STEREOCHEMISTRY OF THE CO-OXIDATION PRODUCTS OF INDENE AND THIOPHENOL

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Abstract—The major primary product of the co-oxidation of indene and thiophenol is *trans*-2-phenylmercapto-1-indanyl hydroperoxide, which spontaneously rearranges to the two racemes of *trans*-2-phenylsulphinyl-1-indanol. Attack by the phenylmercaptyl radical on the indene molecule is, within 5 per cent, exclusively at the 2-position and subsequent addition of oxygen to the intermediate 2-phenylmercaptoindanyl radical is, within the same limits, exclusively a *trans*-addition.

The *cis*- and *trans*-2-phenylmercapto-1-indanols and the related sulphoxides and sulphones have been synthesised. Under certain conditions, the substitution reaction of thiophenate ion with indene bromohydrin is accompanied by migration of the hydroxyl group and production of *trans*-1-phenylmercapto-2-indanol; the sulphoxides and sulphone in this series are also described.

No completely satisfactory interpretation of the stereochemical course of addition of free radicals to olefins has yet been achieved, perhaps because the number of such reactions which have been adequately studied is limited. The results reported here contribute to this subject new experimental data obtained during an investigation of the products of co-oxidation of indene and thiophenol, a model system which simulates in certain ways the behaviour of unstable gum-forming petroleum products derived from catalytic cracking processes.

Kharasch *et al.*[1] identified hydroxysulphoxides as the products of aerial co-oxidation of styrene and other olefins with mercaptans and suggested that hydroperoxides (or peroxy radicals) formed in a free-radical chain constituted intermediates which subsequently underwent rearrangement.

With indene and thiophenol in benzene solution a hydroperoxide is the major primary product of oxidation and the rearrangement to hydroxysulphoxides can be experimentally observed. The syntheses described later in this paper provide reference compounds for the identification of the co-oxidation products and elucidation of their stereochemical configuration.

Co-oxidation of indene and thiophenol

In benzene solution at 20°, the co-oxidation reaction involved indene, thiophenol and oxygen in the molar ratios 1 : 1·06 : 1 and at the end of the reaction 77 per cent of the absorbed oxygen was present as hydroperoxide, which subsequently underwent rearrangement. After complete decay of the hydroperoxide, 85 per cent of the oxygen was found to be present in the two *trans*-2-phenylsulphinyl-1-indanols [(Va) and (Vb)] and 1 per cent in *trans*-2-phenylmercapto-1-indanol (III). With such high yields the precursor of the hydroxysulphoxides must be the hydroperoxide, which, therefore, has the structure (XVI). Confirmation was obtained by lithium aluminium hydride reduction of the peroxide to *trans*-2-phenylmercapto-1-indanol (III).

[1] M. S. Kharasch, W. Nudenberg and C. J. Mantell, *J. Org. Chem.* **16**, 524 (1951).

Although the oxygen accounted for in compounds of completely determined configuration amounts to only 86 per cent of that reacted, it is possible for three reasons to draw conclusions regarding the stereochemistry of this reaction from the yields of hydroxysulphoxides. First, in the rearrangement reaction, 96·7 per cent of the hydroperoxide is converted to hydroxysulphoxides. Secondly, the stereochemical configurations of cis- and trans-hydroperoxysulphides are such that, although close approach of oxygen and sulphur atoms is possible in the trans form, the sulphur atom actually interferes with the rotation of the hydroperoxy group in the cis form, which should therefore have an even greater probability of rearrangement to the stable hydroxysulphoxides. Thirdly, when a paraffinic solvent (e.g. 2:2:4-trimethylpentane) is employed, the hydroxysulphoxides (Va) and (Vb) are rapidly formed and precipitated, but none of the isomers (VIa), (VIb), (XIIa) and (XIIb) nor carbonyl absorption could be detected in the infra-red spectrum of the product.

The only fraction having a spectrum resembling those of the cis-hydroxysulphoxides [(VIa) and (VIb)] was separated by chromatography and amounted to 0·25 per cent of the total product (0·27 per cent of the absorbed oxygen); no trace of the cis-hydroxysulphide (IV) was found. Of the hydroxysulphoxides isolated, 95 per cent have been fully identified as trans-2-phenylsulphinyl-1-indanols in the pure state by m.p. and infra-red spectra or, in admixture with one another by spectra and oxidation to the trans-hydroxysulphone (VII). The remaining 5 per cent were obtained as chromatograph fractions examined only by infra-red absorption, which could detect the presence of 5 per cent of (VIa) or (VIb) and 2 per cent of (XIIa) or (XIIb) in the mixture of (Va) and (Vb). Therefore, allowing for the 3·3 per cent loss to by-products in the rearrangement reaction and the possible uncertainties in the infra-red examinations, it may be concluded that, within 5 per cent, the attack of the phenylmercaptyl radical on the indene molecule is exclusively at the 2-position and that addition of oxygen to the phenylmercaptoindanyl radical in the second step of the chain reaction occurs trans to the phenylmercapto-group:

(XVI)
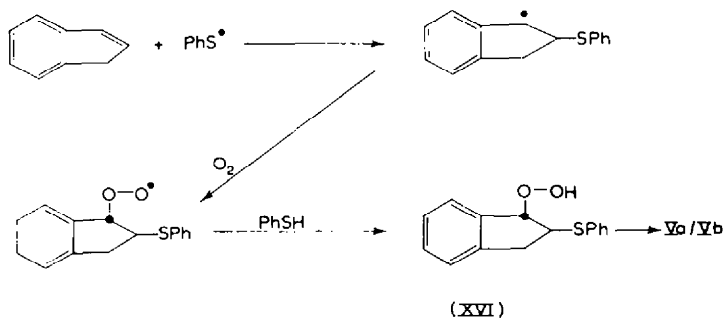
The orientation of the initial attack is the same as in styrene[1] and can be related to the stabilising effect of the adjacent aromatic ring in the 1-indanyl radical.[2,3]

