temperature of the vapors reaches 115°. The distillate is neutralized with 20% sodium carbonate and evaporated to dryness then extracted with absolute alcohol as indicated above. The net yield is 84%.

Esterification proceeds normally in the presence of sulfuric acid. It is entirely superfluous to use anhydrous trifluoroacetic acid as either the 80% solution, or the unrefined sodium salt can be used. The esterification is fast and complete. The operation is best carried out by heating the reagents in a flask fitted with a distilling column. A mixture of ether, ethanol and ester distills at 54–55°, which separates into two layers at about room temperature. From this mixture, the alcohol is removed by repeated washings with a cold concentrated solution of calcium chloride, followed by vigorous agitation with solid calcium chloride and drying over phosphorus pentoxide. The esterification is quantitative, but the yield of pure ester depends markedly on the skill of the operator.

The physical constants listed by Swarts[3] for the acid and the ethyl ester were duplicated.

Difluoroacetic acid was prepared in accordance with the equation

$$CHF_2CH{=}CCl_2 + 2KMnO_4 + 3NaOH \longrightarrow CHF_2CO_2Na + 2NaCl + K_2CO_3 + MnO_2$$

The equipment was that used for the preparation of trifluoroacetic acid. The oxidation was however more exothermic, which led to alterations in the mode of operation. To a stirred solution of 670 g. of potassium permanganate (calcd. 632 g.) and 250 g. of sodium hydroxide (calcd. 240 g.) in three liters of water, 295 g. (2 moles) of $CHF_2CH{=}CCl_2$[6] were added through a dropping funnel. This addition brought the temperature of the liquid rapidly from 28 to 70° where it was held by external cooling while the addition was continued as fast as practicable. The oxidation was virtually complete in three hours. This was verified by heating to 85° and observing that the reflux was free of organic layer. After cooling the working up of the reaction products followed the preceding procedure. The difluoroacetic acid was finally obtained in a 90% mixture with water, which boiled between 125 and 133° as a clear colorless sharp smelling liquid which fumed slightly in the air. The purification to the absolute acid was done via the sodium salt. The net yield was 86%.

The compound is adequately described by Swarts.[3] Its esterification does not require the use of pure acid. Both the crude or the sodium salt have been quantitatively transformed into various esters, the purification of which is mostly a matter of removing entrained alcohol.

Difluorochloroacetic acid was prepared from $CClF_2CCl{=}CCl_2$,[4] in accordance with the equation $3CClF_2CCl{=}CCl_2 + 4KMnO_4 + 14NaOH \rightarrow 3CF_2ClCO_2Na + 4KCl + 5NaCl + 3Na_2CO_3 + 4MnO_2 + 7H_2O$. The apparatus and procedure were substantially those for trifluoroacetic acid, except that an excess of caustic always was avoided. The oxidation was slower, and would not maintain itself, so heat was supplied throughout the operation. After two days, the oxidation was interrupted, despite the fact that it was not yet complete. The material was worked up as indicated above, finally to obtain 47 g. of acid, at the expense of 108 g. of $CClF_2CCl{=}CCl_2$. This is a 70% yield. The acid is described by Swarts.

Summary

For the preparation in high yield of fluorinated acids a method is presented which consists in the alkaline oxidation of an adequately chosen fluorinated olefin. This method is made possible by the resistance of fluorinated acids to the haloform reaction.

COLUMBUS, OHIO RECEIVED NOVEMBER 3, 1943

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[6] This olefin was first made by A. M. Whaley (Research Chemicals, San José, California) by condensing $CHCl{=}CHCl$ and $CHCl_3$ on $AlCl_3$ to $CHCl_2{-}CHClCHCl_2$, removing HCl to obtain $CHCl_2CH{=}CCl_2$ and fluorinating to $CHF_2CH{=}CCl_2$ in the manner previously described.[1]

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

Polarographic Behavior of Chloro and Bromo Complexes of Stannic Tin

BY JAMES J. LINGANE

Since the standard potential of the stannic ion-stannous ion couple is about −0.10 v. *vs.* the saturated calomel electrode one might infer that stannic ion should be easily reducible at the dropping electrode, but actually this is not true. With solutions of stannic tin in 1 to 2 *M* perchloric acid no indication of a reduction wave is obtained before the discharge of hydrogen. In such solutions the predominating ionic species is probably the hexaquostannic ion $Sn(H_2O)_6^{+4}$, and apparently the *rate* of reduction of this ion is so slow that no appreciable reduction occurs during the short life of each mercury drop.

