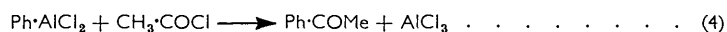
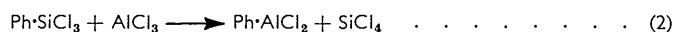
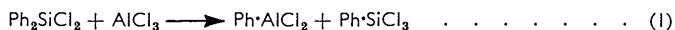


907. *Organosilicon Compounds. Part XXIV.*¹ *An Investigation of Reported Cleavages of Aryl-Silicon Bonds by Aluminium Chloride.*

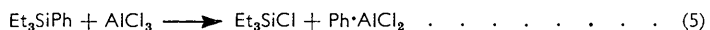
By J. D. AUSTIN, C. EABORN, and J. D. SMITH.

Contrary to earlier reports, aryl-silicon bonds in arylsilicon chlorides are not cleaved by aluminium chloride to give arylaluminium compounds. In the presence of water, acid cleavage occurs; for example, trichlorophenylsilane gives benzene and silicon tetrachloride. In the presence of aluminium chloride, acetyl chloride converts trichlorophenyl- and trichloro-*m*-tolyl-silane into acetophenone and methyl *m*-tolyl ketone, respectively, and phosphorus trichloride converts trichlorophenylsilane into dichlorophenylphosphine, but such reactions probably do not involve organoaluminium intermediates as suggested by earlier workers.

SEVERAL experiments have been thought to demonstrate cleavage of alkyl- or aryl-silicon bonds by aluminium chloride. Thus, when Evison and Kipping treated dichlorodiphenylsilane with aluminium chloride at 70°, silicon tetrachloride distilled out and the residue gave benzene when treated with water, and acetophenone when treated with acetyl chloride.² The results were interpreted in terms of reactions (1)–(4).



Evison and Kipping also obtained silicon tetrachloride, in 80% yield, when they treated tetraphenylsilane with aluminium chloride in chloroform. In a similar experiment, Manulkin³ obtained silicon tetrachloride and steam-distilled the residue to give benzene in 67% yield. He also obtained silicon tetrachloride, in 44% yield, and ethane from tetraethylsilane under similar conditions.³ (Eaborn, however, found that tetraethylsilane did not react with aluminium iodide in the absence of a solvent.⁴) Dolgov and Panina⁵ found that a mixture of aluminium chloride and triethylphenylsilane gave benzene and triethylsilanol on treatment with water, and acetophenone on treatment with acetyl chloride, and suggested that equation (5) represented the initial reaction.



Yakubovich and Motsarev reported that trichlorophenylsilane reacted with aluminium chloride at room temperature to give phenylaluminium dichloride.⁶ For example, they kept a mixture of the two reagents at 25–35° for 48 hr. and on vacuum distillation obtained silicon tetrachloride in 50% yield; treatment of the residue with water gave benzene in 81% yield. In separate experiments, the residue was treated with acetyl chloride to give acetophenone and with phosphorus trichloride to give dichlorophenylphosphine, and they interpreted their results in terms of reactions (2–4) and (6):



Similarly, from trichloro-*p*-chloro- or trichloro-*p*-bromo-phenylsilane they obtained silicon tetrachloride and chloro- or bromo-benzene, *p*-chloro- or *p*-bromo-acetophenone, and *p*-chloro- or *p*-bromo-phenyldichlorophosphine. They interpreted reactions involving

¹ Part XXIII, Eaborn and Niederprüm, *J.*, 1963, 797.

² Evison and Kipping, *J.*, 1931, 2774.

³ Manulkin, *Zhur. obshchei Khim.*, 1948, **18**, 299.

⁴ Eaborn, *J.*, 1949, 2755.

⁵ Dolgov and Panina, *Zhur. obshchei Khim.*, 1948, **18**, 1293.

⁶ Yakubovich and Motsarev, *Zhur. obshchei Khim.*, 1953, **23**, 771, 1547; *Doklady Akad. Nauk. S.S.S.R.*, 1953, **88**, 87.

dichlorodiphenylsilane analogously, in terms of reactions (1)—(3), and they concluded that cleavage of aryl-silicon bonds by aluminium chloride provides a valuable method of preparing arylaluminium compounds.*

More recently, Russell studied the disproportionation of compounds $R\cdot SiMe_3$.⁸ He concluded that organoaluminium intermediates were not involved in the disproportionations, but mentioned that side reactions included cleavages of organosilicon compounds by metal halides. No organoaluminium compounds were isolated but their formation was inferred from hydrolysis products.

