THE PREPARATION OF SULFINIC ACIDS

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CONTENTS

I. INTRODUCTION

Several aliphatic sulfinic acids are known. The low-molecular-weight members are viscous oils which are subject to rapid decomposition. They are usually isolated as their salts, which are considerably more stable than the free acids. The high-molecular-weight aliphatic sulfinic acids can be isolated as crystalline solids (198). They are more stable than the lower members of the series; however, on standing, they also undergo disproportionation (36, 198) according to the following equation:

$$3RSO_2H \rightarrow RSO_2SR + RSO_3H + H_2O$$

Aromatic sulfinic acids are in general more stable than the aliphatic analogs. However, upon long standing, they too tend to decompose as above. Free aromatic sulfinic acids are generally and conveniently obtained by acidifying aqueous solutions of their salts.

Sulfinic acids (and even their salts) tend to be slowly oxidized to sulfonic acids on exposure to air. Their acidity characteristics are somewhat stronger than those of the corresponding carboxylic acids. The ionization constants of benzenesulfinic acid and *p*-toluenesulfinic acid at 25°C. are approximately 2 to 4×10^{-2} (195). Aromatic sulfinic acids appear to be conveniently characterized as thallous salts (108).

An attempt has been made to cover in the following sections the preparations of sulfinic acids which have been reported through the year 1949. Sulfinic acids which were formed as intermediates (as in the synthesis of sulfonic acids) and which were not isolated, or which were obtained as derivatives by changes at other points in the molecule, have been disregarded.

II. REDUCTION OF SULFONYL HALIDES TO SULFINIC ACIDS

Sulfinic acids are most frequently prepared by the action of reducing agents on sulfonyl halides, usually the chlorides (table 1). This is particularly true of

TABLE 1

Reduction of sulfonyl halides (sulfonyl chloride unless otherwise specified) to sulfinic acids

SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
CH_3SO_2H	Zn		(14)
$C_2H_5SO_2H$	Zn		(7, 14, 235)
$(CH_3)_2CHCH_2SO_2H$	Zn		(235)
$(CH_3)_2CHCH_2CH_2SO_2H$	Zn		(221)
$\begin{array}{l}CH_2SO_2H\\ \vert\\ CH_2SO_2H\end{array}$	Zn	53	(165, 221)
CCl_3SO_2H	SO_2		(11)
	K_2SO_3		(250)
	H_2S		(191)
	KCN		(190, 197)
	NaI		(242)
	NH_3 (aqueous)		(197)
$CHCl_2SO_2H$	SO_2 (KOH, alcoholic)		(197)
$C_6H_5CH_2SO_2H$	Zn		(225)
	$NaHg_x$		(225)
			(90)
$C_6H_5SO_2H$			(14, 216)
	Zn	85–95	(289)
			(234)
			(263)
	Zn (NaI)		(102)
	Ca		(17)
	$NaHg_x$		(211, 226)
	Mg (ether)	12.3	(109)
	H_2 (Pd)		(270)
	Na_2SO_3 (NaOH, aqueous)		(175)
	Na_2S		(134)
	Na_2AsO_3		(117)
	NaI		(103)
	NaI ($Na_2S_2O_4$)	81	(242)
	C_6H_5SH (KOH)		(215)
	Methyl sodium camphocarboxylate		(38)
	RMgX	0.5–53	(110, 288)
	$RC{\equiv}CNa$	43–72	(288)
	$(C_6H_5)_2Zn$		(154, 167)
	$(C_6H_5)_2PbS_2$		(264)
	R_2NH, CS_2	80	(34)
	KOH (on sulfonyl iodide)		(232)
	$(C_2H_5)_2Zn$ (on sulfonyl iodide)		(232)

TABLE 1—*Continued*

SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cen	
o-$CH_3C_6H_4SO_2H$	Zn		(285)
	Na_2S		(134)
p-$CH_3C_6H_4SO_2H$	Zn	64–95	(30, 234, 302)
	Na_2SO_3	88	(21, 175, 263)
	$NaHg_x$		(223)
	Mg	69.5–75	(109)
	Sodium acetoacetic ester	70	(166)
	Sodium malonic ester		(166)
	Na_2S		(87, 134)
	As_2O_3 (NaOH)		(115, 117)
	NaI		(103)
	$C_6H_{11}N$, CS_2		(34)
	RMgBr	10.7–67.1	(41, 110, 288)
	$RC\equiv CNa$	48–49	(288)
	C_6H_5MgBr (on sulfonyl bromide)	30.2	(110)
	C_6H_5MgBr (on sulfonyl iodide)	11.8	(110)
	Electrolytic reduction		(74)
p-$ClC_6H_4SO_2H$	Na_2SO_3 (on sulfonyl fluoride)	81	(176)
	Na_2SO_3	80	(175, 176)
	H_2 (Pd)		(270)
	$NaHg_x$		(189, 220)
	Na_2S		(134)
p-$BrC_6H_4SO_2H$	Na_2SO_3		(288a)
	H_2 (Pd)		(270)
	CS_2, $AlCl_3$		(210)
	CS_2, $AlBr_3$ (on sulfonyl bromide)		(210)
o-$IC_6H_4SO_2H$			(10)
p-$IC_6H_4SO_2H$	K_2S		(286)
p-$C_6H_5C_6H_4SO_2H$	$NaHg_x$		(95)
	NaI		(103)
p-$CH_3OC_6H_4SO_2H$	Electrolytic reduction		(75)
	Na_2SO_3		(175)

TABLE 1—*Continued*

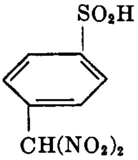
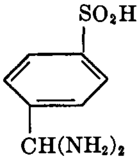
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
o-$HOOCC_6H_4SO_2H$	Na_2SO_3		(60)
m-$HOOCC_6H_4SO_2H$	Na_2SO_3	52	(60, 175)
o-$NCC_6H_4SO_2H$	Zn		(133)
p-$NCC_6H_4SO_2H$	Na_2SO_3	76.1–87.4	(3, 57, 94, 293)
o-$O_2NC_6H_4SO_2H$	Na_2SO_3		(314)
	NH_2NH_2	80	(58)
	$SnCl_4$, HCl, alcohol	90	(47)
m-$O_2NC_6H_4SO_2H$	$SnCl_4$, HCl, alcohol	71.5	(76)
	Na_2SO_3	22.3	(76, 186)
	$C_6H_5NHNH_2$		(67, 184)
	R′SNa		(288a)
p-$O_2NC_6H_4SO_2H$	Na_2SO_3		(315)
	Zn		(240)
	$(NH_4)_2S$		(240)
	Na_2SO_3	41.6–47	(40, 175, 271)
p-$CH_3CONHCH_2C_6H_4SO_2H$	Na_2SO_3	75	(44, 57, 61, 162)
p-$C_6H_5OC_6H_4SO_2H$	Na_2SO_3	87.2	(277)
p-$(C_6H_5CONH)C_6H_4SO_2H$	Na_2SO_3	70	(271)

TABLE 1—*Continued*

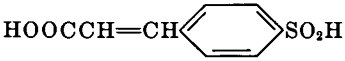
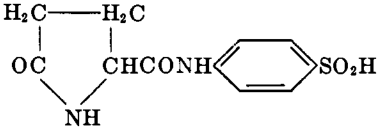
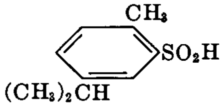
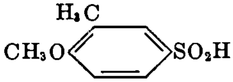
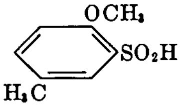
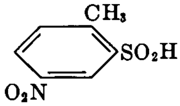
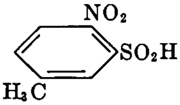
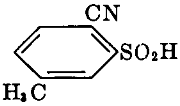
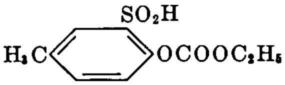
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Na_2SO_3		(175)
	Na_2SO_3		(43)
$3,4\text{-}(CH_3)_2C_6H_3SO_2H$	Zn		(151)
$2,4\text{-}(CH_3)_2C_6H_3SO_2H$	Zn		(151, 152)
	Zn		(18)
	Na_2SO_3	94.6	(169)
	Na_2SO_3		(105)
	Na_2SO_3		(51)
	Na_2SO_3	25	(51)
	Zn		(133)
	Na_2SO_3	55–60	(310)
$2,5\text{-}Cl_2C_6H_3SO_2H$	Na_2SO_3	87.5	(106, 175)
$2,5\text{-}Br_2C_6H_3SO_2H$	Na_2SO_3		(175)

TABLE 1—*Continued*

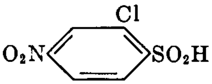
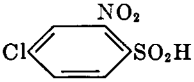
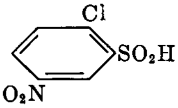
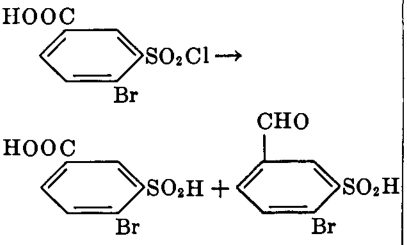
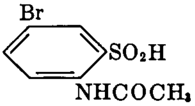
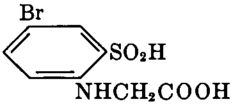
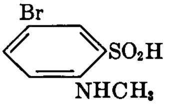
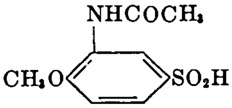
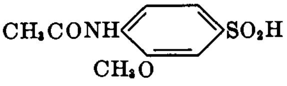
SULFINIC ACID	REAGENT	YIELD *per cent*	REFERENCES
	$SnCl_4$, HCl, alcohol	Quantitative	(47)
	$(C_6H_5NH)_2$		(258)
	Na_2SO_3	70	(174, 175)
	Zn		(24)
	Zn	50	(46)
	Zn		(46)
	Zn		(46)
2,4-$(O_2N)_2C_6H_3SO_2H$	N_2H_4		(59)
	Na_2SO_3		(45)
	Na_2SO_3		(26)

