about the same ratio as that obtained from the reaction of diisobutylene and sulfur.

EXPERIMENTAL

Reactions with sulfur. Two techniques were used to react sulfur with tertiary mercaptans. The first utilized the simple process of dropping mercaptan onto heated sulfur at 200° using an addition rate such that all of the low boiling mercaptan and intermediates were efficiently converted to higher boiling products. A second technique used the addition of preformed alkyl-1,2-dithiole-3-thione to the sulfur before addition of the mercaptan. The added thione served to reduce the viscosity of the sulfur, to increase the mutual solubility of the sulfur and mercaptan, and thus to provide increased conversions.

4-Neopentyl-1,2-dithiole-3-thione, IIIb *and 4-methyl-5-t-butyl-1,2-dithiole-3-thione,* IIIa. Sulfur (160 g., 5.0 moles) was placed in a 500-ml. four-necked flask fitted with a stirrer, thermometer, dropping funnel, and efficient condenser. The condenser was connected to a gas meter to measure evolution of hydrogen sulfide. The sulfur was heated and stirred at 200–220° and 2,4,4-trimethyl-2-pentanethiol (146 g., 1 mole) was added dropwise in 4 hr. Heating and stirring was continued for an additional hour at the end of which 3 moles of hydrogen sulfide had been evolved and reaction had essentially ceased. The crude product was vacuum distilled and after a forecut of intermediate sulfur compounds there was obtained 50 g. boiling at 145–155° (3 mm.). This fraction solidified on standing and was separated into two isomers by fractional recrystallization from pentane and ethanol. 4-Neopentyl-1,2-dithiole-3-thione IIIb, m.p. 85–86°, gave no melting point depression with a sample prepared by the method of Spindt, *et al.*[6] 4-Methyl-5-*t*-butyl-1,2-dithiole-3-thione IIIa, m.p. 79–80°, also was identical to that obtained by the method of Spindt.

Anal. IIIa. Calcd. for $C_8H_{12}S_3$: C, 47.01; H, 5.93; S, 47.06. Found: C, 47.05; H, 5.88; S, 47.00.

Anal. IIIb. Calcd. for $C_8H_{12}S_3$: S, 47.06; mol. wt. 204.3. Found: S, 47.19; mol. wt. 205.

4-Neopentyl-5-t-butyl-1,2-dithiole-3-thione, V. Sulfur (160 g.) and 2,2,4,6,6-pentamethyl-4-heptanethiol (212 g.) were placed in a three-necked 500-ml. flask fitted with a thermometer, stirrer, and a reflux condenser which was attached to a gas meter. The reactants were heated at 190–215° for 5 hr. and 67 l. of hydrogen sulfide were evolved. The crude product was vacuum distilled and 68 g. of thione, b.p. 150–170° (0.1–0.03 mm.) was obtained. This product was identical with that obtained from the direct sulfurization of triisobutylene.[7] Confirming analyses include infrared and ultraviolet spectra, metal complexes with mercuric chloride, silver nitrate, bismuth chloride, and methyl iodide, and the alcoholic potassium hydroxide hydrolysis to pivalic and 4,4-dimethylvaleric acids.[7]

Anal. Calcd. for $C_{12}H_{20}S_3$: S, 36.92; mol. wt. 260.5. Found: S, 36.22; mol. wt. 258, 265.

During the course of a large scale reaction (1 l.) of 2,4,4-trimethyl-2-pentanethiol with sulfur in di-*t*-butylbenzene a side-arm take-off trap was attached to the reflux condenser. This allowed removal of small samples of unreacted thiol and low boiling intermediates. Twenty-milliliter samples were thus removed every half hour and examined by vapor phase chromatography. Small (0.4–1.2%) but definite quantities of a C_8-olefin were observed during the entire course of the reaction (5 hr.). The identity of this olefin was confirmed by extraction of 200 ml. of low boiling condensate with aqueous caustic. The small caustic insoluble layer was separated by ether extraction, the ether extract washed with water, dilute caustic, dilute acid, and then dried over anhydrous sodium sulfate. After careful removal of the solvent the residue was distilled using a micro still and there was obtained 1.1 g. of mixed olefin easily identified by infrared as a mixture of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2. Thermal treatment of the thiol II at reflux temperature gave no evidence for hydrogen sulfide evolution or the consequent formation of olefin.

