in a 4 dm. polarimetric tube. In this way the effluents could be divided into six fractions, each of which was shown by paper chromatography to contain 3–4 constituents.

These fractions, designated A (fastest moving), B, C, D, E, and F, were dried thoroughly *in vacuo* over phosphorus pentoxide. By addition of some dry ethanol to the horny residues, five crystalline substances were separated from A, B, C, and D at room temperature over a period of 10 weeks. From A and B small platelets (XI) could be isolated, which proved to be a condensation product of fructose and methylglyoxal, as will be described elsewhere; from the combined mother liquors diheterolevulosan I (IX) separated followed by small amounts of diheterolevulosan II (X). From C and D tiny amounts of strongly hygroscopic needles (XII) crystallized, $[\alpha]_{\mathrm{D}}^{18}$ +270° (*c* 0.13 in methanol), m.p. 160° (dec.). So far the substance has not been obtained free from impurities. From D, E, and F some traces of small crystals (XIII) separated, $[\alpha]_{\mathrm{D}}^{18}$ approx. −300° (*c* 0.10 in water). The amounts isolated were insufficient to permit purification and elementary analysis.

Nitration of D*-fructose by nitronium sulfate* (Method B): Three grams of D-fructose was dissolved with rapid stirring in 30 ml. of abs. nitric acid at 5° and this temperature kept during the entire procedure; 60 ml. of cold concentrated sulfuric acid was added over a period of 5 min., followed by 100 ml. of dry chloroform. After 2 min. of stirring, the upper chloroform layer was siphoned off, 50 ml. of fresh chloroform was added and the mixture was stirred for 2 min. This procedure was repeated once more and the combined chloroform extracts were repeatedly washed with 300 ml. portions of ice-cooled distilled water, until the aqueous layer was neutral towards litmus. After the first three washings, the chloroform layer was rapidly removed from the aqueous phase disregarding turbidity. To the almost colorless chloroform solution, 0.38 g. of recrystallized *p*-benzoquinone was added. The solution was dried for 4 hr. over anhydrous sodium sulfate and then concentrated *in vacuo* at 30°. There resulted 3.0 g. of a pale yellow sirup (XV) $[\alpha]_{\mathrm{D}}^{18}$ −35° (*c* 2.0 in dioxan) (N = 13.1), which was dissolved in 15 ml. of dioxan, 20 ml. 95% ethanol were added, and the solution was reduced with 10 g. of palladium catalyst. After reduction a yellow sirup was obtained (XVI) that was subjected to paper chromatography (see Fig. 2).

Nitration of D*-fructose in an acetic anhydride mixture.*[3] Three grams of D-fructose was dissolved with rapid stirring in a mixture of 20 ml. abs. nitric acid, 15 ml. acetic acid, and 15 ml. acetic anhydride. The solution rapidly turned yellowish-brown; after 10 min. it was poured into 500 ml. of ice water. The product was extracted by three portions of 100 ml. ether, the combined yellow extracts were washed repeatedly with ice-cooled distilled water until neutral towards litmus. The ethereal solution was dried for 4 hr. over anhydrous sodium sulfate, 0.05 g. *p*-benzoquinone were added, and the ether distilled off. 5.70 g. of a deep yellow sirup (XVII) was obtained, $[\alpha]_{\mathrm{D}}^{16}$ +30 (*c* 7 in methanol), N = 16. By hydrogenolysis of XVII a reddish-brown sirup was formed (XVIII). XVIII was subjected to paper chromatography (see Fig. 2).

Nitration of D*-fructose in presence of phosphorus pentoxide.*[11] Three grams of D-fructose was added to an ice-cooled mixture of 30 ml. abs. nitric acid, 30 ml. of dry chloroform and 6 g. of phosphorus pentoxide. After 5 min. of rapid stirring, 50 ml. of dry chloroform was added and the liquid part of the mixture siphoned off, leaving the phosphorus pentoxide in the reaction flask. The acid mixture was poured into 300 ml. of ice water, and shaken with an additional amount of 100 ml. of chloroform. The chloroform layer was removed and the turbid aqueous layer extracted twice with 100 ml. of ether. The mixed extracts were washed with ice-cooled distilled water until neutral, dried over anhydrous sodium sulfate, 0.02 g. of *p*-benzoquinone were added and the solvents evaporated *in vacuo*. 1.15 g. of an orange colored sirup (XIX) resulted, $[\alpha]_{\mathrm{D}}^{17}$ −3.9°, N = 11.4. The reduction product (XX) of (XIX) was subjected to paper chromatography (see Fig. 2).

