

applied to cinerone as well as to tetrahydropyrene.

U. S. DEPARTMENT OF AGRICULTURE
BELTSVILLE, MARYLAND

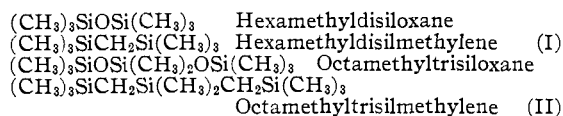
S. B. SOLOWAY
F. B. LAForge

RECEIVED MARCH 5, 1947

NEW COMPOUNDS WITH A SKELETON OF ALTERNATE SILICON AND CARBON ATOMS

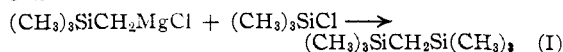
Sir:

We have synthesized compounds of the type $(\text{CH}_3)_n\text{Si}(\text{CH}_3)_2\text{CH}_2)_n\text{Si}(\text{CH}_3)_3$, in which n is 1 or 2. These are *polysilmethylenes*, analogous to polysiloxanes.¹



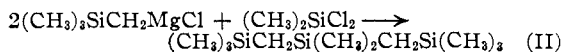
The Grignard reagent was prepared in 95% yield from 61 g., 0.5 mole, of chloromethyltrimethylsilane,² and 12.5 g., 0.5 mole, of magnesium turnings in 150 cc. of dry ether. The reaction flask was cooled in an ice-bath and a solution of 54 g., 0.5 mole, of trimethylchlorosilane in 60 cc. of ether was added during ten minutes. Stirring at ice-bath temperature for three hours was followed by refluxing for twelve hours. Ether was then removed from the reaction mixture by slow distillation during two days. The residue was hydrolyzed with dilute hydrochloric acid, and the product was extracted with ether. Fractional distillation gave 50 g., 0.31 mole, of hexamethyltrisilmethylenes, b. p. 132° at 740 mm., n_D^{20} 1.4170, d_4^{20} 0.7520, a yield of 63%.

Anal. Calcd. for $\text{C}_7\text{Si}_2\text{H}_{20}$: Si, 35.0. Found: Si, 34.9, 34.9.



A similar procedure using 50 g., 0.39 mole, of dimethyldichlorosilane and the Grignard reagent from 98 g., 0.8 mole, of silico-neopentyl chloride gave 58.6 g., 0.25 mole, of octamethyltrisilmethylenes, b. p. 202° at 720 mm., n_D^{20} 1.4414, d_4^{20} 0.8002, a yield of 65%.³

Anal. Calcd. for $\text{C}_{10}\text{Si}_3\text{H}_{28}$: Si, 36.2. Found: Si, 36.2, 36.1.



As an intermediate for the preparation of higher members of this series we have synthesized pentamethylchloromethyltrisilmethylenes (III), b. p. 184° at 732 mm., n_D^{20} 1.4479, in 32% yield from chloromethyltrimethylchlorosilane.⁴

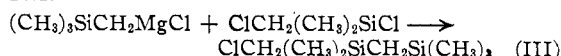
(1) For a recent report on organosilicon nomenclature see *Chem. Eng. News*, **24**, 1233 (1946).

(2) Whitmore and Sommer, *THIS JOURNAL*, **68**, 481 (1946).

(3) The reaction of methylene chloride with silicon-copper has been used to prepare hexachlorodisilmethylenes, pentachlorodisilmethylenes and hexachlorocyclotrisilmethylenes. See Patnode and Schiessler, U. S. Patents 2,381,000 and 2,381,002.

(4) Krieble and Elliott, *ibid.*, **67**, 1810 (1945).

Anal. Calcd. for $\text{C}_7\text{Si}_2\text{H}_{19}\text{Cl}$: Cl, 18.2. Found: Cl, 18.1.



Compounds I and II are interesting from several standpoints. As methylene analogs of hexamethyldisiloxane and octamethyltrisiloxane,⁵ respectively, they will provide valuable data on the relative effects of Si-O-Si and Si-CH₂-Si groupings on physical properties. Chemically, the configuration Si-CH₂-Si is interesting because nothing is known of the effect of two silicon atoms bound to the same carbon atom. Moreover, compounds I and II are, with the exception of tetramethylsilane and hexamethyldisilane, the only completely alkylated silanes with no carbon-carbon bonds. In general, the carbon-silicon bond is more resistant to oxidation than the carbon-carbon bond.⁶

Viscosities in centipoises for hexamethyltrisilmethylenes are as follows: 0°, 0.964; 20°, 0.736; 60°, 0.458. The plot of the logarithms of these values against $1/T^\circ$ has a slope almost identical with that for hexamethyldisiloxane.⁵

(5) Cf. Sauer, *THIS JOURNAL*, **66**, 1707 (1944); Patnode and Wilcock, *ibid.*, **68**, 691 (1946); Hurd, *ibid.*, **68**, 364 (1946); Wilcock, *ibid.*, **68**, 691 (1946); Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).

(6) Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, 1946, p. 19.

DEPARTMENT OF CHEMISTRY
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA.

L. H. SOMMER
G. M. GOLDBERG
J. GOLD
F. C. WHITMORE

RECEIVED MARCH 6, 1947

N,N-DIMETHYL-N'-(α -PYRIDYL)-N'-(α -THEINYL)- ETHYLENEDIAMINE, AN ANTIHISTAMINIC AGENT

Sir:

It has been demonstrated, in several instances, that the replacement of a phenyl group by an α -thienyl group in a physiologically active compound produces an isostere with comparable pharmacological properties¹. In other studies, such an interchange of groups resulted in a diminution of activity² and even in inhibition of a normal biological process³.

Hence, it seemed desirable to ascertain whether the antihistaminic action of N,N-dimethyl-N'-benzyl-N'-(α -pyridyl)-ethylenediamine⁴ (I) would be altered in its thiophene analog (II).

(1) Steinkopf and Ohse, *Ann.*, **437**, 14 (1924); **448**, 205 (1926), for related references see Warren, Marsh, Thompson, Shelton and Becker, *J. Pharmacol. Exptl. Therap.*, **79**, 187 (1943); Blicke and Tsao, *THIS JOURNAL*, **66**, 1645 (1944).

(2) Gilman and Pickens, *ibid.*, **47**, 245 (1925); Tarbell, Fukushima and Dam, *ibid.*, **67**, 1643 (1945); Blicke and Chanin, paper 46 presented before the Medicinal Division of the American Chemical Society, Atlantic City, April, 1946.

(3) du Vigneaud, McKennis, Simmonds, Dittmer and Brown, *J. Biol. Chem.*, **159**, 385 (1945).

(4) Hutterer, Djerassi, Beears, Mayer and Scholz, *THIS JOURNAL*, **68**, 1999 (1946).