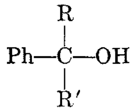
oxonium salt and the resultant carbonium ion by solvation. Thus the hydrogenation of benzhydrol may be explained as a process involving cleavage of the C–O bond of the benzhydrol in the presence of an acid catalyst, the rate of which is enhanced by solvation of the carbonium ion. It appears that the mechanism of the hydrogenation of benzhydrol or aromatic carbinols of formula



$$\mathrm{Ph{-}}\overset{\displaystyle R}{\underset{\displaystyle R'}{\mathrm{C}}}\mathrm{{-}OH}$$

does not involve an intermediate cobalt tricarbonyl, unlike the hydrogenation of aldehydes[9,10] or the hydroformylation of olefins,[11] which are inhibited by CO.

An interesting fact is that benzyl alcohol reacts under oxo conditions to give both toluene and 2-phenylethanol.[4,5] When R and R′ are H as for benzyl alcohol, it is possible that carbon monoxide may insert between the carbon and cobalt of the corresponding complex II, probably owing to less steric hindrance. Benzhydrol, in contrast to benzyl alcohol, gives no homologated product, perhaps owing to steric hindrance in complex II.

**Registry No.**—Benzhydrol, 91-01-0; *p*-methylbenzhydrol, 1517-63-1; *p*-methoxybenzhydrol, 720-44-5; *p*-chlorobenzhydrol, 119-56-2; *p,p*′-dichlorobenzhydrol, 90-97-1; phenylmethylcarbinol, 98-85-1; triphenylcarbinol, 76-84-6.

**Acknowledgement.**—We are indebted to Dr. M. Orchin for his interest and aid in carrying out this work.

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# Methyl(2-thienyl)- and Methyl(2-furyl)cyclopolysiloxanes

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The trimeric, tetrameric, and pentameric methyl(2-thienyl)- and methyl(2-furyl)cyclosiloxanes were prepared and characterized by nmr spectroscopy. All of the possible stereoisomers were detected in the mixtures. In both the 2-thienyl and 2-furyl series, the 2,4,6′-trimethyl-2′,4′,6-triarylcyclotrisiloxane and the 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetraarylcyclotetrasiloxane stereoisomers were isolated and identified by nmr spectroscopic techniques. 2-Thienyl-substituted cyclosiloxanes were found to undergo facile acid-catalyzed cleavage under mild hydrolysis conditions. Base-catalyzed redistribution of thienyl–silicon and oxygen–silicon bonds also was observed.

The synthesis[1,2] and characterization[2-6] of methylphenylcyclopolysiloxanes have been the subject of numerous papers, but relatively little attention has been paid to cyclosiloxanes containing aromatic heterocyclic groups. Mixtures of methyl(2-thienyl)cyclosiloxanes have been reported,[7] but the cyclic trimer, tetramer, and pentamer fractions were not described. Poly(2-thienylsilsesquioxanes) have been prepared.[8] Furyl-substituted siloxanes have not been reported. In this paper we report the synthesis of the methyl(2-thienyl)- and methyl(2-furyl)cyclotrisiloxanes, -cyclotetrasiloxanes, and -cyclopentasiloxanes and the isolation and nmr characterization of some of the individual stereoisomeric trimers, **1** and **2**, and tetramers, **3**–**6** (Chart I).

## Results

Hydrolysis of methyl(2-thienyl)- and methyl(2-furyl)dichlorosilane in aqueous potassium carbonate or potassium bicarbonate solution produced a crude hydrolysate from which the corresponding cyclosiloxanes could be distilled in 46–49% yield. The distillation residue consisted of a brittle resin typical of a cross-linked silicone polymer. Fractional distillation of the cyclosiloxane mixtures afforded the cyclic trimers, tetramers, and pentamer, listed in Table I, together with their physical and analytical data. In the absence of an acid acceptor, hydrolysis of methyl(2-thienyl)-dichlorosilane gave hydrolysate which polymerized to a rubbery polymer upon attempted distillation; thiophene was the only volatile product isolated. In an effort to equilibrate siloxane linkages, distillation of the rubbery polymer over potassium hydroxide was attempted. The only volatile product which could be isolated was methyltris(2-thienyl)silane, identified by elemental, infrared, and nmr analyses. Hydrolysis of methyl(2-thienyl)dichlorosilane in the presence of excess potassium carbonate, followed by distillation of the hydrolysate without prior neutralization, gave a 25% yield of volatiles, the remainder of the product being an intractable polymer. The distillate consisted predominantly of methyltris(2-thienyl)silane and a product tentatively identified as 1,3-dimethyl-1,1,3,3-tetrakis(2-thienyl)disiloxane.

The nmr spectra of the cyclic trimers, tetramers, and pentamer listed in Table I were in agreement with theory, giving a ratio of methyl to ring protons of 1:1. The structures also were confirmed by the infrared spectra, with characteristic[3] Si–O–Si stretching bands noted at 1020 cm$^{-1}$ for the trimers and 1075 cm$^{-1}$ for the tetramers and pentamer.

