two molecules of I by elimination of HF. Its structure was not elucidated.

The mother liquor of the above product was fractionated *in vacuo*. A light yellow oil distilled at 130° (0.4 mm.), which solidified spontaneously. From methanol, white plates of m.p. 59–60° were obtained; yield 7 g. The ultraviolet spectrum of this compound (IV) was practically identical with that of benzalacetophenone.

Anal. Calcd. for $C_{15}H_{11}FO$: C, 79.6; H, 4.9. Found: C, 79.6; H, 5.1.

The 2,4-dinitrophenylhydrazone of this ketone crystallized from butyl acetate in needles of m.p. 274–275°.

Anal. Calcd. for $C_{21}H_{15}FN_4O_4$: C, 62.1; H, 3.7. Found: C, 62.3; H, 3.5.

JERUSALEM, ISRAEL

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

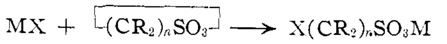
The Chemistry of Sultones. II. Alkylations of Organometallic and Related Compounds by Sultones[1]

BY WILLIAM E. TRUCE AND FRED D. HOERGER[2]

RECEIVED OCTOBER 1, 1954

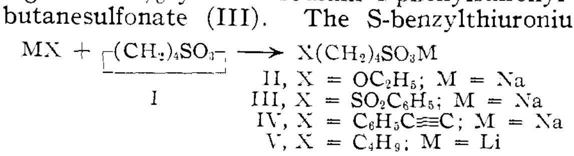
Sodium ethoxide, sodium benzenesulfinate, phenylethynylsodium, *n*-butyllithium and the sodium derivatives of diethyl malonate, ethyl acetoacetate and dibenzoylmethane are alkylated readily by 4-hydroxy-1-butanesulfonic acid sultone. The reaction of 4-hydroxy-1-butanesulfonic acid sultone with phenylmagnesium bromide produces both magnesium 4-phenyl-1-butanesulfonate and magnesium 4-bromo-1-butanesulfonate. The reaction of 2-*o*-hydroxyphenylethanesulfonic acid sultone with phenylmagnesium bromide gives *o*-(β-phenylsulfonylethyl)-phenol.

Helberger and co-workers[3,4] have shown recently that sultones serve as alkylating agents for a variety of nucleophilic reagents, such as alcohols, alkoxides, salts of inorganic and organic acids, amines and the sodium derivative of fluorene. The products of these reactions are substituted alkanesulfonates, but their structures were not established; presumably they arise according to the equation



$$MX + (CR_2)_nSO_3 \longrightarrow X(CR_2)_nSO_3M$$

In order to establish definitely the nature of the products obtained from the reactions of sultones with nucleophilic reagents, the reactions of sodium benzenesulfinate and sodium ethoxide with 4-hydroxy-1-butanesulfonic acid sultone (I) were studied. With sodium ethoxide, a 91% yield of sodium 4-ethoxy-1-butanesulfonate (II) was obtained. This product was characterized by comparison of its *p*-chloro-S-benzylthiuronium salt with an independently synthesized specimen. The independent synthesis involved the reaction of 4-chloro-1-ethoxybutane with aqueous sodium sulfite. The reaction of sodium benzenesulfinate with I gave a 53% yield of sodium 4-phenylsulfonyl-1-butanesulfonate (III). The S-benzylthiuronium derivative of III was identical with the corresponding derivative of a sulfonate independently synthesized from 4-chloro-1-phenylsulfonylbutane and sodium sulfite. These reactions confirm the structures assigned by Helberger to the alkylation products of sultones and establish a similarity in the reactions of sultones and alkyl sulfonates with nucleophilic reagents.



$$MX + (CH_2)_4SO_3 \longrightarrow X(CH_2)_4SO_3M$$

I

II, $X = OC_2H_5$; $M = Na$

III, $X = SO_2C_6H_5$; $M = Na$

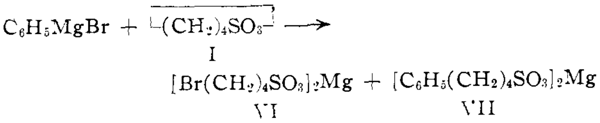
IV, $X = C_6H_5C{\equiv}C$; $M = Na$

V, $X = C_4H_9$; $M = Li$

In the first paper of this series[5] it was shown that C-alkylations are accomplished readily by the use of sultones as alkylating agents in the Friedel–Crafts reaction. Since alkyl sulfonates serve as carbon–carbon alkylating agents for organometallic compounds and since the reactions of sultones with nucleophilic reagents closely resemble the reactions of alkyl sulfonates, it seemed probable that sultones could serve as alkylating agents for carbon–carbon alkylations of organometallic and related compounds.

Carbon–carbon alkylation occurred readily in the reactions of both phenylethynylsodium and *n*-butyllithium with 4-hydroxy-1-butanesulfonic acid sultone (I). With phenylethynylsodium, an 85% yield of crude sodium 6-phenyl-5-hexyne-1-sulfonate (IV) was obtained; purification, however, reduced the yield to about 50%. The structure of IV was established by analysis of its *p*-chloro-S-benzylthiuronium derivative and by catalytic reduction to sodium 6-phenyl-1-hexanesulfonate. The latter compound was synthesized independently from 6-phenyl-1-bromobutane and sodium sulfite. The reaction of *n*-butyllithium with I gave a 58% yield of the very hygroscopic lithium 1-octanesulfonate which was characterized by comparison of its *p*-chloro-S-benzylthiuronium salt with an independently synthesized specimen.

