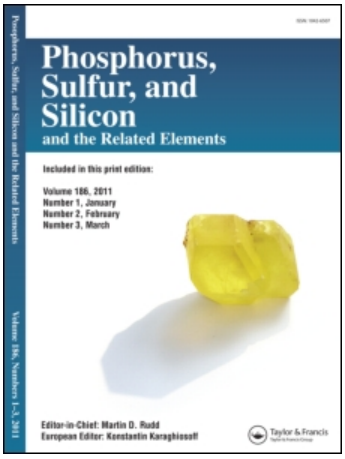

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SYNTHESIS AND REACTIONS OF TRANS-2-(2'-NITROPHENYLTHIO)-1-CHLOROINDANE

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SYNTHESIS AND REACTIONS OF TRANS-2-(2′-NITROPHENYLTHIO)-1-CHLOROINDANE

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The title compound was prepared by addition of 2-nitrobenzenesulphenyl chloride to indene, and proton nmr was used to prove its *trans*-structure. The chloro-substituent could be replaced by ethanol under very mild conditions with retention of configuration owing to anchimeric assistance by the bridging S-atom. Analogous reactions were observed with water and other alcohols (MeOH, Me_2CHOH, Me_3COH, PhSH). Basic nucleophiles caused dehydro-chlorination to the corresponding indenes. Reduction of the nitro-group resulted in intramolecular cyclisation to give a dihydrobenz[b] indeno[1,2-e][1,4] thiazine **9**. Thermolysis of the 2-(2′-nitrophenylthio)-1-azidoindane occurred with ring expansion to give 3-(2′-nitrophenylthio) quinoline. Oxidation of the title compound with *m*-chloroperoxybenzoic acid produced the corresponding sulphone which smoothly underwent reductive cyclisation to a benzindenothiazinesulphone **20**.

The only recorded addition of an aromatic sulphenyl chloride to indene is that reported by Kharasch[1] and coworkers for 2,4-dinitrobenzenesulphenyl chloride. However, no independent proof for the structure of this adduct is given. It is generally accepted that reaction of arene sulphenyl chlorides with alkenes results in a highly stereospecific *trans*-addition involving an episulphonium ion intermediate which adds in a Markovnikov manner.[1,2] We similarly obtained an adduct **2** from indene **1** and 2-nitrobenzene sulphenyl chloride on reflux in acetonitrile to which we assign the trans-structure **2** (R = 2-NO_2) arising from a study of its ^{1}H-n.m.r. spectrum 1. The low field signal in the 300 Hz expanded spectrum of the aliphatic region (cf. spectrum 2) was assigned to H_A as being bonded to an aromatic carbon and a chlorine atom. The coupling constant $J_{A/B}$ is found to be 2 Hz, which is in agreement with the dihedral angle of ca 105° found from inspection of a molecular model of a *trans*-adduct. The *cis*-model with an angle of about 20° would show a well-defined doublet for $J_{A/B}$ of ca 9 Hz. The complex multiplet for H_B results from a small dihedral angle between H_B/H_C resulting initially in a doublet from H_B with a large coupling constant $J_{B/C}$. Each line of this doublet is split into a pair of doublets by H_D leading to a doublet of doublets. Since the dihedral angle between H_D and H_B is roughly the same as between H_A and H_B the coupling constant $J_{B/D}$ will be small. Finally, because H_B is also coupled to H_A each line of the doublet of doublets is split, and because of overlapping H_B appears as a doublet of triplets. By a similar approach the signal multiplicities of the geminal protons H_C and H_D can be interpreted. Further verification was adduced from decoupling H_B which is coupled to all other aliphatic protons. As expected double irradiation of H_B caused H_A to appear as a singlet and H_C and H_D to show up as doublets with $J_{C/D}$ = 16

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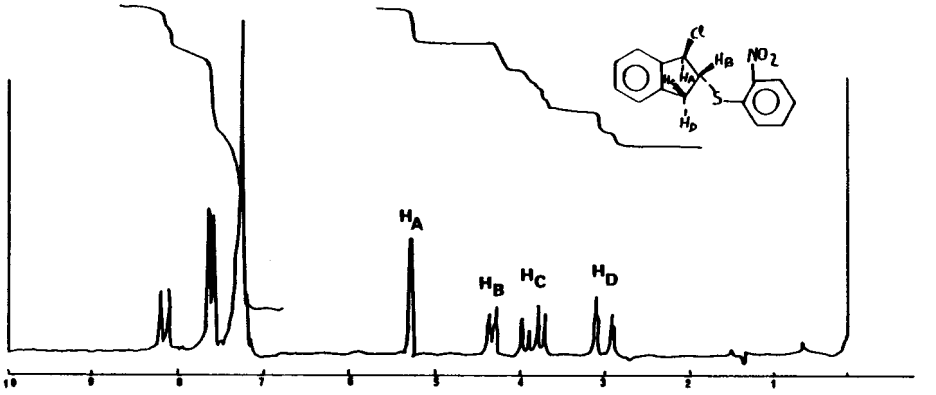
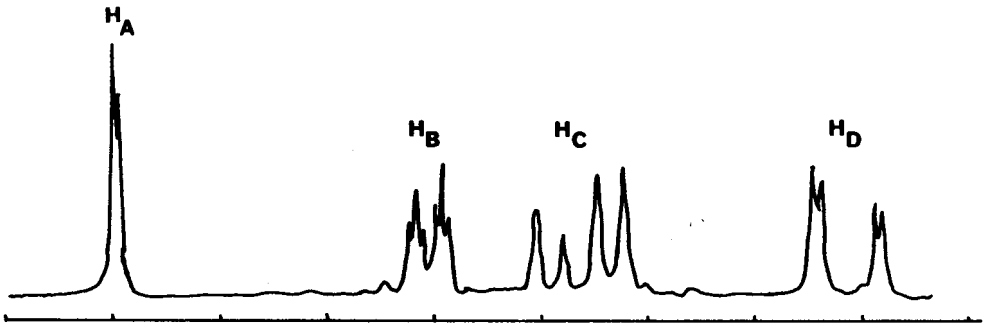


SPECTRUM 1 Trans-2-(2′-nitrophenylthio)-1-chloroindane.

