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Phthalimides. I. Base-catalyzed Lossen Rearrangement and Acid-catalyzed Beckmann Rearrangement with *N*-(Arylsulfonyloxy)phthalimides

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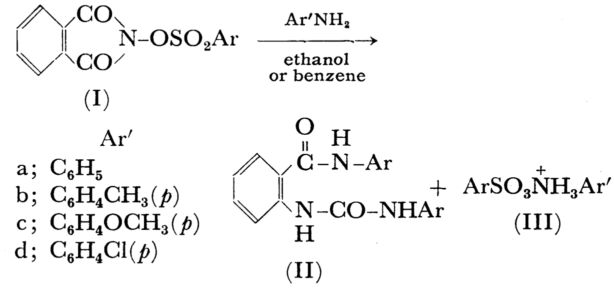
N-(Arylsulfonyloxy)phthalimides undergo base-catalyzed Lossen rearrangement with amines, and amino acids to give *N,N'*-diaryl ureas and amine salts. They behave similarly with phenylhydrazine in alcohol to give a mixture of *N*-hydroxyphthalimide and phenylhydrazine salts. However, *N*-(arylsulfonyloxy)phthalimides undergo isomerization followed by Beckmann rearrangement to give a mixture of 4-aryl-1*H*-2,3-benzoxazin-1-ones and diarylsulfones.

N-(Hydroxy)phthalimides undergo Beckmann rearrangement but fail to undergo Lossen reangement.1) We have reinvestigated the imide rearrangement starting with *N*-(arylsulfonyloxy)phthalimides (I) in order to see the effect of the introduction of *N*-arylsulfonyl group on the mode of rearrangement. It was found that Ia and b undergo base-catalyzed Lossen rearrangement and acid-catalyzed isomerization followed by Beckmann rearrangement.

Lossen Rearrangement of N-*(Arylsulfonyloxy)phthalimides. (A) Rearrangement in the Presence of Amines*: When *N*-(arylsulfonyloxy)phthalimides (Ia and b) are allowed to react with aromatic amines in refluxing benzene, they undergo aminolysis followed by base-catalyzed Lossen rearrangement to give the corresponding mixtures of *N*-[2-(arylcarbamoyl)phenyl]-*N'*-arylureas (IIa—d), and aromatic amine salts of aryl sulfonic acids (IIIa—h).



	Ar'
a;	C_6H_5
b;	$C_6H_4CH_3(p)$
c;	$C_6H_4OCH_3(p)$
d;	$C_6H_4Cl(p)$

	Ar	Ar'
a;	C_6H_5	C_6H_5
b;	C_6H_5	$C_6H_4CH_3(p)$
c;	C_6H_5	$C_6H_4OCH_3(p)$
d;	C_6H_5	$C_6H_4Cl(p)$
e;	$C_6H_4CH_3(p)$	C_6H_5
f;	$C_6H_4CH_3(p)$	$C_6H_4CH_3(p)$
g;	$C_6H_4CH_3(p)$	$C_6H_4OCH_3(p)$
h;	$C_6H_4CH_3(p)$	$C_6H_4Cl(p)$

Structure (II) was confirmed by the following:

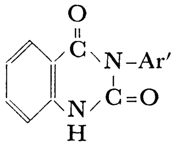
IR spectra: $\nu_{C=O}$ (anilide, 1710—1700 cm^{-1}), $\nu_{C=O}$2) (*N,N'*-diarylureas, 1660—1640 cm^{-1}), and $\nu_{NH's}$ (3300—3200 and 3120—3100 cm^{-1}).

MS of IId: (molecular ion, $m/e=399$).

Pyrolysis of IIa—d to give the corresponding 3-aryl-1,2,3,4-tetrahydroquinazoline-2,4-diones (IVa—d).

Structure (IIIa—h) was confirmed by the following:

(i) IR spectra: $\nu_{\overset{+}{N}H_3}$ (3020—3000 cm^{-1}), $\overset{+}{N}H_3$ asymm.

