6-, 7- and 8-Methyl-5,6,7,8-tetrahydro-3,4-benzocarbazoles (Ib, Ic, Id). The 6- and 7-methyl derivatives were prepared from 4-methyl- and 3-methylcyclohexanone respectively, as described above for Ia. The 8-methyl isomer (Id) was synthesized by the method of Bryant and Plant.[19]

Proof of structure of Ic. *4-Methyl-2-(2-naphthylamino)-cyclohexanone.* (VI). A mixture of 14.8 g. (0.100 mole) of 2-chloro-4-methylcyclohexanone,[17] 14.4 g. (0.100 mole) of 2-naphthylamine, 2.6 g. (0.020 mole) of quinoline, 20 g. of anhydrous sodium carbonate and 75 ml. of cellosolve were heated and stirred under reflux for 1 hr. The cooled reaction mixture was filtered and the solid material washed with a little methanol. Solvent was removed at reduced pressure and the residual slurry diluted with an equal volume of methanol and allowed to stand overnight. Filtration and washing with cold methanol provided 8.8 g. (35%) of 4-methyl-2-(2-naphthylamino)cyclohexanone, m.p. 116–117°. Crystallization from cyclohexane gave colorless crystals of unchanged melting point.

Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.75; H, 7.54; N, 5.65.

7-Methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole (Ic). A solution of 5.00 g. (0.0198 mole) of 4-methyl-2-(2-naphthylamino)cyclohexanone in 100 ml. of 20% absolute ethanolic zinc chloride was refluxed for 18 hr. under nitrogen. The cooled, deep red solution was poured into a mechanically stirred mixture of 150 ml. of concentrated hydrochloric acid and 350 ml. of ice. Filtration, washing with dilute hydrochloric acid and water and drying *in vacuo* gave 4.56 g. of crude product, m.p. 128–135°. Decolorization with Norit and crystallization from ethanol provided 3.51 g. (76%) of colorless needles, m.p. 136.5–138°. A second crystallization raised the melting point to 137–138°. A mixed melting point with a sample prepared as described above showed no depression and the infrared spectra were identical.

The *9-methyl derivatives* (IIa–IId) were prepared by methylation of Ia–Id with methyl iodide in acetone in the presence of concentrated alkali.[9]

Dehydrogenation was carried out as follows: The tetrahydro compound (2 g.), 30% palladium on carbon (0.8 g.) and 25 ml. of xylene were heated at vigorous reflux for 8 to 48 hr. The cooled reaction mixture (diluted with ethyl acetate, when necessary to dissolve precipitated product) was then filtered and evaporated to a thick slurry by heating on the steam bath in a stream of air. The slurry was diluted with hexane, filtered, and crystallized from methanol.

8,9-Dimethyl-3,4-benzocarbazole (IVd) was obtained in impure form by the above treatment. A second dehydrogenation, using *p*-cymene as solvent, followed by crystallization from an ethanol-ethyl acetate mixture gave pure IVd.

BLOOMINGTON, IND.

---

[19] S. A. Bryant and S. G. P. Plant, *J. Chem. Soc.*, 93 (1931).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Studies in Organosilicon Chemistry. XXXV. Preparation of Certain Olefinic and Alkylsilanes

LEONARD D. NASIAK AND HOWARD W. POST

Received October 8, 1958

Several olefinic silanes have been prepared from appropriate Grignard reagents and their infrared spectra are recorded. Hexamethylbis(1,5-chloromethyl)trisiloxane and dimethylallylethoxysilane have also been prepared.

By the action of allylmagnesium bromide on the appropriate chlorosilane, dimethyldiallylsilane, methylphenyldiallylsilane, and diphenyldiallylsilane have been prepared. Similarly, from β methallylmagnesium chloride, dimethylbis(β-methallyl)-silane, methylphenylbis(β-methallyl)silane, and diphenylbis(β-methallyl)silane have been prepared. Cohydrolysis of one molar part of dimethyldichlorosilane and two of dimethylchloromethylchlorosilane yielded hexamethylbis(1,5 - chloromethyl)trisiloxane. Dimethylallylethoxysilane has been prepared by the action of allylmagnesium bromide on dimethyldiethoxysilane. Infrared absorption curves are presented for the first three compounds above.

Discussion. The compounds herein described were needed for the carrying out of certain experiments in the formation of polymeric silicon compounds containing sulfur and reported elsewhere in this journal.[1] In general, the principles involved are not novel, but certain modifications in procedure have been developed which are deemed of value. These modifications are based on procedures already in the literature.[2–9] Two compounds are

---

(1) L. D. Nasiak and H. W. Post, *J. Org. Chem.*, **24**, 000 (1959).

(2) A. D. Petrov, V. F. Mironov, and V. G. Glukhotsev, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk,* 1123 (1954).

(3) A. D. Petrov and V. F. Mironov, *Doklady Akad. Nauk, S.S.S.R.*, **80**, 761 (1951).

(4) A. D. Petrov and G. I. Nikishin, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1128 (1952).

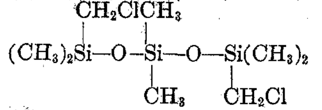
(5) A. D. Petrov and G. I. Nikishin, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 243 (1956).

(6) R. R. McGregor and E. L. Warrick, U. S. Patent **2,507,316** (1950).

(7) J. L. Speier, *J. Am. Chem. Soc.*, **71**, 273 (1949).

