The above experiment was repeated using divinylsilane instead of the silacyclopentadiene. All other variables were held constant, *e.g.*, concentrations, reaction time etc. It became immediately apparent that the rate of reaction of divinylsilane relative to silacyclopentadiene was exceedingly slow. Removal of the solvent (and divinylsilane) left behind a relatively pure sample of bromobenzene as shown by infrared and vapor phase chromatography. There was no trace of phenylated products as was the case with silacyclopentadiene.

1-Phenylsilacyclopentane.—One-half mole of phenylmagnesium bromide (from bromobenzene and magnesium) was added slowly to 77.5 g. (0.5 mole) of 1,1-dichlorosilacyclopentane in ether. After the addition, the mixture was stirred overnight; the precipitated salts were filtered off and the ether removed. The residue was distilled on a Todd column; 25 g. was obtained boiling at 89–90° (2.5 mm.). An additional 8.5 g. was collected at 91–92° (2.5 mm.). The total yield of 1-chloro-1-phenylsilacyclopentane was 33.5 g. (50%). Thirty grams (0.15 mole) of this material was immediately added dropwise to excess lithium aluminum hydride in ether and allowed to stir overnight. Then dilute hydrochloric acid was added until the salts coagulated. After these salts were filtered, they were washed with ether, and the ether removed. The residue was distilled and 11 g. of 1-phenylsilacyclopentane was obtained boiling at 95° (10 mm.), n^{25}_{D} 1.5358. An infrared spectrum of this material showed Si–H and Si-phenyl absorption. An additional 7.5 g. of product was obtained from this reaction boiling at 96–98° (10 mm.); total yield 18.5 g. (80%).

Anal. Calcd. for $C_{10}H_{14}Si$: C, 74.07; H, 8.64; Si, 17.07. Found: C, 74.07; H, 8.74; Si, 17.00.

Hydrogen Determination.—An apparatus was set up to measure hydrogen evolution quantitatively.[17]

Freshly prepared silacyclopentadiene (0.3 g., 0.0036 mole) was weighed out and injected by means of a syringe into a sodium–potassium alloy (0.1 g. of sodium, 0.6 g. of potassium) contained in a small amount of dimethyl ether or diethylene glycol or tetrahydrofuran. Gas evolution was immediate and vigorous. When reaction had ceased, the solution was heated briefly and allowed to cool. The arms of the manometer were then allowed to come to equilibrium. A total of 41.50 ml. of hydrogen[18] at 25° and 748 mm. was collected. This corresponds to a 91% yield of gas.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this work possible.

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[17] The apparatus used was essentially a modified "Grignard machine." See "Advanced Organic Chemistry" by L. F. Fieser and M. Fieser, Reinhold Publishing Corp., New York, N. Y., 1961, p. 422.

[18] Analysis of this gas was made in a Bendix Time-of-Flight Mass Spectrometer.

[CONTRIBUTION FROM THE DOW CORNING CORPORATION, MIDLAND, MICH.]

Redistribution and Reduction Reactions of Alkoxysilanes

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Strong bases have been found to cata e the redistribution of alkyl, aryl, silyl and alkoxy groups attached to silicon. Alkali metals cause reduction of methoxy or phenoxy silicon compounds to form methyl or phenyl silicon compounds. This reduction reaction is a new method of forming carbon–silicon bonds.

The ability of tetra-substituted silanes to undergo disproportionation has long been recognized. Acidic catalysts such as aluminum chloride have been investigated. Russell[1] studied such systems and summarized the results of other investigators. Alkaline catalysts are also known to promote such reactions. Friedel and Ladenburg[2] showed that sodium or very likely the ethoxide ion promoted the disproportionation of triethoxysilane.

$$4HSi(OEt)_3 \longrightarrow SiH_4 + 3Si(OEt)_4$$

The interchange of alkoxy groups between alkoxysilanes[3] and the disproportionation of various alkenylalkoxysilanes[4] have been reported in the presence of alkaline catalysts. Bailey disclosed that disproportionation took place when phenylalkoxysilanes were heated with sodium alkoxides,[5] although alkylalkoxysilanes were unaffected by similar conditions. Redistribution of phenyl groups also has been observed by Beck[6] and others in rearrangements of phenylsiloxanes at high temperatures.

Our work has confirmed the disproportionation of phenylalkoxysilanes disclosed by Bailey. Specifically it was shown that phenyltrimethoxysilane and phenylmethyldimethoxysilane form tetramethoxysilane and methyltrimethoxysilane, respectively, when heated in the presence of catalytic amounts of sodium. The other products of these reactions are materials containing more than one phenyl group attached to silicon:

$$C_6H_5Si(OMe)_3 \longrightarrow (MeO)_4Si + C_6H_5Si(OMe)_3 + (C_6H_5)_2Si(OMe)_2 + (C_6H_5)_3SiOMe + (C_6H_5)_4Si$$

$$(C_6H_5)MeSi(OMe)_2 \longrightarrow MeSi(OMe)_3 + (C_6H_5)_2MeSiOMe + (C_6H_5)_3SiMe$$

At the temperatures employed in the latter experiments (200°), it is significant that the methyl group did not take part in the disproportionation. The actual catalyst in these systems very likely is the hydroxide or methoxide ion generated by reaction of sodium with moisture or free methanol which are certainly present in these systems.

