[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Cleavage of Some Organosilanes by Hydrogen Chloride

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As a result of extensive investigations[2] on the chemical properties of organometallic compounds it has become apparent that cleavage by hydrogen chloride is characteristic of carbon–metal bonds. Since the reaction becomes more difficult as the affinity of the metal for an electron pair increases, the studies have involved, for the most part, derivatives of such metals as mercury, tin and lead. Organosilicon compounds have been the subject of little such investigation although there have been isolated reports of cleavage reactions.[3]

It was thus the purpose of this present work to investigate the general applicability of hydrogen chloride cleavages to organosilanes and to see if, in this sense at least, silicon could be considered metallic. The results would also indicate the agreement of the order of removal of groups from silicon with the series of radicals previously established with other organometallic compounds.[4,5]

After preliminary experiments indicated that cleavage does not occur in solvents such as benzene and chloroform, the medium chosen was glacial acetic acid. This had been used by Kipping and Lloyd[3a] for the cleavage of tetraphenylsilane by hydrogen chloride. The reactions did not present as much difficulty as the similarity of silicon to carbon might suggest. Isolation of the silicon fragment from the products of cleavage of arylsilanes (Table I), such as triphenyl-*p*-anisylsilane, proved to be difficult or impossible but this appeared to be due to the removal of more than one group. This view found support in the ease of isolation of the products when tribenzyl-*p*-anisylsilane was used, the benzyl–silicon bond being stable under the conditions of these experiments. The same difficulty was again encountered, however, when diethyldiphenylsilane and ethyltriphenylsilane were used and where there was opportunity for the removal of more than one group.

Silanes containing three alkyl groups appeared to be compounds of choice for these studies and, with this in mind, tri-*n*-butylphenylsilane was tried. Because of much greater ease of preparation and relatively rapid rate of cleavage the trimethylarylsilanes were eventually chosen (Table II). Another advantage of these compounds which makes them admirably suited for these studies is that the trimethylsilyl chloride produced is volatile and may be captured in a cold trap and the course of the reaction may thus be followed. The order of ease of removal of groups in this series,

TABLE I

HYDROGEN CHLORIDE CLEAVAGE OF SILANES OF THE TYPE $(C_6H_5)_3SiR$

R	Mole	Cleavage time, hours	Yield of products, %
p-Anisyl[a,b]	0.0136	15	Hexaphenyldisiloxane, 1.7 Anisole,[e] 41
2-Thienyl[a,c]	.0132	7	Triphenylsilanol, 12.7
p-Dimethylaminophenyl[d]	.0158	7.5	Triphenylsilanol, 2.3 Dimethylaniline,[f] 76
OH	.0180	15	Benzene,[g] 82
Ethyl[i]	.0278	15	Benzene,[g] 44[h]

[a] Benkeser, Doctoral Dissertation, Iowa State College, 1947. [b] Attempted cleavage in benzene and in chloroform gave 74 and 70% recoveries, respectively, of starting material. [c] Attempted cleavage in benzene gave a quantitative recovery of starting material. [d] Plunkett, Doctoral Dissertation, Iowa State College, 1947. [e] Isolated by distillation from the oil obtained after neutralization of the reaction mixture. Identified as the 2,4-dinitro derivative. [f] Isolated by steam distillation after the reaction mixture was made basic. Identified as the picrate. [g] Collected in a trap immersed in a moderately cold Dry Ice-acetone bath. Identified as *m*-dinitrobenzene. [h] Calculated on the basis of removal of one group. [i] Marsden and Kipping, *J. Chem. Soc.*, **93**, 198 (1908).

