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SUBSTITUENT EFFECTS IN THE CO-OXIDATION REACTION OF INDENE AND AROMATIC THIOLS. EVIDENCE FOR A CLASSICAL-BRIDGED RADICAL EQUILIBRIUM

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Previous investigators of the co-oxidation reaction of indene and thiophenol claim (1) the formation of only trace amounts (0.25%) of the <u>cis</u> - hydroxy sulfoxide, and this result is frequently quoted (2) in the discussion of the stereospecificity of homolytic thiol addition reactions to olefins and in the general consideration of the existence of bridged radical intermediates. Some time ago we have reported (3) that careful quantitative separation of the co-oxidation products of thiophenol and indene leads to the isolation of a 14.3% yield (duplicate results) of the <u>cis</u>-2-phenyl-sulfinyl-1-indanol (<u>anti</u> sulfoxide configuration) when the reaction is carried out in hexane, and that the yields of this isomer increase to 15-18% when benzene is used as a solvent. These results demonstrate that the addition of oxygen to the 2-phenylmercapto-1-indanyl radical is not as stereospecific as previously assumed, and would appear to cast serious doubts concerning the existence of bridged sulfur radicals in this system. However, parallel co-oxidation experiments with <u>p</u>-substituted thiophenols now reveal that the relative yields of the <u>cis</u>-arylsulfinyl-1-indanols (all of the <u>anti</u>-configuration) vary as a function of the electronic character of the <u>p</u>-substituent. Thus, the electron-donating <u>p</u>-methyl group depressed the yield of the <u>cis</u> sulfoxide to 9%, while the electron-withdrawing <u>p</u>-chloro substituent increased the yield of the <u>cis</u> sulfoxide to 19% (all experiments were carried

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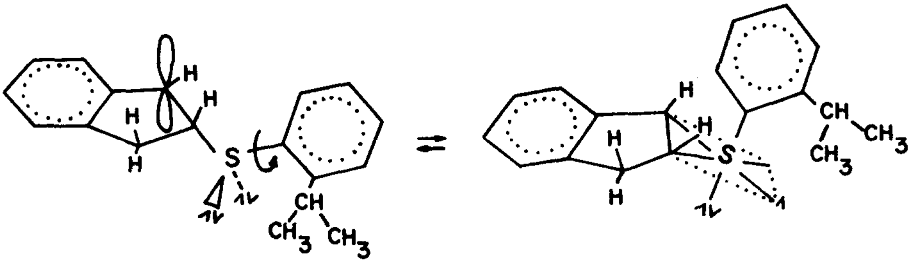
out in hexane). While this work is being expanded to include the effect of additional substituents, these initial results are believed to be noteworthy in view of the current interest in bridged radicals (2,4).

Since the stereochemistry of addition reactions of indene is not complicated by conformational uncertainties inherent to aliphatic and alicyclic olefins, and since the change of p- substituents may be expected to produce insignificant steric effects with regard to the direction of the addition of oxygen to the 2-arylmercapto-1-indanyl radical, the experimentally reproducible and significant variations in the yields of the cis isomers (relative to the trans isomers) must be explained on other grounds. The explanation which is compatible with the results reported here, as well as with the non-stereospecific oxygen addition in the formation of the polymeric indene peroxide (5), on one hand, and the highly stereospecific (6) homolytic addition reaction of methyl deuteriomercaptan to cis and trans 2-butene in the presence of deuterium bromide, on the other, suggest that the bridging capacity of a substituent beta to the radical center is proportional to the electron density at the atom active in the formation of the bridge. The same argument may be invoked to explain the difference in the behavior of vicinal dihalides in the reaction with tin hydrides (7) in which a vicinal bromine appears to form a bridged radical intermediate while a neighboring chlorine does not.

Thus it is concluded that the stereochemistry of the addition reaction of thiols to indene is determined, at least in part, by an equilibrium between classical and bridged radicals, and that the equilibrium concentration of the latter is a function of the electron density at the sulfur atom. In the indene system the radical center is, of course, delocalized over the adjoining benzene ring and this is expected to inhibit to some extent the formation of bridged radicals in comparison with a non-delocalized radical center formed in the addition reaction of 2-butene.

A further result of interest is the isolation of a 13.3% yield of the cis co-oxidation product from the reaction of indene and o-isopropylthiophenol in hexane. On both counts, the favorable effect of the electron-releasing isopropyl group in the formation of the bridged radical, and the steric hindrance introduced by the o-substituent toward the cis approach of oxygen in the classical radical, the relatively high yield of cis co-oxidation product is very surprising. While the effect of other o-substituents is subject of further studies, one may speculate that the primary steric effect exerted by the o-isopropyl group is on the classical-bridged radical equilibrium, and that this effect is so pronounced because the conversion of the classical to the bridged radical involves a rehybridization of the essentially tetrahedral sulfur to a more nearly octahedral (or trigonal bipyramidal) state. Such a rehybridization is accompanied by a decrease in the C-S-C bond angle, and a constriction in the rotational freedom of the *o*-isopropylphenyl group.



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