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Vinylsilicon and 1,2-Dihaloethylsilicon Halogenoids and Esters[1]

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Earlier publications report the closely related halogenoids and perfluoroester $Si(NCO)_4$,[2] $Si(NCS)_4$,[3] $C_2H_5Si(NCO)_3$,[3] $CH_3Si(NCS)_3$,[3] $C_2H_5Si(NCS)_3$,[3] and $C_2H_5Si(OCOCF_3)_3$.[4] Addition of bromine or chlorine to vinyltrichlorosilane furnishes $CH_2BrCHBrSiCl_3$ and $CH_2ClCHClSiCl_3$ respectively,[5] while only a boiling point at diminished pressure and an analysis for silicon characterize $CH_2{=}CHSi(OCOCH_3)_3$.[6]

An E_2 elimination occurs in $CH_2ClCH_2Si(CH_3)_3$, in which the *beta* chlorine is titrated quantitatively with aqueous alkali.[7] Similarly, an acidic *beta* halogen titrates quantitatively in five new halogenoids and esters of the type $CH_2YCHYSiX_3$, in which Y is chlorine or bromine, presented in this paper.

Table I lists the boiling points, densities, refractive indices, molar refractions (calculated[4] and observed values show an average error of 0.46%), and analyses of the following eleven new compounds: $CH_2{=}CHSi(OCOCF_3)_3$, $CH_2{=}CHSi(OCOC_2F_5)_3$, $CH_2{=}CHSi(OCO\text{-}n\text{-}C_3F_7)_3$, $CH_2{=}CHSi(OCOC_2H_5)_3$, $CH_2{=}CHSi(NCO)_3$, $CH_2{=}CHSi(NCS)_3$, $CH_2BrCHBrSi(OCOCF_3)_3$, $CH_2BrCHBrSi(OCOC_2F_5)_3$, $CH_2BrCHBrSi(OCO\text{-}n\text{-}C_3F_7)_3$, $CH_2BrCHBrSi(NCO)_3$, and $CH_2ClCHClSi(NCO)_3$. There is also adequate data for $CH_2{=}CHSi(OCOCH_3)_3$. These colorless compounds all hydrolyze easily and many decompose sufficiently at the normal boiling point to limit the accuracy of the individual boiling point.

A typical perfluoroester such as $CH_2{=}CHSi(OCOCF_3)_3$ has a higher thermal stability and

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(1) Presented at 15th Southwest Regional A. C. S. Meeting, Baton Rouge, La., December, 1959.

(2) G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **62**, 761 (1940).

(3) H. H. Anderson, *J. Am. Chem. Soc.*, **69**, 3049 (1947); **71**, 1801 (1949); **72**, 196 (1950).

(4) H. H. Anderson and T. C. Hager, *J. Am. Chem. Soc.*, **81**, 1584 (1959).

(5) C. L. Agre and W. Hilling, *J. Am. Chem. Soc.*, **74**, 3895, 3899 (1952).

(6) K. C. Frisch *et al.*, *J. Am. Chem. Soc.*, **74**, 4584 (1952).

(7) L. H. Sommer *et al.*, *J. Am. Chem. Soc.*, **68**, 485 (1946); **70**, 2871 (1948).

liquid density and a lower normal boiling point and refractive index than the corresponding halogen-free ester such as $CH_2{=}CHSi(OCOCH_3)_3$. Comparably, distillation under reduced pressure furnishes pure $CH_2BrCHBrSi(OCOCF_3)_3$ but decomposes the supposed $CH_2BrCHBrSi(OCOCH_3)_3$ completely; the latter compound appears to form through reaction of bromine and $CH_2{=}CHSi(OCOCH_3)_3$.

