immediately and was allowed to stand at room temperature overnight. The yellow solid that appeared was collected, washed with CH_3OH, and dried to give 7 g (80%) of **26**, mp 284–287 °C, identical in all respects with the compound previously reported.[4,14,19]

Generation of 2,4,5-Triphenyl-3*H*-pyrrol-3-one (24). A suspension of dimer **26** (62 mg) in CH_2Cl_2 (20 mL) was treated with 0.8 g of freshly prepared nickel peroxide.[20] The violet color of product **24** appeared within minutes, but the mixture was allowed to stand at room temperature overnight. Evaporation of the solvent allowed the isolation of 18.5 mg (57%) of **2,4,5-triphenyl-6*H*-oxazin-6-one (25)**, mp 207 °C (lit.[21] mp 207 °C), identical in all ways with an authentic sample.[21]

When the purple CH_2Cl_2 solution, filtered to remove nickel oxides, and 5 drops of DMAD in 10 mL of toluene were mixed and the solution was refluxed for 4 h (after removal of CH_2Cl_2), the purple color was discharged. Thick-layer chromatography on silica with $CHCl_3$ allowed separation of oxazinone **25** and pyridine **9a** (10 mg), mp 231 °C.

Acknowledgment. We thank Professor D. J. Pasto for many stimulating discussions.

Registry No. **4**, 762-42-5; **8a**, 62224-74-2; **8b**, 75233-32-8; **9a**, 58329-12-7; **9b**, 75233-33-9; **10a**, 75233-34-0; **10b**, 75233-35-1; **11a**, 75233-36-2; **11b**, 75233-37-3; **12a**, 75233-38-4; **12b**, 75233-39-5; **13**, 75233-40-8; **24**, 58329-06-9; **25**, 30237-78-6; **26**, 74149-24-9; benzaldehyde, 100-52-7; diphenylcyclopropenone, 886-38-4.

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Determination of the Stereochemistry in the Addition of Thiols to Indene[1a]

H. Harry Szmant* and Jaime Baeza H.

Department of Chemistry and Chemical Engineering, University of Detroit, Detroit, Michigan 48221

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A methodology for the determination of the stereoselectivity in the addition of thiols to indene is described. The chemical method employs an *S*-deuterio thiol, the thermal elimination reaction of the sulfoxides derived from the adducts, and the determination of the D content in the resulting indene. The preferred spectroscopic method employs 1,1,3-trideuterioindene and the LIS technique in the NMR analysis of the sulfones derived from the thiol–olefin adduct. The methodology employed is illustrated with a set of addition reactions carried out at room temperature under photochemically induced conditions and employing equimolar mixtures of 1,1,3-trideuterioindene and a series of substituted thiophenols. Under these conditions the relative amount of cis adduct increased proportionally with the σ constants of the substituents.

The stereochemistry of the addition of thiols to olefins has been reviewed[1b,2] in the context of the stereochemistry of radical chemistry. In the case of cyclic olefins, most of the results have dealt with systems that contain either a substituent at the double bond, in which the exo or endo approach of the sulfur-containing reagent leads to isomeric products of different stability, or systems in which there is a choice of axially or equatorially substituted intermediates. This is the case when the addition reaction occurs with 4-*tert*-butylcyclohexene,[3] *trans*-Δ^2-octalin,[4] norbornene,[5-7] bornylene,[8] norbornadiene,[9] and related bicyclic olefins[7,10-17] or with 1-chlorocyclohexene,[18,19] 1-chloro-4-*tert*-butylcyclohexene,[20] 2-chloro-4-*tert*-butylcyclohexene,[21] 2-methylnorborn-2-ene,[6] or 1-methylcyclopentene.[22] In all of these olefins there exists a built-in bias with respect to either the preferential approach of the sulfur moiety to the olefinic site or a difference in the relative stability of the potential intermediate species or final products. Our concern here is the relative orientation of the thiyl and hydrogen moieties in the thiol–olefin adduct irrespective of the kinetic or thermodynamic factors induced by the structure of the olefinic reagent. Thus, for our purposes the most appropriate system is an olefin that is symmetrical with regard to the syn or anti approach of the thiol. The isomeric 2-butenes fit this criterium, and these olefins