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING DIVISION OF THE MIDWEST RESEARCH INSTITUTE]

The Phenylation and Methylation of Alkoxychlorosilanes[1]

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The phenylation of diisopropoxydichlorosilane, triisopropoxychlorosilane, and triethoxychlorosilane with chlorobenzene and molten sodium was investigated. The effect of vaiying the reactant ratio on the yield of diphenyldiisopropoxysilane from the reaction of diisopropoxydichlorosilane, chlorobenzene, and molten sodium was studied. The methylation of triethoxychlorosilane and triisopropoxychlorosilane with methyl chloride and molten sodium was studied briefly. During this investigation, four new isopropoxychlorosilanes were prepared and characterized: diisopropoxydichlorosilane, triisopropoxychlorosilane, phenylisopropoxydichlorosilane, and phenyldiisopropoxychlorosilane.

Various modifications of the sodium method of preparing organosilicon compounds have been devised to control the degree of substitution. One approach[3] is based upon limiting the concentration of the organic halide in the reaction mixture by extreme dilution with an inert solvent. A two-stage synthesis[4] in which the organosodium reagent is prepared and treated separately allows much better control. Another approach to controlled substitution is based on the relative reactivities of the silicon-alkoxy and silicon-chlorine bonds toward the organosodium intermediate.

One objective of this study was to determine the effect on the phenylation and methylation reactions due to varying the type of alkoxy groups in the silane starting material. Another objective was to determine the effect of varying the reactant ratio

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(3) E. G. Rochow, *Chemistry of the Silicones*, John Wiley and Sons, N. Y., 2nd Edition, p. 32, 1951.

(4) W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **63**, 93 (1941).

TABLE I

PHENYLATION AND METHYLATION OF ALKOXYCHLOROSILANES

Reactants (mole)	Ratio RCl to Silane	Solvent (ml.)	Approx. Composition of Reaction Mixture (wt. %)[a]	Yield of Desired Product[b]
C_6H_5Cl + Na + $Cl_2Si(O\text{-}i\text{-}Pr)_2$ 0.71 1.50 0.35	2.03:1	Toluene 150	16% $Si(O\text{-}i\text{-}Pr)_4$, 14% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 23% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$, 47% residue	15% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$
C_6H_5Cl + Na + $Cl_2Si(O\text{-}i\text{-}Pr)_2$ 0.71 1.50 0.35	2.03:1	Toluene 150	18% $Si(O\text{-}i\text{-}Pr)_4$, 14% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 22% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$, 46% residue	13% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$
C_6H_5Cl + Na + $Cl_2Si(O\text{-}i\text{-}Pr)_2$ 0.61 1.30 0.35	1.75:1	Toluene 150	15% unchanged $Cl_2Si(O\text{-}i\text{-}Pr)_2$, 3% $C_6H_5Si(O\text{-}i\text{-}Pr)_2Cl$, 9% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 57% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$, 16% residue	61% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$
C_6H_5Cl + Na + $Cl_2Si(O\text{-}i\text{-}Pr)_2$ 0.53 1.10 0.35	1.50:1	Toluene 150	18% unchanged $Cl_2Si(O\text{-}i\text{-}Pr)_2$, 9% $C_6H_5Si(O\text{-}i\text{-}Pr)_2Cl$, 7% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 53% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$, 13% residue	64% $(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$
C_6H_5Cl + Na + $ClSi(O\text{-}i\text{-}Pr)_3$ 0.35 0.85 1.05	0.35:1	None	18% unchanged $ClSi(O\text{-}i\text{-}Pr)_3$ 76% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 6% residue	72% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$
C_6H_5Cl + Na + $ClSi(O\text{-}i\text{-}Pr)_3$ 0.35 0.85 1.05	0.35:1	None	20% unchanged $ClSi(O\text{-}i\text{-}Pr)_3$, 72% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$, 8% residue	64% $C_6H_5Si(O\text{-}i\text{-}Pr)_3$
C_6H_5Cl + Na + $ClSi(OC_2H_5)_3$ 0.35 0.85 0.53	0.70:1	None	60% unchanged $ClSi(OC_2H_5)_3$, 39% $C_6H_5Si(OC_2H_5)_3$, 1% residue	40% $C_6H_5Si(OC_2H_5)_3$
CH_3Cl + Na + $ClSi(O\text{-}i\text{-}Pr)_3$ 0.70 0.85 0.35	2.00:1	Toluene 100	2% unchanged $ClSi(O\text{-}i\text{-}Pr)_3$, 73% $CH_3Si(O\text{-}i\text{-}Pr)_3$, 25% residue	38% $CH_3Si(O\text{-}i\text{-}Pr)_3$
CH_3Cl + Na + $ClSi(OC_2H_5)_3$ 1.5° 1.10 1.00	1.50:1	None	70% unchanged $ClSi(OC_2H_5)_3$, 10% $MeSi(OC_2H_5)_3$, 20% residue	13% $CH_3Si(OC_2H_5)_3$

