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On Fragmentation of Aryl Sulfide Radical Anions during Aromatic SRN1 Reactions¹

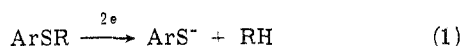
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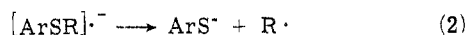
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The photostimulated reaction of ethanethiolate ion with iodobenzene in liquid ammonia produces not only ethyl phenyl sulfide but also thiophenoxide ion and diphenyl sulfide. This shows that the presumed intermediate in the SRN1 mechanism, the ethyl phenyl sulfide radical anion, fragments in part into ethyl radical and thiophenoxide ion. The reactions of *p*-iodoanisole with thiophenoxide ion and of iodobenzene with *p*-methoxythiophenoxide ion both produce phenyl *p*-methoxyphenyl sulfide in good yield without any detectable amount of symmetrical diaryl sulfide, indicating that the phenyl *p*-methoxyphenyl sulfide radical anion intermediate does not fragment appreciably in this system. Reactions of four unsymmetrical phenyl aryl sulfides with acetone enolate ion afford more *m*-methyl-, *p*-methyl-, *m*-methoxy-, or *p*-methoxyphenylacetone than phenylacetone.

Diaryl sulfides and alkyl aryl sulfides are cleaved cathodically or by alkali metals to form an arenethiolate ion and a hydrocarbon (eq 1), the necessary hydrogen atom being derived from the solvent.²⁻⁷

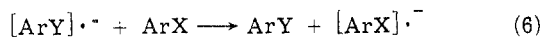
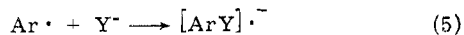
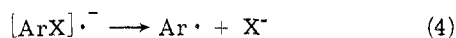
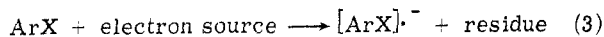


Both stoichiometry⁶ and polarographic data⁷ indicate a two-electron process. However, there is evidence that an alkyl⁶ or aryl⁸ radical is formed as a primary cleavage fragment, as well as the arenethiolate ion. It follows that the aryl sulfide radical anion is the entity which actually fragments (eq 2).



In aromatic substitution by the SRN1 mechanism,⁹ the radical anions of aryl sulfides sometimes appear as intermediates.¹⁰⁻¹⁴ In Scheme I, this radical chain mechanism is

Scheme I



presented in generalized form.¹⁵ When a diaryl sulfide is involved as substrate (ArX), the fragmentation of its radical anion, [ArX]^{·-}, occurs in step 4. When a thiolate ion is involved as nucleophile (Y⁻), the species [ArY]^{·-} formed in step 5 is an aryl sulfide radical anion, and conceivably it might suffer fragmentation before transferring an electron to another substrate molecule in step 6.

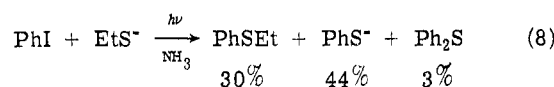
In the present investigation, we address a number of questions suggested by this discussion. If an alkanethiolate

ion is employed as nucleophile Y⁻, will radical anion [ArY]^{·-} fragment before it loses its "extra" electron? If an arenethiolate nucleophile, Ar'S⁻, is employed, with an aryl group different from that in substrate ArX, will the radical anion [ArSAr']^{·-} formed in step 5 fragment to Ar'· and ArS⁻, leading eventually to products Ar₂S and/or Ar'Ar₂S as well as ArSAr'? If an unsymmetrical diaryl sulfide, ArSAr', is used as substrate in photostimulated reaction with acetone enolate ion,¹¹ in what proportions will the two arylacetones ArCH₂COCH₃ and Ar'CH₂COCH₃ be formed? Inasmuch as each of these questions has required separate investigation, we shall present and discuss the results from each before moving on to the next.

I. Reaction of Iodobenzene with Ethanethiolate Ions. Although the photostimulated reaction of iodobenzene with excess thiophenoxide ion in ammonia is quite fast, giving a nearly quantitative yield of diphenyl sulfide in 70 min,¹² that of iodobenzene with ethanethiolate ion is much slower. Under similar conditions, only 60% of iodide ion was released in 90 min. The products from an extended (200 min) reaction included 30% of ethyl phenyl sulfide and 3% of diphenyl sulfide.

