[CONTRIBUTION FROM DOW CORNING CORP.]

Epoxyorganosiloxanes

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Methods were sought for preparing epoxy silicon compounds in which the epoxy-containing group is attached to silicon by a stable Si–C linkage. These have been prepared by: (1) epoxidation of olefinic organosilicon compounds with peracetic acid, and (2) addition of silicon hydrides across the olefinic bond of unsaturated epoxy compounds. A wide variety of epoxy groups on silane or siloxane structures are conveniently prepared in good yield. The epoxy groups and silicon portions of these compounds may react independently of each other in familiar epoxy or siloxane reactions.

Glycidyl silicon ethers have been prepared by the reaction of glycidol with chloro-[1] or acetoxy[2] silanes.

Related structures were postulated as the products of condensation of silanols with hydroxyl groups of commercial epoxy resins.[3] Such glycidyl silicon ethers and silicone modified epoxy resins are stable to heat, but contain Si–O–C bonds that are unstable to hydrolysis or alcoholysis.

A true epoxyorganosilicon compound, $(CH_3)_3SiCH_2CH_2\overline{CHCH_2O}$, was prepared by the reaction of $(CH_3)_3SiCH_2MgBr$ with epichlorohydrin followed by alkali treatment.[4] Two general methods of preparing epoxyorganosilicon compounds are now described: (1) epoxidation of unsaturated organosilicon compounds, and (2) addition of $\equiv$SiH compounds across the double bond of unsaturated epoxy compounds.

$\equiv$SiH compound

$(C_2H_5O)_3SiH$

$(C_2H_5O)_2CH_3SiH$
$C_2H_5O(CH_3)_2SiH$

$(CH_3)_3SiOSi(CH_3)_2H$
$H(CH_3)_2SiOSi(CH_3)_2H$
$H(CH_3)_2SiO[Si(CH_3)_2O]_nSi(CH_3)_2H$
(CH_3HSiO) cyclics
$C_6H_5(CH_3)_2SiH$
$C_6H_5CH_3SiH_2$

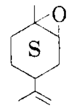
$(C_6H_5HSiO)_n$
$C_6H_5SiH_3$

Unsaturated epoxy compound

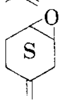
$CH_2{=}CH{-}\overline{CH{-}CH_2O}$
Butadiene monoepoxide

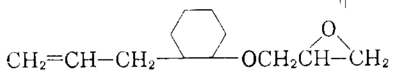
$CH_2{=}CHCH_2OCH_2\overline{CHCH_2O}$
Allyl glycidyl ether

Limonene monoepoxide



Vinylcyclohexene monoepoxide





2-Allylphenyl glycidyl ether

These reactions are adaptable to silanes, alkoxysilanes and siloxanes, but not directly to chlorosilanes.

Epoxidation of vinyl siloxanes with commercial 40% peracetic acid in acetic acid is very sluggish and gives only a poor yield of the vinyl oxide. The simplest member of this series, $\overline{OCH_2CH}Si(CH_3)_2OSi(CH_3)_3$, was recovered in only 20% yield.

Allyl groups on silicon react vigorously with peracetic acid, but are cleaved from silicon to leave condensed siloxanes that give no test for oxirane oxygen.

Unsaturated groups more than two carbons removed from silicon are epoxidized normally by peracetic acid. Internal double bonds react much more readily than terminal olefinic linkages, as has been described for unsubstituted olefins.[5]

Silicon hydrides add across the double bonds of unsaturated epoxy compounds as with other olefins in the presence of peroxide[6] or platinum[7] catalysts. It is notable that the oxirane group does not react under the relatively mild conditions of these additions. Terminal olefins add silicon hydrides more readily than do internal olefins. Usually an excess of the unsaturated epoxy compound is used and yields of epoxyorganosilicon compounds are essentially quantitative based on silicon hydride. Some of the many possible reaction combinations that have been investigated are shown below.

Epoxyorganosiloxanes formed by addition of silanes to epoxy olefins are virtually free of hydroxyl groups and are stable at distillation temperatures exceeding 200°. The oxirane rings are opened under appropriate conditions by active hydrogen compounds such as amines, alcohols, phenols and acids.[8] The resulting hydroxyalkyl amines, ethers or esters in many cases may be isolated by distillation without disrupting or "cutting into" siloxane linkages.