The exchange of phenyl and alkoxy groups attached to silicon was extended to a procedure which could be a useful method of preparing any number of phenyl-containing alkoxysilanes

$$MeSi(OMe)_3 + (C_6H_5)_x\,Si(OMe)_{4-x} \longrightarrow Si(OMe)_4 + (C_6H_5)_y\,MeSi(OMe)_{3-y}$$
$$x = 1, 2;\ y = 0, 1, 2, 3, \ldots$$

These reactions are typical redistribution reactions under which conditions the methyl group does not participate, while the phenyl and methoxy groups are distributed in all possible combinations

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[1] G. A. Russell, *J. Am. Chem. Soc.*, **81**, 4815 (1959).

[2] C. Friedel and A. Ladenburg, *Ann.*, **143**, 124 (1867).

[3] D. F. Peppard, W. G. Brown and W. C. Johnson, *J. Am. Chem. Soc.*, **68**, 77 (1946).

[4] (a) D. L. Bailey and A. N. Pines, *Ind. Eng. Chem.*, **46**, 2363 (1954); (b) A. N. Pines and R. E. Godlewski, U. S. Patent 2,851,474.

[5] D. L. Bailey, U. S. Patent 2,723,983; 2,723,985.

[6] E. W. Beck, W. H. Daudt, H. J. Fletcher, M. J. Hunter and A. J. Barry, *J. Am. Chem. Soc.*, **81**, 1256 (1959).

TABLE I

REACTIONS OF METHYLTRIMETHOXYSILANE

Run no.	Moles MeSi(OMe)$_3$	Catalyst (moles or g.-atom)	Temp., °C.	Time, hours	Products isolated, moles: Me$_2$O	Me$_3$SiOMe	Me$_2$Si(OMe)$_2$	MeSi(OMe)$_3$	Si(OMe)$_4$	Residue, g.
1	3.81	Na (2.9)	230	16	2.06	0.60	0.69	0.14	. .	240[a]
2	3.81	NaOMe (0.22)	230	67	0.46	. .	.29	2.64	. .	33
3	3.5	Na (0.52)	240	5.7	Present	Trace	.44	2.52	0.17	. .[a]
4	3.5	Na (0.52)	250	6.0	0.24	0.03	.69	1.94		62
5	2.72	Na (0.43)	240	87	.64	.05	.54	1.22		68
6	2.5	Na (1.0)	270	4.3	.93	.13	.61	0.65		89[a]
7	2.5	Na (0.52)	270	22	Present	.05	.51	1.3		62
8	2.5	Na (0.52)	270	22	0.56	.05	.47	1.14	.07	[b]
9	2.5	Residue above	270	22	.20	. .	.20	1.63	.20	76[c]
10	2.0	Na (0.52)	250	21	.87	.07	.47	0.84		[d]
11	3.0	K (0.18)	250	15	.14	.02	.54	1.73		
12	2.5	Li (1.0)	270	23	Present	.03	.08	2.02	.09	[a]
13	2.5	(KOSiMe$_2$)$_2$O (0.09)	270	19	0.18	.03	.32	1.57	Present	
14	2.5	Na$_2$O (0.32)	270	16	1.04	.03	.42	1.21	0.11	

[a] Residue contains unreacted alkali metal. [b] Residue used as catalyst in run 9. [c] Residue from both run 8 and 9. [d] Pentene-1 (1.0 mole) was present during this reaction; it was recovered unchanged at the end of the experiment.

among the valences of the $\overset{|}{\underset{|}{-\text{Si}-}}$ and $\overset{|}{\underset{|}{\text{MeSi}-}}$ groups. When these systems contain impurities capable of supplying protons, cleavage of phenyl groups takes place to form benzene.

Alkyl groups have now been found to take part in disproportionations at higher temperatures. Methyltriethoxysilane, heated with sodium at 250°, gave essentially equimolar amounts of dimethyldiethoxysilane and tetraethoxysilane.

$$2\text{MeSi(OEt)}_3 \longrightarrow \text{Me}_2\text{Si(OEt)}_2 + (\text{EtO})_4\text{Si}$$

Essentially all of the sodium was recovered unchanged at the end of the experiment. Methyltriisopropoxysilane and methyltributoxysilane were unaffected when treated under these same conditions.

Methyltrimethoxysilane, when heated at temperatures of 230–280° with an alkali metal or a strong alkali base, forms a mixture of trimethylmethoxysilane, dimethyldimethoxysilane, methyltrimethoxysilane and tetramethoxysilane. In no case was tetramethylsilane detected. Potassium, sodium or lithium metal as well as such bases as sodium methoxide, sodium oxide, sodium methylsiloxanolate $[\text{NaOSiMeO}]_x$, and the dipotassium salt of tetramethyldisiloxane-1,3-diol all bring about the formation of these redistribution products. Weaker bases such as potassium acetate and sodium metasilicate and a less active metal such as calcium proved ineffective.

