Some Free-radical Addition Reactions of Norbornene and Related Compounds

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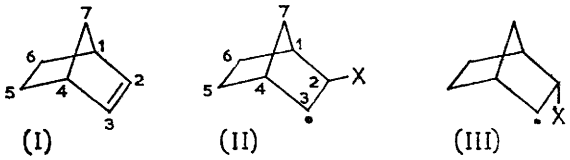
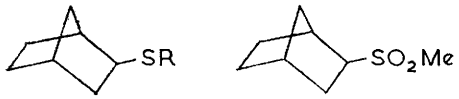
In the additions of methanethiol, 2-methylpropane-2-thiol, thioacetic *S*-acid, benzenethiol, and *S*-deuteriobenzenethiol to norbornene, products of *exo–cis*-addition are formed. *exo-cis*-Addition similarly occurs when benzenethiol adds to 2-methylnorborn-2-ene; the phenylthio-radical attacks the more sterically available 3-position, which affords the more highly substituted intermediate radical. In the addition of benzenethiol to both 2-methylenenorbornane and camphene, chain transfer of the intermediate radicals occurs from the *exo*-direction. When methylene bromide, methyl bromoacetate, and probably ethyl bromoacetate are added to norbornene, products of both *trans*- and *exo–cis*-addition are formed, with the latter predominant. These results are best rationalised on the basis of exclusive *exo* radical attack, since this minimises both steric and torsional strain effects. In the chain-transfer step stereoelectronic interactions between the attacking molecule and the group introduced in the initial radical attack control the *exo*:*endo* ratio for direction of chain transfer leading to product formation. In additions of methylene bromide and methyl bromoacetate these interactions are so great that some chain transfer from the *endo*-side of the radical centre occurs in spite of the increase of torsional strain experienced in the transition state.

If the additions of bromine [1] and hydrogen bromide [2] are omitted from a consideration of free-radical addition reactions of norbornene (I) and related compounds, on the supposition that the possibility of competing ionic and free radical additions cannot be ruled out, *exo* radical attack is found to be the rule.[3] The *exo*-side of norbornene (I) is considered to be sterically more available to attack than the *endo*-side, and steric effects are usually quoted [3] to explain the preference for *exo* attack. The formation of radical (II) rather than (III) by attack of radical X· is additionally favoured, since the formation of (III) would require, in the transition state for its formation, the eclipsing of the C-2 hydrogen of norbornene (I) with the C-1 hydrogen, resulting in disadvantageous torsional strain.[4] However, recent work of Factor and Traylor [5] suggests that there is a rather low limit to the size of the much discussed steric and electronic effects in the norbornyl system, and we considered that a suitably small attacking radical might well give rise to at least some product derived from *endo* radical attack. The smallest alkanethiol, methanethiol



(I) (II) (III)



(IV) R = Bu^t
(V) R = Me
(VII) R = Ac
(VIII) R = Ph
(IX) R = *p*-C_6H_4

(VI)

was chosen, and 2-methylpropane-2-thiol was used for comparison, since it was assumed that the large t-butylthio-radical would invariably afford products derived entirely from *exo* radical attack. The n.m.r. spectra of both the 1 : 1 adducts (IV) and (V) were recorded, and

[1] J. A. Berson and R. Swidler, *J. Amer. Chem. Soc.*, 1953, **75**, 4366; 1954, **76**, 4060; N. S. Zefirov, A. F. Davydova, and Yu. K. Yur'ev, *J. Gen. Chem. U.S.S.R.*, 1965, **35**, 817; J. Mantecón, L. Cortés, E. Payo, and A. Salazar, *J. Org. Chem.*, 1967, **32**, 3796; S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, 1967, **32**, 3727; R. Caple, Fu Mei Hsu, and C. S. Ilenda, *J. Org. Chem.*, 1968, **33**, 4111.

[2] N. A. LeBel, *J. Amer. Chem. Soc.*, 1960, **82**, 623; H. Kwart and J. L. Nyce, *J. Amer. Chem. Soc.*, 1964, **86**, 2601; N. A. LeBel, P. D. Beirne, E. R. Karger, J. C. Powers, and P. M. Subramanian, *J. Amer. Chem. Soc.*, 1963, **85**, 3199.

[3] (*a*) D. I. Davies and S. J. Cristol, *Adv. Free Radical Chem.*, 1966, **1**, 155; (*b*) C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1968, **90**, 5806; (*c*) M. M. Martin and R. A. Koster, *J. Org. Chem.*, 1968, **33**, 3428, and references referred to in these papers.

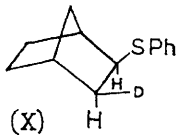
[4] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701.

