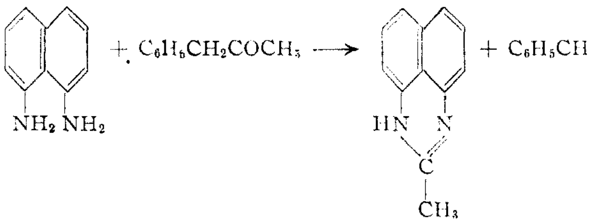

Toluene was identified as one of the products of the reactions.

Experimental[2]

Reaction of *o*-Aminophenol with Benzyl Methyl Ketone.—A mixture of 11 g. (0.1 mole) of *o*-aminophenol and 27 g. (0.2 mole) of benzyl methyl ketone was heated for 6 hours in a flask equipped with an inside thermometer and a condenser set downward for distillation. The temperature of the mixture was rapidly raised so that approximately 200° was reached in the first hour; then heating was continued at a slower rate until 250° was reached at the end of 6 hours.

The slightly yellow distillate (10 g.) which collected in the ice-cooled receiver consisted of two layers. The lower layer (1-2 g.) was found to be water which had formed in the course of the reaction. The entire distillate was then taken up in 25 ml. of ether and dried over anhydrous sodium sulfate. The filtered ether solution was fractioned and the fraction boiling at 110-111° (3 g.) was identified as toluene by oxidation to benzoic acid with potassium permanganate.

The dark brown viscous residue in the reaction flask was further distilled under reduced pressure and the fraction coming over at 135-145° at 114 mm. (10 g.) was crude 2-methylbenzoxazole in 70% yield.

The picrate prepared from this crude material melted at 117-118° and was identified by mixed m.p. with an authentic sample.[3]

Condensation of Benzyl Methyl Ketone with *o*-Aminobenzenethiol.—Nine grams (0.072 mole) of *o*-aminobenzenethiol[4] was mixed with 15 g. (0.11 mole) of benzyl methyl ketone in a flask fitted with an inside thermometer and a condenser set for distillation. The temperature was slowly raised until approximately 250° was reached at the end of 6 hours. The amount of volatile distillate obtained under these conditions was so small that it was not further investigated.

The residue in the reaction flask, subjected to distillation *in vacuo*, yielded 5 g. of a fraction boiling at 120-123° at 20 mm. The picrate prepared from this fraction melted at 153-154° and was identified as 2-methylbenzothiazole picrate by mixed m.p. with an authentic sample.[5]

Condensation of Benzyl Methyl Ketone with 1,8-Naphthalenediamine.—A mixture of 4.74 g. (0.03 mole) of 1,8-diaminonaphthalene[6] and 5 g. (0.047 mole, 20% excess) of benzyl methyl ketone was heated in a small distilling apparatus equipped with a capillary gas inlet tube extending to the bottom, and a receiver cooled by Dry Ice. Nitrogen streaming through this capillary furnished agitation and protected the amine from oxidation. The mixture was heated as before so that a temperature of approximately 315° was obtained at the end of 6 hours.

The distillate (about 2 ml.) collected in the frozen state was first thawed at room temperature into a liquid mixture with two layers; it was then taken up in ether, dried with anhydrous sodium sulfate and fractionated. The fraction boiling at 110-111° (0.5 g.) was identified as toluene by oxidation to benzoic acid with potassium permanganate.

The brown resinous residue in the distilling flask was soluble in alcohol, chloroform, acetone and dioxane. A portion dissolved in hot dioxane was precipitated by pouring into an equal volume of chloroform. The resulting green solid precipitate melted at 210-214° and was identified as 2-methylperimidine[7] by two mixed melting point determinations; *i.e.*, the free perimidine and its oxalate[8] (m.p. 230-232°) with authentic samples.

Brooklyn 6, N. Y. Received August 7, 1950

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[2] All melting points are corrected.

