and 33.5 g. (0.2 mole) of carefully purified dibenzofuran. A slow stream of nitrogen maintained throughout the experiment was found to reduce materially the amount of darkening. The mixture was heated with constant stirring; in the neighborhood of 80° the whole mass became liquid and two layers were formed, the organic layer being on top. The temperature was held at 110° for one hour, during which time most of the water was driven off and a small amount of dibenzofuran steam distilled. The temperature was then raised to 165° and held there for four hours. During this time the rest of the water was driven off and there was a gradual evolution of hydrogen chloride. The reaction mixture darkened appreciably during this time, the two layers became one and a bright yellow solid deposited on the bottom of the flask. The reaction was allowed to cool under nitrogen and then was extracted with 100 ml. of 95% ethyl alcohol to remove all the unreacted dibenzofuran. The residue was then repeatedly extracted with absolute ethyl alcohol until a solution on cooling deposited no crystals. In this manner 5.1 g. of material was extracted which represented a 9% yield of di-4-dibenzofurylthallium chloride.

Anal. Calcd. for $C_{24}H_{14}O_2ClTl$: Tl, 35.5. Found: Tl, 35.3.

The yellow solid which remained after the alcoholic extractions was recrystallized from a large quantity of boiling water and shown to contain only thallium and chlorine.

Anal. Calcd. for Tl_2Cl_3: Tl, 79.5. Found: Tl, 79.9.

No unreacted thallium trichloride was present, as was demonstrated by the failure to obtain the characteristic dark brown precipitate with potassium iodide solution.

To demonstrate the point of entrance into the dibenzofuran nucleus, 2.9 g. (0.005 mole) of the R_2TlCl compound was suspended in 50 ml. of chloroform and 2.5 g. (0.01 mole) of iodine was added. The mixture was stirred and refluxed for five hours, filtered from thallous iodide, and the solvent removed under reduced pressure. The residue was recrystallized twice from methanol to give 1.1 g. or 38% of 4-iododibenzofuran which melted at 69–72° and which gave no depression in a mixed melting point with an authentic sample.

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Thallous Salts as Derivatives of Sulfonic Acids

BY HENRY GILMAN AND R. K. ABBOTT, JR.

Incidental to an examination of organothallium compounds we have observed that thallous salts appear to be reagents of choice for characterizing or derivatizing some sulfonic acids. Hitherto, the best general types for this purpose have been the amines, and the *p*-toluidine[1] and phenylhydrazine[2] salts.

Some advantages of the thallous salts are as follows: (1) They are readily prepared in practically quantitative yields from the sulfonic acid or its sodium salt. (2) They crystallize readily, and preferably from water, to give generally high-melting solids. (3) One of the methods of preparation (from the free sulfonic acid and thallous hydroxide) can be used titrimetrically to get a neutralization equivalent incidental to the preparation of the derivative. (4) The ease of formation of large, well-defined crystals suggests their application in micro-procedures.

Experimental

Procedure: from Free Sulfonic Acid.—The free sulfonic acid (about 0.01 mole) dissolved in a little warm water is titrated with about 0.1 *N* thallous hydroxide solution, using phenolphthalein as an indicator. Thallous hydroxide was prepared from equivalent quantities of thallous sulfate and barium hydroxide, each dissolved in a minimum volume of boiling water. The precipitate of barium sulfate was allowed to digest for three hours on the steam-plate to improve the filtering qualities of the precipitate. The clear solution was then concentrated under reduced pressure, and the normality determined by titration with standard acid.

From the Sodium Sulfonate.—To the sodium sulfonate, dissolved in a small volume of water, is added the calculated quantity of thallous formate[3] dissolved in a few drops of water. In a few cases a precipitate forms immediately in hot solution, but more often crystals are deposited only as the solution cools.

The thallous formate procedure depends on the greater insolubility in water of the thallous sulfonate as compared with the sodium sulfonate. From our present limited studies only two sodium sulfonates could not be used as such. In both these cases, sodium benzenesulfonate and sodium 1,2,3,4-tetramethylbenzene-5-sulfonate, the thallous salt was about as soluble as the sodium salt, and both deposited as the aqueous solution was cooled.

The thallous salts of other acids (including sulfinic, phosphonic, and arsonic types) are being examined.

It might be mentioned that the thallous salts may be particularly suitable for the separation and isolation of isomers. For example, the three tetramethylbenzenesulfonates differ significantly in solubility: thallous 1,2,4,5-tetramethylbenzene-3-sulfonate is very insoluble in water; thallous 1,2,3,4-tetramethylbenzene-5-sulfonate is extremely soluble; and thallous 1,2,3,5-tetramethylbenzene-4-sulfonate is of intermediate solubility in water. Several of the thallous sulfonates described in Table I were prepared from 0.1 g. of the sulfonic acid with customary, non-micro technique. The different crystal forms of the thallous sulfonates should be helpful in any development of micro-analytical procedures.

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(1) Fieser, THIS JOURNAL, **51**, 2460, 2471 (1929).

