but it was difficult to obtain consistent results because of the ready racemization of the acid in solution. The best sample had $[\alpha]^{26}D$ 2.4 ± 0.5° (0.0538 g. in 2 ml. of ethyl acetate, 2-dm. tube). It melted at the same temperature as the racemic acid and the mixed melting point was not depressed. Further studies of the racemization of the salt and the acid will be made and a full description of this work and of the synthesis of 1,4,5-trimethylphenanthrene, m. p. 62.6–63.0°, will be published soon.

THE OHIO STATE UNIVERSITY MELVIN S. NEWMAN
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RECEIVED MARCH 17, 1947

## HYDROGEN CHLORIDE AS A CONDENSING AGENT

*Sir:*

Mr. S. H. McAllister has kindly pointed out to us an error in our paper "Hydrogen Chloride as a Condensing Agent", in THIS JOURNAL, **66,** 1309 (1944), in the statement that the alkylation of toluene with isopropyl chloride using hydrogen chloride as the catalyst resulted in the exclusive formation of the para substituted product. In a duplication of this experiment in the laboratories of the Shell Development Company by Mr. Edwin F. Bullard, it was found by infrared spectral analysis that the monosubstituted product contained 25% ortho, 22% meta, and 53% para. As we do not have the expensive equipment available in the industrial laboratory, our products were kindly analyzed by Mr. F. S. Mortimer of the above mentioned company with the following results: 31 ± 1% ortho, 27 ± 1% meta, and 42 ± 1% para. These analyses have been confirmed by Dr. R. V. Weigand at The Pennsylvania State College by raman spectra with the following results: 38% ortho, 25% meta, and 37% para.

This illustrates the need of caution in giving the ratio of isomers in a product when adequate methods of analysis are not available.

SCHOOL OF CHEMISTRY AND PHYSICS J. H. SIMONS
THE PENNSYLVANIA STATE COLLEGE HAROLD HART
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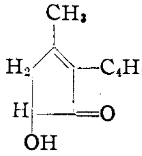
RECEIVED MARCH 29, 1947

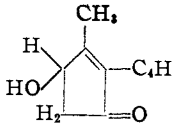
## THE SYNTHESIS OF DIHYDROCINEROLONE

*Sir:*

In a previous communication[1] we reported the synthesis of 1-butyl-5-hydroxy-3-methyl-2-cyclopenten-1-one (I), the structure previously ascribed to dihydrocinerolone.[2] As the α-hydroxyketone (I) was not identical with the dihydro derivative of natural cinerolone, the revised formula 2-butyl-4-hydroxy-3-methyl-2-cyclopenten-1-one (II) was suggested.

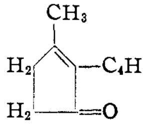


I



II

We have now synthesized the hydroxy ketone identical with dihydrocinerolone. The synthesis was accomplished by the bromination of dihydrocinerone (III) with the employment of N-bromosuccinimide and subsequent hydrolysis of the bromo derivative.



III

Equimolecular quantities of dihydrocinerone and N-bromosuccinimide in carbon tetrachloride were heated under reflux for eighteen hours and, after removal of the insoluble succinimide and the solvent, the crude bromo derivative was hydrolyzed by refluxing with an aqueous suspension of calcium carbonate. This hydrolysis procedure has been employed for the conversion of chlorocinerone to cinerolone. The product had properties in agreement with those of dihydrocinerolone (Table I).

TABLE I

COMPARISON OF THE PROPERTIES OF DIHYDROCINEROLONES

| Dihydrocinerolone | B. p. °C. | B. p. Mm. | $n_D$ | Semicarbazone m.p., °C. | 3,5-Dinitrobenzoate m. p., °C. |
|---|---|---|---|---|---|
| From cinerolone | 115–117 | 1[2] | 1.4958 (22°)[2] | 185[2] | 111 |
| Synthetic | 110–114 | 0.3 | 1.4955 (25°) | 187 | 111 |

The slight difference in melting points of the semicarbazones is probably due to impurities in the natural materials (mixed m. p. 185–187°). A similar difference in the melting points of the 3,5-dinitrobenzoates was initially observed. However, after several recrystallizations the derivative from the natural material melted at the same point as that of the synthetic compound (mixed m. p. 111°).

The substitution of bromine into the 4-position of dihydrocinerone (III) is not unexpected, as Ziegler and co-workers[3] have shown that N-bromosuccinimide characteristically brominates in the allyl position. These results, then, support structure II for dihydrocinerolone.

The action of N-bromosuccinimide is being

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[1] LaForge and Soloway, THIS JOURNAL, **69,** 186 (1947). In column 1, line 8, the position of the hydroxyl group in the name of the compound should read "5" in place of "4."

[2] LaForge and Barthel, *J. Org. Chem.*, **10,** 222 (1945).

[3] Ziegler and co-workers, *Ann.*, **551,** 80 (1942).

applied to cinerone as well as to tetrahydropyrethrone.

U. S. DEPARTMENT OF AGRICULTURE S. B. SOLOWAY
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RECEIVED MARCH 5, 1947

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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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RECEIVED MARCH 6, 1947

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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).