that the salt is sufficiently insoluble in 3 *N* HCl so that the filtrates from the precipitation can be discarded. The present results suggest that recovery of cesium from the filtrate is advisable. Recovery by precipitation of Cs_2SnCl_6 by addition of stannic chloride is recommended.

It had been expected that iron would be found in the impure samples, but only traces of this element were found in even the most highly colored material. A stable compound of thallium chloride and antimony trichloride, $SbCl_3 \cdot 3TlCl$, has been reported[4]; its existence makes the presence of thallium reasonable if unexpected, but inasmuch as the compound was not prepared under conditions comparable to those of the present work, a further investigation is necessary. A full discussion of this question will be given in a subsequent report.

Acknowledgment.—The author wishes to express his appreciation to Mr. Eugene F. Wilda for the spectrographic analyses.

Summary

Evidence has been presented confirming the composition of cesium antimony chloride as constant at $3CsCl \cdot 2SbCl_3$. Color variation in the salt has been shown to be due to the presence of thallium as an impurity.

The solubility of cesium antimony chloride at 25° in hydrochloric acid solutions of concentrations from 2 to 16 molal has been reported.

MADISON, WIS. RECEIVED JUNE 25, 1945

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[4] F. Ephraim and P. Barteczko, *Z. anorg.' Chem.*, **61**, 249 (1909).

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Direct Synthesis of Phenylchlorosilanes

BY E. G. ROCHOW AND W. F. GILLIAM

The general reaction of hydrocarbon halides with elementary silicon to produce alkyl and aryl halosilanes has been described.[1] The purpose of the present investigation is to apply that general reaction to the synthesis of phenyl chlorosilanes from chlorobenzene and silicon, seeking conditions which would permit yields of diphenyldichlorosilane comparable to those obtained by substitution methods.[2]

Experimental

Chlorobenzene and Silicon.—Pure dry monochlorobenzene was introduced at a rate of 7 g. per hour into a heated glass tube of 2.5 cm. internal diameter containing 107 g. of granular pure silicon (99.8% Si). The tube was sealed to a water condenser, a thermocouple was embedded in the silicon, and the tube was heated until the temperature of the charge was 530°. Only slight reaction of the silicon with the stream of chlorobenzene occurred over a period of fifteen hours. When operated at 680° for a period of fifty-four hours, 13 g. of carbon was deposited in the tube and 367 g. of dark condensate was collected. From this liquid there was obtained by distillation 54 g. of silicon tetrachloride, 241 g. of unchanged chlorobenzene, and 65 g. of high-boiling material consisting of phenylchlorosilanes, biphenyl, chlorinated biphenyls and unknown materials of a tarry nature.

A larger glass tube (4 cm. internal diameter) in which was sealed a concentric thermocouple well was then charged with commercial silicon (97% Si) which had been pulverized to 325 mesh size and then sintered in hydrogen. The packed section was 120 cm. long. The tube was heated in an electric furnace to 570 ± 10° and chlorobenzene was introduced at the rate of 12 g. per hour. The products which condensed at water temperature were collected. From 2694 g. of condensate there was obtained by distillation 287 g. of low-boiling material (silicon tetrachloride and benzene), 1834 g. of unchanged chlorobenzene and 473 g. of fuming high-boiling material. Of the latter, 144 g. distilled near the boiling point of diphenyldichlorosilane, but analysis showed that only one-fourth of this was actually diphenyldichlorosilane and the rest was a mixture of chlorinated biphenyls having about the same boiling point. Phenyltrichlorosilane, triphenylchlorosilane and many other unidentified products also were obtained.

Chlorobenzene, Hydrogen Chloride and Silicon.—Apparatus similar to that employed in the preceding experiment was set up, but anhydrous hydrogen chloride was mixed with the chlorobenzene vapor and passed over the heated silicon. A variety of molar proportions of hydrogen chloride to chlorobenzene were employed at several temperatures. At 0.3 mole of hydrogen chloride per mole of chlorobenzene, and at a temperature of 500°, 9.4 g. of phenyltrichlorosilane was obtained per 100 g. of chlorobenzene charged, in one pass through the reactor. Twenty-four grams of silicon tetrachloride per 100 g. of chlorobenzene charged was obtained at the same time, but very little diphenyldichlorosilane.