[a] Not including solvent. [b] Yield calculations based on moles of limited reactant.

TABLE II

PHYSICAL PROPERTIES OF COMPOUNDS INVOLVED IN THIS STUDY

Compound	B.P. (°C/mm.)	n_D^{25}	d_4^{25}	MR$_D$ Calcd.	MR$_D$ Found
$Cl_2Si(O\text{-}i\text{-}Pr)_2$[a]	155/745	1.3960	1.0490	49.58	49.75
$ClSi(O\text{-}i\text{-}Pr)_3$[a]	177/734	1.3898	0.9496	59.97	60.07
$Si(O\text{-}i\text{-}Pr)_4$	62–64/5[b]	1.3844[c]	0.8744[d]	70.36	70.76
$C_6H_5Si(O\text{-}i\text{-}Pr)Cl_2$[a]	99–100/10	1.4868	1.1267	59.38	60.02
$C_6H_5Si(O\text{-}i\text{-}Pr)_2Cl$[a]	113–114/10	1.4669	1.0221	69.77	70.25
$C_6H_5Si(O\text{-}i\text{-}Pr)_3$	110–112/5[e]	1.4488[f]	0.9411[g]	80.16	80.46
$(C_6H_5)_2Si(O\text{-}i\text{-}Pr)_2$	152–154/5[h]	1.5120[i]	0.9973[j]	89.96	90.49
$CH_3Si(O\text{-}i\text{-}Pr)_3$	163/749[k]	1.3830[l]	0.8557	60.34	60.08
$ClSi(OC_2H_5)_3$	156–157/743[m]	1.3884	1.0124	46.08	46.35
$C_6HSi_5(OC_2H_5)_3$	122–124/15[n]	1.4590[o]	0.9904[p]	66.27	66.26
$CH_3Si(OC_2H_5)_3$	142–144/745[q]	1.3887[r]	0.9166[s]	46.45	45.97

[a] New compound. [b] 170°/16 mm.[11] [c] n_D^{20} 1.5136.[11] [d] d_4^{20} 0.9982.[11] [e] 136°/22.[11] [f] n_D^{20} 1.3852.[11] [g] d_4^{20} 0.8754.[11] [h] 170°/16 mm.[11] [i] n_D^{20} 1.5136.[11] [j] d_4^{20} 0.9982.[11] [k] 102°/100 mm.[12] [l] n_D^{25} 1.3869.[12] [m] 155–157°/760.[10] [n] 120°/14 mm.[11] [o] n_D^{20} 1.4611.[11] [p] d_4^{22} 0.9916.[11] [q] 143.5°/760 mm.[13] [r] n_D^{25} 1.3820.[13] [s] d_D^{25} 0.885.[13]

on the reaction of diisopropoxydichlorosilane and chlorobenzene in the presence of molten sodium. The results of this investigation are summarized in Table I.

The phenylation of alkoxychlorosilanes. The phenylation of tetramethoxysilane,[5] chlorotricyclohexoxysilane,[6] and dichlorodimethoxysilane[7] with chlorobenzene and sodium have been reported.

Our study of the phenylation of diisopropoxydichlorosilane by the molten sodium method revealed that higher yields of diphenyldiisopropoxysilane were obtained at lower chlorobenzene to silane molar ratio: 64% at 1.50 to 1; 61% at 1.75 to 1; 13–15% at 2.03 to 1.

