above. The combined reaction mixtures gave a crude yield of 81.9%. Purification by means of the silver salt gave 55.4% of pure acid (m. p. 227–229°).

Acknowledgment.—We gratefully acknowledge the assistance of Dr. Henry Gilman in whose laboratory one of the authors spent several days becoming acquainted with the latest techniques of handling organolithium compounds. We also acknowledge helpful suggestions from Dr. C. G. Stuckwisch.

Summary

The halogen–metal interconversion reaction between the appropriate aryl halide and *n*-butyllithium has been applied on a one millimole scale to the preparation of *p*-aminobenzoic and nicotinic acids marked in the carboxyl groups with C^{14}. These biologically important compounds have been prepared with extremely high specific activities.

Nicotinic acid containing approximately 6 isotopic per cent. of C^{13} in the carboxyl group was also prepared by the same procedure.

LOS ALAMOS, NEW MEXICO RECEIVED JULY 29, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Some Systems of Silicon Halides with Dioxane

BY S. M. SCHOLASTICA KENNARD[1] AND P. A. MCCUSKER

Molecular compounds of dioxane with inorganic halides, in dioxane solution and in the crystalline state, have been the subject of previous studies in these laboratories[2,3] and elsewhere.[4]

Most of these molecular compounds, whose dielectric properties have been studied in solution, appear to be formed as a result of coördination between dioxane and the central atom of the halide. It has been further observed that those halides which coördinated strongly with dioxane in solution also formed relatively stable crystalline complexes. Since silicon tetrachloride gave no evidence of coördination with dioxane in solution, it was considered of interest to determine whether any solid molecular compounds would be formed between silicon tetrahalides and dioxane. For this reason a study was made of the solid–liquid equilibria in silicon tetrahalide–dioxane systems. Dielectric constant and density data were also obtained for silicon tetrabromide in solution. During the course of this work it became desirable to obtain melting point–composition data for the cyclohexane–dioxane system.

Experimental

Preparation and Purification of Materials.—Dioxane was purified as described previously.[2] Silicon tetrabromide was prepared by passing bromine in a stream of nitrogen over granular silicon, in a vertical, 24 mm. Pyrex tube electrically heated. The exothermic reaction was maintained, with slight heating, by a rapid flow of bromine over the heated silicon. Under carefully controlled conditions silicon tetrabromide, essentially free of bromine, was distilled out of the reaction tube. Purification was effected by shaking with mercury and several distillations in a 4 ft. glass helix-packed distilling column. The final product boiled at 154° and was further purified by fractional freezing. The purity was established by separating into two fractions each melting sharply at 5.4°. The melting point reported by Pohland[5] for highly purified silicon tetrabromide is 5.2–5.3°. Silicon tetrachloride was prepared by a similar procedure and purified by fractional distillation. C. P. cyclohexane was refluxed over phosphorus pentoxide and fractionally distilled.

Determination of Melting Points.—Temperatures were measured with a calibrated tenth-degree mercury thermometer. The apparatus for the determination of the melting points was designed for convenience and rapidity in obtaining data. A motor-actuated reciprocating glass ring stirrer surrounded the bulb of the thermometer immersed in the liquid. The system contained a side arm through which measured volumes of liquid could be added from a buret. A thin rubber finger was used to connect the stirring rod and its glass shaft and permitted the complete exclusion of moisture. In a typical determination, a measured volume of liquid was run into the apparatus and a cooling bath placed around the tube. The liquid was cooled and stirred slowly so as to obtain considerable undercooling. In all this work undercooling of from 5 to 10° was readily obtained. The undercooling is an essential feature of this method of determining melting points. By intermittent application of a bath, held at about 10° below the expected melting point, and control of the rate of stirring, sufficient undercooling could be obtained to cause separation of a large quantity of solid in finely divided form. When solid separated, the bath was removed and the mixture allowed to warm up while being vigorously stirred. With finely divided solid and rapid stirring equilibrium between solid and liquid was closely approached. The equilibrium temperature was taken as the point of visible clarification of the mixture and this temperature checked by observation of the increased rate of temperature rise. In all cases these two readings checked within the precision of the thermometer, and numerous checks demonstrated the reproducibility of the data. Subsequent addition of measured volumes of a second component enabled a considerable number of determinations to be made with one original charge. Warming curves were obtained in a similar manner, temperature–time readings being taken during the warming and vigorous stirring of the mixture, after considerable solid had separated.

