

# THE PREPARATION OF SULFINIC ACIDS

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## 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:



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<sup>-2</sup> (195). Aromatic sulfinic acids appear to be conveniently characterized as thallos 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 I

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

SULFONIC ACID	REAGENT	YIELD	REFERENCES
		<i>per cent</i>	
CH <sub>3</sub> SO <sub>2</sub> H	Zn		(14)
C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> H	Zn		(7, 14, 235)
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> SO <sub>2</sub> H	Zn		(235)
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H	Zn		(221)
CH <sub>3</sub> SO <sub>2</sub> H	Zn	53	(165, 221)
CH <sub>3</sub> SO <sub>2</sub> H			
CCl <sub>3</sub> SO <sub>2</sub> H	SO <sub>2</sub>		(11)
	K <sub>2</sub> SO <sub>3</sub>		(250)
	H <sub>2</sub> S		(191)
	KCN		(190, 197)
	NaI		(242)
	NH <sub>3</sub> (aqueous)		(197)
CHCl <sub>2</sub> SO <sub>2</sub> H	SO <sub>2</sub> (KOH, alcoholic)		(197)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> H	Zn		(225)
	NaHg <sub>2</sub>		(225)
			(90)
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> H	Zn	85-95	(14, 216)
			(289)
			(234)
			(263)
	Zn (NaI)		(102)
	Ca		(17)
	NaHg <sub>2</sub>		(211, 226)
	Mg (ether)	12.3	(109)
	H <sub>2</sub> (Pd)		(270)
	Na <sub>2</sub> SO <sub>3</sub> (NaOH, aqueous)		(175)
	Na <sub>2</sub> S		(134)
	Na <sub>2</sub> AsO <sub>3</sub>		(117)
	NaI		(103)
	NaI (Na <sub>2</sub> S <sub>2</sub> O <sub>4</sub> )	81	(242)
	C <sub>6</sub> H <sub>5</sub> SH (KOH)		(215)
	Methyl sodium camphocarboxylate		(38)
	RMgX	0.5-53	(110, 288)
	RC≡CNa	43-72	(288)
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Zn		(154, 167)
	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PbS <sub>2</sub>		(264)
	R <sub>2</sub> NH, CS <sub>2</sub>	80	(34)
	KOH (on sulfonyl iodide)		(232)
	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Zn (on sulfonyl iodide)		(232)

TABLE 1—Continued

SULFINIC ACID	REAGENT	YIELD <i>per cen</i>	REFERENCES
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Zn		(285)
	Na <sub>2</sub> S		(134)
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Zn	64-95	(30, 234, 302)
	Na <sub>2</sub> SO <sub>3</sub>	88	(21, 175, 263)
	NaHg <sub>2</sub>		(223)
	Mg	69.5-75	(109)
	Sodium aceto- acetic ester	70	(166)
	Sodium malonic ester		(166)
	Na <sub>2</sub> S		(87, 134)
	As <sub>2</sub> O <sub>3</sub> (NaOH)		(115, 117)
	NaI		(103)
	C <sub>6</sub> H <sub>11</sub> N, CS <sub>2</sub>		(34)
	RMgBr	10.7-67.1	(41, 110, 288)
	RC≡CNa	48-49	(288)
	C <sub>6</sub> H <sub>5</sub> MgBr (on sulfonyl bro- mide)	30.2	(110)
	C <sub>6</sub> H <sub>5</sub> MgBr (on sulfonyl iodide)	11.8	(110)
Electrolytic re- duction		(74)	
<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub> (on sul- fonyl fluoride)	81	(176)
	Na <sub>2</sub> SO <sub>3</sub>	80	(175, 176)
	H <sub>2</sub> (Pd)		(270)
	NaHg <sub>2</sub>		(189, 220)
	Na <sub>2</sub> S		(134)
<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>		(288a)
	H <sub>2</sub> (Pd)		(270)
	CS <sub>2</sub> , AlCl <sub>3</sub>		(210)
	CS <sub>2</sub> , AlBr <sub>3</sub> (on sulfonyl bro- mide)		(210)
<i>o</i> -IC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H			(10)
<i>p</i> -IC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	K <sub>2</sub> S		(286)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	NaHg <sub>2</sub>		(95)
	NaI		(103)
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Electrolytic re- duction		(75)
	Na <sub>2</sub> SO <sub>3</sub>		(175)

TABLE 1—Continued

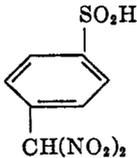
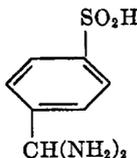
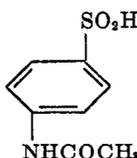
SULFINIC ACID	REAGENT	YIELD <i>per cent</i>	REFERENCES
<i>o</i> -HOCC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>		(60)
<i>m</i> -HOCC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>	52	(60, 175)
<i>o</i> -NCC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Zn		(133)
<i>p</i> -NCC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>	76.1-87.4	(3, 57, 94, 293)
<i>o</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>		(314)
	NH <sub>2</sub> NH <sub>2</sub>	80	(58)
	SnCl <sub>4</sub> , HCl, alcohol	90	(47)
<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	SnCl <sub>4</sub> , HCl, alcohol	71.5	(76)
	Na <sub>2</sub> SO <sub>3</sub>	22.3	(76, 186)
	C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub>		(67, 184)
	R'SNa		(288a)
<i>p</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>		(315)
	Zn		(240)
	(NH <sub>4</sub> ) <sub>2</sub> S		(240)
	Na <sub>2</sub> SO <sub>3</sub>	41.6-47	(40, 175, 271)
<i>p</i> -CH <sub>2</sub> CONHCH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>	75	(44, 57, 61, 162)
<i>p</i> -C <sub>6</sub> H <sub>5</sub> OC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>	87.2	(277)
<i>p</i> -(C <sub>6</sub> H <sub>5</sub> CONH)C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	Na <sub>2</sub> SO <sub>3</sub>	70	(271)

TABLE 1—Continued

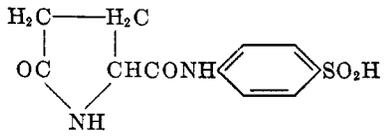
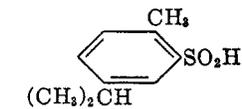
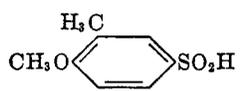
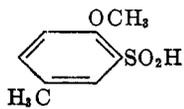
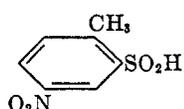
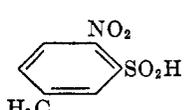
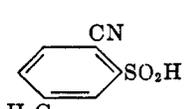
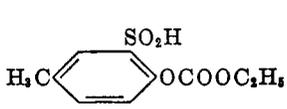
SULFINIC ACID	REAGENT	YIELD	REFERENCES
$\text{HOOCCH}=\text{CH}-\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$\text{Na}_2\text{SO}_3$	<i>per cent</i>	(175)
	$\text{Na}_2\text{SO}_3$		(43)
3,4-( $\text{CH}_3$ ) <sub>2</sub> $\text{C}_6\text{H}_3\text{SO}_2\text{H}$	Zn		(151)
2,4-( $\text{CH}_3$ ) <sub>2</sub> $\text{C}_6\text{H}_3\text{SO}_2\text{H}$	Zn		(151, 152)
	Zn		(18)
	$\text{Na}_2\text{SO}_3$	94.6	(169)
	$\text{Na}_2\text{SO}_3$		(105)
	$\text{Na}_2\text{SO}_3$		(51)
	$\text{Na}_2\text{SO}_3$	25	(51)
	Zn		(133)
	$\text{Na}_2\text{SO}_3$	55-60	(310)
2,5- $\text{Cl}_2\text{C}_6\text{H}_3\text{SO}_2\text{H}$	$\text{Na}_2\text{SO}_3$	87.5	(106, 175)
2,5- $\text{Br}_2\text{C}_6\text{H}_3\text{SO}_2\text{H}$	$\text{Na}_2\text{SO}_3$		(175)

TABLE 1—Continued

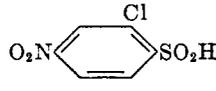
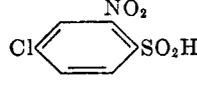
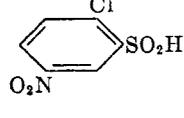
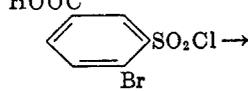
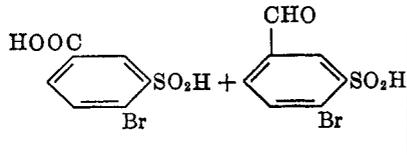
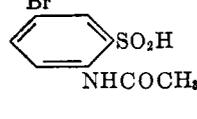
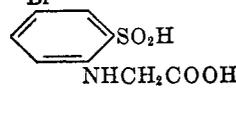
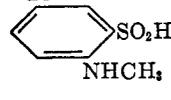
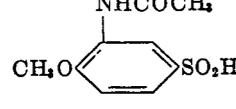
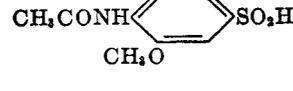
SULFINIC ACID	REAGENT	YIELD	REFERENCES
	SnCl <sub>4</sub> , HCl, alcohol	Quantitative	(47)
	(C <sub>6</sub> H <sub>5</sub> NH) <sub>2</sub>		(258)
	Na <sub>2</sub> SO <sub>3</sub>	70	(174, 175)
	Zn		(24)
			
	Zn	50	(46)
	Zn		(46)
	Zn		(46)
2,4-(O <sub>2</sub> N) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SO <sub>2</sub> H	N <sub>2</sub> H <sub>4</sub>		(59)
	Na <sub>2</sub> SO <sub>3</sub>		(45)
	Na <sub>2</sub> SO <sub>3</sub>		(26)

