on carbon to yield diethyl 3-phenylpimelate, bp 145–150° (0.5 mm), in high yield. The same ester was synthesized by a Reformatsky condensation of ethyl bromoacetate with ethyl 4-benzoylbutanoate to the expected hydroxy diester (86% yield). This ester was dehydrated and reduced as above to yield diethyl 3-phenylpimelate, identical by ir and nmr analysis with that of the product obtained from 1_{LE}.

Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.9; H, 8.2. Found: C, 70.2, 70.3; H, 8.4, 8.4.

3-Phenylpimelic Acid.—Alkaline hydrolysis of the above ester followed by acidification afforded 3-phenylpimelic acid, bp 180–183° (0.004 mm) (bath temperature), in high yield.

Anal. Calcd for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8. Found: C, 66.2; H, 7.1.

The above acid on treatment with thionyl chloride gave the diacid chloride. Upon reaction of the crude diacid chloride in tetrahydrofuran with liquid ammonia the diamide, mp 152–153°, ir bands at 3.0, 6.08 μ (broad), was obtained in high yield after recrystallization from alcohol–benzene.

Anal. Calcd for $C_{13}H_{18}N_2O_2$: N, 12.0. Found: N, 11.8.

Registry No.—1_{MA}, 20633-23-2; 1_{VE}, 20633-26-5; 1_{PE}, 20633-25-4; 1_{NPA}, 26366-16-5; 1_{CUL}, 4055-00-9; 1_{LE}, 20678-81-3; **2**, 2938-68-3; 2_{NE}, 20633-40-3; 3_{UL}, 26366-19-8; 3_{PE}, 20633-29-8; 4_{UL}, 26366-21-2; 4_{NE}, 20633-63-0; 4_{VE}, 26366-23-4; 4_{PE}, 20633-31-2; **6**, 20633-33-4; **7**, 4412-28-6; **8**, 20633-35-6; **9**, 20633-36-7; **10**, 13544-27-9; 2,2-dimethyl-1,5-diphenyl-1,2-dihydropyran, 26372-49-6; diethyl 3-phenylpimelate, 26372-50-9; 3-phenylpimelic acid, 26372-51-0; 3-phenylpimelic acid diamide, 26372-52-1.

Preparation and Reactions of Siloxanylpropanals

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1,1,3,3-Tetramethyldisiloxane or pentamethyldisiloxane with 3,3-dimethoxypropene in the presence of chloroplatinic acid formed mostly the 3,3-dimethoxypropyl along with the corresponding 2,2-dimethoxy-1-methylethyl adducts. Hydrolysis of the former afforded the corresponding siloxanylpropanals. Hydrolysis of the latter caused cleavage of the Si–C bond to form siloxanes and propionaldehyde.

Silanes of the formula $R^1R^2R^3SiH$ add to acetals of acrolein with platinum catalysts to form $R^1R^2R^3SiCH_2CH_2CH(OR)_2$.[1,2] However, no aldehydes have been prepared from these acetals and characterized except for 3-triethylsilylpropanal[2] and 3-diethylmethylsilylpropanal.[3] We wished to prepare compounds having siloxane structures substituted with propanal groups and to study the chemistry of the aldehyde group in such molecules.

Results and Dicussion

Pentamethyldisiloxane and acrolein dimethylacetal (**1**) gave (3,3-dimethoxypropyl)pentamethyldisiloxane (**2**) along with methoxypentamethyldisiloxane (**3**) and 1-methoxypropene (eq 1).

$$Me_3SiOSiMe_2H + \underset{\mathbf{1}}{CH_2{=}CHCH(OMe)_2} \xrightarrow{H_2PtCl_6} \underset{\mathbf{2}}{Me_3SiOSiMe_2CH_2CH_2CH(OMe)_2} + \underset{\mathbf{3}}{Me_3SiOSiMe_2(OMe)} + MeCH{=}CH(OMe) \qquad (1)$$

The formation of 1-methoxypropene and **3** probably occurred by a route shown by eq 2 analogous to that reported for the formation of propene and silicon tetrachloride from allyl chloride and trichlorosilane.[4]

$$Me_3SiOSiMe_2H + CH_2{=}CH{-}CH(OMe)_2 \xrightarrow{Pt} \underset{\mathbf{3}}{Me_3SiOSiMe_2(OMe)} + CH_3CH{=}CH(OMe) \qquad (2)$$