No completely satisfactory theory of free-radical addition to olefins has yet been developed, but, if the interpretation of Goering et al.[4,5] is applicable, the essentially

[2] R. L. Huang, J. Chem. Soc. 1749 (1956).
[3] M. Takahasi, Bull. Chem. Soc. Japan 29, 511 (1956); quoted by H. B. Henbest, Ann. Rep. Chem. Soc. 53, 149 (1956).
[4] H. L. Goering, D. I. Relyea and D. W. Larsen, J. Amer. Chem. Soc. 78, 348 (1956).
[5] H. L. Goering and L. L. Sims, J. Amer. Chem. Soc. 77, 3465 (1955).

trans configuration of the product may be attributed to axial attack on the planar indene molecule in the first step, followed by rapid addition of oxygen in the second step before conformational rearrangement can occur. However, evidence to support this view is lacking.

The stereospecificity of free-radical addition reactions can vary in different systems from purely *trans* additions[6–13] at one extreme, through various intermediate degrees of specificity[4,14] to the other extreme in which *cis* and *trans* additions are equally probable.[15,16,17] This sensitivity to structure and conditions is particularly apparent in a comparison of the co-oxidation of indene and thiophenol with the formation of polymeric indene peroxide.[16] Although the second stages of these two reactions are identical, the latter shows no stereospecificity, while the former is a virtually pure *trans* addition. This implies, in the conformational analysis, that the rate of oxygen addition must be slow compared with the conformational rearrangement in the formation of indene peroxide, but relatively fast (as mentioned above) for the co-oxidation reaction. Unfortunately no data is available on the rates of oxygen addition, because this step is usually not rate-determining in either reaction and the control or measurement of radical concentrations is difficult.

Syntheses in the 2-phenylmercapto-1-indanol series

2-Bromo-1-indanone (I) has been previously prepared by chromic acid oxidation of indene bromohydrin[18,19] and also by bromination of 1-indanone;[20] the structure is therefore well established. Replacement of bromine in (I) by the phenylmercapto-group was straightforward and yielded (II); rearrangement at this stage was most improbable.

Reduction of (II) with lithium aluminium hydride was practically quantitative, yielding a separable mixture of the *trans*- and *cis*-2-phenylmercapto-1-indanols [(III) and (IV)] in the ratio of 4·6 : 1. It was shown that isomer (IV) was unaffected by lithium aluminium hydride under the conditions of the reduction and it is evident that the formation of (III) is favoured, but not through an equilibrium with (IV). The preferential production of (III) must therefore be the result of steric influences and this isomer should be the *trans* form, because approach of the large aluminium complex will be less hindered by the C_6H_5S-group if the attack on the oxygen is made from the opposite side of the molecule.[21]

[6] M. S. Kharasch, J. S. Sallo and W. Nudenberg, *J. Org. Chem.* **21**, 129 (1956).
[7] P. I. Abell, B. F. Aycock and H. L. Goering, *J. Amer. Chem. Soc.* **74**, 3588 (1952).
[8] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.* **14**, 239 (1949).
[9] E. S. Fawcett, *Chem. Rev.* **47**, 219 (1950).
[10] J. Weinstock, Abstr. of Papers 128th Meeting of the American Chemical Society, Minneapolis, Sept. 1955, 0. 19–0.
[11] R. H. Rosenwald, *Symposium on the Use of Additives in Petroleum Fuels.* Division of Petroleum Chemistry, American Chemical Society Meeting, Minneapolis, Sept. 1955.
[12] G. M. Bristow and F. S. Dainton, *Proc. Roy. Soc.* A **229**, 509, 525 (1955).
[13] L. K. J. Tong and W. O. Kenyon, *J. Amer. Chem. Soc.* **71**, 1925 (1949).
[14] F. G. Bordwell and W. A. Hewett, Abstr. of Papers, 126th Meeting of the American Chemical Society, Sept. 1954, p. 6–0.
[15] R. Reimenschneider, *Mh. Chem.* **85**, 1133 (1954).
[16] G. A. Russell, *J. Amer. Chem. Soc.* **78**, 1035 (1956).
[17] S. Winstein and D. Seymour, *J. Amer. Chem. Soc.* **68**, 119 (1946).
[18] C. Courtot, Fayet and Parant, *C. R. Acad. Sci., Paris* **186**, 371 (1928).
[19] F. Ishiwara, *J. Prakt. Chem.* [2], **108**, 194 (1924).
[20] F. S. Kipping, *J. Chem. Soc.* **65**, 480, 500 (1894).
[21] N. L. Paddock, *Chem. & Ind.* 63 (1953).

Attempts were made to prove the *cis–trans* relationship of (III) and (IV) by isomerisation with alkali, but without success. However, proof was obtained by oxidation in stages and isolation of the theoretically required number of isomers at each stage, finally ending with one ketosulphone.

