Addition of Thiols to some 5-Substituted Norborn-2-enes †

By D. I. Davies * and D. J. A. Pearce, Department of Chemistry, King's College, Strand, London WC2R 2LS
E. C. Dart, I.C.I. Ltd., Corporate Laboratory, P.O. Box No. 11, The Heath, Runcorn, Cheshire

Thiols react with 5-substituted norborn-2-ene derivatives to afford 2-*exo*- and 3-*exo*-sulphides by addition across the double bond. Product proportions appear to depend on the relative stability of the intermediate radicals formed by attack at positions 2 and 3 respectively, and, in additions of benzenethiol, also on the variation in the degree of reversibility of radical attack at positions 2 and 3. The addition of thiols to norborn-2-en-5-one forms 2-*exo*-, 3-*exo*-, and 7-*anti*-sulphides, the last having its origin either in the rearrangement of the intermediate formed by radical attack at position 2, or in the formation of a non-classical homoenolised radical by attack at position 2.

THE free-radical addition of tribromofluoromethane to the 5-*endo*-substituted norborn-2-enes (Ia, c, and e) was investigated by Ludwick and Martin,[1] who observed a preference of approximately 1·3 : 1 for radical attack at position 3 relative to attack at position 2. 5-*exo*-Substituents in the norborn-2-enes (Ib and d) were found to have no effect on the site of radical attack, which took place equally readily at positions 2 and 3; thus such substituents, and presumably 5-*endo*-substituents also, seem to have no major polar directing effects on the addition of dibromofluoromethyl radicals. Although the addition of the related trichloromethyl radicals to norbornene has been shown by Huyser[2] not to be reversible, attack of dibromofluoromethyl radicals at position 2 could well become reversible since *endo* intermediate radicals occurs exclusively from the *endo*-direction.

The addition of thiyl radicals to olefins can be a reversible process,[3] but studies of additions to conjugated diolefins[4] and to norbornenes[5] suggest that reversibility is much more significant for aromatic than for aliphatic thiols. We have now studied the addition of thiols to 5-substituted norborn-2-enes. Since such addition should[6] be *exo,cis*, there should be no steric effect of 5-*endo*-substituents governing the chain transfer of intermediate radicals (IV) and (V), and the results should give an indication of the directive effect by 5-substituents on radical attack at positions 2 and 3, and the relative ability of such substituents to stabilise the intermediate radicals (IV) and (V).

The properties and proportions of products formed by the addition of thiols to the 5-substituted norborn-2-enes (Ia, b, f, g, h, and k) are given in Table 1. In almost every case the presence of one or more substituents at position 5 causes a preference for formation of products derived from thiyl radical attack at position 2 rather than position 3.

Studies on free radical additions to olefins[7] and on homolytic aromatic substitution[8] have shown that, in the absence of steric effects, all substituents, regardless of the nature of their electronic effects, stabilise free radicals. Therefore the greater proximity of a 5-substituent to the radical centre in (V) compared to that in (IV) should result in an enhanced stability for (V). Thus if (IV) and (V) resemble closely the respective transition states for their formation, this rationalises the greater preference for the formation of (V). Addition of benzenethiol may be reversible[4,5] and the greater stability of (V; R = Ph) relative to (IV; R = Ph) will reduce the reversibility of the formation of (V; R = Ph) relative to (IV; R = Ph). Thus the preference is further enhanced for chain transfer of (V; R = Ph), with benzenethiol, to give product, and this may account for the greater selectivity in the addition of benzenethiol to compounds (Ia, b, g, and h) compared with the
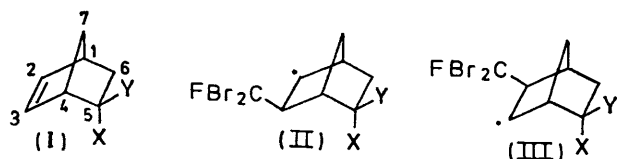
For (II) – (VII) :
a ; X = OAc,Y = H
b ; X = H,Y = OAc
c ; X = O·CO·CF₃,Y = H
d ; X = H,Y = O·CO·CF₃
e ; X = OBz,Y = Me
f ; X = OH,Y = H
g ; X = H,Y = OH
h ; X = Y = Me
k ; X = Y = Cl
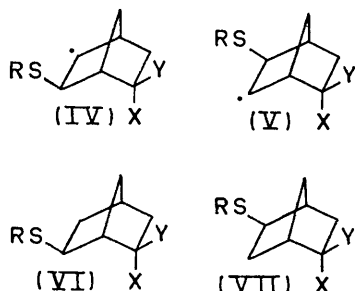
chain transfer at position 3 in the radicals (IIIa, c, and e) is sterically retarded by the presence of the 5-*endo*-substituent, and appreciable chain transfer takes place from the *exo*-direction. The extent of the steric effect is shown by the observation that the *trans* product only is formed in the addition of tribromofluoromethane to norbornene, a reaction in which chain transfer with the

---

† For clarity, all norbornane derivatives in this Paper are numbered with the double bond in the 2,3-position, as exemplified by compounds (I) and (X).