Formation of the latter product suggested the intermediacy of thiophenoxide ion. A further run was performed under the same conditions, the ammonia was allowed to evaporate, and ethyl iodide was added to convert any thiophenoxide ion to ethyl phenyl sulfide. The yield of the latter was thereby raised to 61%, supporting the hypothesis. In a further experiment of similar type, benzyl chloride was added to benzylate the thiophenoxide ion, and 44% of benzyl phenyl sulfide was formed.

The reaction of iodobenzene with ethanethiolate ion, in ammonia under irradiation, thus gives products as indicated in eq 8.



This result is interpreted as follows. Combination of phenyl radical with EtS^- in step 5, Scheme I, forms the ethyl phenyl sulfide radical anion, $[\text{PhSEt}]^-$. In part this transfers an electron to an iodobenzene molecule (step 6), and emerges as ethyl phenyl sulfide. In part it expels ethyl radical, and the resulting thiophenoxide ion reacts partially with iodobenzene by the SRN1 mechanism to form diphenyl sulfide. Much of the thiophenoxide ion, which is generated amid an excess of ethanethiolate ion, does not react but can later be captured by reaction with ethyl iodide or benzyl chloride.

The fate of the expelled ethyl radical is unclear. Many modes of reaction are conceivable. Most of them lead eventually to termination of the radical chain, and therefore to depression of overall reactivity. In these terms one comprehends why ethanethiolate is less reactive than thiophenoxide ion with iodobenzene.

We call attention to some similarity between this ethanethiolate ion reaction and the photostimulated reaction of the cyanomethyl anion with bromobenzene.¹⁷ The latter reaction is also slow, owing to fragmentation of the phenylacetonitrile radical anion to benzyl radical and cyanide ion. The benzyl radical engages in termination steps.

It is noteworthy that the SRN1 mechanism (Scheme I) provides a straightforward interpretation of the phenomenon represented in eq 8, one that is consistent with published information on the reductive cleavage of alkyl phenyl sulfides.²⁻⁸ This constitutes a further instance in which this mechanistic hypothesis has accommodated observations never anticipated when it was formulated.

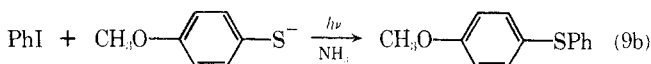
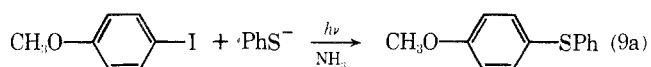
II. Reactions of Aryl Iodides with Arenethiolate Ions. According to the SRN1 mechanism, the same radical anion intermediate should be formed by reaction of ArI with PhS^- as by reaction of PhI with ArS^- , where Ar represents an aryl group other than phenyl. If the experiment is performed both ways, and if there is appreciable fragmentation of $[\text{ArSPh}]^-$, at least one of the symmetrical diaryl sulfides, Ar_2S and Ph_2S , should appear in one experiment or the other.

Let us consider starting with ArI and PhS^- . If $[\text{ArSPh}]^-$ does not fragment as fast as it transfers an electron in step 6, or if it fragments only in the sense of reverting to $\text{Ar}\cdot$ and PhS^- , only the unsymmetrical diaryl sulfide will be formed. On the other hand, if $[\text{ArSPh}]^-$ fragments into $\text{Ph}\cdot$ and ArS^- appreciably, the $\text{Ph}\cdot$ can combine with PhS^- to form $[\text{Ph}_2\text{S}]^-$ and ultimately Ph_2S , and the ArS^- can be attacked by $\text{Ar}\cdot$ (from ArI) to form $[\text{Ar}_2\text{S}]^-$ and ultimately Ar_2S . However, if PhS^- is present in excess over ArI , the latter behavior may be difficult to detect because of the statistical preference for combination of $\text{Ar}\cdot$ with the more abundant thiolate ion.

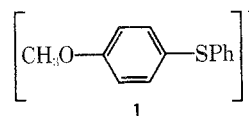
If only ArSPh is formed from ArI and PhS^- because, although $[\text{ArSPh}]^-$ fragments, it does so only to $\text{Ar}\cdot$ and PhS^- , some symmetrical diaryl sulfide(s) should, however, be obtained starting from PhI and ArS^- .

For the experiment to be meaningful, it must also be demonstrated that the symmetrical diaryl sulfides are formed from $\text{ArI} + \text{ArS}^-$ and from $\text{PhI} + \text{PhS}^-$.

