TABLE I (*Continued*)

Ar—N(R)—CO—CH_2—S—X

X = Au			$(R—NH—CO—CH_2—S)_2$				
					%N[a]		
Dec., °C.[11]	Calcd.	Found	M. p., °C.[11]	Purified[b]	Calcd.	Found	Color with $SeOCl_2/H_2SO_4$
208–210	52.3	52.2	82[c]	dil. e	...	...	Red
231	52.3	51.9	171[e]	m	...	...	Red
245	52.3	52.3	186[g]	m	...	...	Brownish red
251	50.4	50.2	185	e	7.21	7.41	Brown
259	50.4	50.2	235	e	7.21	7.19	Yellow
202[h]	44.9	44.7	150	m	5.78	5.73	Reddish purple
246	47.7	47.3	213[j]	m	...	...	Emerald green
260	47.7	47.4	209[l]	e	...	...	Greenish blue
268	48.7	47.9	184	e	...	...	Yellow
256–258[n]	48.3	47.6	176[m]	e	13.26	13.19	Yellow
...	..	..	198[m]	e	13.26	9.11[o]	Yellow
215[5]	51.9	51.1	213	e	7.68	7.67	Blue
238[5]	51.9	50.8	166	dil. e	7.68	7.84	Blue
240[5]	51.9	51.1	202	dil. e	7.68	7.61	Green
202[h,12]	50.1	50.0	126	e	7.14	6.96	Purplish blue
249	50.1	49.9	191[q]	m	...	...	Emerald green
243	48.4	47.7	220–222 (dec.)	AcOH	6.66	6.80	Yellow
284[n]	48.4	47.6	281 (dec.)	AcOH	6.66	6.60	Yellow
274	45.3	44.6	146	e	5.87	5.82	Yellow
276	46.8	45.3	218.5–220.5	AcOH	6.24	6.10	Yellow
268	44.5	43.5	246 (dec.)	m	11.42	11.25	Yellow
231	37.9	37.9	226–228 (dec.)	m	13.03	12.93	Yellow
265	37.5	36.5	236 (dec.)	m	12.79	12.56	Yellow
...	..	..	....	....	...	...	[s]

Crude preparations used for further work without drying, only samples prepared for analysis. [s] Reactions of these carbamyl compounds (see preceding paper), whose corresponding —SH compounds have not been prepared; Ar—N(R)= C_6H_5NH—NH— purplish red turning brown quickly; $C_6H_5N(CH_2C_6H_5)$— purplish red; $As_3OH_2C_6H_4NH$— yellow 2-OH,5—$COOCH_3C_6H_4NH$— yellowish brown.

obtained with selenium oxychloride, but to react only slowly with carbamyl compounds and disulfides, and not at all with the gold salts.[18]

Acknowledgment.—The author is much indebted to Drs. S. M. Gordon and N. Weiner for their interest, and to Mr. Saul Sokol for technical assistance.

Summary

A number of N-arylmercaptoacetamides, the corresponding disulfides and gold-mercaptides have been prepared.

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[18] This color reaction might be of interest in connection with the use of α-mercaptoacetyl-β-naphthylamine, "thionalide," as analytical reagent for heavy metals: Berg and Roebling, *Ber.*, **68**, 403 (1935), and subsequent papers.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Alkylation of Hydrochlorosilanes

BY C. A. BURKHARD AND R. H. KRIEBLE

The peroxide and ultraviolet light catalyzed addition of trichlorosilane to 1-octene was announced recently by Sommer, *et al.*[1] We had concluded a similar investigation when this communication appeared and wish to describe further results at this time concerning the addition of the silicon–hydrogen compounds to olefins.

Kharasch, *et al.*,[2] have reported similar reactions in which carbon tetrachloride, carbon tetrabromide, bromoform, and chloroform add to olefins in the presence of peroxide or white light. Unlike the reactions described by Kharasch, the attempted preparation of β-halogeno-organohalogenosilanes from the interaction of chloro- and bromosilanes with olefins has been unsuccessful.[3]

In contrast to this, trichlorosilane is found to add with ease to olefinic double bonds in the presence of peroxides or ultraviolet light. The reac-

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[1] Sommer, Pietrusza and Whitmore, THIS JOURNAL, **69**, 188 (1947).

