THE CHEMISTRY OF SULTONES AND SULTAMS

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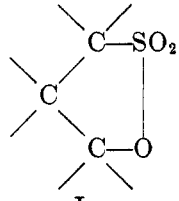
CONTENTS

I. Introduction

Sultones are the cyclic esters derived from hydroxysulfonic acids and are analogous to the lactones of hydroxycarboxylic acids. Most of the sultones have five- or six-membered rings (I, II), which may be saturated or unsaturated.

Similarly, the sultams (III) are analogous to the γ-, δ-, and ε-lactams. No β-sultones or β-sultams have as yet been synthesized.



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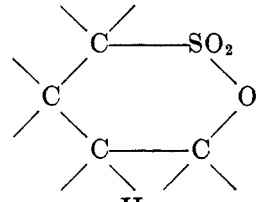

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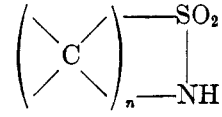
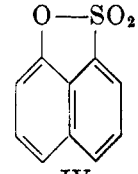


III

The first sultone prepared was 1,8-naphthosultone (IV); this compound was analyzed in 1887 by Schultz (64), who credited C. Mensching with having discovered it. The compound was studied by Erdmann (18), who confirmed the structure and coined the term "sultone."



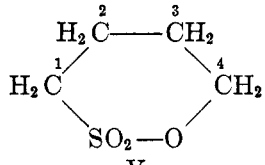
IV

1,8-Naphthosultone

Since the sultones are relatively more reactive than the sultams, they serve as useful materials for the synthesis of detergents (34), dyestuff intermediates (58), and furan derivatives (48).

II. Nomenclature

The nomenclature of sultones and sultams as used in *Chemical Abstracts* (13) may be illustrated by 4-hydroxy-1-butanesulfonic acid sultone (V) (56), α-hydroxy-*o*-toluenesulfonic acid sultone (VI), α-amino-*o*-toluenesulfonic acid sultam (VII), and 1-aminonaphthalene-8-sulfonic acid sultam (IX).



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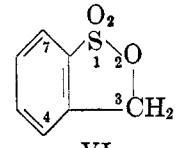

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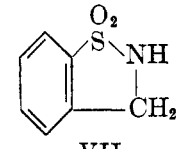

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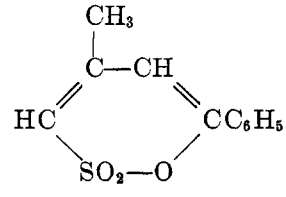
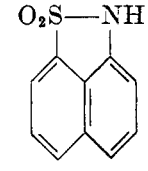


VIII



IX

The name "δ-sultone" is derived from that of the corresponding δ-hydroxysulfonic acid in which the sulfonic acid group is present in the δ-position (47). Therefore, substance VIII is called the sultone of 4-hydroxy-2-methyl-4-phenyl-1,3-butadiene-1-sulfonic acid.

III. Methods of Preparation

A. PREPARATION OF SULTONES

The general method for the preparation of sultones consists in the elimination of the elements of water from the corresponding hydroxysulfonic acid, either by the action of heat (1, 32, 33, 65) or of a mixture of concentrated sulfuric acid and acetic anhydride (46, 47) or by boiling the diazotized solution of an *o*- or peri-aminoarylsulfonic acid (18, 45).

1. Sultones derived from aliphatic sulfonic acids

(a) From aliphatic sulfonic acids prepared from alkyl halides

This method consists in irradiation of the appropriate alkyl halide, usually the chloride, in an atmosphere of sulfur dioxide and chlorine (1, 32, 33). The sulfonyl chloride function of the resulting chlorosulfonyl chloride is hydrolyzed and the reaction mixture heated to 200°C. to give the sultone. The products consist of isomeric dichloroalkanes and a mixture of γ- and δ-sultones. 1-Chloropropane gives the γ-sultone (X) (1, 33) and a mixture of isomeric dichloropropanes

$$CH_2ClCH_2CH_3 + SO_2 + HCl \rightarrow CH_2ClCH_2CH_2SO_3Cl \xrightarrow{H_2O}$$

$$CH_2ClCH_2CH_2SO_3H \xrightarrow[\text{heat}]{-HCl} \underset{\text{X}}{\overset{CH_2CH_2CH_2}{\underset{SO_2\text{——}O}{|\quad|\quad|}}}$$

while 1-chlorobutane gives a mixture of γ- and δ-butanesultones (XI and XIIa) in addition to a mixture of dichlorobutanes. The higher chloroalkanes react similarly (33).

$$\underset{\text{XI}}{\overset{CH_3CHCH_2CH_2}{\underset{SO_2\text{—}O}{|\quad|\quad|}}} \qquad \underset{\text{XIIa}}{\overset{CH_2CH_2CH_2CH_2}{\underset{SO_2\text{————}O}{|\quad|\quad|\quad|}}}$$

(b) From aliphatic sulfonic acids prepared from olefins

Baldeschweiler and Cassar (4b) described an octanesultone which was formed as a byproduct in the olefin–sulfuric acid process for producing secondary and tertiary alcohols. Its properties suggested that it might be the γ-sultone (XIIb), although a bimolecular structure was not completely excluded.

$$\underset{\text{XIIb}}{\overset{CH_2CH_2}{\underset{O\text{—}SO_2}{CH_3(CH_2)_4CH\quad|}}}$$

The sodium and potassium salts of 3-hydroxy-1-octanesulfonic acid were prepared by Shriner, Rendleman, and Berger (64b) as follows:

$$CH_3(CH_2)_4MgBr + CH_2ClCH_2CHO \rightarrow CH_3(CH_2)_4CHOHCH_2CH_2Cl$$

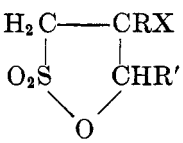
$$\downarrow KI$$

$$CH_3(CH_2)_4CHOHCH_2CH_2SO_3K \xrightarrow{K_2SO_3} CH_3(CH_2)_4CHOHCH_2CH_2I$$

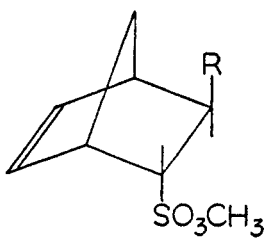
but attempts to cyclize this salt to a γ-octanesultone failed.

Alkenesulfonic acids are readily formed by the addition of the olefin to an equimolecular quantity of dioxane sulfotrioxide in ethylene chloride at 0°C., followed by hydrolysis (9, 10). The reaction of the corresponding alkenesulfonic acid (or its adduct with cyclopentadiene) with bromine water gave the corresponding sultone. Thus, 2-bromo-2-methyl-3-phenyl-1,3-propanesultone (XIIIa: R = CH_3, R′ = C_6H_5, X = Br) is obtained from barium 2-methyl-3-phenyl-2-propene-1-sulfonate (9), and 2-aryl-6-bromo[2,2-1]bicycloheptane-3,5-sultones (XVa) are obtained from the adducts prepared from the methyl esters (XIVa) of 2-arylethene-1-sulfonic acids and cyclopentadiene (57).

$$R'CH_2CR{=}CH_2 \xrightarrow[\text{then } H_2O \text{ and } BaCO_3]{OC_4H_8OSO_3} (R'CH{=}CRCH_2SO_3)_2Ba \xrightarrow[\text{water}]{\text{bromine}}$$

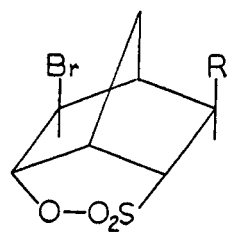


XIIIa



XIVa

R = C_6H_5 or $C_6H_4NO_2$-*p*



XVa

R = C_6H_5 or $C_6H_4NO_2$-*p*

(c) From aliphatic sulfonic acids prepared from α,β-unsaturated aldehydes

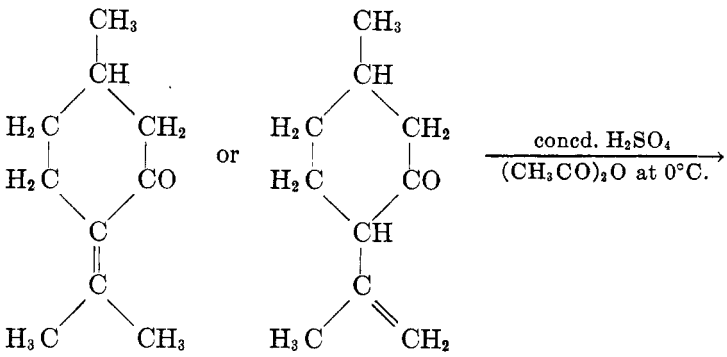
The treatment of α,β-unsaturated aldehydes with sodium bisulfite, followed by reduction with Raney nickel, hydrolysis of the sodium salt, and heating, gives the corresponding sultone (65). Only two sultones—namely, γ-propanesultone (XIIIa: R = R′ = X = H) and β-methyl-γ-propanesultone (XIIIa: R = CH_3, R′ = X = H)—have been prepared by this method.