The relative amount of conversion of methyltrimethoxysilane to dimethyldimethoxysilane and trimethylmethoxysilane is a function of the amount and type of catalyst used as well as of temperature and time. In general, higher temperatures, longer heating periods, larger amounts of catalyst and more active catalysts all give higher conversions of methyltrimethoxysilane. Table I shows the results of a number of reactions of methyltrimethoxysilane with various reagents.

Dimethyldimethoxysilane and sodium at 240° formed a mixture of methyltrimethoxysilane, dimethyldimethoxysilane and trimethylmethoxysilane. Similarly, redistribution of methyl groups occurred when propylmethyldimethoxysilane and sodium were heated at 270° to form propyldimethylmethoxysilane. The observed formation of dipropylmethylmethoxysilane indicates that higher alkyl groups can also participate in redistribution reactions.

This redistribution is unique since the average methyl to silicon ratio of the volatile products is higher than that of the initial mixture. This phenomenon is explained by the observed side reactions which serve to remove methoxy groups and silicon atoms from the volatile product mixture.

Dimethyl ether was formed from all methoxysilanes under conditions that also caused redistribution of an alkyl group. This may result from attack of a methoxide ion on the carbon atom of a methoxysilane.

$$\text{CH}_3\text{O}^- + \text{CH}_3\text{OSi}\equiv \longrightarrow \text{CH}_3\text{OCH}_3 + \ominus\text{O–Si}\equiv$$

Ether formation was not observed in any redistribution involving an ethoxysilane.

The silanolate ion produced by the above reaction may react with another methoxysilane to produce a siloxane.

$$\equiv\text{SiO}\ominus + \text{CH}_3\text{OSi}\equiv \longrightarrow \text{CH}_3\text{O}^- + \equiv\text{SiOSi}\equiv$$

Continuation of these processes can thus lead to a mixture of alkali metal siloxane-silanolates which are essentially alkali metal silicates. Such products were found as residues in these reactions.

When an alkali metal was used to cause disproportionation, reduction also took place at high temperatures. Tetramethoxysilane heated with sodium formed dimethyldimethoxysilane and methyltrimethoxysilane presumably by the steps shown in the equations

$$\text{CH}_3\text{OSi}\equiv + 2\text{Na} \longrightarrow \text{CH}_3\text{Na} + \text{NaOSi}$$

$$\text{CH}_3\text{Na} + \text{CH}_3\text{OSi}\equiv \longrightarrow \text{CH}_3\text{Si}\equiv + \text{NaOCH}_3$$

By the same reaction propyldimethylmethoxysilane and propylmethyldimethoxysilane were formed from propyltrimethoxysilane and sodium. In this case some dipropyldimethoxysilane was recovered, again showing that the propyl group attached to silicon is capable of redistribution.

Dimethyldiphenoxysilane heated with sodium formed sodium phenoxide and a mixture of products which were impossible to separate by fractional distillation. Specific refraction values of various fractions, infrared analysis, and the separation observed by gas–liquid chromatography indicated the presence of mixed silanes and siloxanes containing methyl, phenyl and phenoxy groups on silicon. 1,3-Diphenyltetramethyldisiloxane and phenyldimethylphenoxysilane were identified using gas–liquid chromatography. It is interesting in this case that no redistribution occurred; probably sodium phenoxide is too weak a base to bring about this reaction. Trimethylphenoxysilane was unaffected by similar treatment.

Sodium and tetraethoxysilane formed large amounts of ethylene when heated at 280°. It is believed that rupture of the C–O bond occurred in this system, but the resulting ethylsodium decomposed immediately to ethylene and sodium hydride.[7] The pyrophoric nature of the residue from this reaction supports the presence of sodium hydride. Presumably other higher alkoxy-silanes would also form an olefin with sodium.

When benzyltriethoxysilane was heated to 240° with a small piece of sodium, tetraethoxysilane was formed along with a fraction corresponding to $(C_7H_7)_2Si(OEt)_2$. Specific refraction values and vapor chromatography indicated that partial isomerization to tolyl structures may have occurred. In any event, the benzyl structure is capable of entering into a redistribution reaction.

Sodium and 1,2 - dimethyltetramethoxydisilane formed methyltrimethoxysilane and a mixture of higher polysilanes when heated to the reflux temperature. The reaction in this case was the exchange of the Si–Si bond with the Si–OMe bond.

Experimental

The following properties were recorded for various alkoxysilanes used as starting materials in this study. These materials were prepared by alcoholysis of the corresponding chlorosilane.