[5] A. Factor and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2607.

in each case the H-2 signal was observed as an octet, at τ 7·45 (J 7·7, 4·5, and 1·5 c./sec.) for (V), and at 7·47 (J 8·0, 4·8, and 1·8 c./sec.) for (IV). The 2-protons must be assigned to the *endo*-position, since the couplings are consistent only with such a proton coupling with 3-*endo*-, 3-*exo*-, and 7-*anti*-protons.[6] The 2-*exo*-position is ruled out since increased multiplicity and line width would be expected in this case.[6] G.l.c. indicated that in both reactions only one compound was formed. To provide further confirmation of the *exo*-orientation of the methylthio-group in (V), the sulphide was oxidised to the sulphone (VI) with hydrogen peroxide in methanol or glacial acetic acid. The latter system promotes sulphone epimerisation in hexachloronorbornenes.[7] Both systems gave the same sulphone, but in the n.m.r. spectrum the $SO_2{\cdot}CH_3$ absorption overlaid that of $CH{\cdot}SO_2{\cdot}CH_3$ so that the multiplicity of the latter could not be determined. However treatment of the sulphone with potassium t-butoxide in t-butyl alcohol produced no change, and therefore the group $SO_2{\cdot}CH_3$ in the sulphone (VI) and hence SMe in the sulphide (V) may be concluded to have the more stable *exo*-configuration.

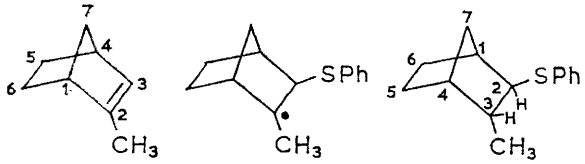
Recent work by van Auken[8] on the additions of thioacetic *S*-acid and benzenethiol to norbornadiene (at −8 to 25°) has shown that appreciable quantities of products derived from *endo* radical attack are formed. We find that the addition of these thiols to norbornene (I), under these conditions, gives a single product in each case. These products, (VII) and (VIII), both showed the H-2 signal as an octet, at τ 6·74 (J 7·4, 4·5, and 2·5 c./sec.) and 6·92 (J 7·5, 4·7, and 1·5 c./sec.), respectively, consistent[6] only with the *exo*-orientation of the S·COMe and SPh groups. The reaction is carried out in the cold presumably so that products which are not necessarily the most stable thermodynamically can be trapped. The reaction is highly exothermic, and the addition of thiols is known to be reversible.[9] Both these factors suggest that products which are more stable thermodynamically will generally be formed. Addition to norbornadiene from the *endo*-side will certainly be more ready than in the case of norbornene (I), since there is less steric interference from the olefinic hydrogens on C-5 and C-6 in norbornadiene compared with that from the 5-*endo*- and 6-*endo*-hydrogens in norbornene (I).

The addition of toluene-*p*-thiol to norbornene (I) was shown by Cristol and Brindell[10] to give exclusively the *exo*-sulphide (IX). This structure, as for the sulphides (IV), (V), (VII), and (VIII), gives no information regarding the direction of chain transfer in the intermediate radical (II; X = $S{\cdot}C_6H_4$-*p*). Related studies by Cristol and Arganbright[11] on the addition of toluene-*p*-thiol to 6-chloroaldrin, and on that of toluene-*p*-sulphenyl chloride to aldrin, indicate that chain transfer from the *exo*-direction is most likely in the addition of thiols to norbornene (I), but are not necessarily conclusive.[3a] This likelihood of *exo* chain transfer is supported by the torsional strain theory of Schleyer.[4] The addition of *S*-deuteriobenzenethiol to norbornene (I) gave a single product (X), the n.m.r. spectrum of which showed the



(X)

2-*endo*-proton signal as a quartet at τ 6·94 (J 7·5 and 1·5 c./sec.). The 2-*endo*–3-*exo* coupling found in the benzenethiol adduct (VIII) had disappeared, showing that in the addition of *S*-deuteriobenzenethiol the intermediate (II; X = SPh) had undergone chain transfer from the *exo*-direction. Thus in the addition of thiols to norbornene (I) both radical attack and chain transfer occur from the *exo*-direction. This observation was further supported by the addition of benzenethiol to 2-methylnorborn-2-ene (XI). The n.m.r. spectrum of the product showed a low-field quartet at τ 7·44 (1H, J



(XI) (XII) (XIII)

5·0 and 2·0 c./sec.) and a doublet at 8·95 (3H, J 6·8 c./sec.). This shows the presence of $CH{\cdot}CH_3$, which suggests that radical attack on 2-methylnorborn-2-ene (XI) occurs at the less hindered end of the double bond to give the more highly substituted, and therefore stabilised, free radical (XII). The stereochemistry of the methyl and phenylthio-groups in the product is determined by the coupling constants for $CH{\cdot}$SPh at τ 7·44, which can only[6] be J(2-*endo*,3-*exo*) and J(2-*endo*,-7-*anti*), so that the phenylthio- and methyl groups are in the 2-*exo*- and 3-*endo*-positions, and the product is therefore 3-*endo*-methylnorborn-2-*exo*-yl phenyl sulphide (XIII). Chain transfer of (XII) with benzenethiol has occurred from the *exo*-direction to obviate the eclipsing of methyl and bridgehead hydrogen in the transition state leading to chain transfer from the *endo*-direction.