The reaction of phenylmagnesium bromide with 4-hydroxy-1-butanesulfonic acid sultone produced a mixture of sulfonates, magnesium 4-bromo-1-butanesulfonate (VI) and magnesium 4-phenyl-1-butanesulfonate (VII). When two moles of the sultone I and one mole of Grignard reagent were employed,



$$C_6H_5MgBr + (CH_2)_4SO_3 \longrightarrow [Br(CH_2)_4SO_3]_2Mg + [C_6H_5(CH_2)_4SO_3]_2Mg$$

I VI VII

$$VI \xrightarrow[2,\ HCl]{1,\ Na_2CO_3} Br(CH_2)_4SO_3H \xrightarrow[-HBr]{} I \xrightarrow{MgBr_2} VI$$

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(1) Abstracted from a portion of the Ph.D. Dissertation of F. D. Hoerger, Purdue University, 1955.

(2) National Science Foundation Predoctoral Fellow, 1953–1954.

(3) J. H. Helberger, *et al.*, *Ann.*, **565**, 22 (1949); **562**, 23 (1949); **586**, 147 (1954); **586**, 158 (1954).

(4) J. H. Helberger, *Reichsamt Wirtshaftaufbau Chem. Br. Pruf. Nr.*, **15** (U. S. Office of Publication Board, P. B. 52013) 269 (1942).

(5) W. E. Truce and F. D. Hoerger, THIS JOURNAL, **76**, 5357 (1954).

the mixture of sulfonates was obtained in 90% yield. By fractional crystallization of this mixture, it was possible to isolate magnesium 4-phenyl-1-butanesulfonate (VII), identified by preparation of its sulfonamide[5] and *p*-chloro-S-benzylthiuronium salt.[5] It was not possible to isolate the bromosulfonate VI from the mixture of sulfonates. The presence of this sulfonate was shown by converting the crude reaction product to a mixture of sulfonic acids; by heating this mixture of sulfonic acids under vacuum, 4-bromo-1-butanesulfonic acid lost the elements of hydrogen bromide and was converted to 4-hydroxy-1-butanesulfonic acid sultone (I) which distilled away from the 4-phenyl-1-butanesulfonic acid.

Even when only one mole of sultone per mole of Grignard reagent was employed, both VI and VII were formed. This suggested that magnesium bromide also should react readily with 4-hydroxy-1-butanesulfonic acid sultone. Under the same reaction conditions as were employed with phenylmagnesium bromide, magnesium bromide and the sultone gave a 97% yield of magnesium 4-bromo-1-butanesulfonate (VI).

The formation of a mixture of sulfonates from the reaction of phenylmagnesium bromide with 4-hydroxy-1-butanesulfonic acid sultone is analogous to the formation of both hydrocarbons and alkyl halides in the reaction of Grignard reagents with alkyl sulfonates.[6-9] The latter reaction has been shown to proceed primarily according to the following equation regardless of whether one or two moles of alkyl sulfonate are used per mole of Grignard reagent

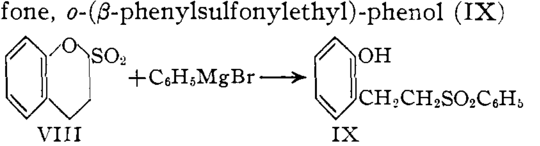
$$ArSO_3R + R'MgX \longrightarrow RR' + RX + (ArSO_3)_2Mg$$

A side reaction in the formation of hydrocarbons and alkyl halides in the reaction of Grignard reagents with alkyl sulfonates is sulfone formation[10,11]

$$ArSO_3R + R'MgX \longrightarrow ArSO_2R' + ROMgX$$

However, no evidence for sulfone formation was observed in the reaction of phenylmagnesium bromide with 4-hydroxy-1-butanesulfonic acid sultone.

In contrast to the behavior of 4-hydroxy-1-butanesulfonic acid sultone with phenylmagnesium bromide, Mustafa and co-workers[12] report that several derivatives of 1-naphthol-8-sulfonic acid sultone react with Grignard reagents to give sulfones. Likewise, we found that the reaction of phenylmagnesium bromide with 2-*o*-hydroxyphenylethanesulfonic acid sultone (VIII) gave a 62% yield of a sulfone, *o*-(β-phenylsulfonylethyl)-phenol (IX)

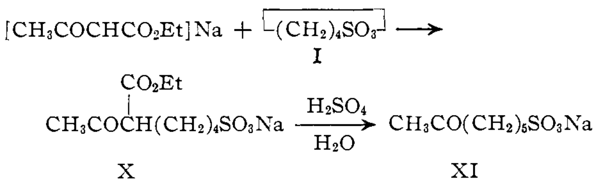


VIII IX

The difference in the mode of reaction of the sultones I and VIII with phenylmagnesium bromide is due to the fact that the sulfonate grouping would have to be displaced from an aromatic carbon atom in VIII in order for alkylation to occur; this is a much more difficult process than the displacement of the sulfonate grouping from an aliphatic carbon atom.