[1] A. G. Ludwick and J. C. Martin, *J. Org. Chem.*, 1969, **34**, 4108.
[2] E. S. Huyser and G. Echegaray, *J. Org. Chem.*, 1962, **27**, 429.
[3] For a general discussion see R. M. Kellogg, *Methods Free-Radical Chem.*, 1969, **2**, 26.

[4] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 3897; W. A. Thaler, A. A. Oswald, and B. E. Hudson, jun., *ibid.*, 1965, **87**, 311.
[5] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1965, **30**, 3003; S. J. Cristol, T. W. Russell, and D. I. Davies, *ibid.*, p. 207.
[6] D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc. (C)*, 1969, 1585.
[7] F. R. Mayo and C. Walling, *Chem. Rev.*, 1940, **27**, 351.
[8] D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47.

addition of 1,1-dimethylethanethiol, for which reversibility is unlikely.[5] In additions of benzenethiol to compounds (I) a single exo-substituent as in (Ib and g) has a greater directing effect than a single endo-substituent as in (Ia and f). This suggests that in intermediates (Vb and g; R = Ph) the 5-exo-substituent is better able to interact and stabilise the radical centre at position 2 than the 5-endo-substituent in intermediates (Va and f; R = Ph). This may be compared with the results [9] of the solvolysis reactions of 5-substituted norborn-2-enes, which show that a 2,3-double bond is better able to assist in the solvolysis of 5-exo- than of 5-endo-substituents.

chloride to (Ih), should not be reversible] does not lead to a similar product ratio although comparable interactions are involved.

(VIII)   (IX)
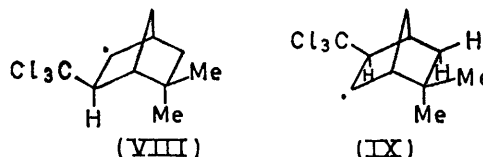
The respective additions of benzenethiol, 1,1-dimethylethanethiol, and methanethiol to 5,5-dichloronorborn-2-ene (Ik) show similar high preferences (1·7 : 1)

TABLE 1

Properties and analysis of 1 : 1 adduct mixtures formed by thiol addition to norbornene derivatives

1 : 1 Adduct mixture [(VI) + (VII)]

5-Substituted norbornene				R	g	Physical properties	Formula	Found (%)		Calc. (%)		G.l.c. analysis			Column and temp. (°C)
No.	g	X	Y					C	H	C	H	% (VI)	% (VII)	(VI):(VII)	
(Ia)	1·52	OAc	H	Ph	2·4	b.p. 126—128° at 0·05 mmHg n_D^{20} 1·5622	C16H18O2S	68·8	7·0	68·7	6·85	43·7	56·3	1:1·3	A, 185
(Ia)	0·76	OAc	H	But	1·1	b.p. 90—94° at 0·1 mmHg n_D^{20} 1·4873	C13H22O2S	64·6	9·15	64·45	9·1	49·0	51·0	1:1·04	A, 140
(Ib)	1·52	H	OAc	Ph	2·4	b.p. 130° at 0·05 mmHg n_D^{20} 1·5600	C16H18O2S	68·45	6·85	68·7	6·85	37·9	62·1	1:1·6	A, 185
(Ib)	1·52	H	OAc	But	2·3	b.p. 94—96° at 0·05 mmHg n_D^{20} 1·4901	C13H22O2S	64·5	9·35	64·45	9·1	50·0	50·0	1:1	A, 140
(If)	2·20	HO	H	Ph	3·9	b.p. 128—130 at 0·02 mmHg n_D^{20} 1·5972	C13H16OS	70·7	7·2	70·9	7·25	42·5	57·6	1:1·35	●
(Ig)	1·10	H	OH	Ph	1·9	b.p. 140—142° at 0·04 mmHg n_D^{20} 1·5937	C13H16OS	71·3	7·15	70·9	7·25	36·6	63·4	1:1·7	A, 185
(Ig)	2·20	H	OH	But	2·9	b.p. 90—94° at 0·05 mmHg m.p. 58—60°	C11H20OS	65·7	9·9	66·0	10·0	49·0	51·0	1:1·04	†
(Ih)	2·40	Me	Me	Ph	4·3	b.p. 98—100° at 0·05 mmHg n_D^{20} 1·5662	C15H20S	77·45	8·4	77·6	8·6	36·2	63·8	1:1·75	C, 180
(Ih)	0·72	Me	Me	But	1·2	b.p. 120—124° at 10 mmHg n_D^{20} 1·4880	C13H24S	73·7	11·2	73·6	11·3	45·76	54·24	1:1·2	C, 120
(Ih)	0·48	Me	Me	Me	0·6	b.p. 40—42° at 0·01 mmHg n_D^{20} 1·5011	C10H18S	70·6	10·5	70·6	10·6	45·47	54·53	1:1·2	C, 100
(Ik)	1·63	Cl	Cl	Ph	2·3	b.p. 118—120° at 0·02 mmHg n_D^{20} 1·5917	C13H14Cl2S	57·15	5·35	57·15	5·15	37·25	62·75	1:1·7	A, 180
(Ik)	1·63	Cl	Cl	But	1·7	b.p. 90—92° at 0·04 mmHg n_D^{20} 1·5672	C11H18Cl2S	52·2	7·1	52·2	7·1	35·49	64·51	1:1·8	A, 140
(Ik)	1·63	Cl	Cl	Me	1·9	b.p. 77—78° at 0·05 mmHg n_D^{25} 1·5530	C8H12Cl2S	45·3	5·75	45·5	5·7	36·80	63·20	1:1·7	C, 120