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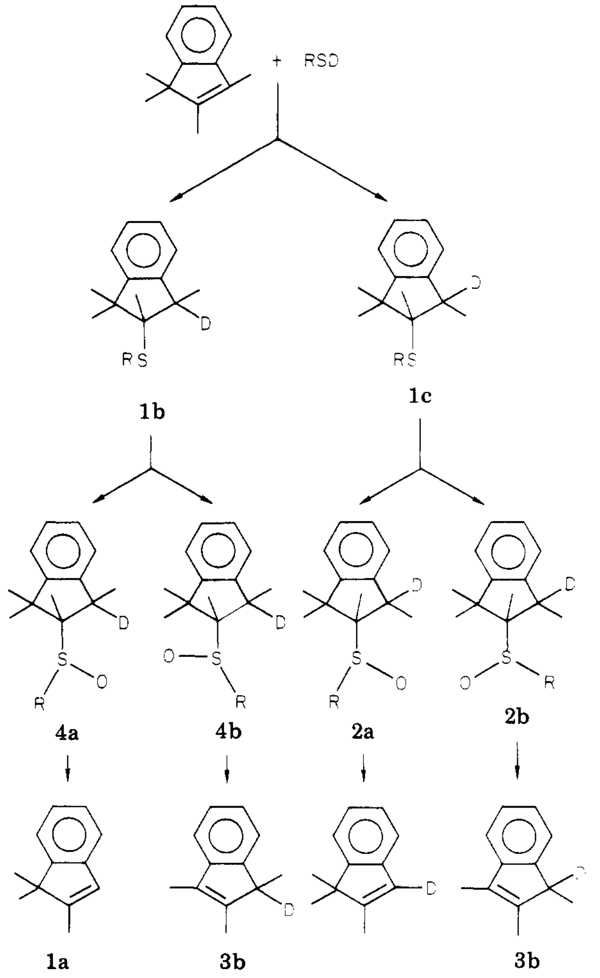
were employed by Skell and co-workers[24,25] in their classical studies of the *S*-deuterio thiol additions in the absence or presence of DBr. Indene also fits the criterium and offers the advantage of revealing the stereochemical results in terms of geometrical rather than optical isomers. Indene has been employed by Dewar and Fahey[25] and by Claros[26] in the stereochemical study of DBr and benzenesulfonyl chloride additions, respectively. In the case of the first-mentioned work, all the methylene proton signals of the adduct appeared in the same range, and the authors assumed,[25] on the basis of a lithium bromide induced isomerization of the adducts, that the outermost and innermost signals of the four peaks corresponded to the trans and cis isomers, respectively. Attempts to confirm these assignments by means of the base-catalyzed elimination of HBr were unsuccessful. In the case of the benzenesulfinyl chloride reaction, the author[26] concluded that the adduct was *trans*-1-chloro-2-(benzenesulfinyl)indane strictly on the basis of the coupling constant of the protons in the 1- and 2-positions. In this paper we describe a similar but unambiguous methodology in the use of indene and its 1,1,3-trideuterio derivative for the determination of the stereochemistry of the addition of some aromatic thiols under a limited set of experimental conditions. The method can be readily applied to other highly symmetrical olefins and to different experimental conditions for the addition reaction.

Results and Discussion

The determination of the stereochemistry of the addition of a thiol to indene employed both chemical and spectroscopic methods.

Chemical Method. The chemical method of differentiating between the cis and trans addition of an *S*-deuterio thiol to indene, i.e., between **1b** and **1c**, is based on the well-established stereospecific cis elimination reaction of sulfoxides[27] (see Scheme I). In the case of the adducts **1b** and **1c**, each can give an isomeric pair of sulfoxides, and the distribution of the elimination products will be governed by the anti or syn orientation[28] of the sulfoxide oxygen. Thus, with the assumption of a negligible isotope effect in the conversion of the trans adduct **1c** to the sulfoxides **2a** and **2b**, the stereospecific elimination reaction of the latter pair is expected to give an equimolar mixture of the monodeuterated indenes **3a** and **3b**. In the case of the cis adduct **1b** we can again assume an insignificant isotope effect in the formation of the corresponding isomeric sulfoxides **4a** and **4b**, and since the elimination reaction of the sulfoxides is carried out to completion, it gives rise to an equimolar mixture of **3b** and undeuterated indene.