In conducting this experiment, we chose *p*-iodoanisole and *p*-methoxythiophenoxide ion as ArI and ArS^- . From their photostimulated reaction with each other we obtained bis(*p*-methoxyphenyl) sulfide in 73% yield. Iodobenzene and thiophenoxide are known to form diphenyl sulfide in 94% yield.¹² *p*-Iodoanisole and potassium thiophenoxide gave 76% of phenyl *p*-methoxyphenyl sulfide, but not a trace of either of the symmetrical diaryl sulfides (eq 9a). The same product was obtained from reaction of iodobenzene with *p*-methoxythiophenoxide ion (eq 9b), again without any symmetrical diaryl sulfide.

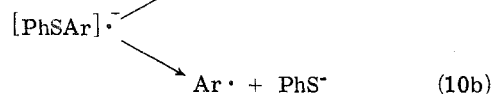
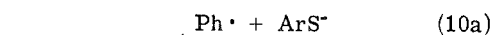


We conclude that in these reactions the intermediate radical anion, 1, transfers an electron to *p*-iodoanisole (eq



9a) or iodobenzene (eq 9b) in step 6 faster than it fragments.

Cleavage of phenyl *p*-methoxyphenyl sulfide by sodium in ammonia or lithium in methylamine is reported to furnish 100% of thiophenol but no *p*-methoxythiophenol.⁴ The implication is that 1 does indeed fragment in the absence of an electron acceptor, such as an aryl iodide, and that it does so in the sense of eq 10b.



III. Reactions of Unsymmetrical Diaryl Sulfides with Acetone Enolate Ions. When an unsymmetrical diaryl sulfide undergoes photostimulated SRN1 reaction with acetone enolate ion, the radical anion of the sulfide is an intermediate and in principle it can split to give either of two pairs of aryl radical and arenethiolate ion (eq 10). The radicals are rapidly captured by acetone enolate ion with ultimate formation of arylacetones.⁸ The relative yields of phenylacetone and the other arylacetone provide a measure of the relative tendencies of the radical anion to sunder in the two ways shown.

This experiment was performed with four different aryl phenyl sulfides. The results are summarized in Table I. An attempt also to perform it with 1-naphthyl phenyl sulfide was frustrated by the very low solubility of this substance in liquid ammonia.

In all cases the yield of phenylacetone is less than of the arylacetone derived from the other aryl moiety in the sulfide employed. This indicates that fragmentation in the sense of eq 10b is favored over that according to eq 10a when Ar is a *m*- or *p*-tolyl or *m*- or *p*-methoxyphenyl group.

On the presumption that transition state theory applies to this situation and that the transition state for fragmentation has some of the character of the products of fragmentation, the preference for route 10b over 10a might arise either from greater stability of $\text{Ar}\cdot$ over $\text{Ph}\cdot$ radical, or of lesser stability of ArS^- as compared to PhS^- anion. The latter factor might be invoked in three of the cases studied, for *m*- and *p*- CH_3 and *p*- OCH_3 increase the $\text{p}K_a$ of thiophenol, but *m*-methoxythiophenol has a lower $\text{p}K_a$ than thiophenol itself.¹⁹ Perhaps substituent effects on aryl radical stability are the more important consideration.

Whatever determines the sense of cleavage of $[\text{PhSAr}]^-$, the preference for route 10b over 10a is not very great. The product yield ratio, $\text{ArCH}_2\text{COCH}_3/\text{PhCH}_2\text{COCH}_3$, varies from 1.2 to 3.1. If transition state theory applies, the difference in free energy between the two fragmentation transition states is at greatest 0.54 kcal/mol.

The cleavage of the four aryl phenyl sulfides of Table I with lithium in methylamine or sodium in ammonia was re-

Table I
Photostimulated Reactions of Unsymmetrical Diaryl Sulfides with Acetone Enolate Ion in Liquid Ammonia

Sulfide	Registry no.	Irradiation time, min	Products, %		Registry no.
			Phenylacetone (103-79-7)	Other arylacetone	
<i>m</i> -CH ₃ C ₆ H ₄ SC ₆ H ₅	13865-48-0	105	39	48 ^a	18826-61-4
<i>p</i> -CH ₃ C ₆ H ₄ SC ₆ H ₅	3699-01-2	105	28	38 ^b	2096-86-8
<i>m</i> -CH ₃ OC ₆ H ₄ SC ₆ H ₅	30723-54-7	75	28	49 ^c	3027-13-2
<i>p</i> -CH ₃ OC ₆ H ₄ SC ₆ H ₅	5633-57-8	90	16	50 ^d	122-84-9

^a *m*-Tolylacetone. ^b *p*-Tolylacetone. ^c *m*-Methoxyphenylacetone. ^d *p*-Methoxyphenylacetone.

ported by Truce, Tate, and Burdge.⁴ For the most part the sense of fragmentation indicated by their studies is qualitatively in agreement with that shown by ours, but the indicated ratios of rupture by paths 10a and 10b differ in quantitative detail.