Hz. Adducts arising from phenyl- and 4-nitrophenylsulphenyl chloride were similarly shown to possess the *trans*-structure **2** (R = H or 4-NO_2)

Reaction of **2** *(R = 2-NO_2) with O-nucleophiles*

Attempted recrystallisation of **2** (R = 2-NO_2) from ethanol caused substitution of the chlorine by EtO. The ease with which this ethanolysis occurred suggested neighbouring group participation by sulphur involving a thi-iranium intermediate **2** → **4** (R = EtO, Ar = C_6H_4—NO_2-2). This was supported when it was found that substitution had occurred with retention of configuration. Since $J_{A/B}$ $J_{B/D}$ = 4 Hz, the ethoxy-compound **4** (R = EtO, Ar = —$C_6H_4NO_2$-2) was assigned *trans*-configuration, since a *cis*-structure is incompatible with these values. An S_N1 process would have given at least some *cis*-product. The chloro-compound **2** (R = 2-NO_2) was also labile when it was attempted to purify it by chromatography on SiO_2 with toluene: it yielded the hydroxy-compound **4** (R = OH, Ar = —$C_6H_4NO_2$-2) by hydrolysis. The best method for preparing the hydroxy-compound **4** (R = OH, Ar = $C_6H_4NO_2$-2) was, however, by a short reflux of the chloro-compound **2** (R = 2-NO_2) in a mixture of THF and water.



SPECTRUM 2 300 Hz expansion oı the aliphatic region in Spectrum 1.

Attempts to convert the *trans*-hydroxycompound into its *cis*-isomer by heating it in thionyl chloride and pyridine caused decomposition. Reflux in thionyl chloride gave as expected only the *trans*-chlorocompound **2** (R = 2-NO_2) and dehydration to the indene **5** occurred readily (96%) in $POCl_3$. Purification of the chloro-compound **2** (R = 2-NO_2) was best carried out by recrystallisation from a mixture of carbon tetrachloride and petrol (b.p. 60–80°C).

Other alcohols (methanol, isopropanol, *tert*-butanol) also gave the ethers **4** (R = OMe, $OCHMe_2$, $OCMe_3$; Ar = $C_6H_4NO_2$-2) respectively. Steric hindrance was no doubt the reason why a one- and two-day reflux time with isopropanol and *tert*-butanol respectively was necessary for conversion into the corresponding ether.

Reaction of **2** *with N-nucleophiles*

Treatment of **2** (R = 2-NO_2) with various secondary (piperidine, pyrrolidine) or primary (benzylamine, cyclohexylamine) amines gave no substitution products. Dehydrochlorination occurred yielding the corresponding amine hydrochloride almost quantitatively but gave only ca 15% of 2-(2′-nitrophenylthio)indene **5** (Ar = $C_6H_4NO_2$-2) and intractable tar. Attempts to improve the yield of the indene **5** were abortive, presumably because its formation entails an unfavourable *cis*-elimination (cf. **2** → **5**) which unsuccessfully competes with an α-elimination leading to a carbene and tar formation. Morpholine, probably owing to its lower basicity, produced a different result under the reaction conditions: the main product was identified as morpholino-2-nitrophenyl sulphide **7** from its analytical and spectral data as well as by an authentic preparation from 2-nitrobenzenesulphenyl chloride and morpholine. In addition morpholine hydrochloride and a small amount of indene were isolated. It thus seems that reaction with basic amines can occur in three different ways, namely by *cis*-dehydrochlorination yielding the indene **5**, by α-dehydrochlorination giving a carbene, and finally as with morpholine attack on sulphur producing the sulphenamide (**6** → **7**) and indene with elimination of chlorine.

By contrast a hot solution of sodium azide in DMSO reacted in high yield with **2** (R = 2-NO_2) to give the *trans*-azide **4** (R = N_3, Ar = $C_6H_4NO_2$-2). Stereochemical assignment was on the basis of an approximate $J_{B/D}$ value (cf. **4**) from the multiplet due to H_B, since the signals from H_C and H_D were superimposed in this case.

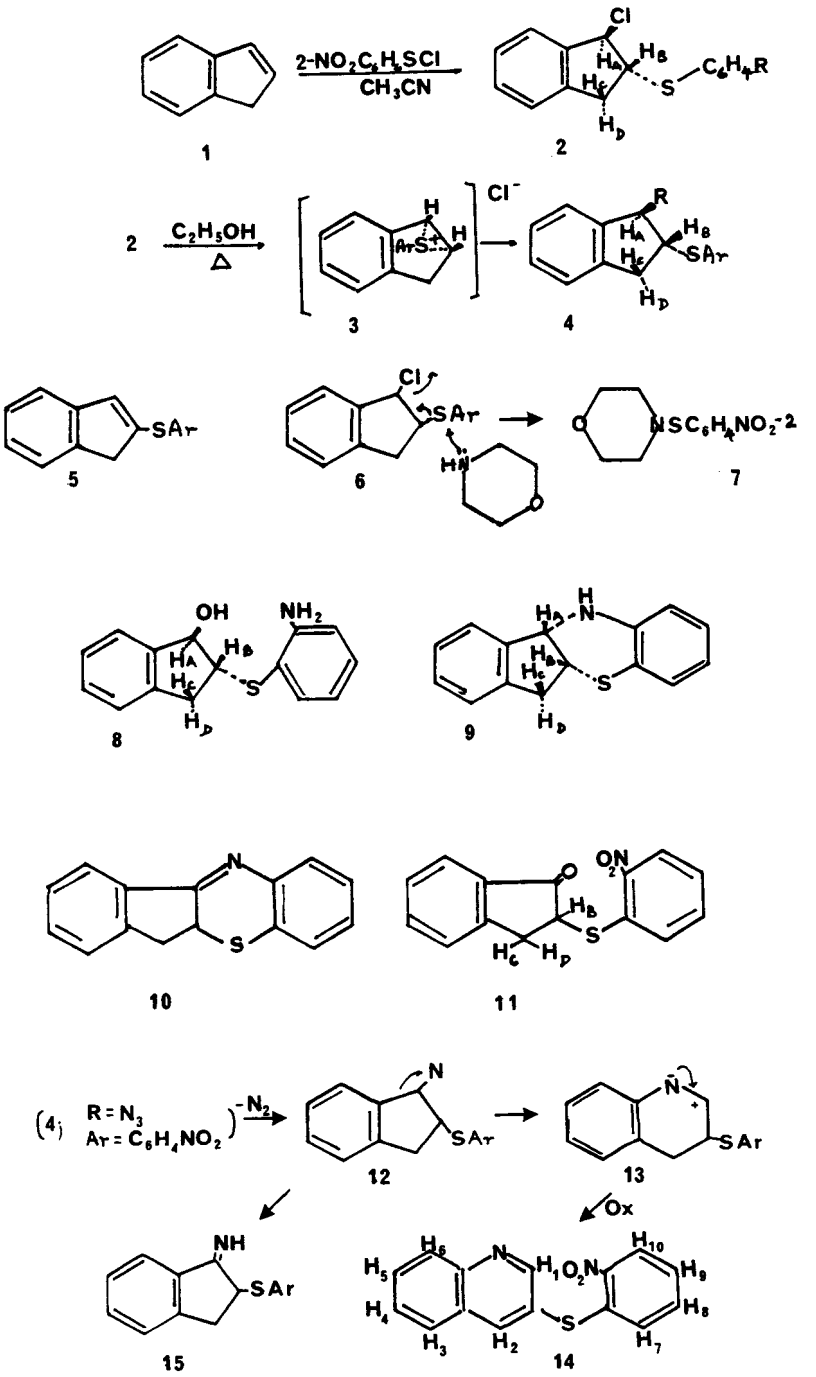
Finally, reaction with sodium thiophenate proceeded smoothly to give *trans*-2-(2′-nitrophenylthio)-1-phenylthioindene **4** (R = SPh, Ar = $C_6H_4NO_2$-2).

