Steric and Electrostatic Effects in the Addition of Thiols to Substituted Norbornenes

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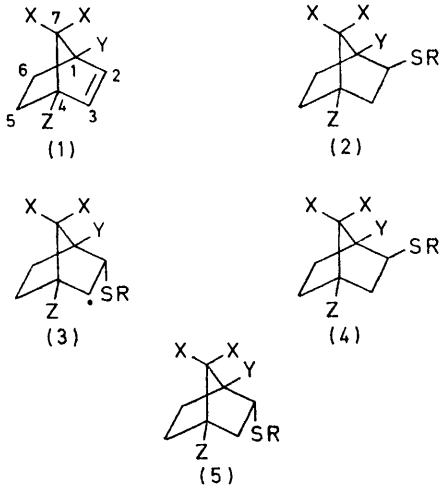
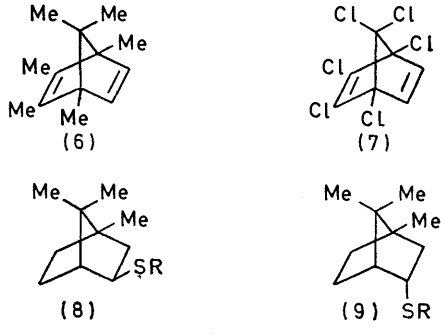
Free radical addition of alkanethiols to 7,7-dimethylnorbornene, bornene, and 1,4,7,7-tetramethylnorbornene and of arenethiols to 1,4,7,7-tetramethylnorbornene to give sulphides is described. The proportions of the products are interpreted in terms of the relative steric and electrostatic interactions between a bridged polycyclic olefin and a thiyl radical approaching from the *exo*- and *endo*-directions respectively. The product sulphides have been oxidised to sulphones; the *exo*-sulphones may be epimerised to give *endo*-sulphones.

ADDITION of benzenethiol, 2-methylpropane-2-thiol, and methanethiol to norbornene (1a) involves virtually exclusive attack by thiyl radicals from the *exo*-direction,[1] and this preference for *exo*- rather than *endo*-attack may be rationalised in terms of torsional strain.[2] An additional factor favouring *exo*-attack is that the steric interactions between 6-*endo*- and 2-*endo*-hydrogen atoms in the transition state leading to the intermediate radical (2a) derived from *exo*-attack are less unfavourable than the interactions between the 6-*endo*-hydrogen atom and a thiyl radical attacking position 2 from the *endo*-direction in the transition state leading to the intermediate radical (3a). A similar preference for *exo*-attack by phenylthio-radicals is found in the addition of benzenethiol to 7,7-dimethylnorbornene (1b).[3,4] This suggests that there is no appreciable steric hindrance to *exo*-attack by the 7-*syn*-methyl substituent in the transition state leading to the intermediate radical (2bj); an observation accommodated by the proposal[4] that two-stage addition reactions to (1b), involving reaction intermediates of small or moderate steric requirements, proceed *via* attack at the corners of the bicyclic ring. In contrast, the addition of 2-methylpropane-2-thiol to 1,2,3,4,7,7-hexamethylnorborna-2,5-diene (6)[5] leads to products of which 96% originate from initial *endo*-attack. This may reflect the absence of any steric hindrance to a thiyl radical attacking (6) from the *endo*-direction [*cf.* norbornene (1a)] compared with the combined steric interaction of bridge and bridgehead methyl substituents in (6) with an incoming *exo*-thiyl radical. The addition of thiols to 1,2,3,4,7,7-hexachloronorborna-2,5-diene (7)[6] gives products derived from *endo*-attack. As chloro- and methyl substituents are of a similar size this parallels the addition of 2-methylpropane-2-thiol to the hexamethylnorbornadiene (6). However, trichloromethyl radicals attack the hexachloronorbornadiene (7) predominantly from the *exo*-direction,[7] as with norbornene (1a),[8] suggesting that factors other than steric can, in certain cases, be of overriding importance in determining the direction of attack. In order to provide further information about these other factors, the addition of thiols to 7,7-dimethylnorbornene (1b), bornene (1c), and 1,4,7,7-tetramethylnorbornene (1d) was investigated.



a; X = H, Y = H, Z = H
b; X = Me, Y = H, Z = H
c; X = Me, Y = Me, Z = H
d; X = Me, Y = Me, Z = Me
e; R = Me
f; R = Pr^i
g; R = Bu^t
h; R = *p*-MeC$_6$H$_4$
j; R = Ph
k; R = *p*-ClC$_6$H$_4$

