[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Chemistry of Sultones. I. Friedel–Crafts Reactions of Sultones[1a]

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RECEIVED APRIL 30, 1954

4-Hydroxy-1-butanesulfonic acid sultone has been synthesized by dehydration of the corresponding hydroxysulfonic acid. Dehydration of 5-hydroxy-1-pentanesulfonic acid, however, gave 4-hydroxy-1-pentanesulfonic acid sultone. These sultones reacted readily with benzene, *p*-xylene, and *p*-dichlorobenzene in the presence of aluminum chloride to give good yields of 4-aryl-1-alkanesulfonates without any rearrangement of the entering side chain. With chlorobenzene, toluene and anisole, mixtures of substitution isomers were formed. 2-*o*-Hydroxyphenylethanesulfonic acid sultone was synthesized and found to be inert in the Friedel–Crafts reaction.

There have been several recent reports of the reactions of lactones with aromatic hydrocarbons in the presence of aluminum chloride to form ω-arylalkanoic acids in good yields.[2–4] Since alkyl sulfonates and sulfates readily undergo the Friedel–Crafts alkylation reaction,[5] there appeared the possibility of utilizing sultones, sulfonic acid analogs of lactones, in the synthesis of arylalkanesulfonic acids.

Dehydration of a hydroxysulfonic acid[6,7] appeared to be the most suitable method of obtaining a simple aliphatic sultone for use in a study of Friedel–Crafts reactions. 4-Hydroxy-1-butanesulfonic acid sultone[8] was prepared in an over-all yield of 82% by the sequence of reactions

$$AcO(CH_2)_4Cl \xrightarrow{Na_2SO_3} AcO(CH_2)_4SO_3Na \xrightarrow[MeOH]{HCl}$$

$$HO(CH_2)_4SO_3H \xrightarrow[vacuum]{\Delta} \underline{(CH_2)_4SO_2O}$$

When tetramethylene chlorohydrin was substituted for 4-chlorobutyl acetate in the above sequence, the sultone was formed in only 58% yield. This lower yield is probably due to a competing reaction in the first step of the synthesis whereby tetramethylene chlorohydrin loses hydrogen chloride and forms tetrahydrofuran. In the reaction of the chlorohydrin with sodium sulfite the odor of sulfur dioxide was observed; this could arise from the action of the liberated hydrogen chloride upon sodium sulfite. The above conclusion is supported by Heine's[9] recent observation that tetramethylene chlorohydrin is hydrolyzed at 40° (in the absence of a catalyst) to give a 75% yield of tetrahydrofuran after "several weeks."

When 5-chloropentyl acetate was subjected to the above sultone synthesis, the expected 5-hydroxy-1-pentanesulfonic acid sultone was not obtained; instead, a previously unreported six-membered ring sultone, 4-hydroxy-1-pentanesulfonic acid sultone (I), was formed in an over-all yield of 49%. The sultone I was hydrolyzed to 4-hydroxy-1-pentanesulfonic acid, which was cleaved with sodium hypoiodite to give iodoform. Additional evidence for the structure of the sultone was furnished by a Friedel–Crafts reaction discussed below. A plausible course for the formation of I is

$$HO(CH_2)_5S\overset{\ominus}{O_3}\overset{\oplus}{H} \longrightarrow \left[H_2\overset{\oplus}{O}(CH_2)_5S\overset{\ominus}{O_3}\right] \xrightarrow{-H_2O}$$

$$\left[CH_3\overset{\oplus}{C}H(CH_2)_3S\overset{\ominus}{O_3}\right] \longrightarrow CH_3\underline{CH(CH_2)_3SO_2O}$$

(I)

That a six-membered ring was formed in preference to a seven-membered ring is not surprising in view of the fact that the dehydration was carried out at about 130°, a temperature that should facilitate isomerization. Ring contractions similar to the above have been observed with seven- and eight-membered lactones.[10]