TABLE I

PHYSICAL PROPERTIES

Compound	B.P.	Mm.	n_D^{20}	Yield, %
$(CH_3)_2Si(CH_2CH{=}CH_2)_2$	135.0–136.0[b]	760	1.4402[c]	78.4
$CH_3Si(CH_2CH{=}CH_2)2C_6H_5$	123.5–124.4[d]	20.5	1.5221[e]	72.1
$(C_6H_5)_2Si(CH_2CH{=}CH_2)_2$	183.8–184.4[f]	16	1.5750[g]	66.4
$(CH_3)_2Si(CH_2C(CH_3){=}CH_2)_2$	71.0–71.6[h]	22	1.4538[i]	64.1
$CH_3Si(CH_2C(CH_3){=}CH_2)_2C_6H_5$[a]	142.8–143.1	20	1.5221	63.3
$(C_6H_5)2Si(CH_2C(CH_3){=}CH_2)_2$[a]	193.8–194.1	14.5	1.5693	59.8
 $\overset{CH_2Cl}{(CH_3)_2Si}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\underset{CH_2Cl}{Si(CH_3)_2}$	136–138[j]	40	1.4275[k]	21
$(CH_3)2Si(CH_2CH{=}CH_2)OC_2H_5$	123.0–123.4[l]	743	1.4020[m]	74.2

[a] New compound. [b] 135.5° (760 mm.),[2] 136.8° (759 mm.).[3] [c] 1.4420.[2,3] [d] 242° (770 mm.).[2] [e] 1.5220.[2] [f] 140.5 (2 mm.).[2] [g] 1.5750.[2] [h] 178.0–178.5° (760 mm.),[4] 176–179° (760 mm.).[5] [i] 1.4515,[4] 1.4556.[5] [j] 141.9° (40 mm.),[6] 142.0° (40 mm.).[7] [k] 1.4283.[6,7] [l] 122.6°–123.2° (743 mm.).[8,9] [m] 1.4080.[8,9]

herein reported for the first time, methylphenylbis(β-methallyl)silane and diphenylbis(β-methallyl)silane.

Infrared absorption curves have been determined for dimethyldiallylsilane, methylphenyldiallylsilane, and diphenyldiallylsilane. An analysis of the salient features of these curves will be found from the data listed in Table II.

TABLE II

INFRARED DATA (MICRONS)

		Bellamy[10]	Found
C=C	Stretching, no conjugation	6.0	6.1
$CH{=}CH_2CH$	Stretching	3.2	3.2
$CH{=}CH_2CH$	Deformation	10.0	10.6
$CH{=}CH_2CH_2$	Deformation (out of plane)	11.0	11.05
$CH{=}CH_2CH_2$	Deformation (in plane)	7.7	7.6
$Si(CH_3)_2$	Stretching	7.9, 12.3–12.5	7.9, 12.2–12.5
$SiCH_3$	Stretching	7.9, 12.3	7.9, 12.3
SiC_6H_5	Vibration	7.0, 8.9	6.9, 9.0

(10) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*," John Wiley & Sons, Inc., New York (1954).

EXPERIMENTAL

Dimethyldiallylsilane. Magnesium turnings (29.6 g., 1.22 moles) under 500 cc. of anhydrous ether in a 2-l. three necked flask equipped with a mercury stirrer, dropping funnel, and reflux condenser were treated, dropwise, with 180.2 g. (1.49 moles) of allyl bromide in 100 cc. of anhydrous ether under steady reflux. After total addition had been accomplished, the mixture was refluxed for an additional 30 min. Dimethyldichlorosilane (40.0 g., 0.31 mole) in 100 cc. of anhydrous ether was added to the above at a rate sufficient to maintain a steady reflux. After total addition the system was refluxed again for an additional 15 hr. It was then hydrolyzed by slow addition to a chilled 25% solution of ammonium chloride. The ethereal layer was washed with water, dried over calcium chloride, and fractionated yielding dimethyldiallylsilane, yield 78.4%, b.p. (lit.) 135.5° (760 mm.),[2] 136.8° (759 mm.),[3] (found) 135.0–136.0° (760 mm.); n_D^{20} (lit.) 1.4420,[2,3] (found) 1.4402.

Methylphenyldiallylsilane. In similar manner, 1.22 moles of magnesium turnings and 1.49 moles of allyl bromide reacted with 1.49 moles of methylphenyldichlorosilane yielding methylphenyldiallylsilane, yield 72.1%, b.p. (lit.) 242° (770 mm.),[2] (found) 123.5–124.4° (20.5 mm.); n_D^{20} (lit.) 1.5220,[2] (found) 1.5221.

Diphenyldiallylsilane. The above procedure was duplicated using 1.49 moles of diphenyldichlorosilane with the isolation of diphenyldiallylsilane, yield 66.4%, b.p. (lit.) 140.5° (2 mm.),[2] (found) 183.8–184.4° (16 mm.); n_D^{20} (lit.)[2] and (found) 1.5750.

Dimethylbis(β-methallyl)silane. Dimethyldichlorosilane (0.31 mole) reacted with 1.22 moles of β-methallylmagnesium chloride as described above, forming dimethylbis(β-methallyl)silane, yield 64.1%, b.p. (lit.) 178.0–178.5° (760 mm.),[4] 176–179° (760 mm.),[5] (found) 71.0–71.6° (22 mm.); n_D^{20} (lit.) 1.4515,[4] 1.4556,[5] (found) 1.4538.

Methylphenylbis(β-methallyl)silane. Methylphenyldichlorosilane (1.49 moles) was treated as above with the formation of methylphenylbis(β-methallyl)silane, yield 63.3%, b.p. 142.8–143.1° (20 mm.), n_D^{20} 1.5221.

Diphenylbis(β-methallyl)silane. In a similar manner, 1.49 moles of diphenyldichlorosilane reacted to form diphenylbis(β-methallyl)silane, yield 59.8%, b.p. 193.8–194.1° (14.5 mm.), n_D^{20} 1.5693.