Scheme I.[a] Chemical Method for the Determination of the Stereochemistry of the Addition of a *S*-Deuterio Thiol to Indene



[a] R = m-$CH_3C_6H_4$.

The experimental conditions for the thermal elimination reaction (with a minimal loss of indene due to polymerization) were established in the case of the sulfoxide of **1a**, and the technique was then applied to the deuterated adducts. The resulting indene was shown by NMR (Figure 1, supplementary material) to be an equimolar mixture of **3a** and **3b**, and undeuterated indene could not be detected. Thus, within the limits of accuracy of this method and under the thermal, i.e., nonphotochemically induced reaction condition employed in the addition of *S*-deuterio-*m*-thiocresol to indene, the adduct was formed in a stereospecifically trans manner.

Spectroscopic Method. The most successful method involved the application of the lanthanide-induced shift (LIS)[37] and aromatic solvent-induced shift (ASIS)[38] techniques in the NMR analysis of a series of sulfones derived from the addition reaction of indene and some substituted thiophenols. The problem was approached from two directions, i.e., by the use of S-deuterated thiophenols or by the use of the deuterated olefin, namely, 1,1,3-trideuterioindene, and the nondeuterated thiol. The latter approach was preferable because it avoids the loss of deuterium during the addition reaction.

Utilization of the NMR spectra of sulfides derived from the addition of the S-deuterated thiophenols to indene for the purpose of the determination of the stereochemistry of the adducts is more difficult unless high-resolution instrumentation is available. By analogy with the sulfide-containing 9,10-ethanoanthracene system,[30,31] it is possible to assign chemical shifts of δ 2.87 and 3.29 to the quartets

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Table I. LIS Effect (ppm) in 2-Indanyl *m*-Methylphenyl Sulfone

proton[a]	$\delta_{\mathrm{DCCl_3}}$[b]	$\delta_{+0.07}$[c]	$\delta_{+0.13}$[c]	$\delta_{+0.16}$[c]	$\delta_{+0.20}$[c]	$\delta_{+0.24}$[c]
H^1	2.42	2.58	2.72	2.77	2.83	2.85
H^2	3.15	4.52	5.22	5.55	5.95	6.22
H^3	3.15	5.30	7.29	7.69	7.52	7.52
H^4	4.01	6.32	8.92	8.79	10.68	11.34
H^5	7.73	9.60	11.63	12.21	12.88	13.32
H^6	7.45	7.65	8.00	8.12	8.25	8.26
H^7	7.12	7.30	7.29	7.69	7.60	7.60

[a] See Figure 7. [b] Concentration of sulfone was 0.23 mmol. [c] Millimoles of $\mathrm{Eu(fod)_3}$ added is given as subscript to δ.

Table II. LIS Effect (ppm) in 2-Indanyl *m*-Methylphenyl Sulfone[a]

proton	$\Delta\delta_1$	$\Delta\delta_2$	$\Delta\delta_3$	$\Delta\delta_4$	$\Delta\delta_5$
H^1	0.16	0.30	0.35	0.41	0.43
H^2	1.37	2.07	2.40	2.80	3.07
H^3	2.15	4.14	4.54	4.37	4.37
H^4	2.31	4.91	5.78	6.67	7.33
H^5	1.87	3.90	4.48	5.15	5.59
H^6	0.20	0.55	0.67	0.80	0.81
H^7	0.18	0.17	0.57	0.48	0.48

[a] The following are values for L_0/S_0 for each $\Delta\delta$: $\Delta\delta_1$, 0.304; $\Delta\delta_2$, 0.565; $\Delta\delta_3$, 0.696; $\Delta\delta_4$, 0.869; $\Delta\delta_5$, 1.04.

produced by the cis and trans proton pairs of **1a**, respectively. Also, in the series of substituted 2-(arylthio)indanes it was found that the coupling constants of the lower field (or trans) protons were higher than those of the higher field (or cis) protons, in agreement with previous observations[33] of that nature. In passing, it is also of interest to note that we observe (Figure 2, supplementary material) a linear relationship between the coupling constants of the higher field protons and the σ values of the substituents in agreement with the expected[34,35] inverse proportionality between the coupling constants of vicinal protons and the electronegativity of the substituents. In any case, the comparison of the NMR spectra of **1a** and **1c** (Figure 3, supplementary material) indicates that the presence of deuterium increases the complexity of the higher field methylene signal, and the spectral differences are not suitable for an analysis of the stereochemistry of the thiol addition.

