added and the solution refluxed for six hours; ammonia was evolved during this operation. The resulting solution was cooled and acidified to congo red with hydrochloric acid. The precipitated suberic acid was collected on a filter and recrystallized from water, m. p. 138–140°; neut. eq., 86.4. There was no depression of the melting point when mixed with an authentic sample of suberic acid.

Hydrolysis of 1,1,1,9-Tetrachlorononane.—A mixture of 500 g. of concentrated sulfuric acid and 15 g. of water was heated to 95° with stirring on a steam-bath, and 133 g. (0.5 mole) of 1,1,1,9-tetrachlorononane was dropped in over a period of one hour. Stirring and heating were continued for three hours. The solution was then cooled, poured on 1200 g. of cracked ice, and extracted with two 100-ml. portions of carbon tetrachloride. The extract was dried over magnesium sulfate and distilled to obtain 55 g. (57% of the theoretical) of a chloro acid, presumably 9-chlorononanoic acid, boiling at 163.5–167° (7.5 mm.); n^{36}D 1.4540; calcd. for $C_9H_{17}O_2Cl$: neut. eq., 192.5; found: neut. eq., 192.8.

Summary

The benzoyl peroxide-initiated reaction of ethylene with carbon tetrachloride gives a series of compounds having the general formula $Cl(CH_2CH_2)_nCCl_3$. When the reaction is carried out at 1500 lb./sq. in. the product is comprised principally of these compounds in which n has the values 1–4. The effect of reaction conditions on the proportions of individual members of this series in the reaction product is described.

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[Contribution from the Department of Chemistry, University of Delaware]

I. The Peroxide-Catalyzed Chlorination of Trimethylchlorosilane and *t*-Butyl Chloride[1]

By J. J. McBride, Jr., and H. C. Beachell

Trimethylchlorosilane has been chlorinated directly by Krieble and Elliot, a mixture of chlorination products being obtained.[2] Chlorination by sulfuryl chloride in the presence of benzoyl peroxide has been applied to various aliphatic hydrocarbons[3] and to certain organosilicon compounds.[4,5] This method of chlorination, however, has not been applied to trimethylchlorosilane, nor to its carbon analog, *t*-butyl chloride, previous to this work. The results are of interest in furnishing further information on the deactivation effect of the $-SiCl$ group on an alpha methyl group. (Sommer and Whitmore report that, like methylchloroform, methyltrichlorosilane cannot be chlorinated in this way.[4]) The chlorination of *t*-butyl chloride by the same method affords a means of comparing the relative effect of a silicon atom and a carbon atom in this reaction

Trimethylchlorosilane.—Refluxing an equimolar mixture of trimethylchlorosilane and sulfuryl chloride in the presence of benzoyl peroxide for several hours gave no detectable amount of chlorination product. When the experiment was repeated, however, using chlorobenzene as an inert diluent to increase the reflux temperature, a 38% yield of chloromethyldimethylchlorosilane was obtained after four hours. The yield of product was increased to 52% by adding the sulfuryl chloride dropwise to the refluxing mixture of trimethylchlorosilane and chlorobenzene. Density and refractive index have been determined for chloromethyldimethylchlorosilane. These are new physical constants for this compound.

In the majority of cases of fractionation of the reaction mixture, it was found that when almost all the chloromethyldimethylchlorosilane had been distilled off and there was a high concentration of higher boiling material left, *i. e.*, chlorobenzene and residue, the temperature dropped abruptly from 116° to about 71° where equilibrium was attained. The boiling point of dimethyldichlorosilane is given as 70°.[6] The identity of the material was established by determination of density, which is given in the literature[6] and by analysis for hydrolyzable chlorine. The presence of dimethyldichlorosilane may be due to disproportionation of chloromethyldimethylchlorosilane at a temperature above its boiling point or to the pyrolysis of unidentified polymeric by-products. No evidence for the presence of higher chlorinated products has been found, and other experimental evidence indicates that the reaction is limited to the introduction of a single chlorine under the conditions of the experiments.

The molar refraction for chloromethyldimethylchlorosilane was calculated by the Lorentz and Lorenz formula using the values obtained for density and refractive index. A value of 34.41 was obtained. This is in excellent agreement with the value of 34.70 obtained by addition of the atomic refraction equivalents. (The value used for silicon is that given by Whitmore for silicon in trimethylchlorosilane.[7])

***t*-Butyl Chloride.**—The chlorination of *t*-butyl chloride was carried out under the same conditions as that of trimethylchlorosilane. When an

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[1] Abstracted from a thesis by J. J. McBride, Jr., submitted to the faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science.

[2] Krieble and Elliot, This Journal, **67**, 1810 (1945).

[3] Kharasch and Brown, *ibid.*, **62**, 925 (1940).

[4] Sommer and Whitmore, *ibid.*, **68**, 485–487 (1946).

[5] Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488–489 (1946).

[6] Rochow, "Chemistry of the Silicones," John Wiley and Sons, New York, N. Y., 1946.

[7] Whitmore, *et al.*, This Journal, **68**, 475 (1946).

equimolar mixture of *t*-butyl chloride and sulfuryl chloride in the presence of benzoyl peroxide was refluxed with chlorobenzene, a 46% yield of 1,2-dichloro-2-methylpropane (b. p. 107–108°) was obtained after three hours. When the sulfuryl chloride was added dropwise to the refluxing mixture, a 59% yield of the chlorination product was obtained after three and one-quarter hours.