[3] Ladenburg, *Ber.*, **9**, 1524 (1876); Phillips, *J. Soc. Chem. Ind.*, **56**, 474T (1937); Wagner, *J. Org. Chem.*, **5**, 139 (1940).

[4] Hofmann, *Ber.*, **13**, 1230-1231 (1880); *ibid.*, **30**, 2260 (1887); Gardner, British Patent 558,877 (1944).

[5] Ochiai and Nisizawa, *J. Pharm. Soc. Japan*, **60**, 132-140 (1940) [*C. A.*, **34**, 5082 (1940)].

[6] Wagner, *J. Org. Chem.*, **5**, 136 (1940); Leonard and Hyson, This Journal, **71**, 1961 (1949). In our preparation we modified the procedure of Wagner: The 1,8 dinitronaphthalene was extensively purified by several recrystallizations and finally a suspension reduced in ethanol with palladium or platinum oxide catalyst in a Parr hydrogenator The reduction took place in a few minutes and the yield was nearly quantitative.

[7] Sachs, *Ber.*, **39**, 3027 (1906).

[8] Sachs, *Ann.*, **365**, 90 (1909).

[Contribution from the Rayon Technical Division, E. I. du Pont de Nemours & Co.]

Reaction of Perfluoroalkyl Chlorides with Silicon

By E. F. Izard and Stephanie L. Kwolek

An attempt has been made to prepare perfluoroalkyl silicon halides by the direct thermal addition of perfluoroalky chlorides to silicon and silicon copper alloy at various temperatures. Below 400°, in which temperature range alkyl halides react, no reaction takes place with the perfluoro compounds. At higher temperatures, 500-1000°, an exothermic reaction takes place but is not addition to silicon to form perfluoro silicon chlorides but appears to be a complete transfer of halogen from carbon to silicon. The volatile reaction products appear to be silicon halides and carbon has been identified in the silicon bed. The smoothness of the reaction suggests that it may be possible to develop the reaction into an analytical method for removing fluorine and other halogens from carbon in volatile fluoro carbons.

Introduction

Recent chemical literature has abundant references to the preparation of various alkyl silicon chlorides and their derivatives which are intermediates in the formation of the alkyl silicones from which the various silicone resins are derived. In recent books Post[1] and Rochow[2] have reviewed the literature of recent years. In general there are two methods for the preparation of these silicone intermediates. An alkyl halide may be converted to a Grignard reagent and this reagent reacted with a silicon compound such as tetraethyl silicate or silicon tetrachloride and the intermediates thus formed converted into alkyl silicon derivatives and ultimately to silicone resins.

The other route is the direct reaction of an alkyl halide with silicon, usually in the form of a silicon-copper alloy. In this case the alkyl halide adds directly to the silicon and the primary reaction product is dialkyl dichlorosilane. By disproportionation this compound may be converted

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[1] H. W. Post, "Silicones and Other Organic Silicon Compounds," Reinhold Publishing Corp., New York, N. Y., 1949.

[2] Eugene G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley & Sons, Inc., New York, N. Y., 1946.

into a variety of alkyl chlorosilanes containing varying amounts of alkyl radicals and chlorine.

Simons, Bond and McArthur[3] attempted to prepare Grignard reagents from trifluoromethyl chloride without success. They were also unable to prepare corresponding trifluoromethyllithium, thus indicating the extreme stability of the carbon–chlorine bond in these fluoro carbon chlorides. More recent work by Emelius and Haszeldine[4] using perfluoroalkyl iodide has resulted in the preparation of perfluoroalkyl mercurial compounds which may be suitable for subsequent conversion to silicon derivatives.

Trifluoromethyl chloride, "Freon 13," and pentafluoroethyl chloride, "Freon 115," were available and it seemed worthwhile to attempt their reaction with silicon–copper alloy under conditions found suitable for alkyl halide addition. It was thought that even though the carbon–chlorine bond is too stable to produce a Grignard reagent it might be sufficiently less stable than the carbon–fluorine bond in such compounds that at proper temperatures addition might take place according to the reaction $2CF_3Cl + Si \rightarrow (CF_3)_2SiCl_2$ and disproportionation products thereof.