The addition of benzenethiol to 2-methylenenorbornane (XIV) afforded a 1 : 1 adduct identical in physical

[6] (*a*) E. Tobler and D. J. Foster, *J. Org. Chem.*, 1964, **29**, 2839; (*b*) P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *ibid.*, 1965, **30**, 2624; R. R. Fraser, *Canad. J. Chem.*, 1962, **40**, 78; E. W. C. Wong and C. C. Lee, *ibid.*, 1964, **42**, 1245; K. C. Ramey, D. C. Lini, R. M. Moriarty, H. Gopal, and H. G. Welsh, *J. Amer. Chem. Soc.*, 1967, **89**, 2401; J. Meinwald and Y. C. Meinwald, *ibid.*, 1963, **85**, 2514; F. A. L. Anet, *Canad. J. Chem.*, 1961, **39**, 789.

[7] J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.* (*C*), 1966, 1498.

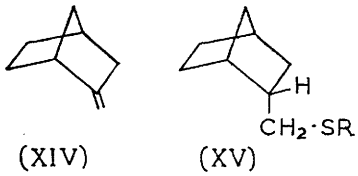
[8] T. V. Van Auken and E. A. Rick, *Tetrahedron Letters*, 1968, 2709.

[9] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, 1965, **30**, 3003.

[10] S. J. Cristol and G. D. Brindell, *J. Amer. Chem. Soc.*, 1954, **76**, 5699.

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

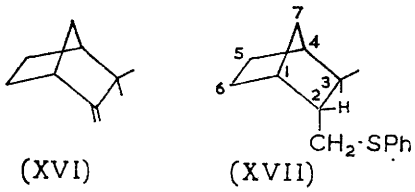
and spectral properties with norborn-2-*endo*-ylmethyl phenyl sulphide (XVa) obtained in two different ways; by the hydrogenation of the Diels–Alder adduct of phenyl allyl sulphide and cyclopentadiene, and from the reaction of 2-*endo*-bromomethylnorbornane with sodium



a; R = Ph
b; R = Et
c; R = MeO·CO·CH$_2$

(XIV) (XV)

benzenethiolate. This indicates that in the addition of benzenethiol to 2-methylenenorbornane (XIV) chain transfer from the *exo*-direction is again the rule. The additions of ethanethiol [9] and of methyl thioglycollate [12] to 2-methylenenorbornane (XIV) also probably afford products (XVb) and (XVc) derived from chain transfer of the intermediate radical from the *exo*-direction. The

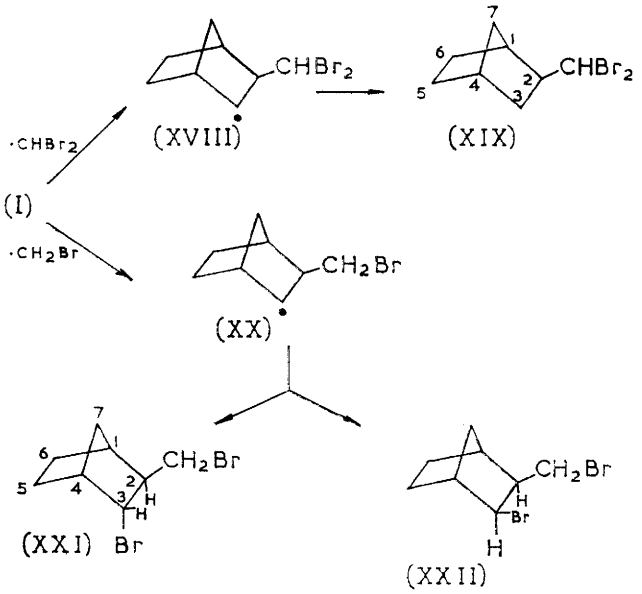


(XVI) (XVII)

addition of benzenethiol to camphene (XVI) also affords a 1 : 1 adduct to which we assign the structure (XVII) since the C*H*$_2$·SPh signal appears as a doublet at τ 7·20 (J 7·6 c./sec.), *cf.* the position for C*H*$_2$·SPh in (XV) [τ 7·15 (d, J 7·5 c./sec.)]. We may thus assume that in both compounds C*H*$_2$·SPh is *endo* and hence H-2 is *exo*. *endo* Chain transfer in the addition of benzenethiol to camphene (XVI) will not be favoured, since in the transition state for the formation of the epimer of (XVII), CH$_2$·SPh would eclipse the bridgehead hydrogen.

