to obtain a (1–6) × 10^{-4} M solution of the amine oxide. Measurement of absorbance at λ_{max} for the *N*-oxide or the rearrangement product began immediately.

Reaction rate constants were calculated from the slope of ln $(A_t - A_\infty)$ vs. time for experiments in which the rate of the disappearance of the *N*-oxide was followed or from ln $(A_\infty - A_t)$ vs. time in cases where the rate of product formation was followed. In all cases the least-squares plots of log $(A_t - A_\infty)$ or log $(A_\infty - A_t)$ vs. time were linear. An Arrhenius plot of ln k vs. $1/T$ gives the energy of activation and the frequency factor from which the entropy of activation could be calculated by using eq 6 and 7.

$$\ln k - \ln A = E_a/RT \quad (6)$$

$$\ln A = \ln (ekT/h) + \Delta S^*/R \quad (7)$$

Least squares plots of ln k vs. $1/T$ for rearrangement of **6a–c** were linear.

Crossover Experiment. A mixture of **6b** and **6c** (0.5 g of each) was dissolved in dioxane and heated at reflux (100 °C) for 3 h (over 3 half-lives of **6c**). The solvent was stripped off, and the resulting residue was analyzed by thin-layer chromatography and showed only two spots corresponding to **7b** and **7c**: R_f (25% benzene–75% petroleum ether 80–100 °C) of **7b**, 0.953; R_f of **7c**, 0.869; authentic **7b**, R_f 0.957; authentic **7c**, R_f 0.871.

Registry No. **5a**, 6574-15-8; **5b**, 10389-51-2; **5c**, 15822-77-2; **5d**, 5320-98-9; **5e**, 15822-71-6; **5f**, 15822-78-3; **5g**, 78019-75-7; **5h**, 78019-76-8; **5i**, 78019-77-9; **5j**, 78019-78-0; **6a**, 40832-54-0; **6a**·HCl, 78019-79-1; **6b**, 40832-53-9; **6b** picrate, 78019-80-4; **6b**·HCl, 78019-81-5; **6c**, 54399-43-8; **6c**·HCl, 78019-82-6; **6d**, 78019-83-7; **6d** picrate, 78019-84-8; **6e**, 78019-85-9; **6e**·HCl, 78019-86-0; **6f**, 78019-87-1; **6f**·HCl, 78019-88-2; **6g**, 78019-89-3; **6g**·HCl, 78019-90-6; **6h**, 78019-91-7; **6h**·HCl, 78019-92-8; **6i**, 78019-93-9; **6i**·HCl, 78019-94-0; **6j**, 78019-95-1; **6j**·HCl, 78019-96-2; **7a**, 78039-75-5; **7b**, 78019-97-3; **7c**, 78019-98-4; **7d**, 78019-99-5; **7e**, 78020-00-5; **7f**, 78020-01-6; **7g**, 78020-02-7; **7h**, 78039-76-6; **7i**, 78020-03-8; **7j**, 78039-77-7; piperidine, 110-89-4; morpholine, 110-91-8; 2-methylpiperidine, 109-05-7; 3-methylpiperidine, 626-56-2; 4-methylpiperidine, 626-58-4; *p*-nitrofluorobenzene, 350-46-9; *o*-nitrofluorobenzene, 1493-27-2.

Thiol–Oxygen Cooxidation Reactions of Cyclopentene, *cis*- and *trans*-But-2-ene, Norbornene, and Norbornadiene

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Thiol–oxygen cooxidation (TOCO) of olefins, followed by reduction of the initially formed hydroperoxides with triphenylphosphine, affords β-hydroxy sulfides in moderate to good yields. The structures of the major products from *cis*- and *trans*-but-2-ene and from cyclopentene indicate that coupling of the intermediate β-thioalkyl radicals with oxygen occurs mainly anti to the sulfur substituent but proceeds too slowly to compete effectively with internal rotation about the C_α–C_β bond. TOCO reactions of aromatic thiols with norbornene involve preferential exo addition of arylthio radicals to the double bond followed by coupling with oxygen in both exo and endo modes; the exo/endo ratio is sensitive to the nature of the thiol. TOCO reactions of norbornadiene afford, inter alia, hydroxy sulfides containing the tricyclene nucleus.

Thiol–oxygen cooxidation (TOCO) reactions[1,2] of olefins and reactive arenes afford convenient and efficient routes to hydroperoxy sulfides or hydroperoxy thioesters and compounds derived therefrom such as hydroxy sulfoxides,[2] aryl thioethers and thioesters,[3] and dihydroarene bis(thioethers).[3] Notable features of TOCO reactions, which can be applied to the preparation of useful synthons,[4-6] are their susceptibility to initiation by free-radical precursors, their propensity to rapidly afford high yields of products, and their relative freedom from side reactions.

These and other features of TOCO reactions are consistent with the free-radical mechanism first enunciated by Kharasch.[7] It involves three chain-propagation steps. In the first (eq 1), addition of thiyl radicals proceeds regioselectively at the less substituted terminus of an olefinic bond, or, in the case of arenes, to a position of high free valence.[3] The regioselectivity of the addition is consistent both with the steric effects of substituents on radical reactions[8,9] and with their expected polar effects[9] on attack by electrophilic species.[10] Rate constants for step 1 are available from studies of free-radical additions of thiols and olefins;[11] typical values of k_1 lie in the range 10^4–10^7 M^{-1} s^{-1}. Recent determinations[12] give values of 2.7 × 10^5 and 2 × 10^8 s^{-1} for k_{-1} in reactions involving elimination of BuS· and PhS· respectively[13] (eq 1-3).

The second propagation step (eq 2) is expected to be very fast. Although rate constants have not been precisely

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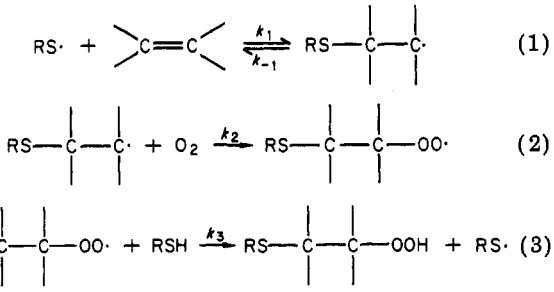
(10) Church, D. F.; Gleicher, G. J. *J. Org. Chem.* **1975**, *40*, 536. Pryor, W. A.; Gojon, G.; Church, D. F. *Ibid.* **1978**, *43*, 793.

(11) Ito, O.; Matsuda, M. *J. Am. Chem. Soc.* **1979**, *101*, 5732, 1815 and references cited.

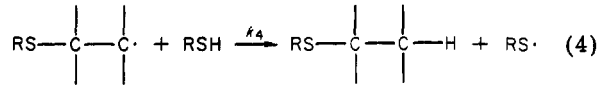
(12) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579.

(13) A value of ca. 4 × 10^5 s^{-1} for the rate constant for β fission of the radical formed by addition of PhS· to methyl methacrylate has been reported.[11] β fission of simple primary or secondary arenethioalkyl radicals would be expected to be more rapid.

0022-3263/81/1946-3638$01.25/0



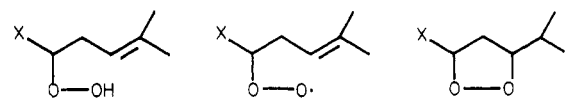
determined, they are known[11] to be larger than 1×10^8 M^{-1} s^{-1} and are probably similar in magnitude to those for coupling of simple alkyl radicals with oxygen ($k \approx 1 \times 10^9$ M^{-1} s^{-1}).[14] In practice, step 2 competes with the atom-transfer process (eq 4) which typically[15] has values of its rate constant (k_4) of $\sim 10^7$ M^{-1} s^{-1}.



The factors important in determining the regio- and stereoselectivity of step 2 have not yet been clearly defined. TOCO reactions of 1,3-dienes give both 1,2- and 1,4-addition products,[5,16] the relative proportions of which appear to reflect the distribution of spin density in the intermediate allylic radical.[10,16] Early reports[17,18] indicated that indene under TOCO conditions undergoes stereospecific trans addition, but other work[2,19] has revealed the formation of significant amounts of cis products in similar reactions. In order to clarify the stereoselectivity of step 2 for typical monoolefinic substrates, we have now studied TOCO reactions of *cis*- and *trans*-but-2-ene, cyclopentene, and norbornene.

