heated to 305° under an atmosphere of methyl chloride. The temperature was raised to 370° to start the reaction, and then dropped to 315° after 1.5 hours. Methyl chloride was introduced at a rate of 30 cc./min. at room temperature. Crystals of dimethyltin dichloride formed in 12 minutes. Over an interval of 862 hours the rate of formation of $(CH_3)_2SnCl_2$ increased slowly to 3.3 g./hr., then declined after 250 hr. to 0.71 g./hr. The addition of fresh tin raised the rate to 2.1 g./hr. but after 400 hr. it declined to 0.81 g./hr. again. The average yield was 1.8 g./hr.

Uncatalyzed Reaction of Methyl Chloride with Tin.—In one example, a small reaction vessel of the same general type was charged with 170 g. of molten tin at 450° under an atmosphere of methyl chloride. The gas input was adjusted to 30 cc./min. Crystals of dimethyltin dichloride formed within 20 minutes, but the gas jet plugged intermittently for the first 120 hours and production during that period was low. Following this period operation was satisfactory at an average yield of 0.58 g./hr. for 774 hr.

Discussion

The observed very high proportion of symmetrical dimethyltin dichloride follows a trend noted in the corresponding reactions with silicon and germanium[7,12] and may be explained in the same way as those found in the case of silicon.[13] A speculative mechanism for the catalyzed reaction is similar to the one proposed for silicon.[14]

$$2Cu + CH_3Cl \xrightarrow{ca.\ 300°} CuCl + CuCH_3 \quad (1)$$

$$Sn + CuCl \longrightarrow (SnCl) + Cu \quad (2)$$

$$CuCH_3 \longrightarrow Cu + CH_3 \quad (3)$$

$$(SnCl) + CH_3 \longrightarrow (CH_3SnCl),\ \text{or} \quad (4)$$

$$(SnCl) + CuCH_3 \longrightarrow (CH_3SnCl) + Cu \quad (5)$$

and so on, until tetra-substitution has occurred. Rearrangement of methyl and chlorine groups at the reaction temperature then results in dimethyltin dichloride almost exclusively.

In the uncatalyzed reaction it could be assumed that tin can split methyl chloride in much the same manner as copper does. Alternatively, the "inert" $5s^2$ electrons of tin allow divalent intermediates which are covalently unsaturated and may absorb more methyl chloride.

$$CH_3Cl + Sn \longrightarrow CH_3SnCl$$

$$\text{(which rearranges to } (CH_3)_2Sn \text{ and } SnCl_2) \quad (6)$$

$$(CH_3)_2Sn + CH_3Cl \longrightarrow (CH_3)_3SnCl \quad (7)$$

$$SnCl_2 + CH_3Cl \longrightarrow CH_3SnCl_3 \quad (8)$$

followed by rearrangement as before. In support of the latter mechanism, yellow polymeric dimethyltin and molten colorless tin(II) chloride have been observed in "uncatalyzed" reactions, and the feasibility of reaction (8) was demonstrated by passing methyl chloride into melted tin(II) chloride, yielding methyltin trichloride.

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(12) E. G. Rochow, This Journal, **70**, 436 (1948).

(13) P. D. Zemany and F. P. Price, *ibid.*, **70**, 4222 (1948).

(14) D. T. Hurd and E. G. Rochow, *ibid.*, **67**, 1057 (1945).

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New Preparative Methods for Organotin Halides

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Received May 9, 1953

During the investigation of the preparation of organotin halides by the direct reaction of an alkyl halide with metallic tin,[1] some new methods for preparing organotin halides were found which represent improvements over the previous methods.[2]

Tin oxide was found to impart an inhibiting effect to the direct reaction of methyl chloride with metallic tin.[1] In an attempt to determine the reasons for the inhibition, methyl chloride was passed through a Pyrex tube containing powdered tin oxide (either with or without copper powder) at 300°. In either case, at the start of the reaction a narrow yellow band formed at the gas-inlet end of the tube and progressed slowly down the tube to the outlet end. During the passage of this band along the tube, trimethyltin chloride was produced. From its color and the known reaction of diethyltin with ethyl chloride to produce triethyltin chloride,[3] we conclude that the material was dimethyltin. Its formation can be postulated as

$$3SnO + 2CH_3Cl \longrightarrow (CH_3)_2Sn + SnOCl_2 + SnO_2$$

The insoluble, non-volatile dimethyltin then absorbs more methyl chloride to form volatile trimethyltin chloride

$$CH_3Cl + (CH_3)_2Sn \longrightarrow (CH_3)_3SnCl$$

Only one-third of the tin thereby is converted to volatile product, leaving a powdered mixture of tin(IV) compounds and causing the reaction zone to move along the tube.