Methyltrimethoxysilane, b.p. 102°, n^{25}_{D} 1.3690, d^{25}_4 0.9388; R_{D} 0.2403, calcd. 0.2397.[8]

Dimethyldimethoxysilane, b.p. 80.2°, n^{25}_{D} 1.3699, d^{25}_4 0.8554; R_{D} 0.2644, calcd. 0.2647.[9]

***n*-Propyltrimethoxysilane**, b.p. 142°, n^{25}_{D} 1.3880, d^{25}_4 0.9318; R_{D} 0.2534, calcd. 0.2554.

Ethyltrimethoxysilane, b.p. 124°, n^{25}_{D} 1.3798, d^{25}_4 0.9451; R_{D} 0.2450, calcd. 0.2483.[10]

Phenylmethyldimethoxysilane, b.p. 105° at 30 mm., n^{25}_{D} 1.4769, d^{25}_4 1.001; R_{D} 0.2822, calcd. 0.2838.

Phenyltrimethoxysilane, b.p. 120° at 30 mm., n^{25}_{D} 1.4710.[11]

Diphenyldimethoxysilane, n^{25}_{D} 1.5404, d^{25}_4 1.078.

***n*-Propylmethyldimethoxysilane**, b.p. 128.6° at 750 mm., n^{25}_{D} 1.3903, d^{25}_4 0.8632; R_{D} 0.2748, calcd. 0.2774.

Phenyldimethylphenoxysilane, b.p. 148° at 13 mm., n^{25}_{D} 1.5450, d^{25}_4 1.022; R_{D} 0.3093, calcd. 0.3083.

Benzyltriethoxysilane was prepared in 58% yield by the reaction of benzyl chloride, magnesium and tetraethoxysilane; b.p. 148° at 26 mm., n^{25}_{D} 1.4628, d^{25}_4 0.9812.[12]

Dimethyldiphenoxysilane was prepared in 84% yield by the reaction of dimethyldichlorosilane and phenol. This material boiled at 94–100° at 1 mm., n^{25}_{D} 1.5310, d^{25}_4 1.0590; R_{D} 0.2922, calcd. 0.2898. Its physical properties and infrared spectrum match those published by Wilson.[13]

1,2-Dimethyltetramethoxydisilane.—A sample of by-product residue from the reaction of methyl chloride with copper silicon (456 g.), boiling at 156–159°, which was known to contain 1,2-dimethyltetrachlorodisilane was placed in a flask fitted with a stirrer and a reflux condenser. Methanol (256 g., 8.0 moles) was added in 50-ml. portions while hydrogen chloride was removed under reduced pressure furnished by an aspirator. On completion of the addition of the alcohol the material was heated to 90° at 40 mm. The resulting crude product had a neutralization equivalent of 230. This material was then heated to 95° and methyl orthoformate (225 g., 2.1 moles) was added slowly. This is essentially the method of Shorr.[14] The mixture was heated 5 hours until the evolution of methyl chloride had ceased and a neutral solution remained in the flask, which was fractionated at 30 mm. pressure. Methyl formate was recovered, followed by 158 g. of unidentified materials boiling up to 86.2° at 30 mm. It was followed by pure 1,2-dimethyltetramethoxydisilane, b.p. 86.2–87° at 30 mm., n^{25}_{D} 1.4166, d^{25}_4 0.9875; R_{D} 0.2544, calcd. 0.2589.

Anal. Calcd. for $(MeO)_2MeSiSiMe(OMe)_2$: Si, 26.8; Si–Si equiv. 210; –OMe, 58.9. Found: Si, 27.48, 27.35; Si–Si equiv. 201; –OMe, 61.

When a few drops of this compound was added to sodium methoxide in methanol, hydrogen and methyltrimethoxysilane were formed. The formation of the latter compound, identified by gas–liquid chromatography, indicated that the disilane was the symmetrical isomer.

Redistribution of Phenyltrimethoxysilane.—Phenyltrimethoxysilane (158.2 g., 0.80 mole) and sodium (4.4 g., 0.19 g.-atom) were heated in a flask equipped with a reflux condenser. At 204° the mixture began to boil. After 100 minutes of gentle refluxing the temperature of the boiling mixture had fallen to 187° and after 18 hours the temperature of the refluxing liquid was 173°. The mixture was placed under a small fractionating column and 31.2 g. of tetramethoxysilane was distilled off. The piece of sodium was then removed, the mixture was acidified by adding trimethylchlorosilane and distilled under reduced pressure. A total of 40.5 g. (0.27 moles) of tetramethoxysilane, identified by its infrared spectrum, was recovered, followed by 67 g. of phenyltrimethoxysilane and 39.0 g. (0.16 mole) of diphenyldimethoxysilane. The diphenyldimethoxysilane had an infrared spectrum identical to that of an authentic sample. This experiment serves to show that the exchange of phenyl and methoxy on silicon takes place at a temperature at least as low as 173°.