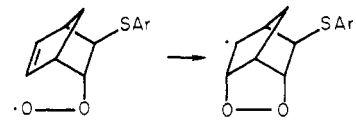
The rate constant[20] for the third propagation step (eq 3) probably has a value of about 5×10^3 M^{-1} s^{-1}. Although this is relatively low, the overall efficiency of the TOCO reaction under normal experimental conditions indicates that step 3 competes effectively with other possible reactions of peroxy radicals. Nevertheless, the opportunity clearly exists to intercept such intermediates by sufficiently rapid alternative inter- or intramolecular processes.

One such process is the ring closure of appropriately constituted alkenylperoxy radicals. Although values of rate constants are not available, the successful formation of cyclic peroxides by treatment of alkyl hydroperoxides (e.g., **1**) with *t*-BuO·[21] indicates that cyclization of **2** to **3** is relatively fast and may well be of comparable rate to the cyclization of analogous carbon-centered radicals ($k \approx 10^5$ s^{-1}).[22] If this is so, it should certainly be possible to observe ring closure of radicals of the general type **4** generated under TOCO conditions. In separate communications[23]



1, X = H **2**, X = H **4**, X = $ArSCH_2$ **3**, X = H **5**, X = $ArSCH_2$

we have described our investigations of such simple systems. The work reported here was initiated to examine the possibility of generating the tricyclic radical **7** from **6**, the architecture of which would appear to favor facile cyclization.

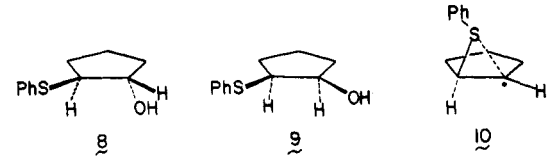


6 **7**

Results and Discussion

TOCO Reactions of Cyclopentene and *cis*- and *trans*-But-2-ene. Preliminary experiments demonstrated that both benzene and hexane–ethyl acetate are good solvents for TOCO reactions; usually we employed hexane–ethyl acetate (4:1). The reactions were initiated by UV irradiation or, more efficiently, by addition of di-*tert*-butyl peroxyoxalate. Two procedures were employed for the isolation of products. One, involving evaporation of the TOCO reaction mixture and chromatography of the residue on silica, afforded mainly hydroxy sulfoxides. In the other, the reaction mixture was treated immediately after completion of the cooxidation with triphenylphosphine which reduces hydroperoxides rapidly and quantitatively to alcohols.[24] Subsequent chromatography gave mainly hydroxy sulfides. Experiments with norbornene and norbornadiene (vide infra) showed that the two methods usually afford consistent information concerning the yields and regio- and stereoselectivity of TOCO reactions.

When the reaction mixture formed by cooxidation of thiophenol with cyclopentene was treated with triphenylphosphine, the only products detected by HPLC and isolated by flash chromatography[25] were the *trans*-hydroxy sulfide **8** (67%) and its cis isomer **9** (11%). The



8 **9** **10**

configurations of the two products were assigned after examination of the effect of a shift reagent on their NMR spectra: the plot of δ(CHOH) – δ(CHS) against [Eu(fod)$_3$] for the cis isomer **9** had a much smaller gradient than that for **8**.

The observation that the TOCO reaction of cyclopentene with thiophenol proceeds mainly (ca. 85%) by trans addition agrees well with data reported by Szmant[2] for the analogous reaction of indene. The simplest explanation for the stereoselectivity of these reactions is that the approach of oxygen toward the cis face of a weakly bridged or "distorted"[26-28] intermediate radical **10** is sterically

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(23) Beckwith, A. L. J.; Wagner, R. D. *J. Am. Chem. Soc.* **1979**, *101*, 7099; *J. Chem. Soc., Chem. Commun.* **1980**, 485.
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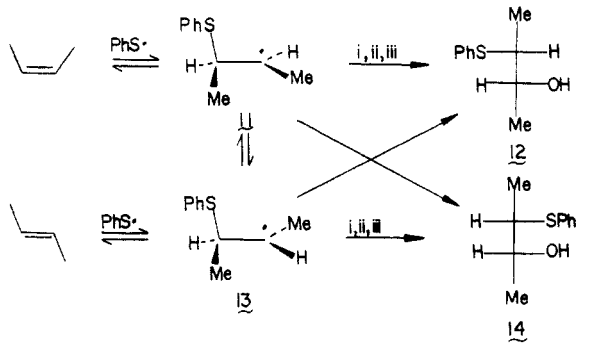
(26) Fischer, H. "Free Radicals"; Kochi, J. K.; Ed.; Wiley: New York, 1973; Vol. 2, p 435.

Scheme I[a]



[a] i, O_2; ii, PhSH; iii, Ph_3P.

hindered by the arylthio group.

Cooxidation of *cis*-but-2-ene with thiophenol gave, after treatment of the initial product with triphenylphosphine, a mixture of the *erythro*-hydroxy sulfide **14** (40%) and its threo isomer **12** (20%).[29] The same products in the same relative proportions were obtained by similar treatment of *trans*-but-2-ene. When the TOCO reaction was conducted with *cis*-but-2-ene in excess, the product mixture contained both *cis*- and *trans*-but-2-ene, with the latter predominating (trans/cis ratio ≈ 2).

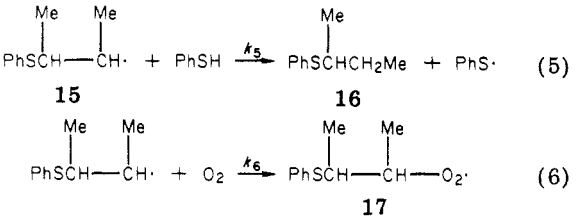
Both the isomerization of *cis*-butene and the formation of **12** and **14** must involve the intermediacy of the conformers **11** and **13** of the initial addition product (Scheme I). The same species have been generated previously by interaction of 2-bromo-3-(phenylthio)butane and tributyltin radicals.[29] Since both the threo and erythro isomers of this bromide give the same ratio of isomers of but-2-ene when treated with tributyltin hydride, Shevlin and his co-workers[29] concluded that interconversion of **11** and **13** is very rapid, that there is a low barrier to internal rotation in such radicals, and that bridging is unimportant.

On the other hand, *cis*- and *trans*-but-2-ene each undergo stereospecific trans addition when treated with CH_3SD and DBr at −78 °C.[30] These results are consistent with the hypothesis[31] that β-thioalkyl radicals have bridged structures and a considerable barrier to interconversion by internal rotation about the C_α–C_β bond. ESR measurements[26-28,32] tend to support this view for they suggest that β-thioalkyl radicals preferentially assume eclipsed conformations such as **11** and **13**. Although they are not symmetrically bridged, they possess distorted structures in which the sulfur atom is displaced from its tetrahedral position toward the radical center, presumably because of homoconjugative interaction between the semioccupied orbital and unoccupied 3d orbitals on sulfur.[26]

The results of the present work indicate that under TOCO conditions the reactions of **11** and **13** with oxygen are not sufficiently fast to compete effectively with their interconversion or with β fission to give the parent olefins. This is not surprising, for although the oxygen coupling reactions have high rate constants (~10^9 M^{-1} s^{-1}), the concentration of oxygen in the reaction mixture is low (ca. 2×10^{-2} M).[33] The relative rates of β fission and oxygen coupling are given by $k_{-1}/k_3[O_2]$, the value of which is ca. 10 if the values of the rate constants given above are correct. Similar considerations lead to the conclusion that substantial equilibration of **11** and **13** will occur even if the rate constant for their interconversion is no greater than 5×10^7 s^{-1}. Thus the results of our experiments are not incompatible with the view that species such as **11** and **13** have partially bridged structures and that there is a barrier to their interconversion.