Thus, oxidation of (III) with peracetic acid yielded a pair of *trans*-hydroxysulphoxides [(Va) and (Vb)], differing only in the orientation about the sulphur atom; similarly, oxidation of (IV) yielded the pair of *cis*-hydroxysulphoxides [(VIa) and
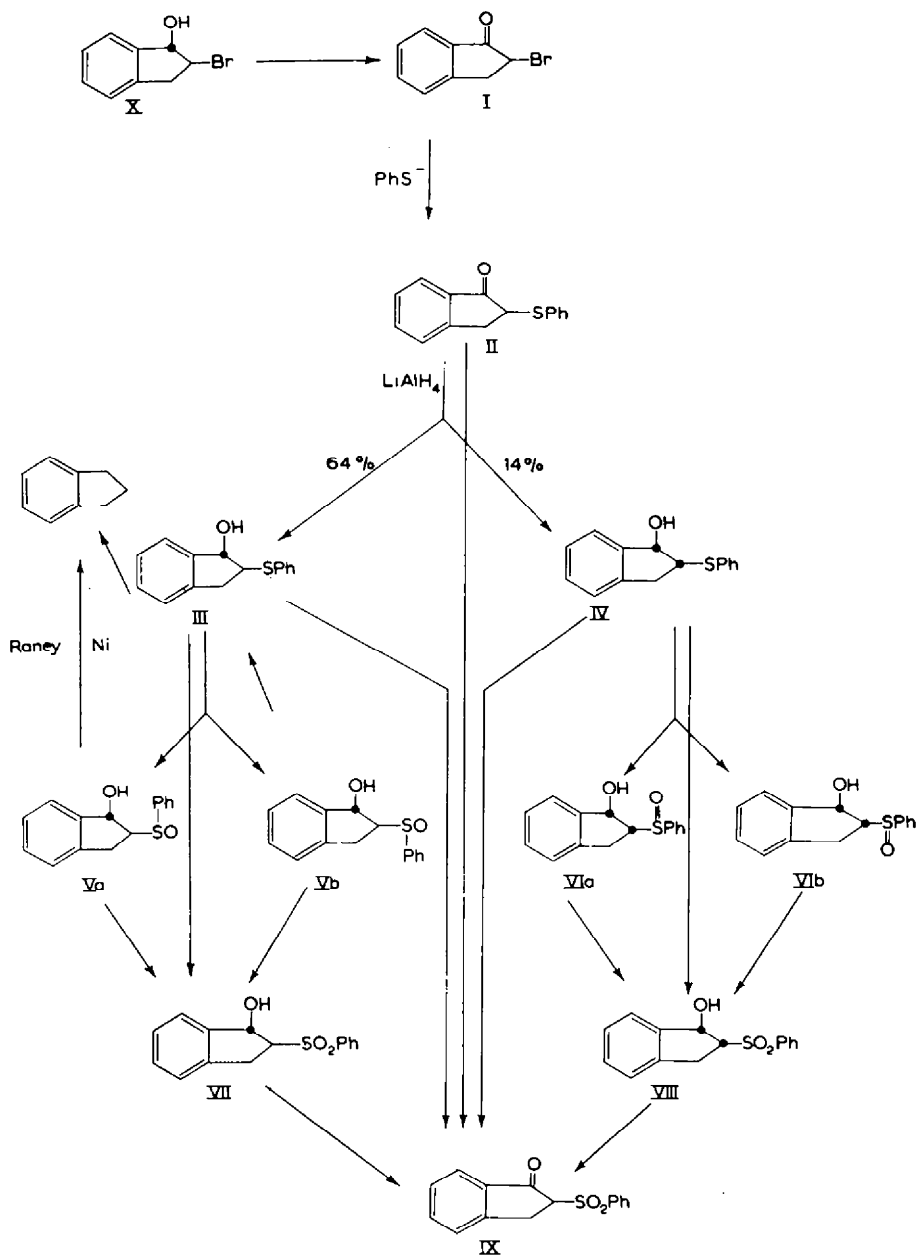
(VIb)]. The relationship between these four isomers with respect to the orientation about the sulphur atom is not known. Further oxidation gave two hydroxysulphones [(VII) and (VIII)], whose *cis–trans* relationship was confirmed by oxidation to the same keto-sulphone (IX).

Attempts to confirm the position of the hydroxyl group by desulphurisation of (III) and (Va) with Raney nickel resulted in complete reduction to indane; by comparison with the desulphurisation of (XI) and (XIIa) (see below) this at least indicates that the hydroxyl group is relatively labile.

The reaction of trans-*indene bromohydrin with sodium thiophenate*

The action of bromine on olefins in aqueous media to form bromohydrins invariably yields the *trans*-isomer[22,23] and, although *cis*-indene bromohydrin is not well characterised, there is no doubt that the indene bromohydrin, m.p. 130°, is the *trans*-isomer.

The reaction between indene bromohydrin and sodium thiophenate was found to be sensitive to reaction conditions; data on the quantities of reactants and products formed are collected in Table 1. In Experiments 1 and 3, although the concentrations were 50 per cent higher in the latter, the proportions were identical, with 6 per cent excess of sodium thiophenate and an additional 12 per cent excess of thiophenol. In both cases the products were mixtures; that from Experiment 1 contained (III), as shown by the isolation of (Va) after oxidation, but from Experiment 3, (IV) must have been the major product, because it separated in the solid state and in amount representing one-third of the total product, although it is the lower melting and more soluble isomer. Direct evidence is lacking, but it is probable that (III) and (IV) were present in both products; however, there is no doubt that the yield of (IV) was appreciably higher in Experiment 3 than in Experiment 1.

In Experiment 2, the excess of sodium thiophenate over the bromohydrin was only 1 per cent, but the reaction medium contained sodium ethoxide derived from the 10 per cent excess of sodium. The product was an oil in which small proportions of (III) and (IV) may have been present, but the major constituent and the sulphoxide (XIIa) obtained from it yielded 2-indanol (XIV) on desulphurisation with Raney nickel. The reaction must therefore have involved migration of the hydroxyl group from the 1- to the 2-position and formation of 1-phenylmercapto-2-indanol (XI).

