bath for 3 hr. The solution was then chilled and poured into 4 ml. of cold 28% ammonia water and stirred. The precipitated amide was purified by three recrystallizations from dilute ethanol and amounted to 0.75 g. (84%) of white crystals, m.p. 129.5–132°, mixture m.p. with amide derived from the benzocoumarin (II).

Anal. Calcd. for $C_{14}H_{25}ON$: N, 6.27. Found: N, 6.15.

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PITTSBURGH 19, PENNA.

[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

Aryl and Alkylchlorodialkoxysilanes[1]

L. W. BREED AND WILLIAM J. HAGGERTY, JR.

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Good yields of chlorodiethoxymethylsilane, suitable for use in alkylation and arylation reactions, are obtained by the ethanolysis of methyltrichlorosilane. The synthesis of chlorodiethoxyphenylsilane, chloro-*p*-chlorophenyldiethoxysilane, and *p*-anisylchlorodiethoxysilane in high yields, and the preparation of their intermediates is described.

In the synthesis of silane monomers for use in high temperature resin systems, it was necessary to prepare certain methyl- and arylalkoxychlorosilanes as intermediates. The alkylation and arylation of these compounds with various organometallic reagents will be described in a subsequent publication.

Although the alcoholysis of silicon tetrachloride has been discussed by numerous investigators, and the stability of the various chlorosilicates against redistribution has been studied, considerably less information is available in the literature regarding the methyl- and arylalkoxychlorosilanes. The reported experimental details are seldom complete, but it appears that, as in the case of the alcoholysis of silicon tetrachloride, mixtures of all possible alkoxychlorosilanes are obtained regardless of the stoichiometry of the reactants, and that yields of individual alkoxychlorosilanes are not high. Treating 6.0 mol. of methyltrichlorosilane with 7.2 mol. of ethanol, Andrianov[2] obtained only 35.9 per cent chlorodiethoxymethylsilane and 21.3 per cent dichloroethoxymethylsilane. Servais[3] reports chlorodiethoxymethylsilane and chlorodiethoxyphenylsilane, but omits properties and yields. Rosnati prepared chlorodimethoxyphenylsilane.[4] Redistribution reactions have been studied both with regard to the preparation and stability of alkoxyalkylchlorosilanes.[2,5,6] It appears that alkoxychloromethylsilanes are more stable than the chlorosilicates against redistribution, and may be distilled at atmospheric pressure without significant changes in their composition.

In our laboratory, the ethanolysis of methyltrichlorosilane resulted in a complex mixture which contained all possible products. However, with a suitable proportion of reactants, chlorodiethoxymethylsilane was obtained in about a 72% conversion. Although the components of the crude alcoholysis mixture were difficult to separate by distillation, the use of an efficient fractionating column gave a 63% yield in fractions suitable for use in alkylation and arylation reactions.

Ethanolysis of aryltrichlorosilanes, however, gave the arylchlorodialkoxysilanes in yields between 88 and 95% even when simpler distillation procedures were used.

The alkoxychlorosilanes were prepared by the action of anhydrous ethanol on the chlorosilane in the absence of any solvent, and the products were collected by fractional distillation. Approximations of the purity of the distillation fractions were carried out by vapor phase chromatography. A sample from each distillation fraction was chromatographed and the identity of each peak was assigned on the basis of the stoichiometry of the starting materials, the known tendency of these systems to form all possible alkoxychlorosilanes, and a comparison of the elution times for the various peaks on the different chromatograms.

With the assumption that peak area is proportional to weight per cent of the component in each fraction on the chromatogram, the weight per cent of each alkoxychlorosilane in all the distillation fractions was calculated. The data are shown in Table I.

In distilling a typical reaction product with a 30-plate Oldershaw column no sharp breaks in the

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(2) K. A. Andrianov, S. A. Golubtsov, and N. P. Lobusevich, *J. Gen. Chem. U.S.S.R.*, **26**, 207 (1956).

(3) R. C. Servais (to Dow Chemical Co.), U. S. Patent **2,485,928**, Oct. 25, 1949.

(4) L. Rosnati, *Gazz. chim. ital.*, **78**, 516 (1948); *Chem. Abstr.*, **43**, 1006 (1949).

(5) Dow Corning Corp., Brit. Patent **653,238**, May 9, 1951; *Chem. Abstr.*, **46**, 1025 (1952).