With the intention of inducing an internal cyclisation we attempted unsuccessfully reduction of the nitro-group in **2** (R = 2-NO_2) with Pd-charcoal and hydrogen. Similarly Goldfarb's method[3] for reducing nitro-compounds in thiophene to obviate poisoning of the catalyst by sulphur was of no avail. However, reduction in aqueous dioxan with iron and ammonium chloride[4] gave a mixture of *trans*-2-(2′-aminophenylthio)-1-hydroxyindane **8** and the cyclised product *cis*-indanobenzthiazine **9** both in ca 25% yield. The coupling of $J_{A/B}$ = 8 Hz in **9** is substantially greater than $J_{B/D}$ 4 Hz which is consistent with its assignment as a *cis*-structure. The formation of the hydroxy-compound **8** could not be suppressed in favour of the thiazine **9** by reducing the amount of water in dioxan. Iron and acetic acid reduction proved an alternative method for making the thiazine **9** in a similar yield to the above method. The compound **9** has recently been described by Liso *et al.*[5] as being

prepared from 1-indanone and 2,2′-dithiodianiline under nitrogen to give the unstable thiazine **10** which on reduction with sodium borohydride furnished **9**. However, the authors do not give an elemental analysis and the m.p. as well as n.m.r. data differ somewhat from our findings. We were unable to repeat the preparation of **9** by this method. Attempts to prepare the unstable intermediate **10** from the indanone **11** by reductive cyclisation with iron and ammonium chloride were also abortive. The indanone itself was conveniently made from the hydroxy-compound **4** (R = OH, Ar = $C_6H_4NO_2$-2) by oxidation with Jones reagent (CrO_3, H_2SO_4) at room temperature. Other oxidising agents (MnO_2, pyridinium chlorochromate) proved much less successful.

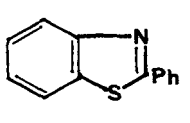
Decomposition of the readily prepared azide **4** (R = N_3, Ar = $C_6H_4NO_2$-2) was thought to provide another possible route to the novel tetracyclic 1,4-thiazine of type **9** by nitrene insertion into the phenyl ring.[6] The azide was, however, inert to irradiation, both by medium and high pressure mercury vapour lamps in quartz or pyrex. Thermal decomposition in 1,2-dichlorobenzene was effective yielding a yellow solid (41% yield). Its M.wt. was 282, i.e. it was formed from the azide **4** (R = N_3, Ar = $C_6H_4NO_2$-2) by loss of possibly N_2H_2. This was taken as evidence for nitrene formation (—N_2) followed by dehydrogenation (—H_2) which was confirmed by the ^1H n.m.r. spectrum in which in contrast with the starting material no aliphatic protons were present. On the basis of its elemental analysis, signals in the ^1H-n.m.r. especially at δ 8.9 and 8.5 with a small coupling constant (< 2 Hz) and a consideration of a feasible mechanism for an aliphatic nitrene, the product was assigned the structure of 3-(2′-nitrophenylthio)quinoline **14**. The mechanism (**4** → **14**, Scheme 1) could be visualized to involve a 1,2-phenyl migration (**12** → **13**) causing expansion from a 5- to a 6-membered ring, followed by aromatisation (**13** → **14**) of the dihydro-quinoline. The nitro-group of the starting material or of any intermediate could feasibly effect this oxidation by analogy with a Skraup synthesis.[7] The high proportion of tarry material can be accounted for by formation of the imine **15**; (Ar = $C_6H_4NO_2$-2) which is one of the usual products in the decomposition of alkyl azides, followed by polymerisation. The ring-enlargement to quinoline is understood as being due to relief of strain in going from a five to a six-membered ring. The phenyl shift (**12** → **13**) is wholly in agreement with migration of an arylgroup in arylalkylnitrenes.[8–10] An unambiguous synthesis was carried out by condensation of 3-thioquinoline with 2-chloronitrobenzene yielding a product identical with our compound **14**. Other attempts at cyclisation made by photolysis and thermolysis of the azide **5** (Ar = $C_6H_4N_3$-2) obtained from the nitro-compound **5** (Ar = $C_6H_4NO_2$-2) by reduction and diazotisation were abortive. The benzoyl derivative **5** (Ar = $C_6H_4NHCOPh$-2) on treatment with polyphosphoric acid gave only 2-phenylbenzthiazole **16** obviously by cleavage of the starting material into 2-mercaptobenzanilide followed by recyclisation.