When hydrogen is not the atom abstracted by intermediate (II) in the chain-transfer step, the end of the molecule involved in this step is larger than hydrogen, and hence stereoelectronic interactions between incoming molecule and the group X already introduced may make chain transfer from the *endo*-direction occur in spite of the unfavourable effect of torsional strain. Thus in the additions of bromotrichloromethane and carbon tetrachloride to norbornene (I) [3b,6a] and aldrin [13] the intermediate radical of type (II; X = CCl_3) undergoes chain transfer from the *endo*-direction by halogen abstraction from the attacking molecule, thus affording the products of *trans*-addition of bromotrichloromethane and carbon tetrachloride. It seemed to us likely that if a reagent could be chosen in which the stereoelectronic interaction between its derived substituent X in intermediate (II) and itself was intermediate between that of CCl_3 and bromotrichloromethane and that of SR and thiols, it might be possible to observe chain transfer of the intermediate (II) from both *exo*- and *endo*-directions leading to products of both *exo*–*cis*- and *trans*-addition. Methylene bromide is known to add in a free-radical manner to olefins,[14] and seemed suitable.

G.l.c. analysis of the product of addition of methylene bromide to norbornene (I) indicated the formation of a 1 : 1 adduct and showed the presence of three products of addition in the ratio 1 : 4 : 5. The n.m.r. spectrum exhibited a very low-field doublet at τ 4·4 (J 9 c./sec.), consistent with C*H*Br$_2$; integration indicated that this peak corresponds to the least abundant isomer, which results from the addition of the dibromomethyl radical to norbornene (I) followed by chain transfer of hydrogen



from another molecule of methylene bromide leading to 2-*exo*-dibromomethylnorbornane (XIX). A poorly resolved triplet at τ 6·28 (J *ca.* 4·5 c./sec.) and a well resolved quartet at 5·77 (J 7·5 and 2·5 c./sec.) in integral ratio 4 : 5 are consistent [6] with the expected patterns for *H*-3-*exo* and H-3-*endo* respectively in the *trans*- and *cis*-adducts (XXI) and (XXII) formed by attack of bromomethyl radicals on norbornene (I) followed by chain transfer of the intermediate radical (XX) with bromine from methylene bromide. In the case of the *trans*-adduct (XXI) the 3-*exo*-proton couples with H-2-*endo* and H-4 (J *ca.* 4·5 c./sec.); expansion of the triplet reveals a small coupling of 1·5 c./sec. superimposed, which is consistent with correlated values [6] for J(3-*exo*,5-*exo*). In the *cis*-adduct (XXII) the couplings correlate [6] with J(3-*endo*,2-*endo*) and J(3-*endo*,7-*anti*) respectively. It thus appears that it is necessary to postulate chain transfer of hydrogen after initial attack by the dibromomethyl radical, in contrast to chain transfer of bromine after attack by a bromomethyl radical. This is reasonable since in the intermediate (XVIII) there is a greater amount of stereoelectronic

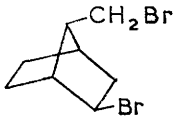
[12] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc.* (*B*), 1966, 1191.

[13] D. I. Davies, *J. Chem. Soc.*, 1960, 3669.

[14] J. I. G. Cadogan, D. H. Hey, and P. G. Hibbert, *J. Chem. Soc.*, 1965, 3950.

interaction between $CHBr_2$ and incoming methylene bromide than in (XX) between CH_2Br and incoming methylene bromide. This results in abstraction of hydrogen by (XVIII) being favoured, since reduction of stereoelectronic interactions in the abstraction stage mitigates the increased energy required to break the stronger C–H rather than the weaker C–Br bond. When the $\cdot CH_2Br$ radical adds, stereoelectronic interactions between (XX) and methylene bromide are less and abstraction of bromine becomes favoured. Thus in the addition of methylene bromide to norbornene (I) addition of the elements of methylene bromide occurs in preference to exclusive chain transfer with bromine as in the addition of methylene bromide to open-chain olefins,[14] in which stereoelectronic factors are much reduced in the chain-transfer step so that the weaker C–Br bond is invariably broken.

