

hydrogenation at 40–45 p. s. i., 5 g. of activated catalyst for 7 g. of the aldehyde was used. In the hydrogenation to butanol-1 at room temperature, 5 ml. of triethylamine, 100 ml. of methanol, 21 g. of crotonaldehyde and 10 g. of the activated catalyst were used under 4000 p. s. i. of hydrogen. In the attempts to selectively hydrogenate cinnamaldehyde to cinnamyl alcohol the ratio of aldehyde to catalyst was 2.6:1.

The copper–chromium oxide catalyst was activated by shaking the catalyst, suspended in methanol, under approximately 4000 p. s. i. of hydrogen at 100° for five minutes. The reaction vessel was then cooled to room temperature and the compound to be hydrogenated was added.

In the hydrogenation of methyl 2-naphthyl ketone, 17 g. was used with 10 g. of activated catalyst in 100 ml. of methanol, under 4000 p. s. i. of hydrogen. The yield of methyl-2-naphthylcarbinol,¹⁴ m. p. 74–75°, from five such hydrogenations was 80.8 g. In the hydrogenations of the naphthoate esters 0.1 mole of the ester was employed with 10 g. of activated catalyst in 100 ml. of methanol, under 300 atmospheres of hydrogen.

Summary

Procedures have been given for the preparation

(14) Lund, *Ber.*, **70**, 1520 (1937).

of the copper–chromium oxide catalyst, having a higher activity than previously described. A method for determining the activity of samples of the catalyst has been described and illustrated by application to samples of catalyst prepared by various procedures.

The catalyst if properly prepared adsorbs approximately 150 ml. of hydrogen per gram of catalyst in the temperature range 80–100° under 4000 p. s. i. The catalyst is thereby activated so that it is effective, even at room temperature, for the hydrogenation of alkene and carbonyl linkages. This catalyst is active for the hydrogenation of carboalkoxy groups of the naphthoic esters from 80° upward.

It has been demonstrated that the copper chromite is not a catalyst for the hydrogenation of aldehydes, ketones, alkenes and esters, at temperatures below 250°, at which the copper–chromium oxide catalyst is normally used.

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RECEIVED DECEMBER 5, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Some Organosilanes

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In connection with some studies on the introduction of functional groups into alkyl- and arylsilanes, it was found desirable to examine the cleavage of the Si–C linkage. This examination involved treatment of the organosilicon compounds with anhydrous hydrogen chloride in refluxing glacial acetic acid.² Table I (Experimental part) shows the products obtained when some selected silanes were subjected to this treatment.

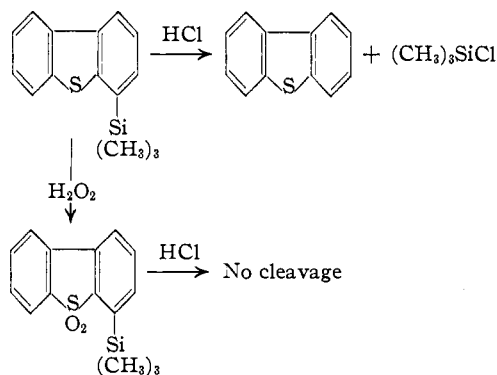
The isolation of hexaphenyldisiloxane from the cleavage of triphenylphenylethynyl-silane was not entirely unexpected since the triphenylsilyl chloride formed by the cleavage reaction would be converted to triphenylsilanol when poured into water and in the presence of the acetic and hydrochloric acids this silanol would condense to form the disiloxane.^{2b} It has not been definitely established, however, whether the acetophenone obtained in this same cleavage came as a result of cleavage of the Si–C bond followed by addition of hydrogen chloride to the phenylacetylene formed, with subsequent hydrolysis to acetophenone or whether addition of hydrogen chloride to the acetylenic linkage preceded cleavage.

Hexaphenyldisiloxane was the only product identified from the cleavage of triphenyl- β -styryl-silane.