Experimental

Apparatus and Materials.—The apparatus used for this work consisted of a vertically mounted "Hevi-Duty" combustion furnace about 18 in. long which was capable of reaching a temperature as high as 1200°. A McDaniel (ceramic) combustion tube of one inch diameter was used. The tube was filled with either silicon–copper alloy or silicon in the form of crushed particles from $^1/_4$" to $^1/_2$" in size. Vertical mounting was preferred to avoid settling or channeling through the reaction bed.

The temperature was determined by a thermocouple strapped to the outside of the combustion tube and insulated with asbestos paper. The tube was equipped with an inlet at the top and an outlet at the bottom. The outlet was connected to a series of traps, finally terminating in a Dry Ice-cooled trap which collected the products of reaction. In most of this work trifluoromethyl chloride, Freon 13, was used and, since it boils at −82°, it would not be stopped by the Dry Ice trap unless reaction had taken place to produce a higher boiling condensate in which the Freon might dissolve.

The cylinder containing the Freon was connected through a bubble counter to the inlet of the combustion tube. After the tube and furnace had been brought to the desired reaction temperature by a Powerstat-controlled source of heat and the tube flushed with nitrogen, a slow stream of the reagent was bubbled through the hot zone. Since the products of the reactions studied were usually hydrolyzable, preliminary evidence of the reaction could be obtained merely by allowing the exit gas to come in contact with moist air or ammonia fumes, in which case the production of a cloud was an indication of a reaction. Freon 13 does not readily hydrolyze in this way.

The only source of silicon–copper alloy available to us conveniently was an 85/15 alloy obtained from the Anderson Chemical Company, Adrian, Michigan. In order to test the suitability of this alloy for production of silicon derivatives a test was first run using methyl chloride as reactant and conditions as described in the literature[1,2] for this reaction.

Reaction of Methyl Chloride with Silicon.—With the tube mounted as described above, heated to a temperature of 315–325° and flushed with nitrogen, a slow stream of methyl chloride was bubbled through the system. Since methyl chloride boils at −24° the Dry Ice trap in this case stopped everything but indication of a reaction was readily obtained by the development of fumes on exposure of the exit gas to moist air or ammonia. Reaction took place at the above temperature but seemed to proceed better at 350°. No attempt was made to determine the identity of the reaction products since the whole purpose of the experiment was to determine the reactivity of this silicon–copper alloy.

Reaction of Perfluoroalkyl Chlorides with Silicon.—A large number of experiments were carried out investigating the reaction of perfluoroalkyl halides with silicon and silicon–copper alloy. Those indicated in Table I are merely representative of the conditions that were studied.

Table I

Reaction of Perfluoroalkyl Chlorides with Silicon

Silicon form	Reagent	Temp., °C.	Result
85/15 alloy	CF_3Cl	360–370	No reaction
85/15 alloy	CF_3Cl	620	Reaction product fumes in air. Chloride ion produced
Metal	CF_3Cl	600	Vigorous reaction
Metal	C_2F_5Cl	600	Reaction material passes Dry Ice trap
Metal	C_4H_7Cl (cyclic)	700	Reaction and depolymn.

On repeated use of the same reaction tube it was evident that the silicon–copper alloy became less reactive and the particles appeared to have a copper colored deposit on the surface after reaction. This suggested that as the silicon was consumed the copper remained behind and finally coated the surface of the silicon sufficiently to cut down on its reactivity. It was found that pure silicon worked just as well at these high temperatures. All subsequent experiments except one were run with pure silicon since it can be used time after time without any diminution in reactivity such as was observed with silicon–copper alloy.