Furthermore, no indication of a reduction wave is observed with stannic tin in sodium hydroxide solution, nor from acidic, neutral, or basic tartrate solutions, nor from acidic oxalate solutions.[1] Apparently the complexes present in these solutions are either too stable, or are reduced too slowly, to permit the occurrence of a wave.

In previous studies it was observed that a rather poorly developed wave is obtained from solutions of stannic tin in 1 *N* perchloric acid containing 0.5 *N* sodium chloride,[2] or from 1 *N* hydrochloric acid.[1] Since the determination of tin from the stannic state is obviously much more convenient than its determination from the stannous state, and since satisfactory conditions for the polarographic determination of stannic tin have not heretofore been described, it seemed worth while to investigate more thoroughly the wave obtained from chloride media. It has been found that when the concentration of chloride ion in the supporting electrolyte is made very large (greater than 4 *M*), so that the *aquo* stannic ion is converted more or less completely into the *chloro* complex, $SnCl_6^{=}$, a very well developed doublet wave is obtained which is entirely suitable for analytical purposes. A fairly well developed doublet wave is also obtained from the reduction of the hexabromostannate ion in concentrated bromide solutions.

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(1) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

Experimental

A stock solution of stannic chloride was prepared by dissolving 6.163 g. of pure tin in a warm mixture of 50 cc. of 12 *N* hydrochloric acid and 25 cc. of 15 *N* nitric acid. The solution was diluted to *ca.* 125 cc., boiled for a few minutes to remove chlorine and oxides of nitrogen, treated with 30 cc. of 12 *N* hydrochloric acid, and diluted to exactly one liter. The final solution was 0.05192 *M* in respect to stannic chloride, about 1 *N* in hydrochloric acid, and it contained a small amount of nitric acid.

Polarograms were recorded according to the usual technique[2] with a calibrated Sargent-Heyrovsky Polarograph. In most cases an H-type cell with a saturated calomel anode[2] was used, and air was removed from the solutions with purified nitrogen. The cell was placed in a water thermostat at 25.00°. The dropping electrode assembly, which included a stop-clock device for measuring *m* automatically, has been described elsewhere.[3]

Results and Discussion

The polarograms of stannic tin in various concentrations of hydrochloric acid (in the presence of 0.005% gelatin) shown in Fig. 1 demonstrate the pronounced effect of the concentration of chloride ion on the character of the stannic wave.

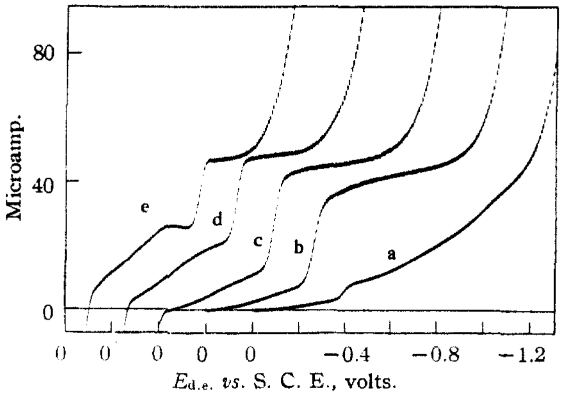

Fig. 1.—Influence of chloride ion concentration on the polarogram of stannic tin. Concentration of stannic chloride was 2.60 millimolar in each case, and 0.005% gelatin was present as a maximum suppressor. Concentrations of hydrochloric acid were (a) 0.2, (b) 1.0, (c) 2.0, (d) 4.0, and (e) 6.0 *N*.

In 0.2 *N* hydrochloric acid an abnormally small wave is observed and a constant limiting current is not attained (curve a). Since in strongly acid solutions which do not contain chloride ion (*e. g.*, 1 *M* perchloric acid) no wave at all is observed, it is clear that the appearance of the wave in 0.2 *N* hydrochloric acid must be due to the formation of mixed *aquo chloro* complexes, such as $Sn(H_2O)_4Cl_2^{++}$, whose rate of reduction at the dropping electrode is faster than that of the hexaquostannic ion. However from the character of curve a it seems evident that the rate of reduction of such *aquo chloro* complexes is still not great enough to permit the attainment of a diffusion controlled limiting current; the steady increase in current beyond the wave is typical of a rate-controlled current. With increasing concentration of chloride ion (curves b to e) a well-defined double wave develops, whose total height becomes constant when the concentration of chloride is greater than about 4 *N*. This reflects the existence of increasing proportions of higher order *chloro* complexes with increasing chloride ion concentration until finally the predominant complex is probably $SnCl_6^{=}$, which is reduced rapidly enough so that the limiting current becomes diffusion controlled.