Kinetic evidence regarding the mechanism of the reaction between *trans*-indene bromohydrin and the thiophenate ion is not available, but it is probable that the reaction lies on the borderline between unimolecular (S_N1) and bimolecular (S_N2), because it is sensitive to reaction conditions.[24,25]

In the presence of sodium ethoxide, ionisation of the hydroxyl group will develop a negative charge on the oxygen; this will promote ionisation at the reaction site and accelerate the S_N1 reaction. In addition, the adjacent —O⁻ group has a strong tendency to participate in the intermediate step[26] and in the present system this would be expected to lead promptly to the formation of epoxide. As shown by direct
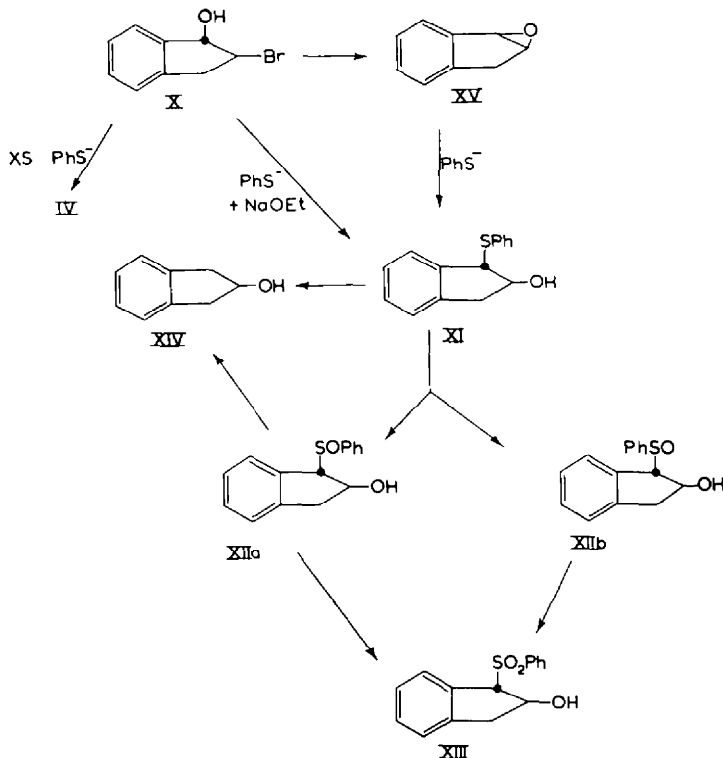
[22] P. D. Bartlett, *J. Amer. Chem. Soc.* **57**, 225 (1935).
[23] P. D. Bartlett and R. V. White, *J. Amer. Chem. Soc.* **56**, 2785 (1934).
[24] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 244 (1935).
[25] E. D. Hughes, *Trans. Faraday Soc.* **37**, 603 (1941).
[26] S. Winstein, *et al., J. Amer. Chem. Soc.* **70**, 816, 821, 828 (1948).

experiment, attack by thiophenate ion on the epoxide (XV) yields as major product the same compound, (XI), obtained in Experiment 2.

With regard to the stereochemical configuration of the rearranged product, it is known[27,28,29,30] that inversion invariably accompanies epoxide formation and also epoxide ring opening so that retention of the *trans*-configuration is expected for the overall reaction. For this reason, the hydroxysulphoxides (XIIa) and (XIIb) and the hydroxysulphone (XIII) are assigned the *trans*-1-substituted-2-indanol structures.

In alcoholic solution, with a small excess of thiophenol, the hydroxyl group will not be ionised; its participation in the transition state and promoting effect on the S_N1 mechanism will be considerably reduced. This condition prevailed in Experiments 1 and 3 and a 50 per cent increase in concentration of the reactants increased the proportion of (IV) in the product. This may be interpreted either as an increased contribution from the bimolecular (S_N2) mechanism or, alternatively, as a result of a shortening of the life of the cation in the S_N1 reaction with consequent increase in the shielding effect of the receding bromide ion. Either interpretation leads to the conclusion that the isomer (IV) favoured by increased concentration is the *cis* form.

If the above interpretations are correct, it should be possible by reducing the dielectric constant of the medium and increasing the thiophenate-ion concentration to inhibit the S_N1 mechanism and promote the S_N2. Experiment 4 was therefore

[27] D. Swern, *J. Amer. Chem. Soc.* **70**, 1235 (1948).
[28] D. Swern, *Organic Reactions* (Ed.-in-Chief Roger Adams) Vol. VII, p. 387. Wiley, New York (1953).
[29] F. G. Bordwell and R. J. Kern, *J. Amer. Chem. Soc.* **77**, 1141, (1955).
[30] S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.* **61**, 1581 (1939).

carried out with a fourfold excess of thiophenate ion and, as solvent, thiophenol containing the minimum amount of ethanol necessary to dissolve the thiophenate. An 89 per cent recovery of product was achieved and it was virtually pure hydroxysulphide (IV). This provides convincing confirmation of the assignments of configuration made on the evidence of yields of isomers from the lithium aluminium hydride reduction of (II), namely, that (III), m.p. 102°, is *trans* and (IV), m.p. 72°, is *cis*.

EXPERIMENTAL*

Infra-red absorption spectra† were recorded for all the substances described. The method of Barnard and Hargrave[31] used for estimation of hydroperoxide and sulph-oxide was modified only by the addition of acetic acid (10 ml) at the same time as the titanous chloride and ammonium thiocyanate, to ensure solubility of the sulphoxides in the aqueous media.