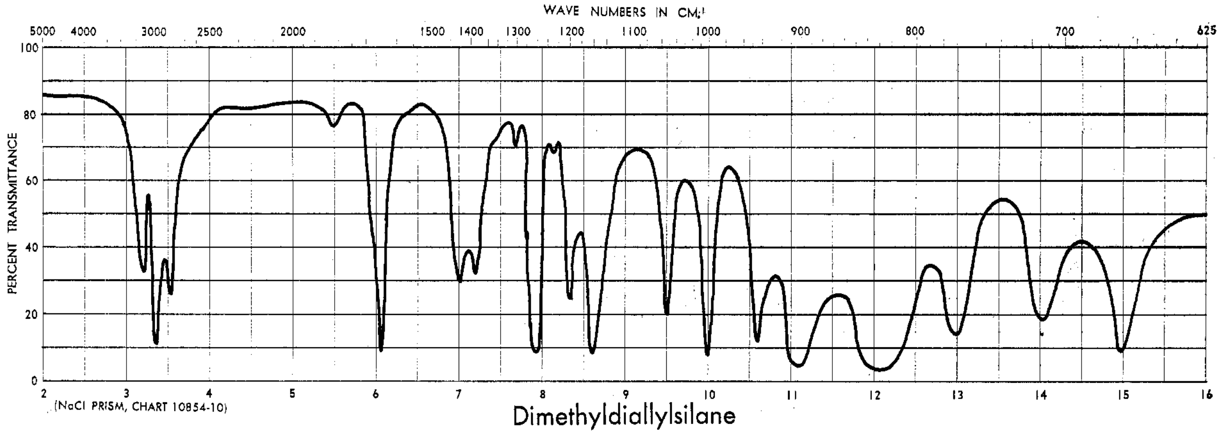
Hexamethylbis(1,5-chloromethyl)trisiloxane. To 252.1 g. (3.0 moles) of sodium bicarbonate in 1 l. of water, contained in a 2-l. flask equipped with stirrer, dropping funnel, and reflux condenser, was added a mixture of 286.1 g. (2.0 moles) of dimethylchloromethylchlorosilane and 129.04 g. (1.0 moles) of dimethyldichlorosilane at a slow rate (1 hr.). Vigorous stirring was necessary. After total addition had been accomplished the stirring was continued until an oily layer had clearly separated (1–2 hr.). The oil was separated and washed with distilled water until neutral to litmus. On fractionation, hexamethylbis(1,5-chloromethyl)trisiloxane was isolated, yield 21%, b.p. (lit.) 141.9° (40 mm.),[6] 142.0° (40 mm.),[7] (found) 136–138° (40 mm.); n_D^{20} (lit.) 1.4283,[6,7] (found) 1.4275.

Dimethylallylethoxysilane. Allylmagnesium bromide (1.22 moles) was prepared as described above and treated with 185.6 g. (1.30 moles) of dimethyldiethoxysilane in 100 cc. or anhydrous ether. Hydrolysis was safely carried out with ammonium chloride solution as before and distillation gave

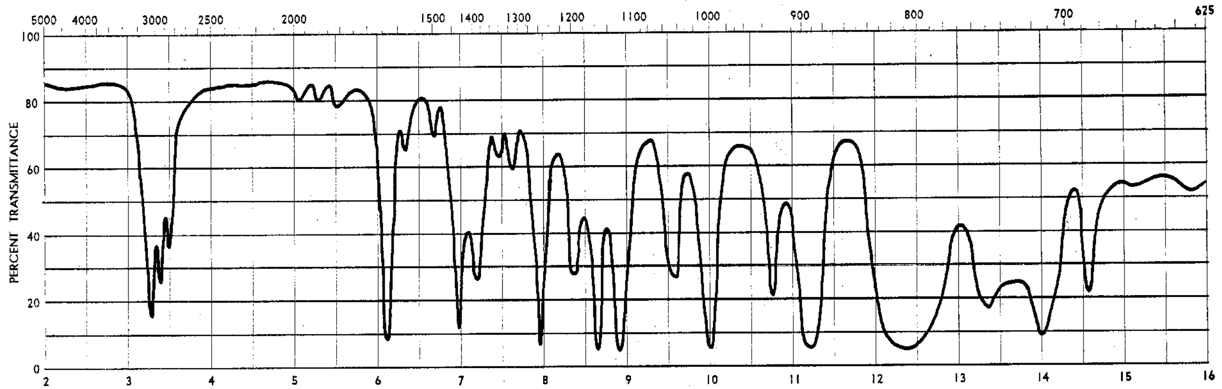
---

(8) J. Swiss and C. E. Arntzen, U. S. Patent **2,595,729** (1950).

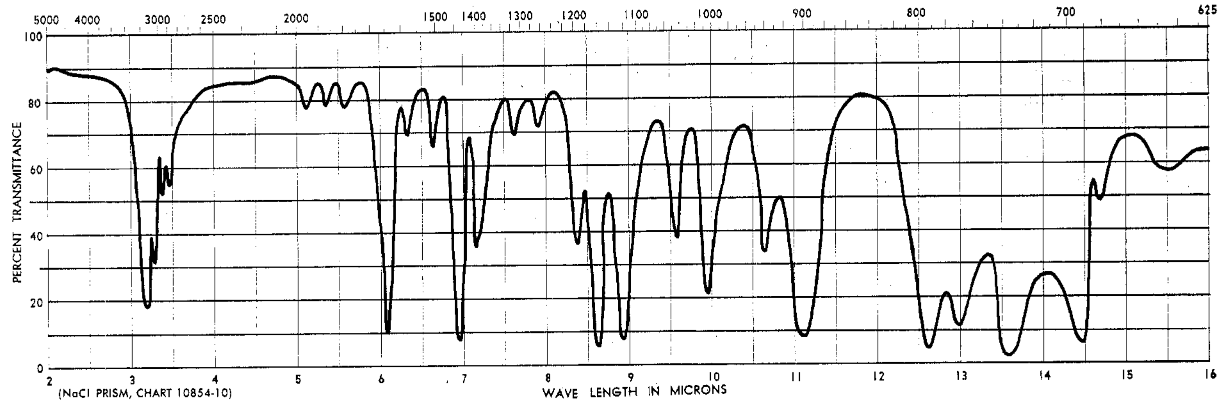
(9) J. Swiss and C. E. Arntzen, Brit. Patent **624,363** (1950).