Hydrolysis of **2** gave 3-pentamethyldisiloxanylpropanal (**4**) (eq 3).

$$\underset{\mathbf{2}}{Me_3SiOSiMe_2CH_2CH_2CH(OMe)_2} \xrightarrow{H_3O^+} \underset{\mathbf{4}}{Me_3SiOSiMe_2CH_2CH_2CH{=}O} \qquad (3)$$

Treatment of **4** with acidic aqueous ethanolic 2,4-dinitrophenylhydrazine gave the bis-2,4-dinitrophenylhydrazone of *sym*-tetramethyldisiloxanedipropanal (**5**) (eq 4).

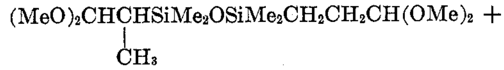
$$\underset{\mathbf{4}}{Me_3SiOSiMe_2CH_2CH_2CH{=}O} \xrightarrow{H_3O^+} \underset{\mathbf{5}}{O(SiMe_2CH_2CH_2CH{=}O)_2} + (Me_3Si)_2O \qquad (4)$$

$$\downarrow \text{2,4-dinitrophenylhydrazine}$$

$$\text{bishydrazone}$$

sym-Tetramethyldisiloxane and **1** gave *sym*-bis(3,3-dimethoxypropyl)tetramethyldisiloxane (**6**) and six other compounds by glc analysis (eq 5). One of these compounds was 1-methoxy-3-(3′,3′-dimethoxypropyl)-tetramethyldisiloxane which was obtained in 10.5% yield. The formation of this compound was expected in light of the formation of **3** during the addition of pentamethyldisiloxane. The five other minor compo-

$$(HSiMe_2)_2O + \underset{\mathbf{1}}{CH_2{=}CH{-}CH(OMe)_2} \xrightarrow{H_2PtCl_6} \underset{\mathbf{6}}{O[SiMe_2CH_2CH_2CH(OMe)_2]_2} +$$



7

$$\underset{\mathbf{7}}{(MeO)_2CH\underset{CH_3}{\underset{|}{C}}HSiMe_2OSiMe_2CH_2CH_2CH(OMe)_2} + MeOSiMe_2OSiMe_2CH_2CH_2CH(OMe)_2 + MeOCH{=}CHCH_3 \qquad (5)$$

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[*] To whom correspondence should be addressed.

(1) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

(2) S. I. Sadykhzade, M. A. Mardanov, Z. B. Sultanova, and R. A. Sultanov, *Azerb. Khim. Zh.*, **6**, 29 (1966).

(3) G. V. Golodnikov and V. V. Shasharina, *Zh. Obshch. Khim.*, **33** (10), 3262 (1963).

(4) J. W. Ryan and J. L. Speier, *J. Amer. Chem. Soc.*, **86**, 895 (1964).

nents accounted for 15 area % of the mixture by glc analysis.

Distillation of a portion of this mixture gave pure *sym*-bis(3,3-dimethoxypropyl)tetramethyldisiloxane (**6**). The forecuts of this product contained an impurity which could be seen by glc analysis. An nmr spectrum of this material contained a doublet at τ 5.85 and the impurity was assigned structure **7**.

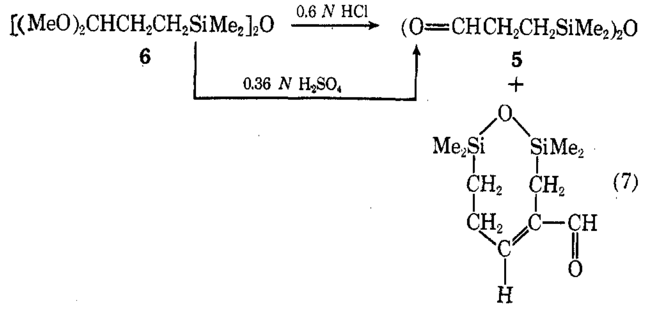
Hydrolysis of a mixture of **6** and **7** gave propionaldehyde and several high boiling compounds in addition to **5** (eq 6).