The two sultones described above readily condense with aromatic compounds in the presence of aluminum chloride to give good yields of 4-aryl-1-butanesulfonates or 4-aryl-1-pentanesulfonates according to the equation

$$ArH + \underline{CHR(CH_2)_3SO_2O} \xrightarrow{AlCl_3} \xrightarrow{Na_2CO_3}$$

$$ArCHR(CH_2)_3SO_3Na$$
$$(R = H \text{ or } CH_3)$$

The reactions of 4-hydroxy-1-butanesulfonic acid sultone with benzene, *p*-xylene and *p*-dichlorobenzene and the reaction of 4-hydroxy-1-pentanesulfonic acid sultone with benzene have been studied. The structures of the sulfonates obtained from these four Friedel–Crafts condensations were proved by comparison of the sulfonamides and either sulfonanilides or S-benzylthiuronium salts with independently synthesized specimens. Except for 4-phenyl-1-butanesulfonate[11] the other sulfonates are unreported and were independently synthesized by lithium aluminum hydride reduction of the appropriate carboxylic acid, conversion of the resulting alcohol to the bromide with phosphorus tribromide, and conversion of the bromide to the sulfonate by means of sodium sulfite.

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[1] (a) Presented at the New York City Meeting of the American Chemical Society, September, 1954. (b) National Science Foundation Fellow, 1953–1954.

[2] R. V. Christian, Jr., THIS JOURNAL, **74**, 1591 (1952).

[3] W. L. Mosby, *ibid.*, **74**, 2564 (1952).

[4] W. E. Truce and C. E. Olson, *ibid.*, **74**, 4721 (1952).

[5] C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 61, 65.

[6] C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, **75**, 748 (1953).

[7] J. H. Helberger, *et al.*, *Ann.*, **562**, 23 (1949); *ibid.*, **565**, 22 (1949).

[8] 4-Hydroxy-1-butanesulfonic acid sultone has been prepared previously in unspecified yield by T. Nilson (*Svensk. Kem. Tid.*, **52**, 324 (1940)) by the action of silver nitrate solution on 4-bromo-1-butanesulfonic acid, but no physical constants were reported for the sultone. Helberger (reference 7) has reported the preparation of a mixture of the sultones of 4-hydroxy-1-butanesulfonic acid and 4-hydroxy-2-butanesulfonic acid, but the isomers were not separated. Recently Helberger (*Ann.*, **586**, 147 (April, 1954)) reported the separation of this mixture and the synthesis of the 1,4-sultone by a method similar to that reported in this paper.

[9] H. W. Heine, *et al.*, THIS JOURNAL, **75**, 4778 (1953).

[10] C. S. Hornberger, *et al.*, *ibid.*, **75**, 1274 (1953); E. E. Blaise and A. Koehler, *Compt. rend.*, **148**, 1772 (1909).

[11] W. E. Truce and J. P. Milionis, THIS JOURNAL, **74**, 974 (1952).

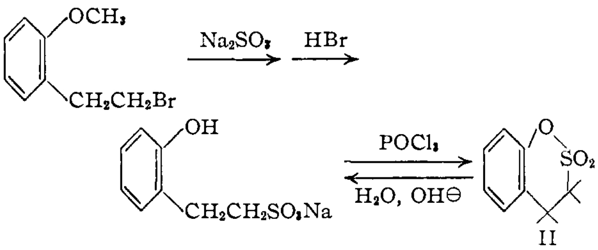
In all of the above Friedel–Crafts reactions the sultone ring opened without any rearrangement of the newly formed side chain in the product. This lack of rearrangement of the side chain is surprising when one considers that many *n*-alkyl sulfates give rise to branched chain products in the Friedel–Crafts alkylation reaction.[12] However, our observations are consistent with the reports that lactones, such as γ-butyrolactone[2,4] and γ-valerolactone,[4] alkylate without carbon skeleton rearrangement, whereas alkyl esters, *e.g.*, *n*-butyl propionate, alkylate[12] with carbon skeleton rearrangement. The formation of straight chain products suggests very strongly that the classical carbonium ion mechanism[12] for Friedel–Crafts alkylations does not operate in the condensations involving sultones. Instead, it appears very likely that there occurs a direct displacement mechanism similar to that proposed by Brown and Grayson[13] for primary halides.