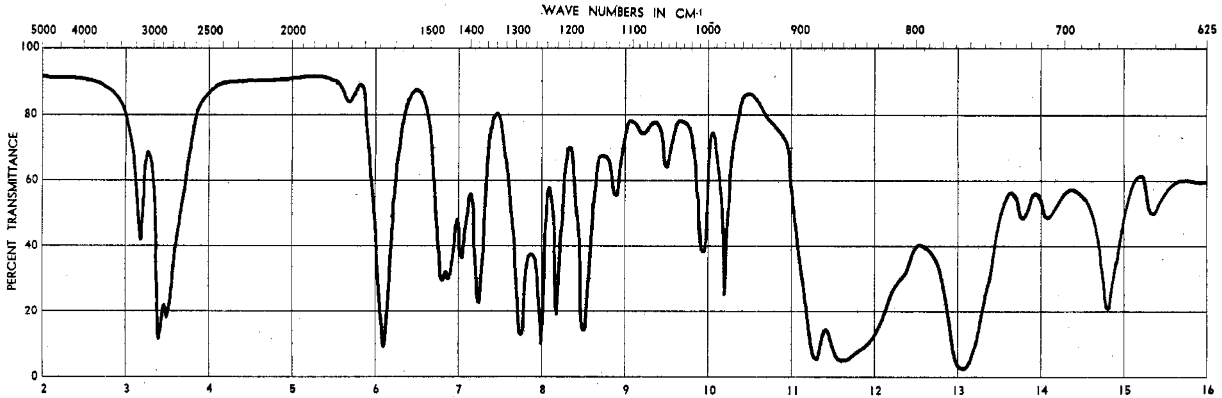
Dimethyldiallylsilane



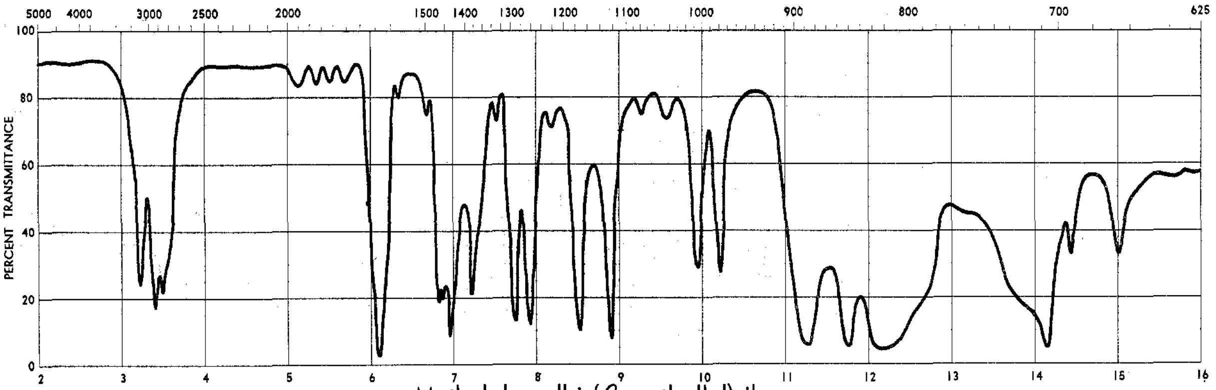
Methylphenyldiallylsilane



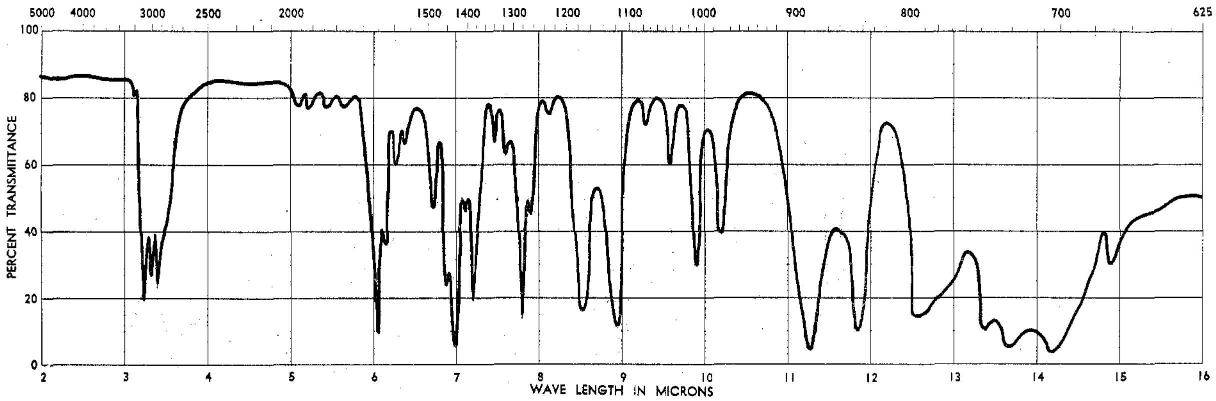
Diphenyldiallylsilane



Dimethylbis(β-methallyl)silane



Methylphenylbis(β-methallyl)silane



Diphenylbis(β-methallyl)silane

dimethylallylethoxysilane, yield 74.2% b.p. (lit.) 122.6–123.2° (743 mm.),[8,9] (found) 123.0–123.4° (743 mm.); n_D^{20} (lit.) 1.4080,[8,9] (found) 1.4020.

Dimethylbis(chloromethyl)silane was purchased from Peninsular ChemResearch, Inc. Dimethyldichlorosilane, methylphenyldichlorosilane and diphenyldichlorosilane were purchased from Dow Corning Corp., Midland, Mich., and found to have satisfactory physical constants.

Buffalo 14, N. Y.

[Contribution from the Department of Chemistry, The University of Buffalo]

Studies in Organosilicon Chemistry. XXXVI. Polymers Containing Sulfur

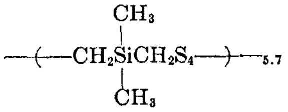
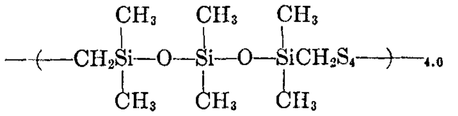
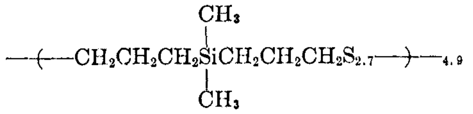
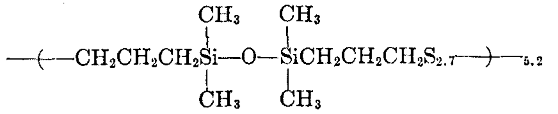
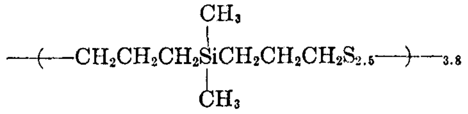
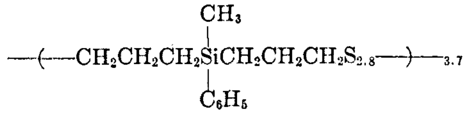
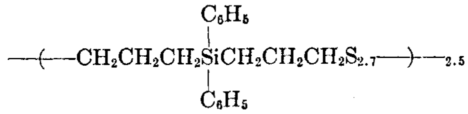
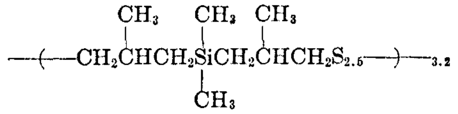
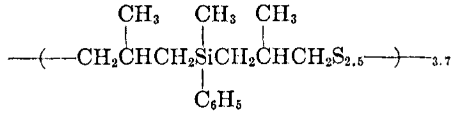
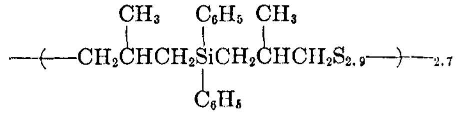
LEONARD D. NASIAK and HOWARD W. POST