In the absence of active hydrogen compounds the siloxane portion of the epoxyorganosiloxanes may undergo alkali-catalyzed rearrangement or "equilibration" without opening the oxirane ring. Alkoxysilane groups may also be hydrolyzed under

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(1) R. W. Martin, U. S. Patent 2,730,532 to Shell Development Company.

(2) K. A. Andrianov and V. G. Dubrovina, *Doklady Akad. Nauk, S.S.S.R.*, **108**, 83 (1956).

(3) S. A. Brady, J. C. Johnson and J. O. Lyons, *Paint Varnish Production*, 25 (1958).

(4) S. Brynolf, *Acta Chem. Scand.*, **10** [5], 883 (1956).

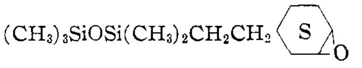
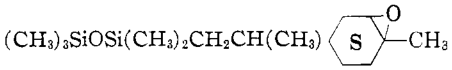
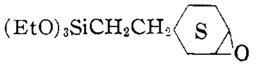
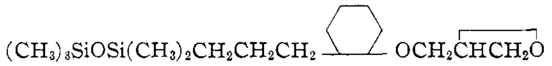
(5) D. Swern, *Chem. Revs.*, **45**, 1 (1949).

(6) J. L. Speier, Ruth Zimmerman and J. A. Webster, THIS JOURNAL, **78**, 2278 (1956).

(7) J. L. Speier, J. A. Webster and G. H. Barnes, *ibid.*, **79**, 974 (1957).

(8) L. Schechter and J. Wynstra, *Ind. Eng. Chem.*, **48**, 86 (1956).

TABLE I

Epoxy silicon compound	Method[a]	B.p. °C.	B.p. Mm.	Dens.[25]	n^{25}D	Epoxy equiv. wt. Calcd.	Epoxy equiv. wt. Obsd.	Si, % Calcd.	Si, % Obsd.
$\mathrm{(CH_3)_3SiOSi(CH_3)_2\overline{CHCH_2O}}$	A	45–50	10	0.877	1.4068	192	212	30.1	29.5
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH(CH_3)\overline{CHCH_2O}}$	B	56–59	8	.850	1.4056	218	..	25.7	25.1
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2CH_2\overline{CHCH_2O}}$	C	78–79	8	.887	1.4180	218	217	25.7	24.6
	B	76–77	7	.881	1.4171	218	227	25.7	25.1
$\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$	B	122–123	11	.915	1.4267	262	257	21.4	..
	A	90–95	0.3	.916	1.4455	272	285	20.7	..
	B	91–92	0.3	.921	1.4450	272	270	20.7	20.4
	B	100–109	0.4	.912	1.4473	300	322	18.7	..
$\mathrm{EtO(CH_3)_2SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$	B	100	3	.947	1.4337	218	227	12.3	..
$\mathrm{(EtO)_2CH_3SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$	B	122–126	5	.978	1.4305	248	256	11.3	11.5
$\mathrm{(EtO)_3SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$	B	122–125	3	1.003	1.4256	278	265	10.1	..
	B	120–130	2	1.014	....	288	310	9.7	..
$\mathrm{(EtO)_2C_6H_5SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$	B	137–141	0.1	1.044	1.4769	310	300	9.0	8.8
	D	145–148	0.2	0.978	1.4805	338	357	16.6	..

[a] Method A = epoxidation; B = SiH addition; C = Grignard with epichlorohydrin; D = phenol with epichlorohydrin.

mild conditions without opening oxirane rings in the same molecule.

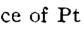
Experimental

Materials.—Commercial chemicals were used without further purification: allyl glycidyl ether (Shell), limonene monoepoxide, distilled grade (Becco), vinylcyclohexene monoepoxide (Union Carbide Chemicals Company), 40% peracetic acid in acetic acid (Becco), butadiene monoepoxide (Columbia Southern Chemical), *o*-allylphenol (Dow), 4-vinylcyclohexene 99% (Phillips).