TABLE 1—Continued

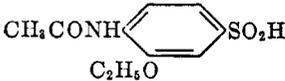
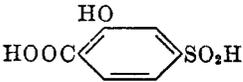
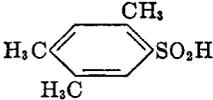
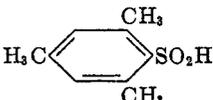
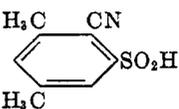
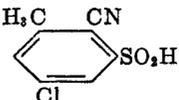
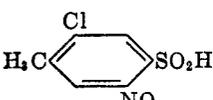
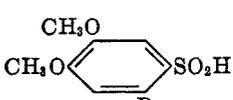
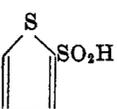
SULFINIC ACID	REAGENT	YIELD <i>per cent</i>	REFERENCES
	Na <sub>2</sub> SO <sub>3</sub>		(26)
	Na <sub>2</sub> SO <sub>3</sub>		(175)
	Na <sub>2</sub> S Zn		(134) (248)
	NaHg <sub>2</sub>		(142)
	Zn		(133)
	Zn		(133)
	N <sub>2</sub> H <sub>4</sub>	97.5	(58)
	Na <sub>2</sub> SO <sub>3</sub>		(182)
	Zn		(19, 300)
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (SO <sub>2</sub> H) <sub>2</sub>	Na <sub>2</sub> SO <sub>3</sub>		(147)
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (SO <sub>2</sub> H) <sub>2</sub>	Electrolytic re- duction Zn	50 60	(75) (8, 234, 283)
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (SO <sub>2</sub> H) <sub>2</sub>	Zn		(283)

TABLE 1—Continued

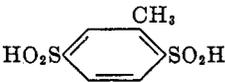
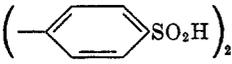
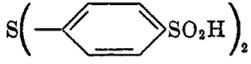
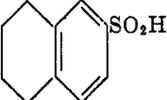
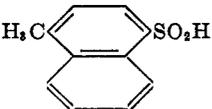
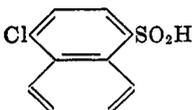
SULFINIC ACID	REAGENT	YIELD	REFERENCES
	Zn	<i>per cent</i>	(283)
$\text{CH}_3\text{C}_6\text{H}_4(\text{SO}_2\text{H})_2$	$\text{Na}_2\text{SO}_3$		(22)
	$\text{Na}_2\text{SO}_3$	60	(10)
	Zn		(31)
	Barium sulfhy- drate		(12)
	$\text{C}_6\text{H}_{11}\text{N}$ , $\text{CS}_2$		(34)
1- $\text{C}_{10}\text{H}_7\text{SO}_2\text{H}$	Electrolytic re- duction $\text{Na}_2\text{S}$ Zn	13.6  Almost quantitative	(75)  (134) (231)
	$\text{NaHg}_z$ $\text{Na}_2\text{SO}_3$ $\text{C}_6\text{H}_5\text{MgBr}$	11	(104) (9) (110)
2- $\text{C}_{10}\text{H}_7\text{SO}_2\text{H}$	$\text{H}_2$ (Pd) Electrolytic re- duction Zn	12.6  Almost quantitative	(270) (75) (231)
	$\text{NaHg}_z$ $\text{Na}_2\text{SO}_3$ RSH	66.4 to quantitative	(104) (9) (261)
	Zn	Very good	(65)
	$\text{Na}_2\text{SO}_3$ $\text{NaHg}_z$ (on sul- fonyl bromide)	91	(15) (104)

TABLE 1—Continued

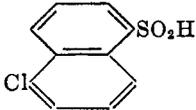
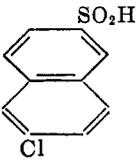
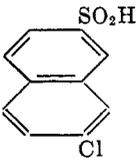
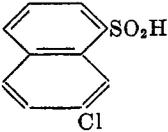
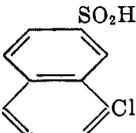
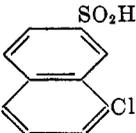
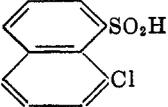
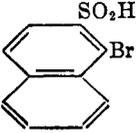
SULFINIC ACID	REAGENT	YIELD	REFERENCES
	$\text{Na}_2\text{SO}_3$	65 <i>per cent</i>	(15, 252)
	$\text{Na}_2\text{SO}_3$	90	(15)
	$\text{Na}_2\text{SO}_3$	94	(15)
	$\text{Na}_2\text{SO}_3$	82	(15)
	$\text{Na}_2\text{SO}_3$	91	(15)
	$\text{Na}_2\text{SO}_3$	77	(15)
	$\text{Na}_2\text{SO}_3$	97	(15)
	$\text{Na}_2\text{SO}_3$	60	(52)

TABLE 1—Continued

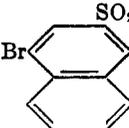
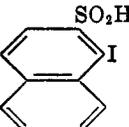
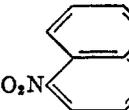
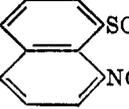
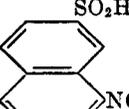
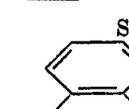
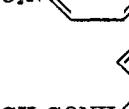
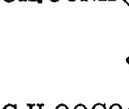
SULFINIC ACID	REAGENT	YIELD	REFERENCES
	NaHSO <sub>3</sub>	<i>per cent</i>	(200)
	Na <sub>2</sub> SO <sub>3</sub>		(10)
	Na <sub>2</sub> SO <sub>3</sub>		(252)
	K <sub>2</sub> SO <sub>3</sub> Na <sub>2</sub> SO <sub>3</sub>	90	(66) (252)
	Na <sub>2</sub> SO <sub>3</sub>		(290)
	Na <sub>2</sub> SO <sub>3</sub>		(290)
	Na <sub>2</sub> SO <sub>3</sub>		(252)
	Na <sub>2</sub> SO <sub>3</sub>		(252)
	Na <sub>2</sub> SO <sub>3</sub>	80	(253)
			

TABLE 1—Continued

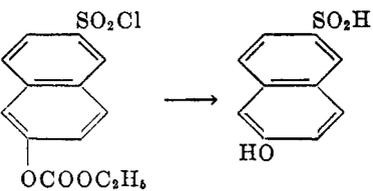
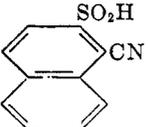
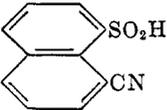
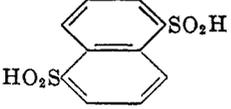
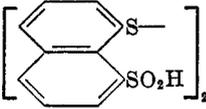
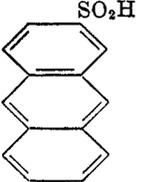
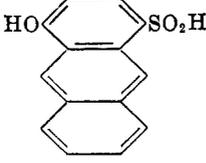
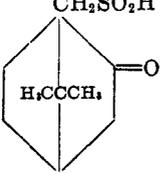
SULFINIC ACID	REAGENT	YIELD	REFERENCES
	Na <sub>2</sub> SO <sub>3</sub>	<i>per cent</i>	(312)
	Zn		(133)
	Zn		(133)
	Zn Na <sub>2</sub> S	50	(56) (54)
C <sub>10</sub> H <sub>6</sub> (SO <sub>2</sub> H) <sub>2</sub>	Zn		(283)
	Na <sub>2</sub> SO <sub>3</sub>		(246)
	Zn Na <sub>2</sub> SO <sub>3</sub>		(123) (123)
	Na <sub>2</sub> SO <sub>3</sub>		(83)
	Zn Na <sub>2</sub> SO <sub>3</sub>	47-70 90	(192, 272) (126, 192)

TABLE 1—Continued

SULFINIC ACID	REAGENT	YIELD <i>per cent</i>	REFERENCES
	$\text{Na}_2\text{SO}_3$		(193)
	Using the well-known methods		(29)
	Zn		(64)
	Zn		(35)

TABLE 1—Continued

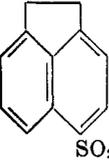
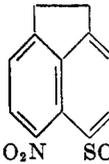
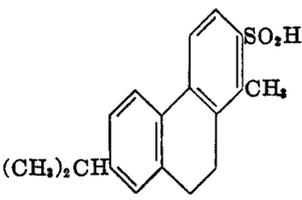
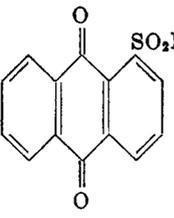
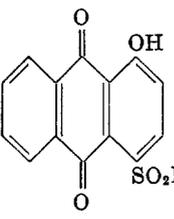
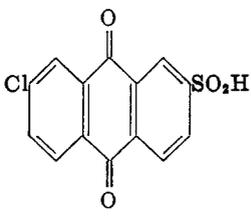
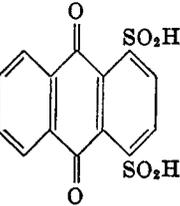
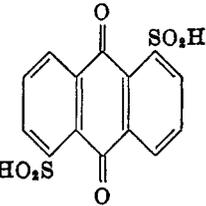
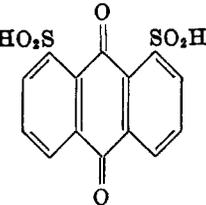
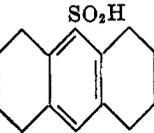
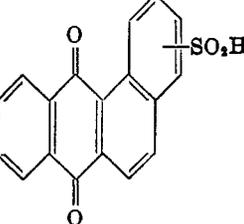
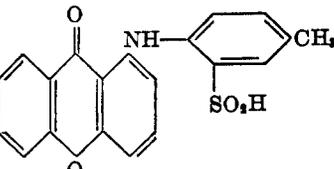
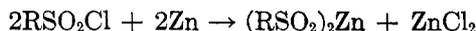
SULFINIC ACID	REAGENT	YIELD <i>per cent</i>	REFERENCES
	Na <sub>2</sub> SO <sub>3</sub>		(25)
	Na <sub>2</sub> SO <sub>3</sub>		(25)
	Zn	57.1	(169)
	Na <sub>2</sub> S		(135)
	Na <sub>2</sub> SO <sub>3</sub> Na <sub>2</sub> S	Changeable, but good	(83) (135)
	Na <sub>2</sub> S		(135)

TABLE 1—*Concluded*

SULFINIC ACID	REAGENT	YIELD	REFERENCES
	Na <sub>2</sub> S	<i>per cent</i> 90.1	(171)
	Na <sub>2</sub> S	83.5	(171)
	Na <sub>2</sub> S	77.5	(171)
	NaHSO <sub>3</sub>		(266)
	Na <sub>2</sub> S		(135)
	Na <sub>2</sub> S		(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



and sodium amalgam is added, the sodium sulfinic acid 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).