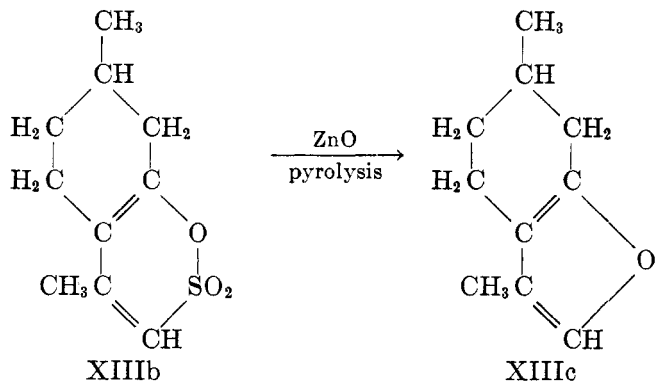
$$CH_2{=}CRCHO \xrightarrow{NaHSO_3} \underset{\displaystyle SO_3Na}{\overset{\displaystyle CH_2CHRCHO}{|}} \xrightarrow{H_2,\ Ni}$$

$$\underset{\displaystyle SO_3Na}{\overset{\displaystyle CH_2CHRCH_2OH}{|}} \xrightarrow[(2)\ \text{heat}\ (-H_2O)]{(1)\ HCl} \text{XIIIa}$$

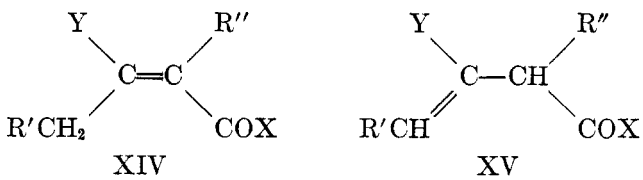
(d) From aliphatic acids prepared from α,β- and β,γ-unsaturated ketones

Interest in the synthesis of sultones from α,β- and β,γ-unsaturated ketones was stimulated by the work of Treibs (67), who described the following reactions with pulegone and isopulegone:

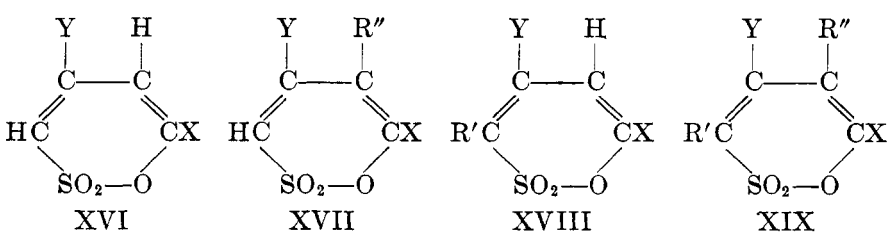




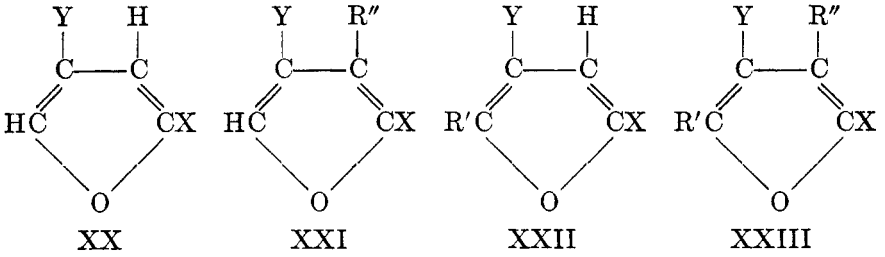
Morel and Verkade (46, 47) obtained δ-sultones by the treatment of α,β- and β,γ-unsaturated ketones having a branching of the carbon skeleton in the β-position (XIV and XV, in which R′, R″, X, and Y represent hydrocarbon residues)



with a mixture of concentrated sulfuric acid and acetic anhydride in the molecular ratio of 1:2 at 0°C. The δ-sultones obtained, with two conjugated double bonds in the hetero-ring, are of the types shown in formulas XVI to XIX (see also table 1).



On pyrolysis these δ-sultones yield sulfur dioxide and furan derivatives of the types shown in formulas XX to XXIII (48) (see also table 1).

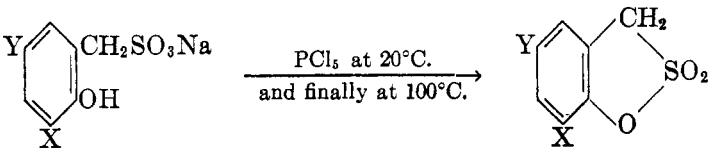


XX XXI XXII XXIII

2. Sultones derived from aromatic sulfonic acids

(a) From 2-hydroxybenzylsulfonic acid

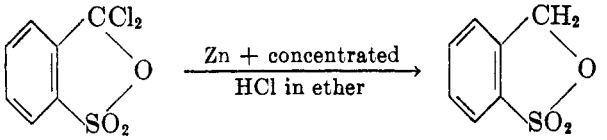
The sultone of 2-hydroxybenzylsulfonic acid, "benzylsultone" (XXIVa), is obtained by heating a diazotized solution of 2-aminobenzylsulfonic acid with dilute sulfuric acid on the water bath (45). XXIVa and its derivatives (XXIVb–XXIVc) may also be prepared by the action of phosphorus pentachloride on the sodium salt of 2-hydroxybenzylsulfonic acid or its derivatives (63).



XXIVa: X = Y = H
XXIVb: X = CH_3, Y = H
XXIVc: X = Y = CH_3

(b) From benzylalcohol-*o*-sulfonic acid

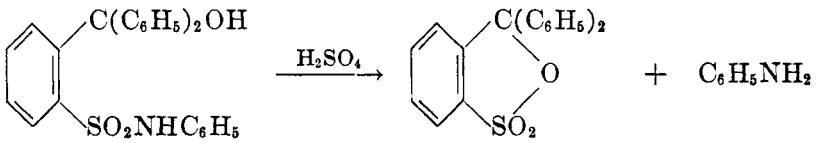
The reduction of the stable chloride (XXV) (m.p. 79°C.) which is obtained by the action of phosphorus pentachloride upon salts of *o*-sulfobenzoic acid leads to the formation of the sultone of benzylalcohol-*o*-sulfonic acid or "tolylsultone" (XXVI) (43).



XXV XXVI
"Tolylsultone"

XXVI can also be obtained by boiling the sodium salt of benzaldehyde-2-sulfonic acid with dimethyl sulfate (31).

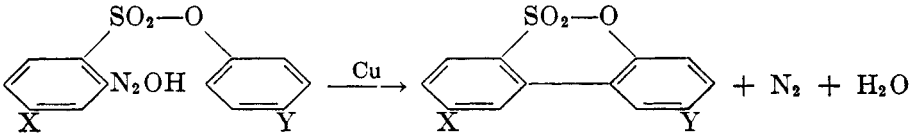
Recently, Mustafa and coworkers (52) obtained XXVIII together with aniline by the action of concentrated sulfuric acid on (N-phenyl-*o*-sulfamyl)-triphenylcarbinol (XXVII). List and Stein (43) prepared XXVIII by the action of XXV upon benzene in the presence of aluminum chloride.



