Nonclassical Condensed Thiophenes. VI. Isothianaphthene 2,2-Dioxides

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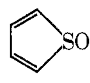
The synthesis and reactions of some derivatives of isothianaphthene 2,2-dioxide (**2**), including its 1-bromo derivative (**3**), its 1,3-dibromo derivative (**4**), and its 1,3-diphenyl derivative (**5**), are described. Of these compounds, only the 1,3-diphenyl derivative **5** was sufficiently stable to be observed directly in solution as an unstable, deep purple substance. The possible role of sulfur d orbitals *vs.* sulfonyl oxygen spiro conjugation in the electronic structure of the isothianaphthene 2,2-dioxide system is discussed. Desulfonylation reactions of some substituted 1,3-dihydroisothianaphthene 2,2-dioxides are also described in the context of this study.

Conjugation of a sulfonyl group with an olefinic or aromatic system has been well documented by many workers. The electronic nature of this effect is not obvious, however, and more than one type of sulfonyl conjugation effect may be invoked, depending upon the structural factors involved. The major complication in sulfonyl conjugation is the possible use of d orbitals by the sulfur atom.[2]

In view of the high instability of thiophene 1,1-dioxide (**1**) as compared to thiophene,[3] it seemed of interest to attempt the synthesis of some derivatives of isothianaphthene 2,2-dioxide (**2**), a system which was unreported at the inception of our work except in the form of reduced derivatives. It was thought that sulfur d orbital participation might be much more important in **2** than in **1**, since nonclassical canonical forms such as **2a** would be stabilized Kekulé structures, in contrast to the classical 4-π *o*-quinonoid structure **2**.



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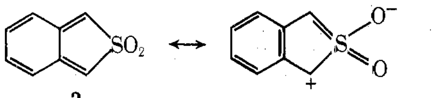


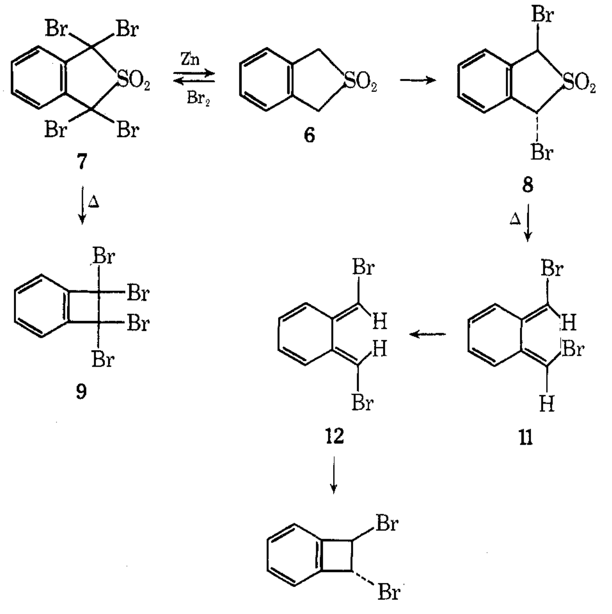
2 **2a**

This paper describes the generation and some reactions of the 1-bromo derivative (**3**), the 1,3-dibromo derivative (**4**), and the 1,3-diphenyl derivative (**5**) of **2**, as well as some aspects of the chemistry of their chemical precursors.[4]

Results

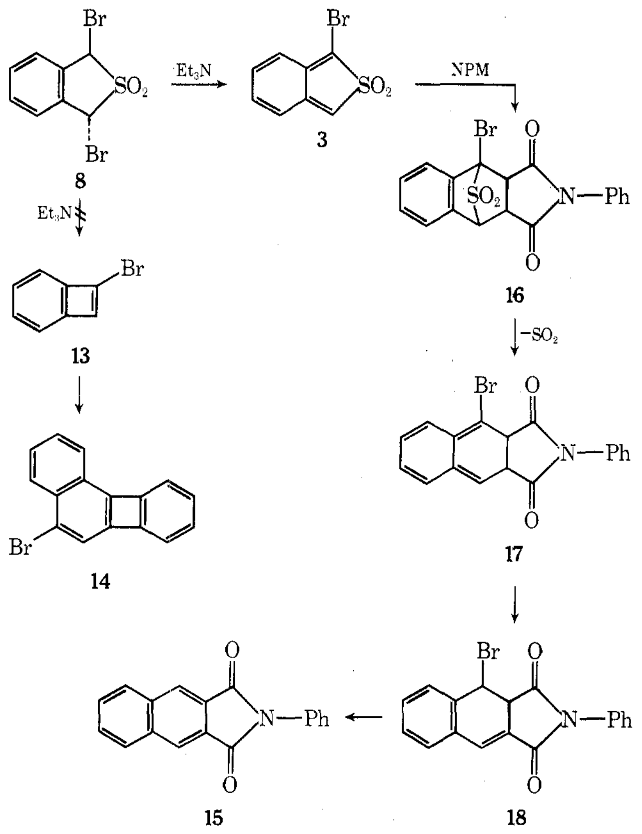
Bromo Derivatives 3 and 4 of Isothianaphthene 2,2-Dioxide (2). The light-catalyzed benzylic bromination of 1,3-dihydroisothianaphthene 2,2-dioxide (**6**)[5] was found to take place smoothly in hot dilute carbon tetrachloride solution. A monobrominated product could not be obtained, but either the tetrabromo sulfone (**7**) or a single dibromo sulfone, presumably the trans isomer **8**, could be prepared. Since gas phase pyrolysis of the parent sulfone **6** affords benzocyclobutene,[6] it was of interest to examine a similar pyrolysis of its brominated derivatives. Indeed, pyrolysis of **7** gave 1,1,2,2-tetrabromobenzocyclobutene, (**9**), while pyrolysis of **8** gave *trans*-1,2-dibromobenzocyclobutene (**10**); yields were modest (<25%), although the reactions were not studied from a preparative point of view. At first glance, application of electrocyclic reaction theory[7] to the formation of the benzocyclobutene **10** would seem to imply that **8** must be the cis isomer rather than the trans. However, pyrolysis of *trans*-**8** would initially produce the less stable *o*-quinodimethane **11**, which at 400° would be expected to rearrange to the more stable isomer **12** before closing on cooling to the observed product **10**.