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.

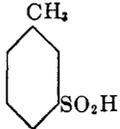
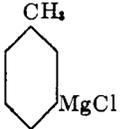
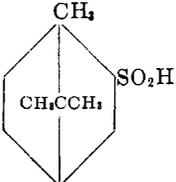
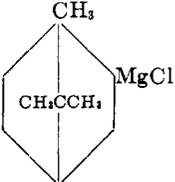
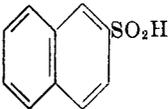
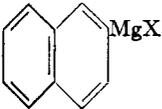
### III. SULFINATION OF ORGANOMETALLIC COMPOUNDS

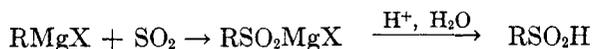
Many aliphatic and aromatic organometallic compounds react with sulfur dioxide to form sulfinic acids (table 2). Hobson (131) was the first to report this type of reaction, using diethylzinc and sulfur dioxide. The more convenient Grignard reagent has been used extensively for the preparation of aliphatic 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

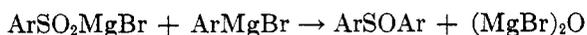
SULFINIC ACID	ORGANOMETALLIC COMPOUND	YIELD	REFERENCES
$\text{CH}_3\text{SO}_2\text{H}$	$(\text{CH}_3)_2\text{Zn}$	<i>per cent</i>	(132)
$\text{C}_2\text{H}_5\text{SO}_2\text{H}$	$(\text{C}_2\text{H}_5)_4\text{Pb}$ $(\text{C}_2\text{H}_5)_2\text{Zn}$ $\text{C}_2\text{H}_5\text{MgX}$ $\text{C}_2\text{H}_5\text{MgBr}$ $\text{C}_2\text{H}_5\text{MgI} (+ \text{SO}_2\text{Cl}_2)$	50-60 (Mg salt)	(78) (131, 306) (260) (144, 155) (209)
<i>n</i> - $\text{C}_3\text{H}_7\text{SO}_2\text{H}$	$\text{C}_3\text{H}_7\text{MgX}$ $\text{C}_3\text{H}_7\text{MgBr}$	50-60 (Mg salt)	(260) (2, 144)
<i>n</i> - $\text{C}_4\text{H}_9\text{SO}_2\text{H}$	$\text{C}_4\text{H}_9\text{MgBr}$ $\text{C}_4\text{H}_9\text{MgBr} (-50^\circ\text{C.})$	69 (Mg salt)	(36) (2, 144)
<i>tert</i> - $\text{C}_4\text{H}_9\text{SO}_2\text{H}$	<i>tert</i> - $\text{C}_4\text{H}_9\text{MgCl}$		(257)
<i>n</i> - $\text{C}_6\text{H}_{11}\text{SO}_2\text{H}$	$\text{C}_6\text{H}_{11}\text{MgBr}$		(2, 144)
<i>i</i> - $\text{C}_6\text{H}_{11}\text{SO}_2\text{H}$	<i>i</i> - $\text{C}_6\text{H}_{11}\text{MgBr}$		(36)
<i>n</i> - $\text{C}_6\text{H}_{13}\text{SO}_2\text{H}$	$\text{C}_6\text{H}_{13}\text{MgBr}$		(2)
<i>n</i> - $\text{C}_7\text{H}_{15}\text{SO}_2\text{H}$	$\text{C}_7\text{H}_{15}\text{MgBr}$		(2)
<i>n</i> - $\text{C}_8\text{H}_{17}\text{SO}_2\text{H}$	$\text{C}_8\text{H}_{17}\text{MgBr}$	41.6 (Mg salt)	(2)
<i>n</i> - $\text{C}_9\text{H}_{19}\text{SO}_2\text{H}$	$\text{C}_9\text{H}_{19}\text{MgBr}$	37.6 (Mg salt)	(2)
<i>n</i> - $\text{C}_{10}\text{H}_{21}\text{SO}_2\text{H}$	$\text{C}_{10}\text{H}_{21}\text{MgBr}$	34.5 (Mg salt)	(2)
<i>n</i> - $\text{C}_{11}\text{H}_{23}\text{SO}_2\text{H}$	$\text{C}_{11}\text{H}_{23}\text{MgBr}$	49.8 (Mg salt)	(2)
<i>n</i> - $\text{C}_{12}\text{H}_{25}\text{SO}_2\text{H}$	$\text{C}_{12}\text{H}_{25}\text{MgBr}$ $\text{C}_{12}\text{H}_{25}\text{MgBr} (-40^\circ \text{ to } -35^\circ\text{C.})$	56.5 (Mg salt) 80 (Mg salt)	(2) (198)
<i>n</i> - $\text{C}_{13}\text{H}_{27}\text{SO}_2\text{H}$	$\text{C}_{13}\text{H}_{27}\text{MgBr}$	38.7 (Mg salt)	(2)
<i>n</i> - $\text{C}_{14}\text{H}_{29}\text{SO}_2\text{H}$	$\text{C}_{14}\text{H}_{29}\text{MgBr}$	39.2 (Mg salt)	(2)
<i>n</i> - $\text{C}_{15}\text{H}_{31}\text{SO}_2\text{H}$	$\text{C}_{15}\text{H}_{31}\text{MgBr}$	43.0 (Mg salt)	(2)
<i>n</i> - $\text{C}_{16}\text{H}_{33}\text{SO}_2\text{H}$	$\text{C}_{16}\text{H}_{33}\text{MgBr}$	57.2 (Mg salt)	(2)
$(\text{CH}_2)_4\text{CHSO}_2\text{H}$	$(\text{CH}_2)_4\text{CHMgBr}$		(28)
$(\text{CH}_2)_5\text{CHSO}_2\text{H}$	$(\text{CH}_2)_5\text{CHMgCl}$ $(\text{CH}_2)_5\text{CHMgCl}$	28	(36, 206) (111)

TABLE 2—Concluded

SULFINIC ACID	ORGANOMETALLIC COMPOUND	YIELD <i>per cent</i>	REFERENCE
			(28)
		50 26 (Na salt)	(27) (143)
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> MgBr (+ SO <sub>2</sub> Cl <sub>2</sub> ) C <sub>6</sub> H <sub>5</sub> MgBr C <sub>6</sub> H <sub>5</sub> Na	50-60 (Mg salt)	(209) (260) (21)
<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> MgBr <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Li	20 68	(287) (287)
<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	<i>m</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Li	54	(287)
<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	<i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> MgBr <i>o</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> Li	50-60 (Mg salt) 56	(260) (287)
<i>p</i> -( <i>n</i> -C <sub>12</sub> H <sub>25</sub> )C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	ArLi	63	(287)
<i>m</i> -( <i>n</i> -C <sub>12</sub> H <sub>25</sub> )C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	ArLi	44	(287)
<i>o</i> -( <i>n</i> -C <sub>12</sub> H <sub>25</sub> )C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	ArLi		(287)
		50-60 (Mg salt)	(260)
(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CSO <sub>2</sub> H	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CNa	Quantitative	(265)
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHSO <sub>2</sub> H	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> C=CHMgBr	33	(233)



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



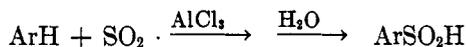
Another side reaction that may be encountered is disproportionation, e.g.,

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 aro-

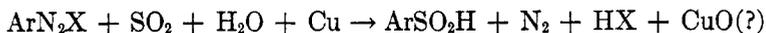


matic hydrocarbon, aluminum chloride, and some hydrogen chloride. An excess of the aromatic compound which is being sulfinated or of carbon disulfide is frequently employed as solvent. Although aluminum chloride is the catalyst most frequently employed, the patent literature also reports the use of boron halides for this purpose (148).

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*-aminobenzenesulfonylides (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).