From the fact that with concentrations of chloride ion greater than about 4 *N* the height of the first wave is one-half the total height of the double wave (compare also Fig. 2) it is evident that the first wave must result from the reduction of the hexachlorostannate ion to the stannous state, and the second wave corresponds to reduction of the chlorostannite ion to the metal. This conclusion is substantiated by the fact that the half-wave potential of the second wave (−0.46 v. in 1 *N* hydrochloric acid) coincides with that observed with stannous tin alone in similar chloride solutions.[1]

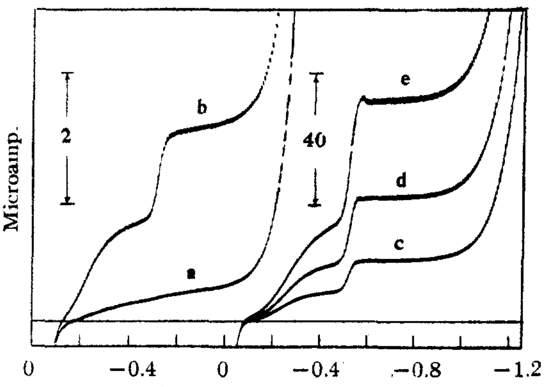

Fig. 2.—Polarograms of various concentrations of stannic chloride in a supporting electrolyte composed of 4 *M* ammonium chloride, 1 *M* hydrochloric acid, and 0.005% gelatin. Concentrations of stannic tin were (a) 0, (b) 0.129, (c) 0.962, (d) 1.98, and (e) 3.58 millimolar (see Table I).

The steep slope of the second wave indicates that the reduction of the chlorostannite ion at least approaches thermodynamic reversibility; the difference between $E_{3/4}$ and $E_{1/4}$ is 0.030 ± 0.005 v., which agrees well with the theoretical value 0.029 v. for a reversible 2-electron reduction.[2,4] On the other hand, the small slope of the first wave shows that the chlorostannate ion is not reduced reversibly at the dropping electrode; *i. e.*,

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[3] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 329 (1944).

[4] J. J. Lingane, *Chem. Rev.*, **29**, 1 (1941).

at points on the first wave the rate at which chlorostannate ion is reduced, as well as the rate at which it diffuses up to the electrode, governs the observed current.

With concentrations of hydrochloric acid between 0.2 and 4 *N*, and concentrations of tin smaller than 0.005 *M*, the half-wave potential of the second wave was found to be a linear function of the logarithm of the chloride ion concentration, the empirical relation being

$$E_{1/2} = -0.464 - 0.10 \log C_{\text{Cl}^-} \qquad (1)$$

Assuming the *chloro* stannous complex to be $SnCl_4^=$, that it is reduced reversibly at the dropping electrode according to $SnCl_4^= + 2e^- + Hg = Sn(Hg) + 4Cl^-$, and that concentrations are equal to activities since data for the correction are not available, the theoretical slope of the plot of $E_{1/2}$ *vs.* log C_{Cl^-} is[2,4] $\Delta E_{1/2}/\Delta \log C_{\text{Cl}^-} = -(4 \times 0.059)/2 = -0.12$ v. The agreement of the observed slope, −0.10 v., with the theoretical value is sufficiently good to show that $SnCl_4^=$ must be the predominant stannous complex under these conditions.

Since a high concentration of chloride ion is essential to optimum development of the chlorostannate wave, but too high a concentration of hydrogen ion is deleterious because the final increase in current (discharge of hydrogen ion) then occurs at a relatively positive potential, experiments were performed with a supporting electrolyte consisting of 4 *M* ammonium chloride and 1 *N* hydrochloric acid. Figure 2 shows polarograms of various concentrations of chlorostannate ion in this supporting electrolyte in the presence of 0.005% gelatin as a maximum suppressor. The wave is seen to be much better developed than in hydrochloric acid alone; in fact this is the only supporting electrolyte of those investigated so far in which a really well developed stannic wave is obtained. The half-wave potential of the first wave is −0.25 v. and that of the second is −0.52 v. *vs.* the saturated calomel electrode.

The data in Table I demonstrate that the limiting current is accurately proportional to the concentration of chlorostannate ion, and hence is diffusion controlled. The average value of the diffusion current constant (6.55) corresponds to a value of 0.73×10^{-5} cm.^{2} sec.$^{-1}$ for the diffusion coefficient of the chlorostannate ion in this particular medium at 25°.

