2-Chloro-1-iodo-1,1,2-trifluoroethane (II) by Ultraviolet Light-Catalyzed Isomerization of I.—Isomerization was carried out in a 5000-ml. Pyrex reactor. The light source was a 100-w. mercury-vapor lamp[12] centrally located in a water-cooled quartz well. The reactor was surrounded by an aluminum can which was wrapped with heating tapes for the experiments above room temperatures. Samples (2.0 ml.) were introduced into the evacuated reactor as liquids by means of a hypodermic syringe through a rubber septum which could be isolated from the flask by a stopcock through which the syringe needle could be inserted. The reaction mixture was removed after irradiation by pumping it through a 25-mm. i.d. by 75-cm. column filled with 1.6-mm. 5-Å. Molecular Sieve pellets.[11] Material passing through the column was condensed in a liquid nitrogen-cooled trap. Total recovery amounted to 85–90%. After irradiation for 1 hr. at room temperature the recovered halocarbons contained 86% I and 13% II, after 3 hr. 72% I and 26% II, after 3 hr. at 65–70° 76% I and 18% II. When the sample size was reduced to 1.0 ml. the recovered material contained 66% I and 26% II. Insertion of a Pyrex sleeve between the lamp and the quartz well completely prevented isomerization. Preparative scale chromatography was employed to obtain pure II which had the following physical properties: n.b.p. 85.4°, log $P_{mm} = 7.66157 - 1714.2/T_{°K}$, ΔH 7448 cal./mole, Trouton ratio 20.8, d_{23} 2.185 g./cc., ultraviolet λ_{max} 270 mμ (ϵ_{max} 307). The n.m.r. spectrum showed one CH resonance at −1.20, one CF resonance at −21.5, and one CF_2 resonance (AB_2 type) at +63.4 and +61.3 p.p.m. The following coupling constants were measured: $J_{CH,CF}$ 48, J_{CH,CF_2} 5.8 and 4.0, J_{CF,CF_2} 21.7 and 20.9, and J_{CF_2} 191 c.p.s. Major infrared absorption bands were at 3.32 (w), 7.52 (m), 7.90 (w), 8.26 (s), 8.60 (sh), 8.80 (vs), 9.08 (s), 9.65 (vs), 10.50 (s), 11.70 (s), 12.00 (sh), 12.60 (m), and 13.55 (vs) μ.

1-Chloro-1-iodo-2,2,2-trifluoroethane (III) by Treatment of I with Aluminum Chloride.—I (1.0 ml., 2.18 g., 0.009 mole) and 0.25 g. (0.0019 mole) of anhydrous aluminum chloride were sealed in an evacuated Pyrex ampoule of about 10-ml. capacity. The ampoule was stored in the dark at the desired reaction temperature (see Table II) for 8 to 24 hr. The ampoule was then opened, and any volatile material in it was vaporized at room temperature and 10^{-6} atm. through a 10-mm. i.d. by 10-cm. bed of 5-Å. Molecular Sieve[11] and condensed in a liquid nitrogen-cooled trap. Pure III was obtained by preparative scale chromatography and had the following properties: n.b.p. 83.5°, log $P_{mm} = 7.58749 - 1678.7/T_{°K}$, ΔH 7284 cal./mole, Trouton ratio 20.4, d_{23} 2.210 g./cc., ultraviolet λ_{max} 275.5 mμ (ϵ_{max} 418). The n.m.r. spectrum showed one CH resonance at −1.30 and one CF_3 resonance at −4.50 p.p.m. The coupling constant between the CH and CF_3 groups was 6.2 c.p.s. Major infrared absorption bands were at 3.32 (w), 7.20 (s), 7.92 (vs), 8.40 (s), 8.62 (s), 9.05 (vs), 11.50/11.60 (m), 12.40 (s), and 15.00 (m) μ.