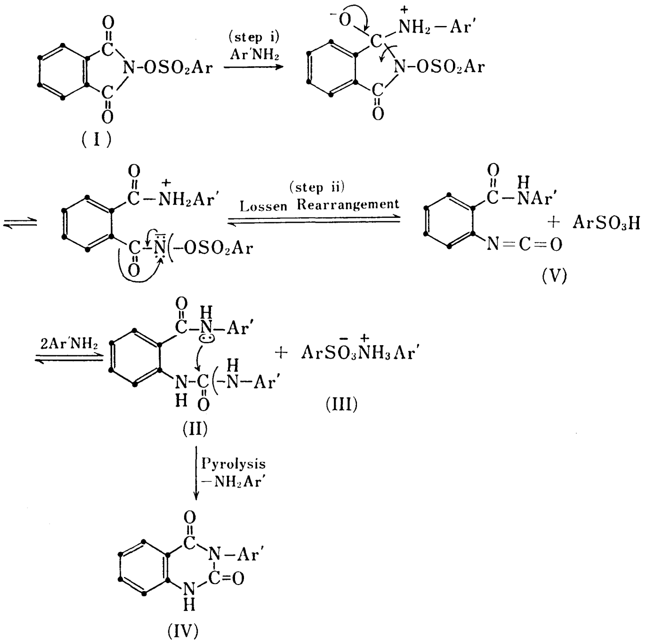


(IV)

a; $Ar'=C_6H_5$, b; $Ar'=C_6H_4CH_3(p)$,
c; $Ar'=C_6H_4OCH_3(p)$, d; $Ar'=C_6H_4Cl(p)$

bending (1600—1575 cm^{-1}), $\overset{+}{N}H_3$3) symm. bending (1500 cm^{-1}).

(ii) Identity with authentic products.4) The above reactions are summarized in the following scheme (Scheme 1).

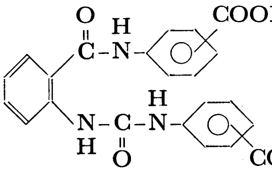


Scheme 1.

(B) Rearrangement in the Presence of Aminobenzoic Acids: *N*-(Arylsulfonyloxy)phthalimides (Ia and b) undergo base-catalyzed Lossen rearrangement with (*p*- and *m*-) aminobenzoic acids to give the corresponding mixtures of *N,N'*-diarylureas (VIa and b) and amino acid salts with sulfonic acids (VIIa—d).

Structure (VI) was confirmed by the following:

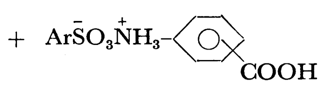
IR spectra: ν_{NH} (3320—3300 cm^{-1}), and $\nu_{C=O}$ (acid, 1720—1700 cm^{-1}).



(VI)

a; COOH(*p*-)

b; COOH(*m*-)



(VII)

a; Ar=C_6H_5, COOH(*p*-)

b; Ar=$C_6H_4CH_3$(*p*-), COOH(*p*-)

c; Ar=C_6H_5, COOH(*m*-)

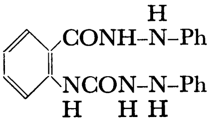
d; Ar=$C_6H_4CH_3$(*p*-), COOH(*m*-)

Structure (VII) was confirmed by the following:

(i) IR spectra: ν^{+}_{NH},[3] (3000 cm^{-1}), and $\nu_{C=O}$ (acid, 1700—1680 cm^{-1}).[5]

(ii) Identity with products obtained by the reaction of arylsulfonic acids (V) with the corresponding amino acids.

(C) Rearrangement in the Presence of Phenylhydrazine: *N*-(Arylsulfonyloxy)phthalimides (Ia and b) undergo base-catalyzed Lossen rearrangement with phenylhydrazine in refluxing ethanol to give mixtures of VIII, and phenylhydrazine salts of sulfonic acids (IX).



(VIII)

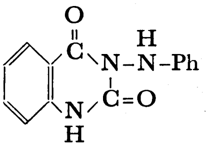
$+ \ Ar\bar{S}O_3\overset{+}{N}H_3NHPh$ (IX)

a; Ar=C_6H_5

b; Ar=$C_6H_4CH_3$(*p*-)

Structure (VIII) was confirmed by the following:

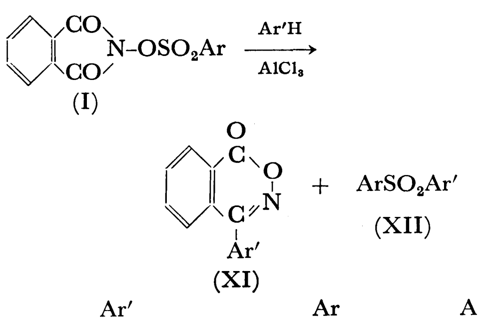
IR spectra: $\nu_{NH's}$ at (3320—3280 cm^{-1}) and $\nu_{C=O's}$ at (1680—1660 cm^{-1}); pyrolysis to give 3-anilino-1,2,3,4-tetrahydroquinazoline-2,4-diones (X).