Ethyl phenyl sulfide was found not to react appreciably with acetone enolate ion under irradiation for 60 min; most of the sulfide remained unreacted. Benzyl phenyl sulfide for the most part survived exposure to acetone enolate ion during 50 min irradiation, and no products with the GLC behavior of phenylacetone or 4-phenyl-2-butanone could be found, though traces of some products did appear, one of them perhaps toluene.

Experimental Section

Reaction of Iodobenzene with Potassium Ethanethiolate. A solution of potassium *tert*-butoxide (*t*-BuOK) in 130 ml of liquid ammonia was prepared from 1.45 g of *tert*-butyl alcohol and 0.75 g of potassium metal with a trace of ferric nitrate. Ethanethiol (1.2 g) was added followed by 0.987 g of iodobenzene. The entire procedure was carried out under nitrogen. The mixture was irradiated under reflux and under a slow stream of nitrogen for 200 min in a Rayonet Model RPR-100 photochemical reactor equipped with 16 ca. 24-W fluorescent lamps emitting maximally at 350 nm. The ammonia was allowed to evaporate and the residue was taken up into diethyl ether and water. The organic phase was separated and dried over anhydrous Na₂SO₄, and the yields of phenyl ethyl sulfide and diphenyl sulfide were determined by GLC on a 1.22-m column of 10% SE-54 silicone rubber on Chromosorb P with diphenyl ether being used as internal standard. Samples of these two products were isolated by GLC and identified by comparison of infrared spectra and GLC retention times with those of authentic samples.

In a similar run, 25 ml of ethanol and 6 ml of ethyl iodide were added after evaporation of the ammonia, the mixture was heated at reflux for 1 hr, the ethanol was removed by evaporation, water and ether were added, and ethyl phenyl sulfide was determined by GLC as above; the yield was 61%.

In a third similar run, after evaporation of the ammonia, 25 ml of ethanol and 3.6 g of benzyl chloride were added, the mixture was heated at reflux for 1.5 hr, water and ether were added, and benzyl phenyl sulfide was determined by GLC to be present in 44% yield, the internal standard being 1-naphthyl phenyl sulfide.

Reactions of Aryl Iodides with Arenethiolate Ions. A solution of 1.02 g of *p*-iodoanisole, 1.55 g of thiophenol and 1.65 g of *t*-BuOK in ca. 125 ml of liquid ammonia, with the *p*-iodoanisole not entirely dissolved, was irradiated in the photochemical reactor (vide supra) for 30 min, during which time the *p*-iodoanisole dissolved. The residue from evaporation of the ammonia was taken up in ether and water, and the ether layer was dried over anhydrous Na₂SO₄ and the solvent removed by evaporation. GLC analysis of the residue on the above column at 200° revealed the presence of a small amount of anisole, about 10% of *p*-iodoanisole, and a major product of longer retention time, but no trace of diphenyl sulfide. Distillation of the residue at reduced pressure afforded 0.69 g (76%) of phenyl *p*-methoxyphenyl sulfide: ¹H NMR (60 MHz, CCl₄) δ 3.78 (s, CH₃), 6.90 (d, *J* = 9 Hz), 7.25 (pseudosinglet, C₆H₅), 7.48 (d, *J* = 9 Hz).

By a similar reaction of iodobenzene with ammonium *p*-methoxythiophenoxide with 120-min irradiation, a substance of identical infrared spectrum, bp 118–120° (0.05 Torr), was obtained in 71% yield; GLC analysis of the crude product indicated about 10% of unreacted iodobenzene and about 5% of a material with reten-

tion time similar to that of the main product, probably the ortho isomer thereof, but no trace of bis(*p*-methoxyphenyl) sulfide.

By a similar reaction of *p*-iodoanisole with potassium *p*-methoxythiophenoxide with 100-min irradiation, a crude product was obtained, GLC analysis of which indicated about 10% of anisole, a little unreacted *p*-iodoanisole, and a major product peak. By distillation at reduced pressure, 73% of bis(*p*-methoxyphenyl) sulfide was obtained. The ¹H NMR spectrum agreed with that reported by Fujisawa and Tsuchihashi.²⁰ The mass spectrum showed a predominant peak at *m/e* 246 (the main product) and substantial peaks at *m/e* 231 and 139, as well as a lesser but significant peak at *m/e* 278 (bis-*p*-methoxyphenyl disulfide).