Addition of Hydrogen Iodide to Chlorotrifluoroethylene.—Chlorotrifluoroethylene (0.011 mole) and hydrogen iodide (0.016 mole) were condensed by means of liquid nitrogen into a 25-ml. stainless steel pressure vessel. After 26 days at ambient temperature the contents of the bomb were vaporized through a small Molecular Sieve[11] bed into a liquid nitrogen-cooled trap. The most volatile portion of the material held by the trap was pumped off until the remaining liquid had a vapor pressure of about 300 mm. at 23°. This liquid weighed 0.31 g. and contained 94.9% II by v.l.p.c. analysis.

1-Iodo-1,2,2,2-tetrafluoroethane (IV).—Pure IV was isolated by preparative scale chromatography from the volatile impurities produced in the preparation of III by treatment of I with anhydrous aluminum chloride, n.b.p. 39.4°, log $P_{mm} = 7.55172 - 1460.1/T_{°K}$, ΔH 6406 cal./mole, Trouton ratio 20.5, molecular weight (by PVT) 230 (theory 228), ultraviolet λ_{max} 262 mμ (ϵ_{max} 306). The n.m.r. spectrum showed one CH resonance at −5.35, one CF resonance at +90.9, and one CF_3 resonance at +0.88 p.p.m. The following coupling constants were measured: $J_{CH,CF}$ 46, J_{CH,CF_3} 5.6, and J_{CF,CF_3} 16.7 c.p.s. Major infrared absorption bands were at 3.40 (w), 7.40 (m), 7.82 (vs), 8.10 (m), 8.85 (vs), 9.20 (vs), 10.15 (w), 11.55 (s), and 14.30 (s) μ.

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[12] Engelhard Hanovia, Inc., 100 Chestnut St., Newark 5, N. J., type Sol #608A-36 operated from a Hanovia #7654-1 reactive transformer was used.

Rearrangement of Hydroperoxide Salts in the Oxidation of α-Trialkysilyl Organometallic Compounds[1]

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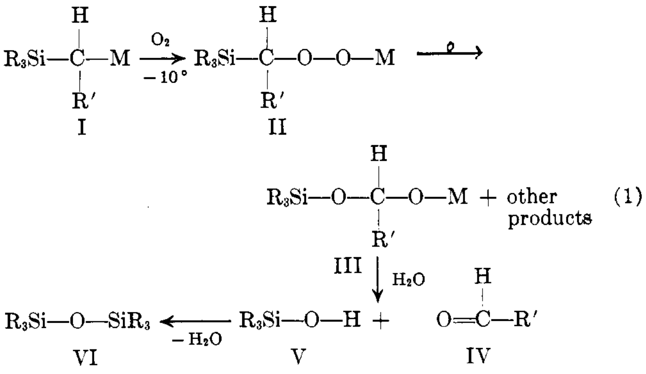
The ready oxidation of a wide variety of metal alkyls to form metal alkoxides by molecular oxygen has been shown to proceed *via* hydroperoxide salt intermediates, R–O–O–M.[2] However, despite the metalloid character of silicon, tetralkylsilanes, such as $(CH_3)_4Si$, are very resistant to the atmospheric oxidation of their carbon–silicon bonds.[3] Therefore, it was of interest to observe an extremely facile oxidation of carbon–silicon linkages when α-trialkylsilyl organometallic compounds (I) were subjected to air oxidation under very mild conditions. Thus, the air oxidation of trimethylsilylmethylmagnesium chloride (Ia) at −10° gave, upon hydrolysis, the expected alcohol, trimethylsilylmethanol, together with large amounts of trimethylsilanol (Va), hexamethyldisiloxane (VIa), formaldehyde (IVa), and higher siloxanes (Chart I). In a similar fashion, the addition products of triethylvinylsilane and diisobutylaluminum hydride (VII and VIII, eq. 2) underwent air oxidation to yield only minor amounts of the expected alcohols, 1-triethylsilylethanol and 2-triethylsilylethanol, respectively. Instead, triethylsilanol (Vb), hexaethyldisiloxane (VIb), and higher siloxanes were obtained as the principal oxidation products (Chart I). Since the relative proportion of adduct VII to adduct