It was thought that sulphones would provide suitable compounds for cyclisation to thiazinesulphones. Oxidation of various sulphides **4** (R = Cl, N_3, OH; Ar = $C_6H_4NO_2$-2) occurred readily with *m*-chlorperoxybenzoic acid in methylene chloride to give the corresponding sulphones **17** (R = Cl, N_3, OH, Ar = $C_6H_4NO_2$-2). The indanone sulphone **18** (Ar = $C_6H_4NO_2$-2) had to be made by oxidation of the hydroxy-compound **17** (R = OH, Ar = $C_6H_4NO_2$-2) with Jones reagent, as direct oxidation of the indanone **11** did not work. In contrast with the sulphide **2**



SCHEME 1

(R = 2-NO_2) the sulphone **17** (R = Cl, Ar = $C_6H_4NO_2$) did not undergo ethanolysis in boiling ethanol, since the neighbouring group participation of sulphur is absent. Treatment with piperidine caused rapid and quantitative dehydrochlorination at room temperature of the chlorosulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2) apparently with *cis*-elimination to give the indenosulphone **19** (R = 2-NO_2). Thus the acidity of the H_B-proton in the sulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2) is sufficiently enhanced to cause olefin formation under much milder conditions than in the corresponding sulphide **2** (R = 2-NO_2). The greater acidity is confirmed by the fact that H_B in **2** appears at δ 4.26–4.4 while in the corresponding sulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2) H_B is located at δ 4.8–5.1. Among the indenosulphones neither the amino-compound **19**; (R = NH_2), nor its acyl derivatives [**19** (R = 2-NHCOPh or 2-NHCHO) could be made to cyclise in polyphosphoric acid or in $POCl_3/SnCl_4$. The azide **19** (R = 2-N_3) obtained by diazotisation of the amine **19** (R = NH_2) gave only amine and tar on decomposition. Only the chlorosulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2) underwent reductive cyclisation with iron and ammonium chloride in aqueous ethanol almost quantitatively to give the *cis*-dihydrobenzindeno[1,4]thiazine sulphone **20**. By oxidation with peracid in the cold the thiazine **9** was converted into the sulphone thiazine **20**.



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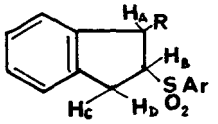

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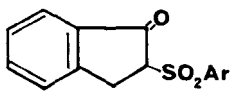

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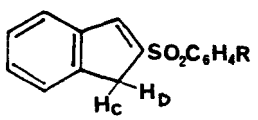

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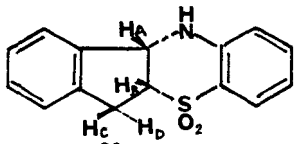

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EXPERIMENTAL

I.r. spectra were measured on a Perkin-Elmer 257 instrument and ^1H n.m.r. spectra on a Varian E M 360 or Perkin Elmer R32 using tetramethylsilane as internal standard. Mass spectra were recorded on an AEIMS 12 or MS 9 instrument. Light petroleum refers to the fraction of b.p. 60-80°C.

2-(2'-Phenylthio)-1-chloroindane. (a) **2** (R = 2-NO_2). A solution of 2-nitrobenzenesulphenyl chloride (39 g) and freshly distilled indene (49 ml) in acetonitrile (350 ml) was refluxed for 3 h and then cooled in ice. The precipitate was filtered off, dried and recrystallised from carbon tetrachloride and light petroleum to give the *chloroindane* **2** (R = 2-NO_2) m.p. 112–13°C (39 g; 62%), ν_{max} (Nujol), 1510, 1330 cm^{-1} (NO_2) (Found: C, 58.95; H, 4.0; N, 4.55. $C_{15}H_{12}ClNO_2S$ requires C, 58.9; H, 4.0; N, 4.6%), m/e 305 (M^+). δ ($CDCl_3$) 5.25–5.4 (1 H, s, H_A), 4.2–4.5 (1 H, H_B), 3.6–4.1 (1 H, H_C), 2.85–3.2 (1 H, m, H_D); cf. discussion for expansion of aliphatic region.

(b) **2** (R = 4-NO_2). Conditions were as for (*a*) using 4-nitrobenzenesulphenyl chloride to give the *chloroindane* **2** (R = 4-NO_2) m.p. 114°C (69%) (Found: C, 59.1; H, 4.1; N, 4.8. $C_{15}H_{12}ClNO_2S$ requires C, 58.9; H, 4.0; N, 4.6%) δ ($CDCl_3$) 7.24–8.34 (m, 8 H arom.), 5.3 (1 H, s, H_A), 4.3–4.46 (1 H, m, H_B), 3.68–4.01 (1 H, m, H_C), 2.8–3.13 (1 H, M, H_D).

(c) **2** (R = H), m.p. 56°C (64%) (Found: C, 69.0; H, 5.0; $C_{15}H_{13}ClS$ requires C, 69.1; H, 5.0%) $\delta(CDCl_3)$, 7.17–7.5 (9 H, m, arom.), 5.26 (1 H, d, H_A), 4.13–4.29 (1 H, m, H_B), 3.51–3.82 (1 H, m, H_C), 2.8–3.16 (1 H, m, H_D), m/e 260 (M^+).

Reaction of **2** *(R = 2-NO$_2$) with O-Nucleophiles.* (a) On recrystallisation from ethanol by short reflux and subsequent cooling 2-(2′-nitrophenylthio)-1-ethoxy-indane **4** (R = OEt, Ar = $C_6H_4NO_2$-2) separated m.p. 84–5°C (81%) (Found: C, 64.3; H, 5.5; N, 4.2. $C_{17}H_{17}NO_3S$ requires C, 64.7; H, 5.4; N, 4.4%), m/e 315 (M^+) δ ($CDCl_3$ (7.0–8.3 (8 H, m, arom.), 4.7–5.0 (1 H, d, H_A), 3.9–4.2 (1 H, H_B), 3.45–3.85 (3 H, H_C and —OCH_2CH_3), 2.7–3.1 (1 H, H_D), 1.0–1.4 (3 H, t, —$OCH_2.CH_3$), $J_{A/B}$ = 4, $J_{B/D}$ = 4, $J_{C/D}$ = 17 Hz.