TABLE II

HYDROGEN CHLORIDE CLEAVAGE OF TRIMETHYLARYL- AND ARALKYLSILANES

$(CH_3)_3SiR$, R	Mole	Reaction time, hours	Yield of cleavage products %	
			$(CH_3)_3SiCl$	RH
2-Thienyl[a]	0.032	1	87	37[e]
p-Anisyl[b]	.045	1	69.5	76[f]
p-Dimethylaminophenyl	.0018	1	67	73.5[g]
p-Tolyl	.0487	1	53.5	62[f]
Phenyl[c]	.0665	6	70	60[h]
p-Chlorophenyl	.045	6	43	48[f]
Benzyl[d]	.0548	15	..	..
β-Phenylethyl[d]	.045	15	..	..

[a] Benkeser and Currie, THIS JOURNAL, **70**, 1780 (1948). [b] Kindly supplied by J. F. Nobis. [c] Benkeser, Doctoral Dissertation, Iowa State College, 1947. [d] Attempted cleavage gave an 80% recovery of starting material. [e] The yield of thiophene was low because of difficulty in isolation. It was identified as 2-nitrothiophene which was prepared according to the procedure of Babasinian, *Org. Syn.*, Coll. Vol. II, 466 (1943). [f] Identified as the 2,4-dinitro derivative. [g] Identified as the picrate. [h] Identified as *m*-dinitrobenzene.

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[2] For general references see Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, pp. 489-579, and Krause and von Grosse, "Die Chemie der metall-organischen Verbindungen," Borntraeger, Berlin, 1937.

[3] (a) Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); (b) Kipping and Martin, *ibid.*, **95**, 489 (1909); (c) Steel and Kipping, *ibid.*, 1431 (1928); (d) Kipping and Cusa, *ibid.*, 1088 (1935); (e) Sommer, Bailey and Whitmore, THIS JOURNAL, **70**, 2869 (1948); (f) Sommer, Tyler and Whitmore, *ibid.*, **70**, 2872 (1948); (g) Gold, Sommer and Whitmore, *ibid.*, **70**, 2874 (1948).

[4] Kharasch and Flenner, *ibid.*, **54**, 674 (1932).

[5] Gilman and Towne, *Rec. trav. chim.*, **51**, 1054 (1932); and THIS JOURNAL, **61**, 739 (1939).

2-thienyl > *p*-anisyl and *p*-dimethylaminophenyl > *p*-tolyl > phenyl > *p*-chlorophenyl > benzyl and β-phenylethyl, is in essential agreement with that established with mercury[4] and lead[5] derivatives. This would seem to indicate that the influence of the central element is not as great as had previously been expected.[4]

The studies on the phenyl, benzyl and β-phenylethyl derivatives had an additional purpose. Whitmore and co-workers[6] have reported the instability of silicon derivatives in which a carbonyl or a hydroxyl group was present *beta* to the silicon. It was thought that a comparison of these three compounds would throw some light on the extent of this effect of groups in the β-position if any unusual activity was noted when the phenyl was so situated rather than attached directly to the silicon or on an α-carbon. Since these compounds followed the pattern which would have been predicted no unusual lability was noted. The phenyl radical was cleaved rather easily from trimethylphenylsilane but no cleavage was noted with the other two compounds. One might have expected removal of a methyl group but apparently greater lability than that possessed by the alkyl radicals is necessary before the C–Si bond is split.

Experimental

Cleavage Procedure. (A) Silanes of the Type $(C_6H_5)_3SiR$.—Dry hydrogen chloride gas was passed into a stirred refluxing solution of 0.0136–0.018 mole of the silane in about 75 cc. of glacial acetic acid during seven to fifteen hours. On cooling, the reaction mixture was neutralized by adding it cautiously to a 20% sodium carbonate solution cooled in ice water. The resulting mixture was extracted with ether and the extracts were dried over sodium sulfate. Removal of the ether left a viscous oil from which the silicon fragment was isolated by crystallization from either petroleum ether (b. p. 60–68°) or a benzene–petroleum ether (b. p., 60–68°) mixture. After purification from these same solvents identification was completed by a mixed melting point with an authentic sample. The other cleavage product was isolated and identified as indicated in Table I.