A study of the effects of varying the amount and the kind of catalyst upon the reaction of benzene and 4-hydroxy-1-butanesulfonic acid sultone was made. Aluminum chloride and ferric chloride were about equally effective for promoting the reaction, but the use of stannic chloride resulted in no reaction at reflux temperature for 24 hours. The optimum ratio of catalyst to sultone was found to be about 1.1; increased amounts of catalyst decreased the yield and resulted in considerable tar formation. Although benzene and γ-butyrolactone in the presence of excess aluminum chloride readily give α-tetralone by cyclization of the intermediate 4-phenylbutyrate,[4] no evidence for cyclization of 4-phenyl-1-butanesulfonate with excess aluminum chloride was observed. Cyclization in the latter case would require formation of a seven-membered ring sulfone, a process which proceeds with some difficulty even with the corresponding sulfonyl chloride.[11]

The condensation of 4-hydroxy-1-butanesulfonic acid sultone also occurred readily with chlorobenzene, toluene and anisole to give sulfonates; the products, however, were mixtures of substitution isomers. The sulfonate obtained from the condensation with chlorobenzene was oxidized with potassium permanganate to a mixture of chlorobenzoic acids which gave the calculated neutral equivalent. From the melting point and water solubility characteristics of this mixture only about half of the product was *p*-chlorobenzoic acid, indicating that very appreciable amounts of *ortho* and/or *meta* substitution occurred during the alkylation reaction. Similar behavior was shown by the alkylation product from toluene. The sulfonate obtained from the alkylation of anisole gave an S-benzylthiuronium salt, m.p. 93–105°, which analyzed correctly for the formula $[HO-C_6H_4-(CH_2)_4SO_3]^{\ominus}$ $[C_6H_5CH_2SC(NH_2)_2]^{\oplus}$, indicating that demethylation occurred during the alkylation reaction.

In proving the structure of the condensation product of *p*-dichlorobenzene and 4-hydroxy-1-butanesulfonic acid sultone, it was desired to obtain β-(2,5-dichlorobenzoyl)-propionic acid as an intermediate by the succinoylation of *p*-dichlorobenzene. It is interesting that this succinoylation could not be effected under a variety of experimental conditions, although the condensation of *p*-dichlorobenzene with 4-hydroxy-1-butanesulfonic acid sultone and with γ-butyrolactone proceeded in 54 and 18% yields, respectively.

Since there are apparently no reports of aryl sulfonates exhibiting the alkylating properties of alkyl sulfonates, 2-*o*-hydroxyphenylethanesulfonic acid sultone (II) was synthesized in order to observe the behavior of a sultone derived from a phenol in the Friedel–Crafts reaction. The following synthesis, which gave an over-all yield of 42%, involved the cyclization of a hydroxysulfonate according to a method previously described by Schetty[14] for preparing 2′-hydroxybiphenyl-2-sulfonic acid sultone. The structure of the sultone was confirmed by hydrolyzing it to the intermediate hydroxysulfonate from which it was formed.



II

As expected, no evidence for alkylation was observed when 2-*o*-hydroxyphenylethanesulfonic acid sultone was treated with benzene, anisole or *m*-xylene in the presence of aluminum chloride; in fact from 68 to 90% of the sultone was recovered unchanged. For the above sultone to serve as a Friedel–Crafts arylating agent, the carbon atom holding the oxygen atom of the sulfonate grouping would have to become positively polarized in order to effect electrophilic substitution. Polarization in this manner is unlikely because the indicated carbon atom is a member of the electron-rich benzene ring. Since aryl sultones react with nucleophilic reagents by cleavage of the sulfur–oxygen bond[15,16] rather than cleavage of the oxygen–carbon bond[7] as in aliphatic sultones, sulfonylation to give a sulfone, rather than alkylation would be a more likely reaction of aryl sultones under Friedel–Crafts conditions. No evidence for sulfonylation was observed however. This is consistent with the report of Schetty[14] that 1-naphthol-8-sulfonic acid sultone can be acylated (in the 4-position) by the Friedel–Crafts procedure without cleavage of the sultone linkage.