(X)

(II) Beckmann Rearrangement of N-*(Arylsulfonyloxy)-phthalimides.* *N*-(Arylsulfonyloxy)phthalimides undergo isomerization to 3-(arylsulfonyloxyimino)-phthalide followed by Beckmann rearrangement with anhydrous aluminium chloride as a Lewis acid.

N-(Arylsulfonyloxy)phthalimides (Ia and b) react with anhydrous aluminium chloride in 1,1,2,2-tetrachloroethane to give a mixture of phthalic acid and arylsulfonic acid (V).



(I) (XI) (XII)

Ar′
a; C_6H_5
b; $C_6H_4CH_3$(*p*-)
c; $C_6H_4OCH_3$(*p*-)
d; C_6H_4Cl(*p*-)

	Ar	Ar′
a;	C_6H_5	C_6H_5
b;	C_6H_5	$C_6H_4CH_3$(*p*-)
c;	C_6H_5	$C_6H_4OCH_3$(*p*-)
d;	C_6H_5	C_6H_4Cl(*p*-)
e;	$C_6H_4CH_3$(*p*-)	$C_6H_4CH_3$(*p*-)
f;	$C_6H_4CH_3$(*p*-)	$C_6H_4OCH_3$(*p*-)
g;	$C_6H_4CH_3$(*p*-)	C_6H_4Cl(*p*-)

It was also found that *N*-(arylsulfonyloxy)phthalimides (Ia and Ib) react with reactive aromatic substrates (benzene, toluene, anisole, and chlorobenzene) in the presence of anhydrous $AlCl_3$ to give the corresponding mixtures of 4-aryl-1*H*-2,3-benzoxazin-1-ones (XIa—d), and diarylsulfones (XIIa—g).

Structure (XI) was confiermd by the following:

(i) IR spectra: $\nu_{C=O}$ in six membered heterocyclic compounds, 1750—1740 cm^{-1}.

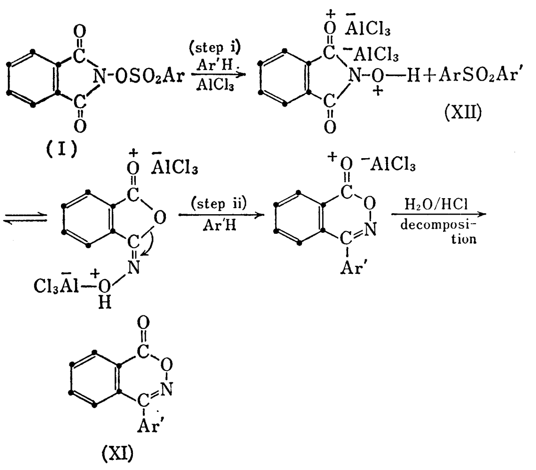
(ii) Identity with authentic products.[6—9]

Structure (XII) was confirmed by the following:

(i) IR spectra: ν_{SO_2} asymm. st. 1320—1310 cm^{-1}.

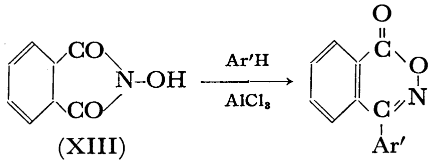
(ii) Identity with authentic products.[10—12]

The reaction is assumed to take place according to Scheme 2.



Scheme 2.

The above scheme was confirmed by the fact that *N*-hydroxyphthalimide (XIII) reacts with aromatic substrates in the presence of anhydrous $AlCl_3$ to give 4-aryl-1*H*-2,3-benzoxazin-1-ones.[1]



(XIII) (XI)

The results show that *N*-(arylsulfonyloxy)phthalimides undergo two types of molecular rearrangement. Lossen rearrangement occurs with amines, amino acids, and hydrazines; isomerization followed by Beckmann rearrangement occurs with Lewis acids such as anhydrous $AlCl_3$.

Experimental

Melting points were not corrected. IR spectra were carried out on an Unicam SP 1200 spectrophotometer by means of KBr Wafer technique.