Experimental

Trimethylchlorosilane.—The trimethylchlorosilane used in this work was purchased from the Dow–Corning Corporation and redistilled, taking the fraction boiling at 57–58° at 760 mm. The boiling point is given as 57.6°.[5]

Chloromethyldimethylchlorosilane.—(a) 100 g. (0.92 mole) of trimethylchlorosilane, 124.2 g. (0.92 mole) of sulfuryl chloride, 0.5 g. of benzoyl peroxide and 200 ml. (220 g.) of chlorobenzene were placed in a 500-ml. round-bottomed flask fitted with a 30-inch reflux condenser surmounted with a cold finger, the inside dimensions of which were 3.5 × 25 cm. This was filled with a salt-ice mixture. Ground glass joints were used throughout. The evolved gases were passed through a drying tube of indicating Drierite into two 1-liter Florence flasks, the first a trap, and the second containing water so that the flow of gas could be observed. The flask was heated with a Glas-Col mantle. The mixture was refluxed vigorously. Gas was evolved at a fairly rapid rate and a gentle reflux was maintained from the cold finger. After three hours the evolution of gas had nearly stopped. The reaction mixture was fractionated in a Whitmore–Fenske total condensation, partial take-off column of about twenty theoretical plates. Twenty-eight grams of unreacted trimethylchlorosilane was recovered and 36 g. of chloromethyldimethylchlorosilane (b. p. 115–117°) obtained before the temperature dropped to 70°. Four grams was obtained between 70 and 131°. Two hundred and seventeen grams of chlorobenzene was recovered and 34 g. of a dark viscous liquid remained in the still pot. The yield based on unrecovered starting material was 38%.

(b) A 500-ml. 3-necked flask was fitted with a 250-ml. dropping funnel, a mercury-sealed stirrer and the reflux system described above. Fifty-four grams (0.5 mole) of trimethylchlorosilane, 0.5 g. of benzoyl peroxide and 108 ml. (119 g.) of chlorobenzene were placed in the reaction flask. The flask was heated as before. When the mixture was refluxing vigorously, sulfuryl chloride was added slowly with stirring over a period of four hours. The mixture was refluxed for two hours more until gas was no longer evolved. Fractionation of the product gave 22 g. of unreacted trimethylchlorosilane, 22 g. of chloromethyldimethylchlorosilane and 107 g. of chlorobenzene. Seventeen grams of tarry residue remained. The yield in this case was 52%.

(c) The chloromethyldimethylchlorosilane obtained in these experiments was redistilled and the middle cut, b. p. 115.2–116° at 762 mm. taken for analysis and determination of physical constants; $n^{20}\text{D}$ 1.4360; $d^{20}{}_4$ 1.0865; *M*D calcd. 34.70; *M*D obs. 34.41. *Anal.* Calcd. for $(CH_3)_2Si(Cl)CH_2Cl$: hydrolyzable Cl, 24.79. Found: Cl, 24.42.

Dimethyldichlorosilane.—A 2.5-g. 71–73° fraction collected in one of the distillations was examined. The following constants were found: $d^{20}{}_4$ 1.0637; $n^{23}\text{D}$ 1.4002; *M*D calcd. 29.42; *M*D obs. 30.09. Rochow gives the density as 1.062 at 20°.[6]

1,2-Dichloro-2-methyl-propane.—Fifty grams (0.39 mole) of *t*-butyl chloride (b. p. 51.0–51.5°), 53.1 g. (0.39 mole) of sulfuryl chloride, 0.5 g. of benzoyl peroxide, and 100 ml. (110 g.) of chlorobenzene were refluxed as in (a). Reaction was practically complete in three hours. The product was fractionated in a Whitmore–Fenske column of about twenty theoretical plates. There was obtained 10.3 g. of unreacted *t*-butyl chloride, 25.2 g. of 1,2-dichloro-2-methylpropane (b. p. 107.1–108.0°, $n^{28}\text{D}$ 1.4316), 101 g. of chlorobenzene and 13 g. of dark, oily residue. This is a yield of 46.3%.

The reaction was repeated as in (b) using 100 g. (0.79 mole) of *t*-butyl chloride, 106.2 g. (0.79 mole) of sulfuryl chloride, 0.5 g. of benzoyl peroxide and 200 ml. (220 g.) of chlorobenzene. Evolution of gas was rapid from the start. Reaction was complete in three hours. Fractionation of the product gave 28.5 g. of unreacted *t*-butyl chloride and 58.5 g. of 1,2-dichloro-2-methylpropane, b. p. 107–108°, $n^{25}\text{D}$ 1.4323. This is a yield of 59%.

Discussion

It appears that *t*-butyl chloride is chlorinated more readily by sulfuryl chloride than is trimethylchlorosilane. This is in accord with the action of the silicon atom as an electron sink.[8]

The deactivating effect on an α-methyl group of a chlorine attached to carbon is evident since the yields of monochlorinated product from *t*-butyl chloride are not nearly so high as those obtained with other types of hydrocarbons and chlorinated hydrocarbons.[3,9]

Summary

Trimethylchlorosilane has been chlorinated by the use of sulfuryl chloride and benzoyl peroxide in the presence of chlorobenzene (as an inert diluent to increase the reaction temperature), to give chloromethyldimethylchlorosilane.

Two new physical constants, density and refractive index, have been determined for chloromethyldimethylchlorosilane. These are: $d^{20}{}_4$ 1.0865; $n^{20}\text{D}$ 1.4360.

t-Butyl chloride has been chlorinated under the same conditions to give 1,2-dichloro-2-methylpropane.

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[8] Whitmore and Sommer, THIS JOURNAL, **61**, 481 (1939).

[9] Kharasch and Brown, *ibid.*, **61**, 2142 (1939).