between the proton and the halogen. This coincides with the usual limit for the transmission of inductive effects along a chain; shielding values for protons further removed on the carbon chain are effectively identical with those for protons in alkanes.

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CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RICHMOND LABORATORY, CALIFORNIA RESEARCH CORPORATION]

Silicate Esters and Related Compounds. I. Synthesis of Certain Tetraalkoxysilanes, Polyalkoxysiloxanes, Bis-(trialkoxysilyl)-alkanes and Related Intermediates[1]

BY J. R. WRIGHT, R. O. BOLT, A. GOLDSCHMIDT AND A. D. ABBOTT

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Methods for the synthesis of silicate esters, disiloxanes (disilicates), trisiloxanes (trisilicates), bis-(trialkoxysilyl)-alkanes, alkoxychlorosilanes, alkoxysilylamines and alkoxysilanols are described. It is shown that the selection of reactants and reaction conditions to obtain a given compound must be based largely on the structure of the hydrocarbon radicals involved. New methods of synthesis and modifications of existing methods were developed to make a number of previously unreported compounds. The present paper describes these preparations. Future papers will describe the properties of the new esters.

Discussion

The shielding of functional linkages by the adjacent alkyl groups accounts for necessary variations in the general procedures to be described for the syntheses of silicates and related intermediates. The degree of shielding determines, for example, the reactivity of the chlorine atom in trialkoxychlorosilanes. It also governs the hydrolytic stability of silicate esters generally. The influence of this steric effect determined the preparation procedures used in the following cases.

Alkoxychlorosilanes and Tetraalkoxysilanes.—Reaction 1 is the most generally applicable for the preparation of these compounds.[2,3]

The concentrations of the individual reaction products depend upon the structure of the alcohol and upon the mole ratio of alcohol to tetrachlorosilane used. Because the rate of reaction decreases as chlorine atoms are successively replaced, lower temperatures tend to reduce the proportion of higher substitution products.

$$\mathrm{SiCl_4} \xrightarrow{\mathrm{ROH}} \text{mixture of } \mathrm{ROSiCl_3} + \mathrm{(RO)_2SiCl_2} + \mathrm{(RO)_3SiCl} + \mathrm{(RO)_4Si} + \mathrm{HCl} \quad (1)$$

Primary and secondary alcohols react readily with no complicating side reactions. However, tertiary alcohols require acid acceptors[4] to prevent dehydration of the alcohol and subsequent hydrolysis of chlorosilane derivatives. Even with this change, tri-(*t*-alkoxy)-chlorosilane is the highest substitution product obtainable by this method even with a large excess of tertiary alcohol.[5]

Temperature and steric hindrance effects for primary and secondary alcohols in reaction 1 are both illustrated by the reaction of three moles of alcohol with one mole of tetrachlorosilane.[6] Straight-chain primary alcohols produce mixtures of all four substitution products with no single one predominating even at −15°. On the other hand, 2-ethylhexanol yields 75 mole per cent. of the trialkoxychlorosilane at −15°. With 2-butanol, 85 to 95 mole per cent. of the trialkoxychlorosilane is obtained at 0°.

Tetraalkoxysilanes. (A) Derived from Primary Alcohols.—Reaction 1 yields tetraalkoxysilane readily when an excess of alcohol is employed. Method 2 is also satisfactory.[7,8] In most cases,

$$\mathrm{(EtO)_4Si} + \text{(Excess) } \mathrm{ROH} \xrightarrow{\mathrm{NaOR}} \mathrm{(RO)_4Si} + 4\mathrm{EtOH} \quad (2)$$

the latter is inferior to the alcoholysis of tetrachlorosilane because of the slow replacement of the fourth ethoxy group. However, reaction 2 was the only satisfactory means found for preparing tetrabenzyloxysilane.[6]