Reaction of N-*(Arylsulfonyloxy)phathalimides with Aromatic Amines in Ethanol.* A mixture of *N*-(arylsulfonyloxy)-phthalimides (I) (0.1 mol) and primary aromatic amines

Table 1. Action of aromatic amines on *N*-(arylsulfonyloxy)phthalimides (Ia and b)

Reactants start amine	Products									
	N-2-(Arylcarbamoyl)-*N*′-arylureas (II)						Amine salts of aryl sulfonic acid (II)			
	No.	Mp, °C	Yield %	M.F.	Analysis Req.	Analysis Found	No.	Mp, °C	Mmp, °C	Yield
Ia Aniline	IIa	218—220	58	$C_{20}H_{17}N_3O_2$	C 72.50 H 5.13	72.3 5.4	IIIa	222	222	60
p-Toluidine	IIb	204—205	54	$C_{22}H_{21}N_3O_2$	C 73.5 H 5.8	74.0 5.0	IIIb	194—196	195	61
p-Anisidine	IIc	208	60	$O_{22}H_{21}N_3O_4$	C 67.53 H 5.37	67.00 5.17	IIIc	168—170	169	64
p-Chloro-aniline	IId	225—226	40	$C_{20}H_{15}N_3O_2Cl$	C 60.0 H 3.75	60.5 3.4	IIId	213—215	214—215	68
Ib Aniline	IIa	218—220	60				IIIe	224—225	223	60
p-Toluidine	IIb	204—205	58				IIIf	184—185	184	48
p-Anisidine	IIc	208	62				IIIg	180	180	61
p-Chloro-aniline	IId	225—226	49				IIIh	230	230	58

(0.4 mol) in ethanol or benzene (20 ml) were heated under reflux for (6 h) and then cooled. The solid product was treated with ethanol and filtered off.

The residual solid was recrystallized from ethanol to give *N*-[2-(arylcarbamoyl)phenyl]-*N*′-arylureas (II) as white crystals. The mother liquor was concentrated by evaporation and trated with a few drops of benzene to give III as a solid product (Table 1).

It was proved to be an amine salt of arylsulfonic acids by mp and mixed mps with authentic samples prepared from the reaction of arylsulfonic acids (Va and b) with the corresponding amines.3)

Pyrolysis of N-[*2-(Arylcarbamoyl)phenyl*]-N′-*arylureas*: *N*-[2-(Arylcarbamoyl)phenyl]-*N*′-arylureas (IIa—d) were heated above their mps on a sand bath for 2 h. The solid product was obtained in sublimed needles and collected in an air condenser. The product was proved to be 3-aryl-1,2,3,4-tetrahydroquinazoline-2,4-diones (IVa—d) by mp and mixture mp and IR spectra.4)

I-B) Reaction of N-(*Arylsulfonyloxy)phthalimides with Aminobenzoic Acids.* A mixture of *N*-(arylsulfonyloxy)-phthalimide (I) (0.1 mol), aminobenzoic acid (0.3 mol) and a few drops of pyridine in benzene (10 ml) was heated under reflux for 4 h, then cooled. The solid product was treated with ethanol and filtered off. The residual solid was recrystallized from acetic acid to give *N*,*N*′-diarylureas (VIa and b) as white crystals (Table 2). The mother liquor was concentrated, and treated with a few drops of benzene to give-VII as a product (Table 2).

It was proved to be arylsulfonic acid salts of aminobenzoic acid by mp and mixture mp.

Reaction of Arylsulfonic Acids (V) with Aminobenzoic Acids: A mixture of arylsulfonic acids (V) (0.1 mol) and aminobenzoic acids (0.3 mol) and a few drops of pyridine in benzene was heated under reflux for 2 h, then cooled. The solid product obtained was filtered off, recrystallized from benzene and a few drops of ethanol were added to give white crystals. It was proved to be arylsulfonic acid salts of aminobenzoic acids by mp and mixture mp.

Reaction of N-(*Arylsulfonyloxy)phthalimides with Phenylhydrazine in Ethanol*: A mixture of *N*-(arylsulfonyloxy)phthalimides (I) (0.1 mol) and phenylhydrazine (0.3 mol) in ethanol was heated under reflux for (3 h), then cooled. The solid product was obtained, filtered off, recrystallized from ethanol to give VIII as white crystals, mp 193 °C. Found: C, 66.6; H, 5.0%. Calcd for $C_{20}H_{19}H_5O_2$: C, 66.48; H, 4.9%.

The mother liquor was concentrated by evaporation. A solid product was obtained. It was proved to be phenyl-