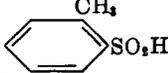
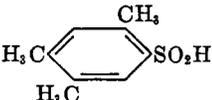
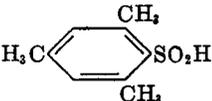
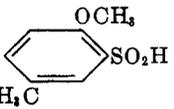
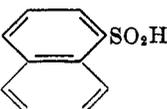
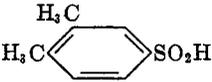
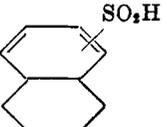
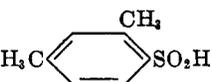
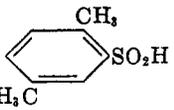
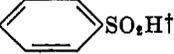
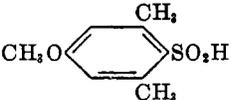
There is evidence that reduction in this process is effected by the copper powder and not by the sulfurous acid employed (97). For best results it is essential to wash the copper first with alcohol and then with ether to remove traces of grease (120). Furthermore, the diazonium sulfate is preferred to 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 sulfonation processes\*

SULFINIC ACID	YIELD	REFERENCES	SULFINIC ACID	YIELD	REFERENCES
$C_6H_5SO_2H$	<i>per cent</i>	(1, 53, 80, 124)		80.5	(160)
	80	(160)	$(CH_3)_2CH$		
	27.4	(273)			
$p-CH_3C_6H_4SO_2H$	94.0	(160)			
	23.6	(273)			
$p-FC_6H_4SO_2H$	75	(119)		71.9	(160)
$p-ClC_6H_4SO_2H$	38.3	(160)			
$p-BrC_6H_4SO_2H$	57.0	(160)			
$p-IC_6H_4SO_2H$	45.6	(161)		65.4	(160)
$p-CH_3OC_6H_4SO_2H$	15.7	(160)			
	<i>ca.</i> 50	(127)		63.4	(160)
	10-13	(273)			
	94.0	(160)			(34)
	81.4	(160)			
	78.2	(160)			
	37.5	(125)	$(CH_3)_2N$ 		(201)
	23.8	(273)	$(C_2H_5)_2N$ 		(201)
			$(C_6H_5)_2C=CHSO_2H$ †	17	(233)

\* 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

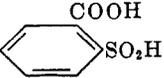
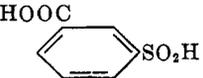
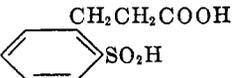
SULFINIC ACID	YIELD	REFERENCES
$C_6H_5SO_2H$	<i>per cent</i> 90 Quantitative	(97) (279) (98, 99, 100, 175)
<i>o</i> - $CH_3C_6H_4SO_2H$	90	(97, 279) (98, 100)
<i>m</i> - $CH_3C_6H_4SO_2H$		(280, 281)
<i>p</i> - $CH_3C_6H_4SO_2H$	80 78	(97) (175) (279)
<i>o</i> - $ClC_6H_4SO_2H$		(118)
<i>m</i> - $ClC_6H_4SO_2H$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

TABLE 4—Continued

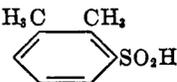
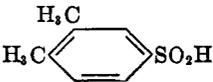
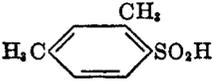
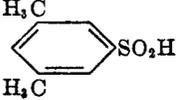
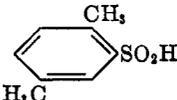
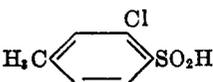
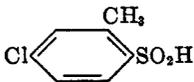
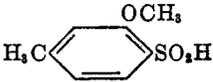
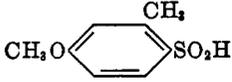
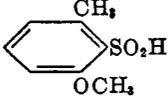
SULFINIC ACID	YIELD	REFERENCES
$o$ -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	<i>per cent</i>	(157)
$p$ -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H	50	(44) (39, 157)
		(205)
		(97, 205)
	71	(97)
		(205)
	Quantitative	(97)
		(268)
		(268)
		(120)
	81	(120)
		(120)

TABLE 4—Continued

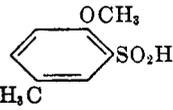
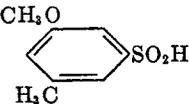
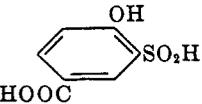
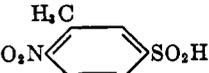
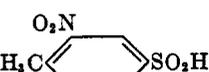
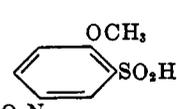
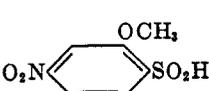
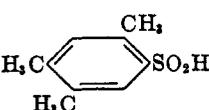
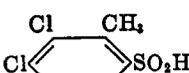
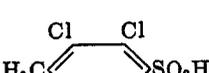
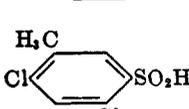
SULFINIC ACID	YIELD	REFERENCES
	<i>per cent</i> 71	(97)
		(120)
		(275)
		(51)
		(51)
	4	(140)
	2	(140)
	57	(97)
		(268)
		(268)
		(268)

TABLE 4—Continued

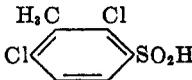
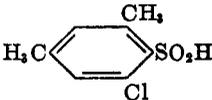
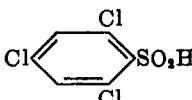
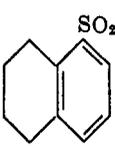
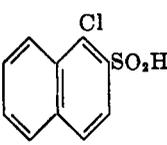
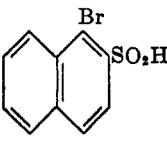
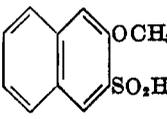
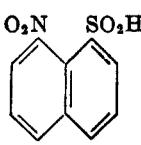
SULFINIC ACID	YIELD	REFERENCES
	<i>per cent</i>	(268)
		(268)
		(268)
	41	(204)
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<p>2-C<sub>10</sub>H<sub>7</sub>SO<sub>2</sub>H</p>	Quantitative (?)	(279) (97)
		(291)
	60	(52)
	97-100	(141)
	35	(308)

TABLE 4—Continued

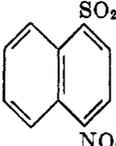
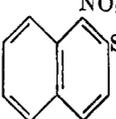
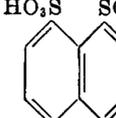
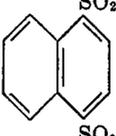
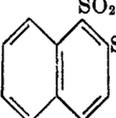
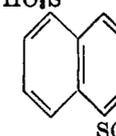
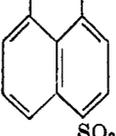
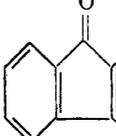
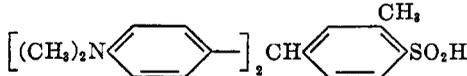
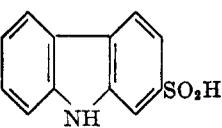
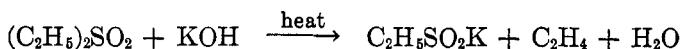
SULFINIC ACID	YIELD	REFERENCES
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 <p>NO<sub>2</sub> SO<sub>2</sub>H</p>		(291)
 <p>HO,S SO<sub>2</sub>H</p>		(246)
 <p>SO<sub>2</sub>H SO<sub>2</sub>H</p>		(97)
 <p>SO<sub>2</sub>H SO<sub>2</sub>H</p>		(97)
 <p>HO,S SO<sub>2</sub>H SO<sub>2</sub>H</p>		(97)
 <p>SO<sub>2</sub>H</p>		(25)
 <p>O SO<sub>2</sub>H</p>	67	(158)

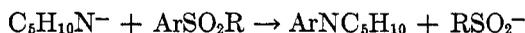
TABLE 4—*Concluded*

SULFINIC ACID	YIELD	REFERENCES
	<i>per cent</i>	
		(98)
		(146)



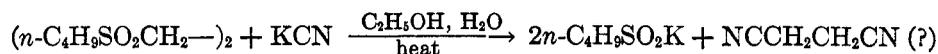
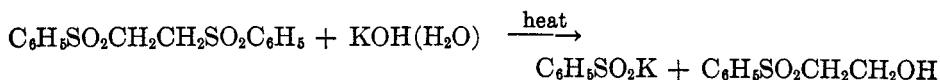
As long as one of the alkyl groups contains less than four carbon atoms, decomposition occurs readily under these conditions. For alkyl sulfones of higher molecular weight, sodium ethoxide is the preferred reagent (73). A large number of symmetrical and unsymmetrical sulfones have been cleaved with sodium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



However, dibenzyl sulfone was not affected.

$\gamma$ -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).

#### 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	
CH <sub>3</sub> SO <sub>2</sub> H	CH <sub>3</sub> SO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	KOH	<i>per cent</i>	(150)	
	CH <sub>3</sub> SO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> - <i>p</i>	C <sub>6</sub> H <sub>10</sub> NH (NaNH <sub>2</sub> )		(33)	
C <sub>2</sub> H <sub>5</sub> SO <sub>2</sub> H	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	KOH (wet)	60	(71)	
		NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	62	(73)	
<i>n</i> -C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> H	<i>n</i> -C <sub>3</sub> H <sub>7</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ( <i>n</i> -C <sub>2</sub> H <sub>7</sub> ) <sub>2</sub> SO <sub>2</sub>	KOH (wet)	69	(72)	
		KOH (wet)	41	(72)	
		NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	60	(73)	
(CH <sub>3</sub> ) <sub>2</sub> CHSO <sub>2</sub> H	( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SO <sub>2</sub>	KOH (wet)	72	(72)	
<i>n</i> -C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> H	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO <sub>2</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> SO <sub>2</sub> CH <sub>2</sub> -) <sub>2</sub>	NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	62	(73)	
		KCN (H <sub>2</sub> O, alcohol)	72	(309)	
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> SO <sub>2</sub> H	( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO <sub>2</sub>	NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	54	(73)	
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ( <i>i</i> -C <sub>5</sub> H <sub>11</sub> ) <sub>2</sub> SO <sub>2</sub>	KOH (wet)		(72)	
		NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	65	(73)	
<i>n</i> -C <sub>8</sub> H <sub>17</sub> SO <sub>2</sub> H	<i>n</i> -C <sub>8</sub> H <sub>17</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ( <i>n</i> -C <sub>8</sub> H <sub>17</sub> ) <sub>2</sub> SO <sub>2</sub>	KOH (wet)	70	(71)	
		NaOC <sub>2</sub> H <sub>5</sub> (alcohol)	62	(73)	
<i>n</i> -C <sub>12</sub> H <sub>25</sub> SO <sub>2</sub> H	( <i>n</i> -C <sub>12</sub> H <sub>25</sub> SO <sub>2</sub> CH <sub>2</sub> -) <sub>2</sub>	NaCN	80	(198)	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -COOH (C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CO	NaOH (H <sub>2</sub> O)		(136)	
		KOH (alcohol)		(88)	
C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SO <sub>2</sub> H	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> )SO <sub>2</sub> CH <sub>2</sub> -CH <sub>2</sub> COOH	NaOH (H <sub>2</sub> O)		(137)	
C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> H	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>10</sub> NH (NaNH <sub>2</sub> )	Good	(33)	
		Na (xylene)		(172)	
		NaHg <sub>2</sub> , alcohol		(222)	
		NaHg <sub>2</sub> , H <sub>2</sub> O		(222)	
		NaHg <sub>2</sub> , H <sub>2</sub> O		(219)	
		NaHg <sub>2</sub> , alcohol		(227)	
		NaOC <sub>2</sub> H <sub>5</sub> , alcohol		72	(73)
		<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ONa		(183)	
		C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>		(69)	
		NaOH (H <sub>2</sub> O)		(121)	
		NaHg <sub>2</sub> , H <sub>2</sub> O		(217, 222)	
KOH (H <sub>2</sub> O)	80	(217, 218)			