The additions of methanethiol and 2-methylpropane-2-thiol to (1b) each afforded single products (g.l.c.),

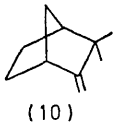


assigned on the basis of their n.m.r. spectra as the *exo*-sulphides (4be) and (4bg); H(2-*endo*) appeared as a doublet of doublets in (4bg) and as a triplet in (4be). The *endo*-isomers (5be) and (5bg) would have shown H(2-*exo*) as a four-spin multiplet.[3,9] It was anticipated that H(2-*exo*) of any *endo*-sulphides (5be) and (5bg)

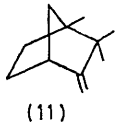
[1] D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc.* (*C*), 1969, 1585.
[2] P. von Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701.
[3] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1968, 1832.
[4] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 201.
[5] E. N. Prilezhaeva, V. A. Azovskaya, A. U. Stepanyants, D. Mondeshka, and R. I. Shekhtman, *Tetrahedron Letters*, 1969, 4909.
[6] J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.* (*C*), 1966, 1498.
[7] D. I. Davies and P. F. Rowley, *J. Chem. Soc.* (*C*), 1969, 424.
[8] E. Tobler and D. J. Foster, *J. Org. Chem.*, 1964, **29**, 2839.
[9] T. J. Flautt and W. F. Erman, *J. Amer. Chem. Soc.*, 1963, **85**, 3212.

present would appear as broad multiplets, which might be obscured by H(2-*endo*) of the major *exo*-sulphides (4be) and (4bg). However, the n.m.r. spectra (100 and 220 MHz) of the products in [$^2H_6$]benzene in [$^2H_6$]-acetone, and in carbon tetrachloride containing a europium complex gave no indication that the *endo*-sulphides (5be) and (5bg) were present, when the spectra were examined in the region of the resonances due to H(2) and the C(7) methyl substituents, respectively.

Consistent with the addition of benzenethiol to bornene (1c),[3] the additions of methanethiol and 2-methylpropane-2-thiol to (1c) gave product mixtures, which on g.l.c. analysis showed two, partly resolved, peaks of approximately equal areas. The n.m.r. spectra of the product mixtures indicated approximately equal amounts of the *exo*-2-bornyl * sulphide [(4ce) or (4cg)] and the *exo*-3-bornyl sulphide [(8e) or (8g)]. Both the *exo*-2-bornyl sulphides (4ce) and (4cg), and *exo*-3-bornyl sulphides (8e) and (8g) showed H(2-*endo*) and H(3-*endo*), respectively, as triplets. The *endo*-2-bornyl sulphides (5ce) and (5cg) would show H(2-*exo*) as a multiplet with a three-spin pattern,[3,9] and the *endo*-3-bornyl sulphides (9e) and (9g) would show H(3-*exo*) as a multiplet with a four-spin pattern.[3,9] Close examination of the n.m.r. spectra of these product mixtures in the region of the resonances due to the methyl groups on the bicyclic ring suggested that the *endo*-sulphides (5ce), (5cg), (9e), and (9g) were present to a small extent (less than 5% of the total), but no accurate estimate could be made. The mixtures of the *exo*-2-bornyl sulphides (4ce) and (4cg) with *exo*-3-bornyl sulphides (8e) and (8g) could not be separated by distillation, t.l.c., or preparative g.l.c. Therefore, for comparison purposes, the pure *exo*-2-bornyl sulphides (4ce) and (4cg) were prepared by the acid-catalysed addition of the respective thiols to camphene (10) in a reaction similar to that used [3] to prepare phenyl *exo*-2-bornyl sulphide (4cj).



(10)



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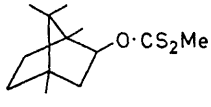


(12)