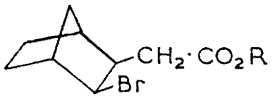
One of the two major products, the *trans*-isomer (XXI), was isolated by preparative g.l.c. Another product was also isolated, but this was not (XXII), the product of *exo–cis*-addition, but probably 2-*exo*-bromo-7-*syn*-bromomethylnorbornane (XXIII), derived from isomerisation of (XXII) on the g.l.c. column. The



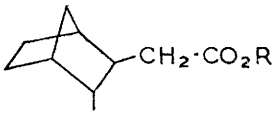
(XXIII)

n.m.r. spectrum of this rearrangement product shows the CH_2Br signal as a doublet at τ 6·74 (J 10 c./sec.). The signal of the 2-proton, which also has a vicinal bromine atom, which appears at τ 6·16 as a poorly resolved multiplet, $W_{\frac{1}{2}}$ *ca.* 15 c./sec., consistent [6] with H-2-*endo* in (XXIII). The stereochemistry of the adducts (XXI) and (XXII) was further confirmed by spin decoupling techniques. The n.m.r. patterns of the 3-protons of the *trans*-adduct (XXI), and of the *exo–cis*-adduct (XXII) in a mixture of (XXI) and (XXII) were examined in this way. For the *trans*-adduct (XXI) irradiation of the frequency of the bridgehead 4-proton at τ 7·56 reduced the H-3 signal to a doublet; coupling between H-4 and H-3 occurs only [6] when H-3 is *exo* and bromine *endo*, as in (XXI), which is thus the favoured structure. For the mixture of *trans*-(XXI) and *exo–cis*-(XXII) H-3 of (XXII) [τ 5·77 (q)] was unaffected when the region τ 7·3—7·5, in which H-4 of (XXII) should absorb, was irradiated. This confirms that H-3 in (XXII) is *endo* and therefore bromine is *exo*.

A brief report of the free-radical addition of ethyl bromoacetate to norbornene (I) was given by Weinstock at a conference.[15] He reported that a single product (XXIVa) of *exo–cis*-addition was formed. Although no details or experimental confirmation were subsequently published, this work has been cited in major texts [16] on



(XXIV)



(XXV)

a; R = Et
b; R = Me

free-radical chemistry as an example of *exo–cis* free-radical addition to norbornene (I). In view of our results with methylene bromide, it seemed desirable to reinvestigate this reaction. G.l.c. of the product showed the presence of two adducts in the ratio of *ca.* 2 : 1. Unfortunately the products could not be identified from the n.m.r. spectrum, since the H-3 signal was overlaid by the quartet due to $CO_2{\cdot}CH_2{\cdot}CH_3$. The addition of methyl bromoacetate gave two adducts in the ratio 4 : 3. The n.m.r. spectrum of the mixture showed the C*H*Br signals of the two adducts as a quartet at τ 5·74 (J 6·2 and 2·0 c./sec.) and a broadened triplet at 6·20 (J *ca.* 4·3 c./sec.). These patterns are consistent [6] with H-3-*endo* and H-3-*exo* in the *exo–cis*- (XXIVb) and *trans*- (XXVb) adducts. The couplings for H-3-*endo* in (XXIVb) correspond [6] to J(3-*endo*,2-*endo*) and J(3-*endo*,7-*anti*), whereas for H-3-*exo* in (XXVb) they correspond to J(3-*exo*,2-*endo*) $\simeq$ J(3-*exo*,4) with the broadening of the pattern due to additional long-range coupling [J(3-*exo*,5-*exo*)]. Integral ratios for H-3 in (XXIVb) and (XXVb) suggest that these products are formed in the ratio 4 : 3. A pure specimen of the *trans*-adduct (XXVb) was isolated by preparative g.l.c. Further evidence of its structure was provided by spin decoupling; the triplet at τ 6·20 corresponding to H-3 coalesced to a poorly resolved doublet when the frequency of H-4 at τ 7·60 was irradiated, thus confirming the *exo*-orientation of H-3; an H-3-*endo*-proton would not be expected to couple with H-4. It is thus a reasonable assumption that in the ethyl bromoacetate addition the *exo–cis*- (XXIVa) and *trans*- (XXVa) adducts are both formed. Mixtures of *exo–cis*- and *trans*-adducts have also been recently reported in the free radical additions of *N*-chlorourethane [17] and dinitrogen tetroxide [18] to norbornene (I).

