c. *Conversion of 1-chloromethyl-1-methylsilacyclopentane to 1,1-dimethylsilacyclopentane.* To 1.70 g. (0.0114 mole) of the chloromethyl isomer was added 3.40 g. (0.22 mole) of sodium iodide in 15 ml. of dried acetone. After 3.5 days at reflux, only a small amount of precipitated sodium chloride was observed. The gas chromatogram of the reaction mixture showed only a small peak (*ca.* 2%) which might correspond to the iodo compound and also showed that the chloromethyl isomer was essentially unaffected by the reaction conditions. The bulk of the acetone was removed by distillation. Ether (10 ml.) was added to the residue and the mixture was washed with water to remove the remaining acetone and sodium salts. The ether solution was then dried with magnesium sulfate.

This ether solution of the chloromethyl isomer (containing *ca.* 2% of its iodo derivative) was added to a mixture of 3.5 g. (0.144 mole) of magnesium turnings, 9.0 ml. of 3*M* methylmagnesium bromide (to consume any acetone or water) and 30 ml. of anhydrous ether. The mixture was heated under reflux for 14 hr. and was then worked up in the standard fashion.

Gas phase analysis of the product exhibited only one major peak, which had a retention time the same as that observed in the chromatogram of 1,1-dimethylsilacyclopentane. The same technique for comparison (at two temperatures and flow rates) was used here as was used with 1-trimethylsilyl-3-butene.

B. *With chlorine gas and ultraviolet light.* Using the same conditions as described in part A, 1.2 g. (0.01 mole) of I was chlorinated for 10 min. while being irradiated with ultraviolet light. The distribution of the monochloro isomers is summarized in Table I. Unchanged starting material was estimated to be 45% of the total reaction mixture.

C. *With sulfuryl chloride without catalyst.* One gram (0.0088 mole) of I and 0.2 g. (0.0088 mole) of sulfuryl chloride (b.p. 69–70°) were heated under reflux for 2.5 hr. The distribution of the monochloro isomers is summarized in Table I. Unreacted starting material was estimated at 87%.

D. *With sulfuryl chloride with benzoyl peroxide.* Using the same conditions as described in part C, with the exception of a 30 min. reflux and the addition of 0.2 g. of benzoyl peroxide, the unchanged starting material was estimated to be 61%. The distribution of the monochloro isomers is summarized in Table I.

Chlorination of 1,1-dimethylsilacyclohexane. A. *With chlorine gas.* Dimethylsilacyclohexane[11] (13.5 g., 0.105 mole) was chlorinated as described in part A. Gas phase analysis showed three peaks: peak 1, retention time 2.8 min., 9%; peak 2, retention time 4.2 min., 69%; peak 3, retention time 5.1 min., 23%. When the reaction mixture was treated with water, peak 1 disappeared from the gas chromatogram and therefore corresponded to the 3-chloro isomer.

The reaction mixture from the treatment with water was pyrolyzed with quinoline in the same manner as described for the monochlorosilacyclopentanes. The gas chromatogram of the distilled mixture showed the absence of peak 3 (therefore corresponding to the 2- or 4-chloro isomer, while peak 2 was the same as before reaction (therefore corresponding to the chloromethyl isomer).

B. *With sulfuryl chloride.* Treatment of 61 g. (0.48 mole of 1,1-dimethylsilacyclohexane with 64.3 g. (0.48 mole) of sulfuryl chloride and 0.1 g. of benzoyl peroxide resulted in the following percentages of monochloro isomers: 3-chloro isomer, 20%; 2- or 4-chloro isomer, 16%; chloromethyl isomer, 64%.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Benzylhalosilanes and α-Bromobenzylhalosilanes

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Bromination of benzylsilane proves somewhat complicated: A deficiency of mercuric bromide furnishes benzylbromosilane; in the dark at 0° two moles of bromine per mole of benzylsilane produces benzyldibromosilane; excess bromine in daylight without a catalyst gives α-bromobenzyltribromosilane; more bromine upon heating yields α,α-dibromobenzyltribromosilane. Reduction of α-bromobenzyltribromosilane with lithium aluminum hydride in ether produces a partial yield of α-bromobenzylsilane, isomeric with the benzylbromosilane already mentioned. Table I lists the properties of these seven new compounds and five others—benzylchlorosilane, benzyliodosilane, *sym*-bis(benzyl)disiloxane, benzyltrifluorosilane, and benzyltriiodosilane.