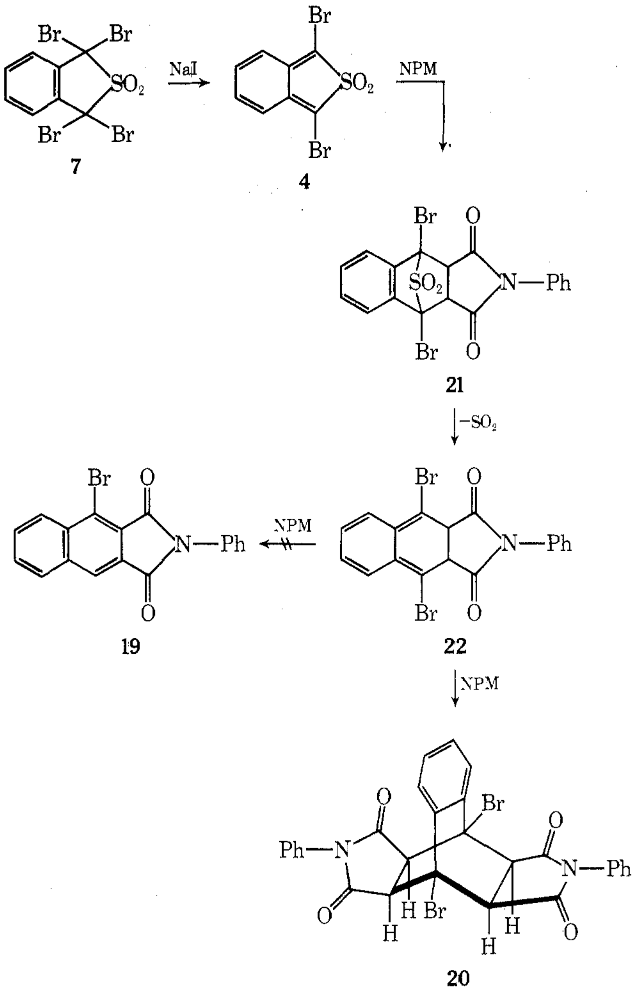
All four bromine atoms of **7** could be removed reductively. Thus, the unhalogenated sulfone **6** was obtained from **7** in good yield after long refluxing with zinc in ethanol.



Treatment of dibromo sulfone **8** with triethylamine at room temperature led to the formation of a brown color with destruction of the starting material; no crystalline reaction product was isolated. In theory, sulfone **8** might have undergone a Ramberg–Backlund reaction to give 1-bromobenzocyclobutadiene (**13**) which, under the basic reaction conditions, would have been transformed into 5-bromobenzo[*a*]biphenylene (**14**).[8] However, thin-layer chromatography revealed no detectible amount of **14**. The fact that base treatment of **8** had instead generated 1-bromoisothianaphthene 2,2-dioxide (**3**) was apparent by running the dehydrobromination reaction in the presence of excess *N*-phenylmaleimide (NPM). The reaction product, isolated in 88% yield, was the known *N*-phenyl-2,3-naphthalimide (**15**).[8] The formation of **15** may be explained by assuming that **3** undergoes a Diels–Alder addition of the dienophile to give the bridged sulfone **16**, which then loses sulfur dioxide to give the *o*-quinodimethane **17**. A 1,5-prototropic shift would convert the latter to the stable benzenoid isomer **18**, which then could lose hydrogen bromide to give the naphthalene derivative **15**.

The reaction of tetrabromo sulfone **7** with sodium iodide generated iodine, but no organic reaction product could be isolated. When the debromination was carried out in the presence of excess NPM, however, a white crystalline product, mp 360°, was formed in high yield (93%). This product was not the expected naphthalimide **19**; its mass spectrum and elemental analysis indicated the composition $C_{28}H_{18}Br_2N_2O_4$, and it was assigned the diimide structure **20**. The endo,endo configuration for **20** is supported by its





nmr spectrum, which shows four equivalent protons α to the carbonyls at δ 4.08, as well as four shielded aromatic protons in the region δ 6.38–6.55. The latter represent the ortho protons of the *N*-phenyl substituents, which are shielded by the bridged benzene ring. An analogous effect has been observed with the endo (but not the exo) NPM adduct of isothianaphthene.[9] The formation of **20** may be explained by assuming that tetrabromide **7** is first debrominated to give 1,3-dibromoisothianaphthene 2,2-dioxide (**4**), which is then trapped by NPM to give the bridged sulfone **21**. Loss of sulfur dioxide from **21** generates the *o*-quinodimethane **22**, which adds a second molecule of NPM stereoselectively to give the observed product **20**. It is interesting to note that the quinonoid intermediate **22** apparently adds NPM faster than it undergoes a 1,5-prototropic shift, a situation in contrast to the related intermediate **17**. The difference may simply be a matter of base catalysis, since **17** (but not **22**) was generated in the presence of triethylamine.