Reactions Summarized in Table I. In a typical reaction, 2.20 g (0.0196 mol) of *t*-BuOK, 1.08 g (0.0186 mol) of acetone, and 0.990 g (0.0046 mol) of phenyl *m*-methoxyphenyl sulfide were dissolved in 150 ml of liquid ammonia, and the mixture was irradiated under reflux in the photochemical reactor described above for 75 min. After standard processing, the product mixture was analyzed by GLC on a 2.44-m column of 3% Carbowax plus 2% Apiezon L with naphthalene and biphenyl being used as internal standards for phenylacetone and *m*-methoxyphenylacetone, respectively.

For calibration of the GLC analysis, authentic samples of *m*-methyl-, *p*-methyl-, *m*-methoxy-, and *p*-methoxyphenylacetone were prepared by photostimulated reactions of the corresponding iodotoluenes or bromoanisoles with acetone enolate ion. *m*-Methylphenylacetone had NMR and ir spectra in agreement with those reported by Thigpen and Fuchs;²¹ MS *m/e* 148 (*M*⁺), 105, 91. *p*-Methylphenylacetone: NMR (CCl₄) δ 2.02 (s, 3 H), 2.45 (s, 3 H), 3.58 (s, 2 H), 7.19 (s, 4 H); ir (film) 1715 (s), 1226 and 1159 (m), 830 and 790 cm⁻¹ (m); MS *m/e* 148 (*M*⁺), 105, 91; the NMR and mass spectra agree with those recorded by Rossi,²² who prepared an authentic sample by the reaction of *p*-methylbenzylcadmium chloride with acetyl chloride. *m*-Methoxyphenylacetone had an NMR spectrum in agreement with two reports in the literature:²³ ir (film) 1705 (s), 1255 (s), 1152 (m), 1055 (m), 781, and 701 cm⁻¹ (m); MS *m/e* 164 (*M*⁺), 121, 107, 91. *p*-Methoxyphenylacetone: NMR (CCl₄) δ 2.01 (s, 3 H), 3.51 (s, 2 H), 3.76 (s, 3 H), 6.7–7.3 (m, 4 H); ir (film) 1705 (s), 1248 (s), 1180 and 1159 (m), 1035 (m), 845 cm⁻¹ (m); MS *m/e* 164 (*M*⁺), 135, 121, 91; the NMR spectrum agrees with that recorded by Rossi,²² who prepared an authentic sample by the method of Heinzelman.²⁴

Acknowledgments. We thank Eric W. Bouldin for technical assistance, and Dr. R. P. Traber for advice.

Registry No.—Iodobenzene, 591-50-4; potassium ethanethiolate, 54669-43-1; phenyl ethyl sulfide, 622-38-8; diphenyl sulfide, 139-66-2; *p*-iodoanisole, 696-62-8; potassium thiophenolate, 3111-52-2; potassium *p*-methoxythiophenoxide, 56830-32-1; bis(*p*-methoxyphenyl) sulfide, 3393-77-9; bis(*p*-methoxyphenyl) disulfide, 5335-87-5.

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- Research supported in part by the National Science Foundation.
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Addition of Singlet Oxygen to Arene Oxides^{1,2}

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Singlet oxygen adds to benzene oxide to afford endo peroxide **2** that readily rearranges to *trans*-benzene trioxide (**3**), and reacts with triphenyl phosphite to afford *trans*-benzene dioxide (**5**). Endo peroxide **2** was also converted into **4**, **6**, and **7**. Indan 8,9-oxide reacts with singlet oxygen to afford endo peroxide **9** that undergoes similar reactions to give **10** and **11**.