TABLE 1—*Continued*

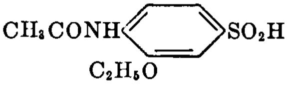
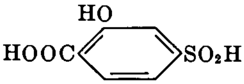
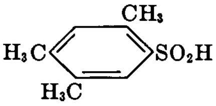
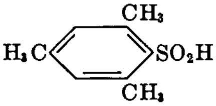
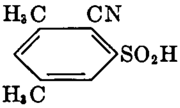
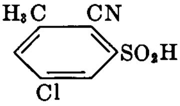
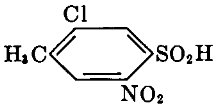
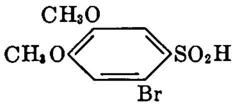
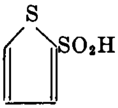
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Na_2SO_3		(26)
	Na_2SO_3		(175)
	Na_2S Zn		(134) (248)
	$NaHg_x$		(142)
	Zn		(133)
	Zn		(133)
	N_2H_4	97.5	(58)
	Na_2SO_3		(182)
	Zn		(19, 300)
o-$C_6H_4(SO_2H)_2$	Na_2SO_3		(147)
m-$C_6H_4(SO_2H)_2$	Electrolytic reduction	50	(75)
	Zn	60	(8, 234, 283)
p-$C_6H_4(SO_2H)_2$	Zn		(283)

TABLE 1—*Continued*

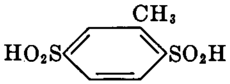
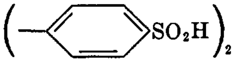
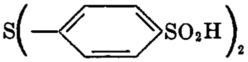
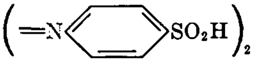
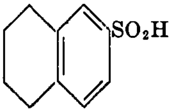
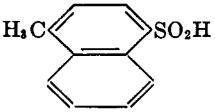
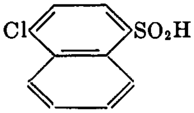
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Zn		(283)
$CH_3C_6H_3(SO_2H)_2$	Na_2SO_3		(22)
	Na_2SO_3	60	(10)
	Zn		(31)
	Barium sulfhydrate		(12)
	$C_6H_{11}N$, CS_2		(34)
1-$C_{10}H_7SO_2H$	Electrolytic reduction	13.6	(75)
	Na_2S		(134)
	Zn	Almost quantitative	(231)
	$NaHg_x$		(104)
	Na_2SO_3		(9)
	C_6H_5MgBr	11	(110)
2-$C_{10}H_7SO_2H$	H_2 (Pd)		(270)
	Electrolytic reduction	12.6	(75)
	Zn	Almost quantitative	(231)
	$NaHg_x$		(104)
	Na_2SO_3		(9)
	RSH	66.4 to quantitative	(261)
	Zn	Very good	(65)
	Na_2SO_3	91	(15)
	$NaHg_x$ (on sulfonyl bromide)		(104)

TABLE 1—*Continued*

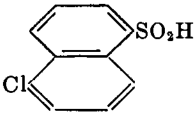
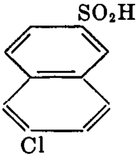
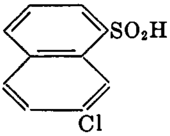
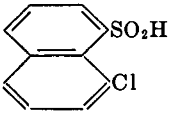
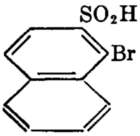
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Na_2SO_3	65	(15, 252)
	Na_2SO_3	90	(15)
	Na_2SO_3	94	(15)
	Na_2SO_3	82	(15)
	Na_2SO_3	91	(15)
	Na_2SO_3	77	(15)
	Na_2SO_3	97	(15)
	Na_2SO_3	60	(52)

TABLE 1—*Continued*

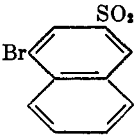
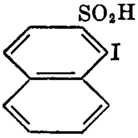
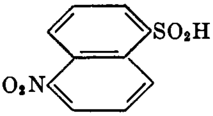
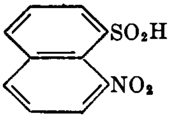
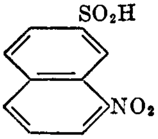
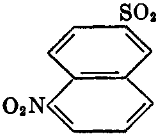
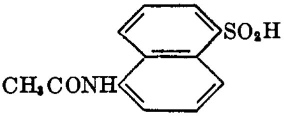
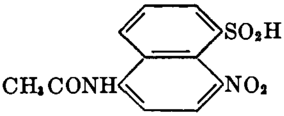
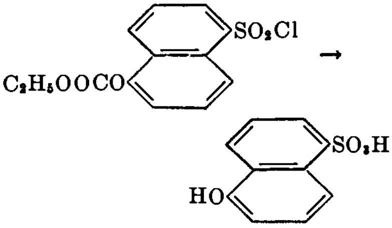
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	$NaHSO_3$		(200)
	Na_2SO_3		(10)
	Na_2SO_3		(252)
	K_2SO_3 Na_2SO_3	 90	(66) (252)
	Na_2SO_3		(290)
	Na_2SO_3		(290)
	Na_2SO_3		(252)
	Na_2SO_3		(252)
	Na_2SO_3	80	(253)

TABLE 1—*Continued*

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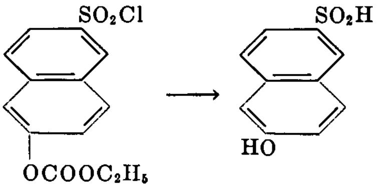
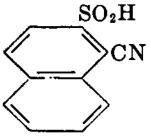
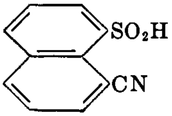
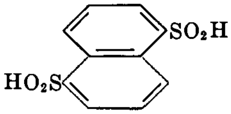
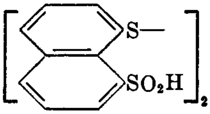
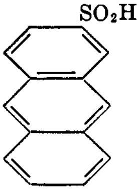
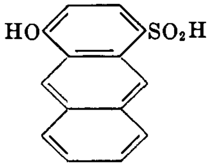
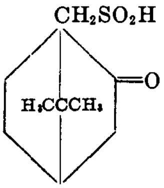
		per cent	
	Na_2SO_3		(312)
	Zn		(133)
	Zn		(133)
	Zn Na_2S	50	(56) (54)
$C_{10}H_6(SO_2H)_2$	Zn		(283)
	Na_2SO_3		(246)
	Zn Na_2SO_3		(123) (123)
	Na_2SO_3		(83)
	Zn Na_2SO_3	47–70 90	(192, 272) (126, 192)

TABLE 1—*Continued*

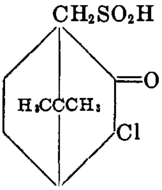
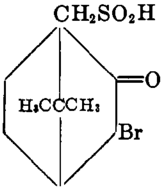
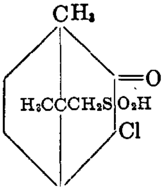
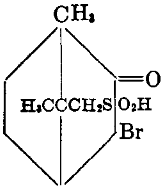
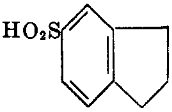
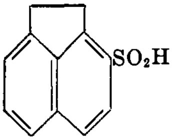
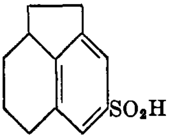
SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Na_2SO_3		(193)
	Na_2SO_3		(193)
	Na_2SO_3		(193)
	Na_2SO_3		(193)
	Using the well-known methods		(29)
	Zn		(64)
	Zn		(35)

TABLE 1—*Continued*

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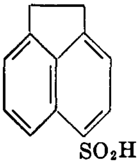
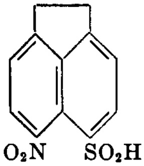
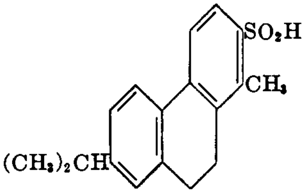
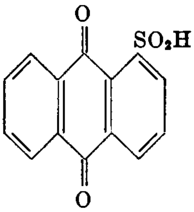
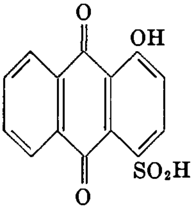
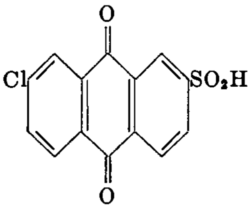
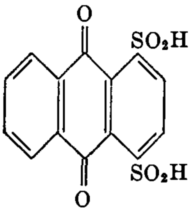
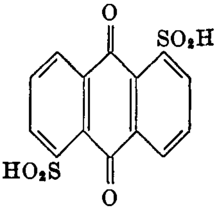
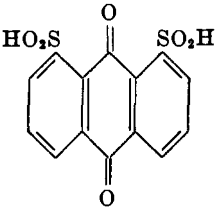
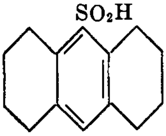
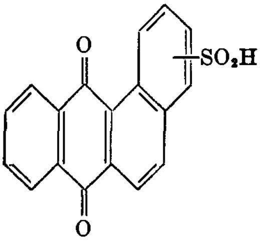
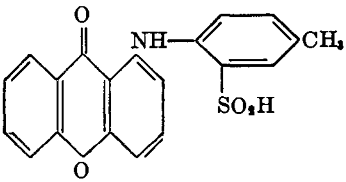
	Na_2SO_3		(25)
	Na_2SO_3		(25)
	Zn	57.1	(169)
	Na_2S		(135)
	Na_2SO_3 Na_2S	Changeable, but good	(83) (135)
	Na_2S		(135)

TABLE 1—*Concluded*

SULFINIC ACID	REAGENT	YIELD	REFERENCES
		per cent	
	Na_2S	90.1	(171)
	Na_2S	83.5	(171)
	Na_2S	77.5	(171)
	$NaHSO_3$		(266)
	Na_2S		(135)
	Na_2S		(135)

the aromatic compounds, owing to the ease of forming aromatic sulfonic acids by direct sulfonation. The first application of this approach to the synthesis of a sulfinic acid was described in 1860 by Kalle, who reduced benzenesulfonyl chloride with diethylzinc (154, 167).

Zinc dust in neutral or basic aqueous or in alcoholic media smoothly effects the reduction (234, 302). If the sulfonyl chloride is dissolved in dry ether or benzene

$$2RSO_2Cl + 2Zn \rightarrow (RSO_2)_2Zn + ZnCl_2$$

and sodium amalgam is added, the sodium sulfinate is formed (211, 223, 226). The reduction can also be performed with calcium in aqueous base (17), with magnesium in ether (109), and with iron or zinc in acetic acid (154).

Sodium or potassium sulfites in aqueous base are widely used (66, 176).

$$RSO_2Cl + Na_2SO_3 + 2NaOH \rightarrow RSO_2Na + NaCl + Na_2SO_4 + H_2O$$

Stannous chloride in hydrochloric acid is an effective reducing agent (47). Many other salts, such as sulfides (134, 135, 240), thiophenolates (215), cyanides (190, 197), iodides (103), and arsenites (115), have been employed.

Reduction has also been brought about by sodium acetoacetic ester (166), sodium malonic ester (166), and organo zinc (154, 167), lead (264), magnesium (110, 288), and sodium (288) compounds.