The sodium derivative of diethyl malonate was alkylated with 4-hydroxy-1-butanesulfonic acid sultone to give a 95% yield of sodium 5,5-dicarbethoxy-1-pentanesulfonate. This sulfonate was identified by its saponification equivalent and by comparison of its *p*-chloro-S-benzylthiuronium derivative with an independently synthesized specimen. 4-Hydroxy-1-pentanesulfonic acid sultone and the sodium salt of diethyl malonate gave a sulfonate in 93% yield. On the basis of saponification equivalent and analysis of its *p*-chloro-S-benzylthiuronium derivative and by analogy with the above alkylation of diethyl malonate, this sulfonate may be assigned the structure of sodium 5,5-dicarbethoxy-4-methyl-1-pentanesulfonate.

The sodium salt of ethyl acetoacetate also was alkylated readily with 4-hydroxy-1-butanesulfonic acid sultone to give an 82% yield of crude sodium 5-carbethoxy-6-oxo-1-heptanesulfonate (X). This sulfonate could not be purified by crystallization from water or alcohol and the saponification equivalent was in error by about 6%. The identity of the product was established, however, by hydrolysis and decarboxylation to sodium 6-oxo-1-heptanesulfonate (XI). The latter compound gave a *p*-chloro-S-benzylthiuronium salt identical with an independently synthesized specimen.



$$[CH_3COCHCO_2Et]Na + \underset{\text{I}}{\overline{\lfloor (CH_2)_4SO_3 \rfloor}} \longrightarrow$$

$$\underset{\text{X}}{CH_3CO\overset{\overset{\displaystyle CO_2Et}{|}}{C}H(CH_2)_4SO_3Na} \xrightarrow[H_2O]{H_2SO_4} \underset{\text{XI}}{CH_3CO(CH_2)_5SO_3Na}$$

The reaction of the sodium salt of dibenzoylmethane with 4-hydroxy-1-butanesulfonic acid sultone gave a sulfonate in 54% yield. Although it was not possible to obtain pure derivatives of this sulfonate, it was shown to be primarily sodium 5,5-dibenzoyl-1-pentanesulfonate (XII); cleavage of the sulfonate with dilute sodium hydroxide gave a 52% yield of benzoic acid and a 50% yield of sodium 5-benzoyl-1-pentanesulfonate (XIII). The identity of XIII was established by analysis of its *p*-chloro-S-benzylthiuronium salt and by Clemmensen reduction to sodium 6-phenyl-1-hexanesulfonate (XIV). The *p*-chloro-S-benzylthiuronium derivative of XIV was identical with the *p*-chloro-S-benzylthiuronium salt of the sulfonate obtained from

$$(C_6H_5CO)_2CHNa + \underset{\text{I}}{\overline{\lfloor (CH_2)_4SO_3 \rfloor}} \longrightarrow$$

$$\underset{\text{XII}}{(C_6H_5CO)_2CH(CH_2)_4SO_3Na} \xrightarrow[2,\ H^+]{1,\ NaOH} C_6H_5CO_2H +$$

$$\underset{\text{XIII}}{C_6H_5CO(CH_2)_5SO_3Na} \xrightarrow[HCl]{Zn(Hg)_x} \underset{\text{XIV}}{C_6H_5(CH_2)_6SO_3Na}$$

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(6) C. M. Suter and H. L. Gerhart, THIS JOURNAL, **57**, 107 (1935).

(7) H. Gilman and L. L. Heck, *ibid.*, **50**, 2223 (1928).

(8) J. W. Copenhaver, *et al.*, *ibid.*, **57**, 1312 (1935).

(9) H. Gilman and H. Robinson, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 47.

(10) H. Gilman and L. L. Heck, THIS JOURNAL, **50**, 2229 (1928).

(11) H. Gilman and J. Robinson, *Bull. soc. chim.*, **45**, 636 (1929).

(12) A. Mustafa, *et al.*, *J. Chem. Soc.*, 384 (1949); 2151 (1949); 1339 (1952).

the catalytic reduction of sodium 6-phenyl-5-hexyne-1-sulfonate (IV).

Abell[13] reports that in the alkylation of dibenzoylmethane with methyl iodide some ethyl benzoate and some phenyl ethyl ketone always are formed; prolonged heating of the reaction mixture increases their formation. Since a longer reaction time was used for the reaction of dibenzoylmethane with I than that reported for the reaction of dibenzoylmethane with methyl iodide, it is quite likely that some of XII is cleaved by sodium ethoxide to give ethyl benzoate and XIII. Thus, the failure to obtain pure derivatives of the product from the dibenzoylmethane–sultone reaction probably results from XII being contaminated with XIII.

Experimental

Sodium 4-Ethoxy-1-butanesulfonate.—To a solution of sodium ethoxide prepared from 2.3 g. (0.10 g. atom) of sodium and 75 ml. of absolute ethanol was added 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone[5]; the resulting solution was refluxed for 46 hours. After cooling the mixture and diluting with 150 ml. of ether, the crystalline sulfonate was filtered. After drying in a vacuum oven, the sulfonate weighed 18.5 g. (91% yield).

p-Chloro-S-benzylthiuronium 4-ethoxy-1-butanesulfonate had m.p. 113–114.5°. A mixed m.p. with an independently synthesized sample (see below) showed no depression.