1 : 1 Adduct

(X) (g)	Thiol	g	Physical properties	Formula	Found (%)		Calc. (%)		% (XV)	% (XVI)	% (XVII)	(XV) : (XVI) : (XVII)	(XV)/(XVI) + (XVII)	Column and temp. (°C)
					C	H	C	H						
1·08	PhSH	1·9	b.p. 122—124 at 0·02 mmHg n_D^{20} 1·5865	C13H14OS	71·4	6·5	71·55	6·4	9·2	77·0	13·8	1: 8·4: 1·5	1/9·9	B, 210
1·08	ButSH	1·9	b.p. 72—74° at 0·05 mmHg n_D^{20} 1·5055	C11H18OS	66·4	9·35	66·65	9·1	21·5	42·8	35·7	1: 2 : 1·65	1/3·65	A, 120

● Product mixture inseparable by g.l.c. and product proportions therefore determined by g.l.c. analysis of the acetylated product mixture [(VIa) + (VIIa); R = Ph] on column A at 185°, and of the oxidised product mixture [(XVa) + (XVIa)] on column B at 120°. † Product mixture inseparable by g.l.c. and product proportions therefore determined by g.l.c. analysis of the acetylated product mixture [(VIb) + (VIIb); R = But] on column A at 140°, and of the oxidised product mixture [(XVb) + (VIb)] on column A at 120°.

The 1·2 : 1 preference for product formation derived from attack at position 2 relative to attack at position 3 in the addition of 1,1-dimethylethanethiol and of methanethiol to 5,5-dimethylnorborn-2-ene (Ih) is similar to that for the 1 : 1 adducts isolated by Osborn et al.[10] from the addition of carbon tetrachloride to (Ih). These workers considered that the ratio reflected the difference between 2-endo-H,6-endo-H interactions in (IX) and 3-endo-H,5-endo-Me interactions in (VIII). However, such interactions seem unlikely to be involved in controlling product proportions, since the addition of 1,1-dimethylethanethiol to 5-endo-norborn-2-enyl acetate [a reaction which, like the addition of carbon tetra-
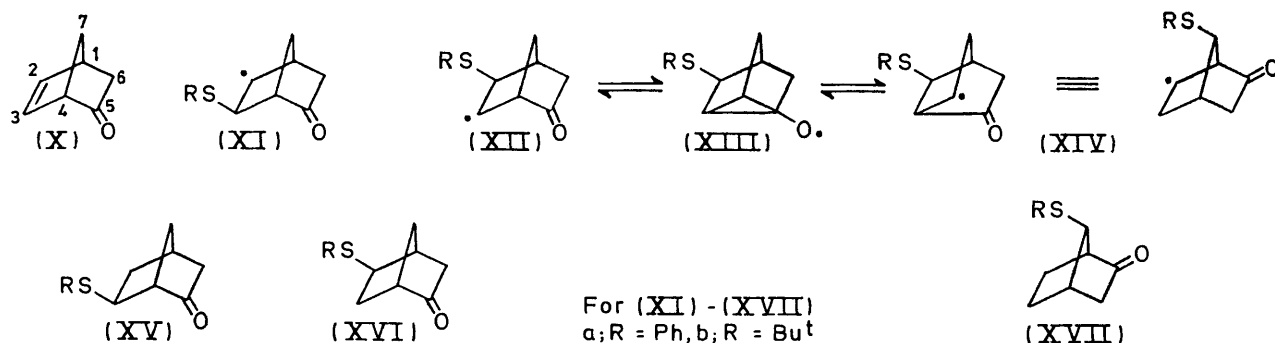
for formation of products derived from attack at position 2 rather than position 3. The best rationalisation for this result is that product formation with all three thiols is controlled by the greater stability and hence ease of formation of (Vk) than of (IVk). The reactivity of these radicals when R = Ph must be such that reversibility is of minimal effect in controlling product proportions. The observation that both 5,5-dimethyl and 5,5-dichloro-substituents in (Ih) and (Ik), respectively, lead to a preference for attack at position 2, in spite of the opposite inductive effects of the respective methyl and chloro-groups, indicates that polarisation of the π-electrons in the double bond by 5-substituents

[9] S. Winstein, K. Walborsky, and K. Schreiber, J. Amer. Chem. Soc., 1950, 72, 5795.