$$[(\mathrm{MeO})_2\mathrm{CHCH_2CH_2SiMe_2}]_2\mathrm{O} + \underset{\mathbf{7}}{(\mathrm{MeO})_2\mathrm{CHCH_2CH_2SiMe_2OSiMe_2CHMeCH(OMe)_2}} \xrightarrow{\mathrm{H_3O^+}} \mathrm{CH_3CH_2CH{=}O} + \underset{\mathbf{5}}{(\mathrm{O{=}CHCH_2CH_2SiMe_2})_2\mathrm{O}} + (\mathrm{O{=}CHCH_2CH_2SiMe_2O})_2\mathrm{SiMe_2} + \text{others} \quad (6)$$

The cleavage of the silicon–carbon bond in β-carbonyl compounds[5–7] accounts for the formation of propionaldehyde from **7**.

Distillation of high-boiling products from hydrolysis of a mixture of **6** and **7** gave pure hexamethyltrisiloxane-1,5-dipropanal. The formation of trisiloxane indicates that a substantial amount of redistribution of dimethylsiloxy groups occurred in the acidic media.

Hydrolysis of **6** using 0.6 *N* hydrochloric acid gave **5** and **8** in a ratio of 1:2 (eq 7). The minor component crystallized on standing.

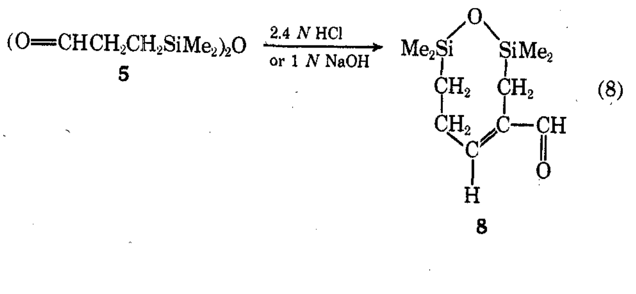


8

The 2,4-dinitrophenylhydrazone of **8** is red, indicative of an α,β-unsaturated carbonyl. A crystalline oxime of **8** was obtained, mp 116–116.5°. The narrow melting point range is indicative of a single configuration; however, it was not determined whether this was the syn or anti form of the oxime.

Refluxing **6** in 0.36 *N* sulfuric acid gave **5** in 95% yield without forming **8**. The best yield of distilled product was 87%. The balance of the product was a viscous residue which was presumably an aldol condensation polymer.

The dialdehyde, **5**, was converted to **8** by either strongly acidic or strongly basic conditions (eq 8).



8

sym-Bis(3-*N*,*N*-dimethylaminopropyl)tetramethyldisiloxane (**9**) was obtained in 78% yield from the reductive alkylation of dimethylamine using **5** (eq 9).

$$\underset{\mathbf{5}}{(\mathrm{O{=}CHCH_2CH_2SiMe_2})_2\mathrm{O}} + \mathrm{Me_2NH} + \mathrm{H_2} \xrightarrow{\text{Pd-C}} (\mathrm{Me_2NCHCH_2CH_2SiMe_2})_2\mathrm{O} \quad (9)$$

The reduction of **5** gave *sym*-bis(3-hydroxypropyl)tetramethyldisiloxane (eq 10).

$$(\mathrm{O{=}CHCH_2CH_2SiMe_2})_2\mathrm{O} + \mathrm{LiAlH_4} \longrightarrow (\mathrm{HOCH_2CH_2CH_2SiMe_2})_2\mathrm{O} \quad (10)$$

The addition of trimethoxysilane to **1** gave 3,3-dimethoxypropyltrimethoxysilane indicating that alkoxysilanes as well as disiloxanes can be used to prepare aldehyde precursors.

Dimethylchlorosilane and **1**, however, gave a mixture of products of which the major silicon-containing products were dimethylmethoxychlorosilane and dimethyldimethoxysilane. The organic products were not identified.