(2) Latimer and Bost, *ibid.*, **59**, 2500 (1937).

(3) The thallous formate used was purchased from the Eastman Kodak Company.

TABLE I

THALLOUS SULFONATES

Thallous salt	M. p., °C.	Formula	Tl analyses, %[4] Calcd.	Tl analyses, %[4] Found
Sulfamate	139-140	H_2O_3NSTl	68.0	68.0
o-Toluenesulfonate	213-216	$C_7H_7O_3STl$	54.3	54.3
p-Toluenesulfonate	226-228	$C_7H_7O_3STl$	54.3	54.1
p-Bromobenzenesulfonate	274-276	$C_6H_4O_3BrSTl$	46.3	46.3
m-Nitrobenzenesulfonate	307-309	$C_6H_4O_5NSTl$	50.3	50.2
Sulfanilate	207-209	$C_6H_6O_3NSTl$	54.3	54.2
2-Bromotoluene-4-sulfonate	220-222	$C_7H_6O_3BrSTl$	44.8	44.5
2-Aminotoluene-4-sulfonate	101-103	$C_7H_8O_3NSTl$	52.3	52.1
2-Naphthoquinone-4-sulfonate	228-232 dec.	$C_{10}H_6O_4STl$	47.9	47.6
d-Camphorsulfonate	267-269	$C_{10}H_{15}O_4STl$	46.8	46.6
1,2,3,4-Tetramethylbenzene-5-sulfonate[5]	260-262	$C_{10}H_{13}O_3STl$	49.0	48.7
1,2,3,5-Tetramethylbenzene-4-sulfonate[5]	283-285	$C_{10}H_{13}O_3STl$	49.0	48.9
1,2,4,5-Tetramethylbenzene-3-sulfonate[5]	340-341 dec.	$C_{10}H_{13}O_3STl$	49.0	48.8
Pentamethylbenzenesulfonate[5]	325-326	$C_{11}H_{15}O_3STl$	47.3	47.1

The sulfonic acid is readily regenerated from the thallous salt by acidification with hydrochloric acid.

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[4] Meyer and Bertheim, *Ber.*, **37**, 2051 (1904).

[5] The authors wish to thank Dr. L. I. Smith for samples of these sodium sulfonates. The melting points reported in Table I are uncorrected.

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The Catalytic Reduction of Dehydrocholic Acid in Presence of Raney Nickel

BY W. M. HOEHN AND H. E. UNGNADE

Dehydrocholic acid has been reduced with palladium and hydrogen in acetic acid, with aluminum amalgam with benzene and ether as the solvent,[1] with sodium amalgam[2] and electrolytically.[3] Ethyl dehydrocholate has been reduced with hydrogen in the presence of a catalyst consisting of nickel or cobalt.[4]

Biological systems also have been studied and it has been found that reductodehydrocholic acid,[5] isoreductodehydrocholic acid[6,7] and 7-hydroxy-3,12-diketocholanic acid,[8] were formed from dehydrocholic acid.

It has now been found that reductodehydrocholic acid is the main product when dehydrocholic acid is reduced in methanol solution with hydrogen in the presence of Raney nickel. Other compounds that have been isolated from the mixture were methyl dehydrocholate and methyl reductodehydrocholate. Yields of reductodehydrocholic acid as high as 85% of the theoretical amount may be obtained when the reduction of dehydrocholic acid in methanol solution is carried out at 105°, under a hydrogen pressure of 3800 lb. No further reduction of reductodehydrocholic acid was observed when it was submitted to a hydrogen pressure of 5800 lb. at a temperature of 230°.

Two typical runs are listed in the following table

Moles of dehydrocholic acid	T, °C.	P	Time, hr.	Products isolated
0.1	110	3800	3	67% reductodehydrocholic acid 20% methyl reductodehydrocholate 12% methyl dehydrocholate
0.2	105	3800	5	85% reductodehydrocholic acid 5% dehydrocholic acid 10% mixture of esters

Physical constants of the pure compounds

Reductodehydrocholic acid, m. p. 187–188° $[\alpha]^{25}D = +30 \pm 1$

Methyl dehydrocholate, m. p. 232–233° $[\alpha]^{25}D = +30 \pm 1$

Methyl reductodehydrocholate, m. p. 152–153° $[\alpha]^{25}D = +32 \pm 1$

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[1] Borsche and Hallwass, *Ber.*, **55**, 3318 (1922).

[2] Schenck, *Z. physiol. Chem.*, **69**, 383 (1910).

[3] Schenck, *ibid.*, **63**, 308 (1909).

[4] Bockmühl, Ehrhart and Ruschig, U. S. Patent 2,143,676 (1939).

[5] Kyoguku, *Z. physiol. Chem.*, **250**, 253 (1937).

[6] Shibuya, *J. Biochem.* (Japan), **17**, 385 (1933).

[7] Yamosaki and Kyoguku, *Z. physiol. Chem.*, **233**, 29 (1935); **235**, 443 (1935).

[8] Mori, *J. Biochem.* (Japan), **29**, 87 (1939).

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