Dielectric Constants and Densities.—These were determined as previously described.[2] The molar refraction for silicon tetrabromide was computed from the density and refractive index data of Pohland[5] and this value used for the electron polarization. Ten per cent. of the electron polarization was taken as the value for the atomic polarization. The method of Hedestrand[6] was used for calculat-

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(1) Sister M. Scholastica, C.S.C. Present address: St. Agnes Convent, Los Angeles, California.

(2) Lane, McCusker and Curran, THIS JOURNAL, **64**, 2076 (1942).

(3) Kelley and McCusker, *ibid.*, **65**, 1307 (1943).

(4) Rheinboldt, Luyken and Schmittmann, *J. prakt. Chem.*, **148**, 81 (1937).

(5) Pohland, *Z. anorg. allgem. Chem.*, **201**, 265 (1931).

(6) Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).

ing the electric moment. Measurements of dielectric constants and densities were made at 25.0°.

Results and Discussion

I. The Silicon Tetrabromide–Dioxane System.—The melting point–composition data for this system are listed in Table I and plotted in Fig. 1. The stable eutectic mixture contains 39.5 mole % dioxane and melts at −11.4°. When pure silicon tetrabromide was undercooled 5° or more a metastable crystalline form frequently separated. This was sufficiently less opaque than the stable form to be readily recognized although the smallness and instability of the crystals did not permit further characterization. In some cases the metastable form would persist until it melted sharply at 2.3°. In other cases, transformation to the stable form melting at 5.4° would occur suddenly. When solutions of composition between pure silicon tetrabromide and the eutectic mixture were undercooled, the stable form of silicon tetrabromide usually separated. Frequently, however, the metastable form separated and persisted until liquefaction was complete. In some instances, after separation of the metastable form, a sudden transition to the stable, higher melting form would occur. Some typical warming curves illustrating the three different modes of behavior are given in Fig. 2. The curve for the melting point obtained when metastable silicon tetrabromide was the solid phase is shown as a broken line in Fig. 1.

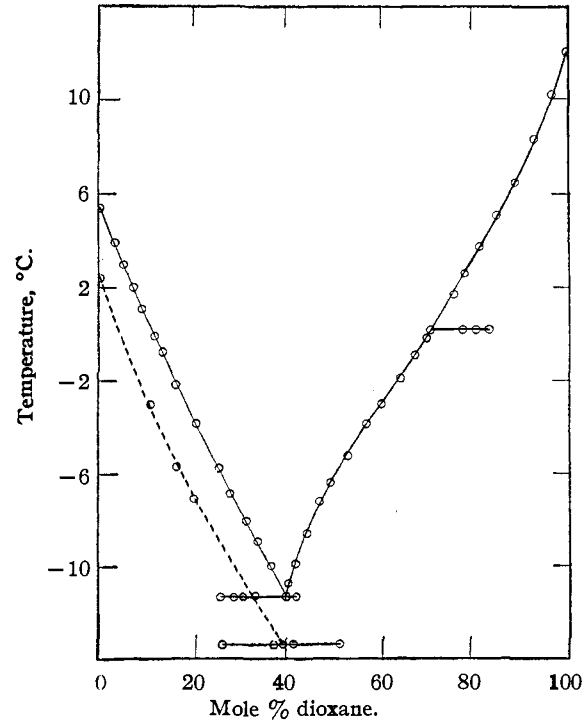

Fig. 1.—Melting point–composition diagram for the silicon tetrabromide–dioxane system.