The phenylation of trialkoxychlorosilanes was carried out in the absence of any solvent by adding chlorobenzene to molten sodium dispersed in the trialkoxychlorosilane. Higher yields of phenyltrialkoxysilane were obtained with triisopropoxy- (68%, average) than with triethoxychlorosilane (40%). An interaction between molten sodium and triethoxychlorosilane was observed which caused an induction period before the reaction was initiated. The exact nature of this interaction is not known. It may have been the formation of a sodium-silane complex or it may have been due to the cleavage of silicon-oxygen bonds. In the runs with triisopropoxychlorosilane, there was no appreciable molten sodium-silane interaction and the reactions were initiated immediately and easily carried to completion.

The methylation of alkoxychlorosilanes. The methylation of tetraethoxysilane,[8] trimethoxychlorosilane,[9] and dimethoxydichlorosilane[9] by the molten sodium method have been reported.

During this study, the methylation of triethoxychlorosilane and triisopropoxychlorosilane were carried out without the use of a catalyst, using molten sodium and methyl chloride. Reactions with both starting materials were difficult to initiate, and it was necessary to add small amounts of ethyl acetate at frequent intervals to sustain the reaction. The yield of methyltrialkoxysilane was higher when triisopropoxychlorosilane with solvent was used (38%) than when triethoxychlorosilane without solvent was used (13%).

The preparation of alkoxychlorosilanes. All of the alkoxychlorosilanes except triethoxychlorosilane which were involved in this work were prepared by the alcoholysis of chlorosilanes. By this procedure, four new alkoxychlorosilanes were prepared: diisopropoxydichlorosilane, triisopropoxychlorosilane, phenylisopropoxydichlorosilane, and phenyldiisopropoxychlorosilane. Triethoxychlorosilane[10] was prepared by the autoclave reaction of acetyl chloride and tetraethoxysilane. Other known[11–13] alkoxysilicon compounds included in this study were isolated from experimental reaction mixtures and characterized.

The physical properties of all the compounds involved in this study are listed in Table II.

EXPERIMENTAL[14]

Preparation of diisopropoxydichlorosilane. To 510 g. (3.0 mole) of tetrachlorosilane at 0° was added 306 g. (5.1 mole)

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[5] C. W. Bondy and K. Reiser, British Patent No. **573,906** (1945).

[6] A. Bowman, *et al.*, British Patent No. **613,648** (1948).

[7] K. Hiratsuka, Japanese Patent No. **5,330** (1951).

[8] L. Tiganik, U. S. Patent No. **2,521,267** (1950).

[9] C. W. Bondy, *et al.*, British Patent No. **612,822** (1948).

[10] D. Peppard, W. Brown, and W. Johnson, *J. Am. Chem. Soc.*, **68,** 70 (1946).

[11] B. Smith, *Svensk. Kem. Tid.*, **71,** 213–217 (1949), *Chem. Abstr.*, **44,** 883 (1950).

[12] M. M. Sprung and F. O. Guenther, *J. Am. Chem. Soc.*, **77,** 6045 (1945).

[13] F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **68,** 475 (1946).

[14] The chlorine content of chlorosilanes was determined by liberating the chlorine as hydrogen chloride by methanolysis and then adding water to the alcoholysate to obtain an aqueous solution of hydrogen chloride which was titrated with 0.1*N* sodium hydroxide using phenolphthalein as an indicator. Molar refractions were calculated from the values of E. L. Warrick, *J. Am. Chem. Soc.*, **68,** 2455 (1948).

of 2-propanol at a rate of 3 to 4 ml./min. The temperature of the reaction mixture was maintained at 0°. After the addition was complete, the reaction mixture was purged with nitrogen for approximately 15 min. while the temperature was gradually increased to 50°. The purged reaction mixture was distilled through a 45-plate, $^3/_4$ in. i.d. Oldershaw column to give 190 g. (29.2%) of diisopropoxydichlorosilane, b.p. 155° at 745 mm., n_D^{25} 1.3960, d_4^{25} 1.0490, MR$_D$ calcd. 49.58, found 49.75.

Anal. Calcd. for $SiC_6H_{14}O_2Cl_2$: Cl, 32.8. Found: Cl, 33.4.

Preparation of triisopropoxychlorosilane. To 748 g. (4.4 mole) of tetrachlorosilane was added 720 g. (12.0 mole) of 2-propanol in a manner similar to that in the preparation of diisopropoxydichlorosilane. Distillation gave 274 g. (26.0%) of triisopropoxychlorosilane, b.p. 177° at 734 mm., n_D^{25} 1.3898, d_4^{25} 0.9496, MR$_D$ calcd. 60.07, found 59.97.