(b) When **2** (R = 2-NO$_2$) was eluted on a silica column with toluene the main product (65%) was 2-(2′-*nitrophenylthio*)-1-*hydroxyindane* **4** (R = OH, Ar = $C_6H_4NO_2$-2) m.p. 147°C (from toluene), ν_{max} (Nujol) 3300, 3200 cm^{-1} (OH) (Found: C, 62.8; H, 4.5; N, 4.8. $C_{15}H_{13}NO_3S$ requires C, 62.7; H, 4.6; N, 4.9%), m/e 287 (M^+). δ (DMSO-D_6) 7.1–8.3 (8 H, m, arom.), 5.9–6.1 (1 H, d, OH), 4.9–5.1 (1 H, t, H_A), 3.85–4.15 (1 H, H_B), 3.50–3.85 (1 H, H_C, 2.6–3.0 (1 H, H_D), $J_{A/B}$ = 4, $J_{B/C}$ = 8, $J_{B/D}$ = 6, $J_{C/D}$ = 16 Hz. On adding D_2O there was no signal at δ 5.9–6.1. A higher yield (88%) was obtained for **4** (R = OH, Ar = $C_6H_4NO_2$-2) on stirring it (20 g) dissolved in a mixture of water (60 ml) and THF (220 ml) on a water-bath for 4 h and then pouring the reaction mixture into water. Recrystallisation was from isopropanol and water.

(c) When **2** (R = 2-NO$_2$) was treated in methanol as in (a) 2-(2′-nitrophenylthio)-1-methoxyindane **4** (R = OMe, Ar = $C_6H_4NO_2$-2) m.p. 71–2°C (62%) was obtained. (Found: C, 63.6; H, 5.0; N, 5.1. $C_{16}H_{15}NO_3S$ requires C, 63.8; H, 5.0; N, 4.65%) m/e 301 (M^+). δ ($CDCl_3$), 7.0–8.2 (8 H, m, arom.), 4.7–4.85 (1 H, d, H_A), 3.95–4.2 (1 H, H_B), 3.5–3.9 (1 H, m, H_C), 3.35–3.5 (3 H, s, OMe), 2.7–3.0 (1 H, H_D), $J_{A/B}$ = 3, $J_{B/C}$ = 8, $J_{B/D}$ = 4, $J_{C/D}$ = 17 Hz.

(d) A solution of **2** (R = 2-NO$_2$) was refluxed in isopropanol for one day. The solvent was driven off and the residue chromatographed on silica with light petroleum/toluene, followed by toluene/diethyl-ether mixture 1 : 1. Finally recrystallisation of the eluate from isopropanol gave 2-(2′-nitrophenylthio)-1-isopropoxindane **4** (R = Me · CHO, Ar = $C_6H_4NO_2$-2), m.p. 84–5°C (45%) (Found: C, 65.8; H, 6.0; N, 4.4. $C_{18}H_{19}NO_3S$ requires C, 65.6; H, 5.8; N, 4.25%), m/e 329 (M^+). δ ($CDCl_3$) 7.1–82. (8 H, m, arom.), 4.9–5.0 (1 H, d, H_A), 3.85–4.2 (2 H, H_B and O*CH*Me_2), 3.5–3.8 (1 H, m, H_C), 2.7–3.0 (1 H, H_D), 1.1–1.4 (6 H, d, OCH*Me*$_2$), $J_{A/B}$ = 4, $J_{B/C}$ = 8, $J_{B/D}$ = 6, $J_{C/D}$ = 17 Hz.

(e) A solution of **2** (R = 2-NO$_2$) in tert-butanol was refluxed for 2 days and evaporated to dryness. Chromatography of the residue on a silica column with toluene/diethyl ether 1 : 1 gave 2-(2′-nitrophenylthio)-1-t-*butoxyindane* **4** (R = Me_3CO, Ar = $C_6H_4NO_2$-2), m.p. 110–11°C (42%). (Found: C, 66.3; H, 6.3; N, 4.0. $C_{19}H_{21}NO_3S$ requires C, 66.45; H, 6.2; N, 4.0%) m/e 343 (M^+). δ ($CDCl_3$) 7.0–8.2 (8 H, m, arom.), 5.0–5.2 (1 H, d, H_A), 38–4.1 (1 H, H_B), 3.4–3.8 (1 H, H_C), 2.7–3.0 (1 H, H_D), 1.1–1.5 (9 H, s, OC*Me*$_3$), $J_{A/B}$ = 5, $J_{B/C}$ = 8, $J_{B/D}$ = 6, $J_{C/D}$ = 17 Hz.

Reaction of **2** *(R = 2-NO$_2$) with N-Nucleophiles.* A solution of **2** (1 g) in acetonitrile (25 ml) and piperidine (0.36 ml) was refluxed for 2 h. The colourless crystals of piperidine hydrochloride were filtered off and the filtrate evaporated to give a brown oil. This was purified by chromatography (alumina) by elution with light petroleum/toluene 1 : 2. The second component off the column was recrystallised from ethanol to give 2-(2′-*nitrophenylthio*)*indene* **5** (Ar = $C_6H_4NO_2$-2), m.p. 118–19°C (15%). (Found: C, 66.6; H, 4.3; N, 5.1. $C_{15}H_{11}NO_2S$ requires C, 66.9; H, 4.1; N, 5.2%) m/e 269 (M^+). δ ($CDCl_3$) 7.1–8.3 (9 H, m, arom.+ olefin.), 3.45–3.65 (2 H, H_C, H_D). Cyclohexylamine or benzylamine gave similar results, *i.e.* the corresponding hydrochloride and **5** (Ar = $C_6H_4NO_2$-2) (ca 10–15%) under these conditions. When a solution of **2** (3.05 g) and morpholine (2 g) in acetonitrile was kept under reflux for 3 h treatment as described for piperidine gave morpholine-2-nitrophenylsulphide **7** m.p. 91°C (0.74 g, 31%). (Found: C, 50.1; H, 5.1; N, 11.6. $C_{10}H_{12}N_2O_3S$ requires C, 50.0; H, 5.0; N, 11.7%) m/e 240 (M^+). δ ($CDCl_3$) 6.9–8.4 (4 H, arom.), 3.5–3.9 (4 H, *CH*$_2$O—) 2.8–3.2 (4 H, $CH_2N<$). Addition of 2-nitrobenzene-sulphenyl chloride (0.04 mol) in dichloromethane (150 ml) to a solution of morpholine (0.09 mol) in dichloromethane (40 ml) over 1 h gave after filtering off the morpholine hydrochloride and evaporation of the filtrate a compound idential to **7** (89%). Some morpholine hydrochloride and indene were also separated and the latter indentified as its picrate,[13] m.p. and mixed m.p. 98°C.