TABLE I

MELTING POINTS OF SILICON TETRABROMIDE–DIOXANE SOLUTIONS

Mole % Dioxane	M. p., °C. Stable	M. p., °C. Metastable	Eutectic, °C. Stable	Eutectic, °C. Metastable	Mole % Dioxane	M. p., °C.
0.0	5.4	2.3			43.2	−8.6
0.7	4.7				44.5	−8.0
2.4	3.9				46.6	−7.2
3.2	3.7				48.3	−6.5
4.5	2.9				50.6	−6.0
6.8	2.0				52.5	−5.4
8.4	1.2	−2.0			52.9	−5.2
10.0	0.4	−3.2			54.6	−4.5
11.1	0.0				56.4	−4.0
12.5	−0.8	−4.2			57.9	−3.6
16.3	−2.2	−5.8			59.9	−3.1
18.9	−3.6				61.2	−2.7
19.8	−3.9	−7.1			63.9	−2.0
25.0	−5.8			−13.5	64.8	−1.6
25.2	−6.1				66.9	−1.1
25.5	−6.3		−11.4		68.9	−0.3
27.0	−6.9				70.6	0.1
28.5	−7.4				73.5	0.9
29.3	−7.7		−11.4		75.5	1.7
31.1	−8.2	−11.1	−11.4		77.4	2.3
32.8	−9.2				79.1	3.0
33.0	−9.0				80.8	3.6
33.6	−9.3				82.4	4.3
35.8	−10.1		−11.4	−13.5	86.4	6.9
36.7	−10.4			−13.5	88.0	5.6
36.9	−10.6				89.2	6.3
38.2	−11.1		−11.4		90.9	7.5
38.7	−11.2		−11.4	−13.5	92.6	8.2
39.6	−10.8				96.6	10.0
40.4	−10.7			−13.5	97.3	10.4
41.0	−9.9				99.6	11.5
42.2	−9.6		−11.4		100.0	11.8

It may be observed that there is an approximately constant difference in the melting points when the two different forms separate, over a range of composition. The metastable eutectic mixture melts at 13.5°.

The silicon tetrabromide–dioxane system is a simple eutectic giving no evidence of strong interaction between the two components except for a slight but definite change of curvature between 60 and 80 mole % dioxane.

Some carefully obtained warming curves for mixtures between 77 and 85 mole % dioxane revealed a reproducible temperature halt in the region 79–83 mole % dioxane. Some representative data from these warming curves are plotted in Fig. 3. A maximum temperature halt shows up at 80 mole % dioxane with temperature halts of shorter duration at neighboring compositions. This behavior is commonly interpreted as due to the existence of a molecular compound with incongruent melting point. Thus the existence of a 1:4 complex between silicon tetrabromide and dioxane is indicated by the warming curve results.

Dielectric Constant and Density Data.—The dielectric constants and densities of dilute solu-

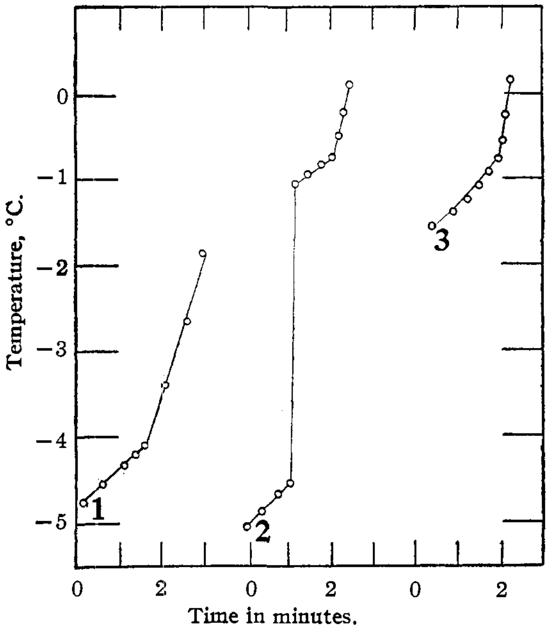

Fig. 2.—Warming curves for 12.5% dioxane in silicon tetrabromide: (1) separation and complete melting of metastable form; (2) separation of metastable form and transformation to stable form before complete melting; (3) separation of stable form.

tions of silicon tetrabromide in dioxane and in carbon tetrachloride were measured and are listed in Table II.