The electrolytic reduction of sulfonyl chlorides in alcoholic sulfuric acid yields some sulfinic acid (75). Hydrogen with a palladium catalyst also produces the acid (270). Hydrazine or phenylhydrazine with sodium hydroxide is effective in some cases (59, 67, 184).

Nitrated arylsulfonyl chlorides have been reduced by stannous chloride and hydrochloric acid (76), sodium amalgam and ether (224), sodium sulfite (186), zinc in alcoholic solution (241), and phenylhydrazine and sodium hydroxide (184) to nitrosulfinic acids. Further reduction to the corresponding aminosulfinic acids can be readily attained (252).

The reduction of sulfonyl fluorides (176) and bromides (104, 210) is also reported. With the iodide, aqueous potassium hydroxide is sufficient for conversion to the sulfinic acid (232, 282).

o-, *m*-, and *p*-Benzenedisulfinic acids have been prepared by reduction of the corresponding disulfonyl chlorides, the *o*-compound by sodium sulfite and sodium hydroxide (146), the *m*- and *p*-isomers by zinc reduction (234, 283), and the *m*-compound also by electrolytic reduction (75). No trisulfinic acids are recorded, although trisulfonyl chlorides are known.

III. SULFINATION OF ORGANOMETALLIC COMPOUNDS

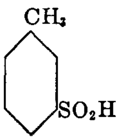
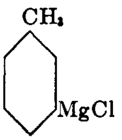
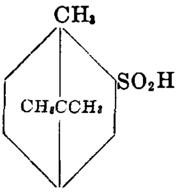
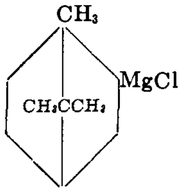
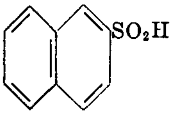
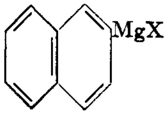
Many aliphatic and aromatic organometallic compounds react with sulfur dioxide to form sulfinic acids (table 2). Hobson (131) was the first to report this type of reaction, using diethylzinc and sulfur dioxide. The more convenient Grignard reagent has been used extensively for the preparation of aliphatic sulfinic acids. The usual procedure is to bubble dry sulfur dioxide through an ether solution of the Grignard reagent. For optimum yields it is desirable to conduct

TABLE 2

Preparation of sulfinic acids via organometallic compounds

SULFINIC ACID	ORGANOMETALLIC COMPOUND	YIELD	REFERENCES
		per cent	
CH_3SO_2H	$(CH_3)_2Zn$		(132)
$C_2H_5SO_2H$	$(C_2H_5)_4Pb$		(78)
	$(C_2H_5)_2Zn$		(131, 306)
	C_2H_5MgX	50–60 (Mg salt)	(260)
	C_2H_5MgBr		(144, 155)
	C_2H_5MgI (+ SO_2Cl_2)		(209)
n-$C_3H_7SO_2H$	C_3H_7MgX	50–60 (Mg salt)	(260)
	C_3H_7MgBr		(2, 144)
n-$C_4H_9SO_2H$	C_4H_9MgBr		(36)
	C_4H_9MgBr (−50°C.)	69 (Mg salt)	(2, 144)
tert-$C_4H_9SO_2H$	*tert*-C_4H_9MgCl		(257)
n-$C_5H_{11}SO_2H$	$C_5H_{11}MgBr$		(2, 144)
i-$C_5H_{11}SO_2H$	*i*-$C_5H_{11}MgBr$		(36)
n-$C_6H_{13}SO_2H$	$C_6H_{13}MgBr$		(2)
n-$C_7H_{15}SO_2H$	$C_7H_{15}MgBr$		(2)
n-$C_8H_{17}SO_2H$	$C_8H_{17}MgBr$	41.6 (Mg salt)	(2)
n-$C_9H_{19}SO_2H$	$C_9H_{19}MgBr$	37.6 (Mg salt)	(2)
n-$C_{10}H_{21}SO_2H$	$C_{10}H_{21}MgBr$	34.5 (Mg salt)	(2)
n-$C_{11}H_{23}SO_2H$	$C_{11}H_{23}MgBr$	49.8 (Mg salt)	(2)
n-$C_{12}H_{25}SO_2H$	$C_{12}H_{25}MgBr$	56.5 (Mg salt)	(2)
	$C_{12}H_{25}MgBr$ (−40° to −35°C.)	80 (Mg salt)	(198)
n-$C_{13}H_{27}SO_2H$	$C_{13}H_{27}MgBr$	38.7 (Mg salt)	(2)
n-$C_{14}H_{29}SO_2H$	$C_{14}H_{29}MgBr$	39.2 (Mg salt)	(2)
n-$C_{15}H_{31}SO_2H$	$C_{15}H_{31}MgBr$	43.0 (Mg salt)	(2)
n-$C_{16}H_{33}SO_2H$	$C_{16}H_{33}MgBr$	57.2 (Mg salt)	(2)
$(CH_2)_4CHSO_2H$	$(CH_2)_4CHMgBr$		(28)
$(CH_2)_5CHSO_2H$	$(CH_2)_5CHMgCl$		(36, 206)
	$(CH_2)_5CHMgCl$	28	(111)

TABLE 2—*Concluded*

SULFINIC ACID	ORGANOMETALLIC COMPOUND	YIELD	REFERENCE
		per cent	
			(28)
		50 26 (Na salt)	(27) (143)
$C_6H_5SO_2H$	C_6H_5MgBr (+ SO_2Cl_2)		(209)
	C_6H_5MgBr	50–60 (Mg salt)	(260)
	C_6H_5Na		(21)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4MgBr$	20	(287)
	p-$CH_3C_6H_4Li$	68	(287)
m-$CH_3C_6H_4SO_2H$	m-$CH_3C_6H_4Li$	54	(287)
o-$CH_3C_6H_4SO_2H$	o-$CH_3C_6H_4MgBr$	50–60 (Mg salt)	(260)
	o-$CH_3C_6H_4Li$	56	(287)
p-(n-$C_{12}H_{25}$)$C_6H_4SO_2H$	ArLi	63	(287)
m-(n-$C_{12}H_{25}$)$C_6H_4SO_2H$	ArLi	44	(287)
o-(n-$C_{12}H_{25}$)$C_6H_4SO_2H$	ArLi		(287)
		50–60 (Mg salt)	(260)
$(C_6H_5)_3CSO_2H$	$(C_6H_5)_3CNa$	Quantitative	(265)
$(C_6H_5)_2C{=}CHSO_2H$	$(C_6H_5)_2C{=}CHMgBr$	33	(233)

$$RMgX + SO_2 \rightarrow RSO_2MgX \xrightarrow{H^+,\ H_2O} RSO_2H$$

the sulfination at low temperatures, i.e., −40° to −35°C. (198). A competing reaction at elevated temperature is sulfoxide formation (41).

$$ArSO_2MgBr + ArMgBr \rightarrow ArSOAr + (MgBr)_2O$$

Another side reaction that may be encountered is disproportionation, e.g., when an excess of sulfur dioxide is used in the preparation of the magnesium salt of the sulfinic acid from 1-dodecylmagnesium bromide, the free sulfinic acid is formed and undergoes disproportionation to the thiolsulfonate and the sulfonic acid (198).

Organolithium compounds have also been employed recently for preparing sulfinic acids (287). They appear to be superior in some respects to the corresponding Grignard reagents.

IV. FRIEDEL–CRAFTS SULFINATION OF AROMATIC COMPOUNDS

Knoevenagel and Kenner (160) first employed this preparation of sulfinic acids. A common procedure is to pass sulfur dioxide into a mixture of the aromatic hydrocarbon, aluminum chloride, and some hydrogen chloride. An excess of the aromatic compound which is being sulfinated or of carbon disulfide is frequently employed as solvent. Although aluminum chloride is the catalyst most frequently employed, the patent literature also reports the use of boron halides for this purpose (148).

$$ArH + SO_2 \cdot \xrightarrow{AlCl_3} \xrightarrow{H_2O} ArSO_2H$$

Several aromatic hydrocarbons and their halogen and alkoxy derivatives (table 3) have been sulfinated successfully by this procedure. The patent literature also refers to the application of this method to *p*-aminobenzenesulfonarylides (245), olefins (299), and aliphatic and alicyclic saturated hydrocarbons (148).

V. REPLACEMENT OF A DIAZONIUM SALT GROUP

Aromatic sulfinic acids may generally be prepared in good yields by treating an acidic solution of a diazonium salt with sulfur dioxide or sulfurous acid in the presence of copper (97, 98) or cuprous salts (50, 99, 100) (table 4).

$$ArN_2X + SO_2 + H_2O + Cu \rightarrow ArSO_2H + N_2 + HX + CuO(?)$$

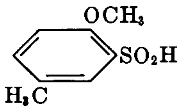
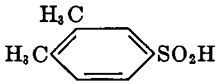
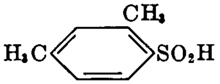
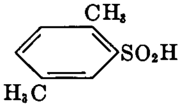
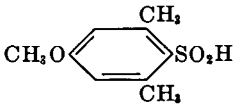
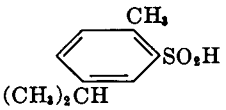
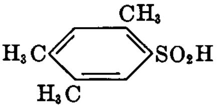
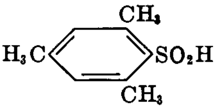
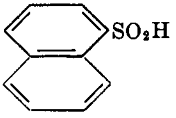
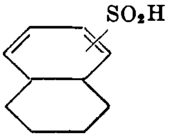
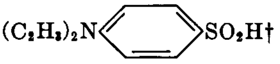
There is evidence that reduction in this process is effected by the copper powder and not by the sulfurous acid employed (97). For best results it is essential to wash the copper first with alcohol and then with ether to remove traces of grease (120). Furthermore, the diazonium sulfate is preferred to the diazonium halide, since the latter tends to yield some aryl halide (97). Another important side reaction is replacement of the diazonium group by a sulfonic acid group. For example, treatment of benzenediazonium sulfate with aqueous sulfurous acid in the presence of cuprous oxide results in a low yield of benzenesulfonic acid (177). Still another possible side reaction is reduction to the corresponding arylhydrazine. The sulfinic acid may be isolated by suitable extraction procedures or by taking advantage of the fact that the ferric salt is frequently sparingly soluble in dilute acid (279).

VI. BASIC CLEAVAGE OF SULFONES

Many aliphatic and aromatic sulfones are cleaved by alkaline reagents to sulfinic acids (table 5). A variety of reagents has been used for this purpose.