Experimental

4-Hydroxy-1-butanesulfonic Acid Sultone.—A mixture of 460 g. (3.65 moles) of sodium sulfite, 1550 ml. of water and 367 g. (2.43 moles) of 4-chlorobutyl acetate[17] was refluxed with stirring for 17 hours and then most of the water was removed under vacuum. The heavy paste remaining was stirred and was refluxed with 1500 ml. of methanol. Through a half-inch delivery tube (a smaller size is readily clogged) an excess of hydrogen chloride was bubbled into the continuously stirred and refluxed solution over a period of 16 hours. The reaction mixture was cooled and filtered.

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[12] For numerous examples, see C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chap. 1.

[13] H. C. Brown and M. Grayson, This Journal, **75**, 6285 (1953).

[14] G. Schetty, *Helv. Chim. Acta*, **32**, 24 (1949).

[15] G. Schetty, *ibid.*, **30**, 1650 (1947).

[16] A. Mustafa and A. M. Gad, *J. Chem. Soc.*, 384 (1949).

[17] J. B. Cloke and F. J. Pilgrim, This Journal, **61**, 2667 (1939).

TABLE I

FRIEDEL–CRAFTS SYNTHESIS OF $ArCHR(CH_2)_3SO_3Na$

						Sulfonamide							
								Analyses, %					
								Carbon		Hydrogen		Nitrogen	
Ar	R	Time, hr.	Temp., °C.	ArH, moles	Yield, %	M.p.,[a] °C.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5[b]	H	12	80	2.25	63	103–104[c,d]	$C_{10}H_{15}NO_2S$	56.31	56.01	7.09	7.11	6.52	6.64
C_6H_5[e]	CH_3	6.5	80	2.0	88	69–70[d]	$C_{11}H_{17}NO_2S$	58.12	58.23	7.54	7.70	6.16	6.26
2,5-$Cl_2C_6H_3$[f,g]	H	11.5	75–80	1.4	54	102–103[d,h]	$C_{10}H_{13}Cl_2NO_2S$	42.55	42.51	4.64	4.74	4.97	5.13
2,5-$(CH_3)_2C_6H_3$[i]	H	54	25	1.5	68	117–119[d,j]	$C_{12}H_{19}NO_2S$	59.69	59.90	7.93	7.91	5.80	5.88
HOC_6H_4[k,l]	H	11	75–80	1.5	89								
ClC_6H_4[m]	H	13	60	1.0	62								
$CH_3C_6H_4$[n]	H	11	50	1.0	58								

[a] Recrystallized from a mixture of benzene and 90–100° petroleum ether. [b] M.p. and mixed m.p. of sulfonanilide, 72–73°. *Anal.* Calcd. for $C_{16}H_{19}O_2S$: N, 4.84. Found: N, 4.92. [c] Lit.[11] m.p. 103–104.5°. [d] No depression of melting point when mixed with an independently synthesized sample. [e] M.p. and mixed m.p. of S-benzylthiouronium salt, 141–142.5°. *Anal.* Calcd. for $C_{19}H_{26}N_2O_3S_2$: N, 7.10. Found: N, 7.10. [f] 200 ml. of nitrobenzene was used as solvent. [g] M.p. and mixed m.p. of S-benzylthiuronium salt, 140–141°. *Anal.* Calcd. for $C_{18}H_{22}Cl_2N_2O_3S_2$: N, 6.24. Found: N, 6.32. [h] This sulfonamide has two crystalline modifications; recrystallized from benzene–petroleum ether it forms plates, m.p. 102–103°, but recrystallized from dilute ethanol it forms needles, m.p. 98.5–99.5°. [i] The reaction mixture was not homogeneous. [j] M.p. of crude sulfonamide, 83–112°. Six recrystallizations were necessary to obtain a sample of m.p. 117–119°. In the first recrystallization of the crude sulfonamide a trace of material, m.p. 161–186°, was isolated. [k] Anisole was used as the starting material. [l] S-Benzylthiuronium salt of sulfonate, m.p. 93–105°. *Anal.* Calcd. for $C_{18}H_{24}N_2O_4S_2$: C, 54.53; H, 6.10; N, 7.07. Found: C, 54.53, 54.43; H, 6.24, 6.20; N, 7.39. [m] *Anal.* Calcd. for $C_{10}H_{12}ClNaO_3S$: Na, 8.50. Found: Na, 8.62. [n] *Anal.* Calcd. for $C_{11}H_{15}NaO_3S$: Na, 9.20. Found: Na, 9.29.