Experimental Section

Reagents.—3,3-Dimethoxypropene was obtained from Shell Chemical Co. The silicon-containing compounds were from Dow Corning Corp. Trimethoxysilane was 75% pure with tetramethoxysilane comprising most of the remainder. *sym*-Tetramethyldisiloxane and dimethylchlorosilane were >98% pure by glc analysis. Pentamethyldisiloxane was prepared from acidic equilibration of *sym*-tetramethyldisiloxane and hexamethyldisiloxane followed by fractionation using a 3-ft Glen-Lab column packed with Podbielniak packing. This compound was 98% pure by glc analysis with hexamethyldisiloxane as the remainder. Chloroplatinic acid hexahydrate (0.1 *M* in isopropyl alcohol) was used as a catalyst.

Analyses.—All gas–liquid chromatographic analyses employed an 8 ft × 0.25 in. stainless steel column packed with 26% Dow Corning SGM-11 on Chromosorb W 80–100 mesh. ^{1}H nmr spectra were obtained on a Varian Associates Model A-60 using $\mathrm{CCl_4}$ as solvent and tetramethylsilane as an internal standard. The nmr data are listed in Table I. Infrared spectra were obtained on a Perkin-Elmer 521 grating spectrometer. Melting points and boiling points are uncorrected. Elemental analyses were by the Dow Corning Analytical Laboratory.

3,3-Dimethoxypropylpentamethyldisiloxane (**2**).—Pentamethyldisiloxane, 160 g (1.08 mol), was added slowly to **1**, 110 g (1.08 mol), that contained 10^{-5} mol of chloroplatinic acid. The temperature rose to 110° during the addition, after which the temperature was held at 100° for 2 hr. Distillation gave 1-methoxypropene [4.5 g (5.8%), bp 42–45°], which formed the 2,4-dinitrophenylhydrazone of propionaldehyde (mp 148–152°, when treated with ethanolic 2,4-dinitrophenylhydrazine), methoxypentamethyldisiloxane [11 g (5.7%); bp 58–60° (80 mm); $n^{25}\mathrm{D}$ 1.3809; $d^{25}{}_4$ 0.825; RD 0.281 (calcd 0.279)], and compound **2** [175 g (65%); bp 136° (80 mm); $n^{25}\mathrm{D}$ 1.4101; $d^{25}{}_4$ 0.8706; RD 0.285 (calcd 0.284); ir ($\mathrm{CCl_4}$) 2830 cm^{-1} ($\mathrm{CH_3O}$); ir ($\mathrm{CS_2}$) 1120 (COC), 1055 (SiOSi), 842 and 753 cm^{-1} ($\mathrm{SiCH_3}$)]. *Anal.* Calcd for $\mathrm{Si_2C_{10}H_{26}O_3}$: Si, 22.4. Found: Si, 22.4.

3-Pentamethyldisiloxanylpropanal (**4**).—A mixture of **2**, 54 g (21.6 mmol), with 250 ml of 0.36 *N* sulfuric acid was refluxed for 7 hr. The organic layer was then separated and the aqueous layer was extracted three times with ether. The organic layer and the ether extract were combined, washed with a dilute solution of sodium bicarbonate and then with water, and dried over sodium sulfate, and the ether was removed *in vacuo*. Distillation of a portion of the residue gave **4**: bp 71° (13 mm); $n^{25}\mathrm{D}$ 1.4109; $d^{25}{}_4$ 0.8925; RD 0.278 (calcd 0.282); ir ($\mathrm{CCl_4}$) 2710 (CH=O), 1725 cm^{-1} (C=O); ir ($\mathrm{CS_2}$) 1050 (SiOSi), 840 and 750 cm^{-1} ($\mathrm{SiCH_3}$). *Anal.* Calcd for $\mathrm{Si_2C_8H_{20}O_2}$: Si, 27.5; C, 47.1; H, 9.88. Found: Si, 27.4; C, 46.9; H, 9.82.

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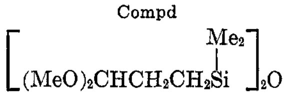
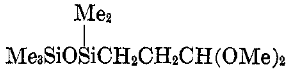
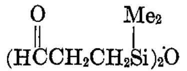
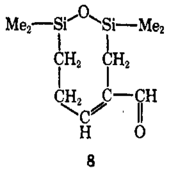
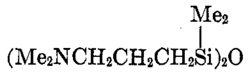
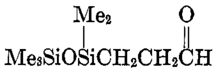
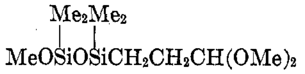
(5) L. H. Sommer and R. P. Pioch, *J. Amer. Chem. Soc.*, **76**, 1606 (1954).