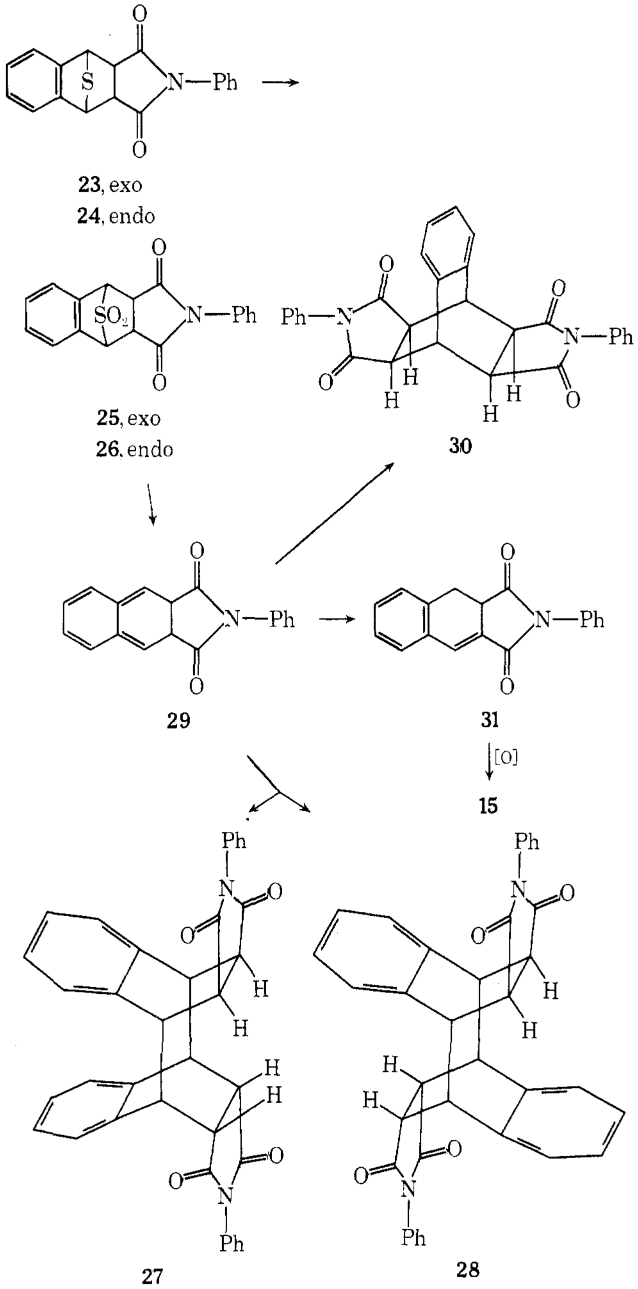
The *N*-Phenylmaleimide (NPM) Adducts of Isothianaphthene 2,2-Dioxide (2). In the chemistry outlined above, NPM adducts (**16** and **21**) of the brominated isothianaphthene 2,2-dioxides **3** and **4** were assumed to be nonisolable intermediates in the formation of compounds **15** and **20** from bromo sulfones **8** and **7**, respectively. Although we were unable to generate and trap the parent isothianaphthene 2,2-dioxide (**2**) in a similar manner, it proved to be quite simple to synthesize both the exo and endo NPM adducts of **2** indirectly and to study some of their reactions. Thus, peracetic acid oxidation of the known NPM-isothianaphthene adducts **23** and **24**[9] afforded the corresponding crystalline exo and endo sulfone adducts **25** and **26**.

The bridged sulfones **25** and **26** were considerably less stable thermally than the parent sulfone **6** of this series; they lost sulfur dioxide readily in a neutral solvent at 150–170° to give a white crystalline dimeric product, mp 360°. On the basis of its composition and its nmr spectrum, this material was assumed to be a 1:1 mixture of the endo,endo head-to-head and endo,endo head-to-tail dimers (**27** and **28**) of the *o*-quinodimethane **29**. In accord with this formulation, the nmr of the product (in CF_3CO_2D) showed singlets at δ 2.78, 3.32, and 3.88 and multiplets at 5.80–6.00 and 6.69–7.00, in a ratio of 1:1:4:4:14. The protons α to the carbonyls in the head-to-head dimer **27** appear at δ 3.32, while the corresponding protons in the dimer **28** are shielded by aromatic rings and appear at δ 2.78. In both dimers, the bridgehead protons are seen at δ 3.88. Evidence that both dimers are endo,endo structures is found in the shielded position (δ 5.80–6.00) of the ortho protons of all the *N*-phenyl groups. Although **27** and **28** were virtually inseparable, several crystallizations effected an enrichment of **27** as shown by nmr.

Thermal decomposition of either sulfone **25** or **26** in the presence of excess NPM led to the formation of an adduct of the intermediary *o*-quinodimethane **29**. This adduct (**30**), like its previously described dibromo analog **20**, was assigned the endo,endo configuration on the basis of its nmr.

In the conversion of dibromo sulfone **8** to imide **15** by NPM and triethylamine, the bridged sulfone **16** was assumed to be an intermediate but could not be isolated. In order to determine if this type of sulfone would be attacked by triethylamine, the model sulfones **25** and **26** were subjected to this reagent at room temperature. Attack did indeed occur, and the naphthalimide **15**, presumably formed *via* the dihydro derivative **31**, was isolated after work-up. A transient yellow fluorescent intermediate, presumably the *o*-quinodimethane **29**, was visible during the reaction. Indeed, when the reaction was run in the presence of NPM, intermediate **29** was effectively intercepted with the formation of the diimide adduct **30** in good yield.

The mechanism of the triethylamine desulfonylation is not entirely clear, but it appears to involve an unusual direct attack of the amine on the strained sulfonyl bridge; elimination of the bridge *via* removal of a proton α to an imide carbonyl would not lead to formation of *o*-quinodimethane **29**. Finally, it is interesting to note that the bicyclic parent sulfone **6** is quite unaffected by long heating with triethylamine, thus attesting to the importance of the strain factor in this desulfonylation reaction.