(B) Derived from Secondary Alcohols.—Method 1 is generally best for this synthesis. However, the reaction is very different from that with primary alcohols because of the relatively slow rate of replacement of the last chlorine atom. The tetrasubstitution stage is reached only after prolonged heating even when an excess of the alcohol is used. An acid acceptor increases this replacement rate. Only the trialkoxychlorosilane could be obtained from 2,4-dimethyl-3-pentanol, apparently because of steric hindrance.[6]

(C) Derived from Tertiary Alcohols.—Breederveld and Waterman[9] reported the preparation of tetra-(*t*-butoxy)-silane by the two steps shown in

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[1] Presented in part at a Meeting of the American Association for the Advancement of Science, Berkeley, Calif., December, 1953.

[2] C. R. Morgan, W. F. Olds and A. L. Rafferty, THIS JOURNAL, **73**, 5193 (1951).

[3] H. W. Post, "Silicones and Other Silicon Compounds," Reinhold Publishing Corp., New York, N. Y., 1949, p. 122.

[4] C. S. Miner, L. A. Bryan, R. P. Holysz and G. W. Pedlow, *Ind. Eng. Chem.*, **39**, 1368 (1947).

[5] H. J. Backer and H. A. Klasens, *Rec. trav. chim.*, **61**, 500 (1942).

[6] Based upon unpublished results from this Laboratory.

[7] H. W. Post, "The Chemistry of Aliphatic Orthoesters," ACS Monograph Series, Reinhold Publishing Corp., New York, N. Y., 1943, p. 133.

[8] D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946).

[9] H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **73**, 871 (1954).

$$\mathrm{SiBr_4 + NaO\text{-}\mathit{t}\text{-}Bu \xrightarrow[80\text{-}100^\circ]{\text{petr. ether}} 3NaBr + (\mathit{t}\text{-}BuO)_3SiBr\ [41\%\ yield]}$$

$$\mathrm{(\mathit{t}\text{-}BuO)_3SiBr + NaO\text{-}\mathit{t}\text{-}Bu \xrightarrow[\text{sealed tube}]{220^\circ,\ 10\ hr.} (\mathit{t}\text{-}BuO)_4Si\ [37\%\ yield] + NaBr} \quad (3)$$

(3). According to Hyde and Curry,[10] this reaction proceeds more readily with silicon tetrafluoride. The reaction between tetrachlorosilane and sodium *t*-butoxide did not yield tetrasubstitution under conditions less drastic than those of (3).[5] Attempts to introduce three tertiary alkoxy groups by reaction 2 were not successful in the present work.

The tri-(*t*-alkoxy)-chlorosilanes will react with either a primary or a secondary alcohol or the corresponding alkali metal alkoxides.[11]

The synthesis of tetraalkoxysilanes containing only one tertiary alkoxy group was shown in the present work to be possible by any one of three following methods. Primary or secondary alkyl groups are represented by R, and tertiary alkyl groups by R′.

$$\mathrm{(RO)_3SiCl + R'OH \xrightarrow{\text{pyridine}} (RO)_3SiOR' + pyridine{\cdot}HCl^{8}} \quad (4)$$

$$\mathrm{(RO)_3SiNH_2 + R'OH \longrightarrow (RO)_3SiOR' + NH_3{}^{4}} \quad (5)$$

$$\mathrm{(RO)_3SiOH + R'NH_2 \xrightarrow{\text{NaOMe}} (RO)_3SiOR' + NH_3{}^{12}} \quad (6)$$

Trialkoxysilylamines and Trialkoxysilanols.—The amines can be made according to equation 7 where R represents primary, secondary or tertiary alkyl groups.[4,6] The reaction is essentially quantitative, and its completion can be recognized by a sudden cessation of heat evolution.

