TABLE I

APPARENT IONIZATION CONSTANTS, DIPHENYLDIAZOMETHANE REACTIVITIES AND ETHYL ESTER SAPONIFICATION RATES OF SUBSTITUTED BENZOIC ACIDS

Substituent	Av. half-point[a,b]	$K_A \times 10^{6c}$	Concn., moles/l.[d]	Half-life,[d] min.	Av. k_1[b,d] l./mole min.	$k_2 \times 10^4$,[b,e] l./mole min.	$k_3 \times 10^3$[b,f] l./mole min.
			0.0487	13.21			
None	5.80 ± 0.01	1.59	.0874	7.29	1.08 ± 0.01	28.7 ± 0.50	8.68 ± 0.50
	(5.75)[g]		.0967	6.22	(1.04)[g]		
			.0800	7.41			
p-(CH₃)₃Si-	5.80 ± 0.01	1.59	.0823	7.35	1.15 ± 0.01	23.3 ± 0.6	9.98 ± 0.44
	(5.85)[g]		.0440	13.71	(1.05)[g]		
			.0810	7.72			
m-(CH₃)₃Si-	6.00 ± 0.02	1.00	.0737	8.69	1.10 ± 0.01	12.6 ± 0.3	6.64 ± 0.08
	(6.01)[g]		.0474	13.22	(1.07)[g]		
p-CH₃-	6.00 ± 0.01 (5.94)[g]	1.00	....	...	....	....	....
p-CH₃O-	6.12 ± 0.02 (6.07)[g]	0.76	....	...	....	....	....

a Reading on pH scale of pH meter calibrated for aqueous buffer solutions at half-neutralization point using glass and saturated calomel electrodes without correction for liquid junction potentials in 50% water–50% ethanol (by volume) solutions at 25°. *b* Standard deviations are appended to the average values. *c* Calculated assuming unit activities and readings of pH meter scale equal to logarithm of reciprocal of hydrogen ion concentrations. *d* For reaction of benzoic acids with diphenyldiazomethane in absolute alcohol solution at 30°. *e* Rate constants for saponification of ethyl esters in 56% acetone (by weight) at 24.9°, see ref. 5b. *f* Rate constants for saponification of ethyl esters in 87.83% ethanol (by volume) at 30.0°, see ref. 5a. *g* Values obtained previously[1] with different apparatus and materials.

The procedures have been described earlier in detail.[1,5] The ethyl esters of m- and p-trimethylsilylbenzoic acids were prepared in 50–57% yields by heating the silver salts of the acids[1] with a slight excess of ethyl iodide in ether; ethyl m-trimethylsilylbenzoate, b.p. 90–91° (1.5 mm.). *Anal.* Calcd. for C₁₂H₁₈O₂Si: C, 64.54; H, 8.12. Found: C, 64.84; H, 8.10. Ethyl p-trimethylsilylbenzoate, b.p. 105–106° (2.7 mm.). *Anal.* Calcd. for C₁₂H₁₈O₂Si: C, 64.54; H, 8.12. Found: C, 64.70; H, 8.11.

The experimental results for the trimethylsilyl derivatives along with those for some reference compounds are given in Table I. A summary of available σ-constant data is presented in Table II. Reasonable experimental agreement was found with the earlier investigation[1] and from all of the results it is clear that the net electrical effect of the trimethylsilyl group on the reactivities of benzoic acids or esters is essentially negligible in the para-position but rather electron-donating in the meta-position. The spread of the meta-σ-values is large compared with what is customarily found[2] and may be related to the bulkiness of the group.[4,8]

TABLE II

σ-CONSTANTS FOR THE TRIMETHYLSILYL GROUP

Reaction[a]	(Meta)	(Para)
Ionization constants in 50% ethanol at 25°	−0.155 (−0.208)[b]	−0.020 (−0.060)[b]
Diphenyldiazomethane rates in absolute ethanol at 30.0°	+0.025 (−0.018)[b]	+0.002 (−0.022)[b]
Alkaline hydrolysis in 87.83% ethanol at 30.0°	−0.040	+0.027
Alkaline hydrolysis in 56% acetone at 24.9°	−0.150	−0.040
Average	−0.080 ± 0.042[c] (−0.113)[b]	−0.008 ± 0.014[c] (−0.041)[b]

a Data for log k₀ and ρ are given elsewhere.[1,2] *b* Ref. 1. *c* Standard deviations.

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(5) (a) K. Kindler, *Ann.*, 450, 1 (1926); (b) E. Tommila and C. N. Hinshelwood, *J. Chem. Soc.*, 1801 (1936).

(6) *Cf.* ref. 5 of J. D. Roberts, R. A. Clement and J. J. Drysdale, THIS JOURNAL, 73, 2181 (1951); C. C. Price and D. C. Lincoln, *ibid.*, 73, 5836 (1951).