If we assume that the stereochemistry of attack by oxygen on **11** or **13** is the same as that (trans/cis ratio of 6) for the radical **10** derived from cyclopentene, it is possible to deduce that the composition of the equilibrium mixture of **11** and **13** is [13]/[11] = 2.6. The difference in free energy between **13** and **11** of 0.6 kcal mol^{-1} appears to be reasonable.[34]

A notable feature of the TOCO reactions of cyclopentene or but-2-ene is their failure to afford appreciable quantities (>5%) of simple thiol addition products (e.g., **16** from but-2-ene). This indicates that the atom-transfer reaction (eq 5) is too slow to compete effectively with the oxygen-



(5)

(6)

coupling process (eq 6). The relative rates of the two processes are given by the expression $d[16]/d[17] = k_5[PhSH]/k_6[O_2]$. In our experiments [PhSH] ≈ 0.05 M and $[O_2]$ ≈ 0.02 M. Since k_6 cannot be much greater than 1×10^9 M^{-1} s^{-1} and $k_5 \approx 1 \times 10^7$ M^{-1} s^{-1}, it follows that $d[16]/d[17] \approx 2 \times 10^{-2}$. Our failure to obtain appreciable quantities of **16** is thus seen to be consistent with expectations based on generally accepted values[14,15] of the rate constants for coupling of alkyl radicals with oxygen and for their reaction with thiols by hydrogen atom transfer.

Norbornene. Previous studies of the free-radical addition of various thiols to norbornene[35] have shown that both the addition of thiyl radical and the transfer of the SH hydrogen atom occur almost exclusively on the exo face. The high stereoselectivity of the atom-transfer process is especially significant, for it demonstrates that the steric and torsional factors[36] disfavoring endo attack are sufficient to outweigh those orbital interactions involving partial sulfur bridging which are conducive to trans addition as exemplified by TOCO reactions of cyclopentene and butene.

Cooxidation of *p*-thiocresol and norbornene in ethyl acetate–hexane afforded mainly the *exo,exo*-hydroxy sulfoxide **24a** (58%) and its endo,exo isomer **26a** (23%); (see Scheme II). ^{13}C NMR spectral data indicated that **24a** was isolated as a single diastereoisomer whereas **26a** comprised a mixture of diastereoisomers in which one component is much more abundant than the other (9:1). The significance of this stereoselectivity will be discussed elsewhere. Minor products from the TOCO reaction were the isomeric hydroxy sulfides **25a** (4%) and **27a** (5%) and the sulfide **19a** (5%). The structures of the products were deduced from their spectral properties and from a series

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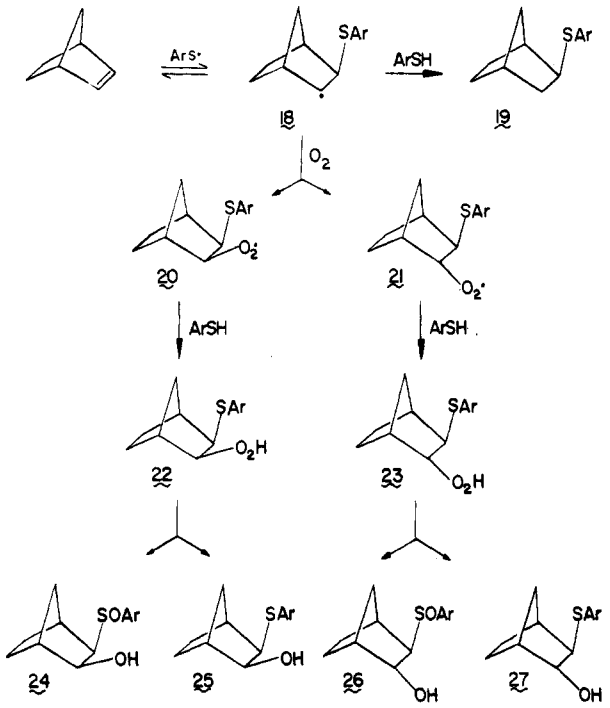
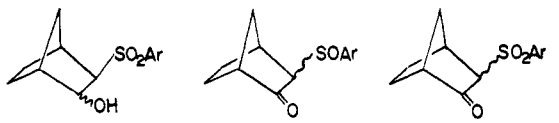
(36) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 699, 701.

Scheme II[a]



[a] a, Ar = p-$CH_3C_6H_4$; b, Ar = o-$CH_3C_6H_4$.

of simple interconversions. Thus **24a** and **26a** were converted into **25a** and **27a**, respectively, on reduction with sodium borohydride–cobalt chloride[37] and to the known[38,39] hydroxy sulfones **28a** and **29a** on oxidation with potassium



28: exo OH 30 31

29: endo OH

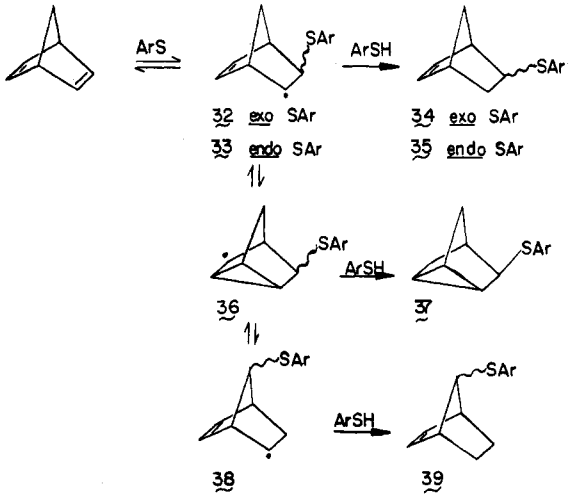
a Ar = p-$CH_3C_6H_4$
b Ar = o-$CH_3C_6H_4$

permanganate. Careful oxidation of either **24a** or **26a** with pyridinium chlorochromate gave the keto sulfoxide **30a** as a mixture of stereoisomers, which was converted into a mixture of stereoisomeric keto sulfones **31a**[38] on further oxidation.

When the TOCO reaction of norbornene with *p*-thiocresol was repeated and the mixture was treated with triphenylphosphine before workup, the only products isolated were the hydroxy sulfides **25a** (54%) and **27a** (41%) and the sulfide **19a** (1%).

The nature and relative yields of the TOCO products from norbornene show that the thiyl radical addition step occurs stereospecifically on the exo face whereas the subsequent coupling with oxygen gives both exo and endo products with some preference for the former.[40] The observation that there is a substantial degree of endo coupling with oxygen is consistent with previous work

Scheme III[a]



[a] Ar = o-$CH_3C_6H_4$.

which indicates that the endo/exo ratio is related to the steric bulk of the reagent and is greatest for coupling with small molecules.[41]

Since our aim of constructing the tricyclic system **7** requires the intermediacy of an endo-peroxy radical, **6**, we investigated the possibility of increasing the degree of endo coupling with oxygen by increasing the steric bulk of the thiyl moiety. Unfortunately, we were unable to isolate pure products from the TOCO reaction of norbornene with *tert*-butyl thiol. However, even the relatively slight change in steric bulk of the thiol brought about by using *o*-thiocresol in place of the para isomer caused a noticeable increase in the degree of endo coupling with oxygen. Thus the TOCO reaction with *o*-thiocresol gave equal total quantities of compounds **24b** (41%) and **25b** (3%) derived from the *exo*-hydroperoxide **22b** and of compounds **26b** (28%) and **27b** (17%) formed from the endo intermediate **23b**. The sulfide **19b** (2%) was also isolated. When triphenylphosphine was added to the reaction mixture before the workup, the products obtained were **25b** (46%), **27b** (46%), and **19b** (2%).

The mechanism for the TOCO reaction of norbornene with *o*- and *p*-thiocresol is set out in Scheme II. As in the case of cyclopentene and butene, the overall rate of β fission of **18** is expected to be faster than its rate of reaction with oxygen, and therefore the exclusive formation of products containing the arylthio substituent in the exo position almost certainly reflects thermodynamic control of the initial step. Other mechanistic features of interest are that the oxygen coupling step is relatively sensitive to steric factors and that the preference for trans addition is much less than is the case for cyclopentene. Undoubtedly, the usual torsional and steric factors disfavoring endo attack in the norbornene system are important. Also, sulfur bridging may be of reduced significance because the semioccupied orbital and the C_β–S bond cannot assume a fully eclipsed relationship.