Co-oxidation of indene and thiophenol. Indene (obtained from Gesellschaft für Teerverwertung, Duisberg-Meiderich) was distilled under nitrogen (oxygen content not greater than 0·001 per cent), b.p. 67°/13 mm, n_D^{20} 1·5765, f.p. −1·549°, purity determined by freezing point[32] was not less than 99·5 per cent. Thiophenol was also distilled under nitrogen before use, b.p. 69°/13 mm, n_D^{20} 1·5899.

A solution of indene (0·046 mole) and thiophenol (0·045 mole) in benzene (150 ml) was shaken in an atmosphere of oxygen at 20 ± 0·1° and 760 ± 5 mm. Absorption of oxygen (0·043 mole) was complete in 85 min and mercaptan was not detectable in the product. Immediately after the oxidation 77 per cent of the absorbed oxygen was present as hydroperoxide and 7 per cent as sulphoxide. On subsequent standing, the hydroperoxide decayed by a second-order law and after 140 hr at 20° the hydroperoxide concentration was virtually zero; concurrently, the sulphoxide concentration rose to a value corresponding to 45 per cent of the absorbed oxygen.

Lithium aluminium hydride reduction of the primary co-oxidation products. Isolation of the hydroperoxide was impracticable owing to the ease with which it decomposed.

The reaction mixture at the end of an oxidation similar to that described above was cooled rapidly to 5°, shaken with anhydrous magnesium sulphate, filtered and added slowly to an ice-cooled suspension of lithium aluminium hydride (4 g) in tetrahydro-furan (150 ml). Hydroperoxide in the solution of co-oxidation products was estimated half-way through the addition by titration of a 2 ml sample (Found: —OOH, 0·029 mole in 150 ml; 69 per cent of the oxygen uptake). The reduction reaction mixture was refluxed for 6 hr, after which time water and sodium hydroxide were added; extraction with benzene yielded, on removal of solvent, 9·05 g of brown solid. Chro-matography on a silica-gel column gave *trans*-2-phenylmercapto-1-indanol (III) (7·19 g, 0·030 mole), identical in infra-red spectrum and m.p. with synthetic material.

Secondary co-oxidation products. Three separate co-oxidations of indene (5·353 g) and thiophenol (4·95 g) in benzene (300 ml) were carried out at 20° (oxygen absorbed: 1·347 g in each), and the combined reaction mixtures were maintained at 20° until decay of the hydroperoxide was complete. In the later stages of the reaction colourless crystals (8·0 g), m.p. 140–145°, were deposited. After 140 hr the supernatant liquid

[31] D. Barnard and K. R. Hargrave, *Anal. Chim. Acta* 6, 23 (1952).
[32] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Res. Nat. Bur. Stand.* 35, 355 (1945).

(solution *A*) was decanted and the deposits, on recrystallisation from benzene, yielded a pure hydroxysulphoxide, m.p. 150° (Found: —OH, 6·50; =SO, 18·20. Calc. for $C_{15}H_{14}O_2S$: —OH, 6·59; =SO, 18·58 per cent), which was identical in m.p. and infra-red spectrum with the synthetic high-melting isomer of *trans*-2-phenylsulphinyl-1-indanol (Va) and did not depress its m.p.

Solution *A* was diluted with an equal volume of *n*-pentane and the resulting white precipitate consisting (infra-red spectrum) of a mixture, m.p. 80–125°, of the *trans*-hydroxysulphoxides (Va) and (Vb) (8·3 g)(Found: —OH, 6·40; =SO, 18·40 per cent), was filtered off.

The benzene–pentane filtrate, after removal of solvent under reduced pressure, left a brown viscous oil, from which a small amount of indene (1·3 g; n_D^{20} 1·5768) was recovered by distillation in high vacuum. On trituration of the residue with carbon tetrachloride crystals separated (8·3 g), consisting of the low-melting *trans*-2-phenyl-sulphinyl-1-indanol (Vb), which after crystallisation from benzene–*cyclo*hexane melted at 99° (Found: —OH, 6·26; =SO, 18·20. Calc. for $C_{15}H_{14}O_2S$: —OH, 6·59; =SO, 18·58 per cent). This material was identical in m.p. and infra-red spectrum with synthetic (Vb) and did not depress its m.p.

Removal of carbon tetrachloride from the remaining solution yielded a viscous oil (8·76 g), which was adsorbed on a column of silica gel and eluted by solvents of increasing polarity. The first two components were diphenyl disulphide (0·6 g; m.p. and mixed m.p. with authentic material, 61°) and *trans*-2-phenylmercapto-1-indanol (III) (0·65 g), identified by infra-red spectrum, m.p. and mixed m.p., 102°. Further quantities of (Va) (1·50 g, m.p. 150)°, were also isolated; other fractions (1·4 g) had spectra closely resembling those of (Va) and (Vb).

The hydroxysulphoxides and hydroxysulphide together accounted for 86 per cent of the oxygen absorbed during co-oxidation. The remaining fractions were not iden-tified, but infra-red spectra indicated the presence of various sulphides, ketones, ketosulphides and ketosulphoxides. One fraction (0·09 g) exhibited an infra-red spectrum approximating closely to those of the *cis*-2-phenylsulphinyl-1-indanols.

Oxidation of the hydroxysulphoxides from co-oxidation. The substances (Va), m.p. 150°, (Vb), m.p. 99°, and the mixture, m.p. 80–125°, separated from the co-oxidation products after decay of peroxide were oxidised in acetic acid solution with a five-fold excess of 30 per cent hydrogen peroxide. All three samples gave theoretical yields of *trans*-2-phenylsulphonyl-1-indanol (VII), identical in their infra-red spectra and showing undepressed m.p. with synthetic material.