TABLE 3

*Preparation of sulfinic acids by Friedel-Crafts sulfination processes**

SULFINIC ACID	YIELD	REFERENCES
	per cent	
$C_6H_5SO_2H$	 80 27.4	(1, 53, 80, 124) (160) (273)
p-$CH_3C_6H_4SO_2H$	94.0 23.6	(160) (273)
p-$FC_6H_4SO_2H$	75	(119)
p-$ClC_6H_4SO_2H$	38.3	(160)
p-$BrC_6H_4SO_2H$	57.0	(160)
p-$IC_6H_4SO_2H$	45.6	(161)
p-$CH_3OC_6H_4SO_2H$	15.7	(160)
	*ca.* 50 10–13	(127) (273)
	94.0	(160)
	81.4	(160)
	78.2 37.5	(160) (125)
	23.8	(273)
	80.5	(160)
	71.9	(160)
	65.4	(160)
	63.4	(160)
		(34)
		(201)
		(201)
$(C_6H_5)_2C{=}CHSO_2H$†	17	(233)

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* Unless otherwise indicated, the reagent employed was sulfur dioxide and aluminum chloride with or without added hydrogen chloride.

† The reagent was thionyl chloride in an inert solvent.

Ethyl sulfone reacts with fused 90 per cent potassium hydroxide at 200°C. to give ethylene and a 60 per cent yield of potassium ethanesulfinate (71). Other low-molecular-weight alkylsulfones react in an analogous manner (71, 72).

TABLE 4

Preparation of sulfinic acids via diazonium salts

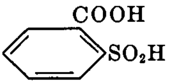
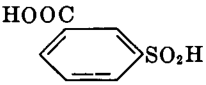
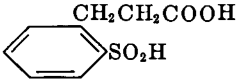
SULFINIC ACID	YIELD	REFERENCES
	per cent	
$C_6H_5SO_2H$	90	(97)
	Quantitative	(279)
		(98, 99, 100, 175)
o-$CH_3C_6H_4SO_2H$	90	(97, 279)
		(98, 100)
m-$CH_3C_6H_4SO_2H$		(280, 281)
p-$CH_3C_6H_4SO_2H$	80	(97)
		(175)
	78	(279)
o-$ClC_6H_4SO_2H$		(118)
m-$ClC_6H_4SO_2H$		(118)
p-$ClC_6H_4SO_2H$		(118, 175)
o-$BrC_6H_4SO_2H$		(118)
m-$BrC_6H_4SO_2H$		(118)
p-$BrC_6H_4SO_2H$		(118)
p-$IC_6H_4SO_2H$		(118)
o-$CH_3OC_6H_4SO_2H$	90	(97)
		(98, 100)
p-$CH_3OC_6H_4SO_2H$	50	(97)
		(175)
o-$C_2H_5OC_6H_4SO_2H$	90	(97)
p-$C_2H_5OC_6H_4SO_2H$	88	(97)
	74	(97)
	67	(60)
		(97, 175)
		(199)

TABLE 4—*Continued*

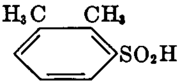
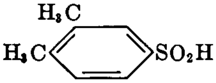
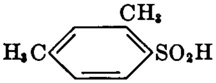
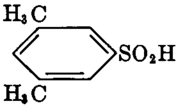
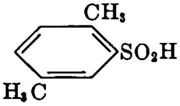
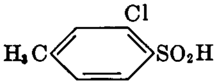
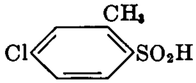
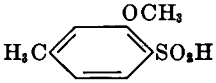
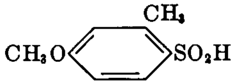
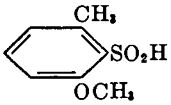
SULFINIC ACID	YIELD	REFERENCES
	per cent	
o-$O_2NC_6H_4SO_2H$		(157)
p-$O_2NC_6H_4SO_2H$	50	(44) (39, 157)
		(205)
		(97, 205)
	71	(97)
		(205)
	Quantitative	(97)
		(268)
		(268)
		(120)
	81	(120)
		(120)

TABLE 4—*Continued*

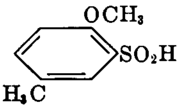
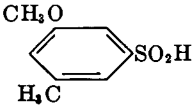
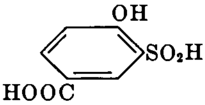
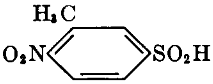
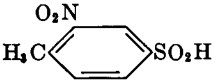
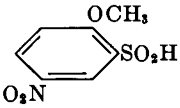
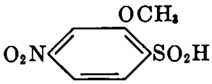
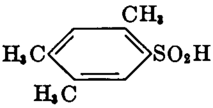
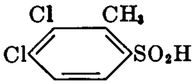
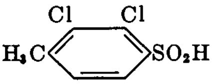
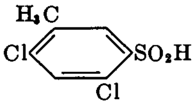
SULFINIC ACID	YIELD	REFERENCES
	per cent	
	71	(97)
		(120)
		(275)
		(51)
		(51)
	4	(140)
	2	(140)
	57	(97)
		(268)
		(268)
		(268)

TABLE 4—*Continued*

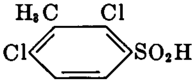
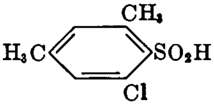
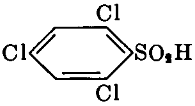
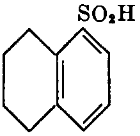
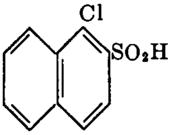
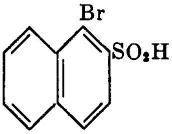
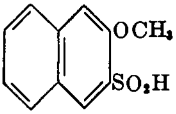
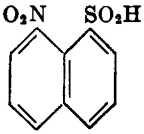
SULFINIC ACID	YIELD	REFERENCES
	per cent	
		(268)
		(268)
		(268)
	41	(204)
1-$C_{10}H_7SO_2H$	Quantitative (?)	(279) (97)
2-$C_{10}H_7SO_2H$	Quantitative (?)	(279) (97)
		(291)
	60	(52)
	97–100	(141)
	35	(308)

TABLE 4—*Continued*

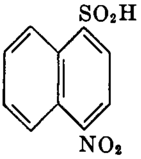
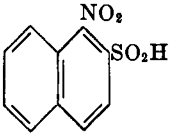
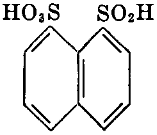
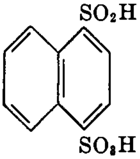
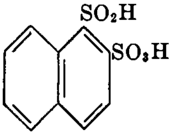
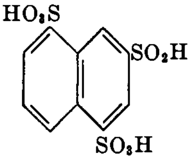
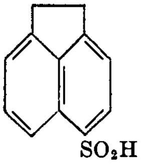
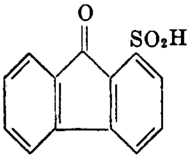
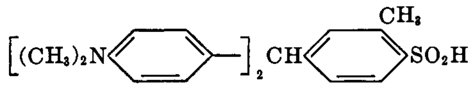
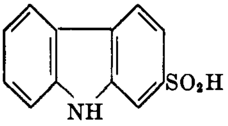
SULFINIC ACID	YIELD	REFERENCES
	per cent	
		(39, 291)
		(291)
		(246)
		(97)
		(97)
		(97)
		(25)
	67	(158)

TABLE 4—*Concluded*

SULFINIC ACID	YIELD	REFERENCES
	per cent	
		(98)
		(146)

$$(C_2H_5)_2SO_2 + KOH \xrightarrow{\text{heat}} C_2H_5SO_2K + C_2H_4 + H_2O$$

As long as one of the alkyl groups contains less than four carbon atoms, decomposition occurs readily under these conditions. For alkyl sulfones of higher molecular weight, sodium ethoxide is the preferred reagent (73). A large number of symmetrical and unsymmetrical sulfones have been cleaved with sodium ethoxide (reaction temperature approximately 235°C.) and the yields are generally good (73).

Phenyl sulfone reacts with sodium amide in piperidine to yield *N*-phenylpiperidine and sodium benzenesulfinate (33). This reagent has also been used to effect the cleavage of *p*-tolyl methyl sulfone and phenyl benzyl sulfone (33).

$$C_5H_{10}N^- + ArSO_2R \rightarrow ArNC_5H_{10} + RSO_2^-$$

However, dibenzyl sulfone was not affected.

γ-Disulfones are usually readily cleaved by alkaline reagents into a sulfinic acid and an alcohol (218, 221, 276). With potassium cyanide, both sulfone groups are generally cleaved (222, 309) and this forms the basis of a useful synthesis of some sulfinic acids (309).

$$C_6H_5SO_2CH_2CH_2SO_2C_6H_5 + KOH(H_2O) \xrightarrow{\text{heat}} C_6H_5SO_2K + C_6H_5SO_2CH_2CH_2OH$$

$$(n\text{-}C_4H_9SO_2CH_2\text{—})_2 + KCN \xrightarrow[\text{heat}]{C_2H_5OH,\ H_2O} 2n\text{-}C_4H_9SO_2K + NCCH_2CH_2CN\ (?)$$

VII. REARRANGEMENT OF CERTAIN *O*-SUBSTITUTED AROMATIC SULFONES AND RELATED TYPES

Aromatic sulfinic acids can be prepared by the rearrangement of certain *o*-hydroxyaryl sulfones, *o*-aminoaryl sulfones, and related compounds, with dilute alkali (table 6).