Norbornadiene. Previous work[42] has shown that norbornadiene is more susceptible to endo radical attack than is norbornene. In order to elucidate the importance of steric factors in reactions of thiyl radicals with nor-

(37) Chasar, D. W. *J. Org. Chem.* **1971**, *36*, 613.
(38) Kleinfelter, D. C.; Squires, T. G.; Mashburn, J. H.; Watsky, R. P.; Brown, S. B. *J. Org. Chem.* **1977**, *42*, 1149.
(39) Although the physical properties of these compounds agree well with those previously reported,[38] there are small differences in ^1H NMR spectral data. It appears that the published data[38] may contain minor typographical errors.
(40) The TOCO reaction involving treatment of the initial product with triphenylphosphine gives an exo/endo ratio of 1.3; without such treatment the ratio is 2. We consider the former figure to be the more reliable.
(41) For a review of stereoselectivity in reactions of norbornyl radicals see: Bartlett, P. D.; Fickes, G. N.; Haupt, F. C.; Helgeson, R. *Acc. Chem. Res.* **1970**, *36*, 177.
(42) For a review of free-radical additions to norbornadiene see: Wilt, J. W. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973, Vol. 1, p 333.

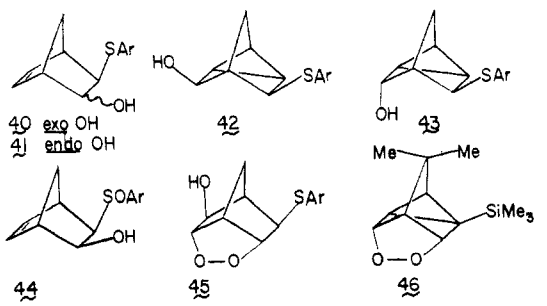
bornadiene, we decided to investigate some simple additions before proceeding to TOCO reactions.

Photoinitiated addition of *o*-thiocresol to norbornadiene gave the *exo*-sulfide **34** (24%), its endo isomer **35** (5%), and the nortricyclene derivative **37** (69%; see Scheme III), the structures of which were assigned by comparison of their spectral properties with published data for thioacetic acid[43] or thiophenol[44] addition products. Since **36** can be formed either from the exo radical **32** or its endo isomer **33**, it is not possible on the basis of these results to determine precisely the exo/endo ratio for attack of *o*-thiocresyl radicals on norbornadiene. However, the ratio of yields of **34** and **35** (34%:35% = 5:1) probably reflects approximately the degree of preference for exo attack. Since the reaction was conducted under conditions of low thiol concentration (0.02 M) the high exo/endo ratio probably reflects thermodynamic control of the addition step.

The other feature of mechanistic interest is the failure of the reaction to produce the 7-substituted compound **39** in substantial yield. There are two possible explanations: either the atom-transfer step **36** → **37** is so rapid that it competes effectively with ring opening of **36**, or ring opening of **36** does occur but proceeds preferentially to **32** and **33** rather than to **38**. A value of the rate constant for the atom-transfer step **36** → **37** is not available, but it seems unlikely to be much greater than that (ca. 10^7 M^{-1} s^{-1})[15] for related reactions in acyclic systems. In view of the high rate constants ($k \approx 10^8$ s^{-1})[46] for ring opening of other nortricyclyl radicals and the low concentration of ArSH employed, we consider the former explanation to be untenable. We conclude that ring opening of **36** does occur under these conditions but proceeds almost exclusively to **32** or **33**, presumably because of their stabilization by interaction of the semioccupied orbital with the β-sulfur atom.

Examination by TLC of the reaction mixture produced by treatment of norbornadiene with *o*-thiocresol under TOCO conditions showed the presence of only two products both of which were peroxidic.[49] However, upon removal of the solvent an intractable mixture of many components was obtained. Prolonged standing of the mixture at low temperature gave a crystalline sample of the hydroxy sulfoxide **44**.

When the complex mixture was treated with sodium borohydride–cobalt chloride, a reagent known to reduce sulfoxides to sulfides,[37] it gave **25b**, **27b**, **37**, **42**, and **43**



which were separated chromatographically. The formation of **25b** and **27b** clearly involves the reduction of the double bonds in **40** and **41**. Separate experiments[47] have shown that sodium borohydride–cobalt chloride efficiently reduces terminal olefins, norbornene, and other compounds containing reactive double bonds.

Treatment with triphenylphosphine or stannous chloride of the initial mixture from the TOCO reaction of *o*-thiocresol with norbornadiene gave the *exo,exo*-hydroxy sulfide **40** (22%) and the tricyclene derivatives **42** (22%), **43** (28%), and **37** (2%). The *endo* alcohol **41** (ca. 3%) was detected but could not be obtained pure. The stereochemistry of the nortricyclenes **42** and **43** was assigned on the basis of their ^1H NMR spectral behavior upon addition of a shift reagent: increasing concentrations of $Eu(fod)_3$ gave much greater differential shift increments[48] for the CHS proton in **43** than for the analogous proton in **42**. Also, as expected, the signals for the two protons at C-7 in **42** moved strongly downfield when shift reagent was added whereas the equivalent protons in **43** did not.

The structures and yields of the major TOCO products from norbornadiene are consistent with the usual mechanism. Thus **42** and **43** must be generated via oxygen coupling of **36**, and **40** must be similarly formed via exo oxygen attack on **32**. In view of the high mobility of the norbornenyl ⇌ nortricyclyl radical equilibrium,[34,42,46] we believe that our results reflect the outcome of oxygen coupling reactions of **32** and **36** at equilibrium concentrations.

The low yield of the alcohol **41** formed by endo attack of oxygen on **32** is perplexing. Although a number of minor unidentified products were detected from the TOCO reaction of norbornadiene and *o*-thiocresol, none of them showed the chromatographic behavior expected of the tricyclic peroxide **45** or its probable decomposition products, even when the reaction was conducted at low temperature. In view of the reported[49] stability of the tetracyclic peroxide **46**, we had expected that **45** should be capable of being isolated. Nevertheless, it is possible that under TOCO reaction conditions **45** was formed but underwent deep-seated fragmentation reactions. The other possibility is that the peroxy radical **6** (Ar = *o*-$CH_3C_6H_4$) required as an intermediate for the formation of **44** was generated to only a minor degree. This would be surprising in view of the fact that the norbornyl radical **18b** undergoes exo coupling with oxygen as readily as endo coupling. However, the low yield of the endo alcohol **41** appears to point in this direction, while separate experiments[23] on acyclic systems indicate that oxygen coupling reactions of arylthio-substituted homoallylic radicals can show unexpected stereoelectronic effects. Further work designed to reveal whether substituted norbornenyl radicals show an unexpectedly high exo/endo ratio in their reactions with oxygen are in progress.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were recorded on a JASCO IRA-1 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL PMX 60 and Bruker WP 80 spectrometers, respectively. GLC was carried out on Perkin-Elmer 990 and Pye 104 instruments. The following columns were employed: column A, 1.8 m × 3 mm, 5% FFAP on Varaport 30 (80–100 mesh); column B, glass capillary, 54 m × 0.5 mm, SP2100. HPLC was carried out on a Chromatronix 3500 instrument fitted with a 24 cm × 2 mm column packed with Lichrosorb (5–10 μm). A UV detector set at λ = 280 nm was used. Merck precoated aluminum sheets (silica HF_{254}) were used for analytical TLC; peroxidic compounds were detected with a ferrous thiocyanate spray reagent.[50] Mass spectra were recorded on an

(43) Van Auken, T. V.; Rick, E. A. *Tetrahedron Lett.* **1968**, 2709.
(44) (a) Cristol, S. J.; Brindell, G. D.; Reeder, J. A. *J. Am. Chem. Soc.* **1958**, *80*, 635. (b) Giese, B.; Jay, K. *Chem. Ber.* **1979**, *112*, 304.
(45) A small amount (ca. 2%) of an unidentified product was detected; it may be the 7-arylthio compound **39**.
(46) Carlsson, D. J.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.
(47) Chung, S.-K. *J. Org. Chem.* **1979**, *44*, 1014.
(48) Kobayashi, T.; Kodama, M.; Ho, S. *Tetrahedron Lett.* **1975**, 655.
(49) Jefford, C. W.; Rimboult, C. G. *J. Am. Chem. Soc.* **1978**, *100*, 6515.
(50) Johnson, R. A.; Nidy, E. G. *J. Org. Chem.* **1975**, *40*, 1680.