The cyclotrisiloxane fraction in both the methyl(2-thienyl)- and methyl(2-furyl) series exhibited three methyl proton singlets, see Table II, expected for a mixture of isomers **1** and **2** having the *cis* and *trans*

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[1] J. F. Hyde and R. C. DeLong, *J. Am. Chem. Soc.*, **63**, 1194 (1941).

[2] R. N. Lewis, *ibid.*, **70**, 1115 (1948).

[3] C. W. Young, P. C. Servais, C. C. Currie, and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

[4] C. B. Moore and H. A. Dewhurst, *J. Org. Chem.*, **27**, 693 (1962).

[5] H. J. Hickton, A. Holt, J. Homer, and A. W. Jarvie, *J. Chem. Soc., Sect. C*, 149 (1966).

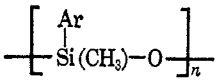
[6] E. D. Pierron, C. F. Hobbs, D. L. Parker, and D. J. Bauer, *J. Heterocyclic Chem.*, **3**, 533 (1966).

[7] P. D. George, U. S. Patent 2,640,818 (June 2, 1953); *Chem. Abstr.*, **47**, 9055 (1953).

[8] K. Olsson and C. Axen, *Arkiv Kemi*, **22**, 237 (1964).

TABLE I

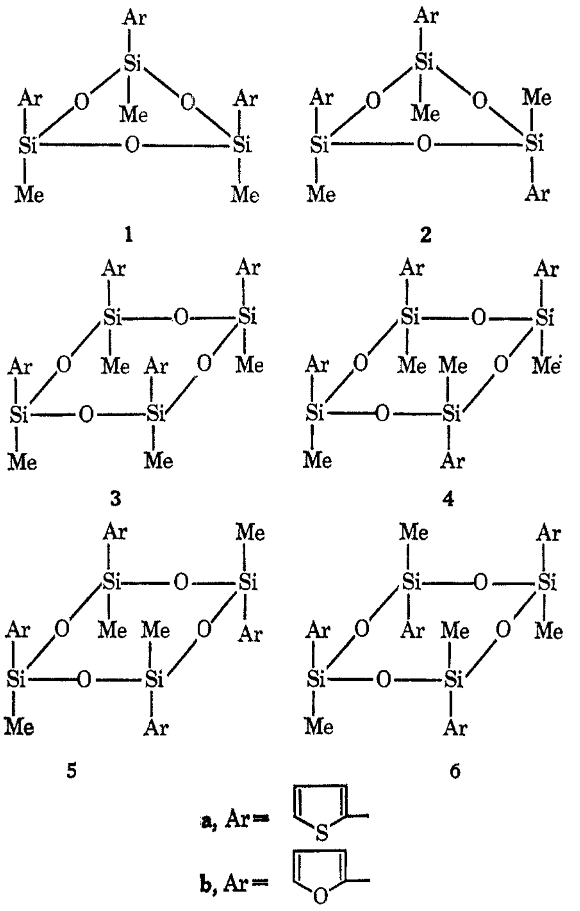
ANALYTICAL AND PHYSICAL DATA OF METHYL(2-THIENYL)- AND METHYL(2-FURYL)CYCLOPOLYSILOXANES



$$\left[\begin{array}{c}\text{Ar}\\ | \\ -\text{Si}(\text{CH}_3)-\text{O}-\end{array}\right]_n$$

| Ar | $n$ | Bp (mm), °C | $n^{25}\text{D}$ | Calcd C, % | Calcd H, % | Calcd Si, % | Calcd Mol wt | Found C, % | Found H, % | Found Si, % | Found Mol wt |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Thienyl | 3 | 141–145 (0.08) | 1.5549 | 42.21 | 4.25 | 19.75 | 427 | 42.14 | 3.92 | 19.75 | 422 |
| 2-Thienyl | 4 | 200–202 (0.13) | 1.5599 | 42.21 | 4.25 | 19.75 | 569 | 42.12 | 4.13 | 19.83 | 563 |
| 2-Thienyl | 5 | 233–235 (0.12–0.20) | 1.5638 | 42.21 | 4.25 | 19.75 | 711 | 42.49 | 4.46 | 20.21 | 740 |
| 2-Furyl | 3 | 108 (0.15) | 1.4915 | 47.59 | 4.79 | 22.26 | 379 | 47.50 | 4.59 | 22.15 | 370 |
| 2-Furyl | 4 | 137 (0.10) | 1.4968 | 47.59 | 4.79 | 22.26 | 505 | 47.80 | 4.79 | 22.37 | 491 |

CHART I



configuration, respectively. The ratio of **1** to **2** was approximately 1:3 in each series. In each series the *trans* isomer **2** was isolated and confirmed by methyl proton chemical-shift assignments. The *trans* assignment in the 2-thienyl series was further substantiated by infrared analysis which showed absorption at 784 cm$^{-1}$ for the *trans* compound compared with absorption at 777 and 784 cm$^{-1}$ for the *cis–trans* mixture.[3]