The situation is not much more favorable when one analyzes the NMR spectra of the sulfides obtained from the addition of *m*-thiocresol and 1,1,3-trideuterioindene (Figure 4, supplementary material) although it is noteworthy that the predominant trans proton signal corresponds approximately to a single methylenic hydrogen and appears in the lower field region.

When sulfides under discussion are converted to the corresponding sulfones, apart from the fact that the relative location of the cis and trans protons is inverted because of the opposite shielding and deshielding effects of the sulfide and sulfone functions, the cis and trans methylenic protons can now be clearly differentiated by means of the LIS effect.[36,37] Figure 5 (supplementary material) shows the effect of the addition of $\mathrm{Eu(fod)_3}$ on the location of the cis and trans protons under discussion, and it is noteworthy that at an equimolar ratio of lanthanide and sulfone, the signals of the trans and cis protons are found at 6.22 and 7.52 ppm, respectively. Other details of the LIS effect are given in Tables I and II and in Figure 6 (supplementary material). These results suggest that the conformation equilibrium favors conformer A over B (Figure 7), presumably because it permits a greater rotational freedom of the aryl group.

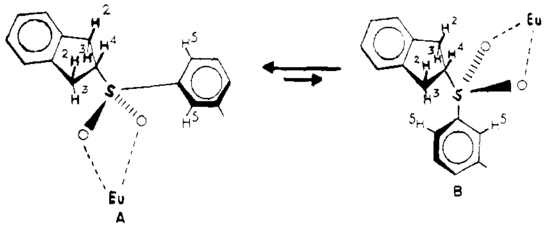

Figure 7. Equilibrium between the two possible conformers of the sulfone–$\mathrm{Eu(fod)_3}$ complex.

A comparison of the NMR spectra of the sulfones of the nondeuterated adduct of indene and *m*-thiocresol with the adducts obtained by using the S-deuterated thiol on one hand and 1,1,3-trideuterioindene on the other hand (Figure 8, supplementary material) demonstrates that the presence of $\mathrm{Eu(fod)_3}$ allows one to clearly identify the cis and trans methylenic protons. The integration of the methylenic signals provides a quantitative estimate of the stereoselectivity in the addition of thiol to olefin.

The ASIS effect[38] was also examined in the case of sulfones derived from the addition of *m*-thiocresol to indene and the above-mentioned deuterated isomers. Figure 9 (supplementary material) illustrates the fact that the replacement of $\mathrm{CDCl_3}$ by $\mathrm{C_6D_6}$ causes large upfield shifts of the $\mathrm{ArSO_2CH}$ and the trans methylenic protons. This suggests that the preferential solvation of the sulfones by $\mathrm{C_6D_6}$ occurs at the positive end of the sulfone dipole of conformer A shown in Figure 7. In the case of the adduct of *m*-thiocresol and 1,1,3-trideuterioindene, the spectrum of the corresponding sulfone indicates the nearly exclusive presence of a single trans methylenic proton at 2.81 ppm in the presence of $\mathrm{C_6D_6}$.

On the basis of these results it is concluded that, for the purpose of a quantitative estimate of the stereoselectivity in the addition of thiols to indene, the most convenient technique utilizes 1,1,3-trideuterioindene and the LIS effect applied to the sulfones derived from the adducts. The application of this method to the determination of the stereoselectivity of the addition as a function of the electronic nature of the substituents present in the aromatic thiol is summarized in Table III and Figure 10. It is apparent that under the photochemically induced reaction conditions chosen for these experiments, the formation of the minority cis adducts is directly proportional to the

