The second mechanism, involving selective inhibition by iodine or iodine chloride, appears more likely. Inhibition of chain reactions of the radical type by iodine has been reported by Stevens[14] and others.[15] That an inhibition mechanism is involved in the iodine-catalyzed chlorination of benzene is substantiated by other observations. Although benzene tetrachloride has not been isolated from chlorination reactions other than those catalyzed by iodine, it has been detected by infrared spectrophotometric examination of benzene hexachloride prepared in the presence of oxygen under conditions resulting in poor chlorine conversion, such as low light intensity.

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[14] H. C. Stevens, U. S. Patent 2,415,971, Feb. 18, 1947.

[15] F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. DeWitt, H. C. Stevens and J. H. Langton, THIS JOURNAL, **72**, 1254 (1950).

DETROIT, MICHIGAN RECEIVED FEBRUARY 20, 1951

[CONTRIBUTION NO. 810 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH AND MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Electric Moments and Structures of Organosilicon Compounds. I. The Aliphatic Carbon–Silicon Bond

BY HENRY FREISER, ROBERT CHARLES, JOHN SPEIER AND MARY EAGLE

The dielectric constants and densities of neopentyl chloride, chloromethyltrimethylsilane, and dichloromethyltrimethylsilane in benzene solution have been determined at 30.0°. The dipole moment values of neopentyl chloride, chloromethyltrimethylsilane and dichloromethyltrimethylsilane have been calculated as 1.93, 2.03 and 2.28 Debye units, respectively. These data permit calculation of the $(CH_3)_3Si-$ group moment as 0.25–0.32 Debye unit. The results are discussed in terms of the large polarizability of the silicon atom.

The interesting properties of organosilicon compounds have merited attention from many investigators. The problem of charge distribution in the organosilicon molecules has been attacked with the hope of shedding light on some of the peculiar behavior of these substances. In this report, there are presented the results of our work with compounds in which silicon is bonded to aliphatic carbon atoms.

Experimental

Chloromethyltrimethylsilane.—This was prepared according to the directions of Whitmore, Sommer and Gold[1] and was purified by fractional distillation through a glass helices packed column, b.p. 97.2°, $n^{25}D$ 1.4148, d^{25}_4 0.8764.

Dichloromethyltrimethylsilane.—This was prepared by the method of Speier and Daubert[2] and was purified by fractional distillation, b.p. 134°, $n^{25}D$ 1.4421, d^{25}_4 1.042.

Neopentyl Chloride.—A sample of purified neopentyl chloride was kindly furnished us by Dr. Leo Sommer of Pennsylvania State College and used without further purification.

Measurements and Calculations.—The procedure used has already been described.[3] The measurements are summarized in Table I where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction f_2 of the substance indicated are given along with the molar polarization and molar refraction. The table also includes the polarization obtained by extrapolation to $f_2 = 0$ of the P_2 values and the dipole moment, μ, calculated therefrom in the usual manner.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES, POLARIZATIONS AND DIPOLE MOMENTS IN BENZENE AT 30°

f_2	ϵ	d	P_2
Chloromethyltrimethylsilane, $MR_D = 35.0$, $\mu = 2.03$ D			
0.00000	2.2627	0.86823	(118.0)
.00997	2.3136	.86814	117.5
.02434	2.3832	.86800	114.7
.03079	2.4141	.86794	113.9
.05442	2.5294	.86772	112.8
Neopentyl chloride, $MR_D = 30.1$, $\mu = 1.93$ D			
0.00000	2.2627	0.86823	(104.8)
.01145	2.3152	.86796	104.6
.02094	2.3568	.86772	102.9
.03752	2.4291	.86731	101.5
.05257	2.4963	.86691	101.0
Dichloromethyltrimethylsilane, $MR_D = 40.0$, $\mu = 2.28$ D			
0.00000	2.2627	0.86823	(144.4)
.01198	2.3428	.87142	143.7
.02128	2.4071	.87391	144.2
.02989	2.4733	.87633	146.9
.04037	2.5365	.87879	142.7