Table 2. Action of aminobenzoic acids on *N*-[arylsulfonyloxy]phthalimides

Reactants start amino acids	Products										
	N,*N*′-Diarylureas (VI)						Aminobenzoic acid salts (VII)				
	No.	Mp °C	Yield %	M.F.	Analysis % Calcd (Found) C	Analysis % Calcd (Found) H	No.	Mp °C	Yield %	M.F.	Analysis, % Calcd (Found) C	Analysis, % Calcd (Found) H
Ia *p*-Amino-benzoic acid	VIa	over 360	75	$C_{22}H_{17}N_3O_6$	63.0 (63.34)	4.06 (3.69)	VIIa	173—175	40	$C_{13}H_{13}NO_5S$	52.42 (53.3)	4.4 (4.6)
Ib *p*-Amino-benzoic acid	VIa	over 360	75				VIIb	295—297	38	$C_{14}H_{15}NO_5S$	54.37 (54.5)	4.85 (4.6)
Ia *m*-Amino-benzoic acid	VIb	over 360	78	$C_{22}H_{17}N_3O_6$	63.0 (63.7)	4.06 (4.2)	VIIc	238—240	43	$C_{13}H_{13}NO_5S$	52.45 (53.3)	4.40 (4.6)
Ib *m*-Amino-benzoic acid	VIb	over 360	78				VIId	253—255	41	$C_{14}H_{15}NO_5S$	54.37 (54.4)	4.85 (4.6)

Table 3. Reaction of anhydrous aluminium chloride in aromatic solvents with *N*-[arylsulfonyloxy]phthalimides

Reactants aromatic solvents	Products: 4-Aryl-1*H*-2,3-benzoxazin-1-ones (XI) No.	Mp °C	Mixed mp °C	Yield %	Ref.	Products: Diarylsulfones (XII) No.	Mp °C	Mixed mp °C	Yield %	Ref.	M.F.	Analysis % Calcd (Found) C	H
Ia Benzene	XIa	160	160	35	5	XIIa	128	127	85	9	—	—	—
Toluene	XIb	158	158	33	6	XIIb	124	123	83	—	$C_{13}H_{12}O_2S$	58.7 (58.3)	4.6 (4.3)
Anisole	XIc	141	140	30	7	XIIc	72	72	84	—	$C_{13}H_{12}O_3S$	62.9 (62.65)	4.84 (4.9)
p-Chlorobenzene	XId	187	186	28	8	XIId	93	93	80	10	—	—	—
Ib Benzene	XIa	160	—	—	—	XIIb	124	—	86	—	—	—	—
Toluene	XIb	158	—	—	—	XIIe	158	157	84	11	—	—	—
Anisole	XIc	141	—	—	—	XIIf	100	98	86	—	$C_{14}H_{14}O_3S$	64.12 (63.72)	5.33 (5.61)
p-Chlorobenzene	XId	186	—	—	—	XIIg	128	127	81	—	$C_{13}H_{11}O_2SCl$	54.6 (54.2)	4.5 (5.0)

hydrazine salt of arylsulfonic acids (IX) by mp and mixed mps.[3]

Pyrolysis of VIII: VIII was heated above its mp on a sand bath for one hour, then cooled. A solid product obtained was filtered off, and recrystallized from ethanol to give a solid product. It was proved to be Xa—d by mp and mixed mp, and IR spectra. The mother liquor was concentrated by evaporation to give an oil.

It was proved to be phenylhydrazine by condensation with benzophenone to give benzophenone hydrazone.

IIA. Action of Anhydrous Aluminium Chloride in Dry 1,1,2,2-Tetrachloroethane on N-*(Arylsulfonyloxy)pathalimides (I).* Anhydrous aluminium chloride was added while stirring to a solution of *N*-(arylsulfonyloxy)phthalimides (I) in dry 1,1,2,2-tetrachloroethane. The reaction mixture was heated under reflux for 1/2 h, and the complex formed was decomposed with ice-cold dilute hydrochloric acid. The solvent was steam distilled. The solution was extracted with ether. The ethereal layer was separated, dried over anhydrous sodium sulfate, and the solvent was concentrated by evaporation.

The solid product obtained was filtered off, recrystallized from ethanol to give white crystals, mp 206 °C. It was proved to be phthalic acid by mp and mixed mp. The mother liquor was concentrated to dryness to give arylsulfonic acids.

IIB. Action of Anhydrous Aluminium Chloride in Aromatic Solvents on N-*(Arylsulfonyloxy)phthalimides.* Anhydrous aluminium chloride (0.6 mol) was added under stirring to a solution of *N*-(arylsulfonyloxy)phthalimide (I) (0.1 mol) in dry aromatic solvents. The reaction mixture was heated under reflux for 1 h, and the complex formed was decomposed with ice-cold dilute hydrochloric acid. The solvent was steam distilled. The residual solid was filtered off.

The crude product was dissolved in ethanol, concentrated, then cooled, and the solid obtained was filtered off and recrystallized from ethanol to give diarylsulfone (XII) as white crystals (*cf.* Table 3).

The mother liquor was concentrated then cooled to give solid product. It was proved to be 4-aryl-1*H*-2,3-benzoxazin-1-ones (XI), (*cf.* Table 3).

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