[2] Kharasch, Jensen and Urry, (*a*) *Science*, **102**, 128 (1945); (b) THIS JOURNAL, **67**, 1864 (1945); (c) *ibid.*, **68**, 154 (1946); (d) Kharasch, Urry and Jensen, *ibid.*, **67**, 1626 (1945).

[3] Scott (U. S. Patent 2,407,181 (Sept. 3, 1946)) reports that a *telomeric* product is obtained in the reaction of ethylene with silicon tetrachloride in the presence of peroxides.

tion appears to proceed exclusively by the addition of the silicon–hydrogen bond. The product is characterized by the fact that: (1) no hydrogen evolution is obtained upon treatment with caustic solution, showing absence of silicon–hydrogen bonds, and (2) the hydrolyzable chlorine content indicates that no silicon–chlorine bonds are lost during the reaction. In this manner isobutyltrichlorosilane, 1-pentyltrichlorosilane, and cyclohexyltrichlorosilane have been prepared from isobutylene,[4] 1-pentene and cyclohexene, respectively.

A further extension of this reaction is demonstrated by the formation of bis-(trichlorosilyl) alkanes from the reaction of either olefinic trichlorosilanes or acetylene with trichlorosilane. By the reaction of vinyl- or allyltrichlorosilane with trichlorosilane, 1,2-bis-(trichlorosilyl)-ethane and 1,3-bis-(trichlorosilyl)-propane, respectively, have been prepared. Acetylene adds two moles of trichlorosilane, forming 1,2-bis-(trichlorosilyl)-ethane. This reaction may be postulated as a two step addition, the first step forming vinyltrichlorosilane followed by a second step, which has already been described, to give 1,2-bis-(trichlorosilyl)-ethane.

$$\mathrm{HC{\equiv}CH + HSiCl \xrightarrow{(C_6H_5CO_2)_2} CH_2{=}CHSiCl_3} \quad (1)$$

$$\mathrm{CH_2{=}CHSiCl_3 + HSiCl_3 \xrightarrow{(C_6H_5CO_2)_2} Cl_3SiCH_2CH_2SiCl_3} \quad (2)$$

The reaction of olefinic halogenosilanes and acetylenes with hydrohalogenosilanes opens a new method for the synthesis of organosilicon compounds having a bridge of carbon atoms between silicon atoms. Examples of previously known Si–R–Si compounds include those in which R is methylene,[5b,c,d] ethylene,[5b,c] pentamethylene[5d] and phenylene.[5a,d] These compounds have been prepared either by a direct synthesis[5b,c] in which a dihalogenohydrocarbon is passed over elemental silicon in the presence of a catalyst or by the Grignard reaction.[5a,d]

In addition to trichlorosilane, it has been shown that methyldichlorosilane (CH_3SiHCl_2) adds in a similar manner, giving organomethyldichlorosilanes. 1- and 2-pentylmethyldichlorosilanes have been prepared by reaction of methyldichlorosilane with 1- and 2-pentene. The extent of reaction is not as great as that obtained with trichlorosilane. Furthermore, when di-*n*-propylmethylsilane is used only very slight reaction is obtained, if any at all. This would indicate that the presence of several negative groups on the silicon bearing the hydrogen is necessary to facilitate the addition of the silicon–hydrogen bond to olefins.

Since both peroxides and ultraviolet light instigate the addition of the silicon–hydrogen bonds to the olefinic double bonds it seems probable that the reaction proceeds by a free radical mechanism. The reaction mechanism postulated by Kharasch[2a,b] has been used by Sommer to account for the formation of 1-octyltrichlorosilane. As pointed out by Kharasch, there is in competition with the reaction forming monomeric products (equation 4) a second reaction which is responsible for the formation of the high boiling materials (equation 5).

$$\mathrm{RCH{=}CH_2 + Cl_3Si\cdot \longrightarrow RCHCH_2SiCl_3} \quad (3)$$

$$\mathrm{R\dot{C}HCH_2SiCl_2 + HSiCl_3 \longrightarrow RCH_2CH_2SiCl_3 + Cl_3Si\cdot} \quad (4)$$

$$\mathrm{R\dot{C}HCH_2SiCl_3 + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2(RCHCH_2)SiCl_3} \quad (5)$$

The ability of an olefin to form monomeric addition products depends, therefore, upon the relative rates of these two reactions. Styrene is an example of an olefin which forms high-boiling products to the exclusion of a monomeric product.

Experimental

The following procedure is typical of that used in this investigation.