Seven earlier publications establish the use of halides and halogenoids of certain transitional elements and elements in regular groups in the total replacement of hydrogen attached to germanium in triethylgermanium hydride,[2] to tin in triethyltin hydride,[2] or to silicon in triethylsilane[2]; or in the partial replacement of hydrogen attached to silicon in diethylsilane,[2] *n*-heptylsilane,[3] cyclohexylsilane,[4] or *n*-butylsilane ; or to germanium in *n*-butylgermanium trihydride or di-*n*-butylgermanium dihydride.[4] Reaction of the appropriate alkylsilane or alkylgermane with a deficiency of mercuric chloride, bromide or thiocyanate or of silver cyanate or thiocyanate or of iodine furnishes partially substituted compounds such as *n*-heptylchlorosilane,[3] diethylbromosilane,[2] cyclohexylisocyanatosilane,[4] cyclohexylisothiocyanatosilane[4] or *n*-butyliodogermane.[4]

This paper, in turn, demonstrates the progressive uncatalyzed bromination of benzylsilane, in which there are two kinds of reactive hydrogen; silane hydrogen (Si-H) is more reactive than methylene hydrogen (CH_2). Silane hydrogen reacts with bromine in the dark to produce either benzylbromosilane or benzyldibromosilane, and should react

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[1] Kindly address communications to this author. Experiments by both authors.

[2] H. H. Anderson, *J. Am. Chem. Soc.*, **79**, 326, 4913 (1957); **80**, 5083 (1958).

[3] H. H. Anderson and A. Hendifar, *J. Am. Chem. Soc.*, **81**, 1027 (1959).

[4] H. H. Anderson, *J. Am. Chem. Soc.*, **81**, 4785 (1959); **82**, 1323, 3016 (1960).

TABLE I

Properties of New Benzylhalosilanes

Compound	B.P.	d_D^{20}	n^{20a}	Mol. Refr. Calcd.	Mol. Refr. Found	Silicon,[b] % Calcd.	Silicon,[b] % Found	Halogen,[c] % Calcd.	Halogen,[c] % Found	H as Si—H Calcd.	H as Si—H Found	Distilled at B.P.	Distilled at mm.
$C_6H_5CH_2SiH_3$	150.3	0.893	1.5207	41.46	41.66	23.0	22.8	—	—	2.47	2.45	91–92	116
$C_6H_5CH_2SiH_2Cl$	186	1.056	1.5317	45.40	45.96	17.9	18.0	22.6	22.4	1.29	1.29	94–95	34
$C_6H_5CH_2SiH_2Br$	208	1.329	1.5587	48.37	48.85	14.0	13.9	39.7	39.9	1.00	1.00	93–94	13
$C_6H_5CH_2SiH_2I$	236.5	1.581	1.6032	54.11	53.93	11.3	11.5	51.1	51.4	0.81	0.81	64–66	1
$C_6H_5CH_2Si$-H_2NCS	253[d]	1.092	1.5929	55.82	55.64	15.7	15.8	32.4	32.5	1.12	1.12	87–88	1
$(C_6H_5CH_2$-$SiH_2)_2O$	307[d]	1.017	1.5464	80.17	80.52	21.7	21.7[e]	—	—	1.56	1.55	130–131	1
$C_6H_5CH_2SiHBr_2$	243.5	1.682	1.5775	55.28	55.49	10.0	10.1	57.1	57.0	0.36	0.35	72–73	1
$C_6H_5CH_2SiF_3$	138.3	1.201	1.4339	37.80	38.21	15.9	—	32.3	32.0	—	—	80–81	101
$C_6H_5CH_2SiI_3$	348	2.428	—	79.41	—	5.62	5.58	76.2	76.3	—	—	160–162	1
$C_6H_5CHBrSiBr_3$	323[d]	2.181	1.6227	69.90	70.77	6.42	6.46[f]	54.8	54.8	—	—	130–132	1
$C_6H_5CBr_2SiBr_3$	354[d]	2.369	1.6514	77.61	79.90	5.44	5.64	46.4	46.9	—	—	154–156	1
$C_6H_5CHBrSiH_3$	213	1.321	1.5659	49.17	49.67	14.0	13.7[g]	39.7	39.6	1.50	1.53	54–55	1