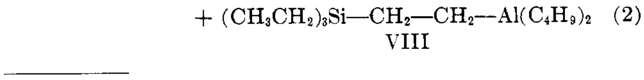
CHART I



$$R_3Si-\underset{R'}{\overset{H}{C}}-M \xrightarrow[-10^\circ]{O_2} R_3Si-\underset{R'}{\overset{H}{C}}-O-O-M \longrightarrow R_3Si-O-\underset{R'}{\overset{H}{C}}-O-M + \text{other products} \quad (1)$$

$$\text{III} \xrightarrow{H_2O} R_3Si-O-H + O{=}\overset{H}{C}-R' ; \quad R_3Si-O-SiR_3 \xleftarrow[-H_2O]{} R_3Si-O-H$$

Ia–VIa, R = CH_3; R′ = H; M = MgCl
Ib–VIb, R = C_2H_5; R′ = CH_3; M = $Al(C_4H_9)_2$



$$(CH_3CH_2)_3Si-\overset{H}{C}{=}\overset{H}{C}H \xrightarrow{(C_4H_9)_2AlH} \underset{\text{VII}}{(CH_3CH_2)_3Si-\underset{Al(C_4H_9)_2}{\overset{H}{C}}-CH_3} + \underset{\text{VIII}}{(CH_3CH_2)_3Si-CH_2-CH_2-Al(C_4H_9)_2} \quad (2)$$

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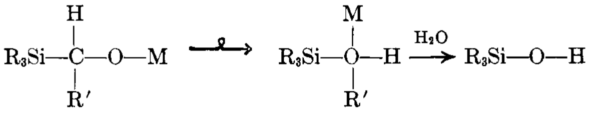
[1] Paper III in the series: Organosilicon Compounds with Functional Groups Proximate to Silicon. Previous papers: *J. Org. Chem.*, **28**, 487, 2870 (1963).

[2] *Cf.* (a) A. G. Davies, "Organic Peroxides," Butterworths Scientific Publications, London, England, 1961, pp. 120–126, 155–160; (b) H. Hock, H. Kropf, and F. Ernst, *Angew. Chem.*, **71**, 541 (1959).

[3] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 123–124.

VIII formed according to eq. 2 has been shown to be 70:30,[4] the oxidation products arose principally from attack on the α-triethylsilyl isomer VII.

To rule out the possibility that carbon–silicon bond cleavage might have occurred in a reaction other than the oxidation process itself, the following control experiments were conducted. First, assurance that no cleavage had taken place during the preparation of the organometallic reagents themselves (Ia, VII, and VIII) was gained by the hydrolysis of aliquots. Only tetramethylsilane and tetraethylsilane were obtained from the respective organometallic systems. Secondly, the metal alkoxides (IX) expected to result upon the oxidation of I, VII, and VIII were prepared independently from the known alcohols and were shown not to undergo readily the rearrangement shown in eq. 3.[5] Thirdly,



$$R_3Si-\overset{\displaystyle H}{\underset{\displaystyle R'}{C}}-O-M \rightsquigarrow R_3Si-\overset{\displaystyle M}{\underset{\displaystyle R'}{O}}-H \xrightarrow{H_2O} R_3Si-O-H \qquad (3)$$

IX

the alkoxide IX ($R = CH_3$, $R' = H$, $M = MgCl$) was shown not to react significantly with molecular oxygen when subjected to the oxidation procedure.[6a]