Chlorobenzene, Silicon and Copper.—Copper had been found to be effective in facilitating the reaction of methyl chloride and silicon to produce dimethyldichlorosilane. A sintered mixture of commercial silicon and copper powders containing 20% Cu was found to react with chlorobenzene at an appreciable rate only above 550°, and the yield of phenylchlorosilanes was poor. When anhydrous hydrogen chloride was mixed with the chlorobenzene as in the previous experiment, phenyltrichlorosilane was obtained in a yield of 12.7 g. per 100 g. of chlorobenzene in a single pass, but the yield of diphenyldichlorosilane remained low. Experiments with sintered pellets containing 10% copper gave similar results.

Further experiments showed that chlorobenzene and bromobenzene would react with a commercial alloy of silicon and copper (50% Cu) in a rotating autoclave above the normal boiling point but below the critical temperature of the halide. To try the same reaction in the vapor phase, lumps of the same alloy (which had stood in the laboratory for over a year and had softened to a friable mass through inter-granular oxidation) were packed in a tube of 4-cm. diameter, and the vapor of chlorobenzene (mixed with 0.0004 g. of anhydrous hydrogen chloride per g. of chlorobenzene) was passed through at elevated temperatures at a rate of 29 g. per hour. The copper–silicon mass was found to have a comparatively high reactivity

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[1] E. G. Rochow, THIS JOURNAL, **67**, 963 (1945).

[2] Kipping and Murray, *J. Chem. Soc.*, 2734 (1927); Polis, *Ber.*, **19**, 1019 (1886); Dilthey and Edvardoff, *ibid.*, **37**, 1139 (1904).

toward this vapor, so high that an acceptable rate of conversion of chlorobenzene to phenylchlorosilanes could be attained at 430°, a temperature low enough to reduce considerably the rate of pyrolysis of the chlorobenzene and the products. From 1092 g. of condensate from the reaction tube (operated at 430°) there was obtained by distillation no silicon tetrachloride, 670 g. of unchanged chlorobenzene, 100 g. of phenyltrichlorosilane, 260 g. of diphenyldichlorosilane and 59 g. of viscous residue. The admixture of hydrogen chloride to the chlorobenzene subsequently was found to be unnecessary when this type of copper catalyst was employed.

When fresh silicon–copper alloy was tried in the same apparatus, the yield of phenylchlorosilanes at 430° was very low. In four experiments the weights of phenylchlorosilanes represented less than 3% of the weights of the condensates obtained from the reaction. Duplicate experiments with the aged alloy consistently gave much higher yields, and it was concluded that the different degrees of reactivity toward chlorobenzene were related directly to the physical and chemical alteration of the silicon–copper mass. The fresh alloy, which was hard and brittle, reacted poorly but the aged alloy, rendered soft and friable by intergranular oxidation, gave high conversions and good yields of diphenyldichlorosilane. The fresh alloy could be made chemically equivalent to the aged alloy by oxidizing it immediately before use; chips were packed loosely in one of the 4-cm. reaction tubes and were heated to 300° in a slow stream of air for fifteen hours. The air flow was then stopped, the temperature was raised to 430°, chlorobenzene was introduced into the tube, and the reaction was found to proceed satisfactorily.

Chlorobenzene, Silicon and Nickel.—Commercial silicon and nickel powders were mixed, pressed and sintered in hydrogen at 900° to obtain pellets containing 10% of nickel.[3] These were packed in a 4-cm. reaction tube and heated to 415° with a stream of chlorobenzene vapor (18 g. per hour) passing through the tube. 2550 g. of condensate yielded 2518 g. of unchanged chlorobenzene and 24 g. of high-boiling liquid consisting principally of biphenyl, phenyltrichlorosilane, diphenyldichlorosilane and tarry substances. The work was repeated several times with the same low yield of phenylchlorosilanes.

Chlorobenzene, Silicon and Antimony.—Sintered pellets containing 10% antimony and 90% commercial silicon were prepared in the same manner as those having copper or nickel except that the sintering temperature was 600°.[3] In an apparatus such as that used for the experiments described above, the silicon–antimony reacted poorly with chlorobenzene, converting only about 1% of it to phenylchlorosilanes in one pass at 405°.

Chlorobenzene, Silicon and Platinum.—Sintered pellets were prepared from a mixture of 90% commercial silicon and 10% platinum by the above method, except that the sintering temperature was 1000°. At 415° the pellets reacted poorly with chlorobenzene vapor, converting less than 1% of the halide to phenylchlorosilanes.