[a] In white light; all compounds are colorless. [b] Weighed as SiO_2 after cautious use of fuming sulfuric and concentrated nitric acids. [c] Halogen available in titration with sodium hydroxide in ethanol; excludes Br as C—Br; average of two runs using Methyl Purple, Chlorphenol Red or Bromcresol Green as indicators. [d] With some decomposition. [e] Also, Calcd.: mol. wt., 258.5. Found: mol. wt. (camphor), 244. [f] Also, Calcd.: mol. wt., 437.9. Found: mol. wt. (naphthalene) 428. [g] Calcd. for $C_6H_5CHBrSiH_3$: mol. wt., 201.2; C, 41.8; H, 4.51; Br, 39.7. Found: mol. wt. (naphthalene), 208; C, 41.6; H, 4.70; Br, 39.6 (unavailable in ethanolic sodium hydroxide).

further to produce benzyltribromosilane with proper stoichiometry. Thereafter, methylene hydrogen reacts fairly easily in daylight to produce α-bromobenzyltribromosilane and then reacts fairly slowly when heated to produce α,α-dibromobenzyltribromosilane. Fortunately mercuric bromide brominates benzylsilane to form benzylbromosilane with a high yield and very little more-highly brominated impurity. With only the third equation not demonstrated, the bromination of benzylsilane is evidently progressive and as follows:

$$C_6H_5CH_2SiH_3 + Br_2 = C_6H_5CH_2SiH_2Br + HBr \quad \text{in the dark at } 0^\circ$$

$$C_6H_5CH_2SiH_2Br + Br_2 = C_6H_5CH_2SiHBr_2 + HBr \quad \text{in the dark at } 0^\circ$$

$$C_6H_5CH_2SiHBr_2 + Br_2 = C_6H_5CH_2SiBr_3 + HBr \quad \text{in the dark at } 0^\circ$$

$$C_6H_5CH_2SiBr_3 + Br_2 = C_6H_5CHBrSiBr_3 + HBr \quad \text{in weak daylight at } 0^\circ$$

$$C_6H_5CHBrSiBr_3 + Br_2 = C_6H_5CBr_2SiBr_3 + HBr \quad \text{with six hours heat in sunlight}$$

Many of these reactions require gradual addition of the bromine; the stoichiometry is vitally important. Dark-colored nonvolatile solid impurities formed in the cleavage of the Si—C bond accompany these last two uncatalyzed brominations moreover, odors indicate the presence of very small amounts of benzyl bromide. An easy uncatalyzed bromination of toluene but not of benzene in daylight indicates absence of any bromination on the benzene ring, and that α-bromobenzyltribromosilane and α,α-dibromobenzyltribromosilane are the correct formulas.

Iodination of benzylsilane furnishes first benzyliodosilane and finally benzyltriiodosilane in the absence of catalyst. A small amount of tetraiodosilane formed demonstrates some rupture of the Si—C bond in this comparatively difficult iodination.

Reduction of α-bromobenzyltribromosilane with lithium aluminum hydride replaces all the Si—Br and at least half the C—Br. The major product is benzylsilane although a 30% yield of α-bromobenzylsilane results. Differentiation between the isomers benzylbromosilane and α-bromobenzylsilane is quite easy, since the halogen in the Si—Br configuration is available in titration with ethanolic sodium hydroxide and the halogen in C—Br is unavailable.