Discussion of Results

In the organosilicon compounds studied the silicon is bonded to three methyl groups and a fourth, substituted methyl group. In order to study the effect of the silicon atom in the electrical charge distribution of these compounds it was decided to consider the $(CH_3)_3Si-$ group as a unit. Thus the two compounds might be written as RCH_2Cl and $RCHCl_2$ where the R symbolizes the $(CH_3)_3Si-$ group. We have assumed that the moment of RCH_2Cl may be calculated, as is that of a disubstituted methane, as the vector sum of the R–C and C–Cl moments each acting in the direction of the tetrahedral bond angle. The moments of the C–H bonds are not considered in this calculation. In order to obtain as exact correspondence as possible, the value of the C–Cl moment was calculated from the dipole moment of neopentyl chloride assuming that the entire value, 1.93 D, resides in the C–Cl bond. Thus, a comparison of the moments of neopentyl chloride and chloromethyltrimethylsilane permits calculation of the $(CH_3)_3Si-C$ group moment. The value, 0.25 D with the silicon atom assumed to be at the positive end of the dipole, is of the same order of magnitude as that reported by Roberts and coworkers[4] based on measurements of halogen nuclear substituted trimethylsilylbenzenes.

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[1] F. C. Whitmore, L. H. Sommer and J. Gold, THIS JOURNAL, **69**, 1976 (1947).

[2] J. Speier and B. F. Daubert, *ibid.*, **70**, 1400 (1948).

[3] R. K. Keswani and H. Freiser, *ibid.*, **71**, 218 (1949).

[4] J. D. Roberts, E. A. McElhill and R. Armstrong, *ibid.*, **71**, 2294 (1949).

The moment of the $(CH_3)_3Si–C_{aliph}$ group was evaluated from the moment of the dichloromethyltrimethylsilane by considering the moment of this compound to be the vector sum of the two C–Cl moments and the $(CH_3)_3Si–C_{aliph}$ moment each acting along the regular tetrahedral bond angle. In order to eliminate as far as possible the effect of inductive interaction of the two chlorine atoms, the moment of the $–CHCl_2$ group, 2.07 *D*, as measured in ethylidene chloride[5] and 1,1-dichloropropane[6] was used in the calculation. This moment was assumed to act along the bisector of the Cl–C–Cl angle. This vector, the resultant of the two C–Cl moment vectors, meets the $(CH_3)_3Si–C_{aliph}$ moment at an angle, β, such that

$$\cos \beta = \sqrt{\frac{2\cos^2 109°28'}{1 + \cos 109°28'}} = 0.5772$$

In this manner, a value of 0.32 *D* for the $(CH_3)_3Si–C_{aliph}$ group is obtained. While this is in fair agreement with the 0.25 *D* value calculated from the chloromethyltrimethylsilane, it is definitely higher. This can be attributed to the high polarizable character of the silicon atom already noted by Curran.[7] It should be noted that solvent effects, which tend to discredit the significance of dipole measurements performed on compounds in solution, are effectively eliminated by comparing compounds of similar structures measured in the same solvent. Compounds in which silicon is bonded to aromatic carbon may be expected to have varying moments,[4] reflecting the ease with which silicon can be electrically distorted. An investigation of organosilicons of this type is under way.

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[5] A. A. Maryott, M. E. Hobbs and P. M. Gross, THIS JOURNAL, **63**, 659 (1941).

[6] P. Gross, *Physik. Z.*, **32**, 587 (1931).

[7] B. C. Curran, R. M. Witucki and P. A. McCusker, THIS JOURNAL, **72**, 4473 (1950).