There thus seemed to be considerable evidence that aryl-silicon and even alkyl-silicon bonds are cleaved by aluminium chloride, with formation of organoaluminium compounds, and such cleavages were the bases of several possible mechanisms suggested for some reactions of organosilicon compounds.⁹ The only report which did not fit into the pattern outlined above was by Rochow and Gilliam, who, while finding that dichlorodiphenylsilane in the presence of aluminium chloride gave silicon tetrachloride and benzene, showed that only small amounts of aluminium chloride were necessary.¹⁰ They concluded that the reaction was complex and cyclic, and that no organoaluminium compounds were formed even as intermediates.^{10,11}

We have reinvestigated the behaviour of mixtures of aryltrichlorosilane and aluminium chloride, and have shown that no reaction occurs when impurities are absent, and that the reactions which take place in the presence of moisture or hydrogen chloride do not involve aryl-aluminium compounds.

EXPERIMENTAL

Materials.—Aluminium chloride (a good commercial grade) was sublimed several times under a vacuum and then fused with aluminium wire in a sealed tube for 12 hr. at 200°. The tube was opened under a vacuum, and the aluminium chloride was sublimed as a white powder (Found: Al, 20.1; Cl, 79.3. Calc. for $AlCl_3$; Al, 20.2; Cl, 79.8%) into a container which was then stored in a nitrogen-filled dry-box.

Aryltrichlorosilanes, $X\cdot C_6H_4\cdot SiCl_3$, fractionally distilled in nitrogen at reduced pressure, were collected in flasks which were sealed and stored in the dry-box; the b. p.s were: (X =) H, 96—98°/20 mm.; *p*-Cl, 78—80°/1.0 mm.; *m*-Me, 116—118°/30 mm. Dichlorodiphenylsilane, similarly purified, had b. p. 160—161°/10 mm. and dichloro-*p*-chlorophenylsilane b. p. 160—162°/1.0 mm.

Vapour-phase chromatography (in a 10-ft. tube at 150° packed with silicone oil on "Embacel," with nitrogen as carrier gas and a detector of the thermal-conductivity type) revealed no impurities in the aryltrichlorosilanes thus purified.

Trichlorophenylsilane and Aluminium Chloride.—(a) At 35°. Trichlorophenylsilane (6.7 g., 32 mmoles) and aluminium chloride (4.2 g., 32 mmoles) were mixed in a 25-ml. flask in the dry-box, and the flask was removed from the box and quickly fitted to a reflux condenser attached to a vacuum-line. The mixture was kept at 35° for 48 hr. (conditions used by Yakubovich and Motsarev⁶), during which the pressure was gradually reduced so that material markedly more volatile than trichlorophenylsilane was transferred to a trap cooled in liquid nitrogen. The amount of material thus collected weighed between 0.10 and 0.20 g. in a series of experiments.

(b) At 70—80°. The previous experiment was repeated except that the mixture was kept at 70—80° for 10 hr. (also conditions used by Yakubovich and Motsarev⁶), but again the amount of volatile material did not exceed 0.20 g. (even though the pressure was ultimately

* Yakubovich and Motsarev also reported that dichlorodiphenylsilane and ferric chloride react to give phenyliron dichloride.⁷ In view of our results with aluminium chloride it seems improbable that ferric chloride cleaves aryl-silicon bonds in this way.

⁷ Yakubovich and Motsarev, *Zhur. obshchei Khim.*, 1953, **23**, 1059.

⁸ Russell, *J. Amer. Chem. Soc.*, 1959, **81**, 4815, 4825.

⁹ Eaborn, "Organosilicon Compounds," Butterworths Scientific Publ., London, 1960, pp. 69, 126—127.

¹⁰ Rochow and Gilliam, *J. Amer. Chem. Soc.*, 1945, **67**, 1772.

¹¹ Rochow, personal communication.

reduced to 1 mm.), and most of this was collected during the first 15 min. of heating; vapour-phase chromatography and infrared spectroscopy showed it to be a mixture of benzene and silicon tetrachloride. Unchanged trichlorophenylsilane, b. p. 96—98°/20 mm., was distilled from the residue in 85% yield, and 90% of the aluminium chloride was recovered subsequently by sublimation.