XXVII XXVIII

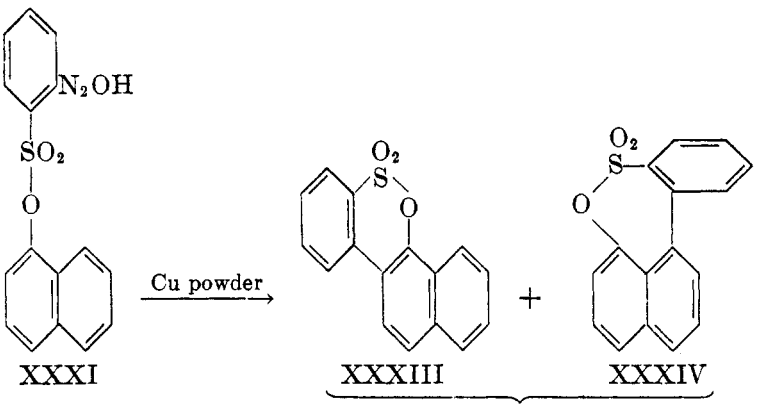
(c) From 2′-hydroxy-2-biphenylsulfonic acid and its derivatives

The sultones illustrated by formula XXX (table 2) are obtained by treatment of the diazotized solutions of aryl esters of *o*-aminoarylsulfonic acids (XXIX) with sodium acetate, followed by copper powder (60).



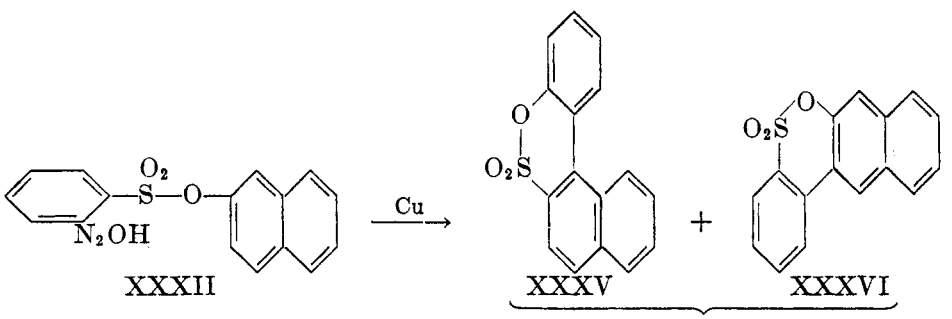
XXIX XXX

XXX (X = Y = H) has also been prepared by the action of 70 per cent sulfuric acid on *o*-phenylphenol, probably via sulfonation and subsequent elimination of water from the intermediate hydroxybiphenylsulfonic acid (14).



XXXI XXXIII XXXIV

(32 per cent yield)



XXXII XXXV XXXVI

(50 per cent yield)

TABLE 1

Sultones prepared from unsaturated ketones

α,β- AND β,γ-UNSATURATED KETONE	δ-SULTONE		FURAN DERIVATIVE	
	Structure	Yield	Structure	Yield
		per cent		*per cent*
XIV: X = Y = CH_3, R′ = R″ = H	XVI: X = Y = CH_3	40	XX: X = Y = CH_3	54
XIV: X = C_2H_5, Y = CH_3, R′ = R″ = H	XVI: X = C_2H_5, Y = CH_3	43	XX: X = C_2H_5, Y = CH_3	35
XIV: X = $C(CH_3)_3$, Y = CH_3, R′ = R″ = H	XVI: X = $C(CH_3)_3$, Y = CH_3	60	XX: X = $C(CH_3)_3$, Y = CH_3	65
XIV: X = CH_3, Y = C_6H_5, R′ = R″ = H	XVI: X = CH_3, Y = C_6H_5	40	XX: X = CH_3, Y = C_6H_5	65
XIV: X = C_6H_5, Y = CH_3, R′ = R″ = H	XVI: X = C_6H_5, Y = CH_3	84	XX: X = C_6H_5, Y = CH_3	16
XIV: X = Y = R″ = CH_3, R′ = H	XVII: X = Y = R″ = CH_3	54	XXI: X = Y = R″ = CH_3	76
Pulegone	XIIIb	61	XIIIc	75
Isopulegone	XIIIb	57	XIIc	75
XIV: X = Y = R′ = CH_3, R″ = H XV: X = Y = R′ = CH_3, R″ = H	XVIII: X = Y = R′ = CH_3	41	XXII: X = Y = R′ = CH_3	71
XIV: X = R′ = CH_3, Y = C_2H_5, R″ = H XV: X = R′ = CH_3, Y = C_2H_5, R″ = H	XVIII: X = R′ = CH_3; Y = C_2H_5	45	XXII: X = R′ = CH_3, Y = C_2H_5	58
XV: X = Y = C_2H_5, R′ = R″ = CH_3	XIX: X = Y = C_2H_5; R′ = R″ = CH_3	Not reported	XXII: X = Y = C_2H_5, R′ = R″ = CH_3	Not reported

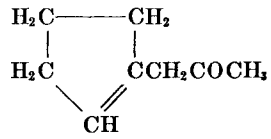
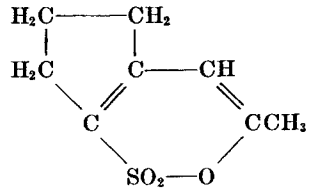
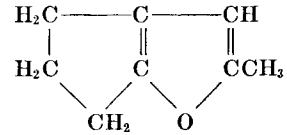
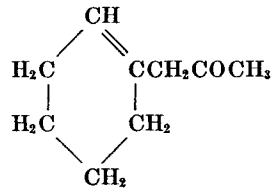
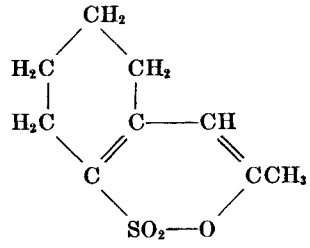
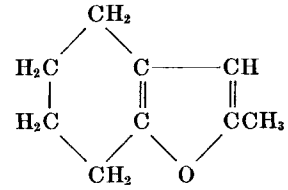
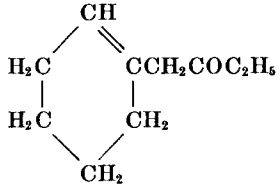
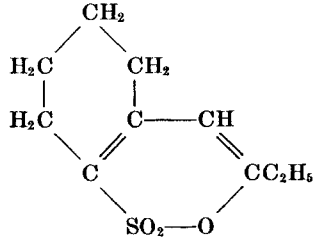
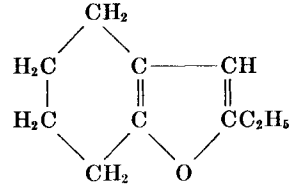
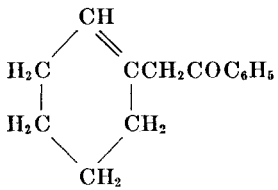
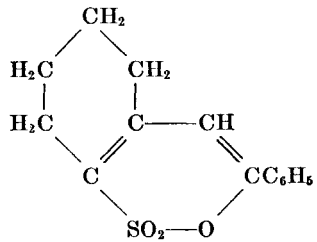
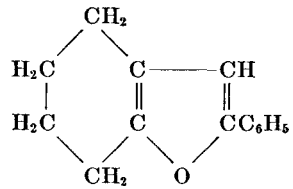
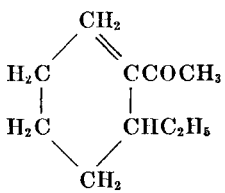
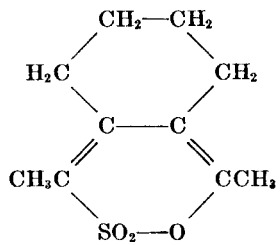
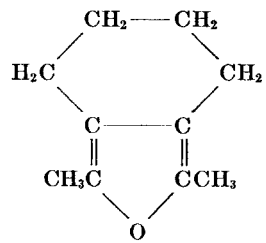
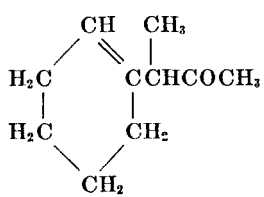
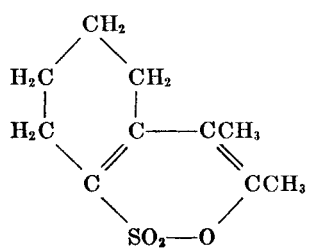
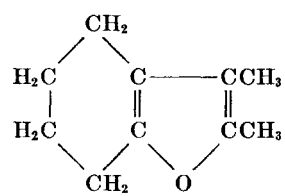
UNSATURATED KETONE THE DOUBLE BOND OF WHICH IS PART OF A RING	SULTONE OBTAINED BY TREATMENT OF THE KETONE WITH A MIXTURE OF CONCENTRATED SULFURIC ACID AND ACETIC ANHYDRIDE	FURAN DERIVATIVE OBTAINED BY PYROLYSIS OF THE SULTONE
	 (Yield not reported)	 (20% yield)
	 (50% yield)	 (74% yield)
	 (26% yield)	 (60% yield)