In a similar way trimethyltin bromide was prepared from methyl bromide and tin oxide, and although no pure trimethyltin iodide was isolated from the analogous reaction of methyl iodide, a small amount of liquid with the expected boiling and freezing ranges was obtained.

Pfeiffer and Heller[4] previously have reported the preparation of compounds of the type $RSnI_3$ by the reaction of RI with tin diiodide. We have extended this method in the present investigation to the combination of methyl chloride and tin dichloride at 300° to give methyltin trichloride.[5] Similarly, in testing the effect of tin dioxide on the reaction between methyl chloride and tin, some tin dioxide was mixed with 8% by weight of copper(II) oxide and treated with methyl chloride at 300°. Within a few hours a considerable quantity of dimethyltin dichloride containing small amounts of tin dichloride was obtained. It seems probable that the tin dioxide is reduced by the methyl chloride to tin oxide and tin dichloride, both of which are capable of reacting with methyl chloride to produce methyltin chlorides. Such a mixture of methyltin chlorides is known to rearrange at the reaction temperature to produce dimethyltin dichloride as the principal product.

Using a reaction vessel of the type described in reference (1) we have found that methyl bromide

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(1) A. C. Smith, Jr., and E. G. Rochow, This Journal, **75**, 4103 (1953).

(2) E. Krause and A. v. Grosse, "Die Chemie der metall-organischen Verbindungen," Chapt. V, Borntraeger, Berlin, 1937, pp. 311–372.

(3) P. Pfeiffer, *Ber.*, **44**, 1269 (1911).

(4) P. Pfeiffer and I. Heller, *ibid.*, **37**, 4619 (1904).

(5) This reaction was carried out on a half-kilogram scale by Mr. John W. Farnham while associated with us in this investigation, and he found that the addition of 10% by weight of copper powder to the melted $SnCl_2$ enabled the reaction to proceed more smoothly and rapidly.

will react with *metallic tin* to form dimethyltin dibromide, but methyl iodide undergoes pyrolysis at the temperatures used with methyl chloride (300–400°) to form free iodine and no detectable amount of dimethyltin diiodide. Instead, some tin diiodide is formed which reacts with methyl iodide to give trimethyltin iodide.[3]

Similar reactions were carried out using ethyl chloride as a reactant, both with and without copper as catalyst.[1] Under conditions similar to those used for the preparation of dimethyltin dichloride, diethyltin dichloride was formed in very small quantities. Lower operating temperatures gave better results, and it was found advantageous to remove the product from the hot reaction zone as rapidly as possible, as by passing a stream of dry nitrogen over the surface of the molten tin and into the condenser. A spray-type reaction vessel was devised in order to obtain the largest possible surface of molten tin for reaction and to remove the product rapidly from the reaction zone. In this apparatus a fine stream of molten tin was sprayed into an atmosphere of ethyl chloride at 350°, and diethyltin dichloride was condensed from the excess gas. The conversion of ethyl chloride was low, due in part to the necessity for blowing two to four liters of ethyl chloride per minute past the atomizing jet of molten tin in order to maintain an adequate spray of metal; only a small part of this ethyl chloride could react in the 2.8 by 60 cm. chamber following the jet.

In the preparation of phenylchlorosilanes[6] it has been found advantageous to add dry hydrogen chloride to the chlorobenzene used. This modification was tested with ethyl chloride and molten tin, but no improvement in the reaction was noted.

The greater difficulty experienced in preparing diethyltin dichloride over that found in preparing dimethyltin dichloride indicated that higher members of the series might be even less readily obtained. Several attempts to prepare *n*-butyltin chlorides and bromides or phenyltin bromides by reactions in sealed tubes or in vessels of the type described in reference 1 were unsuccessful.

Experimental

Trimethyltin Chloride.—A stream of CH_3Cl at 15 cc./min. was passed through a mixture of 20 g. of SnO and 2 g. of Cu at 300°. $(CH_3)_3SnCl$ was formed, which upon recrystallization from benzene gave a melting point of 37.5–39.5° (37° in ref. 2).

Anal. Calcd. for C_3H_9SnCl: C, 18.08; H, 4.55; Cl, 17.80. Found: C, 17.78; H, 4.63; Cl, 18.07.

Trimethyltin Bromide.—*A stream of CH_3Br at 15 cc./min.* was passed through a mixture of SnO and 10% by weight of Cu. The initial reaction temperature rose to 500°, but was dropped rapidly to 300°. About 20 cc. of liquid was collected in 7 hr. The product was fractionally distilled, and $(CH_3)_3SnBr$ was obtained at 163–166° (165° in ref. 2) m.p. 26–27° (27° in ref. 2).