1,3-Diphenylisothianaphthene 2,2-Dioxide (5). The addition of sulfur dioxide to *trans*-1,2-diphenylbenzocyclobutene (**32**) readily affords a 1,3-dihydro-1,3-diphenylisothianaphthene 2,2-dioxide;[10] the latter sulfone can now be assigned the cis stereochemistry **33** on the basis of the application of electrocyclic reaction theory to the addition of dienophiles to **32**.[11,12] Light-catalyzed bromination of **33** could be controlled to give a single monobromo sulfone **34**, mp 198–200°; the stereochemistry of this bromide is uncertain, but it is probably the *cis*-diphenyl isomer; the latter would result by bromine addition to the less hindered side of the benzylic radical derived from **33**. Dibromination of **33** could also be achieved in a similar manner to give a dibromo sulfone **35**, mp 225–227°; the mother liquors contained a lower melting stereoisomer of **35** which was not further examined. Gas phase pyrolysis of **34** and **35** did not give benzocyclobutene derivatives, but instead gave 9-phenylanthracene (**36**) and 9-bromo-10-phenylanthracene (**37**), respectively.[13]

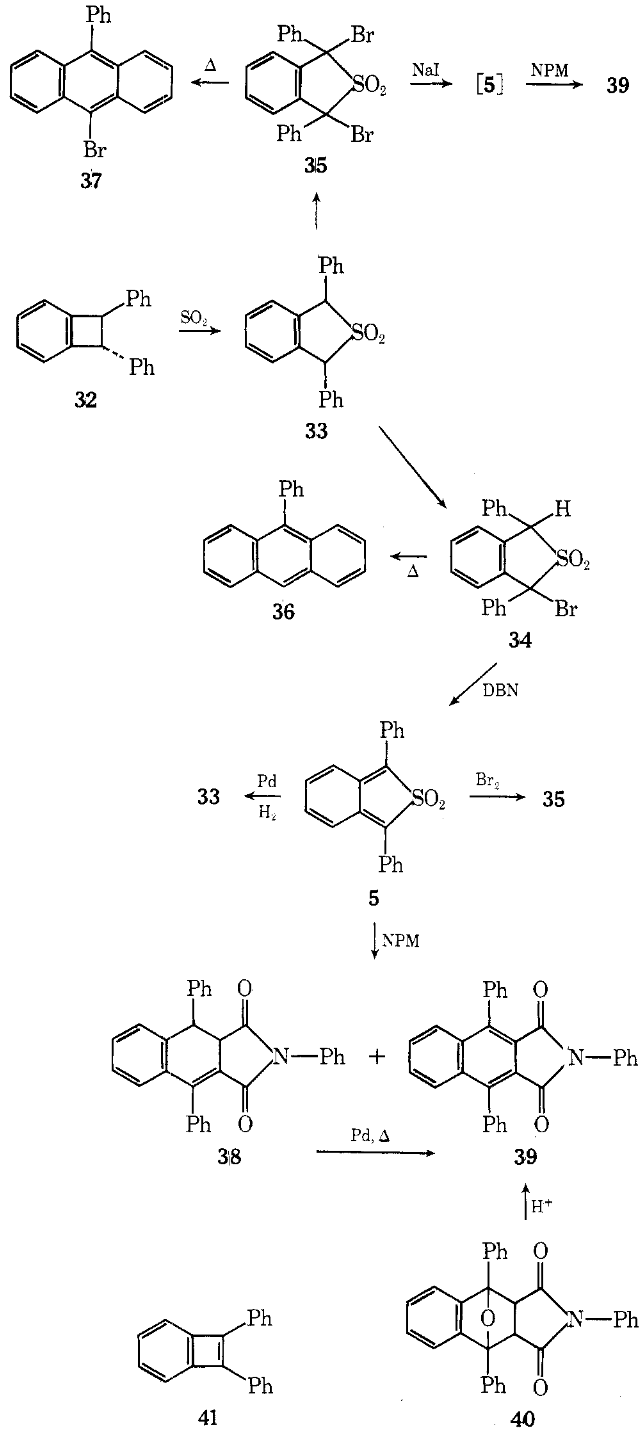
Treatment of monobromo sulfone **34** with a wide variety of bases (*i.e.*, alumina, triethylamine, potassium *tert*-butoxide) produced a purple coloration reminiscent of permanganate; this purple color was attributed to 1,3-diphenylisothianaphthene 2,2-dioxide (**5**) on the basis of the evidence outlined below. Preparatively, the best procedure for preparing **5** involved treatment of bromide **34** with diazabicyclononene (DBN), followed by immediate chromatographic purification on a cooled alumina column. The resulting purple solutions faded after several hours at room temperature, but benzene solutions were essentially unchanged in the frozen state after 1 week. All attempts to isolate the purple sulfone by solvent evaporation caused *discharge of the purple color with the formation of a yellow-orange residue*, from which characterizable constituents were not isolated.

The purple sulfone **5** reacted instantly with *N*-phenylmaleimide (NPM); because of the color change this reaction could be used as a visual titration method for the estimation of the concentration of **5** in a chromatographed solution. In this way also, a value of $\log \epsilon = 2.65$ was determined for the broad visual absorption band of **5** which was centered at 550 nm. A preparative reaction of **5** with NPM gave a difficulty separable mixture of two products. The minor product, $C_{30}H_{21}NO_2$, was assigned the dihydro imide structure **38**; on heating with palladium, it was dehydrogenated to give the major product, $C_{30}H_{19}NO_2$, assigned the structure *N*-1,4-triphenylnaphthalimide (**39**). Imide **39** was identical with material synthesized by the acid dehydration of the adduct (**40**) of NPM and 1,3-diphenylisobenzofuran. The reaction of dibromo sulfone **35** with NPM and sodium iodide also resulted in the formation of imide **39**. The purple color of **5** could be detected when **35** was heated with copper powder in benzene, but this was not a useful method for generating **5** due to the relatively high temperature required.

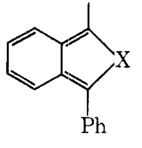
The evidence presented above does not exclude the possibility that the labile purple intermediate from sulfones **34** and **35** may have been the unknown 1,2-diphenylbenzocyclobutadiene (**41**) instead of the unsaturated sulfone **5**. This possibility was eliminated on the basis of two reactions carried out with NPM-analyzed solutions of **5**. In the first reaction, rapid catalytic hydrogenation afforded the parent *cis*-dihydro sulfone **33** in 88% yield. In the second reaction, low temperature addition of bromine afforded the dibromo sulfone **35** in 74% yield.