(c) *With crude trichlorophenylsilane.* When a commercial sample of trichlorophenylsilane (likely to contain hydrogen chloride, and possibly some silanols) was used without purification under the conditions of experiment (b), 1.12 g. of volatile material was collected in 3 hr. It was shown to be a mixture of benzene and silicon tetrachloride.

(d) *With addition of water.* A small amount of water was added to purified trichlorophenylsilane (6.7 g., 32 mmoles) and aluminium chloride (4.2 g., 32 mmoles), and the mixture was heated at 80° under 1 atmosphere of dry nitrogen for 3 hr. in the apparatus described above. Volatile material (shown by vapour-phase chromatography and infrared spectroscopy to be a mixture of silicon tetrachloride and benzene) was then collected at 1 mm., weighed, and treated with water at 0°; weighing, after drying, of the silica produced gave the amount of silicon tetrachloride formed, and the remainder of the volatile material was assumed to be benzene.

From one mole of water were produced two moles each of silicon tetrachloride and benzene, as shown in the following Table.

H ₂ O (mmoles)	2.2	3.3	4.4	5.55	11.1
SiCl ₄ (mmoles)	4.2	6.5	8.4	10.7	21.4
C ₆ H ₆ (mmoles)	4.3	6.3	8.6	10.6	21.2
Cleavage of Ph·SiCl ₃ (%)	13	20	27	33	67.5

(e) *With added water, and varying amounts of aluminium chloride.* A procedure similar to that in experiment (d) was used, but water (3.3 mmoles) was added to a mixture of trichlorophenylsilane (31.8 mmoles) and varying amounts of aluminium chloride. The amount of cleavage of the aryl-silicon bond was independent of the amount of aluminium chloride present, as shown in the following Table.

AlCl ₃ (mmoles)	31.8	21.4	10.4	4.7	3.0
SiCl ₄ (mmoles)	6.5	6.1	6.4	6.4	6.5
C ₆ H ₆ (mmoles)	6.3	6.6	6.5	6.5	6.5

Experiments with Rigorous Exclusion of Moisture.—An all-glass apparatus connected to a vacuum-line was used in experiments involving rigorous exclusion of moisture.

Aluminium chloride (31.8 mmole) was transferred within the dry-box to a tube which was then sealed and attached *via* a break-seal to the vacuum-line. Trichlorophenylsilane (31.8 mmoles) was distilled in the vacuum-system into a trap, A, kept at -78°. The break-seal on the aluminium chloride container was broken and the solid was sublimed into a trap A. With the system under 3 mm. pressure of dry nitrogen, and with a trap B, adjoining trap A, kept at -78° so that volatile material collected in it, trap A, containing the reaction mixture, was heated at 80° for 8 hr. No pressure change occurred, and no material collected in trap B, indicating that no hydrogen chloride, silicon tetrachloride, or benzene was formed.

Similar results were obtained with trichloro-*p*-chlorophenyl-, trichloro-*m*-tolyl-, dichloro-*p*-chlorophenyl-, and dichlorodiphenyl-silane, two moles of aluminium chloride being used with each mole of the diaryldichlorosilanes.

Trichlorophenylsilane and Aluminium Chloride in Chloroform.—Reagent-grade chloroform was shaken with concentrated sulphuric acid, washed with water, stored over anhydrous calcium chloride for 24 hr., and fractionated with exclusion of moisture. The centre fraction, b. p. 60—61°, was collected in a bottle of dark glass which was then stored in the nitrogen-filled dry-box.

In the vacuum-line mentioned above, chloroform (7 ml.) was distilled at 0°, and then redistilled on to a mixture of trichlorophenylsilane (6.7 g., 32 mmoles) and aluminium chloride (4.2 g., 32 mmoles). The mixture was heated at 60° for 3 hr., and material markedly more volatile than trichlorophenylsilane (including the chloroform) was then distilled into a cold trap. The infrared spectrum and vapour-phase chromatographic analysis of the distillate showed that benzene was absent, and no precipitate was obtained when water was added, indicating that silicon tetrachloride was also absent.