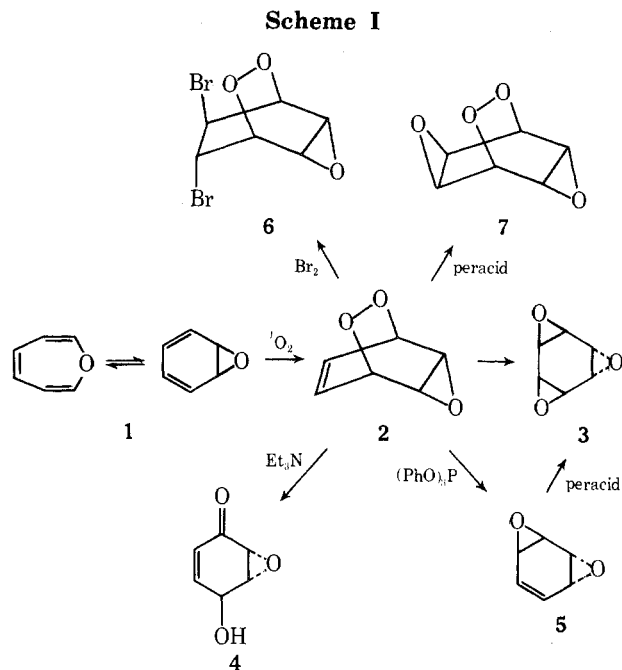
Since the initial reports on the synthesis of *trans*-benzene trioxide (**3**) from rearrangement of the endo peroxide obtained by addition of singlet oxygen to oxepin-benzene oxide (**1**),^{3,4} similar products have been prepared from addition of singlet oxygen to oxidoannulenes⁵ and indene.⁶ The synthesis and chemistry of *cis*-benzene trioxide have been reported.^{5,7-13} *trans*-Benzene dioxide,¹⁴ *cis*-benzene dioxide,¹⁵ and *cis*-benzene dioxide derivatives^{16,17} have also been studied. Of particular interest is the valence bond isomerism of *cis*-benzene trioxide and *cis*-benzene dioxides with the corresponding *cis,cis,cis*-1,4,7-trioxacyclononatriene and 1,4-dioxacins, respectively. A variety of substances related to the benzene oxides described above in which one or more oxygen atom is replaced by carbon, nitrogen, or sulfur have been prepared.^{5,8,11,12,14,18}

Reaction of oxepin-benzene oxide (**1**) with singlet oxygen generated from hypochlorite-hydrogen peroxide by the method of Foote¹⁹ affords, in 37% yield, pure, crystalline endo peroxide **2**, which undergoes quantitative rearrangement to **3** on heating in chloroform at 45° (half-life ~14 hr) or on heating under reflux for 16 hr in ethyl acetate. (Scheme I). Photosensitized oxygenation of **1** with Methylene Blue or Rose Bengal as sensitizer gives mainly phenol.²⁰ Singlet oxygen generated from the adduct of ozone and triphenyl phosphite²¹ also oxygenates **1**, but separation of **2** from triphenyl phosphate is difficult; sublimation of the product mixture affords **3** (17% yield).

The facile rearrangement of **2** to **3** is particularly interesting in view of previously reported rearrangements of 1,4-endo peroxides derived from 1,3-cyclohexadienes that require higher temperature and tend to yield mixtures including hydroxy ketone or epoxy ketone in addition to bis-epoxide.²²⁻²⁴ Photochemical rearrangement of **2**²⁵ affords **3** in only 27% yield. It is our belief that the thermal rearrangement of **2** to **3** is a concerted reaction, but ionic or radical pathways cannot be ruled out completely.

Endo peroxide **2** reacts with triethylamine to give ketol **4**, and with triphenyl phosphite to give *trans*-benzene dioxide (**5**).²⁶ The latter substance is a fairly volatile white solid that readily decomposes on standing. Catalytic hydrogenation (Pd/C) of **5** affords *trans*-1,2-cyclohexanediol.²⁷ Epoxidation of **5** affords **3**.

Reaction of **2** with bromine in chloroform gives dibromide **6** and with peroxytrifluoroacetic acid gives **7**. Both



products are crystalline substances that undergo violent decomposition without melting at ~100°.

The addition of singlet oxygen to indan 8,9-oxide (**8**) is more facile than the photooxygenation of **1**. Thus, photosensitized addition of singlet oxygen to **8** gives **9** in quantitative yield (Scheme II). The more facile addition to **8** as compared to **1** may be due to the greater stability of **8** or the fact that **8** exists entirely in the arene oxide form²⁸ and is not subject to side reactions through the oxepin form. Rearrangement of **9** occurs in ~3 days at room temperature or overnight in refluxing chloroform to give **10** in essentially quantitative yield. The ease of conversion of **9** to **10** is similar to that for conversion of **2** to **3** and suggests that the stereochemistry of the endo peroxy and epoxy groups is the same in **9** and **2**. For establishment of the stereochemistry in **10**, see Experimental Section.

Reaction of **9** with triphenyl phosphite is exothermic and affords *trans*-indan dioxide (**11**). Epoxidation of **11** affords a 2.6:1 mixture of **12** and **10**, respectively.