Thus in the case of additions of methylene bromide, ethyl bromoacetate, methyl bromoacetate, *N*-chlorourethane, and dinitrogen tetroxide to norbornene (I) the situation is intermediate between total *trans* (*e.g.* bromotrichloromethane) and total *cis* (*e.g.* thiols). In the absence of steric factors, the intermediate (II) formed on free-radical attack will favour *exo*-chain transfer to give the product of *exo–cis*-addition, since this will minimise torsional strain factors [4] in the chain-transfer step. When X in (II) is not too large, *e.g.* SR, and the end of the molecule involved in chain trans-

[15] J. Weinstock, American Chemical Society Meeting Abstracts, 1955, **128**, p. 19.
[16] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 267; C. J. M. Stirling, 'Radicals in Organic Chemistry,' Oldbourne, London, 1965, p. 89; C. Walling and E. S. Huyser, *Org. Reactions*, 1963, **13**, 106.
[17] K. Schrage, *Tetrahedron*, 1967, **23**, 3033.
[18] H. Shechter, J. J. Gardikes, T. S. Cantrell, and G. V. D. Tiers, *J. Amer. Chem. Soc.*, 1967, **89**, 3005.

fer is small, then *exo–cis*-addition occurs. However when they are both large (*e.g.* in bromotrichloromethane addition), in the intermediate radical (II; X = CCl_3) the *exo*-CCl_3 group will effectively shield the radical centre sterically from chain transfer with the bromotrichloromethane molecule from the *exo*-direction, and chain transfer will take place from the now more sterically accessible *endo*-side, in spite of the disadvantageous torsional strain. Methylene bromide, methyl bromoacetate, and ethyl bromoacetate seem to be intermediate between these two extremes; chain transfer of the intermediate radical occurs from both directions. In these examples the reason for observation of some chain transfer from the *endo*-direction is likely to be partially steric, owing to interaction between X in (II) and incoming molecule, and partially electronic, since both the group X (original attacking radical) and the end of the molecule required for chain transfer are electron-attracting, and therefore likely to repel each other. It is also possible that a similar electronic effect assists the steric factors in affording virtually exclusive *trans*-addition of bromotrichloromethane and carbon tetrachloride.

EXPERIMENTAL

The n.m.r. spectra (60 Mc./sec.) were recorded with a Perkin-Elmer R10 instrument fitted with the standard accessory for spin-decoupling. Analytical g.l.c. was carried out with a Pye Argon chromatograph fitted with columns (4 ft. × ¼ in.) of 10% Apiezon L on Celite (40—60 mesh). Preparative g.l.c. was carried out with a Varian A-705 instrument, with nitrogen as carrier gas, a flame ionisation detector, and a column (20 ft. × ⅜ in.) of 20% Apiezon L on Chromosorb W (60—80 mesh).

S-*Deuteriobenzenethiol*.—Ethanol (dried over sodium) was distilled from sodium. Sodium (5·85 g.) was then dissolved in this dry ethanol (70 ml.), benzenethiol (27·5 g.) was added, and the mixture was stirred and then evaporated to dryness *in vacuo* to give a colourless solid. This was washed with sodium-dried ether (3 × 200 ml.) and dried in a vacuum oven at 90°. To a suspension of this sodium benzenethiolate in a solution of deuterium oxide (5 g.) in sodium-dried ether (50 ml.) was added freshly distilled acetyl chloride (20 g.), dropwise, under anhydrous conditions. The ether solution was then filtered, the solid was washed with sodium-dried ether (50 ml.), and the filtrate was distilled under reduced pressure, with exclusion of moisture, to yield *S*-deuteriobenzenethiol (12 g.), b.p. 68—72°/19 mm. The n.m.r. spectrum showed no SH peak at τ 6·75 and the compound was therefore assumed to be fully deuteriated.

Free-radical Addition of Thiols to Norbornene (I).—In general approximately equimolar amounts of thiol and norbornene (I) were mixed and kept at room temperature until reaction was complete. The product was then dissolved in ether (20 ml.) and the solution was washed with saturated sodium hydrogen carbonate (2 × 10 ml.) and water (2 × 10 ml.) and dried ($MgSO_4$). After distillation of the solvent the crude product was purified by distillation. In each case g.l.c. analysis at 180—200° indicated that only one compound was formed.

Methanethiol. Norbornene (I) (3·65 g.) was cooled to −70° and methanethiol (5 ml.), similarly cooled, was added dropwise, with shaking. The flask was sealed and allowed to attain room temperature during 4 hr. Excess of methanethiol was then removed by warming to 50°. Distillation of the crude product afforded *methyl norborn*-2-exo-*yl sulphide* (V) (3·2 g.), b.p. 82°/18—20 mm., n_D^{25} 1·5118 (Found: C, 68·05; H, 9·75. $C_8H_{14}S$ requires C, 67·55; H, 9·95%). Oxidation with hydrogen peroxide in either glacial acetic acid or methanol gave *methyl norborn*-2-exo-*yl sulphone* (VI) as white crystals, m.p. 75° (from ethanol) (Found: C, 54·25; H, 8·05. $C_8H_{14}O_2S$ requires C, 55·15; H, 8·1%). The sulphone (VI) (0·2 g.) was recovered unchanged after being heated at 100° for 1 hr. with potassium t-butoxide (0·05 g.) in t-butyl alcohol (5 ml.).