The filtrate was concentrated, and then distilled under 4 mm. pressure; the external pot temperature was gradually raised to 180–200° to give 289 g. of sultone, b.p. 123–127° (4 mm.). After dissolving the sultone in ether and drying over sodium sulfate, redistillation gave 271 g. (82% yield) of product, b.p. 112–113° (1.5 mm.), $n^{25}\text{D}$ 1.4620, d^{25} 1.3322.

Anal. Calcd. for $C_4H_8O_3S$: C, 35.27; H, 5.92; sapon. equiv., 136.2. Found: C, 35.55; H, 6.01; sapon. equiv., 136.7.

A mixture of 2.9568 g. of this sultone and 6 ml. of pyridine was heated on a steam-bath for 1.25 hours. After removal of excess pyridine in a vacuum oven, the residue, m.p. 233–235°, weighed 4.6715 g. (100% yield). Recrystallized from ethanol, the betaine derivative had m.p. 234.5–235.5°.

Anal. Calcd. for $C_9H_{13}NO_3S$: C, 50.21; H, 6.08; N, 6.51. Found: C, 49.87; H, 6.21; N, 6.56.

Preparation of the sultone was achieved in 58% yield according to the above procedure except that instead of using 4-chlorobutyl acetate, 217 g. (2.0 moles) of tetramethylene chlorohydrin and 282 g. of sodium sulfite in 900 ml. of water were refluxed for 7 days (the reflux temperature did not reach 100° until near the end of this period).

4-Hydroxy-1-pentanesulfonic Acid Sultone.—The procedure was essentially the same as for the preparation of 4-hydroxy-1-butanesulfonic acid sultone. The initial reaction consisted of refluxing a mixture of 233 g. (1.41 mole) of 5-chloropentyl acetate[18] and 300 g. (2.38 moles) of sodium sulfite in 900 ml. of water for 40 hours. The yield of sultone, b.p. 121–123° (2 mm.), $n^{25}\text{D}$ 1.4586, was 49%.

Anal. Calcd. for $C_5H_{10}O_3S$: C, 39.98; H, 6.71; sapon. equiv., 150.2. Found: C, 39.78; H, 6.89; sapon. equiv., 149.2.

Heating the sultone with excess pyridine gave a betaine derivative, m.p. 243–244.5° (after recrystallization from ethanol).

Anal. Calcd. for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59; N, 6.11. Found: C, 52.22; H, 6.78; N, 6.22.

The glassy solid obtained by heating the sultone with an equal weight of aniline on the steam-bath for one hour was recrystallized from ethanol to give the compound, $C_6H_5\overset{\oplus}{N}H_2CH(CH_3)(CH_2)_3SO_3^{\ominus}$, m.p. 257–258°.

Hydrolysis of 1.0 g. of the sultone with potassium hydroxide solution and treatment of the resulting hydroxysulfonate with sodium hypoiodite gave 0.83 g. of iodoform, m.p. 119–121° (lit.[19] m.p. 119°).