Received October 8, 1958

A number of polymers containing silicon and sulfur have been prepared by both emulsion and solution techniques. Certain properties of the products were investigated.

Emulsion polymerizations have been carried out on the products resulting from the action of sodium tetrasulfide on dimethylbis(chloromethyl)silane and on hexamethylbis(1,5-chloromethyl)trisiloxane. Similarly, bulk polymerization is herein reported of the products resulting from the addition of hydrogen polysulfide to dimethyldiallylsilane and to dimethylallylethoxysilane. Solution polymerization has been carried out on the products resulting from the addition of hydrogen polysulfide to dimethyladiallylsilane, methylphenyldiallylsilane, diphenyldiallylsilane, dimethylbis(β-methallyl)silane, methylphenylbis(β-methallyl)silane and diphenylbis(β-methallyl)silane. The aver-

TABLE I

Physical Data	Inherent Viscosity	Yield, %	Type
 $-(-CH_2Si(CH_3)_2CH_2S_4-)-_{5.7}$	0.13	68.11	Emulsion
 $-(-CH_2Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2CH_2S_4-)-_{4.0}$	0.13	74.41	Emulsion
 $-(-CH_2CH_2CH_2Si(CH_3)_2CH_2CH_2CH_2S_{2.7}-)-_{4.9}$	0.13	80.4	Bulk
 $-(-CH_2CH_2CH_2Si(CH_3)_2-O-Si(CH_3)_2CH_2CH_2CH_2S_{2.7}-)-_{5.2}$	0.15	46.10	Bulk
 $-(-CH_2CH_2CH_2Si(CH_3)_2CH_2CH_2CH_2S_{2.5}-)-_{3.8}$	0.11	65.4	Solution
 $-(-CH_2CH_2CH_2Si(CH_3)(C_6H_5)CH_2CH_2CH_2S_{2.8}-)-_{3.7}$	0.14	64.1	Solution
 $-(-CH_2CH_2CH_2Si(C_6H_5)_2CH_2CH_2CH_2S_{2.7}-)-_{2.5}$	0.14	70.4	Solution
 $-(-CH_2CH(CH_3)CH_2Si(CH_3)_2CH_2CH(CH_3)CH_2S_{2.5}-)-_{3.2}$	0.08	68.41	Solution
 $-(-CH_2CH(CH_3)CH_2Si(CH_3)(C_6H_5)CH_2CH(CH_3)CH_2S_{2.5}-)-_{3.7}$	0.11	61.8	Solution
 $-(-CH_2CH(CH_3)CH_2Si(C_6H_5)_2CH_2CH(CH_3)CH_2S_{2.9}-)-_{2.7}$	0.11	65.1	Solution

age degrees of polymerization of the above polymers are, respectively, 5.7, 4.0, 4.9, 5.2, 3.8, 3.7, 2.5, 3.2, 3.7, and 2.7.

Calculations of per cent yields are probably too high in all cases. The determinations were very difficult owing to the fact that the samples were small and because of the sticky character of the material itself.

Discussion. Patrick[1] very early reported the preparation of a polysulfide polymer through the interaction of ethylene dichloride and aqueous sodium tetrasulfide. This type of synthesis, as is well known, is to be found in countless other instances and forms the basis for the preparation and manufacture of the various Thiokol elastomers and other products. Modifications of this general procedure have been used for a portion of this work. A wetting agent, Naccosol A, was used to provide maximum contact between monomer and sodium tetrasulfide. Magnesium hydroxide was also introduced. The disagreeable odor which accompanied many of these products could have been due to the presence of mercaptans, even in minute amounts.

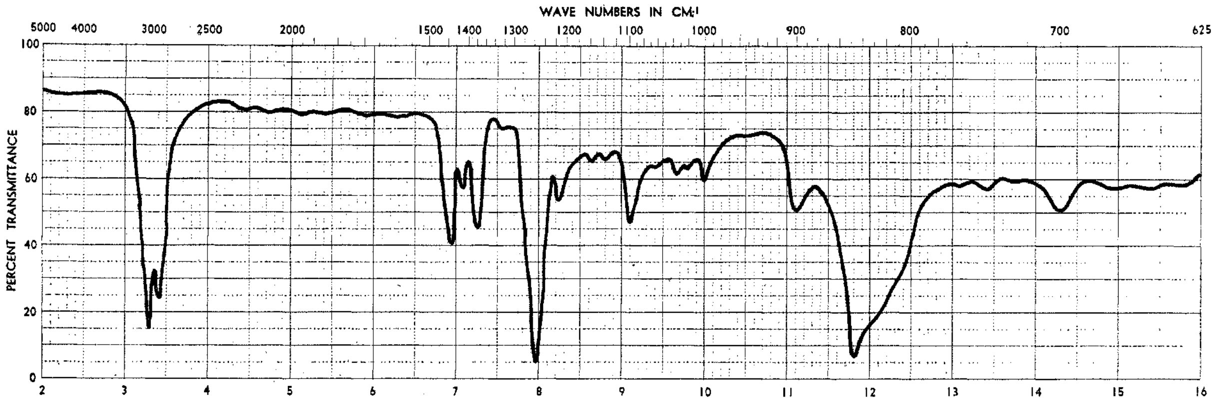
There are several references in current literature to the addition of mercaptans across olefinic double bonds and the use of this type of reaction to synthesize polymeric molecules.[2,3] In each case, addition was reported as having taken place contrary