Redistribution of Phenylmethyldimethoxysilane.—Phenylmethyldimethoxysilane (808 g., 4.43 moles) and sodium (1 g., 0.04 g.-atom) were placed in a flask under a 30-inch fractionating column and heated at 200° for 200 hours while 291 g. (2.14 moles) of methyltrimethoxysilane was removed. The material in the flask was then made slightly acidic with trimethylchlorosilane and rapidly distilled at low pressure. The last fractions from this distillation crystallized. On recrystallization from methanol this material was identified as triphenylmethylsilane, m.p. 66.5–67.5°. The value given in the literature[15] is 68–69°. The yield was 63 g. (0.23 mole). Careful fractionation of the liquid distillate led to the recovery of 72 g. (0.37 mole) of phenylmethyldimethoxysilane, n^{25}_{D} 1.4769, and 135.5 g. (0.59 mole) of diphenylmethylmethoxysilane, n^{25}_{D} 1.5510, d^{25} 1.034.

Anal. Calcd. for $(C_6H_5)_2MeSiOMe$: Si, 12.3; R_{D} 0.3101. Found: Si, 12.32, 12.45; R_{D}, 0.3086.

Methyltrimethoxysilane and Phenyltrimethoxysilane.—Phenyltrimethoxysilane (297 g., 1.5 moles), methyltrimethoxysilane (204 g., 1.50 moles) and sodium methoxide (4.6 g., 0.08 mole) were heated 19 hours at 190–200°. On cooling, the contents of the vessel were filtered to give

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(7) W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **51**, 588 (1929).

(8) D. Seyferth and E. Rochow, *J. Org. Chem.*, **20**, 250 (1955), list the properties of this compound as b.p. 102–103° (768 mm.), n^{25}_{D} 1.3690, d^{25}_4 0.951.

(9) T. Tanaka and R. Okawara, *Bull. Chem. Soc. Japan*, **28**, 365 (1955), report b.p. 82° (760 mm.), n^{20}_{D} 1.3708, d^{20}_4 0.8646.

(10) R. Okawara, *ibid.*, **28**, 360 (1955), reports for this compound b.p. 124.3° (760 mm.), n^{20}_{D} 1.3838, d^{20}_4 0.9488.

(11) L. Tyler, *J. Am. Chem. Soc.*, **77**, 770 (1955), reports for this compound b.p. 108° (20 mm.), n^{25}_{D} 1.4701, d^{25}_{25} 1.067.

(12) W. Melzer, *Ber.*, **41**, 3390 (1908), reports for this compound b.p. 245–250°, d_4 0.9864.

(13) G. Wilson, *J. Org. Chem.*, **24**, 1 17 (1959).

(14) L. M. Shorr, *J. Am. Chem. Soc.*, **76**, 1390 (1954).

(15) E. Larsson and E. van Gilse von der Pals, *Svensk. Kemi. Tids.*, **63**, 177 (1951).

480.6 g. of liquid products. To 373.2 g. of this product mixture was added 8 g. of Me_3SiCl to neutralize any remaining alkali. Vacuum fractionation of this material gave methyltrimethoxysilane (126.2 g., 0.93 mole) boiling at 32° at 45 mm., n^{25}D 1.3680; tetramethoxysilane (73.1 g., 0.48 mole) boiling at 48° at 44 mm., n^{25}D 1.3652, d^{25} 1.026, *R*D 0.2179 (calcd. 0.2199)[16]; phenylmethyldimethoxysilane boiling at 114° at 45 mm., n^{25}D 1.4680, d^{25} 1.0032 (43.7 g., 0.24 mole); and phenyltrimethoxysilane (34.2 g., 0.17 mole) boiling at 127° at 43 mm. The remaining undistilled material was found by infrared analysis to be essentially 38% phenyltrimethoxysilane and 62% diphenyldimethoxysilane.

Methyltrimethoxysilane and Diphenyldimethoxysilane.—Diphenyldimethoxysilane (664.4 g., 2.72 moles), methyltrimethoxysilane (819 g., 6.0 moles) and a solution made by dissolving 0.9 g. of sodium (0.04 g.-atom) in 15 ml. of methanol were placed in a 2900-ml. stainless steel pressure vessel and heated 60 hours at 190°. The products were then filtered and made slightly acidic by adding trimethylchlorosilane. Fractionation of this mixture at atmospheric pressure led to the isolation of benzene boiling at 80° (25 g., 0.32 mole) and methyltrimethoxysilane (524 g., 3.84 moles) boiling at 102–103°. The remainder of the material was then rapidly distilled at the minimum pressure of an oil-pump to give 853 g. of volatile material and 5.4 g. of a tarry residue.

Fractionation of this material at 30 mm. led to the recovery of methyltrimethoxysilane (19.6 g., 0.14 mole), tetramethoxysilane (73 g., 0.48 mole, 23%), phenylmethyldimethoxysilane (229.0 g., 1.26 moles) and phenyltrimethoxysilane (256.9 g., 1.3 moles). The distillation was discontinued at this point. The remaining material in the flask weighed 226 g. and had n^{25}D 1.5410, indicating a high phenyl content.