(6) L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

(7) P. G. Cambell, Ph.D. Thesis, Pennsylvania State University, 1957.

TABLE I
NMR SPECTRAL DATA

Compd	τ	H's	Assignment	Type	Hz (cps)
 $[(MeO)_2CHCH_2CH_2\overset{Me_2}{Si}]_2O$	5.85	2.2	$HC(OMe)_2$	t	7
	6.81	12.0	$COCH_3$	s	
	8.2–8.7	4.0	CCH_2C	m	
	9.3–9.7	4.2	$SiCH_2C$	m	
6	9.94	11.6	$SiCH_3$	s	
 $Me_3SiO\overset{Me_2}{Si}CH_2CH_2CH(OMe)_2$	5.81	1.0	$HC(OMe)_2$	t	7
	6.80	6.1	$COCH_3$	s	
2	8.2–8.7	2.1	CCH_2C	m	
	9.3–9.7	2.0	$SiCH_2C$	m	
	9.94	14.9	$SiCH_3$	s	
 $(H\overset{O}{\overset{\Vert}{C}}CH_2CH_2\overset{Me_2}{Si})_2O$	0.29	2.0	$O{=}CH$	s	
	7.60	4.0	$O{=}CCH_2$	m	
	9.24	4.0	$SiCH_2C$	m	
5	9.91	12.0	$SiCH_3$	s	
 $(H\overset{O}{\overset{\Vert}{C}}CH_2CH_2\overset{Me_2}{Si}O)_2SiMe_2$	0.3	1.6	$O{=}CH$	s	
	7.62	4.0	CCH_2C	m	
	9.25	4.2	$SiCH_2C$	m	
	9.94	18.2	$SiCH_3$	s	
	0.74	0.9	$O{=}CH$	s	
	3.65	1.0	$-CH{=}C$	t	9
	7.2–7.8	2.1	$=CCH_2-$	m	
	8.23	2.0	$SiCH_2C=$	s	
	8.9–9.3	2.1	$SiCH_2CH_2$	m	
	9.96	11.9	$SiCH_3$	s	
8	9.98	11.9	$SiCH_3$	s	
 $(Me_2NCH_2CH_2CH_2\overset{Me_2}{Si})_2O$	7.89	6.0	NCH_3	s	
	7.9	2.0	CCH_2N	m	
	8.4–8.9	2.0	CCH_2C	m	
	9.3–9.7	2.0	$SiCH_2$	m	
	9.96	6.1	$SiCH_3$	s	
 $Me_3SiO\overset{Me_2}{Si}CH_2CH_2\overset{O}{\overset{\Vert}{C}}H$	0.27	1.0	$O{=}CH$	s	
	7.4–7.8	2.0	CCH_2	m	
	9.1–9.4	2.1	$SiCH_2$	m	
4	9.95	14.8	$SiCH_3$	s	
 $MeO\overset{Me_2}{Si}O\overset{Me_2}{Si}CH_2CH_2CH(OMe)_2$	5.79	1.0	$HC(OMe)_2$	t	6
	6.60	3.0	$SiOCH_3$	s	
	6.79	6.0	$COCH_3$	s	
	8.2–8.7	1.9	CCH_2	m	
	9.3–9.7	2.0	$SiCH_2$	m	
	9.92	6.0	$SiCH_3$	s	
	9.98	6.0	$SiCH_3$	s	
$(HOCH_2CH_2CH_2SiMe_2)_2O$	6.24	1.6	OH	s	
	6.54	4.0	OCH_2	t	7
	8.46	4.0	CCH_2	m	
	9.48	4.4	$SiCH_2$	m	
	9.94	12.0	$SiCH_3$	s	

Addition of *sym*-Tetramethyldisiloxane to 1.—To 818 g (8.0 mol) of **1** containing 10^{-4} mol of chloroplatinic acid was added 537 g (4.0 mol) of **9**. The addition required 3 hr and during most of the addition the temperature was 90°. After the addition was complete, the temperature was maintained at 130° for an additional 3 hr. Analysis by glc indicated 75% of the mixture was diadduct. Six peaks accounted for the remainder of the material. One of these peaks was much larger than the others. Distillation identified this major by-product as 1-methoxy-3-(3′,3′-dimethoxypropyl)tetramethyldisiloxane, 112 g (10.5%): bp 76° (4 mm); $n^{25}{}_D$ 1.4108; $d^{25}{}_4$ 0.9259; RD 0.268 (calcd 0.268). *Anal.* Calcd for $Si_2C_{10}H_{26}O_4$: Si, 21.2; C, 45.2; H, 9.84. Found: Si, 21.2; C, 45.1; H, 10.02.