Sodium 2-*o*-Methoxyphenylethanesulfonate.—A mixture of 57 g. (0.45 mole) of sodium sulfite, 38.5 g. (0.18 mole) of 1-bromo-2-(*o*-methoxyphenyl)-ethane[20] (b.p. 108.5–110° (5 mm.), $n^{25}\text{D}$ 1.5579) and 300 ml. of water was refluxed for 20 hours. Upon cooling the reaction mixture there separated 33 g. (77% yield) of the crystalline sulfonate; S-benzylthiuronium salt had m.p. 140.5–142°.

Anal. Calcd. for $C_{17}H_{22}N_2O_4S_2$: N, 7.33. Found: N, 7.47.

Sodium 2-*o*-Hydroxyphenylethanesulfonate.—A mixture of 100 ml. of 48% hydrobromic acid and 32 g. of sodium 2-*o*-methoxyphenylethanesulfonate was refluxed for 9 hours and then evaporated to a thick paste. The S-benzylthiuronium salt of this material, recrystallized from dilute ethanol, had m.p. 156–157°.

2-*o*-Hydroxyphenylethanesulfonic Acid Sultone.—The above crude sodium 2-*o*-hydroxyphenylethanesulfonate was refluxed with 250 ml. of phosphorus oxychloride for 2.5 hours. After cooling, the solution was slowly and cautiously poured on approximately 1000 g. of cracked ice. The dark-colored oily solid was extracted with benzene, the extracts were decolorized to a pale yellow with charcoal and were then concentrated to about 75 ml. Subsequent dilution with petroleum ether and cooling gave a sultone which, recrystallized from benzene–petroleum ether (90–100°), weighed 14.0 g. (42% yield based on 1-bromo-2-(*o*-methoxyphenyl)-ethane) and had m.p. 109–112°; analytical sample, m.p. 111–112°.

Anal. Calcd. for $C_8H_8O_3S$: C, 52.16; H, 4.38; mol. wt., 184. Found: C, 52.45; H, 4.66; mol. wt., 190.

Hydrolysis of the sultone by refluxing with excess potassium hydroxide for 3 hours gave a product whose S-benzylthiuronium salt had m.p. 156.5–157.5° (undepressed by admixture with the corresponding derivative of 2-*o*-hydroxyphenylethanesulfonate).

Anal. Calcd. for $C_{16}H_{20}N_2O_4S_2$: C, 52.15; H, 5.47; N, 7.60. Found: C, 52.01, 52.32; H, 5.39, 5.56; N, 7.56.

General Friedel-Crafts Procedure.—The apparatus consisted of a three-neck 500-ml. round-bottom flask equipped with a sealed mechanical stirrer, a reflux condenser surmounted with a calcium chloride tube, and a half-inch rubber tube connected to a 25-ml. erlenmeyer flask containing the aluminum chloride. In all experiments described in Table I, 0.10 mole of sultone and 0.11 mole of aluminum chloride were used. The sultone and aromatic compound were placed in the flask, the stirrer was started and aluminum chloride was added in portions as rapidly as it dissolved; this required about 0.5 hour and there was usually a slight evolution of heat. The reactants were maintained at the temperature for the length of time specified in Table I, followed by hydrolysis in about 150 ml. of ice-water containing 25 ml. of concd. hydrochloric acid. The aqueous

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(18) J. Cason, *et al.*, *J. Org. Chem.*, **14**, 37 (1949).

(19) R. L. Datta and N. Prosad, THIS JOURNAL, **39**, 453 (1917).

(20) Mme. Ramart-Lucas and J. Hock, *Bull. soc. chim.*, **2**, 327 (1935); S. Sugasawa and H. Sigehara, *Ber.*, **74B**, 459 (1941).

layer was separated from the organic layer, the organic layer was washed twice with water and the combined aqueous solutions were neutralized with sodium carbonate (addition of a drop of octyl alcohol reduces foaming). The aluminum hydroxide was removed by filtration and the resulting filtrate was decolorized if necessary with charcoal and evaporated to dryness on the steam-plate. The resulting residue was extracted with several 200-ml. portions of absolute alcohol. Concentration and chilling of the extract precipitated the crystalline sulfonate which was dried in a vacuum oven to remove absorbed alcohol. The sulfonamides were prepared by treating the sulfonate with an equimolar amount of phosphorus pentachloride at room temperature for two to three hours, heating on the steamcone for 15 minutes, hydrolyzing in ice-water, extracting the resulting sulfonyl chloride with ether and pouring the ether solution into aqueous ammonia.