AEI MS 3074 mass spectrometer operating at 70 eV.

General Methods and Workup Procedures for TOCO Reactions. [**Caution**: since vapors of organic solvents may form explosive mixtures with oxygen in closed systems, all such reactions should be conducted behind safety shields.] All cooxidation reactions were carried out under oxygen (balloon) in vigorously stirred hexane–ethyl acetate (4:1) solutions at ambient temperatures. The solvent was then removed in vacuo and the residue chromatographed. Whenever triphenylphosphine was used in the workup, the solution was allowed to stir for a further 30 min, and the solvent was then removed in vacuo. The residual oil was dissolved in ether (100–200 mL) and cooled in a dry ice–acetone bath for 30 min. The crystalline precipitate of the phosphine oxide was then collected and the ether removed in vacuo to yield a colorless or sometimes pale yellow oil which was subjected to chromatography.

Cooxidation of Thiophenol and *cis*- and *trans*-2-Butene. Thiophenol (1.0 g, 9.09 mmol), *cis*-2-butene (10 g, 0.18 mol), and di-*tert*-butyl peroxyoxalate (47 mg, 0.2 mmol) were cooxidized in hexane–ethyl acetate (100 mL) for 36 h. After triphenylphosphine (2 g, 7.6 mmol) had been added, the excess of 2-butene was distilled into a dry ice–acetone cold trap. GLC (column B, 20 °C) of the distillate revealed the isomers of 2-butene in a trans/cis ratio of 2.0. Preparative TLC (20% ethyl acetate–hexane) of a sample of the oil obtained from the workup gave pure samples of *erythro*- (**14**) and *threo*-3-(phenylthio)-2-butanol (**12**; 60% combined yield). Their ^{13}C NMR spectra were identical with those obtained from authentic samples: erythro, δ 68.4, 51.4, 19.5, 14.7; threo, δ 70.0, 52.0, 19.5, 17.4. Analysis by HPLC (15% ethyl acetate–hexane) of the mixture showed an erythro/threo ratio of 2:1. The cooxidation of *trans*-2-butene with thiophenol gave identical products.

Cooxidation of Thiophenol and Cyclopentene. Cyclopentene (3.0 g, 44 mmol), thiophenol (1.0 g, 9.09 mmol), and di-*tert*-butyl peroxyoxalate (47 mg, 0.2 mmol) were cooxidized in hexane–ethyl acetate (100 mL) for 16 h. After the addition of triphenylphosphine (2 g, 7.6 mmol), the usual workup afforded a colorless oil, flash chromatography (10% ethyl acetate–hexane) of which gave the following compounds in order of increasing polarity.

(a) *cis*-2-(Phenylthio)cyclopentanol (**9**):[51] 190 mg (11%); ^1H NMR (CCl_4) δ 7.5–7.0 (m, 5 H, Ar H), 4.1–3.8 (m, 11 H, CHOH), 3.6–3.1 (m, 1 H, CHS), 2.5–0.4 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 72.0, 54.8, 32.6, 29.2, 21.6.

(b) *trans*-2-(Phenylthio)cyclopentanol (**8**):[51] 1.18 g (67%); ^1H NMR (CCl_4) δ 7.5–7.0 (m, 5 H, Ar H), 4.3–3.8 (m, 1 H, CHOH), 3.6–3.15 (m, 1 H, CHS), 2.6–0.4 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 78.8, 54.2, 33.3, 31.1, 21.9.

Cooxidation of *p*-Thiocresol and Norbornene. Norbornene (6.0 g, 63.33 mmol) and *p*-thiocresol (3.43 g, 23.06 mmol) were cooxidized in ethyl acetate–hexane (100 mL) for 4 h with initiation with a 250-W sun lamp. Evaporation in vacuo gave a pale yellow residue, of which a small sample (323 mg) was subjected to preparative TLC (chloroform). In order of increasing polarity, the compounds obtained were as follows.

(a) 2-*exo*-(*p*-Tolylthio)norbornane (**19a**): 15 mg (5%); spectral properties identical with those of an authentic sample.[52]

(b) 3-*exo*-(*p*-Tolylthio)-2-*exo*-norbornanol (**25a**): colorless oil; 12 mg (4%); ^1H NMR in accord with the literature.[38]

(c) 3-*exo*-(*p*-Tolylthio)-2-*endo*-norbornanol (**27a**): colorless oil; 15 mg (5%); ^1H NMR ($CDCl_3$) δ 4.0 (t, 1 H, CHOH).[53]

(d) 3-*exo*-(*p*-Tolylsulfinyl)-2-*endo*-norbornanol (**26a**): white solid; 78 mg (23%); crystallized from methylene chloride–hexane to give needles, mp 105–115 °C; IR (CH_2Cl_2) 3600 (m), 3400 (m), 1020 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.5 (q, 4 H, Ar H), 4.6 (t, 1 H, H_{2x}), 3.25 (s, 1 H, OH), 2.42 (s, 3 H, $ArCH_3$), 2.6–1.0 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 21.4, 30.1, 35.5, 40.6, 42.6, 72.0, 75.1, 125.0, 130.2, 140.0, 142.0, and small peaks (~10%) at δ 38.6, 43.0, 73.0, 75.9, and 125.5 arising from the diastereoisomer; mass spectrum, *m/e* (relative intensity) 251 ($M + 1^+$, 3%), 142 (8), 141 (15), 140 (95), 139 (15), 126 (6), 124 (21), 123 (15), 121 (5), 112 (6), 111 (44), 110 (7), 108 (6), 95 (6), 94 (8), 93 (2), 92 (100), 91 (80), 90 (6), 89 (8), 67 (75), 66 (16), 65 (40), 59 (28), 57 (34), 55 (32), 53 (30), 51 (27), 50 (5). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25; S, 12.8. Found: C, 67.25; H, 7.21; S, 13.2.

(e) 3-*exo*-(*p*-Tolylsulfinyl)-2-*exo*-norbornanol (**24a**): white solid; 193 mg (58%); on recrystallization from ethyl acetate gave prisms, mp 170–171 °C; IR (CH_2Cl_2) 3320 (m), 1020 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.6 (q, 4 H, Ar H), 4.7 (d, J = 4 Hz, 1 H, OH), 4.3 (m, 1 H, H_{2n}, resolves into a d (J = 6 Hz) after D_2O exchange), 2.9 (dp, J = 6, 2 Hz, 1 H, H_{3n}), 2.5 (s, 3 H, $ArCH_3$), 2.5–0.7 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 21.5, 23.8, 23.7, 34.1, 38.3, 44.5, 76.0, 76.4, 126.2, 130.2, 141.1, 142.6; mass spectrum, *m/e* (relative intensity) 251 ($M + 1^+$, 15), 142 (5), 141 (10), 140 (59), 139 (24), 124 (10), 123 (10), 121 (6), 111 (13), 93 (60), 92 (69), 91 (100), 90 (8), 89 (15), 83 (15), 82 (8), 81 (32), 79 (32), 78 (20), 77 (69), 67 (86), 52 (15), 51 (38), 50 (19). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25; S, 12.8. Found: C, 67.20; H, 7.40; S, 12.7.