Anal. Calcd. for C_3H_9SnBr: C, 14.81; H, 3.70. Found: C, 15.19; H, 3.79.

Trimethyltin Iodide.—Two hundred grams of CH_3I was passed through a tube containing a mixture of SnO and 10% by weight of Cu heated to 350°, at a rate corresponding to 29 cc. of liquid per hour. About 20 cc. of liquid was collected in the receiving flask. The liquid was fractionally distilled giving mostly methyl iodide, but a small amount of liquid boiling at 160–170° (b.p. $(CH_3)_3SnI$ 170° in ref. 2). The freezing range of this fraction was −3 to −5°.

Methyltin Trichloride.—A stream of CH_3Cl at 30 cc./min. was bubbled through molten anhyd. $SnCl_2$ at 365°. About 70 g. of crystalline product was obtained in four days. The product was easily recrystallized from benzene and sublimed readily. An analytical sample was prepared by sublimation into an evacuated vial which was then sealed.

Anal. Calcd. for CH_3SnCl_3: C, 5.00; H, 1.25. Found: C, 5.37; H, 1.47.

Dimethyltin Dichloride.—A stream of CH_3Cl at 10 cc./min. was passed through a mixture of 50 g. of SnO_2 and 4 g. CuO at 300°. A condensate appeared in less than 18 hr., and at 48 hr. a considerable quantity of $(CH_3)_2SnCl_2$ containing some $SnCl_2$ was obtained.

Dimethyltin Dibromide.—A reaction vessel of the type described in ref. 1 was charged with 200 g. of tin at 395° under an atmosphere of CH_3Br. More CH_3Br was bubbled through the molten metal at a rate of 15 cc./min. until a total of 400 g. had been introduced. About 30 cc. of $(CH_3)_2SnBr_2$ was obtained, which was recrystallized from benzene and was found to melt at 75–77° (74–76° in ref. 2). The crystals sublimed at room temperature.

Anal. Calcd. for $C_2H_6SnBr_2$: C, 7.78; H, 1.94. Found: C, 7.79; H, 2.06.

Methyltin Triiodide.—Two hundred grams of CH_3I was bubbled through 200 g. of tin at 385° at a rate of 15 cc. of liquid per hour. Bright orange-red crystals of SnI_2 formed on top of the molten tin, and a suspension of yellow crystals of SnI_4 in a yellow liquid collected in the condenser. The mixture was filtered to remove the solid, and the filtrate was reduced in volume by evaporation. A crop of yellow crystals of CH_3SnI_3 was obtained. The product was recrystallized from benzene and melted at 84–85.5° (86.5° in ref. 2).

Anal. Calcd. for CH_3SnI_3: C, 2.34; H, 0.59. Found: C, 2.86; H, 0.75.

Diethyltin Dichloride.—Molten tin was sprayed in a fine stream into a reaction chamber 60 cm. × 28 mm. heated to 350°, through which preheated C_2H_5Cl was passed. After 5 hr. a yield of 2 g. of $(C_2H_5)_2SnCl_2$ was obtained. The product was recrystallized from benzene and melted at 83–84° (84° in ref. 2).

Anal. Calcd. for $C_4H_{10}SnCl_2$: C, 19.41; H, 4.07. Found: C, 19.25; H, 4.19.

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(6) E. G. Rochow and W. F. Gilliam, THIS JOURNAL, **67**, 1772 (1945).

N-Substituted 2-Nitrocarbazoles[1]

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RECEIVED APRIL 25, 1953

In the investigation of chemical and physical properties of aromatic carcinogens and allied compounds, a series of N-substituted 2-nitrocarbazoles have been prepared. The analogous 2-nitrofluorene has been shown to be carcinogenic to rats.[2]

The physical properties and yields of the compounds are given in Table I. The chemical, physical and biological properties of these compounds are being further studied.

General Procedure.—Two ml. of 66% aqueous potassium hydroxide was added to a solution of 2.12 g. (0.01 mole) of 2-nitrocarbazole[3] in 30 ml. of acetone. To this red-brown solution was added 0.015 mole of RX. The mixture was allowed to stand for 4 hours with occasional shaking. The change in color of the mixture from red-brown to yellow

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(1) This investigation was supported by research grant C-1308 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service

(2) H. P. Morris, C. S. Dubnik, T. B. Dunn and J. M. Johnson, *Cancer Research*, **7**, 730 (1947).

(3) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).