Distillation of a portion of the diadduct gave 475.5 g of *sym*-bis(3,3-dimethoxypropyl)tetramethyldisiloxane (**6**): bp 135–136° (8 mm); $n^{25}{}_D$ 1.4273; $d^{25}{}_4$ 0.9438; RD 0.273 (calcd 0.273). *Anal.* Calcd for $Si_2C_{14}H_{34}O_5$: Si, 16.6; C, 49.7; H, 10.2. Found: Si, 16.3; C, 50.2; H, 10.4.

The fractions immediately preceding **6** were contaminated with **7**. A glc analysis of this material showed more than one compound: bp 134–135° (8 mm); $n^{25}{}_D$ 1.4288. The nmr spectrum of this material contained a doublet (J = 7 Hz) superimposed upon the triplet (J = 7 Hz) of compound **6** at τ 5.85 corresponding to the proton on the carbon bearing the two methoxy groups.

Hydrolysis of 6. A. With Hydrochloric Acid.—A mixture of 10 g (0.03 mol) of **6** and 100 ml of 0.6 N hydrochloric acid was refluxed for 3.5 hr. The mixture was cooled and extracted with ether. The ethereal solution was dried over sodium sulfate and the ether was removed *in vacuo*. The resulting 6.1 g, 84%, of hydrolyzed material was a mixture of **5** and **8** in a ratio of 2:1 based upon glc area per cent. Distillation of 21 g of material obtained in this manner through a Vigreux column gave 2.1 g of material: bp 114–122° (5 mm); $n^{25}{}_D$ 1.4670; $d^{25}{}_4$ 0.971; RD 0.286 (calcd 0.284); ir (CCl_4) 1685 (C═CC═O) 1635 cm^{-1} (C═C), which was 90% **8** with **5** constituting the remainder. Compound **8** crystallized on standing, mp 41–43° (recrystallized from ethanol), and a red 2,4-dinitrophenylhydrazone, mp 214–216°, was obtained in 85% yield. *Anal.* Calcd for $Si_2C_{16}H_{24}N_4O_6$: C, 47.1; H, 5.94; N, 13.4. Found: C, 47.0; H, 6.23; N, 13.4.

A crystalline oxime of **8** was also prepared. From 1.0 g of **8**, 1.0 g (94%) of oxime, mp 84–102°, was obtained. Recrystallization from ethanol-water gave 185 mg, mp 112–116°, and 280 mg, mp 116–116.5°. The fractions after **8** were mixtures of **5** and **8**. The distillation was slow and the total amount of distilled material obtained was 7.0 g. The remaining 12 g of residue was a viscous material which was evidently an aldol condensation polymer. This material did not contain any volatile material and had (C═C—C═O) 1685 and (C═O) 1730 cm^{-1} absorptions in its ir spectrum.

B. With Sulfuric Acid.—A mixture of 130 g (0.38 mol) of **6** in 1 l. of 0.36 N sulfuric acid was refluxed for 6.5 hr. The cooled hydrolysate was extracted with ether and the ethereal solution was dried over sodium sulfate. The ether was removed *in vacuo* and the resulting 92.0 g (0.37 mol, 97%) of **5** was distilled to give 82.8 g (0.335 mol, 87.4%) of pure **5**: bp 93° (0.45 mm); $n^{25}{}_D$ 1.4368; $d^{25}{}_4$ 0.273 (calcd 0.274); ir (CCl_4) 2720 (CH═O) 1730 cm^{-1} (C═O); ir (CS_2) 1250 cm^{-1}; ir ($SiCH_3$) 1050 cm^{-1}

(SiOSi). *Anal.* Calcd for $Si_2C_{10}H_{22}O_3$: Si, 22.8; C, 48.7; H, 8.98. Found: Si, 21.7; C, 48.7; H, 9.16.