TABLE 5—Continued

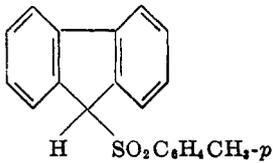
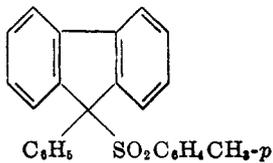
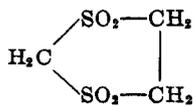
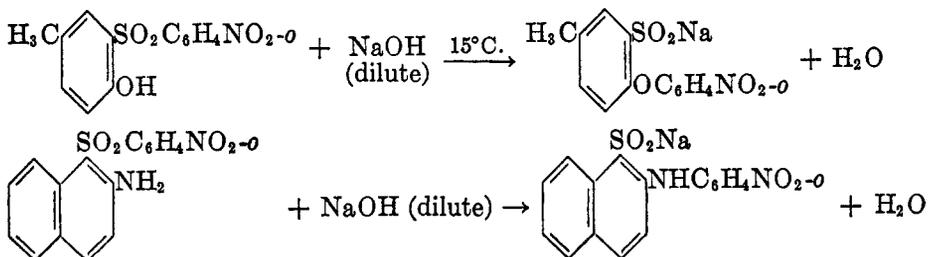
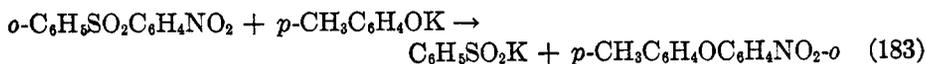
SULFINIC ACID	SULFONE	REAGENT	YIELD	REFERENCES
$C_6H_5SO_2H$ —Contd.	$C_6H_5SO_2CH_2CH(CH_3)-SO_2C_6H_5$ $m-(C_6H_5SO_2)_2C_6H_4$	KOH (H <sub>2</sub> O) NH <sub>3</sub> KHS KCN C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> KOH (H <sub>2</sub> O)	per cent 80	(213, 222) (213, 222) (218) (218, 222) (222) (276)
		KOH		(229)
$p-CH_3C_6H_4SO_2H$	$p-CH_3C_6H_4SO_2CH_3$	KOH	18	(150)
		KOH	20	(150)
$p-CH_3C_6H_4SO_2H$		KOH	64	(150)
	$(p-CH_3C_6H_4SO_2CH_2-)_2$	KOH (H <sub>2</sub> O) NaHg <sub>2</sub> , H <sub>2</sub> O		(218) (222)
	$(p-CH_3C_6H_4SO_2CH=)_2$	C <sub>6</sub> H <sub>5</sub> NHNH <sub>2</sub> (alcohol)		(89, 92)
$p-ClC_6H_4SO_2H$	$p-ClC_6H_4SO_2CH_2CH-(NH_2)COOH$	KOH (H <sub>2</sub> O)		(170)
	$p-ClC_6H_4SO_2CH_2CH-(NHCOCH_3)COOH$	KOH (H <sub>2</sub> O)		(170)
$o-O_2NC_6H_4SO_2H$	$o-O_2NC_6H_4SO_2(CH_2)_2CONHC_6H_5$	NaOH		(70)
$CH_2(COOH)SO_2H$	$(-CH_2SO_2CH_2COONa)_2$	NaOH (H <sub>2</sub> O)	90	(255)
	$(HOOC)CH_2SO_2CH-(CH_3)CH_2SO_2CH_2COOH$	NaOH	90	(256)
$HOCH_2CH_2SO_2CH_2SO_2H$		Ba(OH) <sub>2</sub> , H <sub>2</sub> O		(13)

TABLE 5—Concluded

SULFINIC ACID	SULFONE	REAGENT	YIELD	REFERENCES
HOCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> CH <sub>2</sub> - CH <sub>2</sub> SO <sub>2</sub> H		Ba(OH) <sub>2</sub> , H <sub>2</sub> O	<i>per cent</i>	(13, 294)
CH <sub>3</sub> SO <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )- SO <sub>2</sub> H		NaOH		(145)
		KOH (alcohol)		(82)
HO <sub>2</sub> SCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H + HOCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H		Ba(OH) <sub>2</sub> , H <sub>2</sub> O		(13)
(-SCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H) <sub>2</sub> + HOC <sub>2</sub> H <sub>4</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> - SO <sub>2</sub> H		Ba(OH) <sub>2</sub> , H <sub>2</sub> O		(251)
C <sub>2</sub> H <sub>4</sub> (OH)SO <sub>2</sub> H + HOC <sub>2</sub> H <sub>4</sub> SO <sub>2</sub> C <sub>2</sub> H <sub>4</sub> - SO <sub>2</sub> H		Ba(OH) <sub>2</sub> , H <sub>2</sub> O		(251)

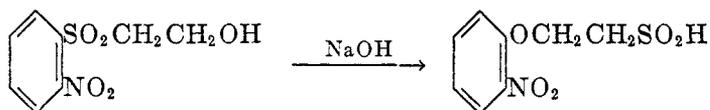


This is apparently a special case of the basic cleavage of sulfones. The relationship becomes more evident when one compares the above reactions with the following ones:

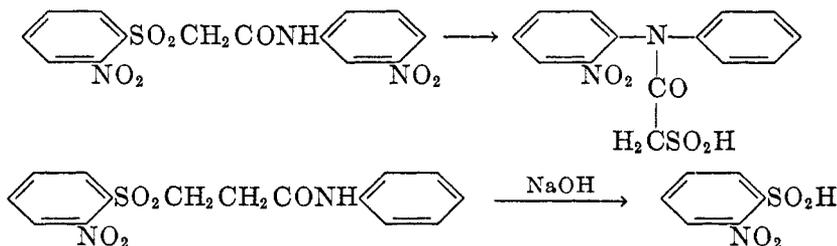


The reaction temperature varies from 15° to 150°C. (approx.), depending on the substituents present and the positions which they occupy. Higher temperatures than those indicated are undesirable, since sulfinic acids tend to lose sulfur dioxide in hot alkali. In general, an *o*- or *p*-nitro or sulfonyl 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.

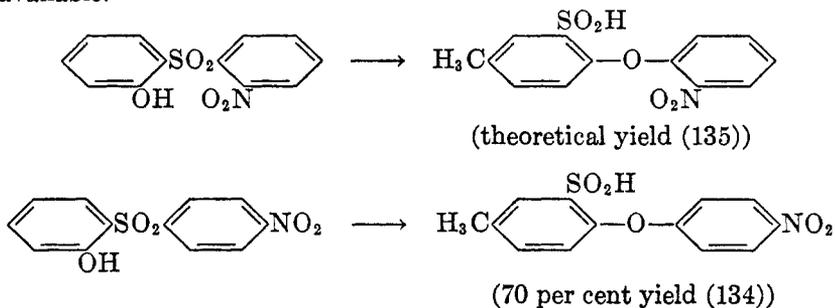
With the hydroxyl group in an aliphatic side chain, rearrangement occurs very rapidly (156).



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.