(B) **Trimethylaryl- and Aralkylsilanes.**—A refluxing solution of the silane in 35–50 cc. of glacial acetic acid was treated with gaseous hydrogen chloride during one to fifteen hours. The condenser outlet was connected to a trap immersed in a moderately cold Dry Ice–acetone bath. The trimethylsilyl chloride which collected in this trap was distilled and identified as trimethyl-9-fluorylsilane.[7] The other product of the cleavage was isolated either by distillation from the trap, as in the case of thiophene or benzene, or from the reaction mixture after neutralization as above. Identification was carried out as indicated in Table II.

Trimethyl-*p*-dimethylaminophenylsilane.—To 0.097 mole of *p*-dimethylaminophenyllithium in 75 cc. of ether was added 9.7 g. (0.09 mole) of trimethylsilyl chloride in 10 cc. of ether. The mixture was refluxed, with stirring, for one hour, Color Test I[8] being positive at the end of that time. After hydrolysis with water and ether extraction the extracts were dried over sodium sulfate. Removal of the ether and fractionation gave 8.3 g. (48%) of material which boiled at 252–253°. This darkened on standing and redistillation gave 5 g. (29%) of material of the same boiling point; $n^{20}\text{D}$ 1.5338; d^{20}_4 0.9249; MR_D[9] calcd. 64.80; and MR_D found, 64.93.

Anal. Calcd. for $C_{11}H_{19}NSi$: Si, 14.50. Found: Si, 14.95.

Trimethyl-*p*-tolylsilane.—To 16.2 g. (0.15 mole) of trimethylsilyl chloride in 50 cc. of ether was added, slowly and with cooling, 0.157 mole of *p*-tolyllithium in 130 cc. of ether. After three hours refluxing the reaction mixture was worked up in the usual manner. Fractionation gave 16.2 g. (66%) of product boiling at 192°; $n^{20}\text{D}$ 1.4910; d^{20}_4 0.8666; MR_D[9] calcd., 54.77; and MR_D found 54.97.

Anal. Calcd. for $C_{10}H_{16}Si$: Si, 17.05. Found: Si, 16.83.

Trimethyl-*p*-chlorophenylsilane.—The procedure of Burkhard[10] for the preparation of this compound from *p*-chlorophenylmagnesium bromide and trimethylsilyl chloride in ether gave only a 29% yield even after forty-three hours reflux. When run for thirty-six hours at 78° after removal of the ether the yield was 43%. The constants, $n^{20}\text{D}$ 1.5090; d^{20}_4 1.0002; MR_D[9] calcd. 55.02; and found 55.01; differ from the reported values of $n^{20}\text{D}$ 1.5128; d^{20}_4 1.0282.

Anal. Calcd. for $C_9H_{13}ClSi$: Si, 15.19; Cl, 19.28. Found: Si, 15.16; Cl, 19.22.

Trimethylbenzylsilane.—Bygden[11] employed benzyltrichlorosilane and methylmagnesium bromide for the preparation of this compound and reported a boiling point of 191.2–191.4° and $n^{20}\text{D}$ 1.4909. In these present studies the reaction between 16.2 g. (0.15 mole) of trimethylsilyl chloride and the Grignard reagent obtained from 31.6 g. (0.25 mole) of benzyl chloride and 6.3 g. (0.26 g. atom) of magnesium was carried out in the absence of solvent. Initially the reactants were stirred for two hours, then heated for thirty-six hours in an oil-bath at 73°, and finally heated to reflux, with stirring, for seven hours after the addition of 50 cc. of ether. Hydrolysis was effected by addition of ammonium chloride solution. Subsequent to ether extraction, drying of the extracts over sodium sulfate, and removal of the ether by distillation there was obtained 18.2 g. (74%) of product boiling at 93° (35 mm.); $n^{20}\text{D}$ 1.4916.