2-*Methylpropane*-2-*thiol*.—A mixture of norbornene (I) (4·7 g.) and the thiol (4·6 g.) was kept at room temperature for 48 hr. Work-up afforded *norborn*-2-exo-*yl t-butyl sulphide* (IV) (8·1 g.), b.p. 99—101°/18—20 mm., n_D^{25} 1·4952 (Found: C, 72·2; H, 11·1. $C_{11}H_{20}S$ requires C, 71·7; H, 10·95%). Oxidation with hydrogen peroxide in methanol gave *norborn*-2-exo-*yl t-butyl sulphone* as white crystals, m.p. 93—95° (from ethanol) (Found: C, 61·2; H, 9·6. $C_{11}H_{20}O_2S$ requires C, 61·1; H, 9·3%).

Benzenethiol. A vigorous exothermic reaction ensued, after a short induction period, when norbornene (I) (4·6 g.) and benzenethiol (5·5 g.) were mixed. Work-up after 1 hr. afforded *norborn*-2-exo-*yl phenyl sulphide* (VIII) (8·2 g.) n_D^{25} 1·5826 (Found: C, 76·5; H, 7·7. $C_{13}H_{16}S$ requires C, 76·4; H, 7·9%). In a subsequent reaction a solution of norbornene (I) in benzene (5 ml.) was cooled to 8° and vigorously stirred. Benzenethiol (1·1 g.) was then added dropwise at such a rate that the internal temperature did not exceed 25°. Work-up after 1 hr. gave unchanged norbornene (I) (*ca.* 0·1 g.) and norborn-2-*exo*-yl phenyl sulphide (VIII), identical with the product obtained before.

Thioacetic S-Acid. The addition of thioacetic *S*-acid (0·8 g.) to norbornene (I) (1·0 g.) was carried out as for the second benzenethiol–norbornene (I) reaction. Work-up afforded S-*norborn*-2-exo-*yl thioacetate* (VII) (0·78 g.), b.p. 55—57°/0·1 mm., $n_D^{23·5}$ 1·5121 (Found: C, 63·3; H, 8·2. $C_9H_{14}OS$ requires C, 63·5; H, 8·3%).

S-*Deuteriobenzenethiol*. The reaction between *S*-deuteriobenzenethiol (2·8 g.) and norbornene (I) (2·3 g.) was not obviously exothermic, and a few drops of a 10% solution of diethyl peroxydicarbonate in dry cyclohexane were used as initiator. After 24 hr. work-up afforded 3-exo-*deuterio-norborn*-2-exo-*yl phenyl sulphide* (X) (3·8 g.), n_D^{23} 1·5824 (Found: C, 75·9; H + D, 8·05; S, 16·0. $C_{13}H_{15}DS$ requires C, 76·0; H, 7·4; D, 1·0; S, 15·6%).

Addition of Benzenethiol to 2-Methylenenorbornane (XIV).—The reaction between benzenethiol (0·67 g.) and 2-methylenenorbornane (XIV) [19] (0·62 g.) was carried out like the addition to norbornene (I), and afforded *norborn*-2-endo-*ylmethyl phenyl sulphide* (XVa) (0·8 g.), n_D^{25} 1·5818 (Found: C, 77·1; H, 8·15. $C_{14}H_{18}S$ requires C, 77·1; H, 8·25%). Specimens for comparison with identical properties were prepared (*a*) by adding 2-*endo*-bromomethylnorbornane [20] to a solution of benzenethiol in ethanolic sodium ethoxide and boiling under reflux for 16 hr.; and (*b*) by catalytic hydrogenation at 1 atmos. (10% palladium–charcoal) of norborn-5-en-2-*endo*-ylmethyl phenyl sulphide prepared [19] by the method of Cristol, Russell, and Davies.

Addition of Benzenethiol to 2-Methylnorborn-2-ene (XI).—

[19] S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, 1965, **30**, 207.
[20] K. Alder and E. Windemuth, *Ber.*, 1938, **71**, 1939.

The addition of benzenethiol (1·6 g.) to 2-methylnorborn-2-ene (XI) [21] (1·6 g.) was exothermic and the product was worked up as in the addition to norbornene (I) to give 3-endo-*methylnorborn*-2-exo-*yl phenyl sulphide* (XIII) (2·3 g.), b.p. 109°/0·3 mm. (Found: C, 77·3; H, 8·45. $C_{14}H_{18}S$ requires C, 77·1; H, 8·25%).