The addition of methanethiol, propane-2-thiol, and 2-methylpropane-2-thiol to 1,4,7,7-tetramethylnorbornene (1d) gave mixtures which were only partly resolved on g.l.c. The ratios of products were also measured from the n.m.r. spectra of the mixtures. The *exo*-sulphides (4de), (4df), and (4dg) showed H(2-*endo*) as a doublet of doublets in each case, whereas the *endo*-sulphides (5de), (5df), and (5dg), showed H(2-*exo*) as multiplets with transannular couplings $J_{2\text{-}exo,6\text{-}exo}$ *ca.* 1·5 Hz, which provides a ready means of distinguishing the *exo*- and *endo*-sulphides.[9,10] The percentages of *exo*- and *endo*-sulphides are recorded in the Table. Since the mixtures of these sulphides were inseparable, the pure *exo*-sulphides were prepared, for comparison, by the acid-catalysed addition of the respective thiols to 1,2,2-trimethyl-3-methylenenorbornane (11); this reaction is comparable to that employed to prepare the the *exo*-2-bornyl sulphides (4ce) and (4cg) from camphene (10). 1,2,2-Trimethyl-3-methylenenorbornane (11) was a by-product in the synthesis of 1,4,7,7-tetramethylnorbornene (1d) from the xanthate (12).[11] The conversion of (11) into the *exo*-sulphides (4de), (4df), and (4dg) confirms the proposals of Tidwell and Traylor [11] concerning the structure of (II).

The results show that there is a preference for *exo*-attack on 1,4,7,7-tetramethylnorbornene (1d). This preference increases as the size of the attacking thiyl radical increases, possibly owing to steric interaction between the 5-*endo*-hydrogen atom and the *endo*-attacking thiyl radical in the transition state leading to the intermediate radical (3c). Equally well, the nucleophilic character of the alkylthio-radicals varies in the order $Bu^tS\cdot > Pr^iS\cdot > MeS\cdot$, and the possibility exists that there is an additional electrostatic effect which favours *exo*-approach with increase in the nucleophilicity of the attacking thiyl radical. The addition of benzenethiol to (1d) in n-heptane as solvent gave more product derived from *endo*-attack than the comparable addition of methanethiol (see Table). This may be due to the greater electrophilic character of the phenylthio-radical and/or to greater steric hindrance to *exo*-approach by phenylthio-radicals than to *endo*-approach. The addition of both toluene-*p*-thiol and *p*-chlorobenzenethiol to (1d) in n-heptane as solvent gave proportionally more product from *endo*-attack than was observed in the addition of benzenethiol. This cannot be a simple steric effect since an examination of molecular models suggests that the presence of a *p*-substituent on the arylthio-radical has little or no effect on the direction of approach of the radical. The addition of thiols to 1,4,7,7-tetramethylnorbornene (1d) is expected to be non-reversible since the relief in steric strain on passing from olefin (1d) to intermediate (2d) and (3d) mitigates against the reverse, elimination reaction.[12] The addition of methanethiol and benzenethiol to (1d) is non-

Yields of *exo*- and *endo*-sulphides formed in the addition of thiols to 1,4,7,7-tetramethylnorbornene (1d)

	Yield of product (%) solvent					
	None		n-Heptane		Benzene	
Thiol	*exo*	*endo*	*exo*	*endo*	*exo*	*endo*
MeSH	65	35	67	33	56	44
Pr^iSH	88	12				
Bu^tSH	100	0				
p-MeC_6H_4·SH			30	70	38	62
PhSH			52	48	29	71
p-ClC_6H_4·SH			33	67	25	75

* *exo*-2-Bornyl, *exo*-3-bornyl, *endo*-2-bornyl, and *endo*-3-bornyl are used respectively to replace the terms isobornyl, epi-isobornyl, bornyl, and epibornyl employed in the older literature.

[10] A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Letters*, 1964, 233.

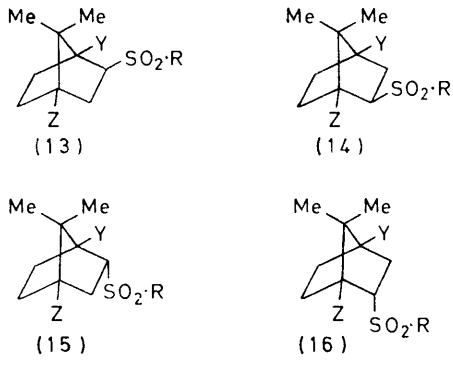
[11] T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2614.

reversible as was demonstrated by a series of reactions, using various concentrations of thiol, in which product ratios were found to be independent of thiol concentration.[12,13]