(6) M. Kumada, *J. Inst. Polytech. Osaka City Univ.*, Ser. C., 2, 139 (1952).

TABLE I

Composition (Wt. %) of Chlorodiethoxymethylsilane Distillation Fractions

Compound Assignment	Fraction No. 1	2	3	4
—	5.28	—	—	—
Methyltrichlorosilane	14.74	0.48	—	—
Dichloroethoxymethylsilane	25.39	2.40	0.12	0.19
Chlorodiethoxymethylsilane	52.41	94.55	97.75	81.80
Methyltriethoxysilane	2.18	2.52	2.15	17.99

head temperature of the distillation column were observed; during the collection of fractions 1 and 4, only a gradual rise in the temperature occurred, suggesting some redistribution during the distillation.

Distillate was collected between 77° and 141°. The normal boiling points recorded in the literature for the possible alkoxychlorosilanes are: Methyltrichlorosilane 65.7[7]; dichloroethoxymethylsilane, 101.2,[6] 99–9.5[2]; chlorodiethoxymethylsilane, 129[6]; 126.5–7.5[2]; and methyltriethoxysilane, 143[7].

It is evident from Fig. 1 that significant quantities of lower boiling materials are found only in fraction 1. The materials in fractions 2, 3, and 4 are all suitable for use in alkylation and arylation reactions. The presence of methyltriethoxysilane may be considered as an inert diluent in these reactions because of the preferential reactivity of organometallic reagents toward silicon-attached chlorine.

Measurement of the areas in Fig. 1, taking into account that the total product accounted for 97.0 weight per cent of the theoretical chlorodiethoxymethylsilane, indicated the approximate yields of the various products. The following per cent conversions were obtained: Methyltriethoxysilane, 6.2; chlorodiethoxymethylsilane, 72; dichloroethoxymethylsilane, 5.1; and methyltrichlorosilane, 2.7. These figures do not include the material which was contained in the distillation residue, mainly additional methyltriethoxysilane and possibly some siloxanes, or certain very low boiling fractions. Taken as chlorodiethoxymethylsilane, the fractions boiling lower than chlorodiethoxymethylsilane represented an 8.6% conversion and those boiling higher, a 16.3% conversion.

Arylchlorodialkoxysilanes, prepared by a similar procedure, include those listed in Table II. Yields of the compounds indicate that the ethanolysis of arylsilanes does not produce as complex a reaction product.

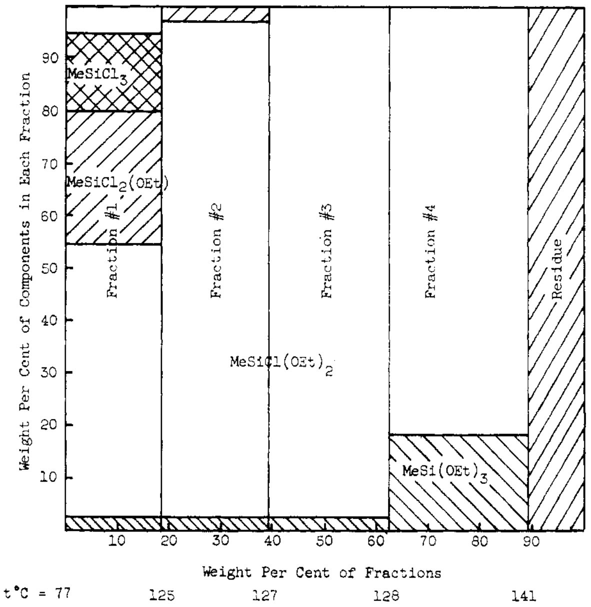

Fig. 1. Composition of distillate from the alcoholysis of methyltrichlorosilane

An attempt was made to prepare chloro-*p*-*N*,*N*-dimethylaminophenyldiethoxysilane by the ethanolysis of a solution *p*-dimethylaminophenyltrichlorosilane in toluene and triethylamine. The attempt was unsuccessful, presumably because of the insolubility of the complex formed between *p*-dimethylaminophenyltrichlorosilane and triethylamine, and a conversion of 45% of the starting material to *p* - dimethylaminophenyltriethoxysilane contaminated with a little of the desired product was obtained.

The aryltrichlorosilanes required for the ethanolysis reactions were prepared by treating silicon tetrachloride with a suitable Grignard reagent. One compound, *p*-*N*,*N*-dimethylaminophenyltrichlorosilane, has not been previously reported.