TABLE 1—*Concluded*

UNSATURATED KETONE THE DOUBLE BOND OF WHICH IS PART OF A RING	SULTONE OBTAINED BY TREATMENT OF THE KETONE WITH A MIXTURE OF CONCENTRATED SULFURIC ACID AND ACETIC ANHYDRIDE	FURAN DERIVATIVE OBTAINED BY PYROLYSIS OF THE SULTONE
	 (68% yield)	 (84% yield)
	 (18% yield)	 (72% yield)
	 (65% yield)	 (81% yield)

(81% yield)

(27% yield)

TABLE 2

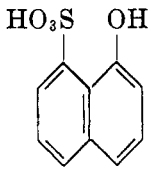
Sultones of 2'-hydroxy-2-biphenylsulfonic acid and its derivatives

XXX		YIELD	MELTING POINT	XXX		YIELD	MELTING POINT
X	Y			X	Y		
		per cent	°C.			*per cent*	°C.
H	H	52	108–109.5	H	$C(CH_3)_2C_2H_5$	23	104.5–105.5
Cl	H	80	175–176	H	Cl	15	163–165
Cl	CH_3	46	220–222	Cl	Cl	16	219–220

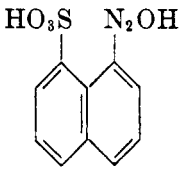
Similar treatment of the diazotized solution of the α-naphthol and β-naphthol esters (XXXI and XXXII) of *o*-aminobenzenesulfonic acid yields an inseparable mixture of isomers (58), presumably the sultones of 2-(1-hydroxy-2(and 8)-naphthyl)benzenesulfonic acids (XXXIII and XXXIV, respectively) in the case of XXXI and the sultones of 2-(2-hydroxy-1(and 3)-naphthyl)benzenesulfonic acids (XXXV and XXXVI, respectively) in the case of XXXII.

(d) From 1-naphthol-8-sulfonic acid and its derivatives

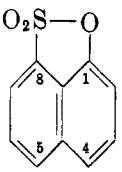
Those naphtholsulfonic acids which have OH and SO_3H groups in the 1,8- or peri-position (XXXVII) form anhydrides, i.e., sultones (64). 1,8-Naphthosultones (XXXIX) are generally prepared by heating the diazotized solutions of 1-aminonaphthol-8-sulfonic acid (XXXVIII) and its derivatives with water, alcohol, or dilute acids (table 3) (18).



XXXVII



XXXVIII



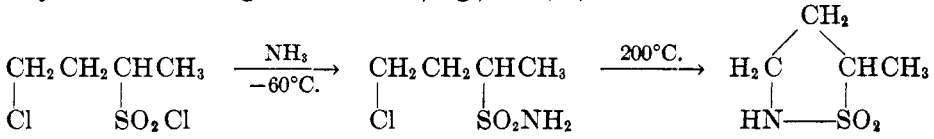
XXXIX

B. PREPARATION OF SULTAMS

Sultams (XLII, XLVI) are generally prepared by the elimination of the elements of water from the corresponding *o*- or peri-aminoarylsulfonic acids through the action of phosphorus oxychloride.

1. Aliphatic sultams

Only two aliphatic sultams have been prepared. These were made by treating the chloroalkylsulfonyl chloride with ammonia and heating the resulting chloroalkylsulfonamide to give the sultam, e.g., XL (33).



XL

(17% yield)

TABLE 3

Sultones prepared from 1-naphthol-8-sulfonic acid and its derivatives

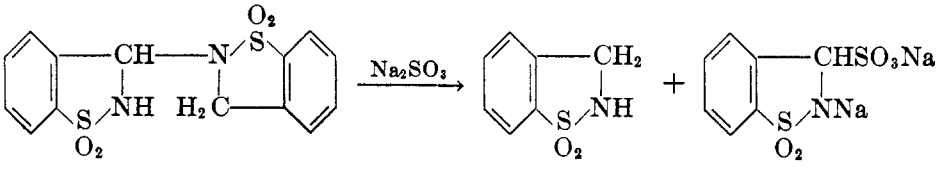
1-NAPHTHOL-8-SULFONIC ACID (XXXVII), 1-DIAZONAPHTHALENE-8-SULFONIC ACID (XXXVIII), AND THEIR DERIVATIVES	1,8-NAPHTHOSULTONE (XXXIX) AND ITS DERIVATIVES	CONDITIONS	REFERENCES
XXXVIII	XXXIX	Boiling with hydriodic acid	(15)
XXXVIII: 4-CH_3	XXXIX: 4-CH_3	Boiling on water bath	(68, 69)
XXXVIII: 5-CH_3	XXXIX: 5-CH_3	Boiling on water bath	(66)
XXXVIII	XXXIX: 4-Cl	Heating with $POCl_3$	(18)
XXXVIII: 4-Cl	XXXIX: 4-Cl	Boiling	(22)
XXXVIII: 5-Cl	XXXIX: 5-Cl	Boiling	(22)
XXXVII: 4-SO_3H	XXXIX: 4-Cl	Chlorine and dilute hydrochloric acid at 30°C., then at 80°C.	(20)
XXXVII: 4-SO_3H	XXXIX: 4-SO_3H	Concentrated HCl at 100°C. or fuming H_2SO_4	(4, 8)
XXXVII: 3-SO_3H	XXXIX: 3-SO_3H	Cold fuming H_2SO_4; H_2SO_4; P_2O_5 and/or $POCl_3$	(3)
XXXVIII: 3-SO_3H	XXXIX: 3-SO_3H	Boiling with dilute H_2SO_4	(7, 19)
XXXVIII: 5-SO_3H	XXXIX: 5-SO_3H	Boiling with dilute H_2SO_4	(24)
XXXVIII: 3,6-$(SO_3H)_2$	XXXIX: 3,6-$(SO_3H)_2$	Boiling	(37)
XXXVII: 3-SO_2H	XXXIX: 3-SO_2Cl	Treatment with $ClSO_3H$	(25)
XXXVII: 4-SO_3H	XXXIX: 4-SO_2Cl	Treatment with $ClSO_3H$	(25)

2. Aromatic sultams

(a) Benzylsultam

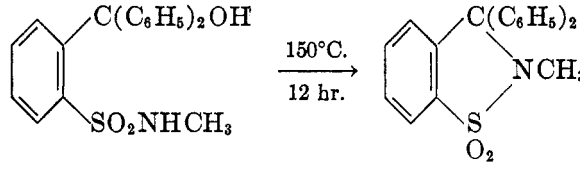
Benzylsultam (XLII) is obtained by the electrolytic reduction of saccharin at 50°C., using high acid concentration and high current density (45).

The action of sodium sulfite on the anhydrobenzylalcohol-*o*-sulfimide of *o*-sulfamidobenzaldehyde (XLI) gives a 92 per cent yield of XLII (38).



XLI XLII

The sultam XLIV is obtained by the action of fuming hydrochloric acid on triphenylcarbinol-*o*-sulfonic methylamide (XLIII) (12).



XLIII XLIV

(b) 1,8-Naphthosultam and its derivatives

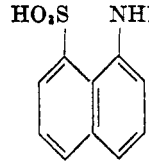
The sodium salt (16) and the potassium salt (23) of 1-aminonaphthalene-8-sulfonic acid and its derivatives (XLV) show a tendency to split off water by the action of phosphorus oxychloride to give 1,8-naphthosultam and its derivatives (XLVI) (table 4).

XLVI (R = H) is also obtained either in 71.2 per cent yield by the action of glucose in aqueous alcoholic sodium hydroxide solution or in 38.2 per cent yield by the action of sodium sulfide in sodium carbonate solution on 1-nitronaphthalene-8-sulfonic acid (70).