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(2) For other cleavage studies see: (a) Kipping and Blackburn, *J. Chem. Soc.*, 1085 (1935); (b) Gilman and Marshall, *THIS JOURNAL*, **71**, 2066 (1949). Numerous references to cleavage reactions are given in this article.

The Si–C bond in 4-trimethylsilyldibenzothiophene is apparently quite unstable toward acidic reagents, as evidenced by the 87% yield of dibenzothiophene obtained when this compound was treated with hydrogen chloride. When this silane was oxidized to 4-trimethylsilyldibenzothiophene-5-dioxide, however, the silicon–carbon linkage was stabilized to a considerable extent, since the dioxide was completely resistant to hydrogen chloride treatment under corresponding conditions.



Further evidence of the stabilizing effect of the –SO₂– group was noted when 4-trimethylsilyldibenzothiophene-5-dioxide was treated with fuming nitric acid and a mononitro-4-trimethylsilyldibenzothiophene-5-dioxide was isolated. A way may have been opened to the direct substitution of other sulfur-containing aryl-alkylsilanes.

TABLE I
HYDROGEN CHLORIDE CLEAVAGE OF SOME ORGANOSILICON
COMPOUNDS

Compound	Products	Yield, %
Triphenylphenylethynylsilane	Acetophenone	67
	Hexaphenyldi- siloxane	32
Triphenyl- β -styrylsilane ^a	Hexaphenyldi- siloxane	21
	Oily material	
4-Trimethylsilyldibenzothio- phene ^b	Dibenzothiophene	87
	Trimethylsilyl chloride	48
4-Trimethylsilyldibenzothio- phene-5-dioxide ^c	No cleavage	
4-Triphenylsilyldibenzothio- phene ^d	No cleavage	

^a Seven grams (0.019 mole) of the silane in 120 cc. of glacial acetic acid was treated as previously described with anhydrous hydrogen chloride. The hexaphenyldisiloxane was identified by a mixed m. p. with an authentic specimen. The oil that remained after extraction of the disiloxane with petroleum ether (b. p., 95–110°) could not be crystallized. It may have been a styrene polymer.

^b Two-tenths mole of 4-trimethylsilyldibenzothiophene in 100 cc. of glacial acetic acid was treated with anhydrous hydrogen chloride. The dibenzothiophene was identified by a mixed m. p. with an authentic specimen. The trimethylsilyl chloride was collected in a Dry Ice-acetone trap attached to the condenser of the cleavage apparatus.

^c A quantitative recovery of starting material was obtained when 1 g. (0.003 mole) of 4-trimethylsilyldibenzothiophene-5-dioxide in 50 cc. of glacial acetic acid was treated with anhydrous hydrogen chloride. ^d Five grams (0.01 mole) of 4-triphenylsilyldibenzothiophene in 120 cc. of glacial acetic acid was treated with anhydrous hydrogen chloride. A 93% recovery of starting material was obtained.

4-Triphenylsilyldibenzothiophene was not cleaved by hydrogen chloride. The greater stability of the (C₆H₅)₃Si-C linkage, as compared to the (CH₃)₃Si-C bond, when attached to the same nucleus, has been noted in other studies.^{2b}

Attempts were made to prepare *o*-hydroxy- and *p*-hydroxyphenyltrimethylsilane for cleavage studies. The results indicated that these compounds are relatively unstable.

Experimental

Hydrogen Chloride Cleavage of Some Organosilicon Compounds.—Table I lists a series of hydrogen chloride cleavages of some new organosilanes. In a typical cleavage experiment, dry hydrogen chloride was passed through a refluxing solution of 4.5 g. (0.012 mole) of triphenylphenylethynylsilane in 100 cc. of glacial acetic acid for fifteen hours. The solution was then poured into water and the resulting mixture extracted with ether. The ether extracts were dried and the ether removed by distillation. Distillation of the residue gave 1 g. (67%) of acetophenone, identified by preparation of the 2,4-dinitrophenylhydrazone (melting point and mixed m. p. 245–246°).

The solid residue remaining after removal of the acetophenone was dissolved in xylene and reprecipitated by addition of petroleum ether (b. p. 95–110°). This solid melted at 223–224° after two recrystallizations from benzene. A mixed melting point with hexaphenyldisiloxane was not depressed. The yield was 1 g. (32%).