$$\mathrm{(RO)_3SiCl + 2NH_3 \longrightarrow (RO)_3SiNH_2 + NH_4Cl} \quad (7)$$

Silanols can be prepared according to equation 8 or 9.[4]

$$\mathrm{(RO)_3SiCl + H_2O \longrightarrow (RO)_3SiOH + HCl} \quad (8)$$

$$\mathrm{(RO)_3SiNH_2 + H_2O \longrightarrow (RO)_3SiOH + NH_3} \quad (9)$$

The nature of the alkyl groups here is of great importance. The primary alkoxysilanols cannot be isolated because they are converted immediately to disiloxanes. Hurd[13] suggested a mechanism for this reaction. Tri-(*sec*-alkoxy)-chlorosilanes in the presence of an excess of water form the silanols at 0° in approximately an 80% yield.[2] At higher temperatures increasing amounts of siloxanes are formed. Only the silanol is formed from tri-(*t*-alkoxy)-chlorosilanes even when treated with boiling water.[6] The reaction of trialkoxysilylamines with water is governed by the same structural considerations as the reaction of corresponding chlorosilanes.

Hexaalkoxydisiloxanes. (A) By Hydrolysis of Trialkoxychlorosilane.—The structure of the alkyl group has a major effect on reaction 10.

$$\mathrm{2(RO)_3SiCl + H_2O \xrightarrow{\text{pyridine}} (RO)_3SiOSi(OR)_3 + 2HCl} \quad (10)$$

Primary trialkoxychlorosilanes are converted to disiloxanes in high yields by the theoretical (or excess) amount of water at room temperature.[2] However, in the synthesis of the hexa-(*sec*-alkoxy)-disiloxanes, the theoretical amount of water must be used, an excess produces silanols. The yield of disiloxane depends upon the reaction temperature, a maximum being obtained at about 50°. At higher temperatures, gel formation sometimes occurs and lower yields of disiloxane result.[6]

With tri-(*t*-alkoxy)-chlorosilanes only silanols are obtained by (10). Hexa-(*t*-butoxy)-disiloxane has been prepared by reaction 11.[5]

$$\mathrm{(\mathit{t}\text{-}BuO)_3SiCl + NaOSi(O\text{-}\mathit{t}\text{-}Bu)_3 \xrightarrow[\text{sealed tube}]{} (\mathit{t}\text{-}BuO)_3SiOSi(O\text{-}\mathit{t}\text{-}Bu)_3 + NaCl} \quad (11)$$

(B) By Hydrolysis of Trialkoxysilylamine.—A satisfactory method is given by reaction 12.[14]

$$\mathrm{2(RO)_3SiNH_2 + H_2O \xrightarrow{\text{base}} (RO)_3SiOSi(OR)_3 + 2NH_3} \quad (12)$$

Either primary or secondary alkoxysilylamines may be used. (Tertiary derivatives were not investigated.) The yield of disiloxane varies markedly with the basic catalyst employed. The best yields are obtained with sodium methoxide.

(C) By Silanolysis of Silylamine.—Asymmetric disiloxanes may be made by method 13.[15] The

$$\mathrm{(RO)_3SiNH_2 + HOSi(OR')_3 \longrightarrow (RO)_3SiOSi(OR')_3 + NH_3} \quad (13)$$

R may be primary or secondary, and R′ may be secondary alkyl groups. (Tertiary compounds were not investigated.) The condensation takes place with the formation of the desired disiloxane exclusively because neither reactant can condense with a like molecule under the conditions used. No evidence of silazane formation was found.

(D) Synthesis from Hexachlorodisiloxane.—The literature contains conflicting data on the method in equation 14 where R can be primary or secondary. Temperatures of the order of 100°

$$\mathrm{Cl_3SiOSiCl_3 + 6ROH \longrightarrow (RO)_3SiOSi(OR)_3 + 6HCl} \quad (14)$$

were found by Abrahamson, *et al.*,[16] to yield no disiloxane. However, Orkin[17] refers to the successful preparation of hexaalkoxydisiloxanes by this method. In the latter case, no data on isolated disiloxanes are given; the viscosity of the stripped reaction product is cited as evidence for these claimed materials. It was found in the present work that disiloxanes can indeed be prepared by (14) although conditions different from those cited previously are required. Table I summarizes data on conditions used and the yields of product obtained. The desirability of removing the hy-

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[10] J. F. Hyde and J. W. Curry, This Journal, **77**, 3140 (1955).