The reaction products from the Freon 13 were considerably more volatile than would have been the case if the expected reaction was taking place and were not adequately trapped by the Dry-Ice cooled trap. A sample of pentafluoroethyl chloride, Freon 115 (b.p. −38°), was used in a subsequent experiment since it was believed that the reaction product therefrom would be much higher boiling and therefore more easily handled. Quite volatile products formed from it also.

A still higher boiling product heptafluoromonochlorocyclobutane was tried in an effort to produce a higher boiling derivative that could be more easily handled. This product is produced by cross-dimerization of tetrafluoroethylene and trifluoromonochloroethylene. Reaction and depolymerization took place.

Collection and Identification of Products.—The unexpected production of highly volatile products from all of the perfluoroalkyl halides indicated that it would be necessary to use a more adequate trapping system and to distil the reaction products to determine their nature. As a result a standard run was made at a temperature of 700° and the product collected in a liquid nitrogen cooled trap. Distillation of this product in a Podbielniak low temperature fractionating still, gave a fraction boiling near −80° which was identified by its infrared spectrum as an impure trifluoromethyl chloride but the nature of the impurity was not established from the infrared absorption. Another fraction boiling near −30° when examined in the infrared, appeared not to be a fluorocarbon and therefore could not be any of the expected reaction products. Other fractions boiled at temperatures up to around 10°. These results caused considerable speculation as to the identity of the products and led to the suspicion that some reaction radically different from the expected one was taking place.

The boiling point of trifluoromonochlorosilane (−70°)[5] is close enough to that of trifluoromonochloromethane, Freon 13 (−82°) to indicate it to be the inpurity in the −80° fraction. The boiling point of difluorodichlorosilane (−32.2°) is very close to that of the principal fraction of unidentified material in the distilled sample. The higher boiling fractions could easily be the silicon derivatives con-

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[3] J. H. Simons, R. L. Bond and R. E. McArthur, This Journal, **42**, 3477 (1940).

[4] H. J. Emelius and R. N. Haszeldine, *J. Chem. Soc.*, 2948, 2953 (1949).

[5] H. S. Booth and C. F. Swinehart, This Journal, **57**, 1333 (1935).

taining less fluorine and more chlorine. All of the silicon halides decompose readily in moist air or ammonia and could account for all the results shown in Table I. In the earlier experiments no tests were made for the presence or absence of fluoride ion in the hydrolyzed products since it has been assumed that the carbon–fluorine bond was too stable to be ruptured by conditions of the reaction being studied. However, after the distillation results were available attention was turned to tests for both chloride and fluoride ions in the hydrolyzed products.

Detailed results of these experiments are shown in Table II. The primary purpose of these experiments was to collect the reaction products in a form that could be analyzed for both fluoride and chloride ions. The reaction products were collected in Dry-Ice cooled methanol in one trap backed up with an aqueous caustic trap. At the conclusion of the run the contents of the two traps were mixed and the products analyzed for the ratio of fluoride ion to chloride ion. The analyses suggest that instead of the expected addition reaction both chlorine and fluorine were being stripped from the carbon by the silicon and that the silicon halides were being hydrolyzed completely to liberate all halogen in ionic form.

TABLE II

Silicon form	Reagent	Temp., °C.	Ratio F^-/Cl^-	Remarks
Metal	CF_3Cl	1000	3/1	Vigorous reacn.
Metal	C_2F_6Cl	1000	*ca.* 5/1	Vigorous reacn.
Metal	CF_3Cl	800	3/1	Exothermic
Metal	CF_3Cl	500	3/1	Slow reacn.

Numerous other runs were made at various temperatures from 500–1000° to determine whether it might be possible that both addition and halogen transfer were taking place in the low temperature reaction. However, analysis of the product always showed approximately 3 moles fluorine to one mole chlorine and no product suggestive of a silicone intermediate was ever isolated.

A sample, taken from the very center of a well-used silicon bed, was burned in the muffle furnace and 90% of the material oxidized away, indicating it to be carbon. In a similar experiment using pure silicon there was a gain in weight in the muffle furnace and some of the silicon was converted to silica.