Trimethyl-β-phenylethylsilane.—To the solvent-free Grignard reagent which had been prepared from 28.1 g. (0.2 mole) of β-phenylethyl chloride in 40 cc. of ether and 5.1 g. (0.21 g. atom) of magnesium turnings in 40 cc. of ether there was added, with cooling in cold water, 16.9 g. (0.157 mole) of trimethylsilyl chloride. After stirring for one hour the mixture was heated in an oil-bath at 70–75° for forty hours without stirring. Fifty cc. of ether was then added and the mixture was hydrolyzed by the addition of a solution of ammonium chloride and finally some dilute (1:3) hydrochloric acid. After extraction and washing the extracts with water they were dried over sodium sulfate. Removal of the ether and distillation of the product gave 16.2 g. (58%) of material which boiled at 211°; $n^{20}\text{D}$ 1.4869; d^{20}_4 0.8657; MR_D[9] calcd. 59.30; and MR_D found 59.21.

Anal. Calcd. for $C_{11}H_{18}Si$: Si, 15.71. Found: Si, 15.69.

Tri-*n*-butylphenylsilane.—To 52 g. (0.25 mole) of redistilled ethyl silicate in 100 cc. of ether was added, at a rate to promote gentle reflux, 0.75 mole of *n*-butyllithium[12] in 600 cc. of ether. The mixture was then stirred for one and one-half hours and refluxed for two and one-half hours. At the end of that time Color Test I[8] was negative and there was then added 0.27 mole of phenyllithium[13] in

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[6] Whitmore Sommer, Gold and Van Strien, THIS JOURNAL, **69**, 1551 (1947).

[7] Benkeser, Doctoral Dissertation, Iowa State College, 1947.

[8] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[9] See Sauer, *ibid.*, **68**, 954 (1946), for the values used in calculating these molecular refractions.

[10] Burkhard, *ibid.*, **68**, 2103 (1946).

[11] Bygden, *Ber.*, **45**, 707 (1912).

[12] (a) The titer of the solution was determined by the double titration procedure of Gilman and Haubein, THIS JOURNAL, **66**, 1515 (1944). (b) For an improved procedure for the preparation of *n*-butyllithium see Gilman and Stuckwisch, *ibid.*, **65**, 1461 (1943).

[13] Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932).

185 cc. of ether. After one and one-half hours of refluxing and stirring the mixture was cooled in an ice-bath and was hydrolyzed by the addition of dilute hydrochloric acid. The reaction was worked up in the usual manner and the ether extracts were dried over calcium chloride. By distillation there was obtained 53 g. of material boiling at 118–140° (1–5 mm.). Redistillation gave 43 g. (62%) of product with a boiling point of 116–118° (0.9 mm.); n^{20}_{D} 1.4891; d^{20}_{4} 0.8719; MR_{D}[9] calcd. 91.73; and found 91.65.

Anal. Calcd. for $C_{18}H_{32}Si$: Si, 10.12. Found: Si, 10.19.

In a later run only a 26% yield of the product was obtained even though the conditions were apparently the same as those described above.

Cleavage of Tri-*n*-butylphenylsilane.—A refluxing solution of 10 g. (0.0363 mole) of the silane in 50 cc. of glacial acetic acid was treated with anhydrous hydrogen chloride for fifteen hours. On cooling, a second layer which was present was separated and taken up in ether. After washing with water the ethereal solution was dried over sodium sulfate. From this solution there was obtained by distillation 0.7 g. of material which boiled at 87–89° (0.35 mm.); n^{20}_{D} 1.4449; and, 2 g. which distilled at 143° at that pressure; n^{20}_{D} 1.4470.

The acetic acid was added slowly to 50 g. of sodium carbonate in 150 cc. of water and the oil which separated was taken up in ether. After drying and removal of the ether the residual liquid was distilled to give 2.2 g. of material which boiled at 85° (0.3 mm.); n^{20}_{D} 1.4442; and 0.7 g. distilling at about 135° (0.3 mm.); n^{20}_{D} 1.4475. All of the latter substance distilled before a definite boiling point could be determined.