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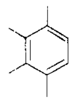
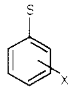
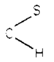
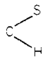
Table III. NMR Spectral Data and Melting Points of 2-Indanyl Aryl Sulfones

	chemical shifts, δ					
X					X	mp, °C
m-CH_3	7.12 (4, s)	7.45 (2, m), 7.73 (2, m)	4.01 (1, m)	3.15 (4, m)	2.42 (s, 3)	107-109
m-CF_3	7.06 (4, s)	8.06 (2, m), 7.71 (2, m)	3.91 (1, m)	3.3 (4, m)		115-117
p-F	7.13 (4, m)	7.13 (2, m), 7.88 (2, m)	3.98 (1, m)	3.29 (4, m)		112-114
p-OCH_3	7.1 (4, s)	6.94 (2, d, J = 9 Hz), 7.8 (2, d, J = 0 Hz)	3.88 (1, m)	3.22 (4, m)	3.82 (3, s)	121-123
p-Cl	7.06 (4, s)	7.46 (2, d, J = 9 Hz), 7.85 (2, d, J = 9 Hz)	3.92 (1, m)	3.21 (4, m)		137-138

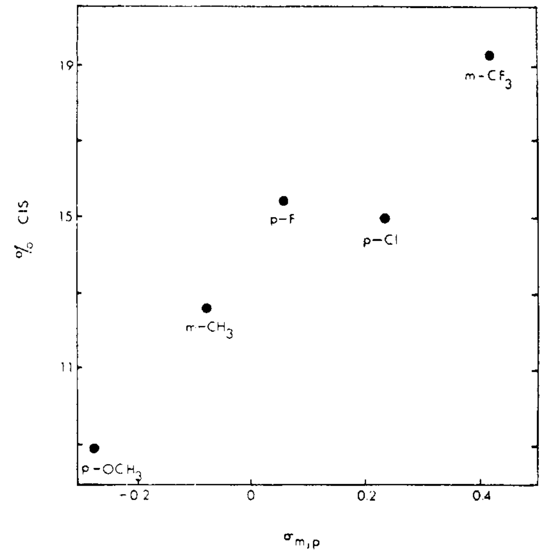


Figure 10. Plot of $\sigma_{m,p}$ values vs. the yield of the cis adducts in the photochemical reaction of 1,1,3-trideuterioindene arylthiols at 32 ± 1 °C.

electron-withdrawing nature of the thiol substituents. The mechanistic implication of these results will be discussed in a future publication.[41]

Experimental Section

The deuterium content in all deuterated reactants was determined by NMR and was found to be in excess of 95% in all cases. The melting and boiling points are uncorrected. The spectra of all compounds (IR and NMR) were consistent with the structure of the compounds.

Materials. 1,1,3-Trideuterioindene was prepared as described by Bergson.[39] The product contained a minimum of 97% and 98% D in positions 3 and 1, respectively. *S*-Deuterio-*m*-thiocresol was synthesized by treating the thiol with deuterium oxide. Indene and the thiols were commercially available.

All the compounds reported here gave satisfactory C, H, and S (±0.2%) microanalytical results (MHW Laboratories).

General Procedures for the Preparation of 2-Indanyl Sulfides. (1) Thermal Reaction. Solutions of 0.02 mol each of indene and thiol in ca. 60–70 cm^3 of solvent were allowed to react during 9 days. For reduction of the competitive TOCO reaction,[40] the reactions were carried out under a nitrogen atmosphere. The reaction was quenched by using a 10% sodium hydroxide solution. For all practical purposes the addition products were analytically pure.

(2) Photochemical Reaction. Equimolecular mixtures of the neat reagents were subjected to black light in an NMR tube. The light source consisted of two General Electric F1578 BL 15-W lamps. For all practical purposes the products were analytically pure.

The indanyl sulfides were purified either by recrystallization from 95% ethanol or by means of column chromatography. The only exception was the trifluoromethyl derivative that was purified by vacuum distillation. The column chromatography employed silica gel G and toluene, followed by ethyl acetate. The toluene eluted the addition product while the ethyl acetate eluted traces of the TOCO products if these were present.

NMR analysis, as well as a comparison with authentic 1-indanyl sulfides prepared from 1-chloroindane, showed the presence of only the anti-Markovnikov products.

2-Indanyl *m*-Methylphenyl Sulfide. This was obtained in a 74% yield after the neat reagents were allowed to react for 5 days.

2-Indanyl *p*-Chlorophenyl Sulfide. This sulfide was synthesized in a 67% yield by using a cyclohexane solution of the reagents over a period of 9 days. The product was recrystallized from 95% EtOH; mp 89–90 °C.