Triphenylphenylethynylsilane.—This compound was prepared according to the method of Plunkett³ from 12.94

g. (0.09 mole) of silicon tetrachloride, 0.272 mole of phenyllithium in 259 cc. of ether, and 0.09 mole of phenylethynyllithium (prepared from 9.55 g. (0.09 mole) of phenylacetylene and 0.09 mole of phenyllithium in 86 cc. of ether). The yield of product melting at 96–98° was 30% (10 g.). When ethyl silicate was used instead of silicon tetrachloride, only a 10% yield of product was obtained.

Triphenyl- β -styrylsilane.—Triphenylsilyl chloride was prepared by treating a suspension of 25 g. (0.1 mole) of triphenylsilanol in 200 cc. of ether with anhydrous hydrogen chloride. The ether was removed by reduced pressure distillation and the crude product dried at 70° under the vacuum of a water aspirator. Recrystallization from petroleum ether (b. p. 95–110°) gave 23 g. (86%) of product melting at 91–94°.

β -Styryllithium was prepared in essential accordance with the procedure of Wright⁴ from 1.26 g. (0.18 g. atom) of finely cut lithium in 10 cc. of ether and 9.15 g. (0.05 mole) of freshly distilled β -bromostyrene in 50 cc. of ether. The total reaction time was twenty minutes. Another preparation of the same size was made simultaneously since it was found that larger preparations than the one described give mostly phenylethynyllithium.^{4,5}

To 17 g. (0.06 mole) of freshly prepared triphenylsilyl chloride in 100 cc. of ether were rapidly added the β -styryllithium solutions. Color Test I⁶ was negative after three hours of refluxing. The solution was treated with water, the ether layer was removed and dried, and the ether was removed by distillation. The remaining oil solidified on cooling, and after recrystallization from petroleum ether (b. p., 65–78°) there was obtained 10 g. (46%) of triphenyl- β -styrylsilane melting at 140–143°. Recrystallization of an analytical sample from ethanol raised the melting point to 146–147°.

Anal. Calcd. for C₂₆H₂₂Si: Si, 7.75. Found: Si, 7.88, 8.13.

4-Trimethylsilyldibenzothiophene.—4-Dibenzothiophenyllithium⁷ was prepared from 37.8 g. (0.2 mole) of dibenzothiophene and 0.23 mole of *n*-butyllithium.⁸ The reaction flask was cooled in ice and 21.6 g. (0.2 mole) of trimethylsilyl chloride in 50 cc. of ether was added dropwise. Color Test I⁶ was still positive at the end of twenty-four and forty-eight hours of refluxing but the addition of a large excess of trimethylsilyl chloride had no effect on the small amount of organometallic compound remaining. The reaction mixture was treated with water and the ether layer removed and dried. After removal of the ether and three fractional distillations of the residue, there was obtained 27 g. (53%) of pure trimethylsilyldibenzothiophene⁹ (b. p., 215–217° (20 mm.)). The following constants were obtained for this compound: *n*_D²⁰ 1.6354; *d*₄²⁰ 1.112; *M*R_D calcd. 82.3; and, *M*R_D found 82.4. (The molecular refraction was calculated using the values of Warrick¹⁰ for silicon and carbon; the value for the C-S-C linkage was calculated from the molecular refraction of thiophene.¹¹)

Anal. Calcd. for C₁₅H₁₀SSi: Si, 10.94. Found: Si, 10.50.

4-Trimethylsilyldibenzothiophene-5-dioxide.—To 5.2 g. (0.02 mole) of 4-trimethylsilyldibenzothiophene in 50 cc. of glacial acetic acid was added 10 cc. of 30% hydrogen peroxide in 15 cc. of glacial acetic acid. The mixture was

(4) Wright, *J. Org. Chem.*, **1**, 457 (1936).

(5) Gilman, Langham and Moore, *THIS JOURNAL*, **62**, 2327 (1940) Wittig and Witt, *Ber.*, **74B**, 1474 (1941).