Epoxybutylsiloxanes. 1. **1-(3,4-Epoxybutyl)-pentamethyldisiloxane.**—The Grignard reagent from 150 g. of $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2Cl}$ (0.82 mole) with excess epichlorohydrin after the manner of Brynolf[4] gave a chlorohydrin. The crude chlorohydrin was dehydrohalogenated by warming with excess 50% aqueous NaOH to 90°, washed with water and distilled through a 3 ft. packed column. A center cut (25 g.) distilling at 79° (8 mm.) was recovered as the desired product, d^{25}_4 0.887, n^{25}D 1.4180, Si 24.6% (calcd. 25.7%), epoxy equivalent weight 217 (calcd. 218).

2. **Pentamethyldisiloxane** (222 g. = 1.5 moles) was refluxed with 140 g. of butadiene monoepoxide (2.0 moles) in the presence of 100 p.p.m. Pt (as $\mathrm{H_2PtCl_6 \cdot 6H_2O}$). The reflux temperature increased from 65 to 103° in 3 hours. The product was fractionated to give two major cuts: (I) 80 g., b.p. 56–59° (8 mm.), d^{25}_4 0.850, b^{25}D 1.4056, Si 25.1% (calcd. for mono-adduct 25.7%), epoxy: none detected by HCl-in-ether titration. (II) b.p. 76–77° (7 mm.), d^{25}_4 0.881, n^{25}D 1.4171, Si 25.1% (calcd. 25.7%), epoxy eq. wt. 227 (calcd. 218).

Infrared examination indicates that (1) and (2)-II are probably the same compound, and that they and (2)-I all contain siloxane linkages and oxirane oxygen, and that olefinic unsaturation and carbonyl groups are absent. (1) and (2)-II are assigned the structure 1-(3,4-epoxybutyl)-pentamethyldisiloxane $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2CH_2\overline{CHCH_2O}}$. (2)-I may be the isomer 2-(3,4-epoxybutyl)-pentamethyldisiloxane $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH(CH_3)\overline{CHCH_2O}}$. (2)-I would be expected to give no apparent HCl consumption since the adduct $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH(CH_3)CHClCH_2OH}$ would lose chlorine by β-elimination with silicon during titration.

2-(7-Oxabicyclo[4.1.0]heptyl)-ethylpentamethyldisiloxane.—1. Addition of $\mathrm{(CH_3)_2HSiCl}$ to 4-vinylcyclohexene in the presence of Pt gave $\mathrm{ClSi(CH_3)_2CH_2CH_2}$ (I) in 90% yield, b.p. 105–110° (10 mm.), d^{25}_4 0.957, eq. wt. 222 (calcd. 203). I cohydrolyzed with 100% excess $\mathrm{Me_3SiCl}$ gave 33% mixed disiloxane $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2CH_2}$ (II), b.p. 85–95° (5 mm.), d^{25}_4 0.882. Epoxidation of 36 g. of II with 20% peracetic acid in acetic acid prepared after the method of Greenspan[9] gave 20 g. (53% yield) of 2-(7-oxabicyclo[4.1.0]heptyl)ethylpentamethyldisiloxane, b.p. 90–95° (0.3 mm.), d^{25}_4 0.915, n^{25}D 1.4455, epoxy eq. wt. 286 (calcd. 272).

2. Pentamethyldisiloxane (74 g., 0.5 mole) was dropped into 3-vinyl-7-oxabicyclo[4.1.0]heptane (vinylcyclohexene monoepoxide) (100 g., 0.8 mole) containing 150 p.p.m. Pt at 130° during 15 minutes. Warming 130–140° was continued 2 hours more, until a portion gave no precipitate with $\mathrm{HgCl_2}$ in alcohol. Distillation gave 125 g. of product, b.p. 91–92° (0.6 mm.), d^{25}_4 0.921, n^{25}D 1.4450, Si, 20.40, 20.38 (calcd. 20.65), epoxy equiv. wt. 270 (calcd. 272). Products 1 and 2 are considered to be the same isomer (product 1 may contain some hydroxy acetate impurity), since SiH addition is preferential at terminal unsaturation,[7] and epoxidation is preferential at internal unsaturation.[5]

Other Pt-catalyzed Additions.—Single products were recovered in substantially quantitative yields by the addition of silanes to limonene monoepoxide, allyl glycidyl ether and *o*-allylphenyl glycidyl ether. Only butadiene monoepoxide gave mixtures of isomeric adducts.