The 2,4-dinitrophenylhydrazone had mp 185–186°. *Anal.* Calcd for $Si_2C_{22}H_{30}N_8O_9$: Si, 9.26; N, 18.4. Found: Si, 9.20; N, 17.9.

The residue, 8.0 g, was similar to that obtained from the hydrolysis with hydrochloric acid.

Hydrolysis of a Mixture of 6 and 7.—A mixture of 1 l. of 0.36 *N* sulfuric acid and 113.9 g (0.336 mol) of **6** and **7** was refluxed for 6 hr. After cooling, the hydrolysate was extracted with ether and the ethereal solution was dried over sodium sulfate and filtered, and the ether was removed *in vacuo*. A cold trap at −80° was used to collect the volatiles. Treatment of these volatiles with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of propionaldehyde, mp 148–152°, mixture melting point undepressed. The resulting 81.5 g (98%) of crude material contained two major components, **5** and hexamethyltrisiloxane-1,5-dipropanal in a ratio of 2:1, as well as several other components by glc analysis. The trisiloxane was separated from **5** by two successive fractional distillations: bp 104° (0.15 mm); $n^{25}{}_D$ 1.4394; $d^{25}{}_4$ 1.000; RD 0.263 (calcd 0.268); 2,4-dinitrophenylhydrazone, mp 172–173°. *Anal.* Calcd for $Si_3C_{24}H_{36}N_8O_{10}$(2,4-dinitrophenylhydrazone): Si, 12.4; C, 42.4; H, 5.31; N, 16.45. Found: Si, 12.5; C, 42.7; H, 5.40; N, 16.2.

Acidic Aldol Condensation of 5.—A mixture of 1.0 g (4 mmol) of **5** and 100 ml of 2.4 *N* hydrochloric acid was refluxed for 4 hr. After cooling the hydrolysate was worked up as described above. The 700 mg (75%) of product was >95% **8** by glc analysis.

Basic Aldol Condensation of 5.—A mixture of 5.0 g (20 mmol) of **5** and 22 ml of 1.0 *N* sodium hydroxide was refluxed for 1 hr. After work-up as described above, 3.5 g (93%) of material was obtained which was a mixture of **8** and **5** in a ratio of 4:1. There were a few additional peaks corresponding to higher boiling products which accounted for *ca.* 5% of the product.

sym-**Bis(3,3-dimethylaminopropyl)tetramethyldisiloxane.**—To 25.8 g (0.105 mol) of **5** in 25 ml of methanol cooled in an ice-water bath was added 61.0 g of 36% dimethylamine in cold methanol (0.49 mol). To this mixture was added 200 mg of 10% palladium on carbon. The mixture was immediately hydrogenated on a Parr apparatus at 39 psig. A pressure decrease to 25.5 psig was noted within 1 hr with no additional pressure decrease in the next 2 hr. The catalyst was removed by filtration. The methanol was removed *in vacuo*. The residue was distilled to give 24.8 g (78%) of *sym*-bis(3,3-dimethylaminopropyl)tetramethyldisiloxane: bp 77–79° (0.05 mm); $n^{25}{}_D$ 1.4351; neut equiv 164.5 (calcd 152.3); ir (CCl_4) 2770 (NMe_2), 1250 (SiMe), 1060 cm^{-1} (SiOSi). There was a small nearby peak in the glc chromatogram which integrated for about 10%, presumably 1-(3′-hydroxypropyl)-3-(3′-dimethylaminopropyl)tetramethyldisiloxane.

3,3-(Dimethoxypropyl)trimethoxysilane.—To 34.1 g (0.33 mol) of **1** at 75° containing 10^{-3} mol of chloroplatinic acid was added slowly 55.0 g of 75% trimethoxysilane (0.33 mol). No reaction was observed for some time after which the silane was added at a rate sufficient to maintain vigorous reflux. The mixture was then heated for an additional hour at 90°. Distillation gave 58 g (77%) of 3,3-dimethoxypropyltrimethoxysilane: bp 77–81° (6 mm); $n^{25}{}_D$ 1.4090; $d^{25}{}_4$ 1.030; RD 0.240 (calcd 0.244); ir (CCl_4) 2840 cm^{-1} (OCH_3); ir (CS_2) 1090 and 1190 cm^{-1} ($SiOCH_3$).