[11] H. Breederveld and H. I. Waterman, *Rec. trav. chim.*, **72**, 166 (1953).

[12] J. R. Wright, U. S. Patent 2,727,054, Dec. 13, 1955.

[13] D. T. Hurd, This Journal, **77**, 2998 (1955).

[14] A. Goldschmidt and J. R. Wright, U. S. Patent 2,758,126, August 7, 1956.

[15] A. Goldschmidt and J. R. Wright, U. S. Patent 2,758,127, August 7, 1956.

[16] E. W. Abrahamson, I. Joffe and H. W. Post, *J. Org. Chem.*, **13**, 275 (1948).

[17] B. A. Orkin, U. S. Patent 2,626,957, January 27, 1953

drogen chloride from the reaction mixture is shown by the increased yields obtained under reduced pressure.

TABLE I

DATA ON HEXA-(2-ETHYLBUTOXY)-DISILOXANE SYNTHESIS BY THE ALCOHOLYSIS OF HEXACHLORODISILOXANE

Run no.	Reaction temperature, °C. Initial	Final	Yield of disiloxane, %
1	100	105	0.0
2	−20	83	11.3
3[a]	−20	25	26.0
4[a,b]	−20	5	54.5
5[a,b]	−20	−5	58.0

[a] Nitrogen passed over reaction mixture during addition period. [b] Reaction mixture under 100 mm. pressure.

Octaalkoxytrisiloxanes and Related Compounds.—Methods used for the synthesis of these compounds are illustrated by these equations

$$2(RO)_3SiOH + Cl_2Si(OR')_2 \xrightarrow{\text{pyridine}} (RO)_3SiOSi(OR')_2OSi(OR)_3 + 2\ \text{pyridine}\cdot HCl \quad (15)$$

where R = secondary or tertiary alkyl and R′ = primary, secondary, or tertiary alkyl groups

$$2(RO)_3SiCl + (HO)_2SiPh_2 \xrightarrow[\text{pyridine}]{\text{2-methyl-}} (RO)_3SiOSi(Ph)_2OSi(OR)_3 + 2\ \text{pyridine}\cdot HCl \quad (16)$$

where R = primary, secondary or tertiary alkyl groups

$$2(RO)_3SiOH + R'_2SiCl_2 \xrightarrow{N_2} (RO)_3SiOSiR'_2OSi(OR)_3 + 2HCl \quad (17)$$

where R = secondary or tertiary alkyl and R′ = primary, secondary or tertiary alkyl groups

$$6ROH + Cl_3SiCH_2CH_2SiCl_3 \longrightarrow [(RO)_3SiCH_2]_2 + 6HCl \quad (18)$$

where R = primary, secondary or tertiary alkyl groups. The synthesis of the bis-(trialkoxysilyl)-ethane in (18) is particularly noteworthy because the reactivity of the hexachloro intermediate is far less than that of hexachlorodisiloxane. The reaction between 2-ethylbutanol and bis-1,2-(trichlorosilyl)-ethane did not take place at 0°, was only moderate at 25°, and could be carried to completion only at 100°.[6]

Experimental Part

Table II is a summary of data on the syntheses of the compounds involved in this work. Three general procedures were used, and the one used for each compound is indicated in the table along with the variations employed. These processes will be described briefly in this section, with the aid of Table II, and references will be made to them in subsequent papers of this series.