TABLE I

DIFFUSION CURRENT CONSTANT OF CHLOROSTANNATE ION

Supporting electrolyte comprised 4 *M* ammonium chloride, 1 *N* hydrochloric acid, and 0.005% gelatin; temp. is 25.00°; $m^{2/3}t^{1/6}$ = 2.86 mg.$^{2/3}$ sec.$^{-1/2}$. The diffusion currents were measured at −0.7 v., and correction has been applied for the residual current (curve a in Fig. 2).

Sn^{+4} Millimolar	i_d Microamp.	$i_d/Cm^{2/3}t^{1/6}$
0.129	2.46	6.65
0.962	18.0	6.55
1.98	36.9	6.53
3.58	66.6	6.52
		Av. 6.55 ± 0.05

It is evident that a supporting electrolyte composed of 4 *M* ammonium chloride and 1 *N* hydrochloric acid is well suited to the polarographic determination of tin. Of the metals with which tin is commonly associated, copper, antimony, bismuth, and lead, whose half-wave potentials are more positive than about −0.6 v., will interfere, but it should be possible to determine small amounts of tin in the presence of large amounts of cadmium or zinc without difficulty. Furthermore, by measuring the second wave it may be possible to determine tin in the presence of equal or smaller amounts of lead. These possibilities are being investigated.

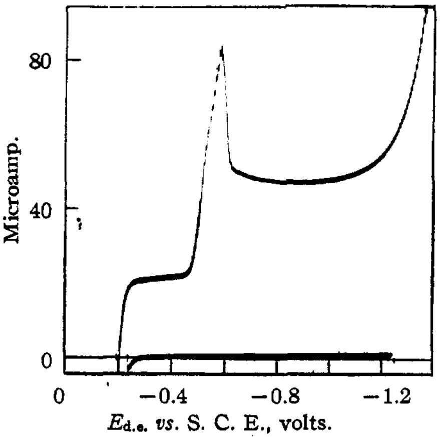


Fig. 3.—Polarogram of 2.48 millimolar stannic tin in a supporting electrolyte composed of 4 *M* ammonium bromide and 0.005% gelatin.

The behavior of stannic tin in a supporting electrolyte containing a high concentration of bromide ion is illustrated by the typical polarogram in Fig. 3. The diffusion current of the first stage of reduction is seen to be much better developed than in the chloride media. However, it should be noted that the half-wave potential of the first wave is not the half-wave potential for the reduction of the bromostannate ion, which doubtless is more positive, but rather it corresponds to the potential of the *anodic* reaction $Hg + 4Br^- = HgBr_4^= + 2e$. Hence the steep slope of the first wave tells nothing about the degree of reversibility of the reduction of the bromostannate ion. The half-wave potential of the second wave is −0.50 v., almost identical with that of the *chloro* complex, but the pronounced maximum causes the second diffusion current to be rather poorly defined.

Since the half-wave potential of lead in a concentrated bromide solution is considerably more negative than −0.4 v., whereas the first diffusion current of the bromostannate ion is completely developed at this potential, this supporting electrolyte may be useful for determining small amounts of tin in the presence of large amounts of lead.

The diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ of the bromostannate ion at 25° in 4 M ammonium bromide in the presence of 0.005% gelatin was found to be 6.52 (total double wave), and hence virtually the same as that of the *chloro* complex in a similar concentration of ammonium chloride.

Summary

In the presence of a very large concentration of chloride ion stannic tin produces a well developed doublet wave, the first part of which results from reduction of the chlorostannate ion to the stannous state and the second corresponds to reduction of the stannous complex to the metal. In a supporting electrolyte composed of 4 M ammonium chloride, 1 N hydrochloric acid, and 0.005% gelatin, the half-wave potentials of the doublet wave are −0.25 and −0.52 v. *vs.* the saturated calomel electrode, and the total diffusion current constant $i_d/(Cm^{2/3}t^{1/6})$ is 6.55 at 25°. The characteristics of the wave are well suited to the polarographic determination of tin.

Stannic tin also produces a well-defined double wave in 4 M ammonium bromide as a supporting electrolyte.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 20, 1945

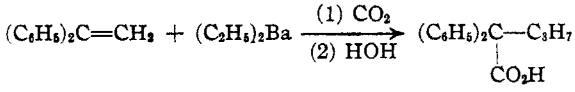
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Organocalcium, -Strontium and -Barium Compounds[1]

BY HENRY GILMAN, A. H. HAUBEIN, GORDON O'DONNELL AND LAUREN A. WOODS

The recent availability of organostrontium[2] and organobarium[3] compounds makes it possible to compare some reactions of these compounds as well as the organocalcium compounds.