PITTSBURGH 13, PENNSYLVANIA

RECEIVED JANUARY 22, 1951

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

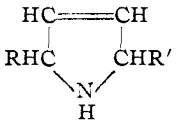
The Structure of Alkyl-Substituted Pyrrolines[1]

BY GORDON G. EVANS[2,3]

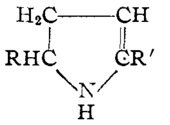
Two isomers each of 2-methyl-, 2,5-dimethyl- and 1,2,5-trimethylpyrroline have been prepared and characterized, and their structures have been established. Each pair of isomers differs only in the position of the double bond in the ring, and in one case the direct conversion of one isomer to the other has been demonstrated. The reduction of homologs of pyrrole with zinc and hydrochloric acid may lead to a mixture of pyrrolines containing the Δ^1- or Δ^2- as well as the Δ^3-isomer, although the product from the reduction of pyrrole itself is homogeneous.

It has long been recognized that, for a pyrroline containing a particular carbon–nitrogen skeleton, various isomers are possible depending on the position of the double bond,[4] but previous work on the preparation of such isomers and the establishment of their structure has been limited to pyrrolines with an aromatic substituent[5] and 1,1-dimethylpyrrolinium salts.[6] The preparation of two isomers each of 2-methyl-, 2,5-dimethyl- and 1,2,5-trimethylpyrroline has now been accomplished.

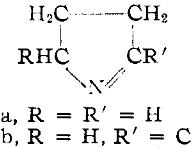
It has generally been assumed[4] that Δ^3-pyrrolines will be formed in the reduction of pyrroles by zinc and an acid (unless an aromatic substituent is present[5,7]) and this assumption has been verified by Treibs and Dinelli[8] for the unsubstituted compound (Ia). Pyrroline preparations involving closure of the ring, on the other hand, have been supposed to yield compounds with the Δ^2 structure (II) or its Δ^1 tautomer (III).[4,9] On very limited evidence, attempts have been made to establish generalizations differentiating the behavior of the two classes.[10,11] The present work necessitates some modification of these views.



Ia, R = R' = H
Ib, R = CH_3, R' = H
Ic, R = R' = CH_3



IIa, R = R' = H
IIb, R = H, R' = CH_3
IIc, R = CH_3, R' = H
IId, R = R' = CH_3



IIIa, R = R' = H
IIIb, R = H, R' = CH_3
IIIc, R = CH_3, R' = H
IIId, R = R' = CH_3

2,5-Dimethylpyrrolines.—The reduction of 2,5-dimethylpyrrole by zinc and hydrochloric acid has been reported by Knorr and Rabe[12] and by Blaise[13] to yield a basic liquid boiling at 106° (736 mm.), whose picrate melts at 107° and which, on treatment with phenyl isocyanate, forms a phenylurea melting at 130°. The present writer, employing

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[1] Most of the results reported in this paper are taken from a thesis submitted by Gordon G. Evans to the Faculty of Arts and Sciences of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1949.

[2] National Research Council Predoctoral Fellow, 1946–1949.

[3] Department of Chemistry, Tufts College, Medford 55, Mass.

[4] G. Ciamician, *Ber.*, **34**, 3952 (1901).

[5] H. P. L. Gitsels and J. P. Wibaut, *Rec. trav. chim.*, **60**, 50 (1941); J. Dhont and J. P. Wibaut, *ibid.*, **63**, 81 (1944).

[6] R. Lukeš and J. Přeučil, *Coll. Czech. Chem. Comm.*, **10**, 384 (1938).

[7] A. Sonn, *Ber.*, **68B**, 148 (1935); *ibid.*, **72B**, 2150 (1939).

[8] A. Treibs and D. Dinelli, *Ann.*, **517**, 170 (1935).

[9] A. Wohl (*Ber.*, **34**, 1914 (1901)) has claimed the formation of a Δ^1-pyrroline by a ring-closure method, but he adduces no evidence in support of this structure.

[10] G. Ciamician, *ibid.*, **37**, 4246 (1904).

[11] L. Mascarelli and G. Testoni, *Gazz. chim. ital.*, **33II**, 312 (1903).

[12] L. Knorr and P. Rabe, *Ber.*, **34**, 3491 (1901).

[13] E. E. Blaise, *Compt. rend.*, **158**, 1686 (1914); E. E. Blaise and A. Cornillot, *ibid.*, **178**, 1617 (1924).