In view of the foregoing observations, the prompt oxidation of carbon–silicon bonds in α-trialkylsilylorganometallic systems can arise reasonably from the formation[2] and rearrangement of the intermediate hydroperoxide salt (II $\rightarrow$ III, eq. 1).[6b] Although the production of higher molecular weight siloxanes indicates that the decomposition of II can pursue more than one course, the scheme portrayed in Chart I is consonant with the unexpected oxidation products observed with both organometallic compounds. This novel peroxide rearrangement in organosilicon chemistry[6c] finds its formal counterpart in the well known acid-catalyzed rearrangement of cumyl hydroperoxide to yield phenol and acetone.[7] Further support for the rearrangement pathway shown in eq. 1 is found in the fact that other oxidations which avoid the formation of II apparently proceed without carbon–silicon bond scission. For example, the oxidation of tris(trimethylsilylmethyl)borane (I, $R = CH_3$; $R' = H$; $M = BR_2'$) and of the hydroboration products from trimethylvinylsilane by means of hydrogen peroxide in alkaline solution takes place normally to yield the expected alcohols.[8]

Finally, as a consequence of the oxidative lability of carbon–silicon bonds in systems such as VII and VIII, air oxidation of the metal hydride adducts of vinylmetalloid systems and the isolation of the corresponding isomeric alcohols is not, in general, a reliable method for determining the mode of addition of metal hydrides to the alkenyl linkage.[4,9]

Experimental

Starting Materials and General Procedures.—The chloromethyltrimethylsilane was obtained from the Peninsular Chemical Co., Gainesville, Florida. The triethylvinylsilane was prepared according to a published procedure.[10] The diisobutylaluminum hydride was synthesized from triisobutylaluminum by the thermal elimination of isobutene[11] and the subsequent distillation of the resulting hydride, b.p. 96–106° (0.1 mm.).

All organometallic reactions were conducted under an atmosphere of dry, oxygen-free nitrogen. The glass apparatus employed was dried beforehand at 200° for several hours and then heated under vacuum after assembly. All reactions solvents were anhydrous, reagent-grade chemicals.

The composition of liquid products was determined by means of a Barber-Colman gas chromatography apparatus, Model 10, with an ionization detector system. The chromatography column consisted of 30% silicone oil on a firebrick support. Infrared spectra were recorded with a Perkin-Elmer infrared spectrophotometer, Model 21, on liquid film samples.

Synthesis of Oxidation Products. A. Known Compounds.—Trimethylsilylmethanol was obtained in two steps from chloromethyltrimethylsilane.[12] Refluxing chlorotrimethylsilane with water provided hexamethyldisiloxane.[13] On the other hand, treatment of chlorotrimethylsilane with ammonia in ether yielded hexamethyldisilazane, which gave upon mild acid hydrolysis trimethylsilanol.[14]

B. **New Compounds. 1-Triethylsilylethanol.**—Although previously reported in the literature,[15] this isomer was prepared in the pure state for the first time by a two-step procedure[4] starting from 1-(triethylsilyl)bromoethane.[16] The bromo compound was treated with silver acetate in hot benzene to produce 1-(triethylsilyl)ethyl acetate and the latter was reduced with lithium aluminum hydride to yield 1-triethylsilylethanol, b.p. 122° (80 mm.), $n^{25}D$ 1.4485.[4]

2-Triethylsilylethanol.—This previously unreported isomer was synthesized by the chloroplatinic acid-catalyzed addition of trichlorosilane to vinyl acetate to provide 2-trichlorosilylethyl acetate and the treatment of the latter compound with excess ethylmagnesium bromide.[4] The resulting 2-triethylsilylethanol boiled at 112° (11 mm.), $n^{25}D$ 1.4510.

Oxidation of Trialkylsilyl Organometallic Compounds. A. Trimethylsilylmethylmagnesium Chloride.—The Grignard reagent was prepared from chloromethyltrimethylsilane and magnesium turnings in anhydrous ethyl ether without any initiator. To ascertain whether any silicon-carbon bond cleavage had occurred during the preparation, a filtered solution of the Grignard reagent was allowed to stand under a nitrogen atmosphere for 20 hr. at room temperature. Usual hydrolytic work-up and vapor phase chromatographic analysis revealed the presence of tetramethylsilane and ether. The former constituted 99.3% of the silicon-containing products; only 0.7% of two unidentified components was detected.