The mixture of olefin, chlorosilane and peroxide was heated in either a glass-lined autoclave or citrate bottle, depending on the vapor pressure of the reaction mixture. In general the charge consisted of 0.5 or 0.75 mole of olefin to one mole of chlorosilane and 0.013–0.026 mole of peroxide. In the acetylene experiment 0.05 mole of peroxide was used. The reactions were carried out by heating the reaction mixture for a period of four to twenty-four hours at 70–100°. After the reaction time had expired the products were separated by rectification, giving unreacted chlorosilane and olefin, addition product, and a high-boiling residue.

The compounds in Table I were tested for the presence of the silicon–hydrogen bond by treatment with alcoholic caustic according to the procedure of Sauer, *et al.*[6] Negative results were obtained in each case.

The assignment of structures to the compounds in Table I has been made by comparing the physical properties of the prepared compounds with known samples. The higher boiling pentylmethyldichlorosilane is given the 1-pentyl configuration by analogy to the results of Sommer[1] with 1-octene. The 2-pentyl configuration was assigned to the lower boiling isomer by comparing the observed and calculated boiling points.[7]

Reaction of Styrene and Trichlorosilane.—A mixture of 135 g. (1.0 *M*) of trichlorosilane, 78 g. (0.75 *M*) of uninhibited styrene,[8] and 10 cc. (0.026 *M*) of diacetyl peroxide in dimethylphthalate was heated for four hours at 100°. Distillation gave trichlorosilane and a small amount of monomeric styrene. An undistillable, glassy solid residue (70 g.) remained. *Anal.* Found: Si, 1.6; Cl, 5.8.

When repeated using a lower temperature, 60–70°, and a more dilute solution, 134 g. (1.0 *M*) of trichlorosilane, 37 g. (0.36 *M*) of uninhibited styrene and 10 cc. (0.026 *M*) of diacetyl peroxide in dimethyl phthalate, 41 g. of a glassy solid high-boiling product was again obtained. No hydrogen evolution could be detected when this product was treated with alcoholic caustic, showing that silicon–

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[4] It is of interest to note that the presence of the hydrogen atom attached to the alkyl-group-bearing doubly bonded carbon is not necessary for the addition of trichlorosilane to olefins. In this way this reaction differs from those described by Kharasch.[2b,d]

[5] (a) Grüttner and Cauer, *Ber.*, **51**, 1283 (1918); (b) Patnode and Schiessler, U. S. Patent 2,381,000 (Aug. 7, 1945); (c) U. S. Patent 2,381,002 (Aug. 7, 1945); (d) Rochow, U. S. Patent 2,352,974 (July 4, 1944).

[6] Sauer, Scheiber and Brewer, THIS JOURNAL, **68**, 962 (1946).

[7] Lewis and Newkirk, *ibid.*, **69**, 701 (1947).

[8] The inhibitor was removed from the styrene by washing first with aqueous sodium hydroxide, then with water until neutral. The styrene was dried over calcium chloride and later distilled *in vacuo*, rejecting the first 50 cc. of distillate.

TABLE I

OLEFIN AND HYDROCHLOROSILANE ADDITION PRODUCTS

Compound	Olefin	B. p., °C.	% Hydrolyzable Cl Calcd.	% Hydrolyzable Cl Found	Yield,[a] %	Conversion,[b] %	Molar[c] ratio	Residue, g.
1-Pentyltrichlorosilane[d]	1-Pentene[e]	166–169	51.9	51.7	73	44	17[i]	8.0
Cyclohexyltrichlorosilane[f]	Cyclohexene[e]	199	48.9	48.4	64	30	8.8[i]	14.9
Isobutyltrichlorosilane[g]	Isobutylene[e]	136	55.5	55.5	..	10	4[j]	..
1-Pentylmethyldichlorosilane	1-Pentene[h]	164–168	38.4	38.3	37	10	3.3[i]	7.0
2-Pentylmethyldichlorosilane	2-Pentene[h]	100[m]	38.4	38.0	71	21	6.2[i]	14.5
1,2-Bis-(trichlorosilyl)-ethane[l]	Vinyltrichlorosilane[e]	199	71.6	70.9	19	19	3.2[i]	5.8
1,3-Bis-(trichlorosilyl)-propane	Allyltrichlorosilane[e]	111[n]	68.5	68.3	83	33	13[i]	..
1,2-Bis-(trichlorosilyl)-ethane[l]	Acetylene[e]	202	71.6	71.2	3	3	[k]	1.0