#### 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

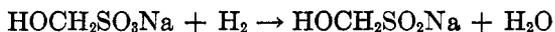


TABLE 6  
Rearrangement of certain *o*-substituted aromatic sulfones and related types

SULFONIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
$o$ -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> OCH <sub>2</sub> CH <sub>2</sub> SO <sub>2</sub> H	$o$ -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	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)

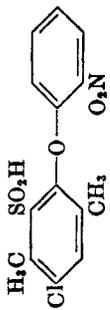
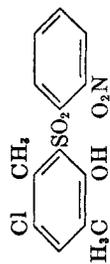
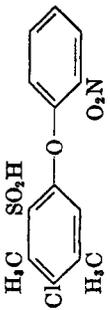
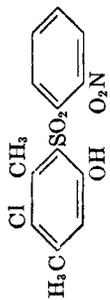
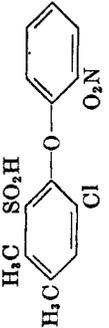
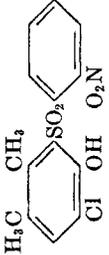
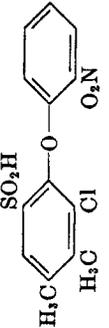
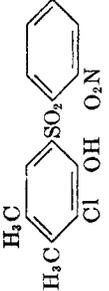
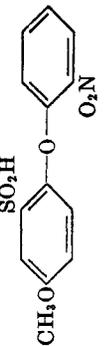
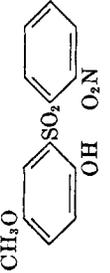
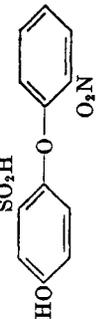
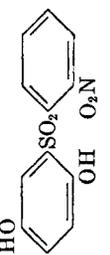
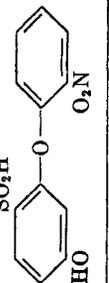
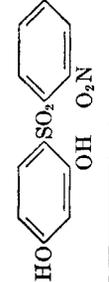
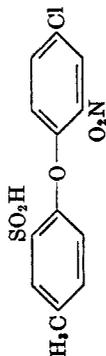
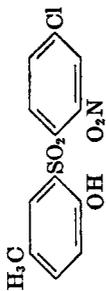
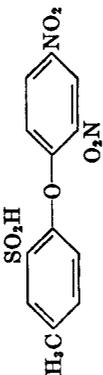
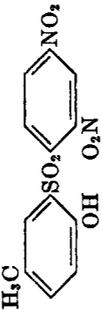
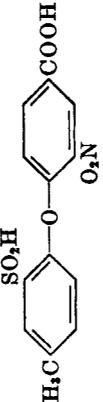
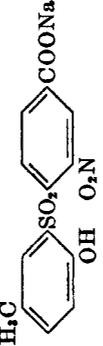
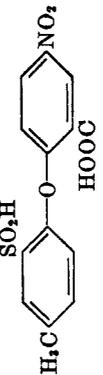
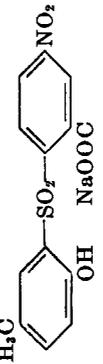
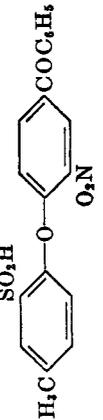
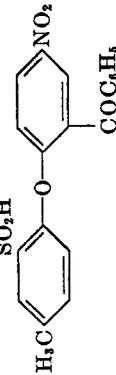
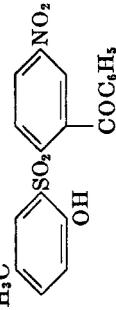
		(196)
		(196)
		(196)
		(196)
		(156)
		(156)
		(156)

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)

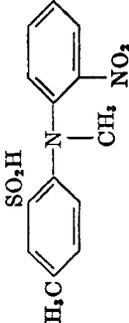
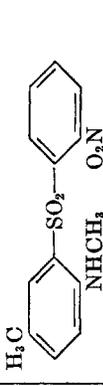
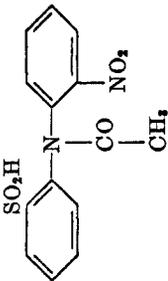
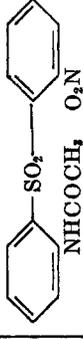
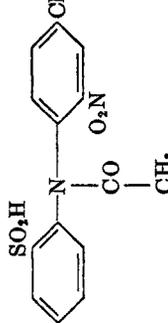
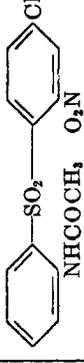
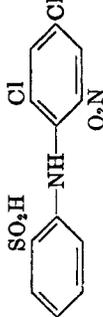
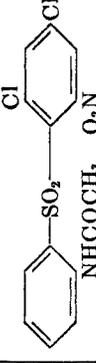
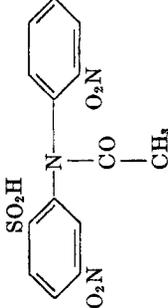
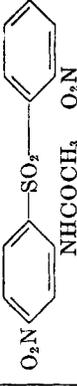
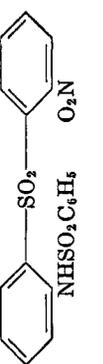
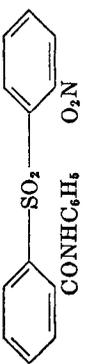
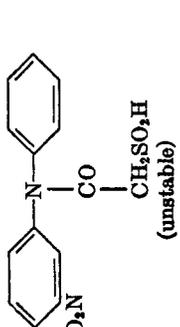
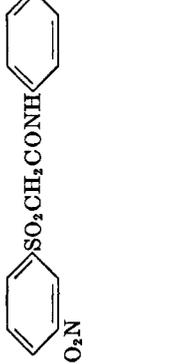
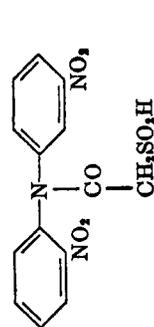
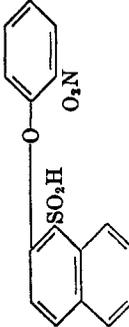
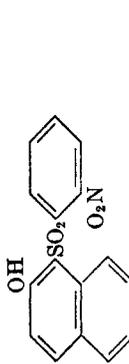
 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), an acetyl group (CO-CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>). The label H<sub>3</sub>C is placed to the left of the structure.</p>	<p>50 per cent aqueous KOH; 70°C.</p>	<p>(298)</p>
 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), an acetyl group (CO-CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	<p>0.5 N NaOH</p>	<p>(69)</p>
 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), an acetyl group (CO-CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	<p>1 N NaOH; boil</p>	<p>(69)</p>
 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), an acetyl group (CO-CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	<p>Dilute aqueous NaOH</p>	<p>(69)</p>
 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), an acetyl group (CO-CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>H-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	 <p>Chemical structure: A central nitrogen atom is bonded to a methyl group (CH<sub>3</sub>), a 4-sulfamoylphenyl group (SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>), and a 2-nitrophenyl group (C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub>).</p>	<p>NaOH</p>	<p>(69)</p>

TABLE 6—Continued

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

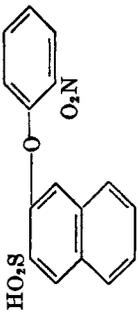
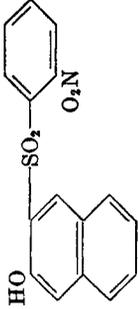
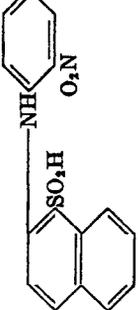
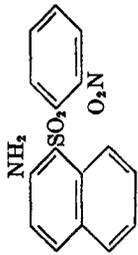
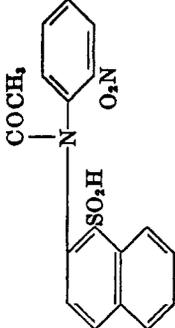
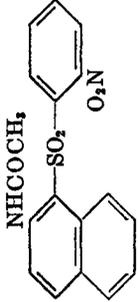
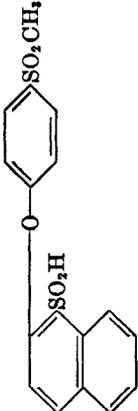
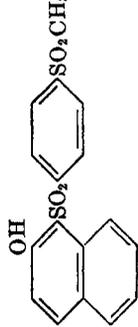
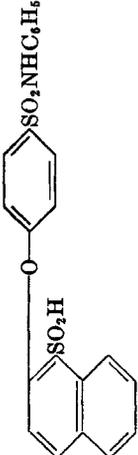
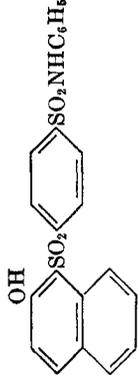
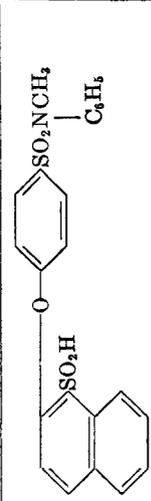
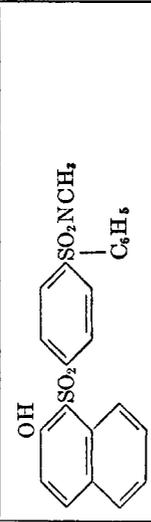
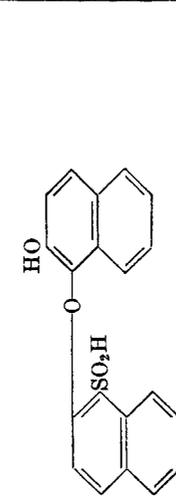
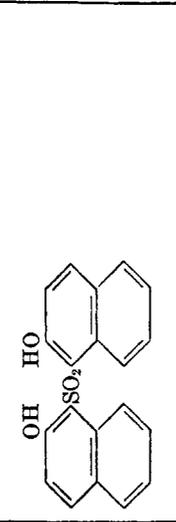
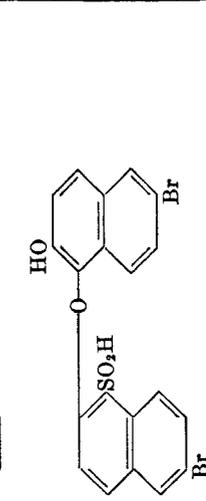
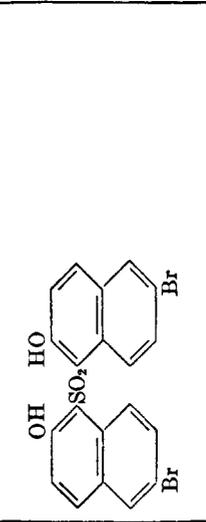
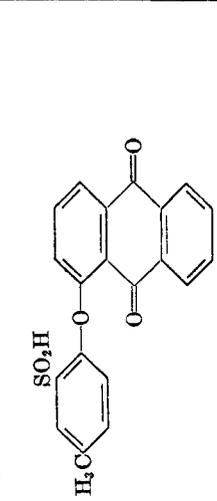
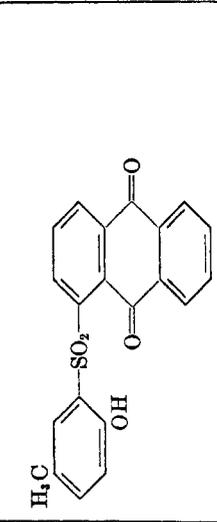
 <p>HO<sub>2</sub>S-O-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	 <p>HO-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	1 <i>N</i> NaOH; 18°C.	(181)
 <p>NH-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	 <p>NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	2 <i>N</i> NaOH; boil	(298)
 <p>COCH<sub>3</sub>-N-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	 <p>NHCOCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NO<sub>2</sub></p>	Warm 2 <i>N</i> NaOH	(298)
 <p>SO<sub>2</sub>H-O-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub></p>	 <p>OH-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub></p>	1 <i>N</i> NaOH; 150°C.	(297)
 <p>SO<sub>2</sub>H-O-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub></p>	 <p>SO<sub>2</sub>NHC<sub>6</sub>H<sub>5</sub></p>	1 <i>N</i> NaOH; 150°C.	(297)