A mixture containing 95 per cent by weight of (VII) and 5 per cent by weight of the *cis* isomer (VIII) began to liquefy at 105° and completely melted at 115°; the crude hydroxysulphone obtained from the mixture m.p. 80–125° melted at 115–117·5°. It is therefore probable that, if the mixture of hydroxy-sulphoxides contained any *cis*-isomers, the proportion was considerably less than 5 per cent.

trans-*Indene bromohydrin* (X). Indene bromohydrin, m.p. 130°, was prepared by the method of Pope and Read.[33]

2-*Bromo*-1-*indanone* (I). A modification of Courtot's method[18] in which chromic acid in acetic acid was employed to oxidise the bromohydrin (0·4 mole) gave a 61 per cent yield of bromoketone, m.p. 33·5–34·5° (Courtot: 38°).

2-*Phenylmercapto*-1-*indanone* (II). The bromoketone (0·2 mole) dissolved in dry

[33] W. J. Pope and J. Read, *J. Chem. Soc.* 101, 758 (1928).

methanol (200 ml) was slowly added, in an atmosphere of nitrogen, to a solution of sodium thiophenate prepared from sodium (5 g), dry methanol (150 ml) and thiophenol (0·196 mole). After 15 min under reflux, 175 ml of methanol was distilled off and refluxing was continued for 1 hr; the reaction mixture was then poured into water (1 l.) and extracted with several portions of benzene. The combined extracts were washed with 5 % sodium hydroxide and water and dried over anhydrous magnesium sulphate. Removal of solvent left a solid residue, which yielded, after repeated crystallisation from *cyclo*hexane, 48·4 g (63 per cent) of a slightly impure product, m.p. 65–67·5°. Recrystallisation from benzene–*cyclo*hexane gave pure 2-*phenylmercapto*-1 *indanone* (II) m.p. 66–67° (Found: C, 74·90; H, 5·20; S, 13·57. Calc. for $C_{15}H_{12}OS$: C, 74·99; H, 5·04; S, 13·31 per cent); *semicarbazone*, m.p. 188° (Found: C, 64·65; H, 4·98; N, 14·31; S, 11·07. Calc. for $C_{16}H_{15}ON_3S$: C, 64·63; H, 5·09; N, 14·14; S, 10·76 per cent); 2:4-*dinitrophenylhydrazone*, m.p. 191° (Found: C, 60·07; H, 3·75; N, 13·17; S, 7·82. Calc. for $C_{21}H_{16}O_4N_4S$: C, 59·99; H, 3·84; N, 13·33; S, 7·61 per cent). The ketosulphide regenerated from the semicarbazone was unchanged in m.p.

trans- *and* cis-2-*Phenylmercapto*-1-*indanol* [(III) *and* (IV)]. A solution of 2-phenyl-mercapto-1-indanone (4·2 g) in sodium-dried ether (30 ml) was slowly added with stirring to a slurry of lithium aluminium hydride (1 g) in dry ether (50 ml) and refluxed for 3 hr. The product (4·08 g, 96 per cent) was isolated in the usual way.[34] Fractional crystallisation from *cyclo*hexane–pentane mixtures yielded the two isomers: trans-2-*phenylmercapto*-1-*indanol* (III), m.p. 102° (2.7 g, 64 per cent). (Found: C, 74·05; H, 5·90; S, 13·38; —OH, 7.2. Calc. for $C_{15}H_{14}OS$: C, 74·37; H, 5·82; S, 13·20; —OH, 7·05 per cent); *phenylurethane*, m.p. 121° (Found: C, 73·19; H, 5·39; N, 4·10; S, 8·85. Calc. for $C_{22}H_{19}O_2NS$: C, 73·10; H, 5·28; N, 3·87; S, 8·87 per cent); and cis-2-*phenylmercapto*-1-*indanol* (IV) m.p. 72° (0·6 g, 14 per cent) (Found: C, 74·49; H, 5·97; S, 13·43; —OH, 7·0 per cent); *phenylurethane*, m.p. 124° (Found: C, 72·91; H, 5·30; N, 4·17; S, 8·80 per cent). The infra-red spectra of the two isomers were much alike, but differed in detail. A mixed m.p. of the phenylurethanes was depressed to 97–105°. Desulphurisation of (III) with Raney nickel yielded indane, identified by refractive index (n_D^{20} 1·5380) and by its retention volume on a gas-chromatography column.

Attempted isomerisation of the trans- *and* cis-2-*phenylmercapto*-1-*indanols*. cis-2-Phenylmercapto-1-indanol (IV) (0·12 g) was heated with lithium aluminium hydride (0·05 g) in sodium-dried ether (7 ml) for 4 hr. After working up in the usual manner, the starting material was recovered (0·11 g), m.p. 70–71°, but with a faint odour of thiophenol.

The hydroxysulphide (IV) (0·5 g) was refluxed under nitrogen for 4 hr with 10 % alcoholic potassium hydroxide (5 ml). After neutralisation with carbon dioxide, filtration and evaporation, the starting material was again recovered (0·45 g), m.p. 70·5–72°.

trans-2-Phenylmercapto-1-indanol (III) (0·2 g) was refluxed with 10 % alcoholic potassium hydroxide (2 ml) for 8 hr. After neutralisation with carbon dioxide and filtration, the brown solution was decolorised with charcoal and evaporated. The infra-red spectrum of the product (0·12 g), m.p. 80–90°, indicated that about 50 per cent had decomposed to an unidentified substance other than (IV).