TABLE 5

Alkaline cleavage of sulfones to sulfinic acids

SULFINIC ACID	SULFONE	REAGENT	YIELD	REFERENCES
			per cent	
CH_3SO_2H	$CH_3SO_2CH_2C_6H_5$	KOH		(150)
	$CH_3SO_2C_6H_4CH_3$-*p*	$C_5H_{10}NH$ ($NaNH_2$)		(33)
$C_2H_5SO_2H$	$(C_2H_5)_2SO_2$	KOH (wet)	60	(71)
		$NaOC_2H_5$ (alcohol)	62	(73)
n-$C_3H_7SO_2H$	*n*-$C_3H_7SO_2C_2H_5$	KOH (wet)	69	(72)
	(*n*-$C_3H_7)_2SO_2$	KOH (wet)	41	(72)
		$NaOC_2H_5$ (alcohol)	60	(73)
$(CH_3)_2CHSO_2H$	(*i*-$C_3H_7)_2SO_2$	KOH (wet)	72	(72)
n-$C_4H_9SO_2H$	(*n*-$C_4H_9)_2SO_2$	$NaOC_2H_5$ (alcohol)	62	(73)
	(*n*-$C_4H_9SO_2CH_2$—$)_2$	KCN (H_2O, alcohol)	72	(309)
$(CH_3)_2CHCH_2SO_2H$	(*i*-$C_4H_9)_2SO_2$	$NaOC_2H_5$ (alcohol)	54	(73)
$(CH_3)_2CHCH_2CH_2SO_2H$	$(CH_3)_2CHCH_2CH_2SO_2C_2H_5$	KOH (wet)		(72)
	(*i*-$C_5H_{11})_2SO_2$	$NaOC_2H_5$ (alcohol)	65	(73)
n-$C_8H_{17}SO_2H$	*n*-$C_8H_{17}SO_2C_2H_5$	KOH (wet)	70	(71)
	(*n*-$C_8H_{17})_2SO_2$	$NaOC_2H_5$ (alcohol)	62	(73)
n-$C_{12}H_{25}SO_2H$	(*n*-$C_{12}H_{25}SO_2CH_2$—$)_2$	NaCN	80	(198)
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2SO_2CH_2CH_2$-COOH	NaOH (H_2O)		(136)
	$(C_6H_5CH_2SO_2CH_2)_2CO$	KOH (alcohol)		(88)
$C_6H_5CH(CH_3)SO_2H$	$C_6H_5CH(CH_3)SO_2CH_2$-CH_2COOH	NaOH (H_2O)		(137)
$C_6H_5SO_2H$	$(C_6H_5)_2SO_2$	$C_5H_{10}NH$ ($NaNH_2$)	Good	(33)
		Na (xylene)		(172)
	$C_6H_5SO_2CH_2CH_2OH$	$NaHg_x$, alcohol		(222)
	$C_6H_5SO_2CH_2CH_2Cl$	$NaHg_x$, H_2O		(222)
	$C_6H_5SO_2CH(CH_3)CH_2OH$	$NaHg_x$, H_2O		(219)
	$C_6H_5SO_2CH_2COCH_3$	$NaHg_x$, alcohol		(227)
	$C_6H_5SO_2CH_2CH_2C_6H_5$	$NaOC_2H_5$, alcohol	72	(73)
	$C_6H_5SO_2C_6H_4NO_2$-*o*	*p*-$CH_3C_6H_4ONa$		(183)
		$C_6H_5NH_2$		(69)
	$(C_6H_5SO_2CH_2CH_2SO_3)_2Ba$	NaOH (H_2O)		(121)
	$C_6H_5SO_2CH_2CH_2SO_2C_6H_5$	$NaHg_x$, H_2O		(217, 222)
		KOH (H_2O)	80	(217, 218)

TABLE 5—*Continued*

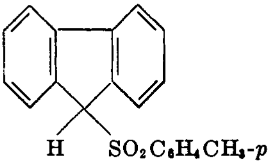
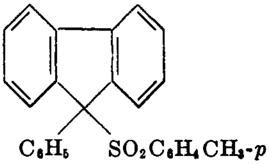
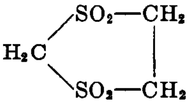
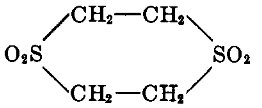
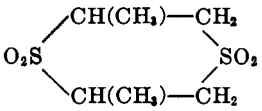
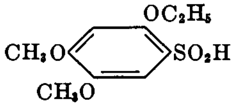
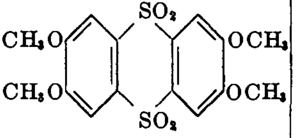
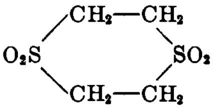
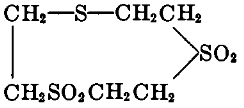
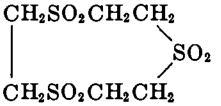
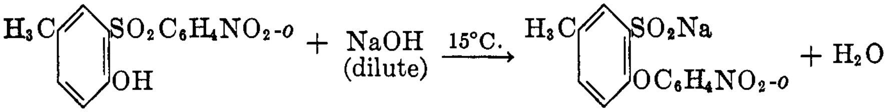
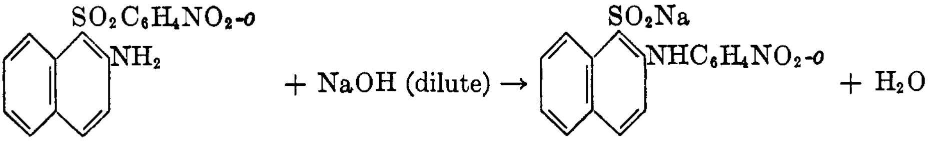
SULFINIC ACID	SULFONE	REAGENT	YIELD	REFERENCES
			per cent	
$C_6H_5SO_2H$—*Contd.*		KOH (H_2O)		(213, 222)
		NH_3	80	(218, 222)
		KHS		(218)
		KCN		(218, 222)
		$C_2H_5NH_2$		(222)
	$C_6H_5SO_2CH_2CH(CH_3)$-$SO_2C_6H_5$	KOH (H_2O)		(276)
	m-$(C_6H_5SO_2)_2C_6H_4$	KOH		(229)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4SO_2CH_3$	KOH	18	(150)
		KOH	20	(150)
		KOH	64	(150)
	(p-$CH_3C_6H_4SO_2CH_2$—$)_2$	KOH (H_2O)		(218)
		$NaHg_x$, H_2O		(222)
	(p-$CH_3C_6H_4SO_2CH$=$)_2$	$C_6H_5NHNH_2$ (alcohol)		(89, 92)
p-$ClC_6H_4SO_2H$	p-$ClC_6H_4SO_2CH_2CH$-$(NH_2)COOH$	KOH (H_2O)		(170)
	p-$ClC_6H_4SO_2CH_2CH$-$(NHCOCH_3)COOH$	KOH (H_2O)		(170)
o-$O_2NC_6H_4SO_2H$	o-$O_2NC_6H_4SO_2(CH_2)_2$-$CONHC_6H_5$	NaOH		(70)
$CH_2(COOH)SO_2H$	(—$CH_2SO_2CH_2COONa)_2$	NaOH (H_2O)	90	(255)
	$(HOOC)CH_2SO_2CH$-$(CH_3)CH_2SO_2CH_2$-$COOH$	NaOH	90	(256)
$HOCH_2CH_2SO_2CH_2$-SO_2H		$Ba(OH)_2$, H_2O		(13)

TABLE 5—*Concluded*

SULFINIC ACID	SULFONE	REAGENT	YIELD *per cent*	REFERENCES
$HOCH_2CH_2SO_2CH_2$-CH_2SO_2H		$Ba(OH)_2$, H_2O		(13, 294)
$CH_3SO_2CH_2CH(CH_3)$-SO_2H		NaOH		(145)
		KOH (alcohol)		(82)
$HO_2SCH_2CH_2SO_2H$ + $HOCH_2CH_2SO_2H$		$Ba(OH)_2$, H_2O		(13)
$(—SCH_2CH_2SO_2H)_2$ + $HOC_2H_4SO_2C_2H_4$-SO_2H		$Ba(OH)_2$, H_2O		(251)
$C_2H_4(OH)SO_2H$ + $HOC_2H_4SO_2C_2H_4$-SO_2H		$Ba(OH)_2$, H_2O		(251)





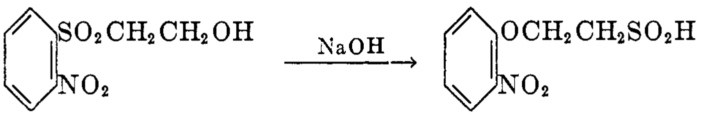
This is apparently a special case of the basic cleavage of sulfones. The relationship becomes more evident when one compares the above reactions with the following ones:

$$o\text{-}C_6H_5SO_2C_6H_4NO_2 + p\text{-}CH_3C_6H_4OK \rightarrow C_6H_5SO_2K + p\text{-}CH_3C_6H_4OC_6H_4NO_2\text{-}o \quad (183)$$

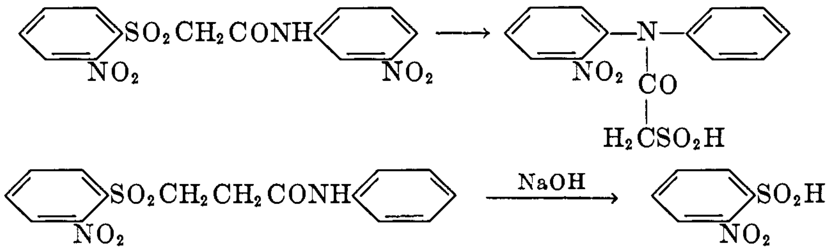
$$o\text{-}C_6H_5SO_2C_6H_4NO_2 + C_6H_5NH_2 \rightarrow C_6H_5SO_2H + o\text{-}C_6H_5NHC_6H_4NO_2 \quad (69)$$

The reaction temperature varies from 15° to 150°C. (approx.), depending on the substituents present and the positions which they occupy. Higher temperatures than those indicated are undesirable, since sulfinic acids tend to lose sulfur dioxide in hot alkali. In general, an *o*- or *p*-nitro or sulfonyl substituent is required in the migrating aryl group for the rearrangement to be successful. More drastic treatment is necessary to bring about the rearrangement of *o*-hydroxy-*p*-sulfonylsulfones than of correspondingly substituted nitrosulfones.

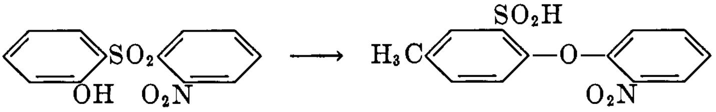
With the hydroxyl group in an aliphatic side chain, rearrangement occurs very rapidly (156).



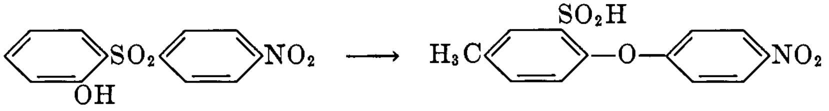
The differences in products obtained from the homologous sulfones below may be due to the less favorable steric relations in the higher member (70).



As the course of the reaction was generally followed by colorimetric methods because of interest in comparative reaction rates (156), not many actual yields are available.



(theoretical yield (135))



(70 per cent yield (134))

VIII. MISCELLANEOUS METHODS

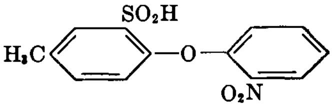
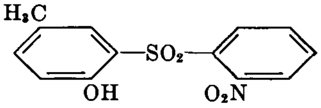
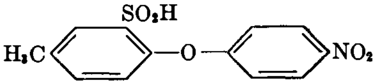
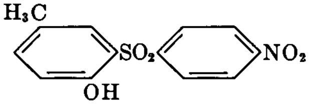
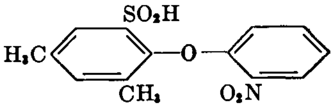
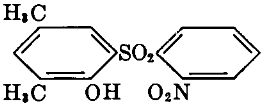
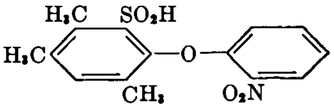
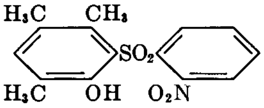
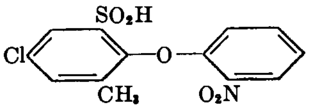
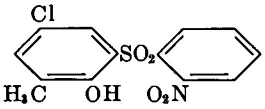
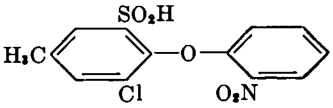
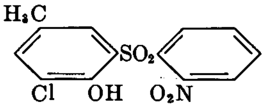
Many other reactions than those listed in the principal sections produce sulfinic acids, several giving excellent yields (table 7).