In general, an excess of epoxy olefin was warmed with 10–200 p.p.m. Pt (added as $\mathrm{H_2PtCl_6 \cdot 6H_2O}$ in *t*-butyl alcohol) at 120–140° with or without toluene solvent while dropping in the $\equiv$SiH compound. The exothermic addition reaction was often sufficient to maintain reaction temperature without outside heat. Precautions were taken to prevent the accumulation of unreacted silane, since a rapid burst of reaction could raise the temperature to a point where violent, exothermic polymerization of epoxy groups would occur. (It was observed that completed epoxysilicon compounds were more stable to heat than were intermediate reaction mixtures.) Warming was continued until no further test for $\equiv$SiH was obtained. The mixtures were then distilled or freed of volatiles to recover the desired products.

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[9] F. P. Greenspan, THIS JOURNAL, **68**, 907 (1946).

TABLE II

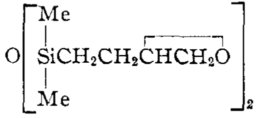
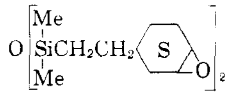
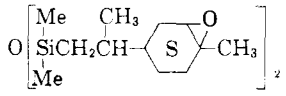
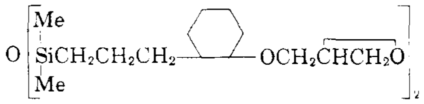
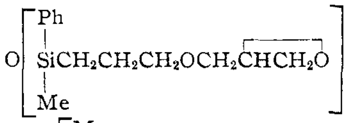
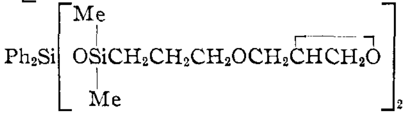
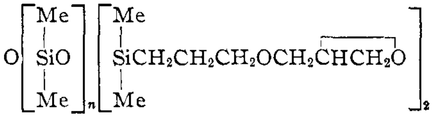
Epoxy siloxane	B.p. °C.	B.p. Mm.	Dens.^{25}	$n^{25}D$	Visc., cs.	Formula wt.	Epoxy equiv. wt.
	110–120	1.5	0.958	1.4429	5	274	145
	190–195	0.6	.993	1.4731	42	382	196
	195–200	.5	.972	1.4742	83	438	227
	.....	..	1.061	1.5184	260	514	263
	.....	..	1.082	1.5200	80	486	244
	.....	..	1.063	1.5011	60	580	282
$PhCH_3Si(CH_2CH_2CH_2OCH_2CHCH_2O)_2$	180–185	.1	1.065	1.5090	35	340	172
							
n = 0	183–187	2	0.995	1.4503	10.8	362	182
1	.....	..	.992	1.4442	11	436	222
2	.....	..	.991	1.4389	11	510	263
3	.....	..	.993	1.4359	12	584	294
4	.....	..	.998	1.4348	14	658	303

TABLE III

MONO ADDUCTS OF $(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CH_2OCH_2CHCH_2O$

Reactant	Catalyst	$(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CH_2OCH_2CH(OH)CH_2X$						
		B.p.		Yield,			Hydroxyl, %	
		°C.	Mm.	%	Dens.^{25}	$n^{25}D$	Theory	Found
Benzoic acid	Dimethylaniline	165–170	0.4	33	1.002	1.4790	4.43	4.05
Phenol	R_4NOH	158–160	.5	60	0.986	1.4738	4.78	5.08
1-Butanol	$SnCl_4$	123–126	.3	90	.913	1.4318	5.06	5.24
Ethylene glycol	H_2SO_4	134–136	.3	20	.975	1.4420	10.5	10.2
Water	H_2SO_4	112–114	.5	15	.976	1.4388	12.1	12.3
$(C_2H_5)_2NH$	None	120–123	.3	90	.900	1.4360	5.06	4.74
t-$C_4H_9NH_2$	Phenol	128–130	.2	70	.906	1.4378	4.2[a]	3.9[a]
Ethylenediamine	Phenol	149–150	.2	55	.959	1.4550	8.7[a]	8.8[a]

[a] Nitrogen.