When a solution of **2** (R = NO_2 5g) in DMSO (80 ml) was heated with sodium azide (1.3 g) at 100°C for 3 h and then poured into a saturated salt solution (400 ml) an oil separated. This was extracted with dichloromethane (4 × 100 ml) and the extract after drying ($MgSO_4$) evaporated to dryness. The remaining solid was purified on alumina with light petrol/toluene 1 : 1 to give 2-(2′-nitrophenylthio)-1-azidoindane **4** (R = N_3, Ar = $C_6H_4NO_2$-2) (4.8 g, 94%), m.p. 111°C ν_{max} (Nujol) 2100 cm^{-1}. (Found: C, 58.0; H, 3.9; N, 18.1. $C_{15}H_{12}N_4O_2S$ requires C, 57.7; H, 3.9; N, 17.9%) m/e 312 (M^+). δ ($CDCl_3$) 7.1–8.2 (8 H, m, arom.), 4.9–5.2 (1 H, d, H_A), 4.0–14.4 (1 H, H_B) 2.9–3.55 (2 H, m, H_C, H_D), $J_{A/B}$ = 6, $J_{B/D}$ = 8 Hz.

2-(2'-Nitrophenylthio)-1-thiophenylindane **4** (*R = SPh, Ar + $C_6H_4NO_2$-2*). A solution of sodium thiophenate (1.3 g) and **2** (3g) in DMSO (115 ml) was kept at 100°C for 2 h and poured into water 700 ml). The liberated oil was taken up in chloroform (6 × 100 ml) and the extracts dried ($MgSO_4$) and evaporated to dryness. The residue was recrystallised from carbon tetrachloride to give the thiophenylindane **4** (R = SPh, Ar = $C_6H_4NO_2$) m.p. 127–28°C (3.1 g, 83%). (Found: C, 66.4; H, 4.4; N, 3.6. $C_{21}H_{17}NO_2S_2$ requires C, 66.5; H, 4.5; N, 3.7%) m/e 379 (M^+). δ ($CDCl_3$) 6.9–8.1 (13 H, m, arom.). 4.85–5.05 (1 H, d, H_A), 4.2–4.5 (1 H, H_B), 2.8–3.4 (2 H, H_C, H_D), $J_{A/B}$ = 6 Hz.

Reduction of **2** (*R = 2-NO_2*). (a) Catalytic: In presence of Pd/C (5% or 10%) or of freshly prepared Raney nickel a solution of **2** in benzene or in acetic anhydride showed only little hydrogen uptake.

(b) With iron and ammonium chloride. To a stirred mixture of reduced iron (3 g), ammonium chloride (0.4 g) in water (25 ml) under reflux was added piecemeal a solution of **2** (5 g) in dioxan (50 ml). After a further 4 h reflux the reaction mixture was filtered hot. The filtrate was poured into water (100 ml) and the mixture extracted with chloroform (3 × 60 ml). The organic extract was washed (water) and dried ($MgSO_4$) and then evaporated to leave a brown oil which was purified and separated into its components on alumina with light petroleum/toluene 1 : 1. The first eluate provided the cis-indanobenzthiazine **9** (0.95 g, 24%), m.p. 97°C ν_{max} 3380 cm^{-1} (NH), recrystallised from isopropanol and water. (Found: C, 75.0; H, 5.7; N, 5.8. $C_{15}H_{13}NS$ requires C, 75.3; H, 5.5; N, 5.9%) m/e 239 (M^+), δ ($CDCl_3$), 6.5–7.4 (8 H, m, arom.), 4.8–5.0 (1 H, d, H_A), 3.7–4.2 (2 H, H_B and NH), 2.8–3.5 (2 H, m, H_C, H_D), $J_{A/B}$ = 8, $J_{B/D}$ 4 Hz. On deuteration 3.7–4.0 (1 H, H_B); lit.[5] m.p. 102–3°C no analysis given.

Further elution with chloroform gave 2-2'-aminophenylthio)-1-hydroxyindane **8** (1.15 g, 27%) m.p. 122°C (CCl_4, ν_{max} 3040–3380 (3 bands) cm^{-1} (OH, NH_2). (Found: C, 69.8; H, 5.8; N, 5.4. $C_{15}H_{15}NOS$ requires C, 70.00; H, 5.9; N, 5.4) m/e 257 (M^+). δ (DMSO-D_6) 6.5–7.5 (8 H, m, arom.), 5.6–5.8 (1 H, d, OH), 5.1–5.5 (2 H, s, NH_2), 4.8–5.0 (1 H, t, H_A), 2.7–3.7 (3 H, m, H_B, H_C, H_D), $J_{H/OH}$ = 6, $J_{A/B}$ = 5 Hz. On deuteration no signals at 5.2–5.5 and 5.6–5.8.

(c) With iron and acetic acid. A mixture of **2** (R = 2-NO_2, 3 g) iron (1.8 g) and acetic acid (50 ml) was kept under reflux with stirring for 1 h. The mixture was then poured into ice/water (400 ml) and extracted with chloroform (3 × 100 ml). After washing and drying ($MgSO_4$) the extract was evaporated to dryness to give an oil which was purified on alumina with light petrol/toluene 1 : 1 to give the thiazine **9** (0.84 g, 36%). The reaction was equally successful if carried out at room temperature overnight.