Anal. Calcd. for $C_{14}H_{23}ClN_2O_4S_2$: C, 43.90; H, 6.05; N, 7.32. Found: C, 43.98; H, 5.97; N, 7.27.

Independent Synthesis of Sodium 4-Ethoxy-1-butanesulfonate.—4-Chloro-1-ethoxybutane was prepared in 50% yield from sodium ethoxide and 1-bromo-4-chlorobutane.[14] The chloroether had b.p. 39–41° (6 mm.), n^{20}D 1.4258 (lit.[15,16] b.p. 50° (13 mm.), n^{15}D 1.4278, n^{20}D 1.4249). A mixture of 20 g. (0.15 mole) of 4-chloro-1-ethoxybutane, 38 g. of sodium sulfite and 130 ml. of water was refluxed with stirring for 20 hours. The reaction mixture was evaporated to dryness and the resulting residue was extracted with about 300 ml. of hot absolute alcohol. Concentration of the alcohol gave 14.5 g. (47% yield) of sodium 4-ethoxy-1-butanesulfonate whose *p*-chloro-S-benzylthiuronium derivative had m.p. 113–114.5°.

Sodium 4-Phenylsulfonyl-1-butanesulfonate.—A solution of 20.0 g. (0.10 mole) of sodium benzenesulfinate dihydrate,[17] 140 ml. of dimethylformamide and 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone was heated with stirring on the steam-cone for 24 hours. After removal of the dimethylformamide under diminished pressure, the resulting residue was washed twice with ether and then was dissolved in water. Concentration of this aqueous solution gave two crops of crystalline sulfonate totaling 12.3 g. Complete evaporation of the filtrate left a residue which was crystallized from absolute alcohol to give an additional 3.5 g. of sulfonate (total yield of 53%).

S-Benzylthiuronium 4-phenylsulfonyl-1-butanesulfonate, recrystallized from dilute ethanol, had m.p. 149–150°. A mixed m.p. with an independently synthesized sample (see below) showed no depression.

Anal. Calcd. for $C_{18}H_{24}N_2O_5S_3$: C, 48.63; H, 5.44; N, 6.30. Found: C, 48.62; H, 5.65; N, 6.37.

Several attempts were made to carry out the reaction of sodium benzenesulfinate in absolute alcohol, aqueous alcohol and acetone as solvents. In refluxing acetone, little or no reaction occurred. Although reaction occurred in ethanol and aqueous ethanol, alcoholysis and hydrolysis of the sultone also occurred; consequently, the product was difficult to purify.

Independent Synthesis of 4-Phenylsulfonyl-1-butanesulfonate.—A mixture of 30 g. (0.15 mole) of sodium benzenesulfinate dihydrate, 76 g. (0.60 mole) of 1,4-dichlorobutane and 200 ml. of 95% ethanol was refluxed with stirring for 22 hours. The mixture was filtered, most of the ethanol was distilled, and the residual oil was poured into 150 ml. of water. After extraction of the organic layer with ether and drying over magnesium sulfate, distillation gave 14.5 g. (41% yield) of 4-chloro-1-phenylsulfonylbutane, b.p. 189–192° (3 mm.). An analytical sample, recrystallized twice from a mixture of benzene and 60--70° petroleum ether, had m.p. 55.5–57°.

Anal. Calcd. for $C_{10}H_{13}ClO_2S$: C, 51.61; H, 5.67. Found: C, 51.75; H, 5.71.

A mixture of 8.0 g. (0.034 mole) of 4-chloro-1-phenylsulfonylbutane, 13.4 g. (0.085 mole) of potassium sulfite, 20 ml. of water and 60 ml. of ethylene glycol was refluxed for 65 hours. The mixture was concentrated to about 50 ml. and upon cooling there separated 10.5 g. of potassium 4-phenylsulfonyl-1-butanesulfonate which was slightly contaminated with potassium sulfite. The S-benzylthiuronium derivative of this sulfonate had m.p. 149–150°.

Sodium **6-Phenyl-5-hexyne-1-sulfonate.**—This reaction was carried out under a nitrogen atmosphere. Phenylethynylsodium was prepared from 2.3 g. (0.10 g. atom) of finely cut sodium, 20.4 g. (0.20 mole) of phenylacetylene and 150 ml. of anhydrous ether according to the method of Gilman and Young.[18] To this suspension of phenylethynylsodium was added dropwise 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone. About 200 ml. of toluene was added and most of the ether was then removed by distillation. The resulting suspension was refluxed with stirring for 18 hours. The precipitated sulfonate was filtered and then washed twice with ether. The crude, slightly yellow, sulfonate weighed 22.1 g. (85% yield). This sulfonate was purified by treatment with charcoal and recrystallization from water or ethanol; the recovery from this sequence was about 60%.

p-Chloro-S-benzylthiuronium 6-phenyl-5-hexyne-1-sulfonate, prepared from the above purified sodium sulfonate, had m.p. 151–153°.

Anal. Calcd. for $C_{20}H_{23}ClN_2O_3S_2$: C, 54.72; H, 5.28; N, 6.38. Found: C, 54.63; H, 5.58; N, 6.48.