(6) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

(7) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(8) Gilman and Stuckwisch, *THIS JOURNAL*, **65**, 1462 (1943).

The titer of the *n*-butyllithium was determined according to the method of Gilman and Haubein, *ibid.*, **66**, 1515 (1944).

(9) 2-Trimethylsilyldibenzothiophene has recently been prepared in these laboratories by Dr. Gabriello Illuminati and was found to be a solid melting at 48°.

(10) Warrick, *THIS JOURNAL*, **68**, 2455 (1946); see also Sauer, *ibid.*, **68**, 954 (1946).

(11) Lange, "Handbook of Chemistry," 6th Edition, Handbook Publishers, Sandusky, Ohio, 1946, p. 976.

(3) Plunkett, Doctoral Dissertation, Iowa State College, 1947.

refluxed at 100° for four hours, during which time an additional 10 cc. of hydrogen peroxide was added. The reaction mixture was poured into water and the crude solid recrystallized from ethanol to give a product melting at 140–143°. A second recrystallization from petroleum ether (b. p., 65–78°) raised the melting point to 146–147°. The yield was 2.5 g. (42%).

Anal. Calcd. for $C_{15}H_{16}O_2SSi$: Si, 9.74. Found: Si, 9.75.

Nitration of 4-Trimethylsilyldibenzothiophene-5-dioxide.—To a suspension of 1 g. (0.0035 mole) of 4-trimethylsilyldibenzothiophene-5-dioxide in 4 cc. of glacial acetic acid and 4 cc. of concentrated sulfuric acid at 5° was added 6 cc. of fuming nitric acid at a dropwise rate. The nitration mixture was stirred at a temperature of 5° for one-half hour and poured into water. The reaction mixture was stirred at room temperature for one hour in another experiment with the same results. There was obtained 1.1 g. (95%) of crude product melting at 180–200°. Recrystallization from ethanol gave 0.4 g. (34%) of a nitrogen-containing product melting at 223–224°. The structure of the compound was not determined, but the reaction illustrated that the C–Si bond was also stable to nitric acid.

Anal. Calcd. for $C_{15}H_{15}O_4NSSi$: Si, 8.43; N, 4.21. Found: Si, 8.72; N, 4.10.

4-Triphenylsilyldibenzothiophene.—Triphenylethoxysilane was prepared by the method of Clark¹² from 41.6 g. (0.2 mole) of tetraethyl orthosilicate and 0.6 mole of phenyllithium in 600 cc. of ether. 4-Dibenzothiophenyllithium was prepared from 55.3 g. (0.3 mole) of dibenzothiophene and 0.29 mole of *n*-butyllithium. The dibenzothiophenyllithium solution was added to the solution of triphenylethoxysilane in a dropwise manner and the resulting mixture refluxed for twenty-one hours. Color Test I⁸ was positive at the end of this time but since an excess of 4-dibenzothiophenyllithium was probably present, the reaction mixture was hydrolyzed with water and dilute hydrochloric acid. The ether layer was separated, dried over calcium chloride, and removed by distillation. The remaining yellow oil solidified after standing overnight. This solid was refluxed with a mixture of 100 cc. of ethyl acetate and 50 cc. of glacial acetic acid. The hot solvent was removed and there remained 7.5 g. of product melting at 181–186°. Recrystallization from ethyl acetate raised the melting point to 193–194°. Dilution of the filtrates and recrystallization of the crude material gave a total pure yield of 6 g. (6.8%). The silane can also be recrystallized from ethanol or dilute acetic acid. In another preparation of the same size when the crude product was distilled, the yield was only 1.4 g.

Anal. Calcd. for $C_{30}H_{22}SSi$: Si, 6.34. Found: Si, 6.06, 6.11.

4-Triphenylsilyldibenzothiophene-5-dioxide.—A mixture of 1.5 g. (0.003 mole) of 4-triphenylsilyldibenzothiophene and 10 cc. of 30% hydrogen peroxide in 20 cc. of glacial acetic acid was refluxed for four hours. There was obtained 1.5 g. (93%) of 5-dioxide melting at 195–210°. Two recrystallizations from ethyl acetate raised the melting point of an analytical sample to 212–213°. The amount of compound remaining after analysis was insufficient for a cleavage test.