Oxidation of 24a to 3-*exo*-(*p*-Tolylsulfonyl)-2-*exo*-norbornanol (28a). Potassium permanganate (400 mg, 2.53 mmol) and 200 mg (0.8 mmol) of the sulfoxide **24a** were vigorously stirred in 1:1 methylene chloride–water (20 mL) at ambient temperature for 15 min. The solution was filtered through a thin pad of Celite, and the organic layer was separated, washed with water (2 × 10 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo left an oil which was pure by TLC and which crystallized on standing to give 120 mg (56%) of **28a**, recrystallization of which from methylene chloride–hexane gave colorless needles: mp 99–100 °C (lit.[38] mp 101–102 °C); the NMR ($CDCl_3$) was in accord with the literature.[38] A similar oxidation of **27a** gave 3-*exo*-(*p*-tolylsulfonyl)-2-*endo*-norbornanol (**29a**): mp 104–105 °C (lit.[38] mp 102–103 °C); the NMR ($CDCl_3$) was in accord with the literature.[53]

Reduction of 24a to 25a. Sodium borohydride (304 mg, 8 mmol) was slowly added to a solution of 200 mg (0.8 mmol) of **24a** and $CoCl_2 \cdot 6H_2O$ (380 mg, 1.6 mmol) in ethanol (20 mL) at 10–15 °C. The solution immediately turned black with vigorous evolution of hydrogen. After the mixture was stirred at ambient temperature for 2 h, water (3 mL) was added, and the solution was heated on a steam bath for 15 min, during which time black granules precipitated. After filtration through a thin pad of Celite, the filtrate was diluted with ether (50 mL) and wathed with water (2 × 10 mL). The ether solution was dried ($MgSO_4$) and the ether evaporated to leave a colorless oil (150 mg, 80%) which was pure by TLC and was found, by spectral comparison, to be identical with **25a**. The hydroxy sulfoxide **26a** was similarly converted to **27a** in 69% yield.

Oxidation of 24a to a Mixture of the Exo and Endo Isomers of 3-(*p*-Tolylsulfoxyl)norbornan-2-one (30a). A solution of the sulfoxide **24a** (1.0 g, 4 mmol) and pyridinium chlorochromate (4 g, 18.6 mmol) in methylene chloride (40 mL) was stirred overnight at ambient temperature. Upon addition of dry ether (100 mL), a black precipitate formed. The supernatant was decanted, the black residue was washed with ether (2 × 50 mL), and the combined brown ether solutions were filtered through a short column of silica. The resultant clear colorless solution when evaporated to dryness gave a white solid, which when recrystallized from ether–hexane, gave a mixture of the stereoisomers of the keto sulfoxide **30a** as prisms: 530 mg (54%); IR (CCl_4) 1755 (s), 1080 (s), 1070 cm^{-1} (s); ^1H NMR (CCl_4) δ 7.3 (q, 4 H, Ar H), 3.1 (m, 1 H), 2.9 (d, J = 3 Hz, 1 H), 2.4 (s, 3 H, $ArCH_3$), 2.3–1.0 (m, 7 H); mass spectrum, *m/e* (relative intensity) 248 (M^+, 8), 81 (100). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.7; H, 7.25; S, 12.8. Found: C, 67.20; H, 7.40; S, 12.7. The stereoisomers were detectable by analytical TLC, but they were not separable on a preparative scale. A similar oxidation of **26a** gave a product with identical physical and spectral properties.

Oxidation of 30a to the Exo and Endo Isomers of 3-(*p*-Tolylsulfonyl)norbornan-2-one (31a). Oxidation of 210 mg (0.85 mmol) of the keto sulfoxide **30a** with $KMnO_4$ (250 mg, 1.6 mmol) in a manner similar to that described for **24a** gave an oil (100 mg, 45%), which analytical TLC showed to be a mixture of two compounds. ^1H NMR ($CDCl_3$) showed two doublets at δ 3.7 (H_{1x}) and 3.3 (H_{1n}) and which integrated as 1:2.[38]

Cooxidation of *o*-Thiocresol and Norbornene. When *o*-thiocresol was cooxidized in a manner similar to that described

(51) Mousseron, M.; Bousquet, H.; Marret, G. *Bull. Soc. Chim. Fr.* **1943**, 84.
(52) Cristol, S. J.; Brindell, G. D. *J. Am. Chem. Soc.* **1954**, *76*, 5699.
(53) Although chemical shifts were identical with those previously reported,[38] the coupling patterns of some signals showed minor differences.

for *p*-thiocresol, the following compounds were obtained in order of increasing polarity on silica.

(a) 2-*exo*-(*o*-Tolylthio)norbornane (**19b**): colorless liquid; 2% yield; bp 120 °C (0.5 mm); IR (film) 1595 (m), 1470 (s), 1450 (s), 1440 (m), 1380 (m), 1315 (m); NMR ($CDCl_3$) δ 7.33–7.0 (m, 4 H, Ar H), 3.33–3.0 (m, 1 H, H_{2n}), 2.5–2.17 (m, with s for $ArCH_3$ at δ 2.33, 5 H), 2.1–1.0 (8 H); mass spectrum, *m/e* (relative intensity) 218 (M^+, 20), 124 (25), 97 (11), 96 (100), 92 (11), 90 (5), 78 (30), 77 (10), 76 (10), 74 (6), 56 (10), 54 (8), 52 (6). Anal. Calcd for $C_{14}H_{18}S$: C, 77.0; H, 8.3; S, 14.7. Found: C, 77.2; H, 8.4; S, 14.7.

(b) 3-*exo*-(*o*-Tolylthio)-2-*endo*-norbornanol (**27b**): colorless oil; 17% yield; bp 130 °C (0.1 mm; bulb to bulb distillation); IR (film) 3400 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 7.33–7.0 (m, 4 H, ArH), 4.0 (t, 1 H, H_{2x}), 2.8 (t, 1 H, H_{3n}), 2.66 (s, 1 H, OH), 2.33 (s, 3 H, $ArCH_3$), 2.3–1.0 (m, 8 H); mass spectrum, *m/e* (relative intensity) 234 (M^+, 36), 125 (8), 124 (100), 111 (10), 93 (19), 91 (10), 81 (5), 79 (8), 67 (13). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.7. Found: C, 71.4; H, 8.1; S, 13.3.

(c) 3-*exo*-(*o*-Tolylthio)-2-*exo*-norbornanol (**25b**): colorless liquid; 13% yield; bp 150 °C (0.3 mm; bulb to bulb distillation); IR (CCl_4) 3480 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 7.33–6.83 (m, 4 H, Ar H), 4.9 (d, J = 6.5 Hz), 1 H, H_{3n}), 3.2 (dp, J = 6.4, 1.6 Hz, 1 H, H_{2n}), 2.5 (s, 1 H, OH), 2.4–2.1 (m, 2 H, with s for $ArCH_3$ at δ 2.33), 2.0–1.5 (m, 6 H); mass spectrum, *m/e* (relative intensity) 234 (M^+, 39), 205 (5), 140 (9), 137 (9), 126 (5), 125 (10), 124 (100), 123 (5), 111 (15), 110 (5), 93 (30), 92 (12), 91 (40), 84 (20), 83 (10), 82 (10), 81 (13), 79 (12), 78 (7), 77 (18), 71 (6), 70 (9), 69 (9), 68 (8), 67 (37), 66 (10), 65 (13), 57 (12), 57 (10), 55 (22), 54 (8), 53 (10), 52 (5). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.7. Found: C, 71.62; H, 7.80; S, 13.4.

(d) 3-*exo*-(*o*-Tolylsulfinyl)-2-*endo*-norbornanol (**26b**): white solid (28% yield) which recrystallized from methylene chloride–hexane; mp 116–122 °C; IR (CCl_4) 3640 (m), 3440 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 8.0–7.6 (m, 1 H, Ar H_{ortho}), 7.5–7.0 (m, 3 H, Ar H), 4.47 (t, 1 H, H_{2x}), 3.2 (s, 1 H, OH), 2.6–2.1 (m, with s for $ArCH_3$ at δ 2.4), 2.0–1.0 (m, 7 H); mass spectrum, *m/e* (relative intensity) 251* ($M + 1^+$, 23), 163 (6), 142 (6), 141 (10), 140 (100), 139 (15), 137 (8), 125 (5), 124 (30), 123 (20), 122 (5), 121 (9), 111 (33), 110 (5), 95 (5), 94 (10), 93 (78), 92 (69), 91 (62), 90 (5), 89 (8), 82 (10), 81 (23), 80 (5), 79 (27), 78 (18), 77 (59), 67 (59), 66 (25), 65 (30), 57 (25), 55 (19), 54 (9), 53 (15), 52 (5), 51 (12), 50 (7). When lower ionization temperatures were applied, $M + 1^+$ decreased, and the M^+ appeared at *m/e* 250. Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.2; H, 7.2; S, 12.8. Found: C, 66.9; H, 7.3; S, 12.8.