Discussion

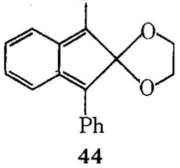
It is clear from the chemistry described above that the isothianaphthene 2,2-dioxide system is highly reactive, like that of thiophene 1,1-dioxide.[3] Direct observation of the long wavelength absorption band of the diphenyl derivative **5** at 550 nm is indicative of some type of sulfonyl conjugation, since the electronically insulated isoindene **42** and the related sulfide **43** have corresponding bands at 444[14] and 388 nm,[4] respectively. At the time of our preliminary report of the generation of **5**,[4] this bathochromic effect in **5** seemed to be an indication of at least a modest degree of d-orbital participation by the sulfonyl sulfur. Subsequently, however, the unstable *o*-quinonoid ketal **44** has been generated and found to have an absorption maximum at



537 nm,[14] a value close to that (550 nm) of **5**. Since the observed conjugation in **44** can only be an example of spiroconjugation,[15] we must revise our earlier opinion[4] and agree with Holland and Jones[14] that spiroconjugation is operative in both **44** and **5**.[16]



42, X = CMe_2
43, X = S



44

In conclusion, it appears that sulfonyl conjugation does exist in the isothianaphthene 2,2-dioxide system but that this effect involves spiroconjugation with the sulfonyl oxygens rather than sulfur d orbital participation. The observed high reactivity of the system is consistent with a spiroconjugation effect.[14,15]

Experimental Section

Melting points are uncorrected. Elemental analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind. The visible spectrum of **5** was determined in benzene solution with a Perkin-Elmer Model 202 spectrophotometer. Nmr spectra were recorded in the indicated solvent (TMS standard) with a Varian A60A spectrometer. Mass spectra and ir spectra (KBr disks) were run using an Atlas CH4 instrument and a Perkin-Elmer Infracord, respectively.

1,3-Dihydro-1,3-dibromoisothianaphthene 2,2-Dioxide (8). A solution of bromine (58 ml of a 0.208 *M* solution) in carbon tetrachloride (150 ml) was added dropwise over 90 min to a refluxing and irradiated (200-W tungsten bulb) solution of 1,3-dihydroisothianaphthene 2,2-dioxide (**6**, 1.0 g)[5,6] in carbon tetrachloride (150 ml). After an additional 30 min of refluxing and irradiation, the solvent was removed *in vacuo* and the product (2.2 g) was crystallized by the addition of 15 ml of 1:1 benzene-cyclohexane. Recrystallization from the same solvent gave pure **8** (1.7 g, 89%): mp 137–138°; nmr ($CDCl_3$) δ 4.42 (s, 2 H).

Anal. Calcd for $C_8H_6Br_2SO_2$: C, 29.45; H, 1.84; Br, 49.15. Found: C, 29.49; H, 1.94; Br, 49.45.

Pyrolysis of 1,3-Dihydro-1,3-dibromoisothianaphthene 2,2-Dioxide (8). Sulfone **8** (0.500 g) was slowly sublimed from a warm flask by a slow nitrogen stream (5 mm pressure), the gas stream being led over a Nichrome wire heated to 400°. The pyrolysate was trapped on a Dry Ice cold finger and purified by ptlc (silica; 1:3 benzene–cyclohexane). White crystals of *trans*-1,2-dibromobenzocyclobutene (**10**, 0.085 g, 22%), mp 52–54° (lit.[17] mp 52–53°), were obtained, which were identical (ir, mixture melting point) with authentic material.

Reaction of 1,3-Dihydro-1,3-dibromoisothianaphthene 2,2-Dioxide (8) with *N*-Phenylmaleimide and Triethylamine. A solution of sulfone **8** (0.050 g) and *N*-phenylmaleimide (0.052 g) in benzene (50 ml) and triethylamine (10 ml) was stirred for 1 day at room temperature under nitrogen. Evaporation of the filtered solution and chromatography of the residue on silica (3:1 benzene–chloroform) afforded *N*-phenyl-2,3-naphthalimide (**15**, 0.036 g, 88%), mp 270–275°, identical (ir, mixture melting point) with authentic material.[8]

1,1,3,3-Tetrabromoisothianaphthene 2,2-Dioxide (7). A solution of bromine (24 g) in carbon tetrachloride (150 ml) was added over 3 hr to a refluxing and irradiated (200-W tungsten bulb) suspension of 1,2-dihydroisothianaphthene 2,2-dioxide (**6**, 5.0 g) in carbon tetrachloride (150 ml). After an additional 3 days of irradiation and refluxing, the solution was evaporated *in vacuo* and the residue was taken up in benzene and decolorized with charcoal. Crystallization from benzene–cyclohexane gave the tetrabromo sulfone **7** (8.5 g, 69%), mp 177–179°.

Anal. Calcd for $C_8H_4Br_4O_2S$: C, 19.72; H, 0.83; Br, 66.20. Found: C, 20.15; H, 0.91; Br, 65.93.

Pyrolysis of 1,1,3,3-Tetrabromoisothianaphthene 2,2-Dioxide (7). Tetrabromo sulfone **7** (0.500 g) was pyrolyzed as described for the dibromo sulfone **8**. Purification of the pyrolysate by ptlc (neutral alumina; benzene–cyclohexane 1:1) gave, after crystallization from methanol, 1,1,2,2-tetrabromobenzocyclobutene (**9**, 0.110 g, 24%), mp 117–119° (lit.[18] mp 117–118°), identical (ir) with authentic material.