Methyltriethoxysilane and Sodium.—Methyltriethoxysilane (500 g., 2.80 moles) and sodium (21.5 g., 0.93 g.-atom) were heated 16.5 hours at 250°. After cooling to 25°, 100 p.s.i. pressure remained in the reactor, due to a mixture of gases which were non-condensable by Dry Ice. Infrared analysis showed these gases to be primarily methane and ethylene. The liquid products were distilled from the bomb and fractionated. There was recovered trimethylethoxysilane, 5.1 g. (0.04 mole), which was identified by its infrared spectrum; dimethyldiethoxysilane, 68.8 g. (0.46 mole), b.p. 113.0°; methyltriethoxysilane, 281.0 g. (1.58 moles), b.p. 144°, and tetraethoxysilane, 98.4 g. (0.47 mole), b.p. 168°. Unreacted sodium remained in the reaction vessel.

Methyltriisopropoxysilane and Sodium.—Methyltriisopropoxysilane (325.0 g., 1.48 moles) and sodium (4.3 g., 0.19 g.-atom) were heated 19 hours at 250°. The volatile contents of the reactor were removed by distilling to a temperature of 250°. On cooling, the reactor contained 3.4 g. of sodium and 11.9 g. of liquid, n^{25}D 1.3862. Fractionation of the liquid product indicated that it was essentially pure methyltriisopropoxysilane, b.p. 169.5°. No other components were detected.

Methyltrimethoxysilane.—The experiments in which methyltrimethoxysilane was heated with various alkali metals and their salts are reported in Table I. The reagents were heated in a 1.4-liter rocking pressure vessel at the indicated temperature for the time reported. After cooling, the volatile products were distilled from the vessel up to the temperature of 250°. The volatile products were analyzed by distillation. In a number of cases dimethyl ether was identified by its infrared spectrum. The residue remaining in the vessel was recovered and weighed. These residues were essentially all white or gray solids. In no case did these residues liberate hydrogen on treatment with alkali, indicating the absence of Si–Si and Si–H bonds.

The pressure of these systems increased as the reaction took place. Beginning with the vapor pressure of methyltrimethoxysilane (290 p.s.i. at 250°) the pressure increased to its final value.

Dimethyldimethoxysilane and Sodium.—Sodium (10 g., 0.43 g.-atom) and dimethyldimethoxysilane (360 g., 2.0 moles) were heated 19 hours at 240°. The volatile products were distilled from the reactor, leaving 28 g. of solid residue which contained some unreacted sodium. Fractionation of the volatile products resulted in the isolation of dimethyl ether which collected in a cold trap (approximately 2 g., 0.05 mole), trimethylmethoxysilane boiling at 57.3° (41.1 g., 0.39 mole), dimethyldimethoxysilane boiling at 82.2° (131.1 g., 1.09 moles), and methyltrimethoxysilane boiling at 102–103° (23.5 g., 0.17 mole).

***n*-Propylmethyldimethoxysilane and Sodium.**—*n*-Propylmethyldimethoxysilane (296.6 g., 2.0 moles) and sodium (12 g., 0.53 g.-atom) were heated 38 hours at 270°. The maximum pressure attained by the system was 438 p.s.i. The volatile products were distilled from the bomb, leaving 53 g. of a white alkaline residue whose neutralization equivalent was 121 and which contained 21.7% silicon. Distillation of the volatile products resulted in the isolation of dimethyl ether, 24.5 g., 0.53 mole (collected in a Dry Ice trap); propyldimethylmethoxysilane, 75.8 g., 0.57 mole, b.p. 111.1–111.3°, n^{25}D 1.3927, d^{25} 0.7860.

Anal. Calcd. for $PrMe_2SiOMe$: Si, 21.24; *R*D, 0.3047. Found: Si, 21.15, 21.27; *R*D 0.3034.

The next component was propylmethyldimethoxysilane, b.p. 129° (80.4 g., 0.54 mole), followed by dipropylmethylmethoxysilane (6 g., 0.04 mole), b.p. 149°, n^{25}D 1.4099, d^{25} 0.7962.

Anal. Calcd. for $Pr_2MeSiOMe$: Si, 17.52; *R*D, 0.3094. Found: Si, 17.23, 17.57; *R*D, 0.3111.

Hydrolysis of about 2 ml. of this material in concentrated hydrochloric acid followed by careful washing and drying formed 1,3-dimethyltetrapropyldisiloxane, n^{25}D 1.4291, d^{25} 0.8354.

Anal. Calcd. for $Pr_2MeSiOSiMePr_2$: Si, 20.46; *R*D, 0.3134. Found: Si, 20.70, 20.73; *R*D, 0.3086.