Optimum Conditions for Friedel–Crafts Reaction of Benzene and 4-Hydroxy-1-butanesulfonic Acid Sultone.—Substitution of 0.11 mole of ferric chloride for aluminum chloride without changing any other conditions gave a 61% yield of sulfonate. Substitution of 0.11 mole of stannic chloride for aluminum chloride gave no sulfonate even though the reflux time was increased to 24 hours.

When the ratio of aluminum chloride to sultone was decreased to 0.5, the yield of sulfonate was only 43%. Increasing the aluminum chloride–sultone ratio to 2.1 and 2.8 decreased the yields to 40 and 16%, respectively, and resulted in considerable tar formation. In the last two cases the benzene layer obtained from hydrolysis of the reaction mixture was dried over sodium sulfate. After distillation of the benzene, three to four grams of a dark colored oil remained, but no crystalline compound could be isolated.

Oxidation of Sodium 4-(Chlorophenyl)-1-butanesulfonate.—A solution of 7.5 g. of the sulfonate obtained from the reaction described in Table I was oxidized with alkaline potassium permanganate. The manganese dioxide was removed and the filtrate acidified. The acid which precipitated, A, was filtered (0.55 g.) and the filtrate extracted with ether; evaporation of ether gave 0.68 g. of acid, B; neut. equiv. of A, 159; neut. equiv. of B, 158.2; calcd. for chlorobenzoic acid, 156.5. The m.p. of A was 239–241°; B had m.p. 123–128°. Lit.[21] values for the m.p. of *o*-, *m*- and *p*-chlorobenzoic acids are 140, 157.5 and 243°, respectively.

Attempted Friedel–Crafts Reactions with 2-*o*-Hydroxyphenylethanesulfonic Acid Sultone.—In a typical reaction a solution of 1.84 g. (0.01 mole) of the sultone, 39 g. of benzene and 2.86 g. (0.021 mole) of aluminum chloride was refluxed for 7 hours. The resulting black solution was hydrolyzed, the layers separated and the organic layer dried over sodium sulfate. After decolorization of the organic layer, 75% of the sultone was recovered unchanged. No sulfonate could be isolated from the aqueous layer. In an identical experiment, except that only 0.011 mole of aluminum chloride was used, 90% of the sultone was recovered unchanged.

An attempted reaction carried out at 120° for 26 hours and utilizing 0.021 mole of aluminum chloride, 0.01 mole of sultone and 0.5 mole of anisole resulted in an 87% recovery of sultone.

Refluxing a solution of 0.01 mole of sultone, 0.011 mole of aluminum chloride and 0.5 mole of *m*-xylene for seven hours resulted in a 68% recovery of sultone.

Independent Synthesis of 4-Arylalkanesulfonates.—The properties of the intermediates utilized in the independent synthesis of the sulfonates are shown in Table II. 4-Arylalkanoic acids were prepared by Friedel–Crafts reaction[2–4] of the appropriate aromatic compound and either γ-butyrolactone or γ-valerolactone. The alcohols reported in Table II were prepared by reducing the corresponding acids with lithium aluminum hydride according to the method of Nystrom and Brown.[22] The bromides reported in Table II were prepared by treating the alcohols with phosphorus tribromide according to the procedure of Shriner and Young[23] for the preparation of *l*-2-bromoöctane.