[10] C. L. Osborn, T. V. Van Auken, and D. J. Trecker, J. Amer. Chem. Soc., 1968, 90, 5806.

cannot be a factor in the observed preference for attack at position 2.

The addition of benzenethiol to norborn-2-en-5-one (X) affords the products (XVa), (XVIa), and (XVIIa) in the ratio 1 : 8·4 : 1·5, whereas in the addition of 1,1-dimethylethanethiol, (XVb), (XVIb), and (XVIIb) are formed in the ratio 1 : 2 : 1·65. Free radical addition to carbonyl groups is known in certain rare cases,[11] and the radical (XII) from attack at position 2 may thus be converted into (XIII); this process can be considered to be the radical equivalent of the carbanion homoenolisation found in analogous systems studied by Nickon.[12] The radical (XIII) can revert on ring opening to afford

via intermediates such as (XVIII). Skell [15] has provided evidence for the involvement of sulphur bridging in the addition of thiols to cyclohexenes, although earlier studies suggest that such bridging may not be important in the addition of aromatic thiols to norbornenes.[16]

When the reaction medium of thiol and norborn-2-en-5-one (X) is diluted with benzene as an inert solvent, there is no effect on product proportions (Table 2) apart from an initial solvent effect in the addition of benzenethiol. This suggests not only that the addition of thiols to norborn-2-en-5-one (X) is non-reversible, but also that product formation can be rationalised in terms of participation of a non-classical homoenolised radical
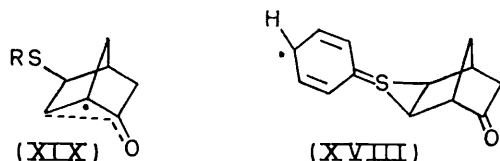

either (XII) or (XIV), from which (XVI) and (XVII) are derived on chain transfer. The results may be accommodated by an equilibrium involving the radical species (XII), (XIII), and (XIV), since related equilibria involving the addition of a radical centre across a carbon–carbon double bond in the same molecule, rather than across a carbon–oxygen double bond, are found in free radical additions to hexachloronorbornadiene [13] and in the additions of tin hydrides to norbornadiene.[14]

Since the major products (XVI) and (XVII) are both derived from radical attack at position 2 in (X), the carbonyl group clearly exerts a powerful directing effect occasioned by the greater stability of radicals derived from attack at position 2. The proportions of products derived from radicals (XII) and (XIV) are dependent on the group R, which must therefore have some control on any equilibrium (XII) ⇌ (XIII) ⇌ (XIV). Sulphur bridging is an attractive explanation for more

product being derived from (XIIa) than from (XIIb), since the phenyl ring may be able to assist in bridging

(XIX) equally as well as by the equilibrium (XII) ⇌ (XIII) ⇌ (XIV).

TABLE 2

Dilution experiments in the addition of thiols to norborn-2-en-5-one (X)

Thiol	Reactants (g)			Product ratio (%)		
	Thiol	(VIII)	C_6H_6	(XVb)	(XVIb)	(XVIIb)
Bu^{t}SH	1·5	1·08	0	21·5	42·8	35·7
	1·5	1·08	0·78	21·9	44·1	34·0
	1·5	1·08	1·56	23·0	44·1	32·9
	1·5	1·08	3·12	21·5	43·6	34·9
	1·5	1·08	78·0	19·0	45·0	36·0
				(XVa) +	(XVIIa)	(XVIa)
PhSH	1·2	1·08	0	22·4		77·6
	1·2	1·08	0·078	29·8		70·2
	1·2	1·08	0·39	32·6		67·4
	1·2	1·08	0·78	31·5		68·5
	1·2	1·08	3·90	29·6		70·4
	1·2	1·08	78·0	31·8		69·2

The assignment of product structures is based on n.m.r. evidence (essential data recorded in Table 3), which is consistent with reported differences in the n.m.r. spectra for *exo*- and *endo*-norbornane derivatives.[17] The products (XVII) are readily distinguished by the narrow multiplet for the C-7 bridge proton. Isomer (XVIIb) was separated from the product mixture [(XVb) + (XVIb) + (XVIIb)] and irradiation at the frequency of this C-7 proton resonance resulted in a

[11] See for example, S. P. Singh and J. Kagan, *Chem. Comm.*, 1969, 1121.

[12] A. Nickon and J. L. Lambert, *J. Amer. Chem. Soc.*, 1962, **84**, 4604; A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *ibid.*, 1963, **85**, 3713.

[13] D. I. Davies, *Chem. Soc. Special Publ.*, No. 24, 1970, 201.

[14] H. G. Kuivila, J. D. Kennedy, R. Y. Tien, I. J. Tyminski, F. L. Pelczar, and O. R. Khan, *J. Org. Chem.*, 1971, **36**, 2083.