Therefore, the results are probably best rationalised by the suggestion that the two substituted arylthio-radicals are more polarised than the unsubstituted phenylthio-radical and can form loose complexes with the n-heptane solvent. The resulting increase in size of the attacking radical species then results in a greater preference for *endo*-approach over *exo*-approach with the *p*-substituted arylthio-radicals. Benzene, as solvent, would be expected to form π-complexes with each of the three arylthio-radicals,[14] increasing the effective size of each to a comparable extent. As shown in the Table, in benzene solution, the proportion of product derived from *exo*-attack of arylthio-radicals increases in the order of nucleophilicity of the radicals p-$MeC_6H_4S\cdot$ > $PhS\cdot$ > p-$ClC_6H_4S\cdot$. Thus, it appears that superimposed on a variety of steric factors controlling *exo*/*endo* product ratios is a smaller factor dependent on electrostatic interaction between attacking radical and olefin. As pointed out by Brown [4] the presence of 7-methyl substituents in (1b) has no appreciable effect on the direction of *exo*-attack by phenylthio-radicals and this observation is now extended to other thiyl radicals. The presence of a single, additional, bridgehead methyl substituent in bornene (1c) also has no appreciable effect on the direction of *exo*-attack by thiyl radicals. Possibly this single, bridgehead methyl substituent distorts the molecule so as to minimise steric effects, although calculations on the related 1-substituted norbornanes have suggested that distortion, due to C(1) substituents alone, is at best very weak.[15] The introduction of a second, bridgehead methyl substituent, in 1,4,7,7-tetramethylnorbornene (1d), leads to the results reported in the Table.[16] Attack of alkylthio-radicals from the *exo*-direction is apparehntly favoured with increase in size of attacking radical. However, with arylthio-radicals the opposite is observed. Therefore it would appear that when steric factors controlling radical attack from both *exo*- and *endo*-directions are of the same magnitude, factors other than steric are important in ordering the relative importance of the two directions of radical attack. In benzene as solvent, the amount of *endo*-attack of arylthio-radicals increases with the electrophilic character of the attacking species. Similarly with alkanethiols the amount of *endo*-attack increases with the electrophilic character.

Each of the mixtures of sulphides formed on the radical addition of thiols to 7,7-dimethylnorbornene (1b), bornene (1c), and 1,4,7,7-tetramethylnorbornene (1d) was oxidised to the corresponding mixture of sulphones using hydrogen peroxide, with ammonium molybdate as catalyst.[17] Similarly, each pure *exo*-sulphide, prepared by the acid catalysed addition of thiol to camphene (10) and to 1,2,2-trimethyl-3-methylenenorbornane (11), was oxidised to the *exo*-sulphone. No evidence was found for any epimerisation during oxidation; the sulphones were identified from examination of their n.m.r. spectra using the same arguments as those on which the structures of the sulphides are based.[3,9,10]

Each sulphone or mixture of sulphones was treated with sodium t-butoxide in t-butyl alcohol under conditions known [3] to epimerise the *exo*-2-bornyl and *exo*-3-bornyl phenyl sulphones [(13b; R = Ph) and (14b; R = Ph)] into the corresponding *endo*-isomers [(15b; R = Ph) and (16b, R = Ph)]. As expected,



each *exo*-sulphone was epimerised to afford the corresponding *endo*-sulphone, confirming that in the presence of 7-methyl substituents, *endo*-sulphones are thermodynamically more stable than *exo*-sulphones.[3,18]

EXPERIMENTAL

N.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer R10 spectrometer, and at 100 and 220 MHz by the P.C.M.U. (Harwell) Service. I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrometer in solution in carbon tetrachloride. Analytical g.l.c. was performed on a Perkin-Elmer F 11 gas chromatograph, fitted with flame ionisation detector, using 2 m × 0·125 in stainless steel columns with nitrogen as carrier gas. The most successful stationary phase for the separation of product aliphatic sulphides was 15% Apiezon L on 80—100 mesh Chromosorb P at 180°; for the aromatic sulphides and all sulphones 5% Apiezon L on 80—100 mesh Chromosorb P at 180°. Preparative g.l.c. was performed on a Pye 105 gas chromatograph, fitted with flame ionisation detector, and a 30 ft × 0·375 in glass column of 25% Embacel 30

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[13] C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144; R. H. Pallen and C. Sivertz, *Canad. J. Chem.*, 1957, **35**, 723.

[14] *Cf.* solvent effects on chlorination reactions, *e.g.* G. A. Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 2977; 1958, **80**, 4987.

[15] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1955.

[16] *Cf.* addition of methanethiol to 1,4-dichloronorbornene, which shows that bridgehead substituents are not sufficient in themselves to bring about *endo*-attack of thiyl radicals; C. K. Alden, D. I. Davies, and P. J. Rowley, *J. Chem. Soc.* (*C*), 1968, 705, and references therein.