Anal. Calcd. for $SiC_9H_{21}O_3Cl$: Cl, 14.8. Found: Cl, 15.5.

A similar run using 816 g. (4.8 mole) of tetrachlorosilane and 732 g. (12.2 mole) of 2-propanol gave 250 g. (24.0%) of diisopropoxydichlorosilane, b.p. 154–156° and 515 g. (41.7%) of triisopropoxychlorosilane, b.p. 176–178°.

Another similar run using 1,020 g. (6.0 mole) of tetrachlorosilane and 900 g. (15.0 mole) of 2-propanol gave 307 g. (23.6%) of diisopropoxydichlorosilane, b.p. 154–156° and 692 g. (47.6%) of triisopropoxychlorosilane, b.p. 176–178°C.

Preparation of triethoxychlorosilane. A mixture of 157 g. (2.0 mole) of acetylchloride and 417 g. (2.0 mole) of tetraethoxysilane were placed in an autoclave and held at 160° for 1 hr. The resulting reaction mixture was flash distilled at reduced pressure to remove any metallic contamination picked up in the autoclave. Distillation gave 119 g. (30%) of triethoxychlorosilane, b.p. 156–157° at 743 mm., n_D^{25} 1.3884, d_4^{25} 1.0124, MR$_D$ calcd. 46.08, found 46.35.

Preparation of phenylisopropoxydichlorosilane and phenyldiisopropoxychlorosilane. To 212 g. (1.0 mole) of phenyltrichlorosilane was added 90 g. (1.5 mole) of 2-propanol in the same general manner previously described. Fractionation of the reaction mixture yielded 45 g. (19.1%) of phenylisopropoxydichlorosilane, b.p., 99–100° at 10 mm., n_D^{25} 1.4868, d_4^{25} 1.1267, MR$_D$ calcd. 59.38, found 60.02.

Anal. Calcd. for $SiC_9H_{12}CCl_2$: Cl, 30.15. Found: Cl, 29.66.

Further distillation gave 64 g. (23.8% yield) of phenyldiisopropoxychlorosilane, b.p., 113–114° at 10 mm., n_D^{25} 1.4669, d_4^{25} 1.0221, MR$_D$ calcd. 69.77, found 70.25.

Anal. Calcd. for $SiC_{12}H_{19}O_2Cl$: Cl, 13.70. Found: Cl, 14.82.

The phenylation of diisopropoxydichlorosilane. To 34.5 g. (1.5 mole) of molten sodium in 150 ml. of toluene was added a mixture of 79.8 g. (0.71 mole) of chlorobenzene and 76 g. (0.35 mole) of diisopropoxydichlorosilane (the molar ratio of chlorobenzene to the silane was 2.03 to 1) at 110°. The addition of the reactant mixture resulted in an immediate temperature rise and a purple color development. The reaction temperature was maintained at 115° by controlling the rate of addition. After the addition was complete, the reaction mixture was maintained at 115° for 0.5 hr. A gelatinous precipitate was removed by centrifugation and washed with toluene, and the washings were added to the supernatant liquid. The solvent and most of the unchanged diisopropoxydichlorosilane were removed by atmospheric distillation. The concentrated reaction mixture was fractionated by a vacuum distillation through an 8 in. section of $^3/_4$ in. i.d. column packed with $^1/_4$ in. Berl saddles to give 16 g. (15.2%) of diphenyldiisopropoxysilane, b.p. 152–154° at 5 mm., n_D^{25} 1.5120, d_4^{25} 0.9973, MR$_D$ calcd. 89.96, found 90.49, and the following: 11 g. of tetraisopropoxysilane, b.p. 62–64° at 5 mm., n_D^{25} 1.3844, d_4^{25} 0.8744, MR$_D$ calcd. 70.36, found 70.76; 9.5 g. of phenyltriisopropoxysilane, b.p. 110–112° at 5 mm., n_D^{25} 1.4488, d_4^{25} 0.9411, MR$_D$ calcd. 80.16, found 80.46; and 32 g. of an unidentified solid residue.