Anal. Calcd. for $C_{30}H_{22}O_2SSi$: Si, 5.95. Found: Si, 5.75.

2-Triphenylsilyldibenzofuran.—To a solution of 0.02 mole of 2-dibenzofuryllithium¹³ was added 4 g. (0.014 mole) of triphenylsilyl chloride. Color Test I⁸ was negative at the end of one hour of refluxing. The reaction mixture was treated with water and the ether layer removed and dried. After removal of the ether a dark oil remained. Extraction of the oil with 25 cc. of absolute ethanol left a solid residue which was recrystallized from petroleum ether (b. p., 95–110°). There was obtained 0.5 g. (8.7%) of

product melting at 124–125°. This quantity was insufficient for a decisive cleavage test.

Anal. Calcd. for $C_{30}H_{22}OSi$: Si, 6.58. Found: Si, 6.59.

Trimethyl-*o*-anisylsilane.—To 27 g. (0.25 mole) of trimethylsilyl chloride in 100 cc. of ether was slowly added a solution of *o*-anisyllithium,¹⁴ prepared from 52 g. (0.277 mole) of *o*-bromoanisole and 4 g. (0.55 g. atom) of lithium. Color Test I⁸ was negative one-half hour after the addition was complete. The reaction mixture was worked up in the usual manner to give 35 g. (71%) of product distilling at 91–93° (15 mm.). The material contained a small amount of *o*-bromoanisole that could be removed only by distillation of the mixture at atmospheric pressure (b. p., 205–206° (733 mm.)). The following constants were determined: n^{20}_D 1.5055; d^{20}_4 0.9587; *MRD* calcd. 56.47; and *MRD* found 55.80.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55. Found: Si, 15.32.

Trimethyl-*p*-anisylsilane.—To 27 g. (0.25 mole) of trimethylsilyl chloride in 100 cc. of ether was added a solution of *p*-anisyllithium¹⁴ (0.25 mole). The reaction mixture was allowed to stir overnight and then treated with water. The pure product was obtained by extraction of the crude material with 500 cc. of water in 50-cc. portions. Other attempts at purification did not remove the small amount of *p*-bromoanisole contaminant. There was obtained 18 g. (40%) of product boiling at 220° (740 mm.). The following constants were observed: n^{20}_D 1.5014; d^{20}_4 0.9398; *MRD* calcd. 56.47; and *MRD* found 56.46. Cleavage of this compound has been reported by Marshall.^{2b}

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.55. Found: Si, 15.48.

Reaction of Trimethylsilyl Chloride with Lithium *o*-Lithiophenoxide.—To a solution of lithium *o*-lithiophenoxide,¹⁵ prepared from 17.3 g. (0.1 mole) of *o*-bromophenol in 50 cc. of ether and 0.2 mole of *n*-butyllithium in 400 cc. of ether, was added 5.4 g. (0.05 mole) of trimethylsilyl chloride. There was no apparent reaction so the mixture was refluxed overnight. After treatment with water and separation of the layers, there was obtained from the ether layer 1 g. (b. p. 90–95°) of a mixture suspected of being trimethylsilanol and hexamethyldisiloxane.¹⁶ There was also isolated 10 g. of phenol boiling at 175–180°, identified by preparation of phenoxyacetic acid (mixed melting point). No trimethyl-*o*-hydroxyphenylsilane was isolated.

Trimethyl-*o*-anisylsilane was treated with sodium metal in the presence of pyridine according to the ether cleavage method of Prey¹⁷ in hopes of obtaining trimethyl-*o*-hydroxyphenylsilane. No phenolic silicon material was obtained.