Table I lists the properties and analyses of the twelve new compounds benzylsilane, benzylchlorosilane, benzylbromosilane, benzyliodosilane, benzylisothiocyanatosilane, *sym*-bis(benzyl)disiloxane, benzyldibromosilane, benzyltrifluorosilane, benzyltriiodosilane, α-bromobenzyltribromosilane, α,α-dibromobenzyltribromosilane, and α-bromobenzylsilane.

Molar refractions in Table I show reasonable agreement, ±0.75%, between calculated and observed values. However, this excludes the compound α,α-dibromobenzyltribromosilane (perhaps slightly impure) which is the most difficult to handle because of the unusually high viscosity and the expected ease of hydrolysis. Calculated molar refractions use 1.95 for Si—F, 17.53 for Si—NCS, 15.82 for Si—I, and the other customary published values,[5] including a Si—Cl of questionable accuracy.

EXPERIMENTAL

Table II lists the preparations of nine new compounds; earlier publications[3,4] describe the equipment, the preparative methods and analysis, and also three different explanations[3] for the reactions of organometallic hydrides with cer-

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(5) A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1854).

TABLE II

PREPARATIONS OF COMPOUNDS

Starting Materials				Reaction Products			
Compound	Wt., g.	Compound	Wt., g.	Chief product	Wt., g.	Yield, %	Other products
$C_6H_5CH_2SiH_3$	6.3	$HgCl_2$^{a}	11.3	$C_6H_5CH_2SiH_2Cl$	5.4	67	Hg, HCl
$C_6H_5CH_2SiH_3$	6.3	$HgBr_2$^{a}	13.5	$C_6H_5CH_2SiH_2Br$	9.5	92	Hg, HBr
$C_6H_5CH_2SiH_3$	8.9	$Hg(NCS)_2$^{b}	23	$C_6H_5CH_2SiH_2NCS$	6.0	46	Hg, $H_3N_3C_3S_3$, $C_6H_5CH_2Si(NCS)_3$^{c}
$C_6H_5CH_2SiH_3$	4.2	Br_2^{d}	16.7	$C_6H_5CH_2SiHBr_2$	7.2	75	HBr
$C_6H_5CH_2SiH_3$	4.5	Br_2^{e}	25	$C_6H_5CHBrSiBr_3$	14.3	89	HBr
$C_6H_5CHBrSiBr_3$	17.4	Br_2^{f}	10	$C_6H_5CBr_2SiBr_3$	10.6	52	HBr
$C_6H_5CHBrSiBr_3$	40	$LiAlH_4$	8	$C_6H_5CHBrSiH_3$	5.5	30	LiBr, $AlBr_3$, $C_6H_5CH_2SiH_3$^{h}
$C_6H_5CH_2SiH_2Cl$	5.6	H_2O^{i}	3	$(C_6H_5CH_2SiH_2)_2O$	4.2	92	HCl
$C_6H_5CH_2SiI_3$	14.3	40% HF^{j}	25	$C_6H_5CH_2SiF_3$	2.6	51	HCl, residues^{j}

[a] Addition in five equal lots over 2 hr. with gentle warming. [b] Use of 16 g. of carbon tetrachloride as solvent; addition of 2 g. of mercuric thiocyanate every 5 min., with 30 min. reflux at end of additions. [c] Probable formula of untested residue weighing 5 g. [d] Addition over 2 hr. in dark with constant very slow flow of bromine. [e] Very slow constant addition of bromine over 3 hr. at 0° in weak daylight. [f] Gentle heating for 6 hr. in sunlight; then addition of 5 g. of bromine with 2 more hr. heating. [g] One hour of reflux in 300 ml. of ether, then gradual addition to 500 ml. of stirred 4*M* hydrochloric acid–ice mixture, next distillation of ether, then drying with anhydrous sodium sulfate and finally fractional distillation. [h] Weight 5.4 g. (48% yield). [i] Use of 3 g. of ethyl bromide as solvent; strong agitation with 3 g. of water twice. [j] One-half hour of vigorous shaking at 75°; next cooling and then extraction with 5 g. of ethyl bromide; next distillation; residues included 0.8 g. of unidentified liquid of b.p. approximately 125° under 1 mm. pressure.

tain halides. Because of the complications involved, it is necessary to present the preparations of benzylsilane and the benzyliodosilanes in detail.