A duplicate run gave 14.0 g. (13.4%) of diphenyldiisopropoxysilane, b.p. 152–154° at 5 mm., n_D^{25} 1.5123, d_4^{25} 1.000, MR$_D$ calcd. 89.96, found 90.10; 11.0 g. of tetraisopropoxysilane, b.p. 62–64° at 5 mm., n_D^{25} 1.3855, d_4^{25} 0.8718, MR$_D$ calcd. 70.8, found 71.1; 9.0 g. of phenyltriisopropoxysilane, b.p. 110–112° at 5 mm., n_D^{25} 1.4464, d_4^{25} 0.9399, MR$_D$ calcd. 80.7, found 80.1; and 28 g. of unidentified solid residue.

A similar run using 29.9 g. (1.3 mole) of sodium in 150 ml. of toluene, 68.6 g. (0.61 mole) of chlorobenzene, and 76 g. (0.35 mole) of diisopropoxydichlorosilane was carried out. The molar ratio of chlorobenzene to the silane was 1.75 to 1. The precipitate was removed by filtration, and the filtrate was fractionated as before to give 57.0 g. (61.3%) of diphenyldiisopropoxysilane, b.p. 150–152° at 5 mm., n_D^{25} 1.5101, d_4^{25} 0.9944, MR$_D$ calcd. 89.96, found 90.20; 15.0 g. of unchanged diisopropoxydichlorosilane, 3.4 g. of phenylisopropoxydichlorosilane, 9.6 g. of phenyltriisopropoxysilane, b.p. 106–107° at 5 mm. and 16.0 g. of an unidentified solid residue.

A similar run using 25.3 g. (1.1 mole) of sodium in 150 ml. of toluene, 59.1 g. (0.525 mole) of chlorobenzene, and 76 g. (0.35 mole) of diisopropoxydichlorosilane was carried out. The molar ratio of chlorobenzene to the silane was 1.5 to 1. The reaction mixture was filtered easily and then fractionated as before to give: 50.0 g. (63.7%) of diphenyldiisopropoxysilane, b.p. 150–152° at 5 mm., n_D^{25} 1.5082, d_4^{25} 0.9952, MR$_D$ calcd. 90.60, found 89.96; 17.1 g. of unchanged diisopropoxydichlorosilane, as calculated from chlorine analysis of the distillate from the atmospheric distillation; 8.5 g. of crude phenyldiisopropoxychlorosilane, collected in a b.p. range of 45–90° at 5 mm.; 6.5 g. of phenyltriisopropoxysilane, b.p. 106–107° at 5 mm., and 12.0 g. of an unidentified solid residue.

The phenylation of triisopropoxychlorosilane. To 19.5 g. (0.85 mole) of molten sodium in 253 g. (1.05 mole) of triisopropoxychlorosilane at 110° was added 39.5 g. (0.35 mole) of chlorobenzene. The reaction was initiated immediately upon addition of the chlorobenzene, and the reaction temperature was maintained at 115° by the rate of addition. Phenyltriisopropoxysilane was isolated in a manner similar to that of diphenyldiisopropoxysilane and was obtained in a 72 per cent yield (71.0 g.), b.p. 137–138° at 20 mm., n_D^{25} 1.4469, d_4^{25} 0.9428, MR$_D$ calcd. 80.16, found 79.65. Also, 17.0 g. of unchanged triisopropoxychlorosilane and 6.0 g. of residue were obtained.

A duplicate run gave 63.0 g. (64%) of phenyltriisopropoxysilane, b.p. 122° at 10 mm., n_D^{25} 1.4482, d_4^{25} 0.9409; 17.0 g. of unchanged triisopropoxychlorosilane and 7.0 g. of residue.

The phenylation of triethoxychlorosilane. To 19.5 g. (0.85 mole) of molten sodium in a mixture of 1.04 g. (0.525 mole) of triethoxychlorosilane and 100 ml. of toluene at 110° was added 39.5 g. (0.35 mole) of chlorobenzene. About 10 ml. of chlorobenzene was added before the reaction was initiated, when there was a rapid temperature increase to 125°. The reaction mixture was cooled, then maintained at a temperature of 120° by the addition rate. After the addition of chlorobenzene was complete, the reaction mixture was maintained at 120° for 15 min. Phenyltriethoxysilane, isolated in a manner similar to that of the diphenyldiisopropoxysilane, was obtained in a 40.0% yield (35.5 g.), b.p. 122–124° at 15 mm., n_D^{25} 1.4590, d_4^{25} 0.9904, MR$_D$ calcd. 66.27, found 66.26. Also, 54.0 g. of unchanged triethoxychlorosilane and 2.0 g. of residue were obtained.