The oxidation of 0.16 mole of the Grignard reagent in 100 ml. of ether solution was conducted in a three-necked, round-bottomed flask fitted with a gas inlet and stirrer, and situated in an ice–sodium chloride cooling bath (−10°). Dry oxygen was introduced at such a rate that no bubbling occurred at the mercury

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[4] The mixture of adducts resulting from the hydride addition has been hydrolyzed with deuterium oxide and the resulting isomeric mixture of monodeuterated tetraethylsilanes has been analyzed by n.m.r. spectroscopy (uncertainty = ±9%): J. J. Eisch and G. R. Husk, unpublished studies.

[5] *Cf.* A. G. Brook, *J. Am. Chem. Soc.*, **80**, 1886 (1958).

[6] (a) A referee has suggested that the observed silicon–carbon bond oxidation may arise from the thermal- or acid-catalyzed decomposition of the free hydroperoxide (II, M = H) obtained upon hydrolytic work-up. However, hydrolyzed samples of the oxidized organometallic solution (I) failed to give a positive test for the presence of peroxides in the potassium iodide–starch procedure. Therefore, significant amounts of II did not survive until the hydrolysis step. (b) Whether the hydroperoxide salt in Chart II decomposes *via* a polar or a free-radical pathway is undetermined. (c) *Cf.* E. Buncel and A. G. Davies, *J. Chem. Soc.*, 1550 (1958), for the reaction of trimethylchlorosilane with perbenzoic acid. The postulated trimethylsilyl perbenzoate is thought to rearrange to give the observed product, dimethylmethoxysilyl benzoate.

[7] B. Barnett, E. R. Bell, F. H. Dickey, F. F. Rust, and W. E. Vaughan; *Ind. Eng. Chem.*, **41**, 2612 (1949).

[8] D. Seyferth, *J. Am. Chem. Soc.*, **81**, 1844 (1959).

[9] *Cf.* L. T. Zakharkin and L. A. Savena, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 253 (1962).

[10] R. Nagel and H. W. Post, *J. Org. Chem.*, **17**, 1379 (1952).

[11] K. Ziegler, H.-G. Gellert, H. Lehmkuhl, W. Pfohl, and K. Zosel, *Ann.*, **629**, 11 (1960).

[12] J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **70**, 1117 (1948).

[13] R. O. Sauer, *ibid.*, **66**, 1707 (1944).

[14] M. F. Shostakovsky, D. A. Kochkin, I. A. Shikhiev, and V. M. Vlasov, *J. Gen. Chem. USSR*, 622 (1955).

[15] (a) C. Friedel and J. M. Crafts, *Ann.*, **138**, 19 (1886); (b) E. Niedzielski, *J. Am. Chem. Soc.*, **62**, 3519 (1940).

[16] E. Larson and L. Knopp, *Acta Chem. Scand.*, **1**, 268 (1947); *Trans. Chalmers Univ. Technol. Gothenberg*, **79**, 7 (1948); *Chem. Abstr.*, **43**, 2929 (1949).

exit bubbler surmounted on the condenser. After an hour oxygen was no longer absorbed by the system and a white precipitate was present in the reaction mixture. With a slow stream of oxygen passing through the system, the reaction mixture was allowed to come to room temperature over a 6-hr. period and maintained there for an additional 6 hr. Hydrolysis of an aliquot and the addition of the potassium iodide–acetic acid reagent gave a negative peroxide test. The suspension was then hydrolyzed with ammonium chloride solution and the separated ether extract was dried over anhydrous calcium sulfate. By means of vapor phase chromatographic analysis of the ether extract and comparison with the retention times and infrared spectra of authentic samples, the following product distribution (mole %) was determined: trimethylsilylmethanol (60), hexamethyldisiloxane (17), unknown A (15), unknown B (3.1), tetramethylsilane (2.7), and trimethylsilanol (2.3). The infrared spectra of unknowns A and B indicated them to be higher molecular weight hydroxyl siloxanes (bands at 1040–1060 and 3400 cm.$^{-1}$).