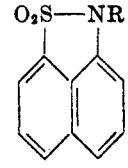
Cumming and Muir (15) have shown that the action of aqueous ammonia on 1-iodonaphthalene-8-sulfonyl chloride resulted in the elimination of hydrogen iodide and ring-closure to form XLVI (R = H), whereas the action of aniline produced 1-iodonaphthalene-8-sulfonanilide which, on treatment with copper

TABLE 4

1,8-Naphthosultam and its derivatives



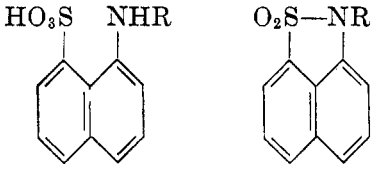
XLV



XLVI

1-AMINONAPHTHALENE-8-SULFONIC ACID DERIVATIVES (XLV)	SULTAM DERIVATIVES (XLVI)	CONDITIONS	REFERENCES
R = C_6H_5	R = C_6H_5	$POCl_3$ at 130°C.	(42)
R = $C_6H_4CH_3$-*p*	R = $C_6H_4CH_3$-*p*	$POCl_3$ at 130°C.	(42)
R = H; 5-CH_3	R = H; 5-CH_3	$POCl_3$ at 105°C. for 10 min.	(68, 69)
R = H; 4-SO_3H	R = H; 4-SO_3H	$POCl_3$	(5, 17, 40)
R = H; 3,6-$(SO_3H)_2$	R = H; 3,6-$(SO_3H)_2$	Fuming H_2SO_4 (25 per cent SO_3)	(17)
R = H; 4,6-$(SO_3H)_2$	R = H; 4,6-$(SO_3H)_2$	Fuming H_2SO_4 (25 per cent SO_3)	(6)

powder in boiling alcohol, gave *N*-phenyl-1,8-naphthosultam (XLVI:R = C_6H_5) (15).



XLV XLVI

IV. Chemical Properties of Sultones and Sultams

A. CHEMICAL PROPERTIES OF SULTONES

The sultones listed in table 1 are well-crystallized substances of low melting points; they distill in a vacuum without decomposition (67) but are readily pyrolyzed when distilled under atmospheric pressure with anhydrous zinc oxide (67) or freshly ignited calcium oxide (48) to form furan derivatives. Those listed in tables 2 and 3 are well-crystallized substances of high melting points.

In general, sultones undergo the sultone ring-opening by the action of hot alkalies (8, 35, 58, 61, 67); they are insoluble in water and cold alkalies, showing the absence of a free sulfonic acid grouping (67).

1. Action with halogens and halogen acids

When bromine in acetic acid is added to a cold solution of XXXIX in acetic acid or to an aqueous solution of the sodium salt of the 4-SO_3H derivative of XXXIX (35) or of XXXVII (20), 4-bromo-1,8-naphthosultone (XXXIX:4-Br) is obtained.

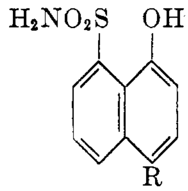
4-Chloro-1,8-naphthosultone (XXXIX: 4-Cl) is obtained either (*1*) by the action of chlorine on XXXIX in the presence of iron powder at 160–200°C. (30) or (*2*) by the action of hot hydrochloric acid alone on the 4-SO_3H derivative of XXXIX (36) or in the presence of manganese on XXXIX at 80–90°C. (30).

2. Action with alkalies

The action of hot alkalies on benzylsultone (XXIVa) (44), tolylsultone (XXVI) (43), 1,8-naphthosultone (XXXIX) and its derivatives (2, 8, 18, 35), and 1,8-naphthosultone-4-ketones (LIX) (table 7) (26, 58, 61, 62) effects the opening of the sultone ring with the formation of the corresponding alkali salt of 2-hydroxybenzylsulfonic acid, benzylalcohol-*o*-sulfonic acid, 1-naphthol-8-sulfonic acid and its derivatives, and 1-naphthol-8-sulfonic acid-4-ketone, respectively.

Shaking the 4-substituted naphthosultone derivatives (table 7) with concentrated ammonia or boiling them mildly with aqueous ammonium carbonate solution produces the corresponding 1-naphthol-8-sulfonamide (XLVII) (26, 58). Similarly, 1,8-naphthosultone-3-sulfonamide (XXXIX: 3-SO_2NH_2) on treatment with ammonia gives 1-naphthol-3,8-disulfonamide (11), whereas 1,8-

naphthosultone-3-sulfonylanilide (XXXIX: 3-$SO_2NHC_6H_5$) gives 1-naphthol-3-sulfonanilide-8-sulfonic acid (XXXVII: 3-$SO_2NHC_6H_5$) (11).



XLVII: R = $COCH_3, COC_2H_5, COCH_2CH_2CH_3, CH_2CH(CH_3)_2$

3. Action with inorganic salts, organic salts, and amines

The sultones (XI) readily form adducts with a variety of inorganic and organic salts, to give derivatives of the corresponding sulfonic acids (XLVIII) (34). Methanol was the usual solvent for these reactions, which are carried out at temperatures ranging from 100 to 150°C. for periods of 1–12 hr. When sodium laurate or oleate was used, the resulting compounds showed excellent detergent properties.

$$\text{XI} + \text{KX} \rightarrow \underset{\underset{\text{XLVIII}}{|\ SO_3K}}{CH_3CHCH_2CH_2X}$$

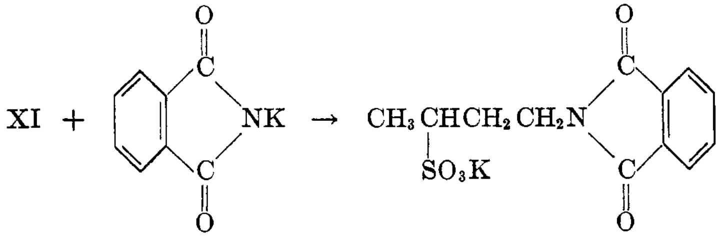
X = I, Br, F, CN, NCS, OC_6H_5, SC_6H_5, SH, and OCOR.

The butanesultones also react with amines to give the inner salts (XLIX). When XLIX (R = H) is heated, a polymeric compound (L) having polysulfonamide character is obtained (34). The value of n was not determined.

$$\text{XI} + RNH_2 \rightarrow \underset{\underset{\text{XLIX}}{|\ SO_3^-}}{CH_3CHCH_2CH_2\overset{+}{N}H_2R}$$

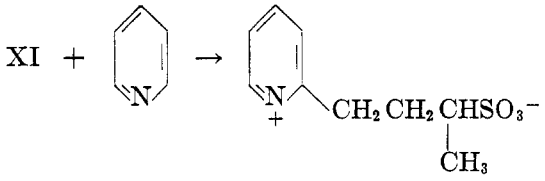
$$\text{XLIX (R = H)} \xrightarrow{230°\text{C.}} \underset{\text{L}}{-NH(SO_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2NH)_nSO_2-}$$

An almost quantitative yield of LI is obtained when XI is allowed to react with potassium phthalimide.



LI

Adducts of the butanesultones (XI) with pyridine, quinoline, and quinaldine form the corresponding inner butanesultones (which may be considered as betaines), e.g., LII in the case of pyridine.



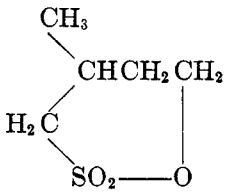
LII

Propanesultone (X) reacts with ammonia to give 1-amino-3-propanesulfonic acid (LIII).

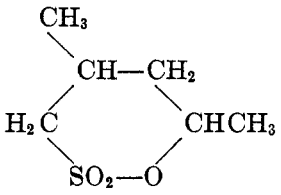
$$X + NH_3 \xrightarrow{-5°C.} NH_2CH_2CH_2CH_2SO_3H$$

LIII

Isopentanesultone (LIV) and isohexanesultone (LV) react, similarly to XI, as alkylating agents, but are less reactive (34).

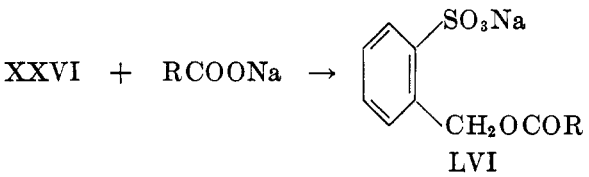


LIV

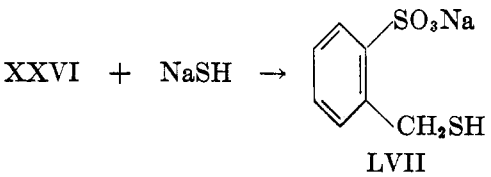


LV

Tolylsultone (XXVI) forms adducts with organic salts to give derivatives of the corresponding sulfonic acid (LVI); with sodium hydrogen sulfide, the adduct LVII is obtained.