[15] P. D. Readio and P. S. Skell, *J. Org. Chem.*, 1966, **31**, 759.

[16] S, J. Cristol and R. P. Arganbright, *J. Amer. Chem. Soc.*, 1957, **79**, 6039.

[17] P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, 1965, **30**, 2624; K. C. Ramey, D. C. Line, R. M. Moriarty, H. Gopal, and H. C. Welsh, *J. Amer. Chem. Soc.*, 1967, **89**, 2401.

narrowing of the multiplets at τ 7·5 and 7·85 for H-1 and H-4 respectively. Although (XVIIa) could not be separated from the product mixture [(XVa) + (XVIa) + (XVIIa)], the H-7 and H-1 signals could be readily picked out in the n.m.r. spectrum of the product mixture,

R = Ph] afforded a mixture of (XVa) and (XVIa), which are among the products of the addition of benzenethiol to norborn-2-en-5-one (X). The products (VIf; R = Ph) and (VIIf; R = Ph) of the addition of benzenethiol to *endo*-norborn-2-en-5-ol (If) were separ-

TABLE 3

N.m.r. data for products *

Compound	R	X	Y	τ Values 2n	3n	5n	5x	J/Hz 2x,3n	2n,3n	2n,3x	2n,7a	3x,3n	3n,7a	5x,6x	5x,6n	5n,6x	5n,6n	5n,7s
(VIa)	Ph	OAc	H		6·3 Octet		5·08 Sextet	5·0	7·9		1·8		1·8	10·5	3·5			
(VIIa)	Ph	OAc	H	6·8 Octet			5·12 Octet		8·25	4·5	1·75	13·2			3·5			
(VIa)	Buᵗ	OAc	H		6·87 Octet		5·15 Sextet	5·0	8·75				1·75	9·5	4·0			
(VIIa)	Buᵗ	OAc	H	7·38 Octet			5·15 Sextet		8·5	4·5	2·0			9·5	4·0			
(VIb)	Ph	H	OAc		6·92 Octet	5·46 m		5·0	9·25				1·5					
(VIIb)	Ph	H	OAc	6·96 Octet		5·46 m			9·00	5·0	2·0							
(VIb)	Buᵗ	H	OAc		7·46 Octet	5·50 Octet		4·0	7·5				1·5			4·5	4·5	2·5
(VIIb)	Buᵗ	H	OAc	7·51 Octet		5·50 Octet			7·5	4·0	1·5					4·5	4·5	2·5
(VIf)	Ph	HO	H		6·09 Octet		5·79 Sextet	5·0	8·0				1·5	10	3·5			
(VIIf)	Ph	HO	H	6·78 Octet			5·84 m		8·25	4·25	1·5	14·2			3·5			
(VIg) †	Ph	H	OH		7·02 Octet	6·26 Octet			7·2	3·6			1·8					
(VIIg) †	Ph	H	OH	7·00 Octet		6·26 Octet			7·2	4·5	1·8							
(VIg)	Buᵗ	H	OH		7·61 Sextet	6·31 Octet		5·0	7·25				2·25			2·5	6·5	1·0
(VIIg)	Buᵗ	H	OH	7·57 Octet		6·35 Octet			8·0	4·5	1·5					2·5	6·5	1·0
(VIh)	Ph	Me	Me		6·37 Octet				8·0	4·0			2·0					
(VIIh)	Ph	Me	Me	6·95 Octet					8·0	5·5								
(VIh)	Buᵗ	Me	Me		6·94 Octet			4·25	8·0				1·5					
(VIIh)	Buᵗ	Me	Me	7·51 Octet					8·25	5·5	1·25							
(VIh)	Me	Me	Me		7·02 Octet			3·75	7·25				1·5					
(VIIh)	Me	Me	Me	7·55 Octet					8·00	5·0	1·75							
(VIk)	Ph	Cl	Cl		6·02 Octet			4·5	8·0			1·75						
(VIIk)	Ph	Cl	Cl	6·81 Octet					8·5	4·75	1·25							
(VIk)	Buᵗ	Cl	Cl		6·60 Octet			5·25	8·5				2·25					
(VIIk)	Buᵗ	Cl	Cl	7·26 m														
(VIk)	Me	Cl	Cl	8·22 Octet	6·68 Octet			4·5	8·0			1·75	1·75					
(VIIk)	Me	Cl	Cl	7·23 Octet				4·5	8·25			1·25						

Compound	R	2n	3n	7a	2n,3x	2n,3n	2n,7a	2x, 3n	3n,7a	4,7a
(XVa)	Ph		6·6 Octet			8·0	1·0	4·75	1·75	0·5
(XVIa)	Ph	6·65 Octet			4·75	8·25	1·75			
(XVIIa) †	Ph			6·85 m				§	§	§
(XVb)	Buᵗ		7·14 Octet		5·25	8·0				
(XVIb)	Buᵗ	7·18 Octet			5·0	8·25				
(XVIIb) †	Buᵗ			7·15 m			1·25		1·25	1·25