---

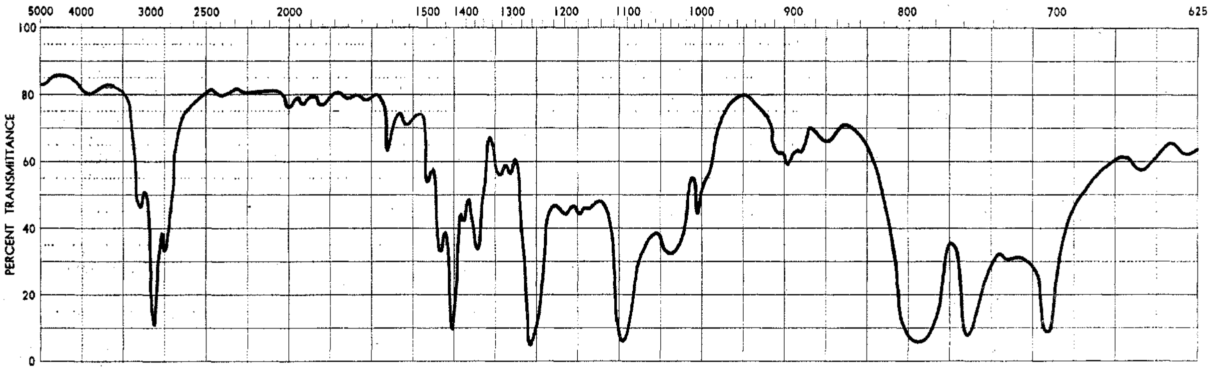
[1] J. C. Patrick, U. S. Patent 1,890,191 (1933).

[2] C. S. Marvel and H. Cripps, *J. Polymer Sci.*, **9**, 52 (1952).

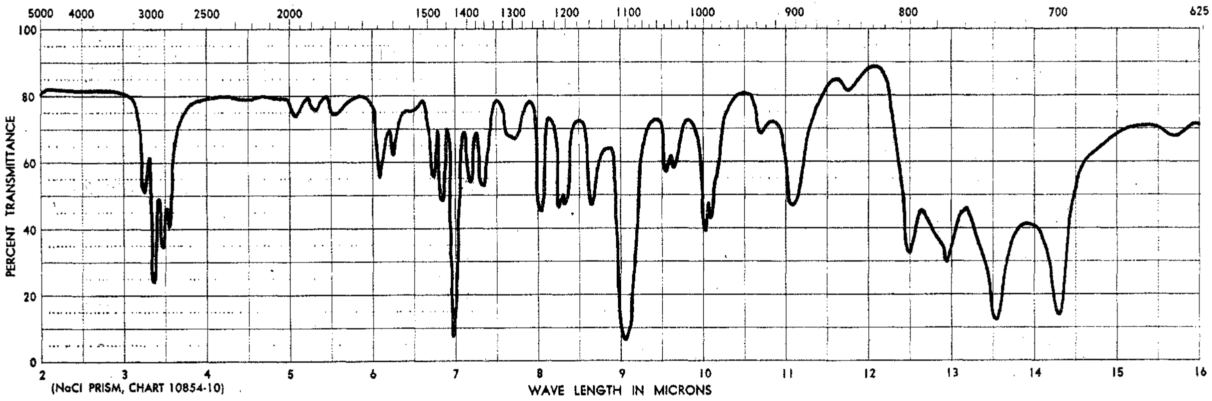
[3] C. Burkhard, *J. Am. Chem. Soc.*, **72**, 1078 (1950).



Polymer from Dimethyldiallylsilane



Polymer from Methylphenyldiallylsilane



Polymer from Diphenyldiallylsilane

to the Rule of Markownikoff. Reasoning by analogy the products reported herein which resulted from the addition of hydrogen polysulfide have been assigned analogous formulas.

The molecular weights of the silicon-carbon-sulfur polymers are admittedly low. However, work is now outlined for the application of more advanced techniques to these procedures which should produce products of somewhat higher degree of polymerization.

Infrared absorption curves have been determined for the products from the bulk polymerization of dimethyldiallylsilane and the solution polymerization of methylphenyldiallylsilane and diphenyldiallylsilane with hydrogen polysulfide.

The provisional interpretation of these curves has already been presented in Part XXXV.[4]

In making calculations as to molar quantities of hydrogen polysulfide, it has been assumed that the compound is a mixture of H_2S_2 and H_2S_3.[5]

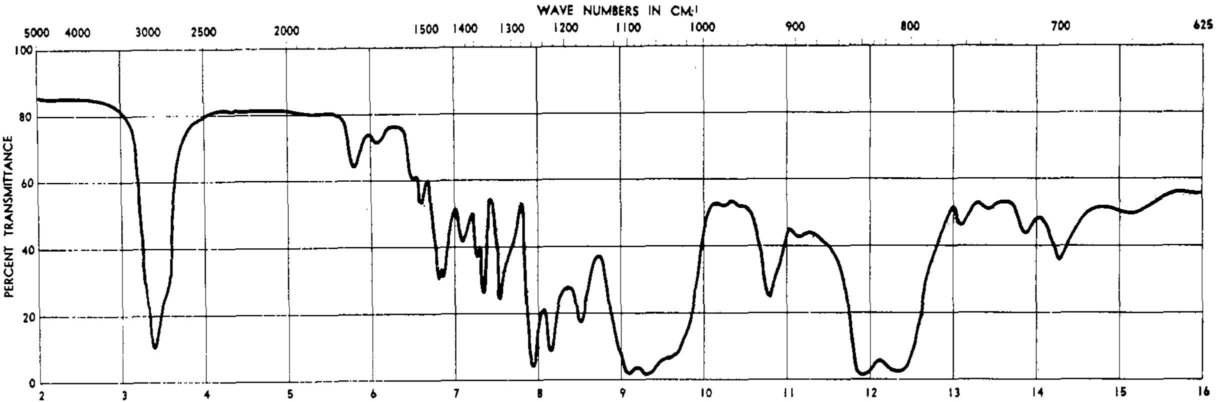
EXPERIMENTAL

Dimethylbis(chloromethyl)silane and sodium tetrasulfide. Anhydrous sodium tetrasulfide (200 g., 0.46 mole) was placed in a 300-cc. three necked flask equipped with stirrer,