The two low boiling fractions were combined and the density was found to be d^{20}_{4} 0.8493; MR_{D}[9] calcd. for tri-*n*-butylsilanol 67.93; and found 67.68.

Anal. Calcd. for $C_{12}H_{28}OSi$: Si, 12.96. Found: Si, 13.12.

The combined higher boiling fractions had a density of d^{20}_{4} 0.8400; MR_{D}[9] calcd. for hexa-*n*-butyldisiloxane 132.06; and MR_{D} found 131.73.

Anal. Calcd. for $C_{24}H_{54}OSi_2$: Si, 13.52. Found: Si, 13.32.

The combined yield of the silanol and the disiloxane represents a cleavage of 72% of the original starting material.

In a later run of the same size as above the condenser outlet was connected to a trap in a Dry Ice–acetone-bath. The reaction was continued for fifteen hours; benzene was collected by the trap during the first eleven hours. The benzene was distilled to give 1.9 g. (68%) boiling at 79–81° and was identified as *m*-dinitrobenzene. The acetic acid solution was worked up by neutralization with 20% sodium carbonate solution to give 2 g. (24%) of the silanol boiling at 81–83° (0.45 mm.); n^{20}_{D} 1.4460; and 5.3 g. (71%) of the disiloxane which boiled at 136–138° (0.5 mm.); n^{20}_{D} 1.4470.

Tri-*n*-butylsilyl Chloride.—This compound was prepared according to the procedure of Whitmore and coworkers[14] for the preparation of triethylsilyl chloride. They reported the preparation of the tri-*n*-butyl derivative by the same method but gave no constants. A 0.079 mole run gave a 51% yield of product boiling at 142–144° (29 mm.); n^{20}_{D} 1.4480; d^{20}_{4} 0.8788; MR_{D}[9] calcd. 71.68; and, MR_{D} found 71.44.

Anal. Calcd. for $C_{12}H_{27}ClSi$: Cl, 15.12. Found: Cl, 15.23.

Tri-*n*-butylsilanol.—The procedure followed was in essential accordance with that of Ladenburg[15] for the preparation of triethylsilanol.

To a vigorously stirred solution of 3 cc. of concentrated ammonium hydroxide in 30 cc. of distilled water was slowly added 3 g. (0.0128 mole) of tri-*n*-butylsilyl chloride. After stirring for one hour the mixture was extracted with ether and the extracts were washed with 10-cc. portions of 1:30 ammonium hydroxide until free of chloride and then with water before drying over sodium sulfate. The ether was removed by distillation and the residual liquid gave 1.5 g. (53%) of product which boiled at 99–99.5° (1 mm.); n^{20}_{D} 1.4470; d^{20}_{4} 0.8505; MR_{D}[9] calcd. 67.93; and MR_{D} found 67.86.

Anal. Calcd. for $C_{12}H_{28}OSi$: Si, 12.96. Found: Si, 13.12.

Hexa-*n*-butyldisiloxane.—In a procedure patterned after the method of Whitmore and co-workers,[16] a mixture of 3 g. (0.014 mole) of tri-*n*-butylsilanol and 1.76 g. (0.007 mole) of iodine was heated to 150° in an oil-bath. During this time some water collected in the condenser. The bath was cooled to 110–120° and was kept there for the remainder of the forty-five minutes reaction time. The mixture was taken up in ether and was shaken with 10% sodium sulfite solution until the iodine color was removed. The aqueous layer was extracted with ether and the combined ethereal solutions were dried over sodium sulfate. After distillation of the ether, 2.2 g. (74%) of the disiloxane was obtained, boiling at 138–140° (0.75 mm.); n^{20}_{D} 1.4470; d^{20}_{4} 0.8372; MR_{D}[9] calcd. 132.06; and MR_{D} found 132.34.

Anal. Calcd. for $C_{24}H_{54}OSi_2$: Si, 13.52. Found: Si, 13.75.