Reaction of 1,1,3,3-Tetrabromoisothianaphthene 2,2-Dioxide (7) with *N*-Phenylmaleimide and Sodium Iodide. A solution of sodium iodide (7.0 g) in dry dimethylformamide (100 ml) was added dropwise at room temperature (nitrogen atmosphere) to a stirred solution of tetrabromo sulfone **7** (3.0 g) and *N*-phenylmaleimide (2.0 g) in dimethyl sulfoxide (10 ml) and dimethylformamide (150 ml). After stirring for an additional 3 days, the mixture was poured into cold water (150 ml) and the free iodine was reduced by adding sodium sulfite. The precipitated solid was recrystallized from chloroform to give white crystals of adduct **20** (3.5 g, 93%), mp 360°: mass spectrum *m/e* 606 (M^+); nmr (DMSO-d_6) δ 4.08 (s, 4 H), 6.38–6.55 (m, 4 H), 7.25–7.55 (m, 10 H).

Anal. Calcd for $C_{28}H_{18}Br_2N_2O_4$: C, 55.45; H, 2.97; Br, 26.41. Found: C, 55.13; H, 2.91; Br, 25.07.

Zinc Reduction of 1,1,3,3-Tetrabromoisothianaphthene 2,2-Dioxide (7). A mixture of tetrabromo sulfone **7** (1.00 g), activated zinc dust (5 g), and ethanol (150 ml) was refluxed (nitrogen) until tlc showed the disappearance of starting material (2 days). Evaporation of the filtered solution, followed by crystallization from methanol and recrystallization from benzene–cyclohexane, gave the debrominated sulfone **6** (0.285 g, 82%), mp 148–150°.

Exo and Endo Sulfones 25 and 26. The exo and endo isothianaphthene adducts **23** and **24** were prepared as described earlier.[9] A mixture of exo adduct **23** (3.0 g) and 40% peracetic acid (100 ml) was stirred for 15 hr at room temperature. The precipitated solid was recrystallized from benzene–hexane to give, in two crops, exo sulfone **25** (3.2 g, 97%): mp 169–171°; nmr (CF_3CO_2D) δ 3.60 (s, 2 H), 5.40 (s, 2 H), and 7.15–7.80 (m, 9 H).

Anal. Calcd for $C_{18}H_{13}NO_4S$: C, 63.75; H, 3.83; N, 4.13. Found: C, 63.57; H, 3.96; N, 4.12.

By an identical procedure, endo adduct **24** (0.60 g) gave pure endo sulfone **26** (0.60 g, 91%): mp 178–181°; nmr (CF_3CO_2D) δ 4.02 (d of d, 2 H), 5.35 (d of d, 2 H), 6.22 (m, 2 H), and 7.10–7.40 (m, 7 H).

Anal. Calcd for $C_{18}H_{13}NO_4S$: C, 63.75; H, 3.83; N, 4.13. Found: C, 63.75; H, 3.96; N, 4.12.

Pyrolysis of Exo and Endo Sulfones 25 and 26. A mixture of exo sulfone **25** (0.150 g) and triethylene glycol dimethyl ether (10 ml) was heated for 30 min at 120° and then at 150–180° for 15 min. The solid which separated on cooling was crystallized from benzene–chloroform to give a mixture of dimers **27** and **28** (0.080 g, 66%), mp 360°. (See Discussion for nmr.)

The identical mixture of **27** and **28** was obtained from endo sulfone **26** in 63% yield under similar conditions.

Anal. Calcd for $C_{36}H_{26}N_2O_4$: C, 78.50; H, 4.73; N, 5.09. Found: C, 78.22; H, 4.81; N, 5.03.

Pyrolysis of Exo and Endo Sulfones 25 and 26 in the Presence of *N*-Phenylmaleimide. A mixture of exo sulfone **25** (0.300 g), *N*-phenylmaleimide (0.600 g), and triethylene glycol dimethyl ether (100 ml) was heated to 180° for 30 min. The cooled solution was poured into water (100 ml) and extracted with chloroform (2 × 100 ml). Evaporation of the dried extract, followed by trituration with pentane, gave a precipitate which was purified by ptlc (silica; benzene–chloroform 1:2), giving white crystalline adduct **30** (0.120 g, 40%): mp 328–330°; nmr (CF_3CO_2H) δ 3.35 (s, 4 H), 3.88 (s, 2 H), 5.8–6.0 (m, 4 H), and 6.6–6.9 (m, 10 H).

The same adduct **30** was obtained in similar yield from endo sulfone **26** under the same conditions.

Anal. Calcd for $C_{28}H_{20}N_2O_4$: C, 75.00; H, 4.46; N, 6.25. Found: C, 74.92; H, 4.62; N, 6.29.

Reaction of Exo and Endo Sulfones 25 and 26 with Triethylamine. Exo sulfone **25** (0.150 g) was stirred under nitrogen with degassed benzene (50 ml), and triethylamine (3 ml) was added through a serum cap; addition of the amine produced an immediate greenish-yellow color and a strong fluorescence. After stirring for 24 hr at room temperature, the product was worked up in the usual manner, followed by ptlc purification (silica; benzene–chloroform 3:1) to give *N*-phenyl-2,3-naphthalimide (**15**, 0.040 g, 33%), mp 275–278° (lit.[8] mp 284–285°), identical with an authentic sample. The same imide **15** was obtained in similar yield from endo sulfone **26** under the same conditions.

Ultraviolet irradiation did not alter the course of this reaction. Thus, when the above experiment was repeated with either exo sulfone **25** or endo sulfone **26** under irradiation conditions (Hanovia high pressure lamp, Pyrex filter), imide **15** was isolated in 67 and 80% yield, respectively.

The reaction of the exo sulfone **25** (0.150 g) with triethylamine (4 ml) in benzene (50 ml) was repeated (30 hr, nitrogen) in the presence of *N*-phenylmaleimide (0.080 g). Direct crystallization of the reaction product from chloroform gave the diimide adduct **30** (0.045 g, 66%), mp 328–330°.

Attempted Reaction of 1,3-Dihydroisothianaphthene 2,2-Dioxide (6) with Triethylamine. A mixture of sulfone **6** (0.300 g), *N*-phenylmaleimide (0.320 g), triethylamine (5 ml), and benzene (75 ml) was refluxed for 4 days. Solvent evaporation, followed by silica chromatography (benzene–cyclohexane 1:1), gave only recovered *N*-phenylmaleimide (0.302 g, 94%) and recovered sulfone **6** (0.285 g, 95%).