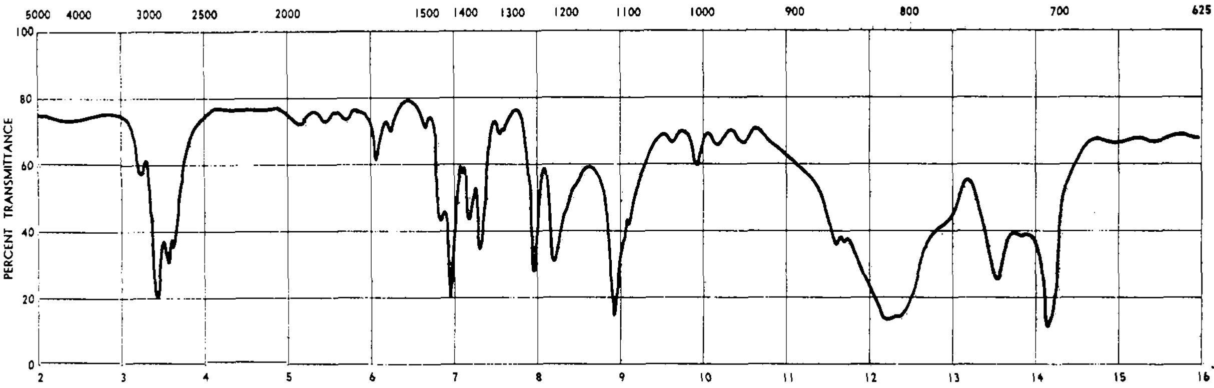
---

[4] Leonard D. Nasiak and Howard W. Post, *J. Org. Chem.*, **24**, 489 (1959).

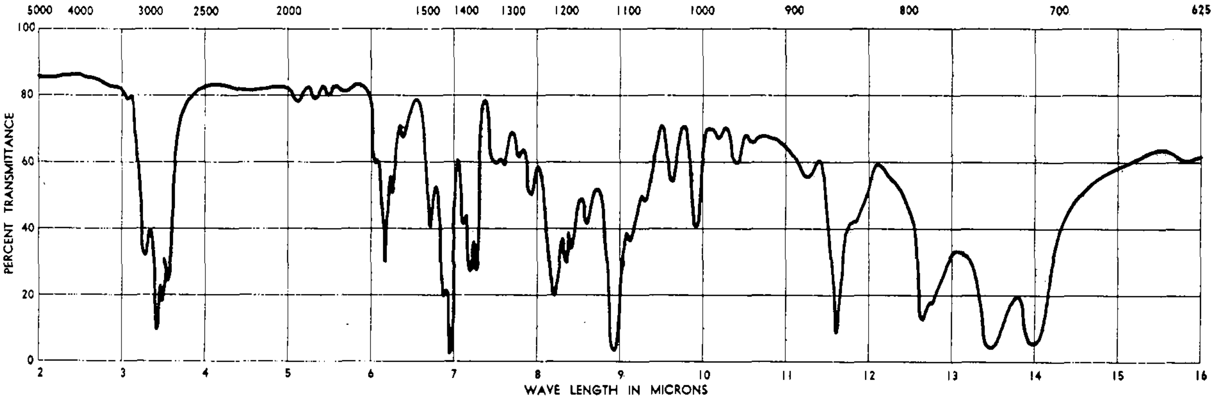
[5] T. Moeller, *Inorganic Chemistry*, John Wiley & Sons, Inc., New York, 1955, p. 516.



Polymer from Dimethylbis(β-methallyl)silane



Polymer from Methylphenylbis(β-methallyl)silane



Polymer from Diphenylbis(β-methallyl)silane

TABLE II

INFRARED DATA, IN MICRONS

		Bellamy[6]	Found
CH	Stretching	3.2	3.3–3.4
$SiCH_3$, $Si(CH_3)_2$	Stretching	7.9	7.9–8.1
		12.3–12.5	12.2–12.5
SiC_6H_5	Vibration	7.0	6.9
		8.9	8.9–9.3
			14.0–14.2

dropping funnel, and reflux condenser, as a 40% aqueous solution. To this solution under vigorous stirring, 1.0 g. of Naccosol A wetting agent and 0.62 g. of sodium hydroxide were added, followed dropwise by 1.55 g. (0.01 mole) of magnesium chloride as a 25% aqueous solution. The system was heated to 60–65° and 20.0 g. (0.13 g. mol.) of dimethylbis(chloromethyl)silane added, dropwise. After complete addition had been accomplished, the mixture was heated to 95–100° and kept at that temperature for 48 hr., with constant stirring. After cooling, the flask was filled with water and the heavy oil extracted with chloroform. After evaporation of the solvent, the viscous tacky oil was heated 4 hr. at 95–100° to facilitate further polymerization, yield 68.1%, based on the silane.

Anal. Calcd. for $(C_4H_{10}SiS_4)_x$: Si, 13.09; S, 37.38. Found: Si, 12.20; S, 36.94; mol. wt. (av.) 1223 (x = 5.7), inherent viscosity (25°) 0.13.

Hexamethylbis(1,5-chloromethyl)trisiloxane and sodium tetrasulfide. In similar manner, the two above named compounds interacted to form an oily polymer, yield 74.4%.

Anal. Calcd. for $(C_8H_{22}Si_3S_4O_2)_x$: Si, 23.21; S, 22.10. Found: Si, 23.75; S, 22.20; mol. wt. (av.) 1456 (x = 4.0), inherent viscosity (25°) 0.13.

---

(6) L. J. Bellamy, *The Infrared Spectra of Organic Molecules*, John Wiley & Sons, Inc., New York, 1954.