TABLE II

INTERMEDIATES IN THE INDEPENDENT SYNTHESIS OF $ArCHR(CH_2)_3SO_3Na$

Compound	Yield, %	B.p. °C.	Mm.	$n^{25}D$
$2,5\text{-}(CH_3)_2C_6H_3(CH_2)_3CO_2H^a$	24	132.5–134	0.5	
$2,5\text{-}Cl_2C_6H_3(CH_2)_3CO_2H^b$	18	148–151	1.0	
$C_6H_5CH(CH_3)(CH_2)_2CO_2H^c$	70	118	0.3	1.5129
$2,5\text{-}(CH_3)_2C_6H_3(CH_2)_4OH^d$	79	101.5–103.5	0.5	1.5189
$2,5\text{-}Cl_2C_6H_3(CH_2)_4OH^e$	87	125.5–128	2	1.5473
$C_6H_5CH(CH_3)(CH_2)_3OH^f$	83	101	1	1.5094
$2,5\text{-}(CH_3)_2C_6H_3(CH_2)_4Br$	72	138	13	1.5329
$2,5\text{-}Cl_2C_6H_3(CH_2)_4Br$	71	121–123	2	1.5609
$C_6H_5CH(CH_3)(CH_2)_3Br^g$	66	93.5–95	1.5	1.5227

[a] Prepared according to the procedure used by Mosby[3] for preparing 4-(2,5-dimethylphenyl)-pentanoic acid. The yield here could likely be increased by a longer reaction time; m.p. 67–69.5°, neut. equiv., 195 (calcd. 192.2); lit.[25] b.p. 175° (2 mm.), m.p. 70°. [b] See below for experimental details and further constants. [c] Procedure of Christian[4]; lit.[4] b.p. 123–126° (0.5 mm.); neut. equiv., 180.1 (calcd. 178.2). [d] *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.82; H, 10.17. Found: C, 80.98; H, 9.95. [e] *Anal.* Calcd. for $C_{10}H_{12}Cl_2O$: C, 54.82; H, 5.52. Found: C, 54.93; H, 5.72. [f] Lit.[26] b.p. 132–133° (11 mm.), $n^{20}{}_{\alpha}$ 1.5164. [g] Lit.[27] b.p. 125° (15 mm.).

The sulfonates were obtained in 80–91% yields by a procedure similar to that described by Clutterbuck and Cohen.[24] The bromide was added to three times the required amount of nearly saturated solution of sodium sulfite and the mixture refluxed with stirring until all of the bromide had dissolved (16–37 hours). Upon cooling in an ice-bath, the sulfonates crystallized from the reaction mixture. The sulfonamides and S-benzylthiuronium salts derived from these sulfonates were identical with those derived from the Friedel–Crafts reaction products described in Table I.

4-(2,5-Dichlorophenyl)-butanoic Acid.—To a solution of 400 g. (2.67 moles) of *p*-dichlorobenzene and 69 g. (0.8 mole) of γ-butyrolactone in 300 ml. of *sym*-tetrachloroethane there was added 128 g. (0.96 mole) of aluminum chloride over a period of one hour. The resulting solution was heated at 85–90° with stirring for 11 hours, allowed to stand at room temperature overnight, heated at 90° for an additional hour, and then hydrolyzed. After drying the organic layer and distilling there was obtained 33 g. (18% yield) of 4-(2,5-dichlorophenyl)-butanoic acid, b.p. 148–151° (1 mm.). An analytical sample recrystallized from petroleum ether (90–100°) had m.p. 69.5–70.5°.

Anal. Calcd. for $C_{10}H_{10}Cl_2O_2$: C, 51.52; H, 4.32; neut. equiv., 233.1. Found: C, 51.77; H, 4.01; neut. equiv., 232.5.

Attempted Preparation of 3-(2,5-Dichlorobenzoyl)-propionic Acid.—A solution of *p*-dichlorobenzene, succinic anhydride and aluminum chloride in *sym*-tetrachloroethane was heated with stirring at 70° for 12 hours, but no crystalline acid could be obtained on working up the reaction mixture. Experiments utilizing nitrobenzene or carbon disulfide in place of *sym*-tetrachloroethane likewise were unsuccessful.

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