TABLE 6—Concluded

SULFINIC ACID	SULFONE REARRANGED	REAGENT	REFERENCES
		1 N NaOH; 150°C.	(297)
		K <sub>3</sub> Fe(CN) <sub>6</sub> and Na <sub>2</sub> S; dilute base	(128) (129) (130) (295)
		NaOH; 150°C.	(296)
		2 N NaOH; 130°C.	(96)

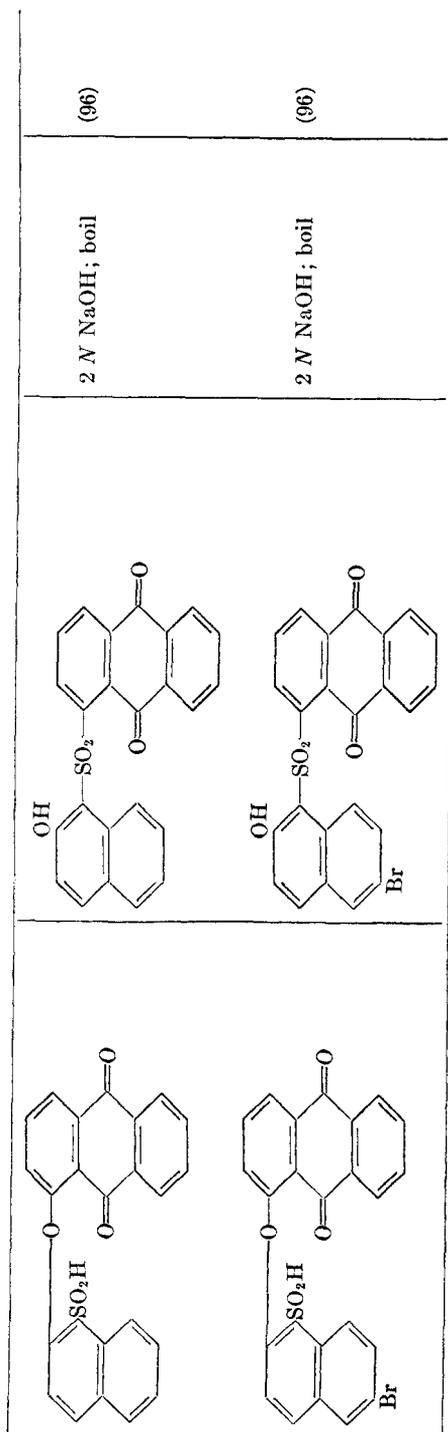
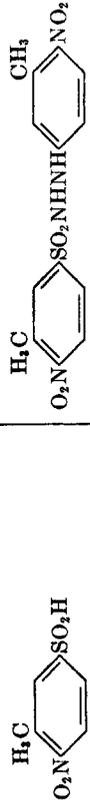
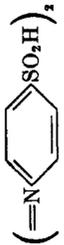


TABLE 7  
Miscellaneous methods

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
	a. Reduction of sulfonates and their derivatives			
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2SO_2NHNH_2$	$H_2O$	<i>per cent</i>	(55)
$C_6H_5SO_2H$	$C_6H_5SO_2NH_2$ $C_6H_5SO_2NHOH$ $(C_6H_5SO_2)_2NOH$ $C_6H_5SO_2NHNHC_6H_5$ $C_6H_5SO_2NHR$	$ArN_2Cl, KOH$ KOH Alkali NaOH NaOH	Quantitative	(63) (244, 259) (4, 164) (67) (77)
$p-CH_3C_6H_4SO_2H$	$p-CH_3C_6H_4SO_2C_6H_5$ $p-CH_3C_6H_4SO_2NH_2$ $p-CH_3C_6H_4SO_2NRR'$	$N_2H_4$ $ArN_2Cl, KOH$ KOH	80 Quantitative	(79) (63) (139)
	$p-NCC_6H_4SO_2NHNH_2$	$NH_2OH$	26	(3)
	$O_2N-C_6H_4-SO_2NHNH-CH_3$	$Ba(OH)_2$		(51)
$1-C_{10}H_7SO_2H$	$C_{10}H_7SO_2NHOH$ or $(C_{10}H_7SO_2)_2NOH$	Alkali		(4, 5)
	$(=N-C_6H_4-SO_2Na)_2$	NaHg <sub>s</sub>		(12)
$C_6H_4(SO_2H)_2$ ( <i>o</i> -, <i>m</i> -, and <i>p</i> -)	$C_6H_4(SO_2)_2NOH$ ( <i>o</i> -, <i>m</i> -, and <i>p</i> -)	$NH_3, H_2O$		(146, 278)

b. Oxidation procedures

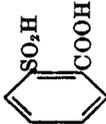
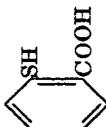
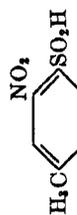
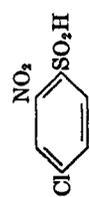
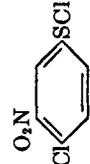
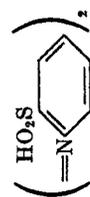
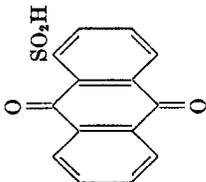
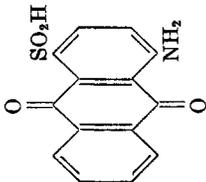
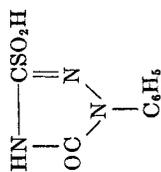
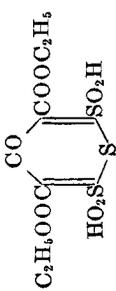
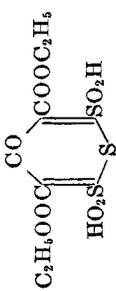
$C_2H_4SO_2H$	$C_2H_4SNa$	Dry $O_2$	(49)
$C_2H_5SO_2H + C_6H_5SO_2H$	$C_2H_5SSC_6H_5$	Alcoholic KOH (air)	(229)
$C_6H_5CH_2SO_2H$	$C_6H_5CH_2SCN$	$Cl_2$ , $0^\circ C$ .	(138, 153)
$C_6H_5SO_2H$	$C_6H_5SCN$	$Cl_2$ , $0^\circ C$ .	(153)
	$C_6H_5SCl$	NaOH	(180)
	$C_6H_5SSC_6H_5$	Alcoholic KOH (air)	(264)
$p-CH_3C_6H_4SO_2H$	$(p-CH_3C_6H_4S-)_2$	Alcoholic KOH (air)	(264)
		$Cl_2$ , $CCl_4$ ; $H_2O$	70 (247)
$p-O_2NC_6H_4SO_2H$	$(p-O_2NC_6H_4S-)_2$	Alcoholic KOH, $C_6H_5CH_2Cl$	(93)
	ArSSAr	$Cl_2$ , NaOH	(316)
		NaOH	(311)
	$o-O_2NC_6H_4SH$	$N_a$	30 (269)

TABLE 7—Continued

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
	ArSOH	Alkali, air K <sub>2</sub> Fe(CN) <sub>6</sub>	<i>per cent</i>	(84) (81)
	ArSOH	Air		(81)
	RSH	Alkaline KMnO <sub>4</sub> 30 per cent H <sub>2</sub> O <sub>2</sub>		(68) (68)
		12 per cent H <sub>2</sub> O <sub>2</sub> ; cold	89	(6)

b. Oxidation procedures—Concluded

c. Disproportionation of thiosulfonates

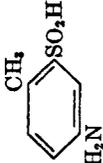
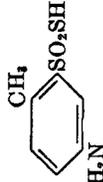
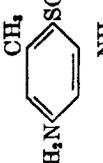
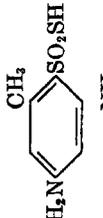
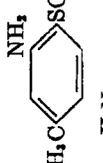
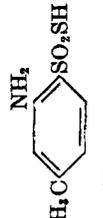
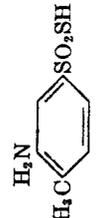
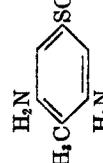
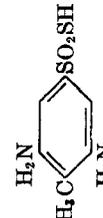
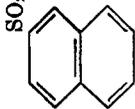
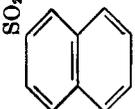
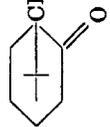
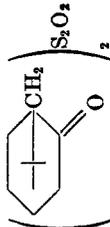
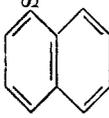
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SH}$	NaOH Na <sub>2</sub> S Na <sub>3</sub> AsO <sub>3</sub> KCN	(114, 232) (114, 232) (114, 232) (114, 232)
$m\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{H}$	$m\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{SH}$	H <sup>+</sup>	(184)
$m\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{H}$	$m\text{-H}_2\text{NC}_6\text{H}_4\text{SO}_2\text{SH}$	NaHg <sub>2</sub> , alkali	(184)
$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{SH}$	KCN HCl	(281) (281)
$p\text{-IC}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-IC}_6\text{H}_4\text{SO}_2\text{SH}$	HCl	(282)
		NaHg <sub>2</sub>	(239)
		NaHg <sub>2</sub> , alkali	(187)
		NaHg <sub>2</sub> , alkali	(180)
		NaHg <sub>2</sub>	(239)
		HCl	(241)