LVI



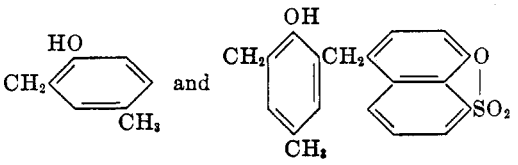
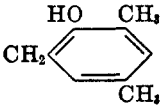
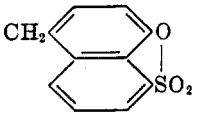
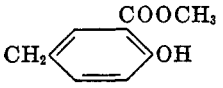
LVII

4. Action with formaldehyde and hydrogen halides

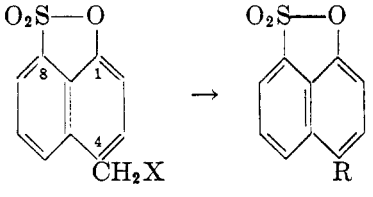
1,8-Naphthosultone (XXXIX) condenses with paraformaldehyde and hydrogen halide in the presence of a condensing agent (zinc chloride) to form

TABLE 5

Preparation of 4-substituted naphthosultones

4-SUBSTITUTED NAPHTHOSULTONES LIX: R=	METHOD OF FORMATION OF LIX FROM LVIII
CH_3	Reduction with zinc dust and acetic acid
$CH_2SO_2C_6H_4CH_3$-*p*	Condensation with the sodium salt of *p*-toluenesulfinic acid
CH_2OH	Boiling with water
CHO	Treatment of the above carbinol with CrO_3 in acetic acid at 65–75°C.
$CH_2C_6H_5$	Treatment with benzene in the presence of anhydrous $AlCl_3$ (Friedel–Crafts reaction)
$CH_2C_6H_4OH$-*p* and $CH_2C_6H_4OH$-*o*	Melting with phenol
	Melting with *p*-cresol
	Melting with 2,4-dimethylphenol
	Condensation with XXXIX in the presence of anhydrous zinc chloride
	Condensation with methyl salicylate in the presence of anhydrous zinc chloride

4-(halomethyl)-1,8-naphthosultones (LVIII) which are valuable intermediates for the production of dyes containing chlorine or bromine (29, 59, 62). 4-Chloromethyl-1,8-naphthosultone (LVIII: X = Cl) is readily converted into other 4-substituted naphthosultone derivatives (LIX) (*cf.* table 5) (59).



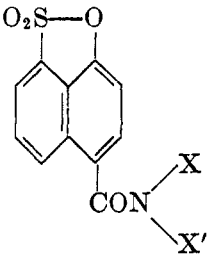
LVIII LIX

TABLE 6

4-Substituted 1,8-naphthosultone-4-carboxylic acid amides (LX)

LX		MELTING POINT	LX		MELTING POINT
X	X′		X	X′	
		°C.			°C.
H	CH_3	255–256	H	1-$C_{10}H_7$	293–294
C_2H_5	C_2H_5	156–158	H	2-$C_{10}H_7$	272.5–273.5
H	C_6H_5	273–275	CH_3	C_6H_5	147–148
H	$C_6H_4CH_3$-*o*	242.5–243.5	C_2H_5	C_6H_5	169.5–170.5

The oxidation of LIX (R = CHO) with chromic acid at room temperature resulted in the formation of 4-carboxy-1,8-naphthosultone (LIX: R = COOH), which is a valuable intermediate for the preparation of 4-substituted 1,8-naphthosultone derivatives (LX) (table 6) via the reaction of amines with the corresponding acid chloride (LIX: R = COCl) (59).



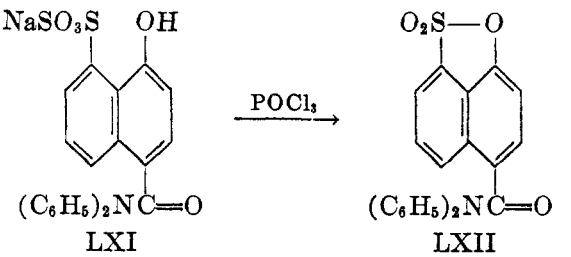
LX

5. Action with acid chlorides (Friedel–Crafts reaction)

1,8-Naphthosultone (XXXIX) can be acylated, aroylated, and arylsulfonated in the 4-position by a Friedel–Crafts reaction to give the corresponding 4-acyl-, 4-aroyl-, and 4-arylsulfonyl derivatives (LIX) (table 7) (26, 27, 28, 58, 61).

Diphenylcarbamyl chloride reacts with 1,8-naphthosultone (XXXIX) in an analogous manner; subsequent treatment of LXI with phosphorus oxychloride yields the sultone substituted in the 4-position (LXII) (58).

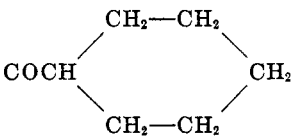
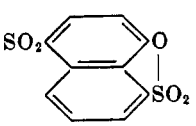
XXXIX + $(C_6H_5)_2NCOCl$ $\xrightarrow[(2)\ NaOH]{(1)\ AlCl_3}$



LXI LXII

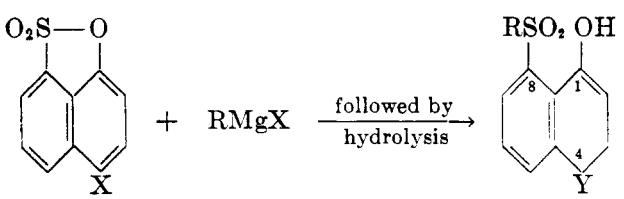
TABLE 7

Products formed from 1,8-naphthosultone by the action of acid chlorides

LIX: R =	MELTING POINT	YIELD
	°C.	*per cent*
$COCH_3$	172–173	74
$COCH_2Cl$	164–165	Not reported
COC_2H_5	160–161	80
$COCH_2CH_2CH_3$	131–132	70
$COCH_2CH(CH_3)_2$	121.5–122.5	36
	134–135	0.5
COC_6H_5	158–159	90
$COC_6H_3Cl_2$-2′,4′	171–172	76
$COC_6H_4NO_2$-3′	236–237	76
$COC_6H_4NO_2$-4′	231–232.5	70
$COC_6H_3(NO_2)Cl$-3′,4′	218–219	55
$SO_2C_6H_5$	206–207	61
$SO_2C_6H_4CH_3$-4′	215–216.5	95
$SO_2C_6H_3Cl_2$-3′,4′	197–197.5	17
$SO_2C_6H_3(COOH)OH$-3′,4′	247–248	3
	292–293	75

6. *Action with Grignard reagents*

Recently, Mustafa and coworkers (49, 51, 52) have found that the action of Grignard reagents on 1,8-naphthosultone and its derivatives (LXIII) effects the opening of the sultone ring and provides a new method of preparing peri-hydroxydiarylsulfones (LXIV) (table 8).



LXIII LXIV

7. *Action with lithium aluminum hydride*

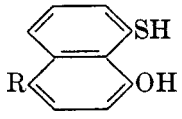
8,8′-Dihydroxy- (LXVIa) and 5,5′-dimethyl-8,8′-dihydroxy-1,1′-dinaphthyl disulfides (LXVIb) (54) are obtained together with 1-mercapto-8-hydroxy-

TABLE 8

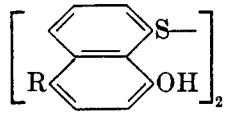
Peri-hydroxydiaryl sulfones prepared from 1,8-naphthosultone and its derivatives