* 100 MHz Spectra of solutions in CCl₄ with Me₄Si as standard unless stated otherwise. n = *endo*, x = *exo*, a = *anti*, s = *syn*. † 220 MHz Spectra of solutions in CDCl₃
‡ 220 MHz Spectra of solutions in C₆D₆. § $W_{\frac{1}{2}}$ 3—4 Hz.

as narrow multiplets at τ 6·9 and 7·52, respectively. Supporting evidence for product structures was provided by the conversion of the product mixtures [(VIf) + (VIIf); R = Ph] and [(VIg) + (VIIg); R = Ph], respectively, formed by the addition of benzenethiol to *endo*-norborn-2-en-5-ol (If) and *exo*-norborn-2-en-5-ol (Ig) into the acetate mixtures [(VIa) + (VIIa); R = Ph] and [(VIb) + (VIIb); R = Ph]. Oxidation of either [(VIf) + (VIIf); R = Ph] or [(VIg) + (VIIg);

ated and converted into the individual acetates (Va; R = Ph) and (VIIa; R = Ph), and also oxidised to afford the ketones (XVa) and (XVIa), respectively. The mixture of products [(VIg) + (VIIg); R = Buᵗ] formed by the addition of 1,1-dimethylethanethiol to *exo*-norborn-2-en-5-ol (Ig) and the separated isomers (VIg; R = Buᵗ) and (VIIg; R = Buᵗ) from the addition to *exo*-norborn-2-en-5-ol (Ig) were similarly converted into their corresponding acetates and ketones

EXPERIMENTAL

N.m.r. spectra were recorded by the P.C.M.U. service at Harwell; where necessary spin decoupling experiments were carried out to confirm proton assignments. Column chromatography was carried out on Woelm neutral alumina, with light petroleum (b.p. 40—60°) followed by ethyl acetate as eluant. For g.l.c. analysis a Perkin-Elmer F11 chromatograph was used fitted with one of the following columns: (A) 2 m × $\frac{1}{8}$ in 2% Versamid 930 on A.W.-D.M.C.S. Chromosorb W (80—100 mesh); (B) 2 m × $\frac{1}{8}$ in 5% Carbowax 20M/TPA on A.W.-D.M.C.S. Chromosorb G (80—90 mesh); (C) 2 m × $\frac{1}{8}$ in 5% Apiezon L on A.W.-D.M.C.S. Chromosorb W (80—100 mesh). Preparative g.l.c. was carried out with a Pye 105 series chromatograph [5 ft × $\frac{1}{4}$ in column of 25% poly(ethylene glycol) 20M on Chromosorb W (60—80 mesh)]. Norborn-5-en-2-yl acetate, b.p. 80—82° at 25 mmHg, n_D^{25} 1·4667, was prepared by Diels–Alder addition of vinyl acetate to cyclopentadiene[18] (lit.,[19] b.p. 72° at 10 mmHg, n_D^{25} 1·4668). The mixture of isomers was separated by preparative g.l.c. at 130° to afford the endo-acetate (Ia), b.p. 86—88° at 30 mmHg, n_D^{25} 1·4662 (lit.,[20] b.p. 99—100° at 35 mmHg; lit.,[18] n_D^{25} 1·4662), and the exo-acetate (Ib), b.p. 76—78° at 15 mmHg, n_D^{25} 1·4642 (lit.,[21] 1·4639). Norborn-2-en-5-one (X), prepared by hydrolysis[22] of 5-chloronorborn-2-ene-5-carbonitrile had m.p. 22—23°, b.p. 76—78° at 38 mmHg (lit.,[22] m.p. 22—23°, b.p. 80—81° at 45 mmHg).

exo- and endo-Norborn-2-en-5-ol (Ig and f).—Crude norbornenyl acetate[18] (30·4 g) was added to a solution of potassium hydroxide (57·6 g) in methanol (160 ml). The mixture was boiled at reflux for 4 h, then poured into water (250 ml) and extracted with ether (3 × 50 ml). The extracts were washed with water (3 × 50 ml), dried (MgSO₄), and evaporated. The residue was distilled to afford norbornenol (16·8 g), m.p. 105—107° (lit.,[18] m.p. 108—109°), which was separated by preparative g.l.c. at 130° [Varian A700 Chromatograph fitted with a 1 m × $\frac{1}{4}$ in column of 8% Carbowax 20M on Chromosorb W (60—80 mesh)] into endo-norborn-2-en-5-ol (If), m.p. 110—112° (lit.,[19] 109·4—110·8°), and exo-norborn-2-en-5-ol (Ig), m.p. 89—90° (lit.,[22] 92—93°), in the ratio 3 : 1. The exo-isomer (Ig) (4·6 g) was also prepared by hydroboration[23] of norbornadiene (18·4 g) with sodium borohydride (1·0 g) in bis-(2-methoxyethyl) ether (25 ml) as reducing agent instead of the recommended[23] lithium borohydride in anhydrous ether.