Dimethylchlorosilane and 1.—To 34.1 g (0.33 mol) of refluxing **1** that contained 10^{-3} mol of chloroplatinic acid was slowly added 31 g (0.33 mol) of dimethylchlorosilane. The catalyst was increased to 10^{-2} mol and the solution refluxed for 20 hr. The mixture did not show a peak in the glc above the peak corresponding to **1**; however, there was a new peak with a shoulder between dimethylchlorosilane and **1**. Distillation gave 10.5 g of this material: bp 68–72°; $n^{25}{}_D$ 1.3808; ir (CCl_4) 2840 cm^{-1} $(OCH_3)_3$; ir (CS_2) 1257 and 803 ($SiCH_3$), 1190 and 1090 ($SiOCH_3$), 480 cm^{-1} (SiCl). The nmr (CCl_4) had peaks at τ 9.58 $(CH_3)_2Si(OMe)Cl$ and 9.91 $(CH_3)_2Si(OMe)_2$ in a ratio of 1.6:1. The material boiling below 68° was a mixture of at least seven compounds and presumably contained methyl propenyl ether.

sym-**Bis(3-hydroxypropyl)tetramethyldisiloxane.**—To 1.0 g (20 mmol) of lithium aluminum hydride in 30 ml of ether was slowly added 3.0 g (12 mmol) of **5**. The excess lithium aluminum hydride was decomposed with methanol and 3 *N* hydrochloric acid after the evolution of hydrogen ceased. The organic layer was separated and dried over sodium sulfate and then the ether was removed *in vacuo* to give 2.8 g of *sym*-bis(3-hydroxypropyl)tetramethyldisiloxane, $n^{25}{}_D$ 1.4495 (lit.[8] $n^{25}{}_D$ 1.4472).

Registry No.—**2**, 26542-45-0; **4**, 26542-46-1; **5**, 26542-47-2; **5** (2,4-DNP), 26599-12-2; **6**, 26542-48-3; **8**, 26542-49-4; **8** (2,4-DNP), 26542-50-7; **8** (oxime), 26542-51-8; 1-methoxy-3-(3′,3′-dimethoxypropyl)tetramethyldisiloxane, 26542-52-9; hexamethyltrisiloxane-1,5-dipropanol, 26542-53-0; hexamethyltrisiloxane-1,5-dipropanol (2,4-DNP), 26542-54-1; *sym*-bis(3,3-dimethylaminopropyl)tetramethylsiloxane, 26-526 97-6; 3,3-dimethoxypropyltrimethoxysilane, 25760-57-0; *sym*-bis(3-hydroxypropyl)tetramethyldisiloxane, 18001-97-3.

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The Reaction of Lithium Acyl Carbonyl Metalates with Organic Halides

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Reaction of lithium acyl tetracarbonylferrates with benzyl halides or acid halides in ether yielded unsymmetrical ketones, while lithium acyl tricarbonylnickelates gave α-benzylacyloins or stilbenediol diesters by reaction with benzyl halides or acid halides, respectively. A dinuclear structure was suggested for lithium acyl tricarbonylnickelates based on the chemical behaviors of the complexes and the results of an infrared study, and furthermore an allusion to alkoxy- or acyloxycarbene metal complexes as precursors to unsymmetrical ketones, α-benzylacyloins, and stilbenediol diesters was made.

Organolithium compounds are reactive toward carbonyl metals and add reductively to the metals even at low temperature to form rather stable anionic metal complexes. Two different aspects of such reactions with organolithium compounds have received recent attention: (1) the synthesis of carbene–transition metal complexes using hexacarbonyls of chromium, molybdenum, and tungsten;[1] (2) the organic synthesis by means of pentacarbonyliron[2,3] and tetracarbonylnickel.[4,5] The carbonyls of iron or nickel are the most reactive toward organolithium compounds. Especially, reactions of alkyl- or aryllithiums with tetracarbonylnickel proceed exothermically even at −70° to

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