LXIII: X =	LXIV: Y =	R	MELTING POINT
			°C.
H	H	C_6H_5	140
H	H	1-$C_{10}H_7$	188
H	H	CH_3	150
H	H	C_2H_5	210
H	H	$C(CH_3)_3$	240
CH_3	CH_3	CH_3	155
CH_3	CH_3	C_2H_5	158
CH_3	CH_3	C_6H_5	170
CH_3	CH_3	1-$C_{10}H_7$	180
$SO_2C_6H_5$	$SO_2C_6H_5$	$C(CH_3)_3$	148–149
$SO_2C_6H_5$	$SO_2C_6H_5$	C_6H_5	282
$SO_2C_6H_5$	$SO_2C_6H_5$	$C_6H_4CH_3$-4″	237–238
$SO_2C_6H_5$	$SO_2C_6H_5$	1-$C_{10}H_7$	218
$SO_2C_6H_4CH_3$-4′	$SO_2C_6H_4CH_3$-4′	CH_3	146
$SO_2C_6H_4CH_3$-4′	$SO_2C_6H_4CH_3$-4′	C_6H_5	260
$SO_2C_6H_4CH_3$-4′	$SO_2C_6H_4CH_3$-4′	$C_6H_4CH_3$-4″	247–248
$COCH_3$	$C(CH_3)_2OH$	CH_3	176
$COCH_3$	$C(C_2H_5)(CH_3)OH$	C_2H_5	158
$COCH_3$	$C(C_6H_5)(CH_3)OH$	C_6H_5	168
$COCH_3$	1-$C_{10}H_7C(CH_3)OH$	1-$C_{10}H_7$	163
COC_6H_5	$C(C_6H_5)(CH_3)OH$	CH_3	170
COC_6H_5	$C(C_6H_5)(C_2H_5)OH$	C_2H_5	181
COC_6H_5	$C(C_6H_5)_2OH$	C_6H_5	164
CH_2Cl	$CH_2C_6H_5$	C_6H_5	169
CH_2Cl	$CH_2C_{10}H_7$-1	1-$C_{10}H_7$	232

naphthalene (LXVa) and 5-methyl-1-mercapto-8-hydroxynaphthalene (LXVb) (50) by the action of lithium aluminum hydride on XXXIX and its 5-methyl derivative, respectively.



LXVa: R = H
LXVb: R = CH_3



LXVIa: R = H
LXVIb: R = CH_3

B. CHEMICAL PROPERTIES OF SULTAMS

Sultams (XLII and XLVI: R = H) (table 4) are well-crystallized substances; their solubility in alkalies is due to the formation of metallic salts. The "imino group" has assumed an acid nature, owing to the influence of the negative SO_2 group. Thus, the hydrogen atom of the imino group can be replaced by an alkyl group by the action of alkyl halide and sodium (16), or by the action of dialkyl sulfate in the presence of sodium hydroxide solution (41); it may be replaced by an acyl or aroyl group by the action of acetic anhydride and/or benzoyl chloride on the sultam (16, 39).

1. Action with halogens

The behavior of 1,8-naphthosultam (XLVI: R = H) towards chlorine presents extensive analogies to that of α-naphthol, a di-, tri-, or pentachloro derivative being obtained depending on the duration and method of chlorination (71). This analogy also extends to the quinones and their derivatives and to the ketochlorides of tetrahydronaphthosultam (72). In general, 1,8-naphthosultam-4-quinone (LXXI) and the 2,3-dichloro- and 2,2,3,3-tetrachloro-1,8-naphthosultam-4-quinones show great resemblance to 1,4-naphthoquinone and the 2,3-dichloro- and 2,2,3,3-tetrachloro-1,4-naphthoquinones, respectively, in their reactions (chart I) (71, 72, 73).

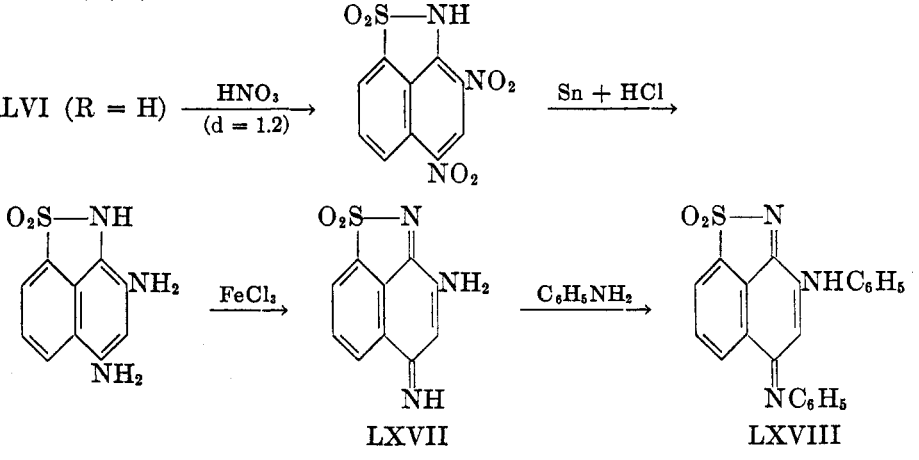
2. Action with alkalies

The sultam ring undergoes ring-opening by the action of hot aqueous alkali hydroxides to give the corresponding alkali salts of 1-aminonaphthol-8-sulfonic acids (XLV) in the case of 1,8-naphthosultam and its derivatives (XLVI) (16, 41). XLVI (R = H), when fused with alkali, gives 8-amino-1-naphthol, and at higher temperatures 1,8-dihydroxynaphthalene is obtained (16).

3. Action with acids

When 1,8-naphthosultam-2,4-disulfonic acid (XLVI: R = H; 2,4-$(SO_3H)_2$) is heated with 20 per cent hydrochloric acid in a sealed tube, the sultam ring is opened and the 2,4-sulfo groups are eliminated, with the formation of XLVI (R = H) (17).

The action of nitric acid on XLVI (R = H) gives the 2,4-dinitro derivative, which is readily reduced to the 2,4-diamino derivative (73). The diamino compound is readily oxidized to 2-amino-1,8-naphthosultam-4-quinonimide (LXVII), which reacts with aniline to give 2-anilino-1,8-naphthosultam-4-quinone anil (LXVIII) (73).



LXVII LXVIII

Similarly, the action of nitric acid on an acetic acid solution of *N*-phenyl-1,8-naphthosultam (XLVI: R = C_6H_5) yields the corresponding 2,4-dinitro derivative (42).

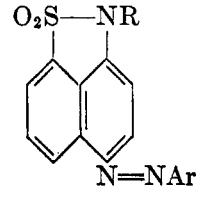
4. Action with inorganic salts and amines

Naphthosultam (XLVI: R = H) forms with the alkaline earths difficultly soluble yellow salts, from which it can be recovered by acidification (16).

The action of aromatic primary amines, e.g., aniline, on 1,8-naphthosultam-3-sulfonic acid (XLVI: 3-SO_3H; R = H) and 1,8-naphthosultam-3,6-disulfonic acid (XLVI: 3,6-$(SO_3H)_2$; R = H) in the presence of hydrochloric acid at about 130–140°C. effects the replacement of the sulfonic acid group in the 3-position by the phenylamino group, with the formation of 3-phenylamino-1,8-naphthosultam (21) and 3-phenylamino-1,8-naphthosultam-6-sulfonic acid, respectively (55).

5. Action with diazo compounds

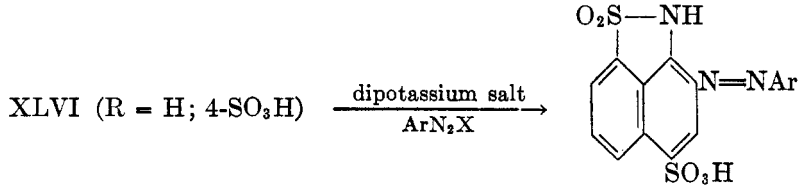
In coupling with diazo compounds XLVI (R = H) and its *N*-substituted derivatives (XLVI: R = CH_3, C_6H_5, and/or $C_6H_4CH_3$-*p*) show great similarity to α-naphthol and its derivatives. The corresponding 4-(arylazo)-1,8-naphthosultam derivatives (LXIX) are obtained (41, 42, 72).



LXIX

LXIXa: R = H, Ar = $C_6H_4NO_2$-4′
LXIXb: R = H, Ar = $C_6H_4SO_3Na$-4′
LXIXc: R = H, Ar = $C_6H_3(NO_2)_2$-2′,4′
LXIXd: R = H, Ar = 1-$C_{10}H_6SO_3H$-4′
LXIXe: R = CH_3, Ar = $C_6H_4NO_2$-4′
LXIXf: R = CH_3, Ar = $C_6H_3(NO_2)_2$-2′,4′
LXIXg: R = CH_3, Ar = $C_6H_2(NO_2)_3$-2′,4′,6′
LXIXh: R = C_6H_5, Ar = $C_6H_3(NO_2)_2$-2′,4′
LXIXi: R = $C_6H_4CH_3$-4″, Ar = $C_6H_3(NO_2)_2$-2′,4′

1,8-Naphthosultam-4-sulfonic acid (XLVI: R = H; 4-SO_3H) shows a greatly diminished tendency to react with diazo compounds when compared with either XLVI (R = H) or 1-naphthol-4-sulfonic acid. It yields *o*-azo dyes (LXXa to LXXb), similarly to the action of 1-naphthol-4-sulfonic acid (40).