Sodium 6-Phenyl-1-hexanesulfonate.—A solution of 1.65 g. of the above sodium 6-phenyl-5-hexyne-1-sulfonate in 80 ml. of 50% methanol was hydrogenated over Raney nickel catalyst at room temperature with an initial hydrogen pressure of 26 pounds. After hydrogen uptake was completed, the catalyst was filtered and the filtrate was concentrated to about 15 ml. From this solution was obtained an 84% yield of *p*-chloro-S-benzylthiuronium 6-phenyl-1-hexanesulfonate, m.p. 148–152°. A further recrystallization raised the m.p. to 152–153.5°.

Anal. Calcd. for $C_{20}H_{27}ClN_2O_3S_2$: C, 54.22; H, 6.14; N, 6.33. Found: C, 54.48; H, 6.40; N, 6.48.

A mixed m.p. with independently synthesized *p*-chloro-S-benzylthiuronium 6-phenyl-1-hexanesulfonate (see below) was not depressed; a mixed m.p. with *p*-chloro-S-benzylthiuronium 6-phenyl-5-hexyne-1-sulfonate, however, was depressed to 116–137°.

Independent Synthesis of Sodium 6-Phenyl-1-hexanesulfonate.—γ-Phenylbutyric acid[19] was converted to 4-phenyl-1-bromobutane according to the procedures described by Truce and Milionis.[20] 6-Phenyl-1-hexanol, b.p. 135–138° (2.5 mm.), n^{25}D 1.5083 (lit.[21,22] b.p. 140–141° (3 mm.), 160–161° (13 mm.)), was prepared in 56% yield from the Grignard reagent of 4-phenyl-1-bromobutane and ethylene oxide according to the method of Dreger.[23] From this alcohol and phosphorus tribromide was prepared, according to the procedure of Shriner and Young,[24] 6-phenyl-1-bromohexane (70% yield), b.p. 120–123° (2 mm.), n^{25}D 1.5250 (lit.[22] b.p. 160–161° (17 mm.)).

Refluxing a mixture of 18.5 g. (0.077 mole) of 6-phenyl-1-bromohexane, 29.1 g. (0.231 mole) of sodium sulfite and 190 ml. of water for 21 hours gave 17.4 g. (86% yield) of sodium 6-phenyl-1-hexanesulfonate; the *p*-chloro-S-benzylthiuronium salt had m.p. 152.5–153.5° after crystallization from dilute ethanol.

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(15) H. Normant, *Compt. rend.*, **231**, 909 (1951).

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(22) J. V. Braun, *Ber.*, **44**, 287 (1911).

(23) E. E. Dreger, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 306.

(24) R. L. Shriner and J. H. Young, This Journal, **52**, 3332 (1930).

S-Benzylthiuronium 6-phenyl-1-hexanesulfonate had m.p.114–115.5° after crystallization from dilute ethanol.

Anal. Calcd. for $C_{20}H_{28}N_2O_3S_2$: C, 58.79; H, 6.91. Found: C, 58.99; H, 6.89.

Magnesium 4-Bromo-1-butanesulfonate.—Magnesium bromide was prepared from 1.24 g. (0.05 g. atom) of magnesium, 8.0 g. (0.05 mole) of bromine and 60 ml. of absolute ether according to the method of Swain and Boyles.[25] To this ethereal solution was added dropwise 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone over 0.33 hours. A precipitate formed as the reaction proceeded. The reaction mixture was refluxed for 2 hours and let stand overnight at room temperature. The ether was decanted and the sulfonate was dissolved in about 100 ml. of hot absolute alcohol. After treatment with charcoal and concentration to about 70 ml., chilling gave 18.1 g. (79% yield) of magnesium 4-bromo-1-butanesulfonate. Complete evaporation of the filtrate gave a slightly tan residue of 4.15 g. (18% yield) which was largely sulfonate. No unreacted sultone could be detected upon distillation of the ether from the reaction mixture.

p-Chloro-S-benzylthiuronium 4-bromo-1-butanesulfonate had m.p. 129–130° after recrystallization from dilute ethanol.

Anal. Calcd. for $C_{12}H_{18}BrClN_2O_3S_2$: C, 34.49; H, 4.34. Found: C, 34.52; H, 4.41.

Conversion of Magnesium 4-Bromo-1-butanesulfonate to 4-Hydroxy-1-butanesulfonic Acid Sultone.—An aqueous solution of 4.56 g. (0.01 mole) of the above magnesium 4-bromo-1-butanesulfonate was treated with a solution of 2.0 g. of sodium carbonate. The magnesium carbonate was filtered and the filtrate evaporated to dryness. Treatment of this residue with about 20 ml. of concentrated hydrochloric acid for a few hours precipitated sodium chloride. After filtration, the resulting solution of sulfonic acid was distilled under vacuum to give 1.2 g. (46% yield) of 4-hydroxy-1-butanesulfonic acid sultone, b.p. 126–128° (4 mm.) (lit.[5] b.p. 112–113° (1.5 mm.)). The sultone was further characterized by the preparation of its pyridine adduct,[5] m.p. 234–235° (lit.[5] m.p. 234.5–235.5°); a mixed m.p. with an authentic sample showed no depression.