TABLE II

METHYL PROTON NMR CHEMICAL-SHIFT DATA FOR METHYLARYLCYCLOPOLYSILOXANES

| Isomer | Methyl positions | Environment[a] | Chemical shift, δ, ppm 2-Thienyl | 2-Furyl | Phenyl[b] |
|---|---|---|---|---|---|
| **1** | 2,4,6 | $2\alpha'$ | −0.55 | −0.50 | −0.52 |
| **2** | 2,4 | $\alpha + \alpha'$ | −0.52 | −0.48 | −0.44 |
|  | 6′ | $2\alpha$ | −0.50 | −0.44 | −0.38 |
| **3** | 2,4,6,8 | $2\alpha' + \beta'$ | −0.53 | −0.46 | −0.51 |
| **4** | 4 | $2\alpha' + \beta$ | −0.48 | −0.42 | −0.43 |
|  | 2,6 | $\alpha + \alpha' + \beta'$ | −0.46 | −0.39 | −0.42 |
|  | 8′ | $2\alpha + \beta$ | −0.34 | −0.29 | −0.20 |
| **5** | 2,4,6′,8′ | $\alpha + \alpha' + \beta$ | −0.41 | −0.35 | −0.32 |
| **6** | 2,4′,6,8′ | $2\alpha + \beta'$ | −0.38 | −0.31 | −0.30 |

[a] After ref 5. Aryl substituents on adjacent and distant silicon atoms are designated α and β. A prime refers to aryl substituents *trans* to the methyl group being considered. [b] See ref 6.

The methyl(2-thienyl)- and methyl(2-furyl)cyclotetrasiloxanes each exhibited six methyl proton singlets, consistent with a mixture of the four stereoisomers **3–6**. Based on the peak assignments shown in Table II, the isomer ratio **3**:**4**:**5**:**6**: was 1:5.7:3.5:1 for the 2-thienyl- and 1.3:4.1:1.7:1 for the 2-furyl-substituted tetramer. Analysis of various distillation fractions of methyl-(2-thienyl)cyclotetrasiloxane demonstrated that the singlet at δ −0.53 belonged to a single isomer, since this peak was absent in some fractions, and that the intensities of the peaks at δ −0.48, −0.46, and −0.34 were always in the ratio of 1:2:1. A crystalline isomer, mp 97.5–98.5°, was isolated from the mixture and was shown to be responsible for the peak at δ −0.38. Similarly, in the methyl(2-furyl) tetramer, the ratio of peak intensities at δ −0.42, −0.39, and −0.29 was shown to be 1:2:1. Further, the peak at δ −0.31 was identified with a crystalline isomer, mp 94–98°, isolated from the tetramer mixture.

## Discussion

The relatively low yields of cyclosiloxanes and large amounts of cross-linked polymer obtained in the hydrolysis of methyl(2-thienyl)- and methyl(2-furyl)dichlorosilanes reflects the ease with which 2-thienyl and 2-furyl substituents undergo acid-catalyzed cleavage from silicon. In the absence of an acid acceptor, cleavage of thienyl groups and subsequent cross-linking is sufficiently extensive that no cyclosiloxanes can be isolated. Under these same conditions, phenyl groups undergo little or no cleavage and excellent yields of the methylphenylcyclosiloxanes are obtained.[2] The facile acid cleavage of 2-thienyl- and 2-furyl-substituted siloxanes thus parallels that observed for the 2-thienyl-[9–11] and 2-furylsilanes.[11]

In an attempt to circumvent acid cleavage and enhance the yield of methyl(2-thienyl)cyclosiloxanes, the hydrolysis of the dichlorosilane was carried out in the presence of excess alkali and the product subjected to distillation without prior neutralization of the silanolate salts. The major products were methyltris(2-thienyl)-silane and 1,3-dimethyl-1,1,3,3-tetrakis(2-thienyl)-disiloxane, indicating that redistribution of 2-thienyl–silicon and oxygen–silicon bonds had taken place. A

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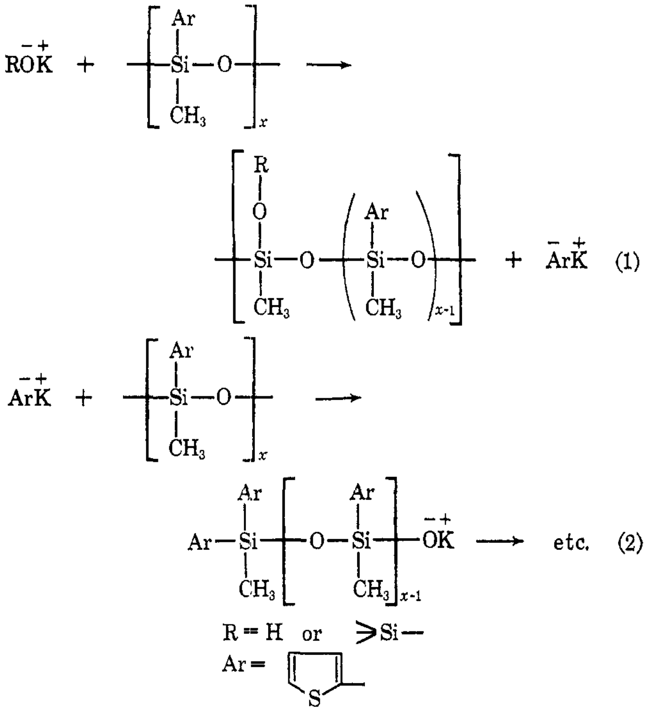
(9) R. H. Meen and H. Gilman, *J. Org. Chem.*, **20**, 73 (1955).
(10) F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 2303 (1959).
(11) C. Eaborn and J. A. Sperri, *ibid.*, 4921 (1961).