[17] P. M. Hardy, H. M. Rydon, and R. C. Thompson, *Tetrahedron Letters*, 1968, 2525.

[18] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1971, **446**.

on 60—80 mesh Chromosorb W at 150°, with nitrogen as carrier gas. Column chromatography was performed on 60—120 mesh silica gel using light petroleum (b.p. 40—60°) as eluant. For t.l.c. basic, neutral, and acidic alumina (Woelm) and silica gel with 2% fluorescent indicator were used. The n.m.r. spectra and physical properties of the sulphides and sulphones prepared in this paper are listed in Supplementary Publication No. SUP 20752 (10 pp, 1 microfiche).*

Preparation of Olefins.—7,7-Dimethylnorbornene [19] (1b), m.p. 42—43°, was prepared from 2-cyclohexylcyclohexanol [20] [55% yield, b.p. 140—150° at 11 mmHg (lit.,[20] b.p. 139—142° at 14 mmHg)]. Bornene [21] (1c), m.p. 112—113° (lit.,[21] 112—113°), was prepared using a zinc–copper couple.[22] A 66 : 34 mixture of 1,4,7,7-tetramethylnorbornene (1d) and 1,2,2-trimethyl-3-methylenenorbornane (11), m.p. 114—115°, was prepared [11] and the individual products (1d), m.p. 117—118°, and (11), m.p. 116—117°, were isolated by preparative g.l.c.

Addition of Alkanethiols to 7,7-Dimethylnorbornene (1b), *Bornene* (1c), *and 1,4,7,7-Tetramethylnorbornene* (1d).—The substituted norbornene (1·0 mmol), alkanethiol (2·0 mmol), and azobisisobutyronitrile (AIBN) (1% by weight) were sealed in a glass tube, and heated at 80° for 30 h. The crude product was analysed by g.l.c. immediately after opening. Excess of thiol was removed by evaporation, and the residue was examined by n.m.r. The product proportions were determined from the relative areas of the peaks due to H(2-*exo*) and H(2-*endo*) of the respective *endo*- and *exo*-sulphide products, and of the peaks due to the methyl groups on the bicyclic structure.

Addition of Arrenethiols to 1,4,7,7-Tetramethylnorbornene (1d).—1,4,7,7-Tetramethylnorbornene (1d) (1·0 mmol) and the arenethiol (1·0 mmol)were dissolved in anhydrous benzene (1·0 ml, 11·2 mmol) or n-heptane (1·65 ml, 11·2 mmol) containing AIBN (1% by weight). The mixture was sealed in a glass tube under nitrogen and heated at 80° for 30 h. The tube was opened and the contents examined by g.l.c.; the contents were then dissolved in carbon tetrachloride (5 ml) and the resulting solution washed with 6N-sodium hydroxide solution (3 × 5 ml) and water (3 × 5 ml), dried ($MgSO_4$), and evaporated. The residue was examined by n.m.r. prior to purification by distillation to give the sulphide mixture (yields 90—95%). These reactions were carried out under nitrogen to prevent the formation of diaryl disulphides (by oxidation of arenethiols in air). In order to prove that the product sulphides were not contaminated with the disulphides, samples of the disulphides were prepared (see below) and found to have g.l.c. retention times significantly different from those of product sulphides.

Preparation of Diaryl Disulphides.[23]—The arenethiol (2·5 mmol) was dissolved in a stirred solution of sodium hydroxide (2·5 mmol) in water (1 ml). Iodine (1·25 mmol) was slowly added, and the mixture stirred until the iodine colour was discharged. The mixture was poured into a saturated solution of sodium thiosulphate (5 ml) and extracted with chloroform (3 × 3 ml); the extracts were dried ($MgSO_4$) and evaporated and the residue recrystallised from methylated spirits. Diphenyl disulphide (80%) had m.p. 62—63° (lit.,[24] 62—63°); bis-*p*-chlorophenyl disulphide (73%) had m.p. 73—74° (lit.,[25] 74°); di-*p*-tolyl disulphide (75%) had m.p. 47—48° (lit.,[26] 47—48°).

Concentration Studies on the Addition of Thiols to (1d).—An approximately M-solution of thiol (methanethiol or benzenethiol) (100 μl), containing AIBN (1 mg), was added to 1,4,7,7-tetramethylnorbornene (1d) (15 mg, 0·1 mmole) under nitrogen in a flask fitted with serum cap. The flask was heated at 80°, and at regular intervals during 48 h the ratio of product isomers was determined by g.l.c. and found not to vary. The isomer ratio was also unaffected by changing the initial thiol concentration from 1 to 2 or 3M, and also by prolonged heating of the product mixture under the conditions of the addition reactions.