A similar experiment with dichlorodiphenylsilane (6.1 g., 24 mmoles) and aluminium chloride (6.4 g., 48 mmoles) also gave no detectable silicon tetrachloride or benzene.

Aryltrichlorosilane with Aluminium Chloride and Acetyl Chloride.—In the usual vacuum-line, acetyl chloride was distilled several times at 0° to remove hydrogen chloride, and then some of it (2.5 g., 32 mmoles) was distilled into a mixture of trichlorophenylsilane (6.7 g., 31 mmoles) and aluminium chloride (4.2 g., 32 mmoles). The mixture was kept at 55° for 4 hr., and volatile material was transferred to a cold trap (and shown by vapour-phase chromatography to be silicon tetrachloride containing a little acetyl chloride) and treated with water at 0°. The silicic acid produced was dried and weighed as silica (1.60 g.), in amount corresponding to formation of silicon tetrachloride in 84% yield. An excess of water was added to the less volatile residue, and benzene-extraction, followed by washing, drying, and distillation of the extract, gave acetophenone (3.4 g., 90%), b. p. 202—204° (semicarbazone, m. p. 199°).

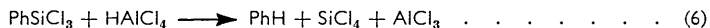
A similar experiment involving trichloro-*m*-tolylsilane gave silicon tetrachloride in 84% yield, and 3-methylacetophenone, b. p. 219—221°, in 81% yield. The ketone was shown to be free from its 2- and 4-isomers by infrared spectroscopy and by vapour-phase chromatography (involving silicone oil on "Embacel" at 185°).

Trichlorophenylsilane with Aluminium Chloride and Phosphorus Trichloride.—Phosphorus trichloride was distilled several times in the vacuum-system and some (4.3 g., 31 mmoles) was then condensed on to a mixture of aluminium chloride (4.2 g., 32 mmoles) and trichlorophenylsilane (6.6 g., 31 mmoles). The mixture was kept at 75° for 8 hr. Volatile material was transferred to a cold trap, identified as silicon tetrachloride, and hydrolysed to give silica (1.54 g., after drying, corresponding to an 81% yield of the tetrachloride). The less-volatile residue was extracted with benzene, and the extract was distilled to give dichlorophenylphosphine, (4.6 g., 82%), b. p. 214—216°; the vapour-phase chromatogram (involving silicone oil on "Embacel" at 130°) of the product had only one peak, with retention time corresponding with that of authentic dichlorophenylphosphine,¹² showing that little, if any, trichlorophenylsilane, which has a different retention time, was present.

DISCUSSION

Some features of the above results, and some comments are as follows:

(1) Contrary to the earlier reports,^{2,3} trichlorophenyl-, trichloro-*p*-chlorophenyl-, and dichlorodiphenyl-silane do not react with aluminium chloride, in the presence or absence of solvent. If water is present, hydrogen chloride is formed by hydrolysis of aluminium chloride (and possibly of the silicon chloride), and the aryl-silicon bonds are then cleaved by the strong acid, HAlCl_4 [reaction (6)] which is known¹³ to destroy carbon-silicon bonds.



(2) Our results are consistent with Rochow and Gilliam's observation that far less than stoichiometric amounts of aluminium chloride effected complete decomposition of dichlorodiphenylsilane.

(3) Earlier reports of cleavage of arylsilicon chlorides by aluminium chloride, with formation of arylaluminium compounds, were probably in error because moisture (or hydrogen chloride) was not rigorously excluded. We think that reports of cleavage of tetra-phenyl-,^{2,3} -benzyl-,² and -ethyl-silane³ by aluminium chloride are probably in error for the same reason. A conclusion that tetraethylsilane was cleaved by aluminium iodide in benzene⁴ is almost certainly in error; the hexaethyldisiloxane isolated after addition of water presumably came from triethyliodosilane formed in aluminium iodide-catalysed cleavage of tetraethylsilane by hydrogen iodide. Evidence for cleavage of triethylphenylsilane by aluminium chloride,⁵ and of trimethylphenylsilane by aluminium chloride or bromide,⁸ also involved isolation of products after addition of water.

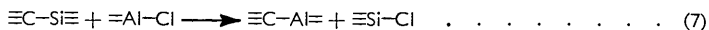
(4) Organoaluminium compounds rapidly convert silicon halides into organosilicon compounds.¹⁴ Our results suggest that reaction (7) is effectively irreversible: if it were an

¹² Buchner and Lockhart, *J. Amer. Chem. Soc.*, 1951, **73**, 755.