EXPERIMENTAL

Chlorodiethoxymethylsilane. In a 3 l. flask equipped with an addition funnel, stirrer, thermometer and Dry Ice cold finger condenser was placed 1500 g. (10 mol.) redistilled commercial methyltrichlorosilane. The contents were cooled to 0° with a Dry Ice bath, then stirred rapidly while 920 g. (20 mol.) of anhydrous ethanol was added dropwise over 3.5 hr. After the addition was complete, nitrogen was bubbled through the mixture, and the temperature was gradually raised to 60° over a 3 hr. period. Purging and heating at 60° were continued for an additional hour. The product was distilled through an Oldershaw column having 30 plates and collected from a distillation head set for 30% take-off. The following fractions were collected: fraction 1, 292 g., b.p. 77–125°; fraction 2, 347 g., b.p. 125–127°; fraction 3, 384 g., b.p. 127–128°; fraction 4, 441 g., b.p. 128–141°; residue, 173 g.

Analysis of the fractions was carried out with a Perkin-Elmer model 154B Vapor Fractiometer using column "C" at 125° with 20 p.s.i. helium.

Arylchlorodiethoxysilanes. Compounds shown in Table II were similarly prepared from the appropriate aryltrichlorosilane except that they were purified by distillation through a 15-in. column packed with berl saddles.

Phenyltrichlorosilane used in the preparation of chlorodiethoxyphenylsilane was redistilled commercial grade.

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TABLE II

ARYLCHLORODIETHOXYSILANES PREPARED AND THEIR PROPERTIES

			Analysis					
		B.P.,	Calcd. (%)			Found		
Compound	Yield	°C./mm.	C	H	Si	C	H	Si
Chlorodiethoxyphenylsilane	95.2	124–126/20	52.06	6.55	12.17	52.68	6.27	12.32 12.27
Chlorodiethoxy-*p*-chlorophenylsilane	88.2	139–142/16	45.28	5.32	10.59	45.41	5.20	10.61 10.82
Chlorodiethoxy-*p*-methoxyphenylsilane	92.4	155–162/14–16	50.64	6.57	10.77	51.10	6.78	10.96 10.58

Other aryltrichlorosilanes were prepared as described below.

p-N,N-dimethylaminophenyltrichlorosilane. A Grignard reagent prepared by the method of Rosenberg[8] from 200 g. (1.0 mol.) *p*-bromo-*N,N*-dimethylaniline in 245 ml. tetrahydrofuran and 27 g. (1.1 g. atoms) magnesium turnings was added dropwise to a stirred solution of 340 g. (2.0 mol.) of redistilled silicon tetrachloride in 1000 ml. heptane which was maintained at 30–40° with an ice bath during the addition. After the product was filtered and concentrated by downward distillation at atmospheric pressure, 104 g. (40.4%) *p-N,N*-dimethylaminophenyltrichlorosilane b.p. 168–171°$_{16\text{ mm.}}$ was obtained as a solid by distillation through a 15-in. Vigreux column.

Anal. Calcd. for $C_8H_{10}Cl_3NSi$: C, 37.73; H, 3.96; Si, 11.02. Found: C, 37.34; H, 4.01; Si, 10.82, 11.00.

Other aryltrichlorosilanes. *p*-Anisyltrichlorosilane was similarly prepared in a 32.4% yield by adding a Grignard reagent obtained from 200 g. (1.4 mol.) *p*-chloroanisole and 37.5 g. (1.5 g. atoms) magnesium in 383 ml. tetrahydrofuran to 476 g. (2.8 mol.) to silicon tetrachloride in 1500 ml. heptane. The product was obtained by fractional distillation and boiled 117–119°/5.5 mm. Literature, 94–97°/1 mm.[8] and 128–130°/15 mm.[9] *p*-Chlorophenyltrichlorosilane was obtained in a 39.4% yield by treating 680 g. (4 mol.) silicon tetrachloride with a Grignard reagent prepared by the method of Burkhard[10] from 383 g. (2.0 mol.) *p*-bromochlorobenzene and 650 ml. anhydrous ether. Fractional distillation gave the product boiling 115–117°/20 mm. Literature, 99–100°/11.[11]

KANSAS CITY 10, MO.

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[10] C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946).

[11] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and V. U. Roshal, *Zhur. Obshcheĭ Khim.*, **26**, 1229–33 (1956); *Chem. Abstr.*, **50**, 14604 (1956).