2-Indanyl *m*-Trifluoromethylphenyl Sulfide. This compound was synthesized in a 70% yield by using 0.02 mol of each reactant in 60 cm^3 of cyclohexane and a reaction time of 9 days. The compound was purified by vacuum distillation: mp 34–35 °C; bp 128–138 °C (0.9 torr).

When a photochemically induced reaction was run at 32 °C, the pure compound was obtained in 90% yield after 24 h.

2-Indanyl *p*-Fluorophenyl Sulfide. This sulfide was obtained in a 46% yield by using 0.02 mol of each reagent in 60 cm^3 of cyclohexane and a reaction time of 9 days. Recrystallization from EtOH (95%) gave the product with a melting point of 58–58.5 °C.

2-Indanyl *p*-Methoxyphenyl Sulfide. This compound was synthesized from the neat reagents over a period of 9 days. The reaction mixture became solid, and the product was recrystallized from 95% EtOH to give a 70% yield of the desired product, mp 52–53 °C.

General Procedures for the Preparation of 2-Indanyl Aryl Sulfones. In a typical reaction 0.0048 mol of the sulfide was stirred overnight at room temperature with 1.15 cm^3 of H_2O_2 (30%) and 17.3 cm^3 of CH_3COOH. The mixture was then heated for 2 h on a steam bath and poured into ice–water. Saturated sodium bicarbonate solution was added carefully to neutralize the acid, and the sulfone was then extracted with dichloromethane. The product was recrystallized from 95% EtOH to give the desired sulfones in yields of 65–75%.

2-Indanyl *m*-methylphenyl sulfone, mp 107–109 °C.

2-Indanyl *p*-methoxyphenyl sulfone, mp 121–123 °C.

2-Indanyl *p*-fluorophenyl sulfone, mp 112–114 °C.

2-Indanyl *m*-trifluoromethylphenyl sulfone, mp 115–117 °C.

2-Indanyl *p*-chlorophenyl sulfone, mp 137–138 °C.

The NMR spectral data of the products described above are given in Table III.

2-Indanyl *m*-Methylphenyl Sulfoxide. The sulfide (0.0169 mol) and 0.0172 mol of sodium periodate were dissolved in 50 cm^3 of a 1:1 mixture of dioxane and water, and the mixture was stirred

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[41] H. H. Szmant, J. Baeza H., R. Nanjundiah, and V. Iyer, manuscript in preparation.

at room temperature for 18 h. The sodium iodate cake was filtered and washed with dichloromethane. The water layer was extracted with three 100-cm^3 portions of methylene chloride. The combined methylene chloride solution solution was dried over Drierite. A 73% yield of crude product (calculated as sulfoxide) was obtained after removal of the solvent. The sulfoxide (70% of the crude product) was separated from the unreacted sulfide by means of a silica gel column using toluene and ethyl acetate as eluents. The sulfoxide (R_f 0.55, TLC silica gel, eluent EtOAc) was recrystallized from 95% EtOH: mp 123–125 °C; NMR (neat) δ 2.41 (s, 3), 3.27 (m, 5), 7.13 (s, 4), 7.14 (m, 4).

***S*-Deuterio-*m*-thiocresol.** *m*-Thiocresol (8 cm^3) was shaken in a separatory funnel with five portions of deuterium oxide (99.8 atom % D). The thiol layer was dried over Drierite. The compound showed a minimum 96% of deuteration by NMR.

***trans*-1-Deuterio-2-indanyl *m*-methylphenyl sulfone**: mp 110–113 °C; NMR δ 2.4 (s, 3), 3.26 (m, 3), 4.02 (m, 1), 7.1 (s, 4), 7.45 (m, 2), 7.72 (m, 2).

***trans*-1-Deuterio-2-indanyl *m*-methylphenyl sulfoxide** was prepared by using sodium periodate as described above. The sulfoxide was shown to contain a minimum of 97% of the expected content of deuterium by NMR: mp 122–124 °C; NMR ($CDCl_3$) δ 2.39 (s, 3), 3.29 (m, 4), 7.13 (s, 4), 7.41 (m, 4).