Reaction of Trimethylsilyl Chloride with Lithium *p*-Lithiophenoxide.—To 43 g. (0.25 mole) of *p*-bromophenol in 200 cc. of ether was rapidly added 0.5 mole of *n*-butyllithium in 470 cc. of ether.¹⁵ Color Test II¹⁸ was negative after the reaction mixture had been refluxed for ninety minutes. To this solution was added 21.6 g. (0.2 mole) of trimethylsilyl chloride in 25 cc. of ether. Color Test I⁸ was negative after two hours. The solution was hydrolyzed with water and dilute hydrochloric acid and the ether layer removed and dried. After removal of the ether there was obtained a variety of material distilling from 81–120°. The lower boiling fractions were identified as phenol (phenoxyacetic acid—mixed melting point) and the higher fractions as *p*-bromophenol (*p*-bromophenoxyacetic acid—mixed melting point). No trimethyl-*p*-hydroxyphenylsilane was found. Trimethyl-*p*-anisylsilane was treated with sodium in pyridine according to the method of Prey¹⁷ but no phenolic silicon compound was isolated.

(14) Gilman, Langham and Jacoby, *ibid.*, **61**, 106 (1939).

(15) Gilman and Arntzen, *ibid.*, **69**, 1537 (1947).

(16) Sauer, *ibid.*, **66**, 1707 (1944). Sauer reports that trimethylsilanol and hexamethyldisiloxane form an azeotropic mixture boiling at 91–92°.

(17) Prey, *Ber.*, **76B**, 156 (1943).

(18) Gilman and Swiss, *THIS JOURNAL*, **62**, 1847 (1940).

(12) Clark, Doctoral Dissertation, Iowa State Collg., 1946.

(13) Gilman, Langham and Willis, *THIS JOURNAL*, **62**, 346 (1940).

Oxidation of Trimethyl-*p*-lithiophenylsilane.—A solution of trimethyl-*p*-lithiophenylsilane was prepared from 1 g. (0.14 g. atom) of lithium in 20 cc. of ether and 16 g. (0.07 mole) of trimethyl-*p*-bromophenylsilane in 100 cc. of ether according to the method of Clark.¹² To this solution was added 0.07 mole of *n*-butylmagnesium bromide. The mixture was cooled to -10° and dry air passed through the solution for three hours. Color Test I⁶ was negative at the end of this time so the reaction mixture was treated with water and dilute hydrochloric acid. There was obtained 3 g. of material distilling at $80-82^{\circ}$ (15 mm.), subsequently identified as phenol (phenoxyacetic acid—mixed melting point).

A study of the results of this reaction and of the two preceding reactions would indicate that *o*-hydroxyphenyl- and *p*-hydroxyphenyltrimethylsilane may be readily hydrolyzable compounds under these experimental conditions. Since Color Test I showed the absence of any organometallic compounds previous to hydrolysis, it is possible that these hydroxyphenyltrimethylsilanes were formed in solution but cleaved to give phenol and trimethylsilanol on hydrolysis.

Triphenyl- α -chloroethylsilane.—To 17.5 g. (0.088 mole) of α -chloroethyltrichlorosilane¹⁹ in 50 cc. of ether was added 0.257 mole of phenyllithium in 216 cc. of ether. The rate of addition was approximately 4 cc. per minute. Color Test I⁶ was negative thirty minutes after the addition was complete. The reaction mixture was worked up in the usual manner to give 6 g. (21%) of product melting at $90-110^{\circ}$. Recrystallization from petroleum ether (b. p., $65-78^{\circ}$), ethanol, and petroleum ether, in the order given, raised the melting point to $129-130^{\circ}$ but reduced the yield to 14% (4 g.).

(19) Sommer and Whitmore, *THIS JOURNAL*, **68**, 485 (1946).

Anal. Calcd. for $C_{20}H_{15}ClSi$: Si, 8.67; Cl, 10.90. Found: Si, 8.69; Cl, 11.01.

This compound was also prepared by treating triphenylethylsilane with sulfuryl chloride in the presence of benzoyl peroxide.²⁰ The yield was 11%.

It was found that triphenyl- α -chloroethylsilane does not react with 10% sodium hydroxide at 100° (one hour), nor did it form a Grignard reagent (one attempt).