similar redistribution also occurred upon distillation of the methyl(2-thienyl)-substituted siloxane polymer over solid potassium hydroxide to give methyltris(2-thienyl)silane. This redistribution reaction is entirely analogous to that observed for methylphenylcyclosiloxanes[12] and can be most simply viewed as occurring by nucleophilic displacement of thiophene by hydroxide or silanolate anion (eq 1), with displacement of siloxy groups by the thienyl anion to give products containing more than one thiophene nucleus per silicon atom (eq 2). Consecutive repetition of this reaction sequence eventually leads to molecules sufficiently small to distil out of the mixture, leaving behind a cross-linked silicone resin. Facile base-catalyzed cleavage of 2-thienyl–silicon bonds in silanes has been observed[9] and opening of siloxane linkages by organometallic reagents is well established.[13]



Nuclear magnetic resonance spectroscopy proved to be a valuable tool for characterizing mixtures of methyl(2-thienyl)- and methyl(2-furyl)cyclosiloxanes as well as individual stereoisomers once the chemical shifts were properly assigned. Previous work[5] on the stereoisomers of methylphenylcyclosiloxanes showed that the chemical shifts of the methyl protons could be estimated from environmental effects. A similar technique was applied to the 2-thienyl and 2-furyl analogs to obtain the assignments given in Table II.

The assignments for the cyclic trimers can be made with certainty since the *trans* isomer (**2**) in each series was isolated and chemical shifts were assigned on the basis of relative intensity. For the cyclic tetramers, the three peaks due to the methyl protons of isomer **4** can be distinguished since their relative ratio remains constant as the composition of the tetramer mixture varies, the shift due to methyl groups in the 2 and 6 positions being assigned on the basis of relative intensity. The remainder of the shifts may then be assigned by comparing the effect of environmental changes in the phenyl series with that in the 2-thienyl and 2-furyl series. Thus, in the phenyl-substituted trimers, the effect of inverting a phenyl group from the *trans* to the *cis* configuration relative to the methyl group, represented by $\alpha - \alpha'$, is found to be about +0.07 ppm from the data in Table II. In the phenyl-substituted tetramers, this $\alpha - \alpha'$ effect is about +0.11 ppm or +0.04 ppm greater than in the trimers. For the 2-thienyl- and 2-furyl-substituted trimers, $\alpha - \alpha'$ is about +0.03 ppm. By analogy to the phenyl series, this would be expected to be about 0.04 ppm greater in the tetramers, or +0.07 ppm. The environment of the methyl groups in isomers **3** and **6** is related to that of the 2,6-methyl group in isomer **4** by $-\alpha + \alpha'$ and $\alpha - \alpha'$, respectively. Hence, the shifts for isomers **3** and **6** should appear at −0.07 and +0.07 ppm, respectively, from that of the 2,6-methyl groups in isomer **4**. Taking the 2-thienyl-substituted tetramers as an example, calculation of the shifts for isomers **3a** and **6a** gives $\delta$ −0.53 and −0.39, respectively, in good agreement with the observed shifts. Furthermore, the methyl groups in the 4 and 8′ positions of isomer **4a** are related by a $2\alpha - 2\alpha'$ effect. This is in agreement with the shifts $\delta$ −0.48 and −0.34 assigned to the methyl groups in these positions on the basis of the observation that the intensity ratio of these peaks remained constant as the composition of the tetramer mixture varied. The remaining peak, $\delta$ −0.41, must be assigned to isomer **5a**. Proof for this assignment is obtained by comparing the shift for isomer **5a** with those for the 4 and 8′ positions of isomer **4a**, which are related by an $\alpha - \alpha'$ and a $-\alpha + \alpha'$ effect, respectively. Inspection of the data in Table II shows that the shifts in the 2-furyl series can be rationalized in exactly the same manner. Furthermore, the $\beta - \beta'$ effect can be calculated and is internally consistent in each of the series. For the phenyl series, $\beta - \beta'$ is +0.08 ppm, for the 2-thienyl series, +0.05 ppm, and for the 2-furyl series, +0.04 ppm.

Identification of the crystalline methyl(2-thienyl)- and methyl(2-furyl)cyclotetrasiloxanes isolated from the respective tetramer mixtures followed from their nmr spectra. The methyl proton shift for the crystalline methyl(2-thienyl)cyclotetrasiloxane appeared at $\delta$ −0.37, which was shown by spiking experiments to shift to $\delta$ −0.38 in the tetramer mixture. This crystalline isomer therefore was isomer **6a**. For the crystalline methyl(2-furyl)-substituted tetramer, the shift appeared at $\delta$ −0.31, corresponding to isomer **6b**.