Diethyldiphenylsilane.—To 15.7 g. (0.1 mole) of diethyldichlorosilane[17] in 50 cc. of dry ether was added 0.21 mole of phenyllithium[13] in 185 cc. of ether. After refluxing for four hours the reaction was hydrolyzed by the addition, with cooling, of water and was worked up in the usual manner to give 18.1 g. (75%) of product distilling at 101–103° (0.3–0.4 mm.); n^{20}_{D} 1.5605; d^{20}_{4} 0.9853; MR_{D}[9] calcd. 79.28; and MR_{D} found 78.92. Previous reports of the preparation of this compound by disproportionation of triethylphenylsilane[18] and by the reaction of ethylmagnesium bromide with diphenyldichlorosilane[3d] gave no constants other than boiling points of 305–315° and 295–298°, respectively.

Cleavage of Diethyldiphenylsilane.—Gaseous hydrogen chloride was passed into a refluxing solution of 10 g. (0.041 mole) of diethyldiphenylsilane in 50 cc. of acetic acid for fifteen hours. At the end of that time the material which had collected in the Dry Ice–acetone trap was distilled to yield 4.4 g. of benzene which boiled at 80–82° and was identified as *m*-dinitrobenzene. This represents a 68% removal of both phenyl groups present in the original molecule. Attempted fractionation of the diethyldichlorosilane to separate it from the acetic acid was not successful.

Tribenzyl-*p*-anisylsilane.—*p*-Anisyllithium[19] was prepared from 2.12 g. (0.3 g. atom) of lithium in 92 cc. of dry ether and 24.8 g. (0.13 mole) of *p*-bromoanisole in 120 cc. of dry ether. The solution was filtered through cotton and was added at a rapid dropwise rate to 27.5 g. (0.082 mole) of tribenzylsilyl chloride[20] in 150 cc. of anhydrous ether. The stirred mixture was refluxed overnight and was then hydrolyzed by the addition of water and was worked up in the usual manner. The product crystallized readily on addition of a small amount of ether and 95%

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[14] DiGiorgio, Strong, Sommer and Whitmore, *ibid.*, **68**, 1380 (1946).

[15] Ladenburg, *Ann.*, **164**, 300 (1872).

[16] Sommer, Pietrusza and Whitmore, THIS JOURNAL, **68**, 2282 (1946).

[17] Purchased from the Dow-Corning Corporation, Midland, Michigan.

[18] Friedel and Ladenburg, *Ann.*, **159**, 259 (1871).

[19] Edward, unpublished studies, Iowa State College.

[20] Martin and Kipping, *J. Chem. Soc.*, **95**, 302 (1909). The needed tribenzylsilanol was prepared in essential accordance with the procedure of Dilthey, *Ber.*, **38**, 4132 (1905), with the exception that instead of several days of standing prior to refluxing the mixture of silicon tetrachloride and benzylmagnesium chloride it was stirred for four hours, refluxed for eighteen hours, and stirred without heating for an additional two hours to give a 58% yield of product which melted at 101–103.5°. No yield is given in the literature.

ethanol and one crystallization from 95% ethanol gave 21.5 g. (66%) of product which melted at 83–85°. Another crystallization did not improve the melting point.

Anal. Calcd. for $C_{28}H_{28}OSi$: Si, 6.84. Found: Si, 7.19.

Cleavage of Tribenzyl-*p*-anisylsilane.—The cleavage of 8 g. (0.0195 mole) of the silane in 40 cc. of glacial acetic acid was carried out in the usual manner. After fifteen hours the solution was cooled and 3.2 g. of a colorless solid was filtered off. This material melted at 131–134° and was evidently slightly impure tribenzylsilyl chloride. It was placed in 20 cc. of water and was allowed to stand overnight to give 2.9 g. of tribenzylsilanol which melted at 101.5–103.5° and did not depress the melting point of an authentic sample.