Addition of Benzenethiol to Camphene (XVI).—Reaction between benzenethiol (3·3 g.) and camphene (XVI) (4 g.) was not exothermic, and was aided by initiation with a few drops of a 10% solution of diethyl peroxydicarbonate in cyclohexane. Work-up after 48 hr. afforded 3,3-*dimethylnorborn*-2-endo-*ylmethyl phenyl sulphide* (XVII) (2·1 g.), n_D^{23} 1·5721, b.p. 130°/0·5 mm. (Found: C, 77·7; H, 9·0. $C_{16}H_{22}S$ requires C, 78·0; H, 9·0%). Oxidation with hydrogen peroxide in methanol afforded 3,3-dimethylnorborn-2-*endo*-ylmethyl phenyl sulphone (0·98 g.), m.p. 73—74° (lit.,[22] 75°).

Addition of Methylene Bromide to Norbornene (I).—A solution of norbornene (I) (9·4 g.), methylene bromide (70 g.), and benzoyl peroxide (0·2 g.) was boiled under reflux under nitrogen for 24 hr. It was then cooled, washed with saturated sodium hydrogen carbonate solution (2 × 100 ml.) and water (3 × 100 ml.), and dried ($MgSO_4$). The excess of reagents was removed by evaporation and the products were distilled to afford a mixture (12·2 g.) of 3-endo-*bromo*-2-exo-*bromomethylnorbornane* (XXI), 3-exo-*bromo*-2-exo-*bromomethylnorbornane* (XXII), and 2-exo-*dibromomethylnorbornane* (XIX), b.p. 104°/0·5 mm., n_D^{25} 1·5574 (Found: C, 36·05; H, 4·7. $C_8H_{12}Br_2$ requires C, 35·85; H, 4·5%). G.l.c. analysis at 150° and n.m.r. integral ratios suggest the formation of (XIX), (XXII), and (XXI) in the ratio 1 : 5 : 4. Preparative g.l.c. at 180° gave 2-*endo*-bromo-3-*exo*-bromomethylnorbornane (XXI), n_D^{21} 1·5598 (Found: C, 35·5; H, 4·8%), and a mixture of 2-*exo*-bromo-3-*exo*-bromomethylnorbornane (XXII) and a product derived from its rearrangement on the gas chromatography column, which is probably 2-exo-*bromo*-7-syn-*bromomethylnorbornane* (XXIII) (Found: C, 35·4; H, 4·2%).

Addition of Methyl Bromoacetate to Norbornene (I).—A solution of norbornene (I) (4·7 g.), methyl bromoacetate (15·3 g.), and benzoyl peroxide (0·1 g.) was heated, under nitrogen, at 80° for 72 hr. The cooled mixture was diluted with ether (50 ml.) and worked up as for the methylene bromide addition to afford a mixture (6·7 g.) of *methyl* 3-exo-*bromonorborn*-2-exo-*ylacetate* (XXIVb) and *methyl* 3-endo-*bromonorborn*-2-exo-*ylacetate* (XXVb), b.p. 92°/0·12 mm., n_D^{25} 1·5138 (Found: C, 48·35; H, 6·1. $C_{10}H_{15}BrO_2$ requires C, 48·6; H, 6·0%). Analytical g.l.c. analysis at 160° and n.m.r. integral ratios suggest that (XXIVb) and (XXVb) are present in the ratio 4 : 3. Preparative g.l.c. at 180° gave methyl 3-*endo*-bromonorborn-2-*exo*-ylacetate (XXVb), b.p. *ca.* 95°/0·15 mm., n_D^{25} 1·5080 (Found: C, 48·85; H, 6·1%). A pure specimen of the *exo–cis* adduct (XXIVb) was not obtained since some isomerization of (XXIVb), possibly to afford a product similar to (XXIII), occurred on preparative g.l.c.

Addition of Ethyl Bromoacetate to Norbornene (I).—A solution of norbornene (I) (4·7 g.), ethyl bromoacetate (20 g.), and benzoyl peroxide (0·1 g.) was heated under nitrogen at 90° for 10 hr. The cooled mixture was diluted with ether (50 ml.) and worked up as in the methylene bromide additions to afford ethyl 3-bromonorborn-2-*exo*-ylacetate (7·1 g.), b.p. 72—80°/0·1 mm., $n_D^{23\cdot5}$ 1·5035 (Found: C, 50·35; H, 6·5. $C_{11}H_{17}BrO_2$ requires C, 50·55; H, 6·55%). G.l.c. analysis at 160° indicated the presence of two compounds, probably the *exo–cis*- (XXIVa) and *trans*- (XXVa) adducts, in the ratio 2 : 1.

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