The hydroxysulphide (III) (0·5 g) was heated in an evacuated sealed tube with 10 %

[34] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.* **69**, 1197 (1947).

alcoholic potassium hydroxide at 100° for 4 hr. After working up with carbon dioxide, the starting material was recovered unchanged, m.p. 101–102°.

trans-2-*Phenylsulphinyl*-1-*indanols* [(Va) *and* (Vb)]. The hydroxysulphide (III) (1·15 g) was oxidised in acetic acid solution with a 10 per cent excess of 30% hydrogen peroxide, the solution being cooled to 5° during addition of the reagent and then allowed to stand at room temperature for 24 hr. By fractional crystallisation of the product (1·23 g, 100 per cent) from benzene–*cyclo*hexane, *the two* trans-2-*phenylsulphinyl*-1-*indanols* were isolated: (Va) (0·31 g), m.p. 149·5–150·5° (Found: C, 69·94; H, 5·65; S, 12·40; =SO, 18·20; —OH, 6·39, 6·50) and (Vb) (0·25 g), m.p. 99° (Found: C, 69·66; H, 5·40; S, 12·40; =SO, 18·20; —OH, 6·26. Calc. for $C_{15}H_{14}O_2S$: C, 69·77; H, 5·46; S, 12·39; =SO, 18·58; —OH, 6·59 per cent). The spectra of the high- and low-melting isomers were similar, but differed in detail. From the m.p. and quantities of the intermediate fractions, it was estimated that the two isomers were formed in equal proportions. Desulphurisation of (Va) with Raney nickel yielded indane.

cis-2-*Phenylsulphinyl*-1-*indanols* [(VIa) *and* (VIb)]. Oxidation of the hydroxysulphide (IV) (2·6 g) by the method used for the *trans* isomer gave a colourless gum (2·3 g) from which were separated *the two* cis-2-*phenylsulphinyl*-1-*indanols*: (VIa) (0·9 g), m.p. 158° (Found: C, 69·36; H, 5·52; S, 12·68) and (VIb, (0·9 g) m.p. 122–123° (Found: C, 69·84; H, 5·61; S, 12·90. Calc. for $C_{15}H_{14}O_2S$: C, 69·77: H, 5·46; S, 12·39 per cent). The infra-red spectra of these two isomers were similar, but differed considerably from those of the isomers (Va) and (Vb).

trans-2-*Phenylsulphonyl*-1-*indanol* (VII). The hydroxysulphide (III) (0·75 g), oxidised in chloroform solution by shaking with acid permanganate solution and working up in the usual manner,[35] yielded trans-2-*phenylsulphonyl*-1-*indanol* (VII) (0·3 g), m.p. 122° (Found: C, 65·55; H, 5·17; S, 11·72. Calc. for $C_{15}H_{14}O_3S$: C, 65·69; H, 5·14; S, 11·66 per cent). The infra-red spectrum showed characteristic hydroxyl and sulphone bands.

cis-2-*Phenylsulphonyl*-1-*indanol* (VIII). Oxidation of (IV), (VIa) and (VIb) in acetic acid solution with five-fold excess of 30% hydrogen peroxide and crystallisation of the products from benzene–*cyclo*hexane gave 95 per cent yields of cis-2-*phenylsulphonyl*-1-*indanol* (VIII), m.p. 131° (Found: C, 65·76; H, 5·24; S, 11·68. Calc. for $C_{15}H_{14}O_3S$: C, 65·69; H, 5·14; S, 11·66 per cent). Mixed m.p. of the three preparations showed no depression.

2-*Phenylsulphonyl*-1-*indanone* (IX). Oxidation of (III), (VII) and (VIII) (2 millimoles) in acetic acid solution with chromic acid (4 millimoles) at 40° (20 min) and permanganate oxidations of (II) and (IV) yielded in all cases 2-*phenylsulphonyl*-1-*indanone* (IX), m.p. 147–148°. The infra-red spectrum of the product from (VII) was consistent with a pure ketosulphone structure (Found: C, 66·23; H, 4·67; S, 12·52. Calc. for $C_{15}H_{12}O_3S$: C, 66·16; H, 4·44; S, 11·77 per cent). *The* 2:4-*dinitro-phenylhydrazone* formed yellow needles from ethyl acetate, m.p. 262° (Found: C, 55·63; H, 3·68; N, 12·38; S, 7·12. Calc. for $C_{21}H_{16}O_6N_4S$: C, 55·74; H, 3·56; N, 12·38; S, 7·08 per cent).

The reaction of trans-*indene bromohydrin with sodium thiophenate*. Four experiments were carried out under different conditions as shown in Table 1; in each an atmosphere of nitrogen was maintained over the reaction mixture. Sodium thiophenate was

(35) J. I. Cunneen, *J. Chem. Soc.* 36 (1947).

TABLE 1. THE REACTION OF *trans*-INDENE BROMOHYDRIN WITH SODIUM THIOPHENATE

Experiment	1	2	3	4
Bromohydrin solution:				
Indene bromohydrin (mole)	0·047	0·665	0·094	0·05
Ethanol (ml)	65	250	110	5
Benzene (ml)	—	200	—	—
Thiophenol (ml)	—	—	—	70
Thiophenate solution:				
Sodium (g-atom)	0·050	0·740	0·100	0·25
Thiophenol (mole)	0·056	0·673	0·112	0·5(50 ml)
Ethanol (ml)	70	350	100	35
Reaction temperature (°C)	Reflux	Reflux	Reflux	50–60
Time of reaction (min)	30	10	45	120
Product:	Oil	Oil		Solid
Yield (per cent of theoretical)	82	71	28 (solid*) 57 (oil)	87 (IV, <2 (other material)
n_D^a	1·6359	1·6368	—†	
Phenylurethane, m.p. (°C)	—	147	124	124
Derived sulphoxides	(Va) (25%)	(XIIa), (XIIb) (44% of each)	(VIa), (VIb) (50% of each)	