TABLE II

DIELECTRIC CONSTANTS AND DENSITIES FOR SILICON TETRABROMIDE SOLUTIONS AT 25°

C_2	ϵ	d
Dioxane solutions		
0.0000	2.208	1.0279
.0106	2.220	1.0545
.0190	2.226	1.0756
.0300	2.234	1.1030
Carbon tetrachloride solutions		
.0000	2.2300	1.5856
.0122	2.2356	1.6035
.2190	2.2389	1.6177

The calculated polarization and electric moments are listed in Table III.

TABLE III

POLARIZATIONS AND ELECTRIC MOMENTS OF SILICON TETRABROMIDE

Solvent	$P_E + A$	$P_{2\infty}$	μ
Dioxane	44.66	51.15	0.55 ± 0.09
Carbon tetrachloride	44.66	45.20	.00 ± .10

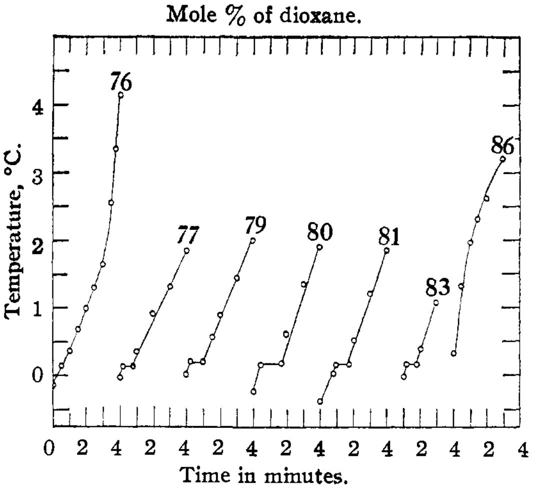

Fig. 3.—Warming curves for some silicon tetrabromide–dioxane solutions.

The value obtained for the electric moment of silicon tetrabromide in carbon tetrachloride is the expected zero value for the tetrahedral structure indicated by electron diffraction,[7] and Raman spectra studies.[8] The value for the electric moment in dioxane is small but is significantly different from zero. A slight but definite electronic interaction between dioxane and silicon tetrabromide is probably responsible for this small moment. The composition of the unstable crystalline compound between silicon tetrabromide and dioxane, indicated by the warming curve data, suggests that interaction at higher temperatures in the same molecular ratio would lead to a zero moment since the moment vectors would cancel. The small electric moment observed for silicon tetrabromide in dioxane is not sufficient evidence to assume extensive interaction between the halide and dioxane in the liquid state. It may, however, indicate a diminished tendency for such interaction with the symmetrical 1:4 complex being partly dissociated.

Measurements of the densities of solutions of silicon tetrabromide in dioxane were made over the whole range of composition. The results obtained are listed in Table IV.

TABLE IV

DENSITY DATA FOR SILICON TETRABROMIDE–DIOXANE

Volume % dioxane	d^{25}_4	Volume % dioxane	d^{25}_4
0.00	2.7715	71.72	1.5141
16.06	2.4853	75.54	1.4483
25.12	2.3236	79.63	1.3770
42.62	2.0184	82.35	1.3312
53.01	1.8380	87.98	1.2342
64.11	1.6457	100.00	1.0279
68.49	1.5703		

Plotting of the density against volume fraction gives a straight line and shows no abnormal change in density at 80 mole per cent. dioxane. This is evidence that no appreciable concentration of the 1:4 complex persists in the liquid state at 25.0°.