Chlorobenzene, Silicon and Silver.—Sintered pellets containing 90% commercial silicon and 10% silver were prepared by pressing the mixed powders and firing in hydrogen at 900°. Such pellets, when heated to 400° in a stream of chlorobenzene vapor (14 g. per hour) in the standardized reaction tube, reacted to produce phenylchlorosilanes in good yields and with a minimum of pyrolytic products. From the first 2187 g. of condensate from one experiment there was obtained by distillation 1813 g. of chlorobenzene, 88 g. of phenyltrichlorosilane, 218 g. of diphenyldichlorosilane, and 60 g. of viscous amber residue. At constant flow of chlorobenzene and constant temperature (400 ± 10°) the yield of phenylchlorosilanes was found to increase with time at first: At the end of twenty-one days of operation a distillation of 2592 g. of crude condensate gave 200 g. of phenyltrichlorosilane and 411 g. of diphenyldichlorosilane. The yield then began to fall off until at the end of seventy days of operation the percentages of phenyltrichlorosilane and diphenyldichlorosilane in the condensate were about equal and had leveled off at 5%. It was considered useless to continue the reaction at 400°, so the temperature was raised to 500 ± 10°, still keeping the same flow of chlorobenzene. The yield of phenyltrichlorosilane soon rose to 16% of the crude condensate, but the yield of diphenyldichlorosilane continued to drop, and tarry products of pyrolysis were obtained in increasing quantity.

Sintered silicon–silver pellets containing 5, 10, and 20% silver were then compared in the same type of reaction tube. The yield of phenylchlorosilanes form the mass containing 5% silver was decidedly lower than the yields from the other two preparations; those from the masses with 10 and 20% silver differed very little.

Effect of Aluminum Chloride.—Commercial silicon contains from $^1/_2$–1% or more of aluminum, and therefore one of the products of the reaction with chlorobenzene is aluminum chloride. This solid product appears at the very start of the run, and thereafter in decreasing amounts as long as phenylchlorosilanes are formed. Some of it sublimes into the cooler portions of the reaction tube and some is washed through the condenser by the stream of chlorobenzene and products. When the condensate is distilled the aluminum chloride begins to react with the phenylchlorosilanes, slowly at first but sufficiently rapidly at the higher temperatures to cause trouble in a slow and careful fractional distillation. The reaction is evidenced by a fluctuation of the vapor temperature, indicating an erratic formation of more volatile substances in the still flask; generally it is first observed as one begins to take off phenyltrichlorosilane (b. p. 201.5°). The nature of this reaction is open to dispute; Evison and Kipping[4] consider that the silicon is stripped of phenyl groups in a series of reactions requiring molar equivalents of the aluminum chloride

$$(C_6H_5)_2SiCl_2 + AlCl_3 = C_6H_5SiCl_3 + C_6A_5AlCl_2$$
$$C_6H_5SiCl_3 + AlCl_3 = SiCl_4 + C_6H_5AlCl_2$$

The present authors have found that much-less-than-molar proportions of aluminum chloride, even 1% or less, will suffice to convert phenylchlorosilanes to silicon tetrachloride and benzene (which are distilled off at once, causing fluctuations of the vapor temperature). The reaction therefore appears to be complex and cyclic in nature. Whatever the mechanism, there can be no doubt of the degradation of desired product. For any but a rapid distillation it is necessary to reduce the content of aluminum chloride to 0.013% or less.[5] Since most of the aluminum chloride in the crude condensate is present as suspended solid, its removal can be accomplished by shaking the mixture with decolorizing charcoal and filtering with suction.

Discussion

The reaction of chlorobenzene with elementary silicon alone is sluggish, and if it is accelerated by heat alone there are obtained many pyrolytic products along with the desired phenyl chlorosilanes. A catalyst therefore is desirable in order to increase the rate of reaction at more moderate temperatures. In this investigation, silver appears to be superior to the other substances which were tried as catalysts; its use in the proportion of about 10% of the silicon by weight leads to acceptable conversions of chlorobenzene to phenylchlorosilanes at 400°. At this temperature the side reactions of chlorobenzene are not troublesome, nor is there excessive deposition of carbon in the tube. Almost all of the chloro-

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(3) This procedure followed that developed by W. I. Patnode for preparing silicon–copper contact masses for the synthesis of methylchlorosilanes from methyl chloride and silicon.

(4) Evison and Kipping, *J. Chem. Soc.*, 2774 (1931).

(5) The authors are grateful to E. H. Winslow and R. M. Lacey for determining aluminum in reactive and non-reactive mixtures.

benzene which enters into reaction appears as phenyltrichlorosilane and diphenyldichlorosilane in the approximate molar proportion of one to three.