Process Ia.—Reactant A is placed in a flask equipped with a thermometer, sealed stirrer, dropping funnel, gas inlet tube and reflux condenser. To ensure anhydrous conditions, the condenser is fitted with a calcium chloride tube on the exhaust end, and the entire apparatus is swept with dry nitrogen. When cooling is indicated in Table II, a salt–ice-bath is used. Reactant B is added dropwise over the required time period, and the flask is heated when needed to complete the reaction. Dry nitrogen is then passed through the liquid to remove liberated hydrogen chloride. The product thus obtained, consisting of a single liquid phase, is fractionated under reduced pressure.

Process Ib.—The apparatus used here is the same as that for process Ia except that nitrogen is employed only for drying the system; none is required during the reaction (no volatile reactant is liberated). A gas inlet tube is needed in those cases where ammonia is one of the reactants. It should be noted from the table that reactant A need not be isolated in most instances from its original preparative mixture. The solvent employed is mixed with reactant A in the flask. Two-phase systems, consisting of a liquid product and a solid hydrochloride salt, result from reactions in which process Ib is used. This system usually is treated by filtration and washing of the precipitate with solvent prior to rectification of the liquid phase. In cases where the desired product is stable to hydrolysis, an alternate method is to dissolve the solid in water. The aqueous phase is then removed, extracted with more solvent, and the combined organic phases dried over anhydrous sodium sulfate prior to rectification.

Process Ic.—The equipment for this process is essentially the same as that for processes Ia and Ib. A gas inlet tube is needed only when one of the reactants is a silylamine which is first made from ammonia and the corresponding chlorosilane. It was found unnecessary to purify the silylamine thus prepared before proceeding with process Ic. Hydrolysis reactions in the presence of an excess of water are involved in this process, and products consisting of two liquid phases, one of which is aqueous, are formed. The organic phase is separated, added to an ether extract of the water phase, dried over anhydrous sodium sulfate, and finally rectified.

Process IIa.—The apparatus for this process is similar to that described for process Ia. The reaction flask is equipped with a thermometer, sealed stirrer, gas inlet tube and reflux condenser fitted with a calcium chloride drying tube on the exhaust end. When a catalyst is used, it is mixed with reactant A in the flask before the addition of reactant B. The reaction mixtures are heated as indicated and then rectified under reduced pressure.

Process IIb.—This method is similar to process IIa, except that a low boiling alcohol is liberated as a by-product instead of a gaseous material. A nitrogen purge is not used, but in cases where the boiling point of the liberated alcohol is near that of one of the reactants, the reaction flask must be fitted with a suitable column to separate this alcohol continuously. When necessary, the product is filtered before rectification.

Process III.—The preparation of hexakis-(2-ethylbutoxy)-disiloxane by the alcoholysis of hexachlorodisiloxane required special apparatus and conditions not needed for the other procedures, and consequently is described as a specific case. Redistilled hexachlorodisiloxane (0.55 mole) was placed in a dry, two-liter flask fitted with a dropping funnel, thermometer, sealed stirrer, gas inlet tube and reflux condenser. The apparatus was dried prior to this addition and the reflux condenser protected from moisture by a calcium chloride drying tube on the exhaust end. Provisions were also made to apply vacuum to the system through the condenser, and to cool the reaction mixture with an acetone–Dry Ice-bath. Dry 2-ethylbutanol (3.6 moles) was added dropwise to the hexachlorodisiloxane over 1.8 hours while maintaining a temperature of −20°. The hydrogen chloride liberated was removed by continuously passing a stream of dry nitrogen through the reaction mixture and by maintaining a vacuum of 100 mm. on the system during the reaction period. Stirring was continued for an additional 1.3 hours under these conditions while the temperature was allowed to rise to −15°. Ammonia was then passed through the mixture to neutralize any remaining hydrogen chloride while agitation was continued for another two hours as the temperature rose to 25°. Excess ammonia was, in turn, removed by sweeping nitrogen through the system. The solid phase was removed by filtration, and the liquid phase subsequently rectified at 0.1 mm.; 207 g. of product (54.5% yield) boiling at 80–82° (n^{20}_D 1.4331) was obtained.