LXXa: Ar = $C_6H_4NO_2$-4′
LXXb: Ar = $C_6H_4OCH_3$-2′

Br2 in
CH3COOH
Cl2 in
CH3COOH
HNO3
(d = 1.32)
SnCl2 +
CH3COOH
Cl2 in CHCl3
Cl2 in CH3COOH
C6H5NH2
C6H5N in
CH3COOH
SnCl2
CH3COOH
NaHSO3
HNO3
(d = 1.4)
moderate chlorination
C6H5NH2

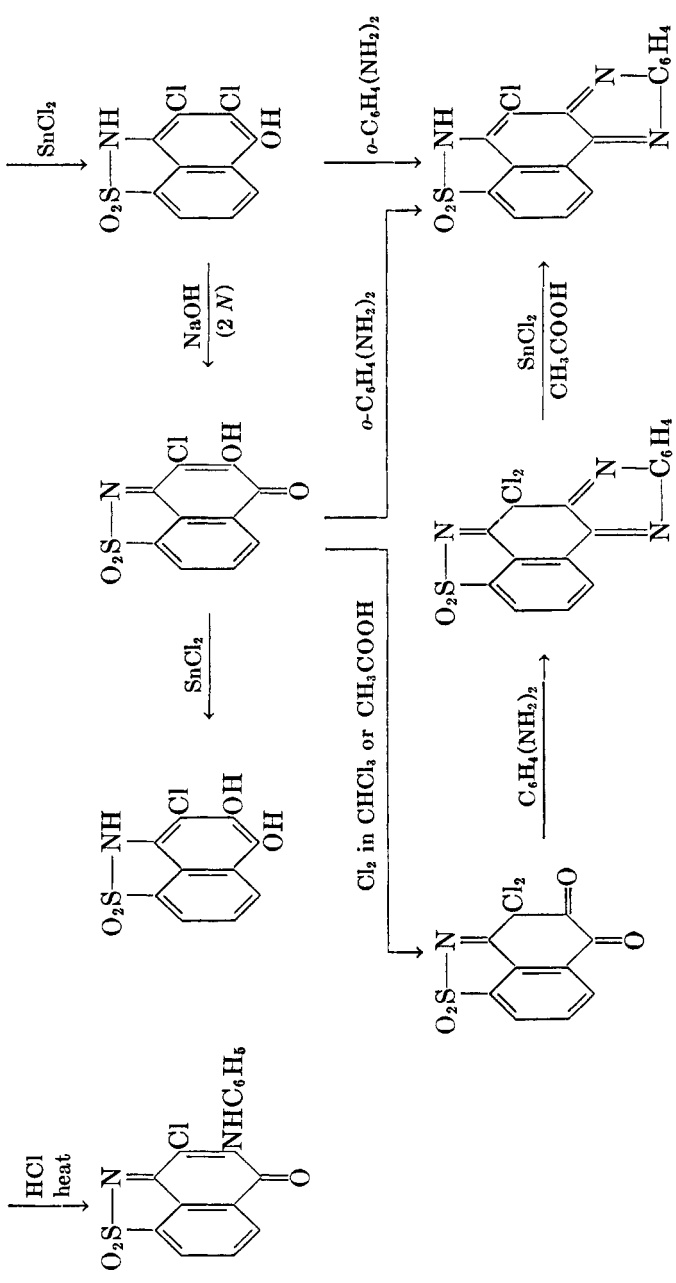
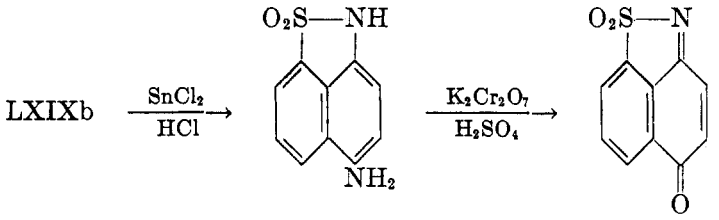


CHART I

Halogen derivatives of 1,8-naphthosultam, hydronaphthosultam, naphthosultamquinone, and ketochlorides of tetrahydronaphthosultam

The azo compound (LXIXb) is readily reduced to 4-amino-1,8-naphthosultam, which is oxidized to 1,8-naphthosultam-4-quinone (LXXI) (72).



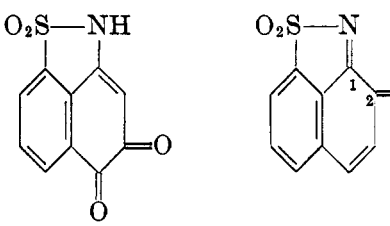
LXXI

6. Action with formaldehyde and hydrogen halides

Similar to XXXIX, XLVI (R = $SO_2C_6H_5$) condenses with paraformaldehyde and hydrogen chloride in the presence of anhydrous zinc chloride to form the 4-chloromethyl-1,8-naphthosultam derivative (XLVI: R = $SO_2C_6H_5$; 4-CH_2Cl), which is readily reduced by the action of zinc dust and acetic acid to the 4-methyl-1,8-naphthosultam derivative (XLVI: R = $SO_2C_6H_5$; 4-CH_3) (50).

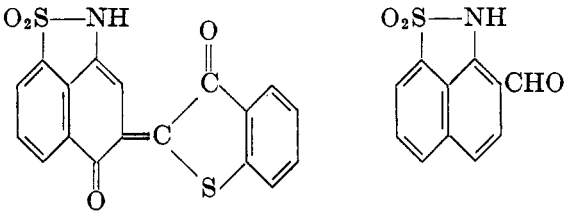
7. Action with α-isatinanilide and with hydroxythionaphthene

XLVI (R = H) and 1,8-naphthosultamquinone (LXXII) might be substituted for phenols in the condensation with α-isatinanilide and/or hydroxythionaphthene to form indigoid dyes. Thus, 2-naphthosultam-2′-indole indigo (LXXIIIa), the formal analog of 2-naphthalene-2′-indole indigo, is obtained in 10 per cent yield by boiling XLVI (R = H) with α-isatinanilide in acetic anhydride (23, 42). The 5′,7′-dibromo derivative (LXXIIIb) is obtained in 32 per cent yield by heating, for several hours, a mixture of XLVI (R = H) and 5,7-dibromoisatin chloride (42). LXXIV is similarly prepared by boiling



LXXII

LXXIIIa: R = H
LXXIIIb: R = Br

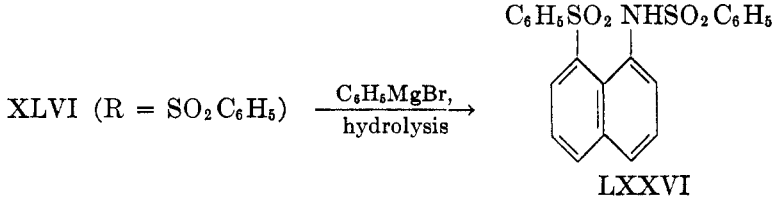


LXXIV LXXV

LXXII with hydroxythionaphthene in acetic acid (23). LXXIIIa is easily decomposed by the action of alkali to give 1,8-naphthosultam-2-aldehyde (LXXV) (42).

8. Action with Grignard reagents

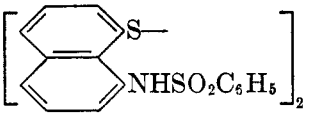
Whereas the sultam ring in the case of XLVI (R = H) and of XLVI (R = CH_3) is stable or almost stable towards the action of phenylmagnesium bromide, it is opened in the case of *N*-benzenesulfonyl-1,8-naphthosultam (XLVI: R = $SO_2C_6H_5$) by the action of phenylmagnesium bromide, yielding 8-benzenesulfonyl-1-benzenesulfonylnaphthylamine (LXXXVI) (53).



LXXVI

9. Action with lithium aluminum hydride

Similar to the behavior of XXXIX towards the action of lithium aluminum hydride, XLVI (R = $SO_2C_6H_5$) is converted to dibenzenesulfonyl-8,8′-1,1′-dinaphthyl disulfide (LXXVII) by the action of lithium aluminum hydride (54). XLVI (R = H) and XLVI (R = CH_3) are proved to be stable or almost stable towards the action of lithium aluminum hydride under similar conditions (50).



LXXVII

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