Reaction of Phenylmagnesium Bromide with 4-Hydroxy-1-butanesulfonic Acid Sultone.—To a solution of phenylmagnesium bromide prepared from 1.22 g. (0.05 g. atom) of magnesium, 7.9 g. of bromobenzene (0.05 mole) and 100 ml. of ether was added dropwise and with stirring 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone. Upon completion of the addition the mixture was refluxed for 2 hours and then allowed to stand overnight at room temperature. About 150 ml. of water containing 5 ml. of hydrochloric acid was added to dissolve the precipitated sulfonates, the ether layer was separated, and the aqueous layer was washed twice with ether. The combined ether extracts were dried and distilled to give 0.5 g. of biphenyl. No evidence for the presence of any sulfone was observed. The aqueous solution of the sulfonates was treated with charcoal and then evaporated to dryness to give 20.3 g. of product. Assuming this to be a mixture of magnesium 4-bromo-1-butanesulfonate and magnesium 4-phenyl-1-butanesulfonate, the yield was 90%.

By the procedure outlined for the conversion of magnesium 4-bromo-1-butanesulfonate, 9.12 g. of the above mixture of sulfonates gave 2.70 g. of 4-hydroxy-1-butanesulfonic acid sultone, b.p. 129–134° (5 mm.). From this sultone was prepared its pyridine adduct, m.p. and mixed m.p. 234–235°.

Another reaction of phenylmagnesium bromide with 4-hydroxy-1-butanesulfonic acid sultone was carried out under conditions identical to those in the above reaction except that twice the weights of all reactants were used. The aqueous solution of sulfonates which was obtained on working up the reaction mixture, however, was crystallized into eight fractions of sulfonates. The first two fractions (combined weight of 7.2 g., 32% yield) were magnesium 4-phenyl-1-butanesulfonate. The identity of this sulfonate was shown by the preparation of 4-phenyl-1-butanesulfonamide and *p*-chloro-S-benzylthiuronium 4-phenyl-1-butanesulfonate, m.p. 138–139°. Mixed melting points of these derivatives with corresponding authentic samples[5] showed no depression. The other six sulfonate fractions were all mixtures which could not be separated by further crystallization from water or alcohol. Attempts to prepare pure *p*-chloro-S-benzylthiuronium salts from these mixtures were unsuccessful.

In another reaction of phenylmagnesium bromide with 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone, the Grignard reagent was prepared from 2.44 g. (0.10 g. atom) of magnesium and 15.7 g. (0.10 mole) of bromobenzene. After working up this reaction mixture there was obtained 40.0 g. of a mixture of crude sulfonates and magnesium bromide. A portion (22 g.) of this crude product was converted to a mixture of sodium sulfonates with sodium carbonate. This mixture of sodium sulfonates was crystallized from water into six fractions with a combined weight of 10.6 g. The first two fractions, weighing 3.45 g. (27% yield), were sodium 4-phenyl-1-butanesulfonate, identified by preparation of its sulfonamide and *p*-chloro-S-benzylthiuronium derivative as described above. The last four fractions of sulfonates were mixtures from which no pure *p*-chloro-S-benzylthiuronium derivatives could be isolated. By the procedure outlined for the conversion of magnesium 4-bromo-1-butanesulfonate, the remaining 18 g. of the above mixture of sulfonates and magnesium bromide gave 1.142 g. of 4-hydroxy-1-butanesulfonic acid sultone, b.p. 129–134° (5.5 mm.).

2-(β-Phenylsulfonylethyl)-phenol.—To a solution of phenylmagnesium bromide prepared from 0.85 g. (0.035 g. atom) of magnesium turnings, 7.85 g. (0.05 mole) of bromobenzene and 45 ml. of ether was added with stirring a solution of 1.84 g. (0.01 mole) of 2-*o*-hydroxyphenylethanesulfonic acid sultone[5] in 45 ml. of benzene. After refluxing for 4.5 hours, the reaction mixture was cooled and was hydrolyzed in dilute hydrochloric acid. The organic layer was separated, washed twice with water, and then dried over magnesium sulfate. Evaporation of the solvent left an oily residue which was dissolved in hot benzene, treated with charcoal, and crystallized by dilution with 60–70° petroleum ether and cooling to give 1.6 g. (62% yield) of crude product, m.p. 106–114°. A further crystallization from benzene–petroleum ether gave 1.3 g. of pure 2-(β-phenylsulfonylethyl)-phenol, m.p. 115.5–117°.

Anal. Calcd. for $C_{14}H_{14}O_3S$: C, 64.09; H, 5.38. Found: C, 64.33; H, 5.63.

The phenol readily dissolved in base and was reprecipitated upon acidification.

Lithium 1-Octanesulfonate.—*n*-Butyllithium was prepared from 1.72 g. of lithium and 13.7 g. of *n*-butyl bromide according to the procedure of Gilman and co-workers.[26] To the filtered *n*-butyllithium solution was added dropwise and with stirring 9.52 g. (0.07 mole) of 4-hydroxy-1-butanesulfonic acid sultone. A white precipitate formed during the addition of the sultone. The reaction mixture was stirred at room temperature for six hours, the solvent was decanted, and the sulfonate was dissolved in hot absolute alcohol. Concentration of the alcohol solution and dilution with ether gave 8.1 g. (58% yield) of the very hygroscopic lithium 1-octanesulfonate.

p-Chloro-S-benzylthiuronium 1-octanesulfonate had m.p. 117–118.5°.

Anal. Calcd. for $C_{16}H_{27}ClN_2O_3S_2$: C, 48.66; H, 6.89; N, 7.09. Found: C, 48.57; H, 7.05; N, 7.02.