Bromination of perfluoroesters at a moderate rate only in sunlight suggests a free radical mechanism.[8] A withdrawal of electrons from the carbon-carbon double bond toward the many fluorine atoms may explain the need for free radicals.

In this paper there are three isocyanates (this term is without proof of structure), $CH_2{=}CHSi(NCO)_3$, $CH_2ClCHClSi(NCO)_3$, and $CH_2BrCHBrSi(NCO)_3$, and only one successful isothiocyanate, $CH_2{=}CHSi(NCS)_3$. There is no success in isolating either $CH_2BrCHBrSi(NCS)_3$ or $CH_2{=}CHSiCl_2NCS$. Gradual addition of silver isothiocyanate to excess $CH_2{=}CHSiCl_3$ furnishes only $CH_2{=}CHSi(NCS)_3$, although there is some indication of an unstable $CH_2{=}CHSiCl_2NCS$. Preparation of $SiCl_3NCS$ is quite straightforward, however.[9] E_2 eliminations[7,8] may possibly explain the reaction of $CH_2BrCHBrSi(NCO)_3$ with fluoride in antimony trifluoride to form silicon tetrafluoride, vinyl bromide, and bromide ion and the reaction of $CH_2BrCHBrSiCl_3$ and 48% aqueous hydrogen fluoride to form silicon tetrafluoride, vinyl bromide, and bromide and chloride ions.

TABLE I

PROPERTIES OF NEW (EXCEPT 4TH) HALOGENOIDS AND ESTERS

Compound	B.P.	d_4^{20}	n^{20a}	Mol. Refr.		Silicon, %[b]		Ester or Halide[c]		Distilled at	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Temp.	Mm.
$CH_2{=}CHSi(OCOCF_3)_3$	144.3	1.503	1.324_7	52.37	52.22	7.13	7.15	86.0	85.8	84–86	70
$CH_2{=}CHSi(OCOC_2F_5)_3$	168	1.567	1.311_2	67.36	67.16	5.16	5.34	89.9	89.5	97–98	50
$CH_2{=}CHSi(OCO\text{-}n\text{-}C_3F_7)_3$	198[d]	1.639	1.312_2	82.35	82.16	4.05	4.04	92.1	92.0	117–118	32
$CH_2{=}CHSi(OCOCH_3)_3$[6]	231[d]	1.167	1.422_6	50.80	50.64	12.09	12.20	76.3	76.3	112–113	1
$CH_2{=}CHSi(OCOC_2H_5)_3$	249[d]	1.098	1.425_7	64.75	63.98	10.24	10.10	79.9	79.7	109–111	1
$CH_2{=}CHSi(NCO)_3$	176.3	1.251	1.458_7	39.44	39.57	15.50	15.28	69.6	69.4	97–98	33
$CH_2{=}CHSi(NCS)_3$	276	1.292	1.640_9	64.31[e]	64.04	12.25	12.20	76.0	76.0	117–118	1
$CH_2BrCHBrSi(OCOCF_3)_3$	195[d]	1.862	1.379_9	68.27	68.95	5.07	5.18	61.2	61.4	131–132	58
$CH_2BrCHBrSi(OCOC_2F_5)_3$	219[d]	1.836	1.355_5	83.26	83.68	3.99	4.05	69.5	69.5	91–92	1
$CH_2BrCHBrSi(OCOC_3F_7)_3$	241[d]	1.856	1.348_5	98.25	98.64	3.29	3.39	74.8	74.8	110–111	1
$CH_2BrCHBrSi(NCO)_3$	264[d]	1.918	1.535_7	55.35	55.43	8.24	8.39	37.0	37.0	137–138	1
$CH_2ClCHClSi(NCO)_3$	248[d]	1.481	1.497_0	49.58	49.81	11.14	11.20	50.0	50.3	117–118	1

[a] In white light. [b] Weighed as silicon dioxide. [c] Average of two close values by titration. [d] Decomposition occurred during measurement of normal boiling point. [e] Using value for Si—NCS derived from Reference 3.