TABLE 7—Continued

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
		KCN		(284)
$C_2H_4SO_2H$	$(C_2H_4)_2S_2O_2$	Zn, alcohol KOH		(214) (214, 238)
$l\text{-HOOCCH(NH}_2\text{)CH}_2\text{SO}_2\text{H}$	$l\text{-[HOOCCH(NH}_2\text{)CH}_2\text{]}_2\text{S}_2\text{O}_2$	NH <sub>3</sub>		(178, 179)
		 SNa	91	(107)
$C_6H_4SO_2H$	$(C_6H_4)_2S_2O_2$	CH <sub>3</sub> MgI C <sub>6</sub> H <sub>5</sub> MgI C <sub>6</sub> H <sub>5</sub> SNa	63 70	(202) (202) (107)
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{S}_2\text{O}_2$	 SNa C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> MgCl C <sub>6</sub> H <sub>5</sub> MgCl CH <sub>3</sub> MgI	60 Quantitative 54 87	(107) (112) (112) (202)

<i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H— <i>Conid.</i>	<i>(p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>2</sub> — <i>Conid.</i>	C <sub>6</sub> H <sub>5</sub> MgI CHNa(COOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHNa(CN)COOC <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> COCHNaCOOC <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>5</sub> CHNaCN <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SNa	76 80-95 80-95 80-95 80-95 90	(202) (37) (37) (37) (37) (107)
			84	(107)
			84	(107)
			72	(107)
			90	(107)
		CH <sub>3</sub> MgI CH <sub>3</sub> MgI <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SNa	90 82 93	(202) (202) (106, 107)
		<i>(m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>2</sub>		
		<i>(p</i> -ClC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>2</sub>		
		<i>m</i> -O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H		
		<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> H		

TABLE 7—Continued

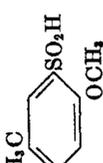
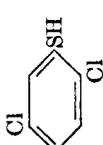
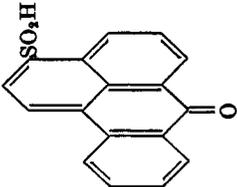
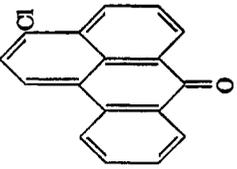
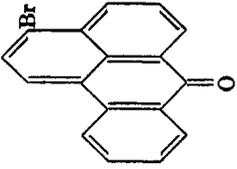
SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
	$\left( \begin{array}{c} \text{H}_3\text{C} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{OCH}_3 \end{array} \right) \text{S}_2\text{O}_2$	$\text{CH}_3\text{MgI}$	68	(202)
$\text{C}_6\text{H}_5\text{SO}_2\text{H}$	$\text{C}_6\text{H}_5\text{SO}_2\text{SC}_2\text{H}_5$	Zn, alcohol		(214)
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SC}_2\text{H}_5$	KOH Ba(OH) <sub>2</sub> Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> KCN K <sub>2</sub> S, alcohol C <sub>2</sub> H <sub>5</sub> SH		(214, 228) (228) (116) (116) (116) (214)
$o\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{NO}_2$	$o\text{-O}_2\text{NC}_6\text{H}_4\text{SH}$	ca. 80	(202)
	$o\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{S} \begin{array}{c} \text{Cl} \\   \\ \text{C}_6\text{H}_4 \\   \\ \text{Cl} \end{array}$	$o\text{-O}_2\text{NC}_6\text{H}_4\text{SH}$	ca. 80	(202)
$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{H}$	$p\text{-ClC}_6\text{H}_4\text{SO}_2\text{SC}_6\text{H}_4\text{NO}_2$		ca. 80	(202)
		$\text{CH}_3\text{COCHN}_a\text{COCH}_3$ $o\text{-O}_2\text{NC}_6\text{H}_4\text{SH}$	89 ca. 80	(37) (202)



TABLE 7—Continued

SULFONIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
d. Nucleophilic displacements—Continued				
		$\text{Na}_2\text{S}_2\text{O}_4, \text{NH}_3$	per cent	(149)
		$\text{Na}_2\text{S}_2\text{O}_4, \text{NH}_3$ $\text{HOCH}_2\text{SO}_2\text{Na}$		(149) (149)
e. Miscellaneous methods				
$\text{C}_2\text{H}_4\text{SO}_3\text{H}$	$\text{C}_2\text{H}_4\text{S}_2\text{O}_4\text{Na}$	$\text{NaOH}$		(62)
$\text{C}_6\text{H}_5\text{CH}_2\text{SO}_3\text{H}$	$\text{C}_6\text{H}_5\text{CH}_2\text{S}_2\text{O}_4\text{Na}$	$\text{NaOH}$		(62)
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	$p\text{-CH}_3\text{C}_6\text{H}_4\text{S}_2\text{O}_4\text{Na}$	$\text{NaOH}$		(62)

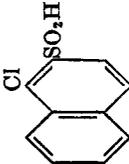
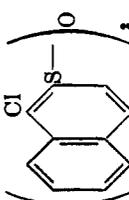
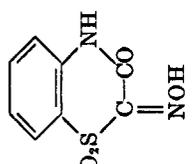
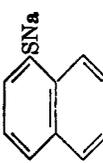
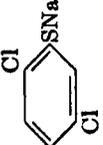
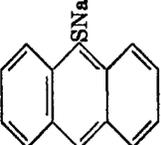
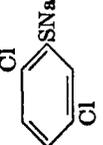
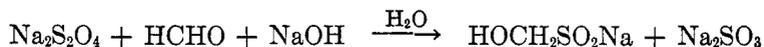
$\begin{array}{c} \text{HN}-\text{C}_6\text{H}_4\text{SO}_2\text{SH}-m \\   \\ \text{HN}-\text{C}_6\text{H}_4\text{SO}_2\text{H}-m \end{array}$	$\begin{array}{c} \text{HN}-\text{C}_6\text{H}_4\text{SO}_2\text{S} \\   \\ \text{HN}-\text{C}_6\text{H}_4\text{SO}_2\text{S} \\ \text{Ba} \end{array}$	HgO	(185)
$\begin{array}{c} \text{NC}_6\text{H}_4\text{SO}_2\text{H}-m \\    \\ \text{NC}_6\text{H}_4\text{SO}_2\text{H}-m \end{array}$	$\begin{array}{c} \text{NC}_6\text{H}_4\text{SO}_2\text{SH} \\    \\ \text{NC}_6\text{H}_4\text{SO}_2\text{H} \end{array}$	NaHg <sub>2</sub> , alkali	(12, 185)
		NaOH	(313)
$p\text{-BrC}_6\text{H}_4\text{CHSCH}_2\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$[p\text{-BrC}_6\text{H}_4\text{CH}_2\text{SSO}_3]^-$	KOH	(274)
$\text{NHCOCOOH}$ 	$[\text{C}_6\text{H}_4\text{CH}_2\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)_2]^+$	HCl, CH <sub>3</sub> COOH	(48a)
$\text{C}_6\text{H}_4\text{SO}_2\text{H}$		$\text{C}_6\text{H}_5\text{SNa}$ , alcohol $(\text{C}_6\text{H}_5\text{S})_2\text{Pb}$	(106) (236, 237)
	$(\text{C}_6\text{H}_5)_2\text{S}_2\text{O}_4$		(106)
		KOH	(228)
		Ba(OH) <sub>2</sub>	(228)
		H <sub>2</sub> S, alcohol	(230)
		C <sub>6</sub> H <sub>5</sub> SH	(236, 237)

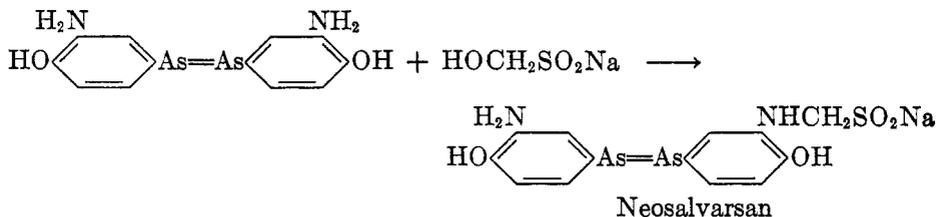
TABLE 7—Concluded

SULFINIC ACID	STARTING COMPOUND	REAGENT	YIELD	REFERENCES
e. Miscellaneous methods—Concluded				
$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{H}$	$(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{S}_2\text{O}_4$	Zn, alcohol KOH, sealed tube $\text{Na}_2\text{CO}_3$ $p\text{-CH}_3\text{C}_6\text{H}_4\text{SNa}$ , alcohol	93	(236) (228) (85) (106)
		 $\text{H}_2\text{C}$	84	(106)
$m\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{H}$ $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{H}$	$(m\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_2\text{O}_4$ $(p\text{-O}_2\text{NC}_6\text{H}_4)_2\text{S}_2\text{O}_4$		84	(106)
			72	(106)
		Alkali, alcohol 	90	(315) (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).



Sodium formaldehyde sulfoxylate is an important industrial reducing agent in vat dyeing. It is also used to introduce the  $\text{CH}_2\text{SO}_2\text{Na}$  group upon nitrogen (254, 301), as in the following example:



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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