5,5-Dimethylnorborn-2-ene (Ih).—5-Methylnorborn-2-ene-5-carbaldehyde (6·8 g) was added to aqueous 64% w/w hydrazine (20 ml), potassium hydroxide (15 g), and ethylene glycol (50 ml). The mixture was boiled at reflux for 5 h (bath temp. 170°), and then distilled, the aqueous distillate being collected up to a b.p. of 120°. The crude product solidified and the aqueous distillate was decanted. A solution of the product in ether was dried (MgSO₄) and evaporated; the residue was distilled to afford 5,5-dimethylnorborn-2-ene (Ih) (3·5 g), b.p. 130—133° at 760 mmHg, m.p. 27—28° (lit.,[24] b.p. 129—130° at 730 mmHg, m.p. 27—28°).

5,5-Dichloronorborn-2-ene (Ik).—Vinylidene chloride (36

g), cyclopentadiene (16 g), and quinol (0·2 g) were mixed and heated in a sealed tube at 185° for 12 h. Distillation of the crude product afforded 5,5-dichloronorborn-2-ene (Ik) (12·2 g), n_D^{30} 1·5079, b.p. 58—62° at 10 mmHg (lit.,[25] b.p. 61—64° at 12 mmHg).

Addition of Benzenethiol to Norbornene Derivatives.—General procedure. The norbornene derivative [(I) or (X)] and benzenethiol (1·1 mol. equiv.) were mixed; after ca. 2 min the temperature rose to ca. 85° during <1 min. After 1 h, when the mixture had cooled to room temperature, the crude product was mixed with aqueous N-sodium hydroxide solution (5 ml). The resultant mixture was extracted with ether (3 × 10 ml); the extract was washed with water (3 × 10 ml), dried (MgSO₄), and evaporated and the crude product was purified by distillation and analysed by g.l.c. Product properties etc. are recorded in Table 1. By preparative g.l.c. at 185° were isolated 3-exo-phenylthionorborn-5-endo-yl acetate (VIa; R = Ph), n_D^{30} 1·5538 (Found: C, 69·05; H, 7·05; S, 11·7. C₁₅H₁₈O₂S requires C, 68·7; H, 6·85; S, 12·2%); 2-exo-phenylthionorborn-5-endo-yl acetate (VIIa; R = Ph), n_D^{30} 1·5523 (Found: C, 68·4; H, 6·7; S, 13·0%); 3-exo-phenylthionorbornan-5-one (XVa), n_D^{30} 1·5831 (Found: C, 71·9; H, 6·7; S, 15·0. C₁₃H₁₄OS requires C, 71·55; H, 6·4; S, 14·7%); and 2-exo-phenylthionorbornan-5-one (XVIa), n_D^{30} 1·5827 (Found: C, 71·6; H, 6·2; S, 15·4%). Column chromatography with 4 : 1 light petroleum (b.p. 40—60°)–ethyl acetate as eluant resulted in separation of 3-exo-phenylthionorbornan-5-endo-ol (VIf; R = Ph), n_D^{30} 1·5859 b.p. 163—164° at 0·02 mmHg (Found: C, 71·0; H, 6·95; S, 15·0. C₁₃H₁₆OS requires C, 70·9; H, 7·25; S, 14·55%), and 2-exo-phenylthionorbornan-5-endo-ol (VIIf; R = Ph), n_D^{30} 1·5845 (Found: C, 70·95; H, 7·06; S, 15·3%).

Addition of 1,1-Dimethylethanethiol and Methanethiol to Norbornene Derivatives.—General procedure. The norbornene derivative [(I) or (X)] and the thiol (1·1 mol. equiv.) were mixed and heated in a sealed tube at 80° for 24 h. The excess of thiol was evaporated off and the crude product was purified by distillation and analysed by g.l.c. (see Table 1). Column chromatography with 2·3 : 1 light petroleum (b.p. 40—60°)–ethyl acetate as eluant allowed separation of 3-exo-t-butylthionorbornan-5-exo-ol (VIg; R = Buᵗ), m.p. 66—68° (Found: C, 65·85; H, 9·9; S, 14·0. C₁₁H₂₀OS requires C, 66·0; H, 10·0; S, 16·0); 2-exo-t-butylthionorbornan-5-exo-ol (VIIg; R = Buᵗ), m.p. 73—74° (Found: C, 66·0; H, 10·0; S, 13·9%); 3-exo-t-butylthionorbornan-5-one (XVb), m.p. 36—37° (Found: C, 66·3; H, 9·05; S, 16·0. C₁₁H₁₈OS requires C, 66·65; H, 9·1; S, 16·15%); 2-exo-t-butylthionorbornan-5-one (XVIb), m.p. 40—41° (Found: C, 66·3; H, 9·05%); and 7-anti-t-butylthionorbornan-5-one (XVIIb), m.p. 32—34° (Found: C, 66·45; H, 8·9%).