Acid-catalysed Addition of Thiols to Camphene (10).[3]—Camphene (10) (13·6 g, 0·1 mol) was dissolved in glacial acetic acid (60 ml) and the thiol (0·1 mol) was added. Concentrated sulphuric acid (14·0 g) was then added and the mixture stirred at room temperature for 7 days. The mixture was poured into water (250 ml) and extracted with carbon tetrachloride (3 × 50 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (3 × 50 ml), dried ($MgSO_4$), and evaporated, and the residue was distilled to separate the respective *exo*-2-bornyl sulphide and *exo*-2-bornyl acetate, b.p. 95—98° at 0·7 mmHg, n_D^{23} 1·4635 (lit.,[27] b.p. 131—138° at 15 mmHg, n_D^{20} 1·4639). The *exo*-2-bornyl sulphides were: *exo*-2-*bornyl methyl sulphide* (4ce), b.p. 64° at 0·6 mmHg (63%) (Found: C, 71·4; H, 10·6. $C_{11}H_{20}S$ requires C, 71·7; H, 10·9%); exo-2-*bornyl t-butyl sulphide* (4cg), b.p. 70° at 0·5 mmHg (77%) (Found: C, 74·6; H, 11·6. $C_{14}H_{26}S$ requires C, 74·3; H, 11·6%).

Acid-catalysed Addition of Thiols to 1,2,2-Trimethyl-3-methylenenorbornane (11).—1,2,2-Trimethyl-3-methylenenorbornane (11) (150 mg, 1·0 mmol) was dissolved in glacial acetic acid (600 μl) and thiol (1·0 mmol) was added. Concentrated sulphuric acid (140 mg) was then added, and the mixture stirred at room temperature for 7 days, poured into water (5 ml), and extracted with carbon tetrachloride (3 × 3 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (3 × 3 ml) and water (2 × 3 ml), dried ($MgSO_4$), and evaporated and the residue was separated by column chromatography to afford successively the tetramethylnorbornyl sulphide, 1,4,7,7-tetramethylnorborn-2-*exo*-yl acetate, b.p. 85—86° at 2 mmHg (lit.,[28] 108—109° at 11 mmHg), τ (60 MHz; CCl_4) 5·4 [q, $J_{2\text{-}endo\text{-}3\text{-}endo}$ 8·0, $J_{3\text{-}exo\text{-}2\text{-}endo}$ 4·0 Hz, H(2-*endo*)], 8·10 (s, $CO_2{\cdot}CH_3$), 9·10, 9·15, 9·17, 9·20 (4s, 4 × Me), and 8·0—9·3 [m, H(3-*exo* and *endo*), H(5-*exo* and *endo*), and H(6-*exo* and *endo*)], $\nu_{max.}$ 1735 cm^{-1} (C=O).

Oxidation of Sulphides to Sulphones.[17]—Each sulphide or mixture of sulphides was oxidised to give the corresponding sulphone(s), the following example being typical. 7,7-Dimethylnorborn-*exo*-2-yl methyl sulphide

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue 20.

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(4be) (120 mg, 0·71 mmol) was dissolved in methanol (3·5 ml) and a solution of ammonium molybdate (78 mg) in 30% (w/v) hydrogen peroxide (1·5 ml) was added. The mixture was stirred at room temperature for 4 days, poured into fresh iron(II) sulphate solution (5 ml), and extracted with carbon tetrachloride (3 × 3 ml). The sulphone solution was washed until free of peroxide, dried ($MgSO_4$), and evaporated. The residue was recrystallised from carbon tetrachloride–light petroleum to afford 7,7-dimethylnorborn-*exo*-2-yl methyl sulphone (99%), m.p. 62—63°.

Epimerisation of Sulphones.[3,18]—A solution of the sulsulphone (1·0 mmol) in t-butyl alcohol (1 ml) was boiled under reflux with sodium t-butoxide (15 mg) for 16 h, poured into water (5 ml), and extracted with carbon tetrachloride (3 × 3 ml). The extracts were dried ($MgSO_4$) and evaporated and the residue was investigated by n.m.r. and g.l.c. to check that epimerisation was complete. The *endo*-sulphones, obtained in yields of 85—90%, were purified by recrystallisation from carbon tetrachloride–light petroleum (or distillation).

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