The isomer ratio **1**:**2** in the cyclotrisiloxanes was determined by nmr spectroscopy to be 1:3.5 and 1:3.2 for the 2-thienyl and 2-furyl series, respectively. This ratio is within experimental error of the ratio of 1:3 expected for random distribution when it is considered that preferential, mechanical losses probably occurred during distillation. For the cyclotetrasiloxanes, the isomer ratio **3**:**4**:**5**:**6**: was 1:5.7:3.5:1 for the 2-thienyl series and 1.3:4.1:1.7:1 for the 2-furyl series; random distribution requires 1:4:2:1. Again, the differences between the observed and random distributions are probably the result of preferential distillation losses.

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[12] E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter, and A. J. Barry, *J. Am. Chem. Soc.*, **81**, 1256 (1959).

[13] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, p 268.

## Experimental Section[14]

**Methyl(2-thienyl)dichlorosilane.**[15]—Methyl(2-thienyl)dichlorosilane was prepared in 63–73% yield by reaction of 2-thienylmagnesium bromide with excess methyltrichlorosilane following the method of George.[16] The product had bp 88–89° (20 mm), $n^{25}_{D}$ 1.5263, neut equiv 97.0 (calcd 98.6). Vapor phase chromatography indicated a purity of 93%. The nmr spectrum had peaks at $\delta$ −0.89 (singlet, -SiCH$_3$), −7.1 (multiplet), and −7.5 (multiplet) in the proton ratio of 3:1:2, respectively.

**Methyl(2-furyl)dichlorosilane.**[15]—A 15% solution of butyllithium (3410 g, 8.0 moles) in hexane (Foote Mineral Co.) was concentrated under vacuum (3700 ml of hexane removed) and then diluted with 2000 ml of anhydrous ether. To this solution, cooled to −50° by means of a solid carbon dioxide bath, was added 544 g (8.0 moles) of furan dissolved in 1500 ml of ether. Stirring was continued and the temperature of the solution was allowed to rise slowly. At 0°, a mild exothermic reaction occurred, causing the temperature to rise to 25°. The mixture then was stirred for a total of 7 hr while maintaining a temperature of 20–25° with external cooling and then was allowed to stand overnight. The resulting slurry was added over a period of 2 hr to a solution of 1800 g (12.0 moles) of methyltrichlorosilane in 4000 ml of ether at −20 to −30°. The mixture was stirred at −30 to −15° for 4.5 hr and then was allowed to warm to room temperature and stand overnight. The mixture was filtered, the solvent removed under vacuum, and the residue distilled to obtain 357 g (24%) of crude product, bp 30–67° (25 mm). Redistillation through a 3-ft, glass helices packed column afforded methyl(2-furyl)dichlorosilane: bp 64–65° (25 mm); $n^{25}_{D}$ 1.4753–1.4757; neut equiv 92.7 (calcd 90.5). The purity was estimated to be 96% by vapor phase chromatography. The nmr spectrum had a singlet at $\delta$ −0.90 (-CH$_3$), two doublets at $\delta$ −6.36 (H$_4$, $J_{3-4}$ = 3.6 cps, $J_{4-5}$ = 1.8 cps[17]), a doublet at $\delta$ −7.0 (H$_3$, $J_{3-4}$ = 3.6 cps[17]), and a doublet at $\delta$ −7.62 (H$_5$, $J_{4-5}$ = 1.8 cps[17]).

**Hydrolysis of Methyl(2-thienyl)dichlorosilane. A. Acidic Conditions.**—A solution of 207.5 g (1.05 moles) of methyl(2-thienyl)dichlorosilane in 200 ml of ether was added dropwise over a 70-min period to 200 ml of water while maintaining the temperature of the reaction mixture at 5–10°. The mixture was separated and the ether solution was washed with saturated sodium bicarbonate solution and then dried over magnesium sulfate. The ether was removed by distillation at reduced pressure to give an oil, the infrared spectrum of which showed weak to moderate absorption at 3690 cm$^{-1}$, indicative of free silanol OH,[3] in addition to a strong Si-O-Si band at 1000–1100 cm$^{-1}$. Upon attempted distillation, the oily product became increasingly viscous and finally gelled at a pot temperature of 260° at 0.3 mm. About 5 g of material, $n^{25}_{D}$ 1.5238, with the characteristic odor of thiophene was recovered from the cold trap. In an attempt to depolymerize the material remaining in the pot, it was triturated with 0.1 g of powdered potassium hydroxide in ether, the ether was removed by distillation, and the rubbery residue was heated to 200° (0.35 mm) for 2.5 hr. The material remained as a rubbery gel. The gel was extracted with ether, the ether removed by distillation at reduced pressure, and the resulting oil distilled through a 14-in. Vigreux column to give 16.5 g (16% yield, based on thiophene groups) of material: bp 133–145° (0.10 mm); $n^{25}_{D}$ 1.6328. The infrared spectrumi ndicated the presence of methyl groups attached to silicon (1258 and 785 cm$^{-1}$)[3] and substituted thiophene groups (3040, 3060, 1550–1800, 1500, and 715 cm$^{-1}$).[18] The nmr spectrum exhibited a methyl proton singlet at $\delta$ −0.86 ($J_{\mathrm{Si}^{29}-\mathrm{H}^{1}}$ = 7 cps) and thiophene ring proton multiplets centered at $\delta$ −7.0 and −7.4 in the proton ratio of 1:1:2, respectively. The nmr and infrared data and elemental analysis were consistent with methyltris(2-thienyl)silane.