(d) Preparation of the thiazine **9** by Liso's method[5] was abortive. 2-(2'-Nitrophenylthio)-1-indanone **11**. To a solution of the hydroxycompound **4** (R = OH, Ar = $C_6H_4NO_2$; 22.75 g) in acetone (455 ml) maintained at 15–17°C was added dropwise with stirring Jones reagent (13.36 g CrO_3, 11.5 ml H_2SO_4 and 38.5 ml water). The acetone solution was decanted from the solids and evaporated to dryness. The residue was taken up in water and extracted with chloroform (4 × 100 ml). The combined chloroform extracts were washed (water) and dried ($MgSO_4$) and finally evaporated to give the yellow indanone **11** (18.2 g, 81%) m.p. 131°C (from ethanol) ν_{max} 1720 cm^{-1} (CO). (Found: C, 63.0; H, 4.1; N, 5.0. $C_{15}H_{11}NO_3S$ requires C, 63.2; H, 3.9; N, 5.0%) m/e 285 (M^+) δ ($CDCl_3$) 7.2–8.4 (8 H, m, arom.), 4.3–4.6 (1 H, m, H_B), 3.6–4.1 (1 H, m, H_C), 2.9–3.4 (1 H, m, H_D). Oxidation with pyridinium chlorochromate gave **11** in a yield of 65%.

Reductive cyclisation of the indanone **11** with iron and ammonium chloride to give **10** was abortive.

3-(2'-Nitrophenylthio)quinoline **14** (*Ar = $C_6H_4NO_2$-2*). (a) The azide **4** (R = N_3, Ar = $C_6H_4NO_2$-2, 1.9 g) was thermolysed at 160–170°C dissolved in 1,2-dichlorobenzene (120 ml) for 1 h. The mixture after cooling was evaporated to dryness and the residual oil chromatographed on alumina with light petrol/toluene 1 : 1 giving the title *quinoline* (0.7 g, 41%) m.p. 121°C recrystallised from light petroleum and carbon tetrachloride. (Found: C, 63.6; H, 3.7; N, 10.1. $C_{15}H_{10}N_2O_2S$ requires C, 63.8; H, 3.6; N, 9.9%) m/e 282 (M^+). δ ($CDCl_3$) 6.8–9.0 (10 H, m, arom.), 8.9 (H_1d), 8.5 (1H d), 8.0–8.4 (H_6 and H_{10} m), 7.6–8.0 (H_3 m), 7.1–7.4 (H_8 and H_9 m), 6.8–7.0 (H_7 m), $J_{H1/H2}$ = 2 Hz.

(b) A mixture of 3-mercaptoquinoline[10] (1 g) and potassium carbonate (5 g) anh. in benzene was made to react with 1-chloro-2-nitrobenzene (1 g) with stirring at 50°C for 6 h. After removal of the solids the organic solution was taken to dryness and the residue chromatographed on alumina as in (a) to give the title compound (0.88 g, 50%) identical with the product obtained in (a) (ir, n.m.r., mixed m.p.).

(c) Attempts to prepare **14**; (Ar = $C_6H_4NO_2$-2) by photolysis of the azide **4** (R = N_3, Ar = $C_6H_4NO_2$-2) in pyrex or quartz in various solvents up to 20 h gave only starting material.

Abortive Cyclisation Reactions. (a) The nitroindene **5** (Ar = $C_6H_4NO_2$-2) was converted into 2-(2'-aminophenylthio) indene **5** (Ar = $C_6H_4NH_2$-2) (86%), m.p. 53°C, ν_{max} 3360, 3250, 3150 (NH_2). (Found C, 75.4; H, 5.4; N, 5.6. $C_{15}H_{13}NS$ requires C, 75.3; H, 5.5; N, 5.9%). m/e 239 (M^+) by reduction with iron and ammonium chloride essentially as described for **2** above. Conventional diazotisation followed by adding the diazonium solution to a solution of sodium azide and sodium acetate in water gave the 2-(2'-azidophenylthio)indene **5** (Ar = $C_6H_4N_3$-2) (71%), m.p. 63°C, ν_{max} 2100 cm^{-1} (N_3) δ ($CDCl_3$) 6.9–7.6 (8 H, m, arom.), 6.7–6.8 (1 H, s), 3.3–3.5 (2 H, s). (The elemental analysis was unsatisfactory).

Photolysis and thermolysis of the azide resulted in extensive tar formation from which no products were isolated.

(b) The N-benzoyl-2-(2′-aminophenylthio)indene (2 g) **5** (Ar = $C_6H_4NHCOPh$-2), m.p. 94°C (Found: C, 76.7; H, 5.0; N, 4.4. $C_{22}H_{17}NOS$ requires (C, 76.9; H, 5.0; N, 4.1%) ν_{max} 3270 (NH) 1700 (>CO) cm^{-1}, obtained (85%) from the amino-compound **5** (AR = $C_6H_4NH_2$-2; cf. above) in the usual way, was stirred at 100°C in polyphosphoric acid (40 g) for 1 h and the mixture poured into water. The precipitate was taken up in chloroform and after drying the solution the solvent was evaporated to give an oil. On purification (alumina, light petroleum/diethyl ether) the eluted solid proved to be 2-phenylbenzothiazole **16** (0.58 g, 47%) m.p. and lit.[7] m.p. 113–14°C; other attempts at cyclisation of the benzoyl derivative ($POCl_3$, P_2O_5 in xylene) proved also unsuccessful.

Preparation of 2-(2′-Nitrophenylsulphone)indanes **17**. In a typical oxidation a mixture of the 1-chloroindane **2** (10 g), *m*-chloroperoxybenzoic acid (17 g) and dichloromethane (230 ml) was kept under reflux for 9 h. After cooling the solids were filtered off. The filtrate was washed with sodium hydrogen carbonate (5% solution), dried ($MgSO_4$) and finally evaporated to yield 2-(2′-nitrophenylsulphone-1-chloroindane **17** (R = Cl, m.p. 156°C, 92%) (petroleum ether b.p. 80–100°C/ethyl acetate) ν_{max}, 1150, 1320 cm^{-1} (>SO_2) (Found: C, 53.3; H, 3.5; N, 4.0. $C_{15}H_{12}ClNO_4S$ requires C, 53.3; H, 3.6; N, 4.2%) m/e 3.37 (M^+). δ ($CDCl_3$) 7.2–8.3, m, arom.), 5.6–5.8 (1 H, d, H_A), 4.8–5.2 (1 H, m, H_B), 3.4–3.7 (2 H, H_C, H_D), $J_{A/B}$ = 6 Hz. In a similar way (except for **18**, cf. below) the following sulphones were prepared from the corresponding thio-compounds:

2-(2′-Nitrophenylsulphone)-1-azidoindane **17** (R-N_3, Ar = $C_6H_4NO_2$-2; m.p. 163°C, 98%) (Found: C, 52.35; H, 3.7; N, 16.4. $C_{15}H_{12}N_4O_4S$ requires C, 52.3; H, 3.5; N, 16.3%) m/e 344 (M^+) δ ($CDCl_3$ 7.3–8.5 (8 H, m, arom.), 4.7–5.1 (2 H, H_A, H_B) 3.6–4.0 (1 H, H_C), 3.0–3.4 (1H, H_D).