***cis*-1,3-Dihydro-1,3-diphenylisothianaphthene 2,2-Dioxide (33).** This compound was prepared by the following modification of the literature method.[10] A stream of sulfur dioxide was passed through a solution of *trans*-1,2-diphenylbenzocyclobutene (4.80 g) in ether (50 ml) at room temperature for a period of 1 hr. The precipitated solid was recrystallized from methylene chloride–petroleum ether to give, in two crops, sulfone **33** (4.80 g, 82%), mp 233–235° (lit.[10] mp 232–234°).

1,3-Dihydro-1-bromo-1,3-diphenylisothianaphthene 2,2-Dioxide (34). A solution of bromine (0.513 g) in carbon tetrachloride (100 ml) was added dropwise over 2 hr to a refluxing and irradiated (200-W tungsten bulb) solution of *cis*-sulfone **33** (1.00 g) in carbon tetrachloride (150 ml). After an additional 30 min of refluxing and irradiation, the solvent was removed *in vacuo* and the product was crystallized by the addition of 1:2 benzene–cyclohexane. Two recrystallizations from benzene gave pure bromo sulfone **34** (0.700 g, 58%): mp 198–200°; nmr ($CDCl_3$) δ 5.23 (s, 1 H), 7.2–7.8 (m, 14 H).

Anal. Calcd for $C_{20}H_{15}BrO_2S$: C, 60.15; H, 3.76; Br, 20.05. Found: C, 59.95; H, 3.81; Br, 20.16.

Pyrolysis of 1,3-Dihydro-1-bromo-1,3-diphenylisothianaphthene 2,2-Dioxide (34). Sulfone **34** (0.300 g) was slowly sublimed from a warm flask by a slow stream of nitrogen (8 mm pressure), the gas stream being led over a Nichrome wire heated to 350°. The pyrolysate, which was collected on a Dry Ice–acetone cold finger, was purified by ptlc (neutral alumina, benzene) to give 9-phenylanthracene (**36**, 0.100 g, 53%), mp 151–152° (lit.[13] mp 154–156°), identical (ir, mixture melting point) with an authentic sample.

1,4-*N*-Triphenyl-2,3-naphthalimide (39). A mixture of 1,3-diphenylisobenzofuran (0.300 g), *N*-phenylmaleimide (0.200 g), and benzene (25 ml) was refluxed for 1 hr at room temperature. Evaporation of the solvent, followed by chromatography (silica; benzene–chloroform 1:1), afforded adduct **40** as white crystals (0.400 g, 91%), mp 205–207°.

Anal. Calcd for $C_{30}H_{21}NO_3$: C, 81.25; H, 4.74; N, 3.16. Found: C, 81.06; H, 4.99; N, 3.19.

Adduct **40** (0.100 g) was added to concentrated sulfuric acid (10 ml) at 0°. After 10 min, the yellow solution was poured into ice water (100 ml) and the precipitate was crystallized from benzene–chloroform 1:1 to give imide **39** (0.90 g, 92%), mp 292–293°.

Anal. Calcd for $C_{30}H_{21}NO_3$: C, 84.75; H, 4.48; N, 3.29. Found: C, 84.80; H, 4.50; N, 3.19.

Generation and Reactions of 1,3-Diphenylisothianaphthene 2,2-Dioxide (5). (a) Reaction of 5 with *N*-Phenylmaleimide. A solution of diazabicyclononene (DBN, 1.92 g) in benzene (50 ml) was added dropwise under nitrogen to a stirred solution of bromo sulfone **34** (2.00 g) and *N*-phenylmaleimide (1.92 g) in degassed benzene (100 ml). Each drop of base produced a purple color which was discharged almost immediately. After an additional 1 hr of stirring, the mixture was acidified by adding 10% sulfuric acid (75 ml). The usual work-up of the organic phase, followed by crystallization from benzene–methylene chloride, gave a crystalline mixture (1.11 g, 52%) of adducts **38** and **39**. An aliquot was separated by ptlc (silica; benzene–chloroform 1:1) to give the two crystalline components. The first component, mp 292–293°, was identical (ir, mp) with the naphthalimide **39** prepared from 1,3-diphenylisobenzofuran (see above). The second component, mp 180–185°, was the dihydro imide **38**.

Anal. Calcd for $C_{30}H_{21}NO_2$: C, 84.29; H, 4.92. Found: C, 84.32; H, 4.83.

Dehydrogenation of dihydro imide **38** was accomplished by heating a sample (0.050 g) with an equal weight of 10% palladium–charcoal for 1 hr at 250–290° under nitrogen. Sublimation of the product, followed by crystallization from benzene, afforded the naphthalimide **39** (0.035 g, 70%), mp 292–293°, identical (ir, mp) with an authentic sample.

(b) Hydrogenation of 5. Diazabicyclononene (0.340 g) was added in one portion to a degassed mixture of bromo sulfone **34** (0.519 g), benzene (10 ml), and chloroform (3 ml). After 3 min, the deep purple solution was chromatographed on a column prepared from neutral alumina and deoxygenated cold benzene. The column was eluted rapidly with benzene under pressure, the purple band being collected and made up to 100 ml with benzene. One quarter of the purple solution was removed and titrated visually with *N*-phenylmaleimide in benzene, indicating formation of the purple sulfone in about 64% yield. The remainder of the purple solution was hydrogenated at once (hydrogen at 40 psi) using 200 mg of 5% palladium–charcoal as catalyst. After 10 min, the colorless solution was worked up and purified by silica chromatography (benzene–chloroform 1:1 eluent) to give white crystals of *cis*-1,3-dihydro-1,3-diphenylisothianaphthene 2,2-dioxide (**33**, 0.175 g, 88%), mp 234–236°, identical (ir, mp) with an authentic sample.