*Anal.* Calcd for $C_{13}H_{12}S_3Si$: C, 53.37; H, 4.14; mol wt, 292.5. Found: C, 53.46; H, 4.28; mol wt, 292 (mass spectroscopy).

**B. Basic Conditions.**—To a solution of 201.6 g (1.46 moles) of potassium carbonate in 600 ml of water was added dropwise with vigorous stirring over a period of 95 min a cold solution of 287.8 g (1.46 moles) of methyl(2-thienyl)dichlorosilane in 500 ml of ether. The reaction mixture was maintained at 5–10° during the addition of the chlorosilane and for an additional 3 hr; it then was allowed to warm to 20° with stirring for 1 hr. The mixture was separated, the aqueous layer extracted with ether, and the combined ether solutions stripped of ether at reduced pressure to a pot temperature of 60° (30 mm), leaving a white solid residue. The infrared spectrum of the solid exhibited a broad band of strong intensity centered at ~3300 cm$^{-1}$ indicative of associated silanol OH,[3] in addition to bands at 1040–1100 cm$^{-1}$, suggesting a lower degree of condensation than that obtained under acidic conditions.

The solid material was heated to 280° under vacuum, water was evolved, and the material became fluid. The resulting liquid was distilled through a 14-in. Vigreux column to obtain 96.0 g (46% yield) of material boiling up to 250° (15 mm); the pot residue was a hard, brittle resin.

The distillates from several such runs were combined and carefully fractionally distilled through a 3-ft. Todd Vigreux column to obtain 2,4,6-trimethyl-2,4,6-tris(2-thienyl)cyclotrisiloxane, 2,4,6,8-tetramethyl-2,4,6,8-tetrakis(2-thienyl)cyclotetrasiloxane, and 2,4,6,8,10-pentamethyl-2,4,6,8,10-pentakis(2-thienyl)cyclopentasiloxane. The physical properties and analytical data for these materials are summarized in Table I. The nmr data for the trimer and tetramer fractions are given in Table II; the pentamer fraction had six methyl proton singlets at $\delta$ −0.51, −0.48, −0.43, −0.42, −0.32, and −0.17. The infrared spectra showed characteristic absorption at 1260 (Si-CH$_3$),[3] 1220 and 1087 (thienyl),[18] and 784 cm$^{-1}$. The trimer fraction also exhibited absorbance at 777 and a Si-O-Si stretching band at 1020 cm$^{-1}$; the latter was shifted to 1075 cm$^{-1}$ in the tetramer and pentamer fractions.

When the hydrolysis of methyl(2-thienyl)dichlorosilane was carried out in the presence of excess potassium carbonate and the excess base was not neutralized, the yield of distillate was lower, more resinous pot residue was formed (~75%), and the resulting distillate contained, in addition to the cyclic trimer, tetramer, and pentamer, two new materials, bp 136–138° (0.35 mm), $n^{25}_{D}$ 1.6226, and bp 175–182° (0.03 mm), $n^{25}_{D}$ 1.5957. The product, bp 136–138° (0.35 mm), was identified as methyltris(2-thienyl)silane on the basis of its nmr and infrared spectra and vpc retention time which were identical with those of methyltris(2-thienyl)silane obtained by the potassium hydroxide catalyzed rearrangment of methyl(2-thienyl)cyclosiloxanes except for additional small impurity peaks at $\delta$ −0.1 to −0.7 in the nmr and at 1275 cm$^{-1}$ in the infrared. The higher boiling product, bp 175–182° (0.03 mm), contained 10–15% of close-boiling impurities which could not be removed by fractional distillation or preparative scale vapor phase chromatography. Although a satisfactory elemental analysis could not be obtained, the material was tentatively identified as 1,3-dimethyl-1,1,3,3-tetrakis-(2-thienyl)disiloxane on the basis of its infrared and nmr spectra. Characteristic bands were observed at 1259 (Si-CH$_3$),[3] 1218 (thienyl),[18] 1087 and 1069 (Si-O-Si),[3] and 780 cm$^{-1}$ (Si-CH$_3$ or monosubstituted thiophene). The infrared spectrum was similar to that of the methyl(2-thienyl)cyclotetrasiloxanes except that the relative intensities of the bands at 1259, 1218, 1087, and 1069 cm$^{-1}$ varied in a way consistent with the expected differences in the ratio of thiophene, methyl, and siloxane groups. The nmr spectrum exhibited methyl proton resonance at $\delta$ −0.66 (singlet, $J_{\mathrm{Si}^{29}-\mathrm{H}^{1}}$ = 7.5 cps) and aromatic proton resonance at $\delta$ −7.03 (2 doublets, $J$ = 3.4 and 4.5 cps), −7.30 (2 doublets, $J$ = 1.0 and 3.4 cps), and −7.46 (2 doublets, $J$ = 4.5 and 1.0 cps) corresponding to protons at the 4, 3, and 5 positions of the thiophene ring, respectively.[17] The ratio of methyl to thienyl