Sodium 1-octanesulfonate was prepared independently in 90% yield from 1-bromoöctane and aqueous sodium sulfite. This sulfonate gave a *p*-chloro-S-benzylthiuronium derivative with m.p. 117–118.5°. A mixed melting point of this compound with the derivative obtained from the above lithium sulfonate showed no depression.

Sodium 5,5-Dicarbethoxy-1-pentanesulfonate.—To a solution of sodium ethoxide prepared from 2.3 g. (0.10 g. atom) of sodium and 60 ml. of absolute ethanol was added 24 g. (0.15 mole) of diethyl malonate and then 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone. The solution was refluxed with stirring for 18 hours. The reaction mixture was diluted with 100 ml. of benzene and cooled in an ice-bath to induce crystallization. After filtration and drying there was obtained 30.3 g. (95% yield) of sodium 5,5-dicarbethoxy-1-pentanesulfonate; the saponification equivalent of this product was 164 (calcd. for $C_{11}H_{19}NaO_7S$, 159.2).

p-Chloro-S-benzylthiuronium 5,5-dicarbethoxy-1-pen-

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(25) C. G. Swain and H. B. Boyles, THIS JOURNAL, **73**, 870 (1951).

(26) H. Gilman, *et al.*, *ibid.*, **62**, 2327 (1940).

tanesulfonate had m.p. 93.5–94.5° after two recrystallizations from dilute ethanol.

Anal. Calcd. for $C_{19}H_{29}ClN_2O_7S_2$: C, 45.92; H, 5.88; N, 5.64. Found: C, 45.99; H, 5.66; N, 5.83.

Independent Synthesis of Sodium 5,5-Dicarbethoxy-1-pentanesulfonate.—To a solution of sodium ethoxide prepared from 4.6 g. (0.20 g. atom) of sodium and 120 ml. of ethanol was added 48 g. (0.30 mole) of diethyl malonate and then 86 g. (0.40 mole) of tetramethylene dibromide. The solution was refluxed until neutral, most of the ethanol was distilled, and the residue was poured into water. After extracting the organic layer with ether and drying over sodium sulfate, distillation gave 16 g. (28% yield) of diethyl 4-bromobutylmalonate, b.p. 92–94° (2 mm.).

A mixture of 15 g. of the above diethyl 4-bromobutylmalonate, 24.1 g. of sodium sulfite and 150 ml. of water was refluxed for 70 hours. Extraction with ether gave 6.2 g. of unreacted bromide. The aqueous layer was evaporated to dryness and the residue was extracted with hot absolute ethanol to give 5.0 g. (43% yield) of sodium 5,5-dicarbethoxy-1-pentanesulfonate. A mixed m.p. of the *p*-chloro-S-benzylthiuronium derivatives of this sulfonate and of the sulfonate obtained from the reaction of diethyl malonate with 4-hydroxy-1-butanesulfonic acid sultone showed no depression.

Sodium 4-Methyl-5,5-dicarbethoxy-1-pentanesulfonate.—This compound was prepared from diethyl malonate and 4-hydroxy-1-pentanesulfonic acid sultone[5] in 93% yield by the same procedure as was used for the preparation of sodium 5,5-dicarbethoxy-1-pentanesulfonate. The saponification equivalent of the product was 166 (calcd. for $C_{12}H_{21}NaO_7S$, 166.2).

p-Chloro-S-benzylthiuronium 4-methyl-5,5-dicarbethoxy-1-pentanesulfonate had m.p. 98–100° after recrystallization from dilute ethanol.

Anal. Calcd. for $C_{20}H_{31}ClN_2O_7S_2$: C, 47.00; H, 6.11; N, 5.48. Found: C, 46.89; H, 6.37; N, 5.63.

Sodium 5-Carbethoxy-6-oxo-1-heptanesulfonate.—To a solution of sodium ethoxide prepared from 2.3 g. of sodium and 60 ml. of absolute ethanol was added with stirring 13.0 g. (0.10 mole) of ethyl acetoacetate and then 13.6 g. (0.10 mole) of 4-hydroxy-1-butanesulfonic acid sultone. The solution was refluxed for 20 hours during which time a gelatinous precipitate formed. After cooling and diluting with ether, filtering, and drying, there was obtained 23.5 g. (82% yield) of waxy, slightly yellow-colored sulfonate. The saponification equivalent was 271 (calcd. for $C_{10}H_{17}NaO_6S$, 288). Several attempts to prepare the S-benzylthiuronium, the *p*-chloro-S-benzylthiuronium and the *p*-toluidine derivatives of this sulfonate were unsuccessful.

Sodium 6-Oxo-1-heptanesulfonate.—A solution of 11.5 g. of the above sodium 5-carbethoxy-6-oxo-1-heptanesulfonate in 50 ml. of 25% sulfuric acid was refluxed for 8 hours. The solution was neutralized with base and evaporated to dryness. The resulting residue was extracted twice with 100-ml. portions of hot absolute ethanol. Concentration of the ethanol extracts gave 7.1 g. of sodium 6-oxo-1-heptanesulfonate.

p-Chloro-S-benzylthiuronium 6-oxo-1-heptanesulfonate had m.p. 93–95° after two recrystallizations from dilute ethanol. A mixed m.p. with an independently synthesized sample (see below) showed no depression.