The acetic acid solution was added to about 50 cc. of water and was steam distilled to remove the anisole. The residue in the flask deposited crystals which, after purification from a chloroform–petroleum ether (b. p. 60–68°) mixture, proved to be 2 g. of the silanol with a melting point of 103–104°. Thus, the total silanol isolated was 4.9 g. (79%).

The steam distillate was extracted with ether and the combined extracts were washed with dilute sodium carbonate solution and dried over sodium sulfate. Removal of the ether and distillation of the residue gave 1.8 g. (84%) of anisole which was identified as the 2,4-dinitro derivative.

Cleavage of Tetra-*o*-tolyldisilanediol.—The cleavage of 5 g. (0.011 mole) of the diol, prepared according to the procedure of Smart,[21] in 35 cc. of acetic acid was carried out in the usual manner during fifteen hours. After about thirty minutes the reaction mixture deposited a white solid which remained throughout the course of the reaction and was filtered off at the end. This material did not melt, showed only a very slight darkening when heated, and was immediately dissolved by hydrofluoric acid. It weighed 1.3 g. and was thus a quantitative yield of silica.

The material which had collected in the cold trap was added to 20% sodium carbonate solution and, after extraction, drying and removal of the ether, there was obtained 1.7 g. of liquid of rather indefinite boiling point which was identified as toluene by conversion to 2,4-dinitrotoluene. This represents a 43% yield of toluene based on the removal of all four of the groups.

Distillation of the acetic acid from the reaction mixture did not leave any residue. Attempted nitration of the toluene, which co-distilled, by four hours of refluxing of the acetic acid solution with 8 cc. of fuming nitric acid was unsuccessful, only a very small amount of material which appeared to be crude *p*-nitrobenzoic acid being obtained.

Acknowledgment.—The authors are grateful to Dr. Robert A. Benkeser and William J. Meikle for their assistance.

Summary

Organosilanes have been shown to undergo cleavage by anhydrous hydrogen chloride, a reaction characteristic of organometallic compounds. The order of ease of removal of radicals is in essential agreement with the series previously established with organic derivatives of mercury and lead.

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[21] Smart, unpublished studies, Iowa State College.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Pore Structure in Activated Charcoal. I. Determination of Micro Pore Size Distribution

BY A. J. JUHOLA[1,2] AND EDWIN O. WIIG

I. Determination of Micro Pore Size Distribution

A knowledge of the pore size distribution is important in the evaluation of charcoals as catalyst carriers and in the interpretation of physical adsorption. The need for such knowledge in the development of better gas mask charcoals prompted a search for a method of determining pore diameters and volumes. During the period December, 1943, to July, 1945, a practical method was developed at the Division 10 Central Laboratory of the National Defense Research Committee at Northwestern Technological Institute. Since then a more fundamental study of pore structure has been continued in this Laboratory in an attempt to clarify the many points of uncertainty in the method.

Briefly, to determine a complete pore size distribution curve four quantities need to be determined (1) Total Pore Volume, which is equal to the volume of the charcoal by mercury displacement minus the volume of the charcoal by helium displacement, (2) Submicro Pore Volume, which is equal to the volume of charcoal by liquid water displacement minus the volume of the charcoal by helium displacement, (3) Micro Pore Size Distribution by application of the Kelvin equation to the desorption side of the water adsorption isotherm, and (4) Macro Pore Size Distribution, by measuring the quantities of mercury forced, at known pressures, into the pores of the charcoal. The sum of the submicro, micro and macro pore volumes makes up the total pore volume. The micro pore diameter range is believed to be between 10 and 30 Å. and the macro pore range between 30 and 100,000 Å. It was first thought that the submicro pore volume was the volume of pores below about 10 Å. but experimental evidence obtained later seems to indicate that it is not due to small pores but to void space between sorbed water molecules, since the closest packing cannot be attained in pores whose diameters are only 2 to 10 molecular diameters. The present paper, the first of a series concerned with pore size and pore distribution in charcoal, deals with the applica-

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