applied to cinerone as well as to tetrahydropyrethrone.

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NEW COMPOUNDS WITH A SKELETON OF ALTERNATE SILICON AND CARBON ATOMS

Sir:

We have synthesized compounds of the type $CH_3[Si(CH_3)_2CH_2]_nSi(CH_3)_3$, in which *n* is 1 or 2. These are *polysilmethylenes*, analogous to polysiloxanes.[1]

$(CH_3)_3SiOSi(CH_3)_3$ Hexamethyldisiloxane
$(CH_3)_3SiCH_2Si(CH_3)_3$ Hexamethyldisilmethylene (I)
$(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_3$ Octamethyltrisiloxane
$(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_3$ Octamethyltrisilmethylene (II)

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 hexamethyldisilmethylene, b. p. 132° at 740 mm., $n^{20}D$ 1.4170, d^{20} 0.7520, a yield of 63%.

Anal. Calcd. for $C_7Si_2H_{20}$: Si, 35.0. Found: Si, 34.9, 34.9.

$$(CH_3)_3SiCH_2MgCl + (CH_3)_3SiCl \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_3 \quad (I)$$

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 octamethyltrisilmethylene, b. p. 202° at 720 mm., $n^{20}D$ 1.4414, d^{20} 0.8002, a yield of 65%.[3]

Anal. Calcd. for $C_{10}Si_3H_{28}$: Si, 36.2. Found: Si, 36.2, 36.1.

$$2(CH_3)_3SiCH_2MgCl + (CH_3)_2SiCl_2 \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_3 \quad (II)$$

As an intermediate for the preparation of higher members of this series we have synthesized pentamethylchloromethyldisilmethylene (III), b. p. 184° at 732 mm., $n^{20}D$ 1.4479, in 32% yield from chloromethyldimethylchlorosilane.[4]

Anal. Calcd. for $C_7Si_2H_{19}Cl$: Cl, 18.2. Found: Cl, 18.1.

$$(CH_3)_3SiCH_2MgCl + ClCH_2(CH_3)_2SiCl \longrightarrow ClCH_2(CH_3)_2SiCH_2Si(CH_3)_3 \quad (III)$$

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–CH_2–Si groupings on physical properties. Chemically, the configuration Si–CH_2–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 hexamethyldisilmethylene are as follows: 0°, 0.964; 20°, 0.736; 60°, 0.458. The plot of the logarithms of these values against $1/T°$ has a slope almost identical with that for hexamethyldisiloxane.[5]

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(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 hexachlorodisilmethylene, pentachlorodisilmethylene and hexachlorocyclotrisilmethylene. See Patnode and Schiessler, U. S. Patents 2,381,000 and 2,381,002.

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

(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.

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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 properties[1]. In other studies, such an interchange of groups resulted in a diminution of activity[2] and even in inhibition of a normal biological process[3].

Hence, it seemed desirable to ascertain whether the antihistaminic action of N,N-dimethyl-N'-benzyl-N'-(α-pyridyl)-ethylenediamine[4] (I) would be altered in its thiophene analog (II).

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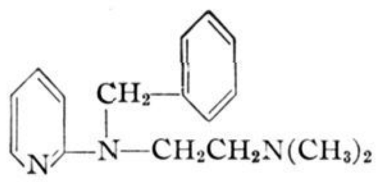
(1) Steinkopf and Ohse, *Ann.*, **437**, 14 (1924); **448**, 205 (1926); for related references see Warren, Marsh, Thompson, Shelton and Becker, *J. Pharmacol. Exptl. Therap.*, **79**, 187 (1943); Blicke and Tsao, THIS JOURNAL, **66**, 1645 (1944).

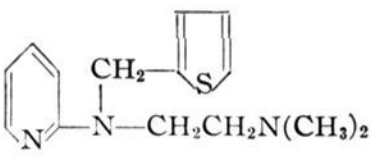
(2) Gilman and Pickens, *ibid.*, **47**, 245 (1925); Tarbell, Fukushima and Dam, *ibid.*, **67**, 1643 (1945); Blicke and Chanin, paper 46 presented before the Medicinal Division of the American Chemical Society, Atlantic City, April, 1946.

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

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



I



II (36)

The synthesis of II was accomplished by condensing the previously described[4,5] N,N-dimethyl-N′(α-pyridyl)-ethylenediamine with α-thienyl cholride.[6] The product, b. p. 173–175° at 3 mm., n^{25}_D 1.5835 was obtained in a 64% yield. *Anal.* Calcd. for $C_{14}H_{19}N_3S$: N, 16.09. Found: N, 16.12. The monohydrochloride melted at 161–162°. *Anal.* Calcd. for $C_{14}H_{20}N_3SCl$: N, 14.12. Found: N, 14.16. The methiodide had m. p. 156–157° (dec.). *Anal.* Calcd. for $C_{15}H_{22}N_3SI$: N, 10.42. Found: N, 10.39.

Preliminary pharmacological data[7] indicate that, experimentally in animals, II exhibits the same order of antihistaminic activity as I. The toxicity of both compounds is approximately equal.

Additional information concerning II and other homologs will be published at some future date.

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[5] Whitmore, Mosher, Goldsmith and Rytina, *ibid.*, **67**, 393 (1945).

[6] Blicke and Leonard, *ibid.*, **68**, 1934 (1946).

[7] Roth, Richards and Shepperd, *Federation Proc.*, in press (1947).

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t-BUTYLSILICON COMPOUNDS

Sir:

From *t*-butyllithium[1] and silicon tetrachloride we have synthesized in 55% yield the first tertiary alkyl silicon compound, *t*-butyltrichlorosilane, m. p. 98–99°, b. p. 133° at 740 mm. *Anal.* Calcd. for $C_4H_9SiCl_3$: Si, 14.6; Cl, 55.6; mol. wt., 191. Found: Si, 14.7; Cl, 55.7; cryoscopic mol. wt. in benzene, 189.

t-Butyltrichlorosilane is unusual. It is a white waxy solid which becomes granular on standing and sublimes readily at room temperature, giving well-defined fern-like crystals (Fig. 1). It is less easily hydrolyzed than other alkyltrichlorosilanes.

Fig. 1.—Photograph of crystals of sublimed *t*-butyltrichlorosilane by Dr. M. L. Willard, H. Francis, G. Kauffman, T Reissmann.

With methylmagnesium bromide the above compound gives a 61% yield of *t*-butyltrimethylsilane, m.p. 75–77°, b. p. 103° at 740 mm.

Anal. Calcd. for $C_7H_{18}Si$: Si, 21.6; mol. wt., 130. Found: Si, 21.7; mol. wt., 132.

It is a white waxy solid with faint camphoric odor. It sublimes readily to crystals resembling those in Fig. 1. Distillation of *t*-butyltrimethylsilane from hot concd. sulfuric acid gave a product with unchanged m. p., thus indicating a high degree of inertness of the C–Si bond.

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[1] Organolithium compounds have been used to make organosilicon compounds: Fleming and Laurens, U. S. Patent 2,386,452, (1945); *C. A.*, **40**, 603 (1946); Gilman and Clarke, THIS JOURNAL, **68**, 1675 (1946).

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