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[14] Melting points were determined on a Reichert hot-stage melting point apparatus and are corrected. Boiling points are uncorrected. All infrared spectra were recorded neat and as dilute solutions (approximately 1–2%) in carbon disulfide on a Beckman IR-5 spectrophotometer. All nmr spectra were recorded on a Varian A-60 nmr spectrophotometer in carbon tetrachloride with tetramethylsilane ($\delta$ 0.00 ppm) as internal standard. A concentration of 30–33% (v/v for liquids and wt/v for solids) was employed. The chemical shifts of singlets were measured at peak half-heights. Molecular weights were determined osmometrically in benzene unless otherwise indicated. Vapor phase chromatograms were obtained on a 21 ft × 0.25 in. column, 12% Dow Corning high vacuum silicone grease on 45–50 mesh Chromosorb P.

[15] We are grateful to Dr. E. S. Blake and Mr. J. A. Webster of Monsanto Research Corp. for the preparation of this material.

[16] P. D. George, U. S. Patent 2,640,833 (June 2, 1953); *Chem. Abstr.*, **48**, 5227 (1954).

[17] R. F. M. White in "Physical Methods in Heterocyclic Chemistry," Vol. II, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, pp 114–128.

[18] A. R. Katritzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry, Vol. II, A. R. Katritzky, Ed., Academic Press Inc., New York, N. Y., 1963, pp 199–207.

protons was 6:13 (calcd 6:12). Several small impurity peaks at $\delta$ −0.05 to −0.55 were noted.

**2,4,6′-Trimethyl-2′,4′,6-tris(2-thienyl)cyclotrisiloxane** (**2a**).—Careful fractional distillation of the cyclotrisiloxane fraction from above afforded a pure sample of the higher boiling isomer: bp 145° (0.08 mm); $n^{25}_{D}$ 1.5544; mp 37–38° (from nitromethane). The nmr spectrum exhibited two methyl proton singlets at $\delta$ −0.52 and −0.50 in the ratio of 2:1; the ratio of thienyl to methyl protons was 1:1. Characteristic bands in the infrared spectrum were noted at 1260 (Si–CH$_3$),[3] 1220 and 1087 (thienyl),[18] 1020 (Si–O–Si, trimer),[3] and 784 cm$^{-1}$ (*trans* trimer).[3]

**2,4′,6,8′-Tetramethyl-2′,4,6′,8-tetrakis(2-thienyl)cyclotetrasiloxane** (**6a**).—The cyclotetrasiloxane mixture was fractionally distilled. Upon standing, the higher boiling fractions deposited a crystalline isomer, mp 97.5–98.5° (from methanol). The nmr spectrum of this isomer consisted of a sharp methyl proton singlet at $\delta$ −0.37, in addition to two doublets at $\delta$ −7.09 ($J$ = 3.4 and 4.6 cps), two doublets at $\delta$ −7.34 ($J$ = 1.0 and 3.4 cps), and two doublets at $\delta$ −7.51 ($J$ = 1.0 and 4.6 cps) corresponding to ring protons at the 4, 3, and 5 positions, respectively.[17] The ratio of methyl to thienyl protons was 1:1. Spiking experiments demonstated that the methyl proton peak was shifted to $\delta$ −0.38 in the tetramer mixture. The isomer was assigned the structure of **6a**, 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetrakis(2-thienyl)-cyclotetrasiloxane. No other crystalline isomers could be obtained from the tetramer mixture.

**Hydrolysis of Methyl(2-furyl)dichlorisilane.**—To a solution of 200.2 g (2.0 moles) of potassium bicarbonate in 500 ml of water was added over a 1-hr period a solution of 90.5 g (0.5 mole) of methyl(2-furyl)dichlorosilane in 150 ml of ether. The mixture was stirred vigorously at 5–10° while the ethereal solution of methyl(2-furyl)dichlorosilane was introduced below the surface of the aqueous solution by means of a filter tube extending to the bottom of the reaction flask. The mixture then was allowed to warm to room temperature and stand overnight. The organic layer was separated, treated with 5% acetic acid solution to acidify any silanolate salts present, and then washed with water until the washings had a constant pH of 6 (indicator paper). The ether was removed under reduced pressure and the residue distilled up to a pot temperature of 300°[19] to obtain 30.9 g (49%) of mixed methyl(2-furyl)cyclopolysiloxanes, bp 100–210° (0.35 mm). The pot residue consisted of a brittle resin. The crude product from two such runs was combined and fractionally distilled to obtain 2,4,6-trimethyl-2,4,6-tris(2-furyl)cyclotrisiloxane and 2,4,6,8-tetramethyl-2,4,6,8-tetrakis(2-furyl)cyclotetrasiloxane; vapor phase chromatography indicated purities of 98 and 99%, respectively. Analytical and physical property data are listed in Table I. A higher boiling fraction, bp 170–171° (0.15 mm), believed to be the cyclic pentamer, was not isolated in sufficient quantity or purity to permit accurate analysis. The infrared spectra of the trimer and tetramer fraction exhibited characteristic bands at 1270, 785 and 745 (Si–CH$_3$),[3] and 1205, 1125, and 1010 cm$^{-1}$ (furyl);[18] Si–O–Si absorption at 1020 cm$^{-1}$ in the trimer fraction was shifted to 1090 cm$^{-1}$ in the tetramer fraction.