EXPERIMENTAL

Starting materials included special preparations of silver cyanate, silver isothiocyanate, $AgOCOCH_3$, $AgOCOC_2H_5$, $AgOCOCF_3$, $AgOCOC_2F_5$, $AgOCO\text{-}n\text{-}C_3F_7$, and freshly sublimed antimony trifluoride, and included vinyltrichlorosilane from Dow Corning Corp., Midland, Mich. All reactions were in a room in which the partial pressure of water vapor was under 10 mm.

Vinyltri(iso)cyanatosilane. Reflux of 33 g. of AgNCO and 9.15 g. of $CH_2{=}CHSiCl_3$ in 35 ml. of carbon tetrachloride for 1 hr., followed by filtration, washing of silver salts and then fractional distillation gave 8.75 g. (85% yield) of $CH_2{=}CHSi(NCO)_3$, the center fraction of which had the properties in Table I.

Vinyltriisothiocyanatosilane. Similarly, 10.0 g. of $CH_2{=}CHSiCl_3$ and 40 g. of AgNCS in 30 ml. of carbon tetrachloride furnished 12.3 g. (86% yield) of $CH_2{=}CHSi(NCS)_3$; the center fraction had the properties in Table I.

Vinyltripropionoxysilane and vinyltriacetoxysilane. Similarly, $CH_2{=}CHSiCl_3$ and an excess of $AgOCOCH_3$ or $AgOCOC_2H_5$ in carbon tetrachloride furnished chlorine-free $CH_2{=}CHSi(OCOCH_3)_3$ or $CH_2{=}CHSi(OCOC_2H_5)_3$, respectively.

Vinyltris(trifluoroacetoxy)silane, vinyltris(pentafluoropropionoxy)silane, and vinyltris(heptafluoro-n-butyroxy)silane. Typically, 6.30 g. of $CH_2{=}CHSiCl_3$ and 34.2 g. (a 30% excess) of $AgOCOCF_3$ in 35 ml. of carbon tetrachloride similarly furnished 9.0 g. (60% yield) of $CH_2{=}CHSi(OCOCF_3)_3$.

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(8) Jack Hine, *Physical Organic Chemistry*, McGraw-Hill, New York, 1956. Especially pages 185 and 428.

(9) H. H. Anderson, *J. Am. Chem. Soc.*, 67, 223 (1945).

1,2-Dibromoethyltri(iso)cyanatosilane. Gradual addition of 3.39 g. of bromine to 3.88 g. of $CH_2{=}CHSi(NCO)_3$ in a 10-ml. stoppered flask, mainly in artificial light at 0° but with a little daylight at the end, left a slight excess of free bromine. After transfer and subsequent removal of free bromine under 30 mm. pressure, then fractional distillation as in Table I gave 6.15 g. (84% yield) of $CH_2BrCHBrSi(NCO)_3$, the center cut of which had a moderate viscosity and the properties listed.

1,2-Dichloroethyltri(iso)cyanatosilane. A slow, 80-min. passage of chlorine gas, until the solution no longer absorbed chlorine, into 9 g. of $CH_2{=}CHSi(NCO)_3$ at 0° in sunlight finally gave 11.8 g. (94% yield) of $CH_2ClCHClSi(NCO)_3$. Table I lists the center fraction, a portion of which hydrolyzed slowly at first but later moderately rapidly in water at 25°.