***cis*-1,1,3-Trideuterio-2-indanyl *m*-methylphenyl sulfide**: mp 42–43 °C; NMR ($CDCl_3$) δ 2.13 (s, 3), 3.32 (m, 1), 4.05 (d, 1), 7.16 (m, 8).

***cis*-1,1,3-Trideuterio-2-indanyl *p*-Methoxyphenyl Sulfide.** A mixture of 0.4 g (0.0034 mol) of 1,1,3-trideuterioindene and 0.48 g (0.0034 mol) of *p*-methoxythiophenol was photolyzed at 32 °C in an NMR tube. The reaction was complete after 48 h and gave 0.76 g of product that was purified by column chromatography to give 0.61 (70% yield) of the trideuterated sulfide: mp 121–123 °C; NMR ($CDCl_3$) δ 3.17 (m, 1), 3.68 (s, 3), 3.85 (m, 1), 6.72 (m, 2), 7.04 (s, 4), 7.3 (m, 2).

***cis*-1,1,3-Trideuterio-2-indanyl *p*-Fluorophenyl Sulfide.** A mixture of 0.4 g (0.0034 mol) of 1,1,3-trideuterioindene and 0.44 g (0.0034 mol) of *p*-fluorothiophenol was photolyzed for 48 h at 32 °C in an NMR tube. Purification of 0.78 g of product by column chromatography gave 0.65 g (77.4% yield) of the desired product: mp 58–59 °C; NMR ($CDCl_3$) δ 3.21 (m, 1), 3.95 (m, 1), 4.19 (m, 8).

***cis*-1,1,3-Trideuterio-2-indanyl *m*-(Trifluoromethyl)phenyl Sulfide.** A mixture of 0.33 g (0.0028 mol) of 1,1,3-trideuterioindene and 0.49 g (0.0028 mol) of *m*-(trifluoromethyl)thiophenol was photolyzed for 48 h at 32 °C in an NMR tube. Purification by column chromatography of 0.7 g of product gave 0.65 g (78.2% yield) of deuterated sulfide: mp 34–36 °C; NMR ($CDCl_3$) δ 3.32 (m, 1), 4.04 (m, 1), 7.04 (s, 4), 7.32 (s, 3), 7.53 (s, 1).

***cis*-1,1,3-Trideuterio-2-indanyl *p*-Chlorophenyl Sulfide.** A mixture of 0.36 g (0.003 mol) of 1,1,3-trideuterioindene, 0.43 g (0.003 mol) of *p*-chlorothiophenol, and 0.3 cm^3 of hexane was photolyzed. The reaction was complete in 24 h. The solvent was removed, and crystallization of the residue from 95% EtOH gave 0.52 g (66% yield) of the desired product: mp 87–89 °C; NMR ($CDCl_3$) δ 3.26 (m, 1), 3.45 (m, 1), 7.12 (s, 4), 7.17 (s, 4).

***cis*-1,1,3-Trideuterio-2-indanyl aryl sulfones** were obtained in 65–85% yields from the corresponding sulfides by oxidation with H_2O_2 in acetic acid overnight. The melting points and NMR data are shown in Table III.

Thermolysis of the 1-Indanyl Sulfoxides. The thermolyses of the deuterated and undeuterated sulfoxides were carried out by using 0.27 M solutions of the compounds in dodecane. The solution was placed in a 50-cm^3 round-bottomed flask, degassed by using seven freeze–pump–thaw cycles (to reduce the polymerization of the expected indene), and then heated for 1 h until a maximum of 152 °C was reached. The thermolysis product codistilled under vacuum with the solvent. The thermolysis product of the nondeuterated sulfoxide gave a clean spectrum of indene while the deuterated compound clearly showed only half the area for the lower field proton relative to the area of the higher field proton. This corresponds to a 1:1 mixture of 1-deuterio- and 3-deuterioindene.

Lanthanide Study. Increasing amounts of $Eu(fod)_3$, tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione)europium(III), were added to a solution of 0.23 mmol of sulfone in 0.5 cm^3 of $CDCl_3$ until a 1:1 ratio was reached. Me_4Si was used as an internal standard. The spectrum was recorded by means of a Varian A60-A instrument with the temperature of the probe at approximately 40 °C. The results are recorded in Tables I and II and in Figures 5 and 6 (supplementary material).