Dimethyldiallylsilane and hydrogen polysulfide (*bulk*). A mixture of 28.06 g. (0.20 mole) of dimethyldiallylsilane and 16.44 g. (0.20 mole) of hydrogen polysulfide in a 200 cc. beaker equipped with stirrer and thermometer became homogeneous at about 70° when heated in an oil bath, forming a yellow viscous polymer. The temperature was raised to 125–130° and maintained at that level for 4 hr. with constant stirring or until almost all hydrogen sulfide had been evolved (lead acetate paper test). The color of the polymer had meanwhile changed to a deep red with concurrent increase in viscosity and tackiness. The product cooled to a semisolid mass which was washed twice with two 30-cc. portions of methyl alcohol to extract organic materials and dissolved in a minimum amount of chloroform to precipitate as much as possible of dissolved sulfur. The solution was chilled in an ice chest, filtered, and the solvent evaporated. This separation was repeated giving finally a red, viscous tacky polymer, yield 80.4%.

Anal. Calcd. for $(C_8H_{18}SiS_{2.7})_x$: Si, 12.29; S, 37.71. Found: Si, 11.01; S, 38.04; mol. wt. (av.), 1121 ($x = 4.9$); inherent viscosity (25°) 0.13.

Dimethylallylethoxysilane and hydrogen polysulfide (*bulk*). The interaction of these two compounds, as described in the preceding experiment, produced a polymeric product in 46.1% yield.

Anal. Calcd. for $(C_{10}H_{24}Si_2S_{2.7}O)_x$: Si, 18.53; S, 28.47. Found: Si, 17.01; S, 28.46; mol. wt. (av.) 1505 ($x = 5.2$); inherent viscosity (25°) 0.15.

Dimethyldiallylsilane and hydrogen polysulfide (*solution*). A mixture of 42.10 g. (0.30 mole) of dimethyldiallylsilane and 27.13 g. (0.33 mole) of hydrogen polysulfide in 50 cc. of benzene in a 250-cc. beaker equipped with stirrer and thermometer and heated in an oil bath, was warmed slowly until the benzene had boiled off. A yellow, viscous polymer remained. This polymer was heated at 125–130° for 4 hr. with constant stirring or until very little hydrogen sulfide was being evolved (lead acetate paper test). It cooled to a semisolid mass which was worked up as were the preceding products giving a red, viscous tacky polymer, yield 65.4%.

Anal. Calcd. for $(C_8H_{18}SiS_{2.5})_x$: Si, 12.62; S, 36.05. Found: Si, 11.85; S, 36.91; mol. wt. (av.) 856 ($x = 3.8$), inherent viscosity (25°) 0.11.

Methylphenyldiallylsilane and hydrogen polysulfide (*solution*). In like manner, these two compounds reacted to form a polymer of similar physical appearance, in 64.1% yield.

Anal. Calcd. for $(C_{13}H_{20}SiS_{2.8})_x$: Si, 9.49; S, 30.37. Found: Si, 9.30; S, 31.01; mol. wt. (av.) 1084 ($x = 3.7$); inherent viscosity (25°) 0.14.

Diphenyldiallylsilane and hydrogen polysulfide (*solution*). These two compounds reacted, as described above, to give a similar red viscous tacky polymer, yield 70.4%.

Anal. Calcd. for $(C_{18}H_{22}SiS_{2.7})_x$: Si, 7.99; S, 24.43. Found: Si, 7.94; S, 24.91; mol. wt. (av.) 872 ($x = 2.5$); inherent viscosity (25°) 0.14.

Dimethylbis(β-methallyl)silane and hydrogen polysulfide (*solution*). The reaction between these two compounds was carried out as has already been described to yield an orange-red viscous tacky polymer, yield 68.4%.

Anal. Calcd. for $(C_{10}H_{22}SiS_{2.5})_x$: Si, 11.21; S, 31.99. Found: Si, 10.87; S, 34.95; mol. wt. (av.) 810 ($x = 3.2$); inherent viscosity (25°) 0.08.

Methylphenylbis(β-methallyl)silane and hydrogen polysulfide (*solution*). The Interaction of these two compounds resulted in the formation of a similar orange-red viscous tacky polymer, yield 61.8%.

Anal. Calcd. for $(C_{15}H_{24}SiS_{2.5})_x$: Si, 8.98; S, 25.63. Found: Si, 8.49; S, 24.98; mol. wt. (av.) 1141 ($x = 3.7$); inherent viscosity (25°) 0.11.

Diphenylbis(β-methallyl)silane and hydrogen polysulfide (*solution*). Using the experimental conditions outlined above, these two compounds interacted to form an orange-red, tacky polymer yield 65.1%.

Anal. Calcd. for $(C_{20}H_{26}SiS_{2.9})_x$: Si, 7.29; S, 23.83. Found: Si, 7.73; S, 24.10; mol. wt. (av.) 1052 ($x = 2.7$); inherent viscosity (25°) 0.11.

Organosilicon reagents were prepared as described in Part XXXV.[3] Hydrogen polysulfide was prepared by adding 150 cc. of a 40% aqueous solution of sodium tetrasulfide to 500 cc. of hydrochloric acid in a 1-l., three necked flask equipped with stirrer, dropping funnel, and thermometer. The flask was first immersed in a Dry Ice–acetone bath and the acid cooled to −10° to −15°. Agitation was necessary at all times during the addition. After total addition had been attained, the mixture was poured into 1 l. of water and the heavy oily product (hydrogen polysulfide) was separated.

Silicon was determined by incinerating with cold fuming sulfuric acid (15%), heating at low heat for 2 hr., then 1 hr. at maximum heat. After partial cooling, the sample was treated with 3 or 4 drops of fuming sulfuric acid and 5 drops of fuming nitric acid, then again heated slowly increasing to high, for 3 to 4 hr. or until the residue was white. Platinum crucible and contents were then heated to red heat.

Sulfur was determined in the Parr peroxide bomb. Molecular weights were determined by the depression of the freezing point in benzene and inherent viscosity, in dilute solution, by an Ostwald viscometer at 25°. Solutions of 0.1 g. of polymer in 25 cc. of purified chloroform were used.

Sodium tetrasulfide was obtained through the courtesy of Hooker Electrochemical Co., Niagara Falls, N. Y. Wherever anhydrous sodium tetrasulfide was needed, water of crystallization was removed by boiling with toluene.

BUFFALO, N. Y.