Anal. Calcd. for $C_{15}H_{23}ClN_2O_4S_2$: C, 45.62; H, 5.87; N, 7.10. Found: C, 45.85; H, 5.99; N, 7.10.

Independent Synthesis of Sodium 6-Oxo-1-heptanesulfonate.—To a solution of sodium ethoxide prepared from 5.75 g. (0.25 mole) of sodium and 190 ml. of absolute ethanol was added 58.5 g. (0.45 mole) of ethyl acetoacetate and then 80 g. (0.47 mole) of tetramethylene chlorobromide. The solution was refluxed for 1.5 hours and most of the alcohol then was distilled. The residual oil and salt were dissolved in water and extracted with ether. After drying the extracts over magnesium sulfate, distillation gave 12.1 g. (22% yield) of ethyl α-(4-chlorobutyl)-acetoacetate, b.p. 117–119° (2 mm.), n^{25}_D 1.4523.

Anal. Calcd. for $C_{10}H_{17}ClO_3$: C, 54.42; H, 7.77. Found: C, 54.10; H, 8.08.

A mixture of 9.0 g. of ethyl α-(4-chlorobutyl)-acetoacetate and 67 ml. of 10% sulfuric acid was refluxed for 5.5 hours. The mixture was extracted several times with ether. The extracts were washed with bicarbonate and dried over magnesium sulfate. Distillation gave 3.6 g. of unreacted ester and 1.8 g. (29% conversion, 48% yield) of 7-chloro-2-heptanone, b.p. 99–102°, n^{30}_D 1.4420.

Anal. Calcd. for $C_7H_{13}ClO$: C, 56.57; H, 8.82. Found: C, 56.90; H, 8.99.

The semicarbazone of 7-chloro-2-heptanone had m.p. 112.5–114.5° dec.

Anal. Calcd. for $C_8H_{16}ClN_3O$: C, 46.71; H, 7.84. Found: C, 46.98; H, 8.05.

Refluxing a mixture of 1.0 g. of 7-chloro-2-heptanone, 2.5 g. of sodium sulfite and 15 ml. of water for 24 hours gave 0.8 g. of sodium 6-oxo-1-heptanesulfonate. The *p*-chloro-S-benzylthiuronium derivative of this sulfonate had m.p. 93–95°.

Sodium 5,5-Dibenzoyl-1-pentanesulfonate.—To a stirred solution of 15.7 g. (0.07 mole) of dibenzoylmethane in 200 ml. of absolute ethanol was added a solution of sodium ethoxide prepared from 1.54 g. (0.067 mole) of sodium and 50 ml. of absolute ethanol. To this stirred solution was added 9.11 g. (0.067 mole) of 4-hydroxy-1-butanesulfonic acid sultone. The solution was refluxed for 20 hours and then concentrated to about 100 ml. After addition of 200 ml. of ether and cooling, 10.8 g. of sulfonate was obtained. Complete evaporation of the filtrate left a residue which was recrystallized from water to give an additional 3.0 g. of sulfonate (combined yield of 13.8 g., 54%). Attempts were made to prepare the *p*-chloro-S-benzylthiuronium and the S-benzylthiuronium derivatives of this material, but they could not be purified.

A solution of 6.38 g. (0.0167 mole) of the above sulfonate, 1.34 g. of sodium hydroxide and 50 ml. of water was refluxed for 3 hours. The solution was acidified and then extracted with ether. Evaporation of the ether gave 1.05 g. (52% yield) of benzoic acid, m.p. and mixed m.p. 121.5–122.5° after one recrystallization from water. The aqueous solution was concentrated to give 2.45 g. (50% yield) of sodium 5-benzoyl-1-pentanesulfonate.

p-Chloro-S-benzylthiuronium 5-benzoyl-1-pentanesulfonate had m.p. 150–151.5°.

Anal. Calcd. for $C_{20}H_{25}ClN_2O_4S_2$: C, 52.56; H, 5.51: N, 6.13. Found: C, 52.74; H, 5.79; N, 6.16.

In another experiment, 6.8 g. of sodium 5,5-dibenzoyl-1-pentanesulfonate was cleaved with sodium hydroxide according to the above procedure. After extraction of the benzoic acid, the solution was evaporated to dryness to leave a residue of sodium 5-benzoyl-1-pentanesulfonate and sodium chloride. This residue was then subjected to the Clemmensen reduction according to the procedure of Martin.[27] After completion of this reaction, the reaction mixture was neutralized with sodium carbonate and the zinc carbonate was filtered. The filtrate was evaporated to dryness and the residue was extracted with 150 ml. of hot absolute alcohol. Cooling and filtering of the alcohol extracts gave a sulfonate which was washed twice with 100-ml. portions of acetone and then was recrystallized from ethanol. The yield of sodium 6-phenyl-1-hexanesulfonate was 1.05 g. (22% based on sodium 5,5-dibenzoyl-1-pentanesulfonate). The *p*-chloro-S-benzylthiuronium salt of this sulfonate had m.p. 152–153.5°. A mixed m.p. with independently synthesized *p*-chloro-S-benzylthiuronium 6-phenyl-1-hexanesulfonate was not depressed. A mixed m.p. with *p*-chloro-S-benzylthiuronium 6-phenyl-6-oxo-1-hexanesulfonate, however, was depressed to 134–143°.

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[27] E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 164.