¹³ George, U.S.P. 2,802,852/1957; *Chem. Abs.*, 1957, **51**, 17,982.

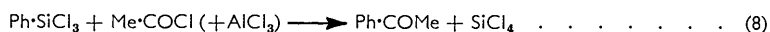
¹⁴ B.P. 689,436; *Chem. Abs.*, 1954, **48**, 3992; Hurd, *J. Amer. Chem. Soc.*, 1945, **67**, 1545; Lengyel and Székely, *Z. anorg. Chem.*, 1956, **287**, 273; Brown, U.S.P. 2,762,824/1957; *Chem. Abs.*, 1957, **51**, 7412.

equilibrium lying detectably to the right, cleavage would occur if the silicon halide were removed continuously.



(5) In view of our results, we doubt the accuracy of Manulkin's report³ that tetraethyl-, tetrabutyl-, and tetraphenyl-stannane are cleaved by aluminium chloride. Cleavage of the much weaker carbon-lead bonds by aluminium chloride has been suggested,¹⁵ and it is more likely since carbon-lead bonds are known¹⁶ to be more readily cleaved by electrophilic reagents than carbon-tin and carbon-silicon bonds. However, it should be noted that no organoaluminium compounds have been isolated from such reactions: Gilman and Apperson, for example, inferred their formation from the benzophenone produced by addition of benzoyl chloride, and the benzene produced by addition of water to a mixture of tetraphenylplumbane and aluminium chloride.¹⁵

(6) In the presence of aluminium chloride, trichlorophenylsilane reacts with acetyl chloride and phosphorus trichloride to give acetophenone and dichlorophenylphosphine, respectively reactions (8) and (9):



Trichloro-*m*-tolylsilane with acetyl chloride and aluminium chloride analogously gives 3-methylacetophenone, the non-production of 2- and 4-isomers indicating the direct replacement of the trichlorosilyl by the acetyl group, rather than acetylation followed by acid cleavage, or acid cleavage to give toluene which is then acetylated. (In some of the experiments^{2,6} in which acid-cleavage of $\text{X}\cdot\text{C}_6\text{H}_4\text{-Si}$ bonds was followed by addition of acetyl chloride, some of the ketone $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{COMe}$ may, of course, have come from direct acetylation of the compound $\text{X}\cdot\text{C}_6\text{H}_5$.)

There is no reason to believe that organoaluminium compounds are involved as intermediates in these reactions. Electrophilic reagents which cleave aryl-hydrogen bonds also cleave aryl-silicon bonds, and usually much more rapidly,¹⁶ and reactions (8) and (9) are to be regarded as direct cleavages of Ph-SiCl_3 bonds by the complexes $\text{CH}_3\cdot\text{COCl}\cdot\text{AlCl}_3$, $\text{PCl}_3\cdot\text{AlCl}_3$, analogous to cleavage of Ph-H bonds in Friedel-Crafts acetylation and dichlorophosphinylation of benzene. The displacements of the trichlorosilyl group may involve cyclic mechanisms, as in (I) and (II).



(7) There is now no basis for the suggested mechanisms⁹ of aluminium halide-catalysed reactions of organosilicon compounds involving initial cleavage of carbon-silicon bonds by aluminium halide to give organoaluminium compounds (though such mechanisms cannot be positively ruled out).

(8) Our results remove the previously noted anomaly¹⁷ that, although carbon-silicon bonds are reported to be destroyed by aluminium chloride, several aluminium chloride-catalysed reactions of organic groups attached to silicon proceed without complications.

The experimental work described was carried out at the University of Leicester. We thank Albright and Wilson (Mfg.) Ltd. for a maintenance award (to J. D. A.), and Mr. J. S. Hughes, of Midland Silicones Ltd., for his interest and encouragement.

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[Received, April 11th, 1963.]

¹⁵ Gilman and Apperson, *J. Org. Chem.*, 1939, **4**, 162.

¹⁶ Ref. 9, pp. 146-157; Eaborn and Pande, *J.*, 1960, 1566.

¹⁷ Ref. 9, pp. 127, 146, 155.