2-(2′-Nitrophenylsulphone)-1-hydroxyindane **17** (R = OH, Ar = $C_6H_4NO_2$-2, m.p. 167°C, 75%) (Found: C, 56.6; H, 4.2; N, 4.2. $C_{15}H_{13}NO_5S$ requires C, 56.4; H, 4.1; N, 4.4%). ν_{max} 1140, 1340 (>SO_2) m/e 31917$^+$.

2-(2′-Nitrophenylsulphone)-1-indanone **18** (Ar = $C_6H_4NO_2$-2; m.p. 178°C, 81%) Found: 56.8; H, 3.5; N, 4.5. $C_{15}H_{11}NO_5S$ requires C, 56.8; H, 3.5; N, 4.4%) ν_{max} 1710 (>CO), 1140, 1335 cm^{-1} (SO_2) δ ($CDCl_3$ 7.2–8.3 (8 H, m, arom.), 5.1–5.3 (1 H, m, H_B), 3.4–4.2 (2 H, H_C, H_D) m/e 317 (M^+). Oxidation of the sulphone **17** (R = OH, Ar$C_6H_4NO_2$-2) with Jones reagent as described for the indanone **11** had to be applied.

Preparation of 2-(2′-arylsulphone)indenes **19**. (a) To a solution of the 1-chloroindanesulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2, 8.7 g) in tetrahydrofuran (260 ml) was added piperidine (2.8 ml) at room temperature with stirring over 10 min. The white precipitate of piperidinium hydrochloride which formed was filtered off. The filtrate was evaporated to leave a solid which was dissolved in chloroform. The solution was washed (water) and dried ($MgSO_4$) and yielded on driving off the solvent the 2-(2′-nitrophenylsulphone)indene **19** (R = 2-NO_2) (m.p. 157°C; 7.7 g i.e. 99%, recrystallisable from ethanol. (Found: C, 59.6; H, 3.6, N, 4.8. $C_{15}H_{11}NO_4S$ requires C, 59.8; H, 3.7; N, 4.7%) δ (DMSO-D_6) 7.3–8.5 (9 H, m, 8 arom., 1 olefinic H), 3.7–3.9 (2 H, s, H_C, H_D).

(b) the above indene **19** (R = 2-NO_2) with iron and ammonium chloride in a water/ethanol mixture as described for **8** yielded 2-(2′-aminophenylsulphone)indene **19** (R = 1-2-NH_2, m.p. 155°C, 98%) ν_{max} 3450, 3350 cm^{-1} (NH_2) (Found: C, 66.3; H, 4.95; N, 5.1. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%) m/e 271 (M^+) δ ($CDCl_3$) 6.5–8.0 (9 H, m, 8 arom. 1 olefinic), 4.8–5.3 (2 H, br., NH_2, removable by deuteration), 3.5–3.7 (2 H, s, H_C, H_D). Its N-benzoyl derivative **19** (R = 2-NHCOPh) had m.p. 145°C (Found: C, 70.4; H, 4.6; N, 3.7. $C_{22}H_{17}NO_3S$ requires C, 70.4; H, 4.6; N, 3.7. Its formyl derivative **19** (R = 2-NHCHO) had m.p. 168° (Found: C, 64.0; H, 4.4; N, 4.45. $C_{16}H_{13}NO_3S$ requires C, 64.2; H, 4.4; N, 4.7%)

(c) Diazotisation of the amine **19** (R = 2-NH_2) followed by addition of sodium azide as described for **4**; (R = N_3, Ar = $C_6H_4NO_2$-2) gave the azide **19** (R = N_3, m.p. 124°C, 36%) (Found: C, 66.8; H, 4.0; N, 13.8. $C_{15}H_{11}N_3O_2S$ requires C, 66.7; H, 3.7; N, 14.1%).

Cyclisation Attempts with Sulphones. (a) The sulphones **19**; (R = 2-NH_2, 2-NHCOPh, 2-CHO) could not be made to cyclise in polyphosphoric acid or in a mixture of $POCl_3/SnCl_4$ under various conditions. Treatment of the amine **19** (R = NH_2) with various bases was also unsuccessful as was decomposition (thermal or photo-) of the azide **19** (R = N_3).

(b) Reduction of the chlorosulphone **17** (R = Cl, Ar = $C_6H_4NO_2$-2, 5 g) with iron (2.7 g) and ammonium chloride (0.32 g) in a mixture of water (50 ml) and ethanol (500 ml) was carried out by reflux for 9 h. The mixture was filtered hot and the filtrate evaporated to dryness leaving a white residue which was recrystallised from dioxan/water to give the cis-dihydrobenzindeno[1,2-e][1,4-]thiazinesulphone **20** (m.p. 262°C, 3.66 g, 91%) ν_{max} 3350 (NH), 1150, 1340 (SO_2) cm^{-1} (Found: C, 66.3; H, 4.9; N, 5.4. $C_{15}H_{13}NO_2S$ requires C, 66.4; H, 4.8; N, 5.2%) m/e 271 (M^+) δ (DMSO-D_6 7.15–7.6 (7 H, m, arom.),

7.0–7.15 (1 H, s, NH, no signal on deuteration), 6.6–7.0 (1 H, m, arom.), 5.2–5.45 (1 H, d, H_A), 4.2–4.6 (1 H, m, H_B), 3.1–3.4 (2 H, H_C, H_D), $J_{A/B}$ = 8, $J_{B/D}$ = 2 Hz.

Oxidation of **9** with *m*-chloroperoxybenzoic acid in chloroform for 24 h at room temperature gave sulphone **20** (56%).

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