The methylation of triisopropoxychlorosilane. A mixture of 19.5 g. (0.85 mole) of sodium, 84.0 g. (0.35 mole) of triisopropoxychlorosilane, and 100 ml. of toluene was heated to 110°. The methyl chloride (35.0 g., 0.70 mole) was introduced beneath the surface of the reaction mixture at a rate of 0.5 g./min. It was necessary to initiate and to maintain the reaction by the addition of 5 ml. of ethyl acetate (in 0.5 ml. portions) during a 3-hr. reaction period. After removal of the precipitate, the filtrate was distilled through a 10-plate, 1 in. i.d. Oldershaw column to give 27.0 g. (37.7% yield) of methyltriisopropoxysilane, b.p. 163° at 749 mm. n_D^{25} 1.3830,

d^{25}_4 0.8557, MR$_D$ calcd. 60.34, found 60.08, 2.0 g. of unchanged triisopropoxychlorosilane and 7.0 g. of residue.

The Methylation of Triethoxychlorosilane. A run similar to that of the methyltriisopropoxysilane was carried out using 25.0 g. (1.1 mole) of sodium, 93.5 g. (0.5 mole) of triethoxychlorosilane, and 75.0 g. (1.5 mole) of methyl chloride. Again it was necessary to add ethyl acetate in small portions to maintain a reaction. Methyltriethoxysilane was obtained in 12.9% yield (11.5 g.), b.p. 142–144° at 745 mm., n^{25}_D 1.3887, d^{25}_4 0.9166, MR$_D$ calcd. 46.45, found 45.97. Also, 80.5 g. of unchanged triethoxychlorosilane and 23.0 g. of residue were obtained.

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[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY[1] AND TEMPLE UNIVERSITY]

Higher Alkyl Monoethers of Mono- to Tetraethylene Glycol[2a,b]

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The mono-*n*-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers of mono- to tetraethylene glycol, $R(OCH_2CH_2)_iOH$, were synthesized from alkyl halides or tosylates or by alkali-catalyzed reaction of alcohols with ethylene oxide. In the dodecyl, tetradecyl, and hexadecyl series, freezing-point minima occurred at $i = 3$. The distribution of products in oxyethylation of tetradecanol followed the equations of Weibull and Nycander, with a distribution constant of 3.0.

In view of the industrial importance of mixtures of monoalkyl ethers of polyethylene glycol, it would be useful to have available individual members of this class. One objective of this investigation was therefore to synthesize the mono-*n*-dodecyl, tetradecyl, hexadecyl, and octadecyl ethers of mono- to tetraethylene glycol and to report their characterizing constants.

Some of the members of this group of sixteen compounds have been previously reported. The Williamson reaction has been used to prepare glycol ethers for nicotine synergism studies.[4] Ethylene glycol mono-*n*-dodecyl ether was synthesized from the alkyl bromide and glycol[5] and ethylene glycol mono-*n*-octadecyl ether from the alkyl tosylate.[6] More recently the stepwise synthesis of mono- to tetraethylene glycol mono-*n*-dodecyl ethers by the acid-catalyzed addition of ethylene oxide to the next lower homolog was reported.[7] Alkali-induced oxyethylation,[8,9,10] common for the preparation of adducts having various average degrees of polymerization, has been seldom employed for the preparation of individual glycol ethers.[11]

Three methods of synthesis were used in the present work: the alkyl halide and alkyl tosylate methods and the alkali-catalyzed oxyethylation of alcohols.

Distribution of Products. The distribution of products is a point of interest in reactions like oxyethylation. When polymer chains are built up ideally from a fixed number of propagating units by a sequence of kinetically identical additions of monomer, size distribution has been shown by Flory[12] to be described by Poisson's formula:[13]

$$\frac{n_i}{n_\infty} = e^{-v}\frac{v^i}{i!} \qquad (1)$$

Although the conditions producing Poisson distribution are indeed found in the reaction of ethylene glycol with ethylene oxide,[14] reactions in which all steps are kinetically different, as in the ammonia-ethylene oxide reaction and the chlorination of methane, require much more complicated mathematics, as shown by Natta and Mantica.[15]

Regarding the assumption of kinetic identity of all steps as an oversimplification and the formulas of Natta as very cumbersome, Weibull and Nycander[14] suggested a compromise treatment for the reaction of an alcohol with ethylene oxide. They proposed that all hydroxyl groups bound to an oxy-

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