Epoxyethylpentamethyldisiloxane.—Addition of 95 g. of (40%) peracetic acid to 88 g. (0.5 mole) of vinylpentamethyldisiloxane and 5 g. of sodium acetate at room temperature caused no temperature rise. The mixture was stirred at 40–50° for 8 hours. After washing with water and filtering to remove gelled particles 45 g. of oily liquid was recovered. Fractional distillation through a 2 ft. packed column gave 17 g., b.p. 20–30° (10 mm.) and 17 g., b.p. 45–50° (10 mm.), d^{25}_4 0.877, $n^{25}D$ 1.4068, Si 30.1%, epoxy equiv. wt. 210; calcd. for epoxyethylpentamethyldisiloxane, Si, 29.5%, epoxy eq. wt. 190.

Diallyldimethylsilane with Peracetic Acid.—Seventy g. (0.5 mole) of $(CH_2{=}CHCH_2)_2Si(CH_3)_2$ in 100 ml. of benzene was stirred at 10° while dropping in 190 g. of commercial 40% peracetic acid containing 8 g. of sodium acetate. After an exothermic reaction during addition, the mixture was warmed to 20–30° for 1 hour. The product was washed three times with water and distilled to 60° (1 mm.) (no distillate 25–60° (1 mm.)). 32 g. of oily residue remained, visc., 276 cs., Si 24.18%, epoxy—none detected by HCl-in-ether method. Calcd. for bis-(epoxypropyl)-dimethylsilane 16.3% Si. Evidently many of the allyl groups were cleaved from silicon under the influence of peracetic acid.

3-[2-(2,3-Epoxypropoxy)-phenyl]-propylpentamethyldisiloxane.—Addition of pentamethyldisiloxane to 2-allylphenol gave 2-[3-(pentamethyldisiloxanyl)-propyl]-phenol, b.p. 110° (0.2 mm.), d^{25}_4 0.019, $n^{25}D$ 1.5430, visc. 24 cs. A solution of 113 g. of substituted phenol (0.4 mole) in 54 g.

of epichlorohydrin (0.6 mole) was dropped with stirring into 80 g. of 25% aqueous NaOH (0.5 mole) at 35–45°, and stirred 1 hour more at 70–80°. The mixture was poured into water and washed until neutral. Distillation of the organic layer gave 90 g. of product (60%), b.p. 145–148° (0.2 mm.), d^{25}_4 0.978, n^{25}_D 1.4805, visc. 17 cs., epoxy eq. wt. 357, calcd. 338.

Monoepoxysilicon compounds prepared by various methods are described in Table I. Diepoxysiloxanes prepared by addition of ≡SiH to olefinic epoxy compounds are described in Table II.

Reactions of Epoxysiloxanes. 1. Addition of Active Hydrogen Compounds.—The monoepoxydisiloxane $\mathrm{(CH_3)_3SiOSi(CH_3)_2CH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$ was used to study the reactions of various active hydrogen compounds with epoxysiloxanes. The resulting hydroxyalkyl substituted disiloxanes were stable to distillation temperatures over 170°. No indication was observed of hydroxyl groups "cutting into" the siloxane linkage to form cyclic silaethers and hexamethyldisiloxane. Difficulty was observed in getting reaction between water or ethylene glycol and the epoxysiloxane because of mutual insolubility.

One hundred g. (1.06 moles) of phenol and 1 g. of benzyltrimethylammonium hydroxide (40% solution in methanol) were refluxed with 50 g. of toluene while dropping in 78 g. of 3-(2,3-epoxypropoxy)-propylpentamethyldisiloxane. The mixture was refluxed 8 hours and then distilled through an 8″ packed column to recover 65 g. of a center cut (60% yield), b.p. 158–160° (0.5 mm.), d^{25}_4 0.986, n^{25}_D 1.4738, Si 15.93, 15.90% (calcd. for mono-adduct 15.72%), hydroxyl 5.08% (calcd. 4.78%). Infrared examination of recovered toluene detected only a trace of hexamethyldisiloxane (less than 0.5 g. total).

Various mono-adducts to 3-(2,3-epoxypropoxy)-propylpentamethyldisiloxane are described in Table III.

2. Hydrolysis.—3-(2,3-Epoxypropoxy)-propyltriethoxysilane (10 g., 0.036 mole) was initially insoluble in water, but after shaking with 90 g. of water for 4 hours at *p*H 3–5 (acetic acid) a clear solution resulted. The solution was stable indefinitely at this *p*H, but an oily precipitate settled out when the solution was made slightly alkaline. After 24 hours the oily layer was taken up in toluene, dried by azeotroping water with part of the toluene. Analysis of the residue indicated that 0.035 epoxy equivalent remained.