1,2-Dibromoethyltris(trifluoroacetoxy)silane, 1,2-dibromoethyltris(pentafluoropropionoxy)silane, and 1,2-dibromoethyltris(heptafluoro-n-butyroxy)silane. Typically, gradual addition of 2.46 g. of bromine to 6.40 g. of $CH_2{=}CHSi(OCOCF_3)_3$ at 0° in sunlight—the reaction was very slow in artificial light—left a very slight excess of free bromine. After transfer and then removal of bromine under 30 mm. pressure, fractional distillation showed the essential absence of $CH_2{=}CHSi(OCOCF_3)_3$ and furnished 7.9 g. (88% yield) of $CH_2BrCHBrSi(OCOCF_3)_3$, the center fraction having the properties in Table I. Similarly, 2.27 g., a slight deficiency, of bromine and 10.07 g. of $CH_2{=}CHSi(OCO\text{-}n\text{-}C_3F_7)_3$ gave 11.6 g. (94% yield) of $CH_2BrCHBrSi(OCO\text{-}n\text{-}C_3F_7)_3$. A comparable process furnished $CH_2BrCHBrSi(OCOC_2F_5)_3$.

Brominations of vinyltriacetoxysilane and vinyltriisothiocyanatosilane. Similarly, 3.52 g. of bromine and 5.19 g. of $CH_2{=}CHSi(OCOCH_3)_3$ easily furnished a colorless, very viscous liquid, presumably $CH_2BrCHBrSi(OCOCH_3)_3$, but distillation under 1 mm. pressure gave total decomposition and much solid residue. Bromine and $CH_2{=}CHSi(NCS)_3$ reacted, but distillation under 1 mm. pressure produced a liquid and also a solid, probably $Si(NCS)_4$.

Reactions of 1,2-dibromoethyltrichlorosilane. Carefully purified $CH_2BrCHBrSiCl_3$ had normal b.p. 220°, d_4^{20} 2.046, n^{20} 1.5369, mol. refr. 49.04 (calcd. 48.95), also b.p. 142–143° under 75 mm. pressure. A vigorous reaction between 16 g. of $CH_2BrCHBrSiCl_3$ and 16 g. of gradually added 48% hydrofluoric acid occurred at 10° in a polyethylene vessel; silicon tetrafluoride and hydrogen bromide were among the escaping gases and no organosilicon layer such as $CH_2BrCHBrSiF_3$ remained in the polyethylene vessel. Evidently the reaction products were silicon tetrafluoride, hydrogen chloride, hydrogen bromide, and vinyl bromide, all uncondensed gases.

Reflux of 10 g. of $CH_2BrCHBrSiCl_3$ in 30 ml. of carbon tetrachloride with 20 g. of AgNCO for an hour ultimately gave 2.0 g. of nearly pure $Si(NCO)_4$, b.p. 188°, d_4^{20} 1.450 and n^{20} 1.4629, and 2.6 g. of crude $CH_2BrCHBrSi(NCO)_3$, b.p. 254°, n^{20} 1.5160 and d_4^{20} 1.810, with large NCO and medium hydrolyzable bromide.

Similarly, $CH_2BrCHBrSiCl_3$ and $AgOCOCF_3$ finally gave a low fraction of b.p. 135° and n^{20} 1.302 and a small higher fraction of b.p. 174° and n^{20} 1.3166; both fractions were bromine-free and extremely hydrolyzable. Evidently a contaminated $CH_2{=}CHSi(OCOCF_3)_3$ was present.

Reaction of 1,2-dibromoethyltri(iso)cyanatosilane and antimony trifluoride. Six grams of $CH_2BrCHBrSi(NCO)_3$ and 3.8 g., an excess of freshly sublimed antimony trifluoride reacted spontaneously at 25° but formed no gases condensing at 0°. No organosilicon compounds remained in the mixture of antimony salts. Evidently the products were $Sb(NCO)_3$, antimony tribromide, silicon tetrafluoride and vinyl bromide, the latter perhaps swept through the condenser by the silicon tetrafluoride gas.

Analytical. All halogenoids or esters with the vinyl group gave satisfactory titrations with ethanolic sodium hydroxide. A light-medium orange-red of cresol red indicator stable for 15 seconds was satisfactory for the titration of $CH_2ClCHClSi(NCO)_3$ and the $CH_2BrCHBrSiX_3$ types; the endpoint fades with time. Because the *beta* halogen is quantitatively acidic, the halogen or ester attached to silicon is 75.0% of the observed acidity.

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