(e) 3-*exo*-(*o*-Tolylsulfinyl)-2-*exo*-norbornanol (**24b**): white solid (41% yield), which recrystallized from methylene chloride–hexane; mp 129–130 °C; IR (CCl_4), 3680 (w), 3360 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 8.2–7.8 (m, 1 H, Ar H_{ortho}) 7.6–7.1 (m, 3 H, Ar H), 4.47 (s, 1 H, OH), 4.3 (d, J = 6.4 Hz, 1 H, H_n), 2.95 (dp, J = 6.4, 1.6 Hz, 1 H, H_n), 2.5 (s, 3 H, $ArCH_3$), 2.3–0.7 (m, 8 H); mass spectrum, *m/e* (relative intensity) 250 (M^+, 3), 234 (7), 140 (100), 124 (14), 111 (18), 94 (8), 93 (35), 92 (23), 91 (15), 81 (9), 77 (6), 67 (20), 57 (6). Anal. Calcd for $C_{14}H_{18}O_2S$: C, 67.2; H, 7.3; S, 12.8. Found: C, 67.2; H, 7.4; S, 12.7.

Cooxidation of *o*-Thiocresol and Norbornadiene. Method A. Norbornadiene (1.0 g, 10.86 mmol), *o*-thiocresol (670 mg, 5.4 mmol), and di-*tert*-butyl peroxyoxalate (47 mg, 0.2 mmol) were stirred in hexane–ethyl acetate (270 mL) for 24 h. Workup with triphenylphosphine (1.41 g, 5.4 mmol) and subsequent preparative TLC (15% ethyl acetate–hexane) gave the following compounds in order of increasing polarity.

(a) 3-(*o*-Tolylthio)tricyclo[2.2.1.$0^{2,6}$]heptane (**37**), 23 mg (2%).

(b) 3-*exo*-(*o*-Tolylthio)-2-*exo*-norborn-5-enol (**40**): colorless oil; 276 mg (22%); bp 150 °C (0.2 mm, Kugelrohr); IR (CCl_4) 3460 cm^{-1} (m); ^1H NMR (CCl_4) δ 7.2–6.7 (m, 4 H, Ar H), 6.1–5.8 (m, 2 H, olefinic), 3.8 (d, J = 6 Hz, 1 H, H_{2n}), 3.1 (dp, J = 6.4, 1.6 Hz, 1 H, H_{3n}), 3.0 (br s, 1 H, OH), 3.0–2.6 (m, 2 H, H_{7a}, H_{7a}); mass spectrum, *m/e* (relative intensity) 232 (M^+, 10), 168 (5), 167 (11), 166 (100), 137 (18), 124 (10), 105 (7), 92 (25), 91 (10), 79 (11). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; S, 13.8. Found: C, 72.37; H, 6.69; S, 14.2.

(c) A pale yellow oil (110 mg), analytical HPLC (20% ethyl acetate–hexane) of which revealed a mixture of six compounds, present in about equal amounts. The ^1H NMR (CCl_4) showed multiplets at δ 7.2–6.7 (aryl H) and 6.5–6.1 (olefinic H). The integration of aryl/olefinic signals was 2:1. A triplet at 4.1 ppm was assigned to the endo alcohol **41** (H_{2x}) by analogy with **27a** and **27b**. [As **40** exhibits extremely close spectral similarities to **25a,b**, it is reasonable to assume the same for **41**.]

(d) 3-*exo*-(*o*-Tolylthio)-5-*endo*-tricyclo[2.2.1.$0^{2,6}$]heptanol (**43**): colorless oil; 350 mg (28%); bp 140 °C (0.2 mm, Kugelrohr); IR (CCl_4) 3420 cm^{-1} (m); ^1H NMR (CCl_4) δ 7.33–6.7 (m, 4 H, Ar H), 3.8 (br s, 1 H, H_{5x}), 3.7 (s, 1 H, H_{3n}), 3.4 (s, 1 H, OH), 2.3 (s, 3 H, $ArCH_3$), 2.0–1.65 (m, 2 H), 1.5–0.9 (m, 4 H); mass spectrum, *m/e* (relative intensity) 232 (M^+, 44), 166 (14), 150 (16), 124 (32), 123 (6), 121 (14), 119 (34), 117 (36), 109 (20), 108 (9), 92 (10), 91 (45), 84 (8), 82 (14), 81 (29), 80 (11), 79 (100), 69 (10), 68 (8), 67 (18), 56 (10), 56 (16), 53 (8). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; S, 13.8. Found: C, 72.10; H, 6.88; S, 14.1.

(e) 3-*exo*-(*o*-Tolylthio)-5-*exo*-tricyclo[2.2.1.$0^{2,6}$]heptanol (**42**): colorless oil; 275 mg (22%); bp 143 °C (0.22 mm, Kugelrohr); IR (CCl_4) 3380 cm^{-1} (m); ^1H NMR (CCl_4) δ 7.2–6.7 (m, 4 H, Ar H), 3.7 (br s, 1 H, H_{5n}), 3.4 (s, 1 H, OH), 3.03 (s, 1 H, H_{3n}), 2.3 (s, 3 H, $ArCH_3$), 2.0–1.67 (m, 3 H), 1.5–1.0 (m, 3 H); mass spectrum, *m/e* (relative intensity) 232 (M^+, 12), 122 (59), 121 (11), 119 (8), 107 (42), 106 (24), 105 (5), 89 (74), 87 (6), 81 (78), 80 (12), 79 (100), 78 (17), 77 (73), 68 (8), 67 (8), 66 (9), 65 (33), 63 (17), 55 (14), 54 (5), 53 (29), 52 (8), 51 (24), 50 (5). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.37; H, 6.94; S, 13.8. Found: C, 72.11; H, 6.82; S, 14.0.

Method B. Without Triphenylphosphine Workup. *o*-Thiocresol (1.2 g, 9.7 mmol) and norbornadiene (1.34 g, 14.56 mmol) were cooxidized with initiation by UV irradiation (black light fluorescent lamp) in hexane–ethyl acetate (500 mL) for 20 h, and the oil obtained upon solvent removal was then allowed to stand at −15 °C for 2 days. A white crystalline solid appeared, which was washed with ethyl acetate and recrystallized from methylene chloride–hexane to give 3-*exo*-(*o*-tolylsulfinyl)-2-*endo*-norborn-5-enol (**46**) as prisms: 221 mg (9%); mp 184 °C; IR ($CHCl_3$) 3360 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 8.0–7.7 (m, 1 H, Ar H_{ortho}), δ 7.5–6.9 (m, 3 H, Ar H), 6.2–5.7 (ddd, J = 7, 5, 3 Hz, 2 H, olefinic), 5.05 (d, J = 4 Hz, 1 H, OH), 4.4–4.2 (m, 1 H, H_{2n}, resolves into a d, J = 6.4 Hz, after D_2O exchange), 3.1–2.8 (br s, 1 H), 2.85 (dp, J = 6.4, 1.6 Hz, 1 H, H_{3n}), 2.45 (s, 3 H, $ArCH_3$), 2.4–2.0 (m, 2 H), 1.6 (d, J = 10 Hz, 1 H); mass spectrum (ionization temperature 105 °C), *m/e* (relative intensity) 250 (15), 249 (100), no M^+, 166 (17), 91 (7), 79 (6); ionization temperature 90 °C, *m/e* (relative intensity) 249 (100), 248 (M^+, 30). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.7; H, 6.5; S, 12.9. Found: C, 68.0; H, 6.5; S, 12.8.