Tetramethoxysilane and Sodium.—Tetramethoxysilane (400 g., 2.64 moles) and sodium (53 g., 2.3 g.-atoms) were heated 2 hours at 220° and then 18 hours at 230°. A slow increase in pressure was observed at the lower temperature. The final pressure in the system was 363 p.s.i. at 223°. The volatile products of the reaction were removed by distillation, leaving a white friable residue weighing 192 g. in the bomb. The residue contained only a trace of sodium. Fractionation of the volatile products resulted in the isolation of dimethyl ether (83.9 g., 1.82 moles) which was collected in a Dry Ice trap and identified by its infrared spectrum, followed by a possible trace of trimethylmethoxysilane. The next component was dimethyldimethoxysilane boiling at 81–82° (19.3 g., 0.16 mole), followed by methyltrimethoxysilane boiling at 102–103° (77.6 g., 0.58 mole). The final component identified was unreacted tetramethoxysilane boiling at 121° (44.5 g., 0.29 mole).

***n*-Propyltrimethoxysilane and Sodium.**—Sodium (28.5 g., 1.24 g.-atoms) and *n*-propyltrimethoxysilane (400 g., 2.44 moles) were heated 20 hours at 278°. The volatile products were then distilled from the reactor, leaving 156 g. of a gray solid residue which was alkaline and contained some unreacted sodium. The infrared spectrum of this material showed the presence of Si–CH_3, Si–OMe and a rather strong Si–$CH_2CH_2CH_3$ band. It also showed a very heavy Si–O–Si absorption characteristic of SiO_2 and silicates. Its analysis showed Si, 20.1; C, 23.2; H, 5.90.

Fractionation of the volatile components of the system resulted in the isolation of dimethyl ether (67.3 g., 1.46 moles) which collected in a Dry Ice trap followed by *n*-propyldimethylmethoxysilane (11.4 g., 0.09 mole), b.p. 109–112°, n^{25}D 1.3926, d^{25} 0.7981, *R*D 0.2988 (calcd. 0.3034). The next component to distil was *n*-propylmethyldimethoxysilane (61.0 g., 0.41 mole) boiling at 128–130°, n^{25}D 1.3911, d^{25}_{4} 0.8671, *R*D 0.2741 (calcd. 0.2774). Continued fractionation produced *n*-propyltrimethoxysilane (77.2 g., 0.47 mole) boiling at 140.8°, n^{25}D 1.3886, d^{25}_{4} 0.9278, *R*D 0.2574 (calcd. 0.2554). The next component to distil was dipropyldimethoxysilane (35.1 g., 0.20 mole) boiling at 166–167°, n^{25}D 1.4071, d^{25} 0.8634. Voronkov[17] gives b.p. 169.3 at 760 mm., n^{20}D 1.4088, d^{20}_{4} 0.8764 for this compound.

Anal. Calcd. for $Pr_2Si(OMe)_2$: Si, 15.93; *R*D 0.2859. Found: Si, 16.1; *R*D, 0.2852.

Dimethyldiphenoxysilane and Sodium.—Dimethyldiphenoxysilane (412 g., 1.69 moles) and sodium (43 g., 1.87 g.-atom) were heated 24 hours at 265–272°. After cooling

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[16] M. G. Voronkov and B. N. Dolgov, *Zhur. Priklad. Khim.*, **24**, 93 (1951), give as the properties of this compound n^{20}D 1.3681, d^{20}_{4} 1.033.

[17] M. G. Voronkov and A. Ya. Yakubovskaya, *Zhur. Obshchei Khim.*, **25**, 1124 (1955).

and opening the vessel, the contents were filtered to remove solid sodium phenoxide and some small pieces of sodium. The liquid products, which weighed 258 g., were then carefully fractionated at 4 mm. The first material collected from this fractionation was shown to be a mixture of phenyldimethylphenoxysilane and dimethyldiphenoxysilane by its infrared spectrum and by vapor phase chromatography. In this case the chief component of the mixture had a retention time identical to that of an authentic sample of phenyldimethylphenoxysilane. Chromatographic analysis of some of the last materials to distil from this reaction mixture indicated that one of the components was 1,3-diphenyltetramethyldisiloxane. Infrared analysis of this sample also confirmed the presence of a phenyl–silicon bond.

Tetraethoxysilane and Sodium.—Tetraethoxysilane (350 g., 1.68 moles) and sodium (42 g., 1.82 g.-atoms) were heated 24 hours at 260°. A slow pressure increase was observed, reaching a maximum of 580 p.s.i. at 259° at the end of the heating period. On opening the pressure vessel a non-condensable gas was recovered whose infrared spectrum showed that it was ethylene. The liquid fractions contained no compounds with an ethyl–silicon bond.