Benzylsilane. Gradual addition of 2.2 l. of 0.7 *M* benzylmagnesium chloride to 1400 g. of silicon tetrachloride in 600 ml. of ether over a period of 3 hr., then storage overnight, next filtration and washing, and then fractional distillation produced 410 g. of crude benzyltrichlorosilane, b.p. 215°. Thereupon, the preparation included gradual addition of 390 g. of benzyltrichlorosilane over 1 hr. to 65 g. of lithium aluminum hydride dissolved in 700 ml. of ether, next 3 hr. reflux, then a very slow pouring of the ether solution with constant stirring into 1200 ml. of 4*M* hydrochloric acid–ice mixture (enough to maintain acidity), next separation of the ether layer and finally fractional distillation. Fractional distillation in a 50-cm. column 10 mm. in i.d. filled with cut-up steel gauze furnished 185 g. (87% yield) of crude benzylsilane, 140 g. of which had the b.p. 91–92° under 116 mm. pressure. Table I lists the properties of a 45 g. center cut, which had a weak aromatic odor. Storage of benzylsilane was in sealed glass tubes with little air present. The end fraction of the benzylsilane contained 10 g. of *sym*-diphenylethane, later purified by fractional freezing to a m.p. of 47° and a b.p of 281°, and to a very low Si-H content.

Benzyliodosilane and benzyltriiodosilane. Gradual addition of 35 g. of iodine, added in 5-g. portions one every 25 min., to 18 g. of benzylsilane over 3 hr. with gentle warming and then fractional distillation gave 5 g. of unchanged benzylsilane, 9 g. (25% yield) of crude benzyliodosilane, b.p. 100–116° under 15 mm., and approximately 20 g. of higher boiling material evidently largely a mixture of benzyldiiodosilane and benzyltriiodosilane. Two fractional distillations of the benzyliodosilane under first 15 mm. and then 1 mm. pressure furnished a 3.6 g. center cut for the study of properties. Reflux of the 20 g. of mixed benzyldiiodosilane and benzyltriiodosilane with more iodine, until a slight excess of iodine remained, produced a liquid containing some dark solid not decolorized by reflux with 2 g. of fine copper wire. Total distillation and then fractional distillation furnished approximately 3.5 g. of tetraiodosilane, a white solid of m.p. above 100° and of b.p. below 155° at 1 mm. pressure, and then 30.6 g. (43% yield) of benzyltriiodosilane, the center-boiling 11 g. of which served for study of the properties. An altered method of addition of benzyliodosilane was necessary in the analysis for silane hydrogen.

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[CONTRIBUTION FROM THE SILICONE PRODUCTS DEPARTMENT, GENERAL ELECTRIC CO.]

Silanols and Cyclosiloxanes from Difunctional Cyanoalkylchlorosilanes

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The preparation of methyl(β-cyanoethyl)silanediol, methyl(γ-cyanopropyl)silanediol, and phenyl(β-cyanoethyl)silanediol is reported. These were condensed to polymers, and crystalline methylcyanoethyl and phenylcyanoethyl cyclic tetramers were isolated. Some new thoughts are presented on the probability of formation of the various stereoisomeric forms of cyclic oligomers of the $(RR'SiO)_n$ type.

Cyanoalkylsilicon compounds have been of considerable interest in recent years, as potential raw materials for making silicone elastomers with improved resistance to swelling and disintegration by certain fuels and solvents.[2,3] The cyanoethylsilanes are of particularly practical interest since

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