium (150 ml, 0.225 mole) was added dropwise to a solution of *p*-dibromobenzene (54.1 g, 0.225 mole) in 1 liter of tetrahydrofuran at −70°. The reaction mixture was kept at −70° for 2 h, and without allowing the temperature to rise; a solution of 1,3-dichlorotetramethyldisiloxane (22.8 g, 0.112 mole) in 50 ml of tetrahydrofuran was added. At 0° the contents were washed with saturated ammonium chloride solution and the combined organic and ether washings dried over sodium sulfate. The organic layer was evaporated down to 45 g of crude oil. Vacuum distillation yielded 33 g (66%) product.

1,3-*Bis(p-thiolphenyl)tetramethyldisiloxane (VI)*. As above, *p*-bromothiophenol (42.1 g, 0.223 mole) in 150 ml of tetrahydrofuran was added to n-butyllithium (304 ml, 0.456 mole) at −70°. The reaction temperature was not allowed to exceed −30° over a 3 h period. At −70° a solution of 1,3-dichlorotetramethyldisiloxane (20.8 g, 0.202 mole) in 100 ml of tetrahydrofuran was added and the contents stirred for 1 h. At −60° the reaction mixture was poured into 1 liter of acidified ammonium chloride solution and its pH adjusted to 2 with concentrated hydrochloric acid. The combined ether and organic layers were dried over sodium sulfate and evaporated down to 55 g of yellow oil. A short head distillation gave 39.0 g (55%) product.

1,3-*Bis(p-carboxyphenyl)tetramethyldisiloxane (VII)*. In a similar manner, n-butyllithium (71 ml, 0.107 mole) was added to a solution of 1,3-bis(*p*-bromophenyl)-tetramethyldisiloxane (23.8 g, 0.54 mole) in 500 ml of tetrahydrofuran which had been cooled to −70°. Over a 3 h period the maximum temperature allowed was −5°. At −70° dry ice crushed under argon was added and the mixture allowed to warm to 0°. The organic layer and ether extracts from the acid hydrolysis, using 400 ml of saturated ammonium chloride solution (pH 6), were dried over sodium sulfate and evaporated under vacuum to 23.4 g of crude product. The product was separated from a methanol solution as an oil by addition of water and solidified (15.0 g) under vacuum. The product was then recrystallized from hexane.

REFERENCES

1 V. BAŽANT, V. CHVALOVSKÝ AND J. RATHOUSKÝ, *Organosilicon Compounds*, Academic Press, New York, Vol. 2, Pt. 2, 1965.
2 G. GREBER AND M. L. HALLENSLEBEN, *Makromol. Chem.*, 83 (1965) 148.

3 V. BAŽANT, V. CHVALOVSKÝ AND J. RATHOUSKÝ, *Organosilicon Compounds*, Academic Press, N. Y., Vol. 1, 4.3, 1965.
4 D. W. LEWIS AND G. C. GAINER, *J. Amer. Chem. Soc.*, 74 (1952) 2931.
5 G. C. GAINER, T. CREEK AND D. W. LEWIS, *U. S. Pat.*, 2,891,981, 1959.
6 H. GILMAN, H. N. BENEDICT AND H. HARTZFIELD, *J. Org. Chem.*, 19 (1954) 419.
7 P. A. MCCUSTER AND T. OSTDICK, *J. Amer. Chem. Soc.*, 80 (1958) 1103.
8 I. HAIDUC AND H. GILMAN, *J. Organometal. Chem.*, 14 (1968) 79.
9 P. J. MOEHS AND B. C. PANT, in preparation.
10 A. L. SMITH, *Spectrochim. Acta*, 116 (1960) 87.
11 R. E. SACHER, D. H. LEMMON AND F. A. MILLER, *Spectrochim. Acta, Part A*, 23 (1967) 1169.
12 W. E. DAVIDSOHN, B. R. LA LIBERTE, C. M. GODDARD AND M. C. HENRY, in preparation.