Benzyltriethoxysilane and Sodium.—Benzyltriethoxysilane (214 g., 0.84 mole) was gently refluxed in the presence of 0.5 g. of sodium. The temperature of the refluxing liquid decreased from 240° to 190° during a 10-hour period. The liquid was cooled, the pellet of sodium was removed, and the liquid was acidified by adding trimethylchlorosilane. On distillation the following fractions were recovered: tetraethoxysilane (50.4 g.) boiling at 93° at 30 mm., $n^{25}D$ 1.3872, d^{25} 0.9298, RD 0.2532, (calcd. 0.2499); benzyltriethoxysilane, 96.5 g., boiling at 150° at 30 mm., $n^{25}D$ 1.4621, d^{25} 0.9825, RD 0.2799 (calcd. 0.2795); $(C_7H_7)_2Si(OEt)_2$, b.p. 176° at 5 mm., $n^{25}D$ 1.5146, d^{25} 1.024, RD 0.2939; $(C_7H_7)_2Si(OEt)_2$, b.p. 203° at 5 mm., $n^{25}D$ 1.5082, d^{25} 1.0437, RD 0.2864. The calculated RD value for dibenzyldiethoxysilane is 0.2935. The calculated RD value for ditolyldiethoxysilane is 0.2862. Vapor phase chromatograms of these two fractions showed two components present. The total yield of these two fractions was 53.3 g.

1,2-Dimethyltetramethoxydisilane with Sodium. At Lower Temperature.—1,2-Dimethyltetramethoxydisilane (105 g., 0.50 mole) was heated to reflux (164°) with about 0.1 g. of sodium. The temperature of the boiling liquid slowly decreased to 146°. The liquid was cooled and placed under a fractionating column. Fractionation of the material resulted in the recovery of 18.2 g. of methyltrimethoxysilane, b.p. 102–103°, $n^{25}D$ 1.3698, d^{25} 0.9458. The material in the flask was filtered to give 84.8 g. of a clear white liquid whose Si–Si equivalent was 163. The Si–Si analysis shows that both the starting material and the final residue contain 0.52 equivalent of silicon bonded to silicon. The residue therefore must contain materials such as a trisilane or higher polysilane.

At 250°.—A mixture of 1,2-dimethyltetramethoxydisilane (136.6 g., 0.65 mole) and sodium (12 g., 0.53 g.-atom) was heated 16.5 hours at 250°. The pressure within the vessel rose rather sharply during the warming up period and showed a slow rise from 203 to 297 p.s.i. at constant temperature. There were recovered from the products Me_2O (10 g., 0.22 mole) which collected in a Dry Ice trap; Me_3SiOMe, b.p. 57° (5.6 g., 0.05 moles); $Me_2Si(OMe)_2$, b.p. 81–82° (39.1 g., 0.32 mole); and $MeSi(OMe)_3$, b.p. 102–103° (31.8 g., 0.23 mole). There remained a non-volatile residue weighing 62 g. This residue was a gray solid containing some pieces of unreacted sodium.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., PLASTICS DIVISION, SPRINGFIELD, MASS.]

Reactions of Phosphorus Halides with Active Metals in Polar Solvents. I. Cleavage of Tetrahydrofuran with Formation of a Phosphorus–Carbon Bond[1]

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It has been found that phosphorus halides react with active metals in polar solvents. The course and products of the reactions are dependent upon (1) the valence state of the phosphorus, (2) the number of halogen atoms on the phosphorus and (3) the solvent. Diphenylchlorophosphine, magnesium and tetrahydrofuran react to form diphenyl-4-hydroxybutylphosphine (I). The structure of this product was demonstrated, and mechanistic considerations point to a cyclic transition state rather than a radical or anionic intermediate.

It has been discovered that phosphorus halides react with active metals such as magnesium zinc and lithium in polar solvents. The generality of the reaction for phosphorus halides was shown by experiments using phosphorus oxychloride ($POCl_3$), phosphorus trichloride (PCl_3), phenyldichlorophosphine ($C_6H_5PCl_2$), diphenylchlorophosphine [$(C_6H_5)_2PCl$], diphenylphosphinyl chloride [$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}Cl$], phenylphosphonyl dichloride ($C_6H_5\overset{\overset{O}{\uparrow}}{P}Cl_2$), methyldichlorophosphine (CH_3PCl_2), methylphosphonyl dichloride ($CH_3\overset{\overset{O}{\uparrow}}{P}Cl_2$), phenylchloromethylphosphinyl chloride ($C_6H_5\underset{\underset{Cl}{|}}{\overset{\overset{O}{\uparrow}}{P}}CH_2Cl$), and phosphorus pentachloride with magnesium in solvents such as: tetrahydrofuran, acetone, acetonitrile, chloroform and ethyl acetate. In each case, there was no reaction if any of the three components were absent. When all three components were present, there was an immediate, spontaneous reaction in which the metal was consumed, and the solvent was caused to reflux. Solvents such as benzene, carbon tetrachloride, diethyl ether, dioxane, dimethoxyethane and furan gave no reaction.

Although the reaction of these halides with the metals is a general one, the course of the reaction appears to depend upon (a) the number of halogen atoms which are attached to the phosphorus atom, upon (b) the oxidation state of the phosphorus, and upon (c) the solvent. For these reasons, this initial paper is confined to the reaction of diphenylchlorophosphine with lithium or magnesium and tetrahydrofuran.

Results

When lithium or magnesium, diphenylchlorophosphine and tetrahydrofuran are mixed, there is an immediate, spontaneous reaction which sus-

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