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(7) Spitzer, Howell and Schomaker, THIS JOURNAL, **64**, 62 (1942).

(8) Trumpy, *Z. physik*, **68**, 675 (1931).

II. The Cyclohexane–Dioxane System.—While few solid–liquid equilibrium diagrams are available in the literature for systems containing dioxane, the system with water has been investigated.[9,10] In this system a considerable change occurs in the curvature of the liquids at approximately the same temperature as observed in the silicon tetrabromide–dioxane system. Since molecular interaction is probable between the highly polar water and dioxane, comparable data were sought for a substance which should be completely inert to dioxane. Cyclohexane was chosen for this purpose, since its melting point was convenient and its geometric similarity to dioxane would minimize steric factors influencing the composition of the solid phase. The melting point data for this system are listed in Table V and diagrammed in Fig. 4.

TABLE V

MELTING POINTS OF CYCLOHEXANE–DIOXANE SOLUTIONS

Mole % dioxane	M. p., °C.	Mole % dioxane	M. p., °C.
0.0	6.5	41.7	−3.1
4.5	1.2	48.2	−2.0
8.7	−2.6	49.6	−1.6
12.9	−6.5	56.2	−0.8
16.1	−8.9	59.2	−0.4
19.3	−11.0	60.2	−0.3
22.3	−8.9	66.7	0.9
25.3	−7.7	72.7	2.3
27.6	−7.0	76.7	2.9
31.8	−5.7	81.5	4.4
35.6	−4.5	86.5	6.0
35.8	−4.7	91.5	7.7
37.5	−4.0	95.9	9.7
39.5	−3.7	100.0	11.8

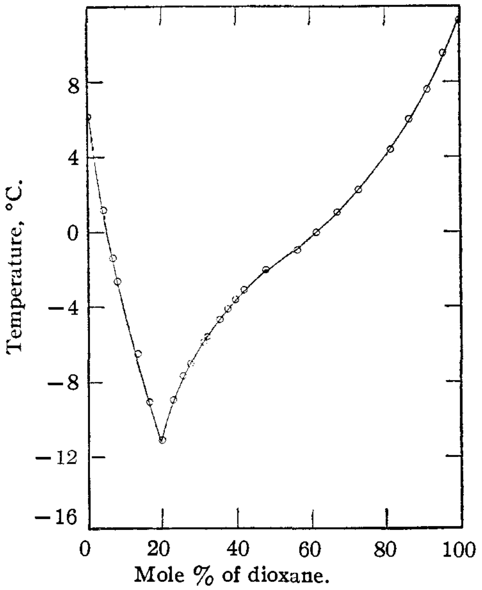

Fig. 4.—Melting point–composition diagram for the cyclohexane–dioxane system.

This system gives a eutectic at −11.1° containing 19 mole % dioxane. The same type of curvature change in the liquidus appears in this system as in the silicon tetrabromide–dioxane and water–dioxane systems, and in the same approximate temperature range, −1° to +2°.

TABLE VI

MELTING POINTS OF SILICON TETRACHLORIDE–DIOXANE SOLUTIONS

Mole % dioxane	M. p., °C.	Mole % dioxane	M. p., °C.
18.1	−11.9	62.0	1.3
22.0	−9.8	62.4	1.2
24.9	−8.3	62.5	1.2
28.2	−7.0	64.0	1.6
30.6	−6.0	64.2	1.8
34.0	−4.9	66.4	2.1
38.0	−3.9	67.4	2.2
42.2	−2.9	70.3	2.8
44.5	−2.2	72.4	3.3
47.8	−1.7	73.8	3.7
48.8	−1.4	74.6	3.9
51.9	−0.8	77.0	4.5
52.7	−0.7	80.0	5.3
54.7	−0.3	82.2	6.0
57.0	0.0	84.0	6.6
57.5	.3	88.2	7.8
59.5	.4	90.1	8.6
59.9	.7	92.0	8.9
60.4	.7	93.4	9.3
61.8	.8	94.5	9.6

III. The Silicon Tetrachloride–Dioxane System.—For the purpose of comparison, a portion of the solid–liquid equilibrium diagram for silicon tetrachloride–dioxane was worked out.