The acidified aqueous extract from the reaction mixture work-up was treated with a solution of 5,5-dimethyl-1,3-cyclohexanedione in alcohol. The colorless precipitate was collected and recrystallized from alcohol. The dimedone derivative melted at 189–190° and did not depress the melting point of an authentic sample of the dimedone derivative of formaldehyde (m.p. 189–190°).

B. **The Adduct of Triethylvinylsilane and Diisobutylaluminum Hydride.**—A three-necked, round-bottomed flask, equipped with a pressure-equalized addition funnel, stirrer, and gas-inlet tube and maintained under a nitrogen atmosphere, was charged with 20.0 g. (0.144 mole) of diisobutylaluminum hydride. After the hydride had been heated to 75°, the triethylvinylsilane (19.2 g., 0.134 mole) was added dropwise over a period of 30 min. The colorless mixture was stirred for an additional 3.25 hr. and then cooled to 0°. The mixture was hydrolyzed cautiously by the dropwise addition of water. After gas evolution had ceased, 6 *N* sulfuric acid was added to dissolve the aluminum hydroxide. The mixture was extracted with ether and the organic layer was washed with sodium bicarbonate solution and with water. The dried ether extract was freed of ether by fractional distillation to yield 18.4 g. (95%) of product. This was shown to be pure tetraethylsilane by v.p.c. and infrared spectral examination. No evidence for the presence of residual vinyl compound or of higher boiling dimers could be obtained.

In a run similar to the foregoing, the resulting organoaluminum adduct was diluted with 100 ml. of pure, dry hexane and cooled in an ice bath. Dry air (previously passed through two drying tubes filled with Linde Molecular Sieves and one tube charged with Ascarite) was passed over the surface of the stirred organoaluminum solution. The temperature was slowly raised to 55° over the total oxidation period of 8 hr. The cooled solution was then treated with ammonium chloride solution and the resulting suspension filtered from the aluminum hydroxide. The hydrocarbon layer was dried and then fractionally distilled to remove the hexane and isobutyl alcohol. The total yield of residue, based upon the calculated yield of alcohols, was 71%. Of this, 30% proved to be a 5.3:2.1:1.0 mixture of triethylsilanol (identified by elemental (Found: C, 54.27; H, 12.22.) and infrared spectral analyses), 1-triethylsilylethanol, and 2-triethylsilylethanol, and 70% was shown to be a mixture of hexaethyldisiloxane and higher molecular weight, carbonyl-containing hydroxyl siloxanes by infrared examination: prominent bands at 3400 and 1030–1100 cm.$^{-1}$ and modest bands at 1730–1750 cm.$^{-1}$.

Attempted Rearrangements. A. **Trimethylsilylmethanol.**—Assurance that the magnesium salt of trimethylsilylmethanol was not undergoing rearrangement or oxidation, leading to carbon–silicon bond cleavage, was obtained by treating the alcohol with ethylmagnesium chloride in ether. The resulting suspension was stirred for 20 hr. under nitrogen. Subsequent hydrolytic work-up gave only the unchanged alcohol.

Passage of oxygen gas through an ether suspension of trimethylsilylmethoxymagnesium chloride for 12 hr. gave upon work-up trimethylsilylmethanol containing only 0.6% of hexamethyldisiloxane.

B. **(Triethylsilyl)ethanol.**—Treatment of the two isomeric alcohols individually with triisobutylaluminum in hexane solution yielded the respective aluminum alkoxides. Subsequent hydrolytic work-up allowed the pure alcohols to be recovered unchanged.

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