Triphenyl- β -chloroethylsilane.—To 13.35 g. (0.068 mole) of β -chloroethyltrichlorosilane¹⁹ was added 0.203 mole of phenyllithium in 155 cc. of ether. The reaction flask was cooled in ice during the addition and Color Test I⁶ was negative when the addition was complete. There was obtained 1 g. (5.2%) of product melting at $124-125^{\circ}$ after recrystallization from petroleum ether (b. p., $65-78^{\circ}$). A mixed melting point with triphenyl- α -chloroethylsilane melted between 90 and 100° .

Anal. Calcd. for $C_{20}H_{15}ClSi$: Si, 8.67. Found: Si, 8.60. The cleavage of these chloroethylsilanes was not examined because of secondary reactions observed, incidental to a related study.^{2b}

Summary

Hydrogen chloride cleavage studies have been made on a number of new organosilicon compounds. The stabilizing effect of a sulfone group in 4-trimethylsilyldibenzothiophene-5-dioxide was particularly noted. Evidence for the instability of *o*-hydroxyphenyl- and *p*-hydroxyphenyltrimethylsilane has been presented.

(20) For a discussion of the general use of sulfuryl chloride, see Kharasch and Brown, *ibid.*, **62**, 926 (1940).

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RECEIVED JUNE 24, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

The Ternary Systems Magnesium Chloride–Dioxane–Water, Cadmium Chloride–Dioxane–Water and Cupric Chloride–Dioxane–Water

BY J. ARNDT WEICKSEL AND CECIL C. LYNCH

In the further study of ternary systems of metal chlorides–dioxane–water,^{1,2} the systems magnesium chloride–dioxane–water, cadmium chloride–dioxane–water and cupric chloride–dioxane–water have been examined. In these systems we should expect some compound formation with dioxane, since a didioxanate of magnesium chloride,³ a monodioxanate, and hemidioxanate of cadmium chloride,^{3,4} and a mono and didioxanate of cupric chloride^{3,5} have been reported in the literature. A preliminary examination of the cupric chloride–dioxane–water system showed several color changes in the solid phase over a wide range of dioxane concentration, indicating the probability of an interesting phase system.

Preparation of Materials

Dioxane.—Technical 1,4-dioxane from the Eastman Kodak Company was purified by the

(1) Lynch, *J. Phys. Chem.*, **46**, 366 (1942).

(2) Bogardus and Lynch, *ibid.*, **47**, 650 (1943).

(3) Rheinboldt, Luyken and Schmittman, *J. prakt. Chem.*, **149**, 30 (1937).

(4) Jahasz and Yntema, *THIS JOURNAL*, **62**, 3522 (1940).

(5) Heines and Yntema, *Trans. Kentucky Acad. Sci.*, **7**, 85 (1938); *Chem. Abs.*, **35**, 1717 (1941).

method described by Eigenberger.⁶ The product was kept over metallic sodium, from which it was distilled when needed.

Saturated Solutions.—These were made from reagent chemicals and analyzed for chloride. The calculated solubilities agreed well with the literature values, as follows

	Solubility, per cent. anhydrous salt by weight	
	Found	Literature value
MgCl ₂	35.41	35.36 ⁷
CdCl ₂	54.67	54.64 ⁸
CuCl ₂	42.85	43.6 ⁹

Anhydrous Chlorides.—Magnesium chloride was made from the hydrated dioxanate by heating in a rapid stream of anhydrous hydrogen chloride for two hours. *Anal.* 99.5% MgCl₂. Cupric chloride was made by heating the dihydrate for 24 hours at 110° . *Anal.* 99.8% CuCl₂.

Apparatus

All solutions were prepared in two hundred and

(6) Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

(7) Kupper, *Caliche*, **8**, 467 (1927); *C. A.*, **21**, 3713 (1927).

(8) Hering, *Ann. chim.*, [11] **5**, 483 (1936).

(9) Chretien and Weil, *Bull. soc. chim.*, [5] **2**, 1577 (1935); *C. A.*, **30**, 2475 (1936).