* (IV)
† Dehydration occurred during distillation of the oil and it was not investigated further.

prepared by dissolving clean sodium in ethanol containing thiophenol and a solution of the bromohydrin was added slowly with stirring. After a period for reaction, the bulk of the solvent was removed at low pressure and the residue was taken up in ether or benzene and 5–7% aqueous sodium hydroxide. Excess of thiophenol was removed from the organic layer by extraction with alkali, followed by water washing and drying over anhydrous magnesium sulphate; the solvent was finally removed under reduced pressure. The liquid products from Experiments 1 and 2 were distilled in vacuum; the solid products from Experiments 3 and 4 were crystallised from *cyclo*hexane–pentane. Phenylurethanes and sulphoxides were prepared from the various products by the usual methods.

Investigation of the product from Experiment 2. The product from Experiment 2 was a viscous orange oil, n_D^{20} 1·6368 (Found: —OH, 6·9. Calc. for $C_{15}H_{14}OS$: —OH, 7·05 per cent), with an infra-red spectrum showing bands characteristic of hydroxyl and sulphide but no other oxygen- or sulphur-containing groups. A phenylurethane was obtained in good yield, m.p. 146–147°, not depressed on admixture with the phenylurethane of the product obtained by the action of sodium thiophenate on indene epoxide (see below).

The hydroxysulphide oil (2·14 g) dissolved in ethanol (150 ml) was refluxed for 2 hr with Raney nickel (40 g). After filtration, the bulk of the solvent was removed by distillation through a 35 cm column packed with Fenske helices. The residue yielded

0·55 g (50 per cent of theoretical) of 2-indanol, m.p. 68–69°, phenylurethane, m.p. 131·5–132·5°.

The product from Experiment 2 must therefore be a mixture of isomeric hydroxy-sulphides, the major component of which is *trans*-1-phenylmercapto-2-indanol (XI).

trans-1-*Phenylsulphinyl-2-indanols* [(XIIa) *and* (XIIb)]. Oxidation of the product from Experiment 2 (10 g) in acetic acid solution with 10 per cent excess of 30% hydrogen peroxide gave a pale-yellow viscous oil (10 g). Trituration with benzene separated a solid (4·6 g), m.p. 145–148°, which on recrystallisation from benzene yielded the *high-melting isomer* of trans-1-*phenylsulphinl-2-indanol* (XIIa), m.p. 157–158° (Found: C, 70·03; H, 5·39; S, 12·13; —OH, 5·9; =SO, 18·0. Calc. for $C_{15}H_{14}O_2S$: C, 69·77; H, 5·46; S, 12·39; —OH, 6·59; =SO, 18·58 per cent). The mixed m.p. with the hydroxysulphoxide (VIa), m.p. 158°, was depressed to 110–120°.

Evaporation of the mother-liquors left a solid (4·0 g), m.p. 125–129°, which yielded on crystallisation from *cyclo*hexane–benzene (50:50), the *low-melting isomer of* trans-1-*phenylsulphinyl-2-indanol* (XIIb), m.p. 133–134·5° (Found: C, 70·13; H, 5·58; S, 12·51. Calc. for $C_{15}H_{14}O_2S$: C, 69·77; H, 5·46; S, 12·39 per cent). By desulphuri-sation of the high-melting isomer (0·6 g in 80 ml of ethanol) with Raney nickel as described for the product of Experiment 2, the same 2-indanol, (0·06 g, 20 per cent m.p. 68–69°, and its phenylurethane, m.p. 131–132°, were obtained.

The final mother-liquors contained a solid (0·7 g), m.p. 99–110°, raised by cry-stallisation from benzene-*cyclo*hexane to 113·5–114·5°; mixed m.p. with the hydroxy-sulphone (XIII) (see next paragraph) was not depressed.

trans-1-*Phenylsulphonyl-2-indanol* (XIII). Oxidation of the hydroxysulphoxides (XIIa) and (XIIb) in acetic acid with excess of 30% hydrogen peroxide gave theoretical yields of trans-1-*phenylsulphonyl-2-indanol* (XIII); the m.p. of the two samples and their mixed m.p. were 114–115° (Found: C, 65·72; H, 4·92; S, 11·86. Calc. for $C_{15}H_{14}O_3S$: C, 65·69; H, 5·14; S, 11·66 per cent). A mixed m.p. with the hydroxysulphone, m.p 122°, was depressed to 97–110°.

trans-1-*Phenylmercapto-2-indanol* (XI). Indene epoxide (0·35 mole), prepared by the method of Boeseken[36] was treated with sodium thiophenate (0·36 mole) in 50% aqueous ethanol, following the procedure of Bordwell and Kern.[29] The product (9·05 g) was a pale-yellow viscous oil, n_D^{20} 1·6294 (Found: —OH, 6·0 Calc. for $C_{15}H_{14}OS$: —OH, 7·05 per cent). Although the product was evidently impure owing to partial dehydration, the *phenylurethane* of trans-1-*phenylmercapto-2-indanol* was obtained in 70 per cent yield, m.p. 143–146°, raised by crystallisation from *cyclo*-hexane to 146–147° (Found: C, 72·90; H, 5·30; N, 4·28; S,8·67. Calc. for $C_{22}H_{19}O_2NS$: C, 73·10; H, 5·28; N, 3·87; S, 8·87 per cent).

[36] J. Boeseken and C. van Loon, *Proc. Kon. Akad. Wet., Amst.* **20**, 1186 (1918); *Chem. Abstr.* **13**, 314 (1919).