3. Alcoholysis.—3-(2,3-Epoxypropoxy)-propyltrimethoxysilane (47 g., 0.2 mole) was warmed with 2-methoxyethanol (50 g., 0.66 mole) while slowly removing distillate at 65–75° through a 12″ packed column. After no more low boiling distillate came over the residue was distilled to recover intermediate fractions and 30 g. of best product, b.p. 160–165° (0.1 mm.), d^{25}_4 1.077, n^{25}_D 1.4408, epoxy equiv. wt. 358 (calcd. for $\mathrm{(CH_3OCH_2CH_2O)_3SiCH_2CH_2CH_2OCH_2\overline{CHCH_2O}}$, 368).

MIDLAND, MICHIGAN

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

The Chemistry of Borazene. II. The Synthesis of N-Trimethyl-B-trialkoxyborazenes and N-Trimethyl-B-triphenoxyborazene[1]

BY MILDRED J. BRADLEY,[2] GEORGE E. RYSCHKEWITSCH AND HARRY H. SISLER

RECEIVED OCTOBER 1, 1958

N-Trimethyl-B-trichloroborazene reacts smoothly with the sodium salts of alkyl alcohols and of phenols to give the B-alkoxy- and B-phenoxyborazenes. By this method the following new compounds have been prepared: N-trimethyl-B-trimethoxyborazene, N-trimethyl-B-triethoxyborazene, N-trimethyl-B-tri-*n*-propoxyborazene, N-trimethyl-B-triisopropoxyborazene, N-trimethyl-B-tri-*n*-butoxyborazene, N-trimethyl-B-tri-*t*-butoxyborazene and N-trimethyl-B-triphenoxyborazene.

Most borazene derivatives have been prepared by starting with the appropriate substituent on nitrogen and boron and then synthesizing the ring. Very few reactions of borazenes in which other borazenes are produced without ring synthesis have been investigated. In general, water cleaves the borazene ring. However, under carefully controlled conditions N-triphenyl-B-trichloroborazene and N-tri-*p*-anisyl-B-trichloroborazene react with three equivalents of water to yield the B-trihydroxy derivatives[3,4]; N-tri-*p*-tolyl-B-trichloroborazene gives only ring cleavage in moist benzene.[5] The chlorine atoms of trichloroborazene may be replaced by cyanide, nitrite, nitrate, bromide and thiocyanate by metathesis with the appropriate silver or sodium salts.[6]

The work reported here gives a simple method for the synthesis of B-alkoxy- and B-phenoxyborazenes through the reaction of N-trimethyl-B-trichloroborazene with sodium alkoxides or phenoxide. Under similar conditions addition of alcohols and phenol to the chloroborazene results only in ring cleavage.

Experimental

N-Trimethyl-B-trichloroborazene.—N-Trimethyl-B-trichloroborazene was prepared by the reaction of boron trichloride with methylamine hydrochloride in refluxing chlorobenzene.[7,8]

Sodium Alkoxides.—Fisher dry, "purified" sodium methoxide was used without further purification. Commercial sodium phenoxide was washed with ether and heated under vacuum to 200° to remove the phenol. The other salts were prepared by the reaction of metallic sodium or sodium hydride with the anhydrous alcohols in a dry, nitrogen atmosphere and vacuum evaporation of the excess alcohols from the salts at 100°. Care must be exercised in removing the excess isopropyl and *t*-butyl alcohols from their gelatinous reaction products in order to remove as much alcohol as possible without forming large amounts of sodium oxide and the respective ether.

N-Trimethyl-B-trialkoxyborazene and N-Trimethyl-B-triphenoxyborazene.—In a typical experiment, 0.15 g. equiv. of N-trimethyl-B-trichloroborazene was placed in a two-necked, angle type, 250-ml. round bottom flask along

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[1] The most recently recommended names for these compounds are 1,3,5-trimethyl-2,4,6-trialkoxyborazine and 1,3,5-trimethyl-2,4,6-triphenoxyborazine.

[2] Abstracted from the Ph.D. Dissertation of Mildred J. Bradley submitted to the University of Florida, 1958, and available from University Microfilms, Ann Arbor, Michigan.

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