Oxidation of the Alcohols (VIf and g) and (VIIf and g) to the Ketones (XV) and (XVI) (cf. Ref. 26).—The following example typifies the procedure. Chromium trioxide (6·2 g, 62 mmol) was added during 15 min to stirred, ice-cold pyridine (70 ml). The adduct mixture [(VIf) + (VIIf); R = Ph] (4·3 g, 2·0 × 10⁻² mol) was added in one portion to the chromium trioxide–pyridine complex and the resultant mixture was stirred vigorously for 30 min, then

[18] K. Alder and H. F. Rickert, Annalen, 1939, **543**, 1.
[19] J. D. Roberts, E. R. Trumbull, jun., W. Bennett, and R. Armstrong, J. Amer. Chem. Soc., 1950, **72**, 3116.
[20] J. C. Davis, jun., and T. V. Van Auken, J. Amer. Chem. Soc., 1965, **87**, 3900.
[21] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, J. Amer. Chem. Soc., 1962, **84**, 3918.

[22] H. Krieger, Suomen Kem., 1963, B**36**, 68; P. K. Freeman, D. M. Ballo, and D. J. Brown, J. Org. Chem., 1968, **33**, 2211.
[23] G. Zweifel, J. Amer. Chem. Soc., 1965, **87**, 3900.
[24] S. Beckman and R. Bamberger, Annalen, 1953, **580**, 198.
[25] R. E. Lidov, U.S.P. 2,635,979 (Chem. Abs., 1953, **47**, 6596).
[26] J. R. Holum, J. Org. Chem., 1961, **26**, 4814.

kept at room temperature with stirring for 24 h, and finally added to water (250 ml). This mixture was extracted with ether (3 × 200 ml); the extracts were combined, dilute hydrochloric acid (50 ml) was added, and the precipitate of pyridine hydrochloride was filtered off. The ether solution was washed with water (2 × 50 ml), dried (MgSO$_4$), and evaporated to leave a viscous liquid, which was distilled to afford a mixture (3·85 g), n_D^{30} 1·5864, b.p. 130—134° at 0·10 mmHg of 3-*exo*-phenylthionorbornan-5-one (XVa) and 2-*exo*-phenylthionorbornan-5-one (XVIa) (Found: C, 71·25; H, 6·3; S, 14·0. Calc. for C$_{13}$H$_{14}$OS: C, 71·55; H, 6·4; S, 14·7%). A similar oxidation of [(VIg) + (VIIg); R = Ph] gave (XVa) + (XVIa). The individual isomers (VIf; R = Ph), (VIIf; R = Ph), (VIg; R = Bu^t), and (VIIg; R = Bu^t) gave the respective ketones (XVa), (XVIa), (XVb), and (XVIb).

Acetylation of the Alcohols (VIf *and* g) *and* (VIIf *and* g).— The following is a typical procedure. Acetyl chloride (8·7 g, 0·011 mol) was added dropwise over 30 min to an ice-cold stirred solution of the mixture [(VIg) + (VIIg); R = Bu^t] (2·0 g, 0·01 mol) in pyridine (20 ml). The resultant mixture was then stirred at room temperature for 2 h. The precipitate of pyridine hydrochloride was filtered off and washed with pyridine, and the filtrate and washings were evaporated. The residue was distilled to afford a mixture (2·58 g), b.p. 136—140° at 0·1 mmHg, n_D^{30} 1·4908, of 3-*exo*-t-butylthionorborn-5-*exo*-yl acetate (VIb; R = Bu^t) and 2-*exo*-t-butylthionorborn-5-*exo*-yl acetate (VIIb; R = Bu^t) (Found: C, 64·25; H, 9·3; S, 13·7. Calc. for C$_{13}$H$_{22}$O$_2$S: C, 64·45; H, 9·1; S, 13·2%). Similarly, acetylation of [(VIf) + (VIIf); R = Ph], [(VIg) + (VIIg); R = Ph], and [(VIf) + (VIIf); R = Bu^t] and the individual isomers (VIf; R = Ph), (VIIf; R = Ph), (VIg; R = Bu^t), and (VIIg; R = Bu^t) afforded the respective acetates [(VIa) + (VIIa); R = Ph], [(VIb) + (VIIb); R = Ph], [(VIa) + (VIIa); R = Bu^t], (VIa; R = Ph), (VIIa; R = Ph); 3-exo-*t-butylthionorborn*-5-exo-*yl acetate* (VIb; R = Bu^t), n_D^{25} 1·4926 (Found: C, 65·0; H, 9·3; S, 12·3. C$_{13}$H$_{22}$O$_2$S requires C, 64·45; H, 9·1; S, 13·2%); and 2-exo-*t-butylthionorborn*-5-exo-*yl acetate* (VIIb; R = Bu^t), n_D^{25} 1·4916 (Found: C, 64·85; H, 9·2; S, 14·8%).