Addition of *o*-Thiocresol to Norbornadiene. *o*-Thiocresol (1.8 g, 4.5 mmol) and norbornadiene (2.0 g, 21.7 mmol) were stirred under N_2 in a water bath at ambient temperature for 1 h. Removal of the excess norbornadiene in vacuo gave a pale yellow oil (3.05 g, 97%), analysis of which by GLC (column A, 185 °C) revealed four compounds in the ratio 2:24:5:69. A portion of the oil (1 g) was subjected to column chromatography on 10% silver nitrate–silica. Elution with ether–hexane (1:1) gave 3-(*o*-tolylthio)tricyclo[2.2.1.$0^{2,6}$]heptane (**37**): colorless oil; 650 mg (63%); bp 105 °C (0.3 mm, Kugelrohr); IR (film) 1595 (m), 1590 (m), 1470 (s), 1450 (s), 1440 (m), 1380 cm^{-1} (m); ^1H NMR (CCl_4) δ 7.7–6.8 (m, 4 H, Ar H), 3.1 (br s, 1 H, H_{3n}), 2.3 (s, 3 H, $ArCH_3$), 2.2–1.8 (m, 2 H), 1.5–1.0 (m, 6 H); mass spectrum, *m/e* (relative intensity) 216 (M^+, 75), 150 (85), 136 (9), 135 (40), 124 (28), 123 (7), 121 (7), 119 (7), 95 (51), 94 (11), 93 (100), 92 (12), 91 (88), 79 (12), 78 (19), 77 (86), 67 (17), 66 (10), 65 (18). Anal. Calcd for $C_{14}H_{16}S$: C, 77.7; H, 7.5; S, 14.8. Found: C, 77.8; H, 7.6; S, 14.5. Further elution with ethyl acetate–methanol (9:1) gave 2-*exo*-(*o*-tolylthio)norborn-5-ene (**34**): colorless oil; 185 mg (18%); bp 145 °C (0.6 mm, Kugelrohr); IR (CCl_4), 1590 (m), 1470 (s), 1455 (m), 1445 (m), 1335 cm^{-1} (s); ^1H NMR (CCl_4) δ 7.5–6.8 (m, 4 H, Ar H), 6.15–5.8 (br s, 2 H, olefinic), 3.1–2.6 (m, 3 H, H_{2n}, H_1, H_4), 2.25 (s, 3 H, $ArCH_3$), 1.9–1.3 (m, 4 H); mass spectrum, *m/e* (relative intensity) 216 (M^+, 20), 152 (5), 151 (10), 150 (100), 149 (9), 136 (5), 135 (65), 105 (5), 93 (17), 91 (19), 77 (12), 66 (5), 65 (9). Anal. Calcd for $C_{14}H_{16}S$: C, 77.7; H, 7.5; S, 14.8. Found: C, 77.9; H, 7.4; S, 15.0. A further portion of the oil (300 mg) was partitioned between 20% $AgNO_3$(aq) (20 mL) and ether (20 mL). The silver nitrate layer was washed with ether (20 mL), diluted with 30% NH_3(aq) (20 mL) and extracted with ether (2 × 20 mL). This ether extract was in turn extracted with 20% $AgNO_3$(aq) (20 mL). The silver nitrate extract was treated as above to give an ether solution, which was dried ($MgSO_4$) and concentrated to give a

pale yellow oil (45 mg). Analysis by GLC (column A, 185 °C) now revealed a 2:1 mixture of **34** and of the compound which had originally accounted for 5% of the mixture. ^1H NMR (CCl_4) revealed a doublet of triplets at 3.5 ppm.[43] The less abundant of the two compounds was therefore **35**.

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Registry No. **8**, 65756-04-9; **9**, 78086-89-2; **12**, 10277-53-9; **14**, 10277-52-8; **19a**, 78019-30-4; **19b**, 78019-31-5; **24a**, 78019-32-6; **24b**, 78019-33-7; **25a**, 61376-30-5; **25b**, 78019-34-8; **26a**, 78086-90-5; **26b**, 78086-91-6; **27a**, 61376-28-1; **27b**, 78086-92-7; **28a**, 61376-36-1; **29a**, 61376-34-9; **30a** (isomer 1), 78019-35-9; **30a** (isomer 2), 78086-93-8; **31a** (isomer 1), 61348-92-3; **31a** (isomer 2), 61348-91-2; **34**, 78019-36-0; **35**, 78019-37-1; **37**, 78019-38-2; **40**, 78019-39-3; **41**, 78086-94-9; **42**, 78019-40-6; **43**, 78086-95-0; **44**, 78019-41-7; thiophenol, 108-98-5; *o*-thiocresol, 137-06-4; *p*-thiocresol, 106-45-6; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; cyclopentene, 142-29-0; norbornene, 498-66-8; norbornadiene, 121-46-0.

Stereochemistry and Mechanism of Hydride Abstraction from Organostannanes[1]

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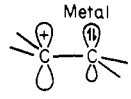
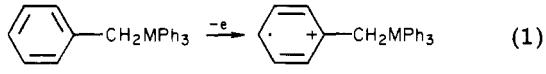
The reaction of trityl cation with *threo*-3-deuterio-2-(trimethylstannyl)butane to produce 2-butenes was shown to proceed with about 99% anti stereochemistry. The primary and secondary isotope effects are 3.7 and 1.1, respectively. These data are interpreted in terms of a hydride-abstraction mechanism leading to a σ–π-conjugated carbocation which subsequently loses the trimethyltin group.

The stabilizing interaction of carbon metal σ bonds with electron-deficient π systems has been demonstrated by



σ–π (vertical stabilization)

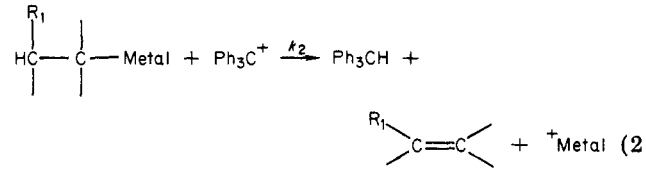
observing the low ionization potentials of allyl and benzyl metal compounds.[2-4] These studies afforded estimates



(1)

of the resonance electron-donating abilities of the groups CH_2MR_3 and CH_2HgX where M = Si, Ge, Sn, or Pb. Expressed as $\sigma^+_{CH_2M}$ in the linear free-energy relationship $\Delta IP = \rho\sigma^+$, the values range from –0.4 for CH_2SiPh_3 to –1.2 for $CH_2HgC_6H_{11}$ compared to $\sigma^+_{p\text{-}NH_2} = -1.3$, indicating a powerful electron donation by C–metal σ–π conjugation.[2a] Such resonance stabilization, observable in vertical ionization has been called "vertical stabilization"[2a] to contrast the resonance nature of this stabilization to the neighboring-group participation in which a nucleophilic center moves closer to the cationic center. These spectroscopic results and their interpretation offer an attractive explanation of the "β effect"[5] in organometallic chemistry.

Among the many chemical processes which tend to generate a positive charge β to a carbon–metal bond (the β effect) and thus partake of this σ–π conjugation, the dehydrometalation of alkyl metal compounds with trityl cation[6] stands out as both structure sensitive and well behaved[7,8] (eq 2).



(2)

Kinetic studies of this reaction in our laboratories[7] and those of Reutov, Uglova, and co-workers[8c] have revealed several characteristics which are indicative of the heterolytic process. The reaction is characterized by the following: (1) almost quantitative yields of Ph_3CH and olefin;[8d] (2) accurately second-order kinetics, first order in each reagent;[7,8d] (3) increasing k_2 as the metal becomes more electropositive[7] ($\log k_2 = \rho\sigma^+_{CH_2MMe_3}$ + constant; M = Pb > Sn > Ge > Si); (4) an increase in k_2 when R_1 is a resonance electron-donating substituent;[2a,c,8c] (5) an increase in k_2 with electron withdrawal by Y in $YPhC^+Ph_2$[8c] ($\log k_2 = \rho\sigma^+_Y$ + constant); (6) a primary isotope effect of $k_H/k_D = 2.5$–4;[8b] (7) relative insensitivity to solvent polarity;[8d] (8) a requirement of a periplanar transition state.[2a] These observations indicate that hydride removal occurs at the transition state which is stereochemically rigid and has carbenium ion character.

However, the stereochemistry of the reaction is not established nor is there a clear indication which of the three likely mechanisms (eq 3–5) occurs with organometallic compounds.

(1) (a) Taken from the Ph.D. Thesis of S.J.H., University of California at San Diego, 1975. The National Science Foundation supported this research (Grant MPS73-08414), and the NMR facilities which were used were supported by the National Institutes of Health (Grant RR00708).

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