ASIS Effect. The solvent shift displacements of equal concentrations of the two solvents $CDCl_3$ and C_6D_6 were studied by using Me_4Si as the internal standard. This study was realized for 2-indanyl *m*-methylphenyl sulfone, *trans*-1-deuterio-2-indanyl *m*-methylphenyl sulfone, and *cis*-trideuterio-2-indanyl *m*-methylphenyl sulfone. The results are recorded in Figure 9 (supplementary material).

Registry No. 2-Indanyl *m*-methylphenyl sulfide, 75102-56-6; 2-indanyl *p*-chlorophenyl sulfide, 62702-97-0; 2-indanyl *m*-trifluoromethylphenyl sulfide, 75102-57-7; 2-indanyl *p*-fluorophenyl sulfide, 75102-58-8; 2-indanyl *p*-methoxyphenyl sulfide, 75102-59-9; 2-indanyl *m*-methylphenyl sulfone, 75102-60-2; 2-indanyl *p*-methoxyphenyl sulfone, 75102-61-3; 2-indanyl *p*-fluorophenyl sulfone, 75102-62-4; 2-indanyl *m*-(trifluoromethyl)phenyl sulfone, 75102-63-5; 2-indanyl *p*-chlorophenyl sulfone, 75102-64-6; 2-indanyl *m*-methylphenyl sulfoxide, 75102-65-7; *S*-deuterio-*m*-thiocresol, 75111-52-3; *m*-thiocresol, 108-40-7; *trans*-1-deuterio-2-indanyl *m*-methylphenyl sulfone, 75111-53-4; *trans*-1-deuterio-2-indanyl *m*-methylphenyl sulfoxide, 75111-54-5; *cis*-1,1,3-trideuterio-2-indanyl *m*-methylphenyl sulfide, 75111-55-6; *cis*-1,1,3-trideuterio-2-indanyl *p*-methoxyphenyl sulfide, 75111-56-7; 1,1,3-trideuterioindene, 770-96-7; *p*-methoxythiophenol, 696-63-9; *cis*-1,1,3-trideuterio-2-indanyl *p*-fluorophenyl sulfide, 75111-57-8; *p*-fluorothiophenol, 371-42-6; *cis*-1,1,3-trideuterio-2-indanyl *m*-(trifluoromethyl)phenyl sulfide, 75111-58-9; *m*-(trifluoromethyl)thiophenol, 937-00-8; *cis*-1,1,3-trideuterio-2-indanyl *p*-chlorophenyl sulfide, 75111-59-0; *p*-chlorothiophenol, 106-54-7; *cis*-1,1,3-trideuterio-2-indanyl *m*-methylphenyl sulfone, 75111-60-3; *cis*-1,1,3-trideuterio-2-indanyl *m*-(trifluoromethyl)phenyl sulfone, 75111-61-4; *cis*-1,1,3-trideuterio-2-indanyl *p*-fluorophenyl sulfone, 75111-62-5; *cis*-1,1,3-trideuterio-2-indanyl *p*-methoxyphenyl sulfone, 75111-63-6; *cis*-1,1,3-trideuterio-2-indanyl *p*-chlorophenyl sulfone, 75111-64-7.

Supplementary Material Available: Figure 1, NMR spectra of indene; Figure 2, plot of σ vs. J_{cis} for 2-indanyl sulfides; Figure 3, NMR spectra of 2-indanyl *m*-methylphenyl sulfide and *trans*-1-deuterio-2-indanyl *m*-methylphenyl sulfide; Figure 4, NMR spectra of 2-indanyl *m*-methylphenyl sulfide and *cis*-1,1,3-trideuterio-2-indanyl *m*-methylphenyl sulfide; Figure 5, LIS effect in 2-indanyl *m*-methylphenyl sulfone; Figure 6, δ vs. L_0/S_0 effect for 2-indanyl *m*-methylphenyl sulfone; Figure 8, NMR spectra for *cis*-1,1,3-trideuterio-2-indanyl *m*-methylphenyl sulfone; Figure 9, ASIS effects for 2-indanyl *m*-methylphenyl sulfone and 1-deuterio-2-indanyl *m*-methylphenyl sulfone in $CDCl_3$ and C_6D_6 (8 pages). Ordering information is given on any current masthead page.