Direct Synthesis of Organotin Halides. I. Preparation of Dimethyltin Dichloride[1]

BY A. C. SMITH, JR.,[2] AND EUGENE G. ROCHOW

RECEIVED MAY 4, 1953

Organotin halides have been known for a hundred years,[3] and many compounds of the type R_a-SnX$_{4-a}$ have been synthesized. With the exception of two sealed-tube syntheses of iodides,[4,5] all preparations have been by indirect and often difficult methods.[6]

The direct synthesis of organosilicon and organogermanium halides[7] led to a study of the direct synthesis of organotin halides.[8] The effects of several metals as catalysts was studied by placing each metal over a thin film of evaporated tin on a microscope slide and heating the slide in an atmosphere of methyl chloride for one-half hour at 300°. Any unusual reactivity of the metallic couple was indicated by reaction and removal of the tin at the junction of the two metals. Copper proved to be the most promising catalyst, with some activity also exhibited by silver and gold. Mercury, iron, selenium, arsenic, titanium, antimony, tellurium, calcium, magnesium, zirconium, aluminum, chro-

(1) From a thesis submitted by A. C. Smith, Jr., to the Graduate School of Arts and Sciences of Harvard University.

(2) Metal and Thermit Fellow at Harvard University 1949–1950.

(3) C. Lowig. *Ann.*, 84, 309, 313 (1852).

(4) A. Cahours, *ibid.*, 114, 373 (1860).

(5) Karantassis and Basileiados, *Compt. rend.*, 205, 460 (1937).

(6) An extensive discussion is given in E. Krause and A. v. Grosse, "Die Chemie der metall-organischen Verbindungen," Chapt. V, Borntraeger, Berlin, 1937, pp. 311–372.

(7) E. G. Rochow, THIS JOURNAL, 67, 963 (1945); 69, 1729 (1947).

(8) The experiments reported herein were conducted in the period 1949 to 1951. After a full account had been prepared, U. S. Patent 2,625,559 in the same field, (Frederick A. Smith, assigned to Union Carbide and Carbon Corp.) appeared on Jan. 13, 1953. The present paper is a condensed version dealing almost entirely with those aspects of our work not touched upon by the F. A. Smith patent. Full details of our own work are available in the thesis of reference (1).
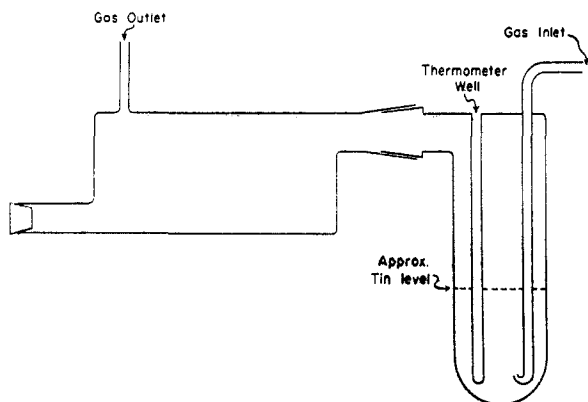
Fig. 1.—Dimensions: reaction chamber, 65 × 200 mm.; condenser (body), 80 × 200 mm.

mium, silicon, manganese, cobalt, nickel, zinc, cadmium, germanium, lead, bismuth and iodine gave no indications of being good catalysts, although the mercury dissolved the coating of tin.

Following this survey, methyl chloride was passed through molten tin[9] at various temperatures, with various proportions of copper added to the tin as catalyst. Reaction occurred at the melting point of the tin (232°) and up to 450°, with the range of 300–350° being optimum. The product was practically pure dimethyltin dichloride,[10] together with very small amounts of trimethyltin chloride and methyltin trichloride. At optimum conditions, a yield of 0.3 g. of dimethyltin dichloride per hour could be obtained from an input of 10 cc. per minute (1 g. per hr.) of methyl chloride, most of the excess methyl chloride being recoverable at the output.

Under the operating conditions employed, it could be expected that copper(II) chloride, copper(II) oxide, copper(I) oxide, tin(II) chloride, tin(II) oxide, and tin(IV) oxides might be present as impurities at the start or be formed to some extent during operation. Each of these substances was tested separately for its effect both on the induction period of the reaction and on its continued operation. Of these, only tin(II) oxide showed any marked effect, and that was to increase the induction period, an effect also noticed when the molten tin stood in contact with air before admitting methyl chloride. Treatment of the tin with hydrogen before admitting methyl chloride materially reduced the induction period.

The effects of zinc, lead, sodium, mercury and water on the starting and the progress of the reaction then were studied. Of these, only sodium showed any pronounced effect, and that was to cause an increased output of trimethyltin chloride and a corresponding retention of chlorine as sodium chloride in the reaction vessel.

The useful duration of the reaction was shortened by the accumulation of residues in the reaction mixture, particularly at the surface of the tin. When-

(9) Anal. 0.01% Fe, 0.01% Pb, 0.02% Zn, no As or Cu. Another source provided 99.981% pure tin containing 0.004% Pb, 0.001% Cu, 0.007% Sb, and 0.008% Fe, but this did not react readily with CH₃-Cl until 0.2 to 1.0% of Zn was added.