TABLE II

DATA ON PROCESSES FOR SYNTHESES OF CERTAIN SILICATE ESTERS AND RELATED COMPOUNDS

Reaction product		Process	Reactant A, moles	Reaction materials Catalyst or solvent	Reactant B, moles		Reaction conditions N_2 purge	Temp., °C.	Time, hr.	Conv., %	Mm.	Results Boiling point °C.	$n^{20}D$
$(2\text{-BuO})_3\text{SiCl}$	Ia	SiCl_4	3.0	None	2-BuOH	9.0	Yes	-5^{f}	2.0	86	2.0	76.5–78	1.4098^{a}
$(2\text{-BuO})_3\text{SiNH}_2$	Ib	$(2\text{-BuO})_3\text{SiCl}^{e}$	1.2	800 ml. petr. eth.	NH_4	Excess	No	$25\text{–}45^{h}$	4.0	87	5.0	93	1.4138^{b}
$(2\text{-BuO})_3\text{SiOH}$	Ib	$\text{H}_2\text{O}/\text{C}_5\text{H}_5\text{N}$	22.0/1.3	None	$(2\text{-BuO}_3)\text{SiCl}$	1.0	No	10–13	1.0	83	3.0	90–92	1.4132^{c}
$(2\text{-BuO})_3\text{SiOH}$	Ic	$(2\text{-BuO})_3\text{SiNH}_2^{e}$	1.1	800 ml. petr. eth.	H_2O	27.8	No	10^{f}	0.5	81	5.0	107.5–108.5	1.4132^{f}
								10–25	1.0				
$(2\text{-BuO})_4\text{Si}$	Ia	SiCl_4	1.0	None	2-BuOH	5.1	Yes	-10 to 15^{f}	1.75	54	5.0	108	1.4076^{i}
								100	4.0				
$(2\text{-BuO})_3(t\text{-BuO})\text{Si}$	IIa	$(2\text{-BuO})_3\text{SiOH}^{e}$	0.50	1 g. NaOMe	$t\text{-BuNH}_2$	0.55	Yes	$25\text{–}91^{g}$	5.0	73	5.0	120	1.4075^{j}
$(\text{PhCH}_2\text{O})_4\text{Si}$	IIb	$(\text{EtO})_4\text{Si}$	4.5	10 g. Na	PhCH_2OH	26.8	No	130–175	12.0^{d}	70	0.2	215–221	MP 32.5°
$[(2\text{-EtBuO})_3\text{Si}]_2\text{O}$	Ic	$\text{H}_2\text{O}/\text{C}_5\text{H}_5\text{N}$	16.6/1.9	None	$(2\text{-EtBuO})_3\text{SiCl}^{e}$	1.05	No	$26\text{–}35^{f}$	1.0	56	0.2	195	1.4331^{k}
								35	4.0				
$[(2\text{-EtBuO})_3\text{Si}]_2\text{O}$	Ic	$(2\text{-EtBuO})_3\text{SiNH}_2^{e}$	0.62	350 ml., petr. eth.	H_2O	22.2	No	25–30	3.0	52	1.0	188	1.4331
				1 g. NaOMe				42^{g}	1.5				
$[(2\text{-EtBuO})_3\text{Si}]_2\text{O}$	III	$(\text{Cl}_3\text{Si})_2\text{O}$	0.55	None	2-EtBuOH	3.6	Yes	-20^{f}	1.8	55	0.1	180–182	1.4331
								-20 to 5^{f}	1.3				
								25	2.0				
$[(2\text{-BuO})_3\text{Si}]_2\text{O}$	Ib	$(2\text{-BuO})_3\text{SiCl}^{e}$	0.39	100 ml. benzene	$\text{H}_2\text{O}/\text{C}_5\text{H}_5\text{N}$	0.33/1.0	No	15^{f}	1.0	61	1.0	139–141	1.4132^{l}
								25^{g}	0.5				
$[(2\text{-BuO})_3\text{Si}]_2\text{O}$	IIa	$(2\text{-BuO})_3\text{SiNH}_2^{e}$	0.30	None	$(2\text{-BuO})_3\text{SiOH}$	0.60	Yes	149–160	12.0	36	1.5	145.5–146.5	1.4132
$[(2\text{-BuO})_3\text{SiO}]_2(2\text{-BuO})_2\text{Si}$	Ib	$(2\text{-BuO})_3\text{SiOH}/$ $\text{C}_5\text{H}_5\text{N}^{e}$	0.98/1.3	400 ml. petr. eth.	$(2\text{-BuO})_2\text{SiCl}_2$	0.38	No	25–72	1.0	45	1.0	187–188	1.4178^{m}
								80	6.0				
$[(2\text{-BuO})_3\text{SiO}]_2\text{SiPh}_2$	Ib	$\text{Ph}_2\text{Si(OH)}_2/$ $2\text{-MeC}_5\text{H}_4\text{N}$	0.67/2.0	400 ml. benzene	$(2\text{-BuO})_3\text{SiCl}$	1.37	No	25–60	1.0	28	1.0	256–258	1.4638^{n}
								140^{g}	2.0				
$[(2\text{-MeBuO})_3\text{SiCH}_2]_2$	Ia	$(-\text{CH}_2\text{SiCl}_3)_2$	0.33	None	2-MeBuOH	2.2	Yes	25	1.5	94	0.1	220	1.4346^{o}
								$25\text{–}80^{g}$	4.0				