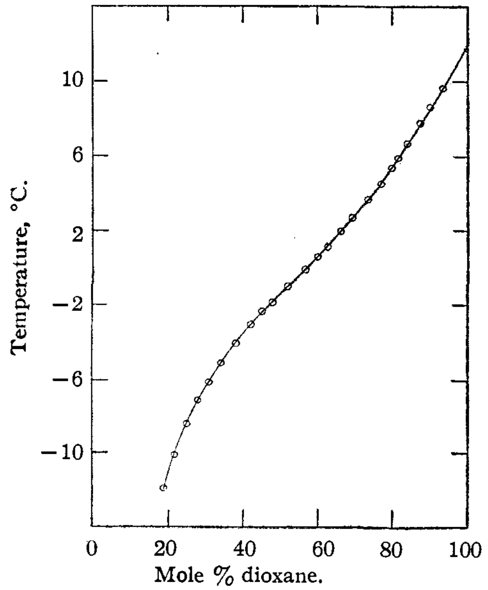

Fig. 5.—Melting point–composition diagram for a portion of the silicon tetrachloride–dioxane system.

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[9] Gillis and Delaunois, *Rec. trav. chim.*, **53**, 186 (1934).

[10] Hovorka, Schaeffer and Dreisbach, THIS JOURNAL, **58**, 2264 (1936).

The selected portion includes all compositions at which molecular compound formation might reasonably be expected to occur. The melting point data for this system are listed in Table VI and are diagrammed in Fig. 5.

An examination of the diagram shows a considerable degree of similarity with the silicon tetrabromide and cyclohexane systems with dioxane. No stable compound is indicated and the same type of curvature change occurs in the liquidus at about the same temperature.

Previous determinations[2] of the electric moment of silicon tetrachloride in dioxane gave zero value. If the small moment obtained for silicon tetrabromide in dioxane is attributed to an electronic interaction between the halogens and the donor oxygens of dioxane, the zero value of the moment for silicon tetrachloride in dioxane would indicate a lessened tendency for such interaction. Attempts to obtain reproducible warming curves for silicon tetrachloride–dioxane solutions in the neighborhood of 80 mole % dioxane were unsuccessful.

Summary

1. Melting point–composition diagrams for the systems of silicon tetrabromide, silicon tetrachloride and cyclohexane with dioxane have been determined.

2. A metastable form of solid silicon tetrabromide, m. p. 2.3°, has been observed.

3. Thermal analysis of the system silicon tetrabromide–dioxane indicates the existence of an unstable 1:4 complex.

4. A characteristic curvature change in the liquidus for several systems containing dioxane was found to occur at approximately 0°.

5. Dielectric constant and density data indicate a small degree of electronic interaction between silicon tetrabromide and dioxane. The electric moment of silicon tetrabromide in carbon tetrachloride was found to be 0.0.

NOTRE DAME, IND. RECEIVED NOVEMBER 20, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phenyl and Ethoxy Silicon Isocyanates

BY GEORGE S. FORBES AND HERBERT H. ANDERSON

This paper describes two complete series of new mixed silicon isocyanates. The phenyl silicon isocyanates were prepared from phenylchlorosilanes and silver isocyanate, and the three ethoxy silicon isocyanates from ethoxychlorosilanes and silver isocyanate.

Preparation of Phenyl Silicon Isocyanates.—In the usual manner,[1] each phenylchlorosilane was changed into the corresponding isocyanate through reaction with an excess of silver isocyanate; the yields varied from 75 to 90%. All three phenyl silicon isocyanates were distilled at 3 mm. pressure through a plain column 4 mm. i. d. and 300 mm. long. Triisocyanate, collected from 101 to 102°; diisocyanate, 142–143°; monoisocyanate, 177.5–178.5°.