(10) White crystals, easily sublimed at 20 to 50°, m.p. 106° (ref. 6 gives 90°). Anal. Calcd. for C₂H₆SnCl₂: C, 11.34; H, 2.84; Cl, 32.28. Found: C, 11.15; H, 3.00; Cl, 32.21.

ever considerable residue appeared, the yield of dimethyltin dichloride decreased and the product became increasingly contaminated with by-products and with tarry material. The residues were found to be composed chiefly of copper–tin intermetallic compounds and porous carbon. By operating the reaction between pure tin and methyl chloride at the optimum conditions determined with copper as catalyst, it was found that dimethyltin dichloride could be produced less dependably but in favorable yields without a catalyst. The accumulation of harmful residues was so greatly reduced that the reaction vessels did not become choked nor the reaction inhibited, but there was usually an induction period. The reaction was inhibited by tin(II) oxide, but relatively uninfluenced by tin(II) chloride. The reaction appears to be catalyzed or aided by the product, which, because of its volatility, escapes readily from the reaction zone. Before any product appears, very small amounts of inhibiting substances may divert the methyl chloride into other reactions. Such substances may very well be those which accelerate the pyrolysis of methyl chloride,[11] for if the reaction with tin is delayed in getting started the "right" way, the accumulation of carbon from pyrolysis of methyl groups accelerates further pyrolysis and keeps the reaction going in the "wrong" way. Experiments indicated that extended surface areas (of fritted glass distributors, finely-divided carbon, particulate residues, etc.) interfered in this way.

Many different reaction vessels were tried, but those using molten tin were preferred because they presented a fresh surface of the metal to the incoming methyl chloride. The most extreme attempt in this direction involved spraying a fine jet of molten tin into an atmosphere of methyl chloride at 300–350°. The reaction was successful in that dimethyltin dichloride was produced, but the yields were extremely low because a stream of two to four liters of gas per minute was necessary to atomize the liquid tin. This large volume gave a very short reaction time, and most of the tin agglomerated on the walls, which acted as baffles. A tower of large diameter and considerable length probably would be necessary to get high conversions.

The type of reaction vessel found to be most generally adaptable to laboratory experiments consisted of a vertical cylinder 6.5 × 20 cm., into which were sealed a gas delivery tube and a thermometer well. A horizontal outlet near the top connected through a 24/40 joint to an inclined air-cooled condenser 8 × 20 cm. in which the crystals collected. The product was removed by melting the crystals and collecting the liquid from a delivery tube at the lower end. The reaction chamber held approximately 1 kg. of tin; the condenser about 100 g. of product. Nearly a hundred experiments were carried out in such vessels, in the manner indicated below.

Experimental

Copper-catalyzed Reaction of Methyl Chloride with Tin.— In one example, a vessel of the type described was charged with 1400 g. of tin and 130 g. of copper powder, and was
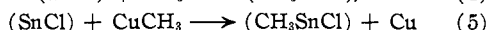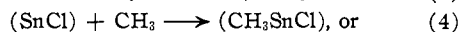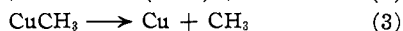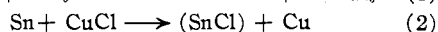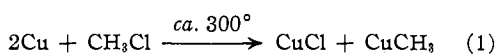
(11) K. Weisler. Chem. Z., 52, 182 (1928).

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 $(CH_3)_2$-$SnCl_2$ 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.
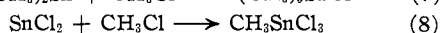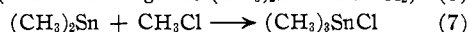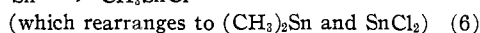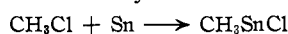
Discussion

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]

$$2Cu + CH_3Cl \xrightarrow{ca.\ 300°} CuCl + CuCH_3 \quad (1)$$
$$Sn + CuCl \longrightarrow (SnCl) + Cu \quad (2)$$
$$CuCH_3 \longrightarrow Cu + CH_3 \quad (3)$$
$$(SnCl) + CH_3 \longrightarrow (CH_3SnCl), or \quad (4)$$
$$(SnCl) + CuCH_3 \longrightarrow (CH_3SnCl) + Cu \quad (5)$$

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.

$$CH_3Cl + Sn \longrightarrow CH_3SnCl$$

(which rearranges to $(CH_3)_2Sn$ and $SnCl_2$) (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.

(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

$$3SnO + 2CH_3Cl \longrightarrow (CH_3)_2Sn + SnOCl_2 + SnO_2$$
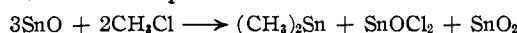
The insoluble, non-volatile dimethyltin then absorbs more methyl chloride to form volatile trimethyltin chloride

$$CH_3Cl + (CH_3)_2Sn \longrightarrow (CH_3)_3SnCl$$
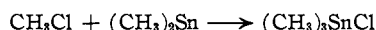
Only one-third of the tin thereby is converted to volatile product, leaving a powdered mixture of tin(IV) compounds and causing the reaction zone to move along the tube.

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

(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.