Copper also is a catalyst for the reaction of chlorobenzene with silicon, but is not as effective as silver in the lower concentrations. In the form of a 50% copper–silicon alloy disintegrated by intergranular oxidation, the copper brings about an acceptable conversion of chlorobenzene to phenylchlorosilanes at 430°, yielding diphenyldichlorosilane as the principal product. Variations in yield have been noticed with different batches of the contact mass, possibly because of variations in the degree of oxidation and hence in the extent of disintegration. More investigation of the metallurgical changes which take place upon oxidation is necessary before an assured reactivity toward chlorobenzene can be brought about by a fixed sequence of operations.

The effect of hydrogen chloride in expediting the reaction of elementary silicon and chlorobenzene could not be called catalytic, because the chlorine appears in the product. The hydrogen chloride undergoes a simultaneous reaction which attaches the chlorine to silicon atoms and in some way facilitates the reaction of the chlorobenzene. Since its use in effective proportions leads to the formation of considerable silicon tetrachloride and phenyltrichlorosilane, hydrogen chloride could more logically be used in a direct synthesis of substituted trichlorosilanes, where extra chlorine is necessary.

The separation of diphenyldichlorosilane prepared by direct synthesis is complicated by the necessity of removing aluminum chloride, which presumably would not be present in preparations by other methods. While the use of aluminum-free silicon would obviate the necessity of such removal, it seems easier and more economical to use the commercial grades of silicon and to carry out the filtration procedure as described. Once this has been done the phenylchlorosilanes may be distilled at atmospheric pressure without decomposition. In this investigation no evidence has been found to support the inference that the phenylchlorosilanes must be distilled at reduced pressure to maintain their purity.[6]

Heretofore only the reduced-pressure boiling points have been given for diphenyldichlorosilane and triphenylchlorosilane. The normal boiling points for all the phenylchlorosilanes, as determined on the products from these experiments, are: $C_6H_5SiCl_3$, 201.5° cor.; $(C_6H_5)_2SiCl_2$, 305.2 cor.; $(C_6H_5)_3SiCl$, 378.0 cor.

Summary

The general reaction of hydrocarbon halides with elementary silicon is applied to the direct synthesis of diphenyldichlorosilane from chlorobenzene and commercial silicon. The effects of various catalysts are described, and conditions for carrying out the reaction and for separating the phenylchlorosilanes by distillation at atmospheric pressure are given.

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(6) Krause and von Grosse, "Die Chemie der Metallorganischen Verbindungen," Borntraeger Geb., Berlin, 1937, pp. 274, 276.

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[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. III. Systems Containing More than Two Monomers

BY CHEVES WALLING AND EMORENE R. BRIGGS

The theory of copolymerization recently developed by Alfrey and Goldfinger,[1] Mayo and Lewis,[2] and Wall[3] may be extended to the case of n monomers and the composition of product expressed in terms of the initial composition of the reaction mixture and the $n(n - 1)$ monomer reactivity ratios[2] involved. This fact has been pointed out by Alfrey and Goldfinger, who have developed the expression for the initial polymer composition in a system of three monomers.[4] This paper contains a discussion of the more general case of n monomers, and experimental work on combinations of styrene, methyl methacrylate, acrylonitrile, and vinylidene chloride, for which the necessary monomer reactivity ratios are now available.[5]

Differential Equation for Copolymerization of *n* Monomers.—If n monomers, A, B, C, . . ., N, are allowed to copolymerize, their rates of disappearance (making the same assumptions as in the copolymerization of two monomers[2]) are given by the system of equations

$$\frac{-d[A]}{dt} = k_{aa}[A][A\cdot] + k_{ab}[A][B\cdot] + \ldots + k_{an}[A][N\cdot] \qquad (1a)$$

$$\frac{-d[B]}{dt} = k_{ba}[B][A\cdot] + k_{bb}[B][B\cdot] + \ldots + k_{bn}[B][N\cdot] \qquad (1b)$$

. . . .

$$\frac{-d[N]}{dt} = k_{na}[N][A\cdot] + k_{nb}[N][B\cdot] + \ldots + k_{nn}[N][N\cdot] \qquad (1n)$$

where $[A\cdot]$, $[B\cdot]$, . . ., $[N\cdot]$ are concentrations of growing polymer chains ending in A, B, . . ., N type radicals, respectively, and k_{ij}, in general, is the rate constant for reaction of monomer I with

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(1) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944).

(2) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944).

(3) Wall, *ibid.*, **66**, 2050 (1944).

(4) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 322 (1944).

(5) Lewis, Mayo and Hulse, THIS JOURNAL, **67**, 1701 (1945).