Among the reduction procedures, the one most important industrially is the reduction of sodium formaldehyde bisulfite to "sodium formaldehyde sulfoxylate." The patent literature records the extension of this reaction to higher

$$HOCH_2SO_3Na + H_2 \rightarrow HOCH_2SO_2Na + H_2O$$

TABLE 6

Rearrangement of certain o-substituted aromatic sulfones and related types

SULFINIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
o-$O_2NC_6H_4OCH_2CH_2SO_2H$	*o*-$O_2NC_6H_4SO_2CH_2CH_2OH$	Aqueous NaOH	(156)
		1 *N* NaOH; 18°C.; theoretical yield	(181)
		0.066 *N* NaOH; 50°C.	(156)
		2 *N* NaOH; 90°C.; 70 per cent yield	(183)
		Dilute aqueous NaOH; warm	(156, 196)
		2 *N* NaOH; 18°C.	(196)
		2 *N* NaOH; 50–60°C.	(196)
		2 *N* NaOH; 50–60°C.	(196)

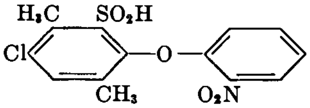
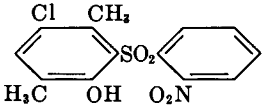
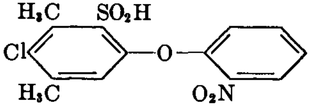
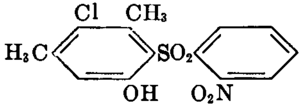
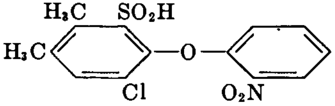
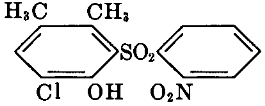
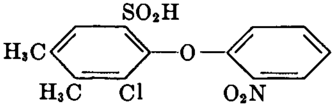
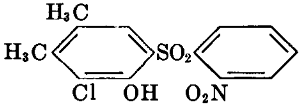
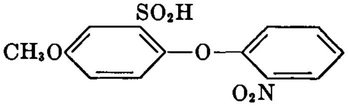
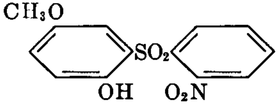
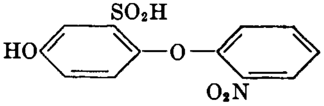
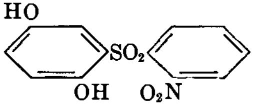
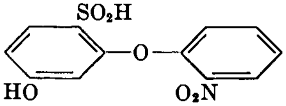
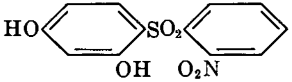
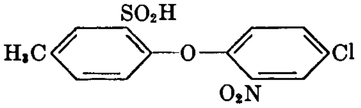
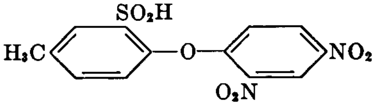
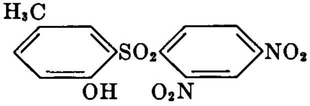
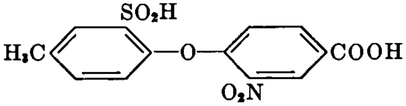
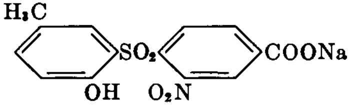
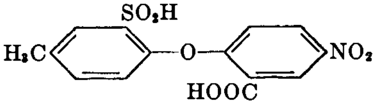
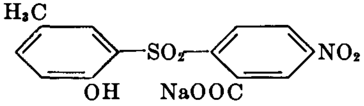
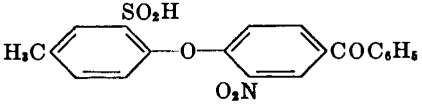
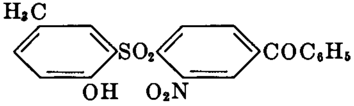
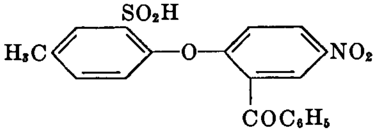
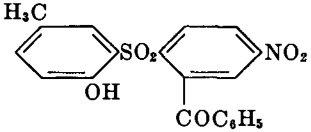
		2 *N* NaOH; 18°C.	(196)
		2 *N* NaOH; 18°C.	(196)
		2 *N* NaOH; 18°C.	(196)
		2 *N* NaOH; 50–60°C.	(196)
		0.066 *N* NaOH; 50°C.	(156)
		0.066 *N* NaOH; 50°C.	(156)
		0.066 *N* NaOH; 50°C.	(156)

TABLE 6—*Continued*

SULFINIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
		0.066 *N* NaOH; 50°C.	(156)
		0.066 *N* NaOH; 50°C.	(156)
		Dilute NaOH; 50°C.	(96)
		Dilute NaOH; 50°C.	(96)
		Dilute NaOH; 50°C.	(96)
		Dilute NaOH; 50°C.	(96)

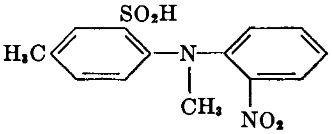
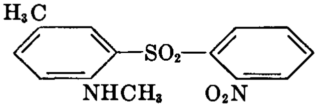
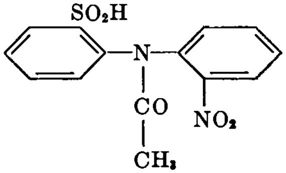
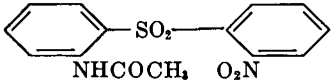
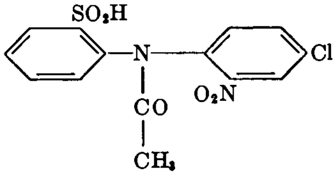
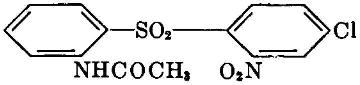
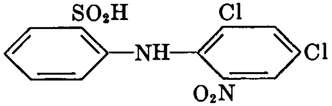
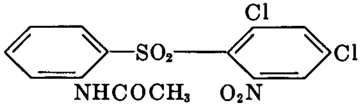
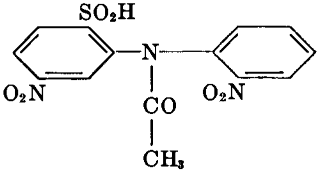
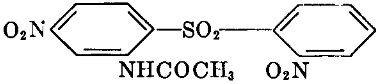
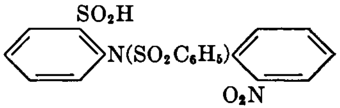
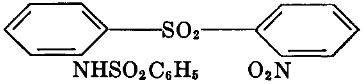
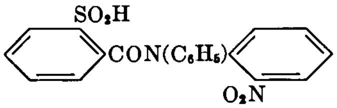
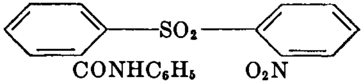
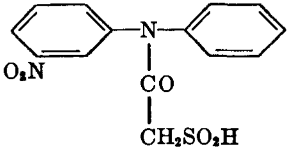
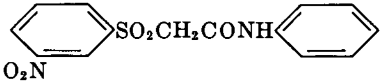
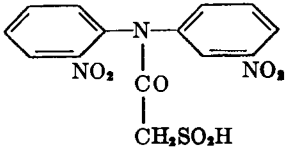
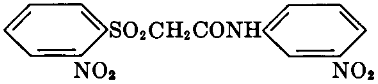
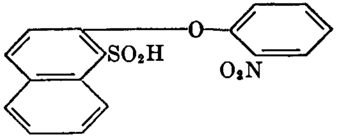
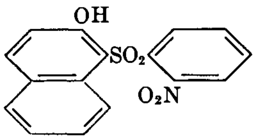
		50 per cent aqueous KOH; 70°C.	(298)
		0.5 *N* NaOH	(69)
		1 *N* NaOH; boil	(69)
		Dilute aqueous NaOH	(69)
		NaOH	(69)

TABLE 6—*Continued*

SULFINIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
		NaOH	(69)
		NaOH	(70)
 (unstable)		NaOH	(70)
		NaOH	(70)
		0.66 *N* NaOH; 50°C.	(156)

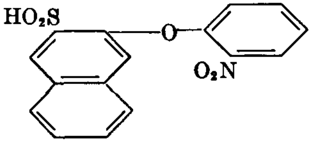
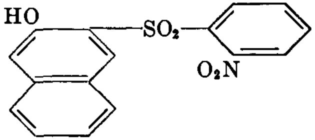
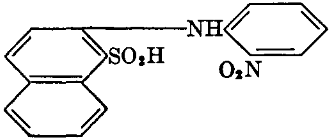
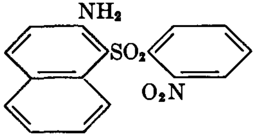
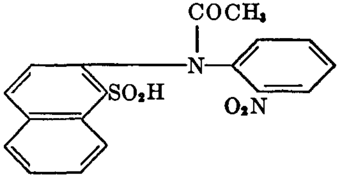
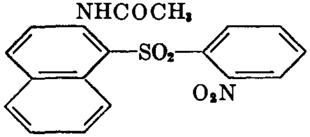
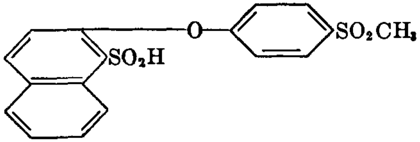
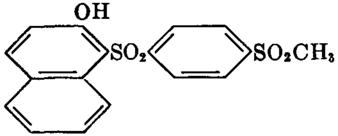
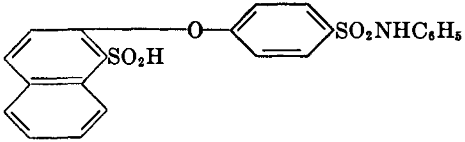
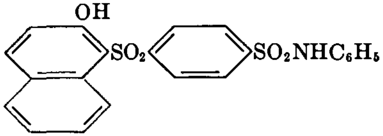
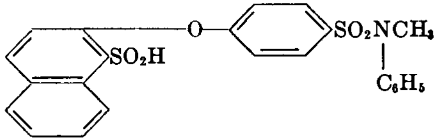
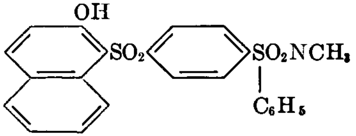
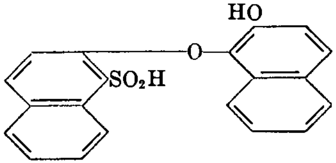
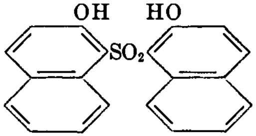
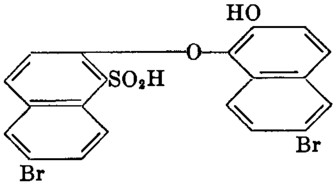
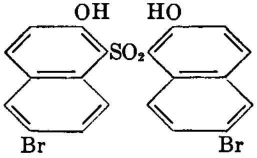
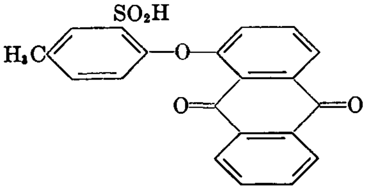
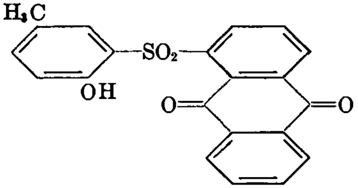
		1 *N* NaOH; 18°C.	(181)
		2 *N* NaOH; boil	(298)
		Warm 2 *N* NaOH	(298)
		1 *N* NaOH; 150°C.	(297)
		1 *N* NaOH; 150°C.	(297)