It was observed at these high temperatures that with everything at a steady state an increase in flow of Freon 13 would cause a substantial increase in the temperature recorded by the thermocouple without any change in power input, indicating the reaction to be quite exothermic.

Data available in the literature show that the reaction $CF_3Cl + Si = C + SiF_3Cl$, would be highly exothermic. For example for the reaction

$$Si + 2F_2 = SiF_4 \quad -\Delta H = 365 \text{ kcal.}$$

and for the reaction

$$C + 2F_2 = CF_4 \quad -\Delta H = 165 \text{ kcal.}$$

Therefore for the reaction

$$CF_4 + Si = SiF_4 + C \quad -\Delta H = 200 \text{ kcal./25°}$$

and for the closely related reaction

$$CF_3Cl + Si = SiF_3Cl + C \quad -\Delta H \text{ would be nearly 200 kcal./25°}$$

These results demonstrate the impossibility of producing a trifluoromethylsilicon halide by direct reaction of silicon and trifluoromethyl chloride. Although the experiments were not sufficiently quantitative to show conclusively that the exchange of halogen goes to completion, the ease with which this exchange takes place and its exothermic nature make it appear quite probable that the reaction could be readily developed into an analytical method for fluorine and chlorine in volatile perfluorocarbons.

BUFFALO, N. Y.

RECEIVED SEPTEMBER 25, 1950

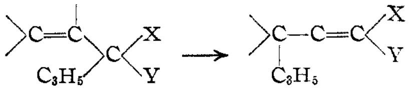
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Kinetics of the Rearrangement of Ethyl Isopropenyl Allylmalonate[1a]

BY GERALD R. ALDRIDGE[1b] AND GEORGE W. MURPHY

The kinetics of the rearrangement of ethyl isopropenyl allylmalonate has been studied in the liquid phase over the temperature range 145–200°. The reaction is first order and proceeds to virtual completion. The heat and entropy of activation, 28,400 cal./mole and −13.5 e.u., respectively, lie close to the values reported by Foster, Cope and Daniels for similar rearrangements. The entropy of activation is somewhat lower than expected, and is interpreted in terms of steric factors.

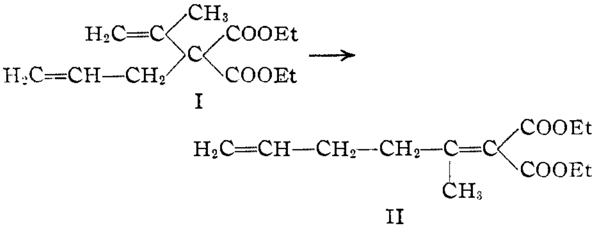
Cope, Hoyle and Heyl[2] have shown that the rearrangement



X and Y = CN or COOEt

is a general one and have suggested that the mechanism is the same for all compounds having the essential skeleton structure. The most likely mechanism was thought to involve a cyclic intermediate, and this hypothesis received support from the kinetics evidence of Foster, Cope and Daniels[3] on three rearrangements.

Cope, Hofmann and Hardy[4] have shown that the rearrangement



I

II

proceeds somewhat below the temperature 200°. This rearrangement appeared to the present authors to be a logical one to investigate further by the kinetics approach, since Foster, Cope and Daniels' work did not include a compound where both X and Y were –COOEt groups.

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[1] (a) An abstract of a thesis presented by Gerald E. Aldridge to the faculty of the University of Wisconsin in partial fulfillment of the requirements for Master of Science, 1950. (b) American Cyanamid Co., Stamford, Conn.

[2] Cope, Hoyle and Heyl, THIS JOURNAL, **63**, 1843 (1941).

[3] Foster, Cope and Daniels, *ibid.*, **69**, 1893 (1947).

[4] Cope, Hofmann and Hardy, *ibid.*, **63**, 1852 (1941).