Physical Properties and Analyses of Phenyl Silicon Isocyanates (see Table I).—Dynamic vapor pressure measurements were made on each of the three compounds—six values on the triisocyanate, five on the diisocyanate and four on the monoisocyanate. Frozen phenyl silicon triisocyanate melted over the range −50 to −20°, approximately. Possibly two solid forms were present; diphenyl silicon diisocyanate supercooled to −70°, but formed a crystalline solid of sharp m. p. after addition of a small clay chip to promote crystallization; triphenyl silicon isocyanate supercooled less than 20°. Needless to say, vigorous stirring was essential in obtaining melting points. When shaken with water, the triisocyanate hydrolyzed slowly at first and then with increasing speed; the diisocyanate hydrolyzed at a moderate rate only, even with vigorous shaking; the monoisocyanate, however, hydrolyzed very slowly, if at all. Analyses employed the Dumas method for nitrogen, combustion for carbon and hydrogen, and the hydrolysis and ignition of the triisocyanate to obtain silica as the end-product. Calcd. for $(C_6H_5)Si(NCO)_3$: Si, 12.2; C, 46.8; H, 2.2. Found: Si, 12.3; C, 47.1; H, 2.3. Calcd. for $(C_6H_5)_2Si(NCO)_2$: N, 10.5; H, 3.8. Found: N, 10.8; H, 3.5. Calcd. for $(C_6H_5)_3Si(NCO)$: N, 4.6; H, 5.0. Found: N, 4.4; H, 5.3 The observed molecular weights in camphor solution were 212, 250 and 290, respectively, corresponding to the calculated values 231, 266 and 301.

Preparation of Ethoxy Silicon Isocyanates.—Methanol reacts with silicon isocyanate to produce methoxy silicon isocyanates,[2] the boiling points of which are 15° apart; however, the reaction between ethanol and silicon isocyanate yields products difficultly separable. It was much easier to obtain the desired products from the ethoxychlorosilanes. Ethoxytrichlorosilane, prepared from tetrachlorosilane and ethanol, boiled at 102.1° at 758 mm.[3]; diethoxydichlorosilane boiled at 137.4–137.6° at 754 mm.[3] Triethoxychlorosilane boiled from 154 to 157°,[4] even upon repeated distillation on a plain column 4 mm. i. d., 125 cm. long; apparently redistribution limited the purity of the sample. Following the general method,[1] a solution of the individual ethoxychlorosilane in benzene was heated with a 30% excess of silver isocyanate for thirty minutes at 90°, and then filtered with washing of the silver salts; benzene was removed by distillation at atmospheric pressure. The middle fraction of ethoxy silicon triisocyanate boiled at 178.5° uncor. at 764 mm. with little variation; that of diethoxy silicon diisocyanate boiled at 174.8–174.9° uncor. at 760 mm. in a column without spiral or packing, and 4 mm. i. d. and 50 cm. long.

Triethoxy silicon isocyanate could not be purified by distillation alone; the main contaminant was probably diethoxy silicon diisocyanate, the boiling point of which is only 2.5° higher, and the minor contaminant was the more easily removed ethyl orthosilicate (tetraethoxysilane). The first preparation showed a b. p. of 173.5°, d^{20}_4 1.025 and n (index of refraction) 1.3933, leading to R (molar refraction, n^2 formula) 47.82 ml., none of which agreed with values interpolated in the series. A product of apparently higher purity was next obtained by treatment of the above material with ethanol in excess. Prob-

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[1] Forbes and Anderson, THIS JOURNAL, **62**, 761 (1940).

[2] Forbes and Anderson, *ibid.*, **66**, 1703 (1944).

[3] Peppard, Brown and Johnson, *ibid.*, **68**, 70 (1946), reported 101.5-102.0°, 136.0-136.5° and 156.0-156.5°, respectively, at 760 mm.