[a] Yield, based on the unrecovered olefin. [b] Yield, based on olefin charged. [c] Yield, in moles of adduct per mole of peroxide. [d] 1-Pentyltrichlorosilane has been reported by Whitmore, *et al.* [THIS JOURNAL, **68,** 475 (1946)], and 2-pentyltrichlorosilane by Bygden [Inaug. Diss. Uppsala (1916)], and Melzer [*Ber.*, **41**, 3390 (1908)]. [e] With trichlorosilane. [f] Palmer and Kipping [*J. Chem. Soc.*, 1020 (1930)], prepared this silane by the Grignard reaction. [g] Bygden, *Ber.*, **44B,** 2640 (1911); Inaug. Diss., Uppsala, 1916. [h] With methyldichlorosilane. [i] 30% Diacetyl peroxide in dimethyl phthalate. [j] *t*-Butyl perbenzoate. [k] Benzoyl peroxide. [l] This compound has been characterized by Patnode and Schiessler [U. S. Patent 2,381,000 (Aug. 7, 1945)], m. p. 27–28°. [m] Pressure 100 mm. [n] Pressure 20 mm.

carbon bonds had been formed. *Anal.* Found: Si, 1.9; Cl, 4.9.

Acknowledgment.—The authors wish to thank Mr. L. B. Bronk and Miss M. Clarke for analytical data.

Summary

1. Isobutyl-, 1-pentyl and cyclohexyltrichlorosilane and 1-, and 2-pentylmethyldichlorosilane have been prepared by the peroxide-catalyzed addition of trichlorosilane or methyldichlorosilane to the corresponding olefin.

2. 1,2-bis-(Trichlorosilyl)-ethane and 1,3-bis-(trichlorosilyl)-propane have been prepared by the addition of trichlorosilane to vinyl- and allyltrichlorosilane, respectively.

3. 1,2-bis-(Trichlorosilyl)-ethane has been prepared by the addition of trichlorosilane to acetylene.

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Cyclic Dimethylpolymethylenedioxysilanes

BY R. H. KRIEBLE AND C. A. BURKHARD

An investigation of the reactions of organohalogenosilanes and organoalkoxysilanes with glycols has been made. Several of the dimethylpolymethylenedioxysilanes have been isolated and characterized. These compounds are the silicon analogs of the cyclic acetals and ketals.

The acetals derived from glycols constitute a typical bifunctional system, in which either cyclic or polymeric forms are obtained depending on the number of atoms in the possible ring structure. The formals have been studied by Hill and Carothers,[1] who found that trimethylene and tetramethylene formals, prepared by acetal interchange from the glycols and dibutyl formal, were largely in the form of the cyclic monomers of six and seven membered rings, respectively. The formals of glycols bearing more widely separated hydroxyls were all polymeric, and on pyrolysis gave cyclic monomer in only trace amounts (with the exception of the polyformal of triethylene glycol which on pyrolysis gave in good yield the cyclic monomer of eleven ring atoms). Similar ring-chain relations are found in the acetals[2] and benzals[3] of glycols. There is less information concerning the polymethylene ketals of acetone. The cyclic ethylene ketal is readily formed in the presence of acid catalysts, the equilibrium constant of formation being 0.14.[4] The cyclic trimethylene ketal is formed only with difficulty due to an unfavorable equilibrium constant.[5] No mention is made of polymeric products in either case. The cyclic tetramethylene ketal apparently has not been reported.

A striking difference between the dimethylpolymethylenedioxysilanes and the formally analogous carbon compounds discussed above is the ease with which the silanes are prepared in the form of cyclic compounds even though the ring size is as large as eleven atoms. The new ring compounds are listed in Table I.

All the compounds but V have been prepared by

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(1) Hill and Carothers, THIS JOURNAL, **57**, 925 (1935).

(2) Hill and Hibbert, *ibid.*, **45**, 3124 (1923).

(3) Franke and Gigerl, *Monatsh.*, **49**, 8 (1938).

(4) Böeseken and Hermans, *Rec. trav. chim.*, **40**, 525 (1921).

(5a) Böeseken and Hermans, *Ber.*, **55B**, 3758 (1922).

(5b) Salmi and Rannikko, *ibid.*, **72B**, 600 (1939).