[a] % Cl calcd. 12.57, found 12.7. [b] % Si calcd. 10.65, found 10.24; % N calcd. 5.33, found 5.13. [c] Mol. refraction calcd. 70.16, found 70.5. [d] 96% of theor. EtOH given off. [e] Not purified. [f] Cooling required. [g] Heating necessary. [h] Drop in temperature denotes end of reaction. [i] % Si calcd. 8.75, found 8.98. [j] % Si calcd. 8.75, found 8.74. [k] Mol. refraction calcd. 192.38, found 191.82. [l] % Si calcd. 11.0, found 10.64. [m] % Si calcd. 13.7, found 13.97. [n] % Si calcd. 11.88, found 11.99. [o] % Si calcd. 9.35, found 9.34.

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RICHMOND, CALIF.

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

γ-Ray Initiated Reactions. II. The Addition of Silicon Hydrides to Alkenes[1]

BY A. M. EL-ABBADY[2] AND LEIGH C. ANDERSON

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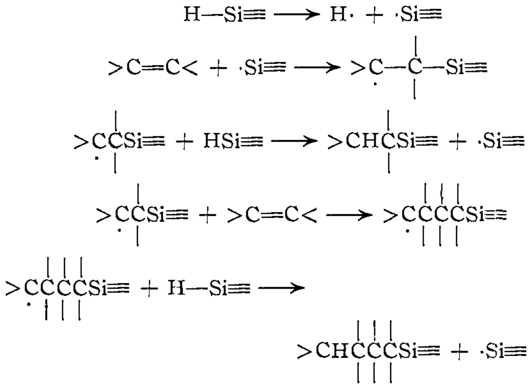
Trichlorosilane and methyldichlorosilane add to the double bond of certain alkenes in the presence of γ-rays as initiator. These compounds include octene-1, isobutylene, butene-2, 2-methyl-2-butene, cyclopentene, cyclohexene, 1-methylcyclohexene, allyl chloride, allyl acetate, allyl cyanide, *cis*-1,2-dichloroethylene, 3,3,4,4,4-pentafluoro-1-butene, 2-methyl-3,3,-4,4,4-pentafluoro-1-butene, 3,3,4,4,5,5,5-heptafluoro-1-pentene and 2-methyl-3,3,4,4,5,5,5-heptafluoro-1-pentene. Ethyl cinnamate, diethyl fumarate, indene and *trans*-stilbene were unreactive. Styrene and α-methylstyrene gave high-boiling silicon polymers. In addition to the isolation of the saturated monomeric adducts, some high-boiling alkylsilyl substituted derivatives were also obtained. Some of the adducts obtained in this way were converted to their tetraalkylsilyl derivatives or hydrolyzed to form polysiloxanes. On hydrolysis 3,3,4,4,5,5,5-heptafluoro-1-pentyltrichlorosilane gave unexpectedly a liquid siloxane.