**2,4,6′-Trimethyl-2′,4′,6-tris(2-furyl)cyclotrisiloxane** (**2b**).—Upon standing, the cyclotrisiloxane mixture deposited crystals, mp 47–48° (from nitromethane). The nmr spectrum of this crystalline isomer showed methyl proton resonance at $\delta$ −0.48 and −0.45 in the ratio of 2:1 and the compound was assigned the structure of 2,4,6′-trimethyl-2′,4′,6-tris(2-thienyl)cyclotrisiloxane, isomer **2b**.

**2,4′,6,8′-Tetramethyl-2′,4,6′,8-tetrakis(2-furyl)cyclotetrasiloxane** (**6b**).—The cyclotetrasiloxane mixture, upon standing for several months, deposited a crystalline isomer, mp 94–98° (from methanol). Based on its nmr spectrum (sharp methyl proton singlet at $\delta$ −0.31), the crystalline isomer was identified as 2,4′,6,8′-tetramethyl-2′,4,6′,8-tetrakis(2-furyl)cyclotetrasiloxane (**6b**).

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[19] When the reaction was repeated on a 5-mole scale and distillation of the product attempted, a strongly exothermic reaction, accompanied by violent gas evolution and carbonization of the pot residue, occurred at 260–280°.

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# Reductions in the 7-Substituted Norbornadienyl System. A Synthesis of *syn*-7-Substituted Norbornenes[1]

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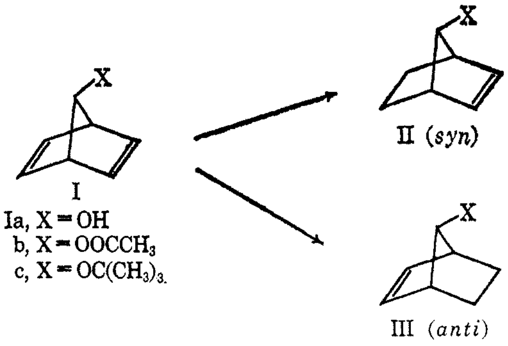
Catalytic reduction of 7-substituted norbornadienes yields primarily the *syn* product. The ratio of *syn/anti* product (with a fixed 7 substituent) is strongly dependent on the type of catalyst used for reduction. Thus, the *syn/anti* product ratio varies from a low of 1.2/1 with a Pd–C catalyst to essentially an infinite ratio (no detectable *anti* isomer) with the use of a platinum catalyst. Isolation of *syn*-7-acetoxynorbornene from both 7-acetoxynorbornane and a small amount of *anti*-7-acetoxynorbornene is readily accomplished by complexation of the *syn* isomer with Ag$^+$. This separation is aided by a high ratio of complexation constants of *syn*-acetate/*anti*-acetate, ≅ 11/1. This synthesis of the *syn*-acetate from 7-acetoxynorbornadiene, coupled with a previous synthesis of the *anti* isomer, leads to both *syn*- and *anti*-norbornenyl derivatives from a common precursor.

As part of a continuing study of the chemistry of 7-substituted norbornadienes and norbornenes, convenient syntheses for the *syn* and *anti* isomers of the latter compounds were desired. Potential routes to these structures appeared to be the specific reduction of either the *anti* or the *syn* double bond of the corresponding norbornadienes[2] (eq 1) by means of the properly selected chemical or catalytic reducing system. In a previous publication, the reduction of 7-substituted norbornadienes (Ia–c) by the chemical reducing agent, diimide (N$_2$H$_2$), to yield *anti*-7-substituted norbornenes (IIIa–c) as the exclusive norbornene product has been reported.[3] This paper describes the preparation of the *syn*-7 isomers (IIa–c) by the hydrogenation of these dienes in the presence of transition metal catalysts.



I

Ia, X = OH
b, X = OOCCH$_3$
c, X = OC(CH$_3$)$_3$

II (*syn*)

III (*anti*)

(1)

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[1] Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p O-10.

[2] These compounds may be readily prepared according to published synthetic procedures: P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

[3] W. C. Baird, Jr., B. Franzus, and J. H. Surridge, *J. Am. Chem. Soc.*, **89**, 410 (1967).