TABLE 6—*Concluded*

SULFINIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
		1 *N* NaOH; 150°C.	(297)
		K$_3$Fe(CN)$_6$ and Na$_2$S; dilute base	(128) (129) (130) (295)
		NaOH; 150°C.	(296)
		2 *N* NaOH; 130°C.	(96)

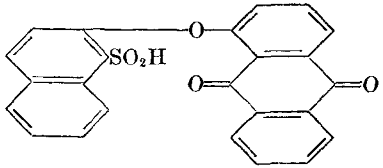
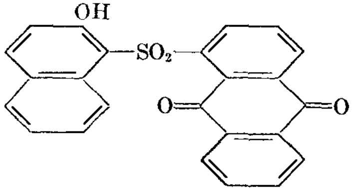
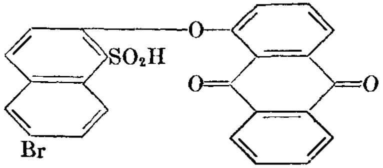
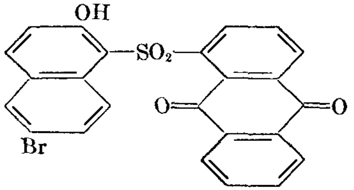
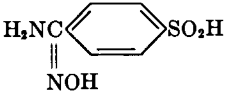
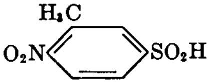
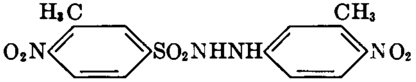
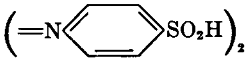
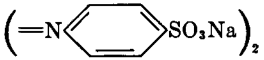
		2 *N* NaOH; boil	(96)
		2 *N* NaOH; boil	(96)

TABLE 7

Miscellaneous methods

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
a. Reduction of sulfonates and their derivatives				
			per cent	
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2SO_2NHNH_2$	H_2O		(55)
$C_6H_5SO_2H$	$C_6H_5SO_2NH_2$	ArN_2Cl, KOH	Quantitative	(63)
	$C_6H_5SO_2NHOH$	KOH		(244, 259)
	$(C_6H_5SO_2)_2NOH$	Alkali		(4, 164)
	$C_6H_5SO_2NHNHC_6H_5$	NaOH		(67)
	$C_6H_5SO_2NHR$	NaOH		(77)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4SO_3C_6H_5$	N_2H_4	80	(79)
	p-$CH_3C_6H_4SO_2NH_2$	ArN_2Cl, KOH	Quantitative	(63)
	p-$CH_3C_6H_4SO_2NRR'$	KOH		(139)
	p-$NCC_6H_4SO_2NHNH_2$	NH_2OH	26	(3)
		$Ba(OH)_2$		(51)
1-$C_{10}H_7SO_2H$	$C_{10}H_7SO_2NHOH$ or $(C_{10}H_7SO_2)_2NOH$	Alkali		(4, 5)
		$NaHg_x$		(12)
$C_6H_4(SO_2H)_2$ (o-, m-, and p-)	$C_6H_4(SO_2)_2NOH$ (o-, m-, and p-)	NH_3, H_2O		(146, 278)

b. Oxidation procedures

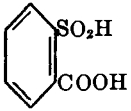
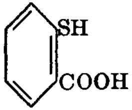
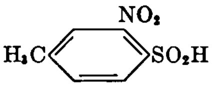
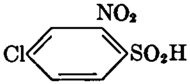
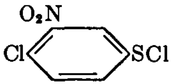
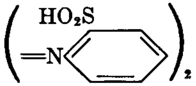
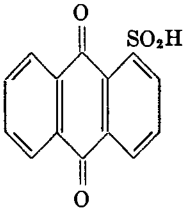
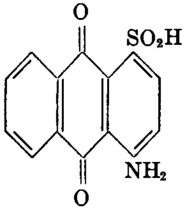
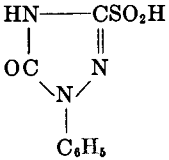
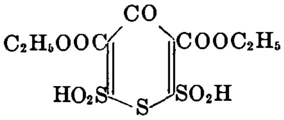
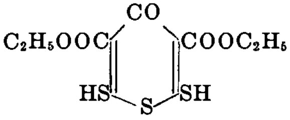
$C_2H_5SO_2H$	C_2H_5SNa	Dry O_2		(49)
$C_2H_5SO_2H + C_6H_5SO_2H$	$C_2H_5SSC_6H_5$	Alcoholic KOH (air)		(229)
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2SCN$	Cl_2, 0°C.		(138, 153)
$C_6H_5SO_2H$	C_6H_5SCN	Cl_2, 0°C.		(153)
	C_6H_5SCl	NaOH		(180)
	$C_6H_5SSC_6H_5$	Alcoholic KOH (air)		(264)
p-$CH_3C_6H_4SO_2H$	$(p\text{-}CH_3C_6H_4S\text{—})_2$	Alcoholic KOH (air)		(264)
		Cl_2, CCl_4; H_2O	70	(247)
p-$O_2NC_6H_4SO_2H$	$(p\text{-}O_2NC_6H_4S\text{—})_2$	Alcoholic KOH, $C_6H_5CH_2Cl$		(93)
	ArSSAr	Cl_2, NaOH		(316)
		NaOH		(311)
	o-$O_2NC_6H_4SH$	Na	30	(269)

TABLE 7—*Continued*

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD *per cent*	REFERENCES
b. Oxidation procedures—*Concluded*				
	ArSOH	Alkali, air $K_3Fe(CN)_6$		(84) (81)
	ArSOH	Air		(81)
	RSH	Alkaline $KMnO_4$ 30 per cent H_2O_2		(68) (68)
		12 per cent H_2O_2; cold	89	(6)

c. Disproportionation of thiolsulfonates

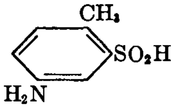
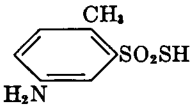
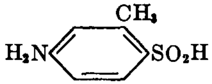
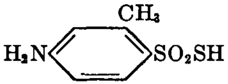
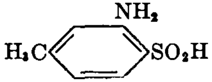
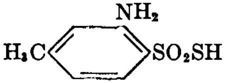
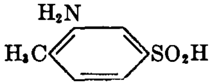
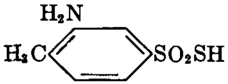
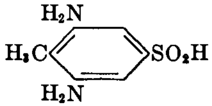
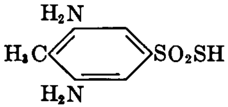
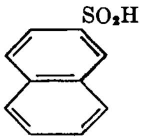
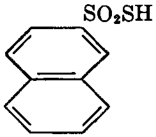
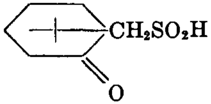
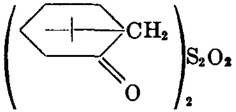
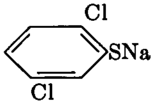
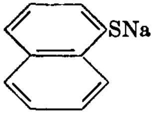
p-$CH_3C_6H_4SO_2H$	*p*-$CH_3C_6H_4SO_2SH$	NaOH Na_2S Na_3AsO_3 KCN		(114, 232) (114, 232) (114, 232) (114, 232)
m-$O_2NC_6H_4SO_2H$	*m*-$O_2NC_6H_4SO_2SH$	H^+		(184)
m-$H_2NC_6H_4SO_2H$	*m*-$H_2NC_6H_4SO_2SH$	$NaHg_x$, alkali		(184)
p-$ClC_6H_4SO_2H$	*p*-$ClC_6H_4SO_2SH$	KCN HCl		(281) (281)
p-$IC_6H_4SO_2H$	*p*-$IC_6H_4SO_2SH$	HCl		(282)
		$NaHg_x$		(239)
		$NaHg_x$, alkali		(187)
		$NaHg_x$, alkali		(180)
		$NaHg_x$		(239)
		HCl		(241)

TABLE 7—*Continued*

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
c. Disproportionation of thiolsulfonates—*Continued*				
			per cent	
		KCN		(284)
$C_2H_5SO_2H$	$(C_2H_5)_2S_2O_2$	Zn, alcohol KOH		(214) (214, 238)
l-$HOOCCH(NH_2)CH_2SO_2H$	*l*-$[HOOCCH(NH_2)CH_2]_2S_2O_2$	NH_3		(178, 179)
			91	(107)
$C_6H_5SO_2H$	$(C_6H_5)_2S_2O_2$	CH_3MgI C_6H_5MgI C_6H_5SNa	63 70	(202) (202) (107)
			60	(107)
p-$CH_3C_6H_4SO_2H$	$(p\text{-}CH_3C_6H_4)_2S_2O_2$	$C_6H_5CH_2MgCl$ C_6H_5MgCl CH_3MgI	Quantitative 54 87	(112) (112) (202)