Several publications have disclosed the addition of silicon hydrides to a number of alkenes under the activation of peroxides and ultraviolet light.[3] Recently two reports have appeared on such type of addition to fluorine-containing alkenes.[4] These involve the addition of silicon hydrides to tetrafluoroethylene photochemically and to chlorotrifluoroethylene, trifluoropropene, 1,1,2-trichloro-3,-3,3-trifluoropropene and 2,3,3,4,4,4-hexafluorobutene using peroxides and ultraviolet light. The yields of the products varied appreciably and were dependent both on the experimental conditions and on the nature of the reactants.

The present investigation differs primarily from the above work in that the reaction was carried out using γ-rays from a 3.0 kilocurie Co^{60} source as initiator at room temperature and also since additional alkenes were used. Trichlorosilane and methyldichlorosilane were added to some simple alkenes. The reaction was clean and went almost quantitatively, giving the expected adducts (Table I). Similarly the reaction was carried out on a number of alkenes which have functional groups and fluorine atoms (Tables II and III).

Other investigators have postulated that the addition of silicon hydrides to alkenes is a free-radical chain reaction. Their proposed mechanism for this reaction[5,3a] includes the steps



$$\text{H—Si}\equiv \longrightarrow \text{H}\cdot + \cdot\text{Si}\equiv \qquad (1)$$

$$>\text{C=C}< + \cdot\text{Si}\equiv \longrightarrow >\dot{\text{C}}\text{—C—Si}\equiv \qquad (2)$$

$$>\dot{\text{C}}\text{CSi}\equiv + \text{HSi}\equiv \longrightarrow >\text{CHCSi}\equiv + \cdot\text{Si}\equiv \qquad (3)$$

$$>\dot{\text{C}}\text{CSi}\equiv + >\text{C=C}< \longrightarrow >\dot{\text{C}}\text{CCCSi}\equiv \qquad (4)$$

$$>\dot{\text{C}}\text{CCCSi}\equiv + \text{H—Si}\equiv \longrightarrow >\text{CHCCCSi}\equiv + \cdot\text{Si}\equiv \qquad (5)$$

In the work being reported in this paper, the rate of the reaction of simple alkenes to form the monomeric products (equation 3) was predominant. But in case of other alkenes as allyl chloride, allyl acetate and *cis*-1,2-dichloroethylene it was found that the second reaction, which is responsible for the formation of high-boiling materials (equation 4), was a strong competitor. Styrene and α-methylstyrene formed high-boiling products to the exclusion of monomeric products. The lesser reactivity of methyldichlorosilane toward alkenes (Table III) was not unexpected because of the difference in the electrophilic character of the methyl derivative. Although the addition of silicon hydrides to 1-alkenes has been shown by other investigators to yield the 1-isomer exclusively,[3a] the addition compound of trichlorosilane to allyl cyanide could be either $CNCH_2CH_2CH_2SiCl_3$ (I) or $CNCH_2CH(CH_3)SiCl_3$ (II) or a mixture of them.[6] In order to distinguish between the two structures, the product prepared in this work was converted to the trimethyl acid amide derivative which was found to have properties identical with those of γ-trimethylsilylbutyric acid amide which is described in the literature.[7] By analogy, the addition com-

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[2] On leave from the Department of Chemistry, University College for Girls, A'in Shams University, Cairo, Egypt, under a travel grant as a Fulbright Visiting Scholar.

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