(c) Addition of Bromine to 5. A solution of chromatographed purple sulfone **5** was prepared from bromo sulfone **34** (0.400 g) and DBN (0.248 g) in the general manner described in the above hydrogenation experiment; *N*-phenylmaleimide titration of one quarter of the solution indicated a 50% yield of **5** from bromo sulfone **34**. The remainder of the purple solution was cooled quickly to −67° (Dry Ice–methylene chloride) and bromine (0.16 g) was added. After warming to room temperature, the usual work-up, followed by ptlc (silica; benzene–chloroform 1:1) afforded white crystals (0.179 g, 74%) of the high melting isomer of dibromo sulfone **35**, mp 225–227°, identical with material prepared by the bromination of *cis*-1,3-dihydro-1,3-diphenylisothianaphthene 2,2-dioxide (**33**).

Anal. Calcd for $C_{20}H_{14}Br_2O_2S$: C, 50.20; H, 2.92; Br, 33.47. Found: C, 50.41; H, 3.08; Br, 33.19.

1,3-Dibromo-1,3-diphenylisothianaphthene 2,2-Dioxide (35). A solution of bromine (0.50 g) in carbon tetrachloride (100 ml) was added dropwise over 2 hr to a refluxing and irradiated (200-W tungsten bulb) solution of *cis*-sulfone **33** (0.50 g) in carbon tetrachloride (150 ml). After an additional 1 hr of refluxing and irradiation, solvent removal, chromatography on alumina (benzene), and repeated crystallization from benzene gave 0.300 g (41%) of dibromo sulfone **35**, mp 225–227°, identical with the bromine addition product of purple sulfone **5** (see above). The benzene mother liquors gave a further 200 mg (27%) of crystals, mp 215–217°; this material was slightly different spectrally (ir, nmr) and appeared to be an impure stereoisomer of the 225° dibromide.

Reactions of 1,3-Dibromo-1,3-diphenylisothianaphthene 2,2-Dioxide (35). (a) With Sodium Iodide. Sodium iodide (0.4 g) in dry dimethylformamide (15 ml) was added to a solution of dibromo sulfone **35** (1.00 g) and *N*-phenylmaleimide (0.40 g) in dry dimethylformamide (30 ml) under nitrogen at room temperature. After 10 hr, the reddish solution was poured into water and the product was worked up in the usual manner, iodine being removed by a sodium sulfite wash. After silica chromatography (benzene–chloroform 1:1), crystallization from benzene–pentane gave, as white crystals (0.325 g, 37%), triphenylnaphthalimide **39**, mp 292–293°, identical (ir, mp) with material prepared (see above) from 1,3-diphenylisobenzofuran.

(b) Pyrolysis. Dibromo sulfone **35** (0.500 g) was pyrolyzed as described for monobromo sulfone **34**; the hot wire temperature was 400°. Purification by ptlc (silica, benzene) gave, after crystallization from benzene, yellow crystals (0.075 g) of 9-bromo-10-phenylanthracene (**37**), mp 145–147°.

Anal. Calcd for $C_{20}H_{13}Br$: C, 72.01; H, 4.13; Br, 23.61. Found: C, 72.58; H, 4.36; Br, 23.96.

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Registry No.—**5**, 23398-54-1; **6**, 2471-91-2; **7**, 53092-82-3; **8**, 53092-83-4; **9**, 26448-34-0; **10**, 14420-75-8; **15**, 21815-18-9; **20**, 53092-60-7; **23**, 13129-12-9; **24**, 13129-13-0; **25**, 53092-61-8; **26**, 53152-37-7; **27**, 53092-62-9; **28**, 5312-38-8; **30**, 53092-63-0; **33**, 53152-39-9; **34**, 21815-15-6; **35**, 21815-16-7; **36**, 602-55-1; **37**, 23674-20-6; **38**, 21815-17-8; **39**, 4209-87-4; **40**, 27594-00-9; *N*-phenylmaleimide, 941-69-5; triethylamine, 121-44-8; sodium iodide, 7681-82-5.

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Preparation and Basicities of Substituted *N,N*-Diethyl- and *N,N*-Dimethylaniline Oxides[1]

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Twelve *meta*- and *para*-substituted *N,N*-dimethylanilines and eleven similar *N,N*-diethylanilines and the corresponding *N*-oxides have been prepared. pK_a values of the amine oxides in water have been determined. They were very well correlated in the Hammett equation *vs.* σ^n, indicating that there is little or no conjugation from the ring through the nitrogen to the oxygen. The ρ values are entirely consistent with a reaction center one atom removed from the benzene ring (ρ = 0.907 for the dimethyl case and ρ = 0.91 for the diethyl case).

In contrast with heterocyclic amine oxides the chemistry of *N,N*-dialkylated aniline oxides has remained largely undeveloped since the original studies of Bamberger,[3] with the exception of the Polonovski reaction[4-7] (*N,N*-dimethylaniline oxide plus acetic anhydride).

Amine oxides are unusual both in their physical properties and in the variety of chemical reactions they can undergo. The reactions of dialkylaniline oxides that have been observed, but for which there are no modern, published mechanistic studies, are the Cope elimination,[8] the rearrangements observed upon treatment with nitrous[2,9] or sulfurous acids,[2,10,11] the deoxygenations and/or rearrangements resulting from treatment with various nonmetal oxides[12] and chlorides,[13] and deoxygenation with alkyl halides.[14,15] The rates of reaction of substituted *N,N*-dialkylaniline oxides can be used to obtain information about the mechanistic nature of these reactions. Since the kinetic behavior of *N*-oxides in protic solvents must involve acid–base ionization, the values of the K_a's must be known before actual rate constants can be determined.

A continuing interest in these compounds, their reactions, and the mechanics of their reactions led to the syntheses and pK_a studies of *N,N*-dimethylaniline oxides (**3**) and *N,N*-diethylaniline oxides (**4**) described here.