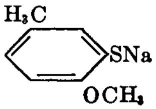
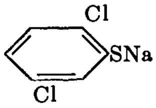
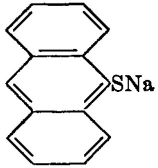
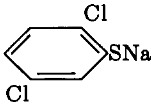
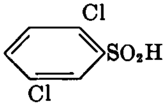
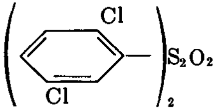
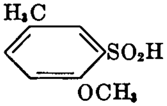
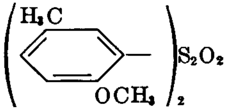
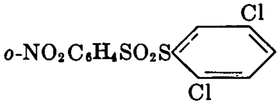
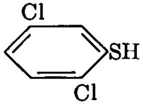
p-$CH_3C_6H_4SO_2H$—*Contd.*	(p-$CH_3C_6H_4)_2S_2O_2$—*Contd.*	C_6H_5MgI	76	(202)
		$CHNa(COOC_2H_5)_2$	80–95	(37)
		$CHNa(CN)COOC_2H_5$	80–95	(37)
		$CH_3COCHNaCOOC_2H_5$	80–95	(37)
		$C_6H_5CHNaCN$	80–95	(37)
		p-$CH_3C_6H_4SNa$	90	(107)
			84	(107)
			84	(107)
			72	(107)
m-$O_2NC_6H_4SO_2H$	(m-$O_2NC_6H_4)_2S_2O_2$		90	(107)
p-$ClC_6H_4SO_2H$	(p-$ClC_6H_4)_2S_2O_2$	CH_3MgI	90	(202)
		CH_3MgI	82	(202)
		p-$CH_3C_6H_4SNa$	93	(106, 107)

TABLE 7—*Continued*

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
c. Disproportionation of thiolsulfonates—*Continued*				
			per cent	
		CH_3MgI	68	(202)
$C_6H_5SO_2H$	$C_6H_5SO_2SC_2H_5$	Zn, alcohol		(214)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4SO_2SC_2H_5$	KOH		(214, 228)
		$Ba(OH)_2$		(228)
		$Na_2S_2O_3$		(116)
		KCN		(116)
		K_2S, alcohol		(116)
		C_2H_5SH		(214)
	p-$CH_3C_6H_4SO_2SC_6H_4NO_2$-$o$	o-$O_2NC_6H_4SH$	*ca.* 80	(202)
o-$NO_2C_6H_4SO_2H$		o-$O_2NC_6H_4SH$	*ca.* 80	(202)
			*ca.* 80	(202)
p-$ClC_6H_4SO_2H$	p-$ClC_6H_4SO_2SC_6H_4NO_2$-o	$CH_3COCHNaCOCH_3$	89	(37)
		o-$O_2NC_6H_4SH$	*ca.* 80	(202)

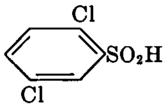
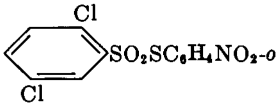
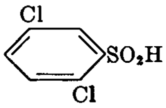
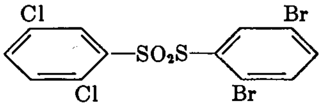
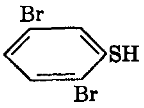
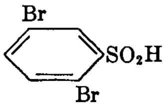
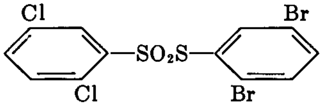
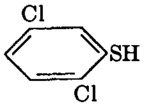
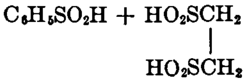
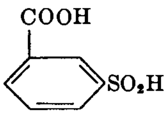
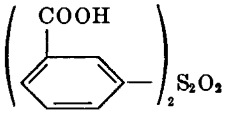
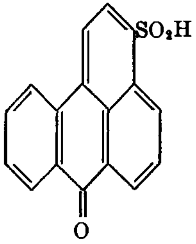
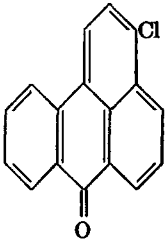
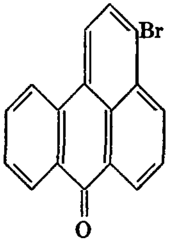
		$CHNa(COOC_2H_5)_2$ $CH_3COCHNaCOCH_3$ $o\text{-}O_2NC_6H_4SH$	92 84 *ca.* 80	(37) (37) (202)
			*ca.* 80	(202)
			*ca.* 80	(202)
 $C_6H_5SO_2H + HO_2SCH_2\text{—}CH_2SO_2H$	$(C_6H_5S_2O_2CH_2)_2$	Zn, alcohol KOH, alcohol NH_3, aqueous		(230) (230) (230)
		$p\text{-}CH_3C_6H_4SNa$		(106)
		d. Nucleophilic displacements		
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2Cl$	$Na_2S_2O_4$, NaOH		(91)
$(p\text{-}HOC_6H_4)_3CSO_2H$	$(p\text{-}HOC_6H_4)_3COH$	$Na_2S_2O_4$, NaOH		(262)
$(p\text{-}H_2NC_6H_4)_3CSO_2H$	$(p\text{-}H_2NC_6H_4)_3COH \cdot HCl$	$Na_2S_2O_4$, NaOH	60	(262, 305)
$[p\text{-}(CH_3)_2NC_6H_4]_3CSO_2H$	$[p\text{-}(CH_3)_2NC_6H_4]_3COH$	$Na_2S_2O_4$, NaOH		(303, 304)
$[p\text{-}(CH_3)_2NC_6H_4]_2C(C_6H_5)SO_2H$	$[p\text{-}(CH_3)_2NC_6H_4]_2C(C_6H_5)OH$	$Na_2S_2O_4$, NaOH		(304)

TABLE 7—*Continued*

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD *per cent*	REFERENCES
	d. Nucleophilic displacements—*Continued*			
		$Na_2S_2O_4$, NH_3		(149)
		$Na_2S_2O_4$, NH_3 $HOCH_2SO_2Na$		(149) (149)
	e. Miscellaneous methods			
$C_2H_5SO_2H$	$C_2H_5S_2O_3Na$	NaOH		(62)
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2S_2O_3Na$	NaOH		(62)
p-$CH_3C_6H_4SO_2H$	p-$CH_3C_6H_4S_2O_3Na$	NaOH		(62)

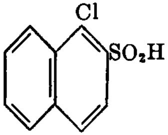
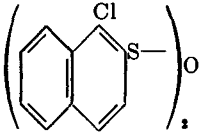
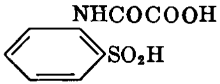
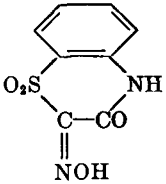
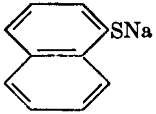
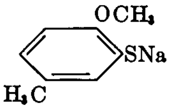
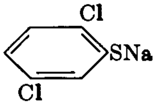
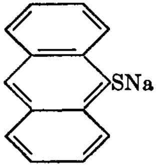
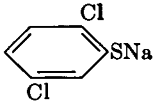
$\begin{array}{l}HN-C_6H_4SO_2SH\text{-}m\\ \vert\\ HN-C_6H_4SO_2H\text{-}m\end{array}$	$\begin{array}{l}HN-C_6H_4SO_2S\diagdown\\ \vert\qquad\qquad\qquad\quad Ba\\ HN-C_6H_4SO_2S\diagup\end{array}$	HgO		(185)
$\begin{array}{l}NC_6H_4SO_2H\text{-}m\\ \Vert\\ NC_6H_4SO_2H\text{-}m\end{array}$	$\begin{array}{l}NC_6H_4SO_2SH\\ \Vert\\ NC_6H_4SO_2H\end{array}$	$NaHg_x$, alkali		(12, 185)
		NaOH		(313)
$\begin{array}{l}p\text{-}BrC_6H_4CHSCH_2C_6H_5\\ \qquad\qquad\vert\\ \qquad\quad SO_2H\end{array}$	$[p\text{-}BrC_6H_4CH_2SSO_3]^-$ $[C_6H_5CH_2N(C_6H_5)(CH_3)_2]^+$	KOH	7–16	(274)
		HCl, CH_3COOH		(48a)
$C_6H_5SO_2H$	$(C_6H_5)_2S_2O_4$	C_6H_5SNa, alcohol		(106)
		$(C_6H_5S)_2Pb$		(236, 237)
			60	(106)
		KOH	64	(228)
		$Ba(OH)_2$	64	(228)
		H_2S, alcohol		(230)
		C_6H_5SH		(236, 237)

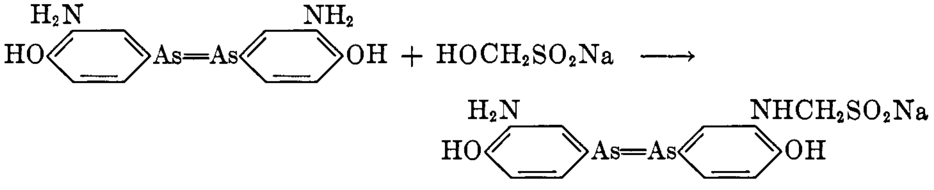
TABLE 7—*Concluded*

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
e. Miscellaneous methods—*Concluded*				
			per cent	
p-$CH_3C_6H_4SO_2H$	(*p*-$CH_3C_6H_4)_2S_2O_4$	Zn, alcohol		(236)
		KOH, sealed tube	93	(228)
		Na_2CO_3		(85)
		p-$CH_3C_6H_4SNa$, alcohol	90	(106)
			84	(106)
			84	(106)
			72	(106)
m-$O_2NC_6H_4SO_2H$	(*m*-$O_2NC_6H_4)_2S_2O_4$	Alkali, alcohol		(315)
p-$O_2NC_6H_4SO_2H$	(*p*-$O_2NC_6H_4)_2S_2O_4$		90	(106)

aldehydes (267). Reagents include zinc dust and acetic acid (249) and hydrogen in the presence of a nickel catalyst (267). Another process employs formaldehyde and sodium dithionite (307).

$$Na_2S_2O_4 + HCHO + NaOH \xrightarrow{H_2O} HOCH_2SO_2Na + Na_2SO_3$$

Sodium formaldehyde sulfoxylate is an important industrial reducing agent in vat dyeing. It is also used to introduce the CH_2SO_2Na group upon nitrogen (254, 301), as in the following example:



Neosalvarsan

Sulfonates, sulfonamides, and several other sulfonic acid derivatives have also been reduced by various reagents to sulfinic acids.

Thiolsulfonic acids and thiolsulfonates (1,2-disulfoxides) may be disproportionated to sulfinic acids with excellent yields in many of the recorded cases.

Oxidation procedures include oxidations of disulfides, sulfenic acids and derivatives, and mercaptans. Nucleophilic displacements, of halogen or hydroxyl groups principally, with sodium dithionate are for the most part recorded for dye compounds. A few reactions which do not fit into the above schemes are recorded at the end of table 7.

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