Tetrahedron Letters No. 27, pp 2719 - 2722, 1972. Pergamon Press. Printed in Great Britain.

STERIC AND ELECTROSTATIC EFFECTS IN THE FREE RADICAL ADDITION OF THIOLS TO NORBORNENES

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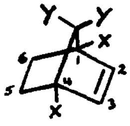
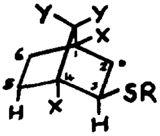
(Received in UK 11 May 1972; accepted for publication 25 May 1972)



(I)



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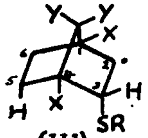

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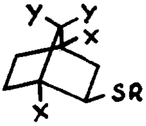

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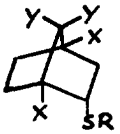
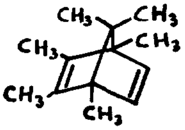


(V)



(VI)

For I - IV a, X = Y = H ; b, X = H, Y = CH_3 ; c, X = Y = CH_3

The addition of thiophenol, *t*-butanethiol, and methanethiol to norbornene (Ia) involves a virtually exclusive attack by thiyl radicals from the *exo*-direction.[1] This preference for *exo* attack relative to *endo* attack may be rationalised in terms of torsional strain,[2] and by the less unfavourable steric interactions between 5-*endo* and 3-*endo* protons in the radical (IIa) derived from *exo* attack [or more properly the transition state leading to the formation of (IIa)] than between the 5-*endo* proton and the 3-*endo*-SR group in the radical (IIIa) derived from *endo* attack. A similar preference for *exo*-attack is involved in the addition of thiophenol,[3,4] *t*-butanethiol,[5] and methanethiol[5] to 7,7-dimethylnorbornene (Ib). As Brown[3] has pointed out, a 7-*syn* methyl group in (Ib) is over the centre of the double bond and therefore does not seriously interfere with the *exo* attack of thiyl radicals on the end of the double bond at the corner of the bicyclic system.

In the addition[6] of _t_-butanethiol to hexamethylnorbornadiene (VI) a 96:4 preference for _endo_ attack occurs, which may be explicable by steric interference of the bridge and bridgehead methyl groups with _t_-butanethiyl radicals attacking from the _exo_ direction, and the lack of any _endo_ protons to interfere sterically with a _t_-butanethiyl radical attacking from the _endo_ direction. These factors favourable to _endo_ attack would appear to be sufficient to overcome the unfavourable torsional strain that such _endo_ attack involves.

Table

Percentages of _exo_-sulphide (IVc) and _endo_-sulphide (Vc) formed in the addition of thiols to 1,4,7,7-tetramethylnorbornene (Ic)

Thiol	% Sulphides[7]	
RS-H	_exo_ (IVc)	_endo_ (Vc)
MeS-H	68	32
$(CH_3)_2CHS$-H	87	13
$(CH_3)_3CS$-H	95	5
_p_-$CH_3C_6H_4S$-H	37	63
C_6H_5S-H	28	72
_p_-ClC_6H_4S-H	23	77

The addition of thiols to 1,4,7,7-tetramethylnorbornene (Ic) affords mixtures of _exo_-sulphide (IVc) and _endo_-sulphide (Vc), and the composition of the mixtures formed with the different thiols are given in the Table. _Endo_ attack by an alkanethiyl radical on (Ic) leads to an intermediate (IIIc) in which the 3-_endo_-SR group has an unfavourable steric interaction with the 5-_endo_-H. This coupled with the disadvantageous torsional strain for _endo_ attack leads to a preference for _exo_ attack by alkanethiyl radicals in spite of the unfavourable interactions of an alkanethiyl radical, attacking from the _exo_ direction, with bridge and bridgehead methyls. The preference for _exo_ attack increases with the increase in size of the alkanethiyl radical. An examination of molecular models shows that in the intermediate (IIIc, R = _t_-Bu) but not in (IIIc, R = Me) the 3-_endo_-SR substituent can have some steric interaction with the 6-*endo*-H as well as with the 5-*endo*-H, which may account for the almost exclusive *exo* attack by *t*-butanethiyl radicals.

The nucleophilic character of the alkanethiyl radicals varies in the order $(CH_3)_3CS\cdot$ > $(CH_3)_2CHS\cdot$ > $CH_3S\cdot$, and the possibility therefore exists that an electrostatic effect could also be operative which directs the more nucleophilic radicals increasingly towards the *exo* face of the double bond. To test this suggestion some aromatic thiols have been added to tetramethylnorbornene (Ic) and the proportions of *exo*-sulphide (IVc) and *endo*-sulphide (Vc) are given in the Table. Steric effects in the attack of $C_6H_5S\cdot$ should be similar to those in the attack of $(CH_3)_2CHS\cdot$, and therefore the preference for *endo* attack with $C_6H_5S\cdot$ radicals, compared with a preference for *exo* attack with $(CH_3)_2CHS\cdot$ radicals would appear to indicate that an additional effect, other than steric, is involved. The $C_6H_5S\cdot$ radical should be highly polarizable, and it is difficult to predict its electrostatic properties, compared to those of an alkanethiyl radical, as it approaches the olefin (Ic). The three aromatic thiyl radicals vary only in the nature of the *p*-substituent, so that steric effects in the approach of these radicals to (Ic) will be similar. Therefore the observed variation in the proportions of *exo* and *endo* attack by these radicals may be due to the variation in the electrostatic interaction of these radicals with the *exo* and *endo* sides of (Ic) as the *para* substituent in the attacking radical is changed. As in the alkanethiol addition the percentage of *exo* attack increases with increasing nucleophilic character of the attacking radical *p*-$CH_3C_6H_4S\cdot$ > $C_6H_5S\cdot$ > *p*-$ClC_6H_4S\cdot$

These results clearly suggest that the direction of radical attack on norbornene (Ia) and substituted norbornenes (Ib, c) may be dependent on both steric and electrostatic interactions between attacking radical and olefin.

REFERENCES

1. D.I. Davies, L.T. Parfitt, C.K. Alden, and J.A. Claisse, *J.Chem.Soc.(C)*, 1969, 1585.
2. P. von R. 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. Product sulphides (IVb, R = *t*-Bu, H-2-*endo* τ 7.45q, J = 9.0, 6.0 Hz and (IVb, R = Me, H-2-*endo* τ 7.50t, J = 7.5 Hz) are the sole identifiable products in the addition of *t*-butanethiol and methanethiol respectively to 7,7-dimethylnorbornene (Ib).

6. E.N. Prilezhaeva, V.A. Azovskaya, A.U. Stepanyants, D. Mondeshka, and R.I. Shekhtman, *Tetrahedron Letters*, 1969, 4909.

7. Based on n.m.r. and g.l.c. analysis of product mixtures.
   (IVc), R = alkyl, H-2-*endo* near τ 7.50q, J = 8.5, 6.0 Hz
   (IVc), R = aryl, H-2-*endo* near τ 6.85q, J = 8.5, 6.0 Hz
   (Vc), R = alkyl, H-2-*exo* near τ 7.30 octet, J = 11.0, 4.5, 2.5 Hz
   (Vc), R = aryl, H-2-*exo* near τ 6.70 octet, J = 10.0, 4.5, 2.5 Hz