Addition to Olefinic Linkage.—Diethylbarium like diethylstrontium[2] adds readily to 1,1-diphenylethylene. The mode of addition was established by carbonation.

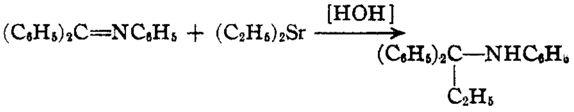


$$(C_6H_5)_2C{=}CH_2 + (C_2H_5)_2Ba \xrightarrow[\text{(2) HOH}]{\text{(1) CO}_2} (C_6H_5)_2\underset{\displaystyle CO_2H}{\underset{|}{C}}{-}C_3H_7$$

However, diethylbarium did not add to stilbene, in contrast to the known addition of n-butyllithium[4] and phenylisopropylpotassium[5] to this compound.

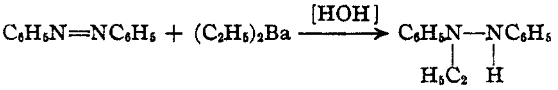
Diethylbarium and ethyllithium, but not diethylstrontium, add to a limited extent to styrene, and the acid obtained subsequent to carbonation is α-phenyl-n-valeric acid.

Addition to Benzophenone-anil.—The Grignard reagent reacts very slowly with benzophenone-anil, and when the reaction is forced the special type of lateral-nuclear 1,4-addition occurs.[6a] However, the more reactive phenylalkali compounds show 1,2-addition to the azomethylene linkage to give triphenylmethylaniline.[6b] As might have been predicted, diethylstrontium and diethylbarium, like ethyllithium, add to the azomethylene linkage.



$$(C_6H_5)_2C{=}NC_6H_5 + (C_2H_5)_2Sr \xrightarrow{[HOH]} (C_6H_5)_2\underset{\displaystyle C_2H_5}{\underset{|}{C}}{-}NHC_6H_5$$

Addition to Azobenzene.—Several products are formed by the reaction of azobenzene with RM compounds, and the relative reactivity of the organometallic compound determines rather uniquely the nature of the product, the very reactive types giving hydrazines.[6c] Diethylstrontium and diethylbarium add to give 1-ethyl-1,2-diphenylhydrazine, which was identified after rearrangement, as N-ethylbenzidine.



$$C_6H_5N{=}NC_6H_5 + (C_2H_5)_2Ba \xrightarrow{[HOH]} C_6H_5\underset{\displaystyle H_5C_2}{\underset{|}{N}}{-}N\underset{\displaystyle H}{\underset{|}{}}C_6H_5$$

Metalation.—Diethylbarium metalates anisole in the ortho-position to give, subsequent to carbonation, o-methoxybenzoic acid. However, the metalation of methyl phenyl sulfide by diethylstrontium and diethylbarium was unusual. It has been shown that the metalation of methyl phenyl sulfide by n-butyllithium takes place laterally[7]

$$C_6H_5SCH_3 + n\text{-}C_4H_9Li \xrightarrow[\text{HOH}]{\text{CO}_2} C_6H_5SCH_2CO_2H$$

No lateral metalation was observed with diethylstrontium and diethylbarium; instead orthonuclear metalation occurred

$$C_6H_5SCH_3 + (C_2H_5)_2Sr \xrightarrow[\text{(2) HOH}]{\text{(1) CO}_2} o\text{-}HOOCC_6H_4SCH_3$$

An equally unexpected metalation occurred in the reaction between dibenzothiophene and di-

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[1] Paper LVIII in the series: "The Relative Reactivities of Organometallic Compounds": the preceding paper with L. A. Woods is in THIS JOURNAL, **67**, 520 (1945).

[2] Gilman, Meals, O'Donnell and Woods, *ibid.*, **65**, 268 (1943).

[3] Gilman and Woods, *ibid.*, **67**, 520 (1945).

[4] Ziegler, Crössmann, Klein and Schäfer, *Ann.*, **473**, 35 (1929).

[5] Ziegler and Bähr, *Ber.*, **61**, 253 (1928).

[6] (a) Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929); (b) Gilman and Kirby, *ibid.*, **63**, 2046 (1941); (c) Gilman and Bailie, *J. Org. Chem.*, **2**, 84 (1937).

[7] Gilman and Webb, THIS JOURNAL, **62**, 987 (1940).