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Stereochemistry of Free-radical Additions in the Bicyclo[2.2.1] heptene and Bicyclo[2.2.1]heptadiene Series

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The stereochemistry of free-radical additions to norbornene and norbornadiene systems is examined. The dependence of the direction of radical attack on the degree of substitution of the bicyclene, and on the position and steric and electronic effects of the substituents is discussed. A mechanism of radical rearrangement of the corresponding norbornene radicals is considered. 109 references.

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1. INTRODUCTION

Among the various bridged cyclic hydrocarbons the system containing a norbornene skeleton is one of the most interesting and also closest to important natural compounds of the terpene type. The rigid fixed geometry of bicyclo[2.2.1]heptane and its derivatives leads to distortion of the valence angles and hence to the establishment of a different type of strain. This in turn brings about an unusual interaction of the electronic and steric effects of the substituents and the reactivity of the latter is closely connected with their position in the molecule.

Owing to the extensive development and use of modern methods of separation and identification of compounds it has recently become possible to find more precisely the structure of intermediate products and also the stereochemical results of the behaviour of these systems under various conditions. Exceptions to the stereochemical rules previously thought to be firmly established are now being found. For example, there is now very extensive discussion of the nature of norbornyl cations, instances of non-stereospecific addition of polar reagents are being reported, and the question of the possible existence of non-classical 7-norbornyl radicals is being discussed.

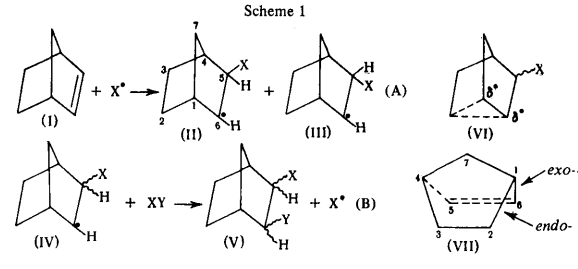
Davies and Cristol [1] have already reviewed the addition of free radicals to norbornene and norbornadiene systems but only dealt with the literature up to 1963. The relatively extensive investigation of such reactions and especially of their stereochemical aspect began again after 1963 and a critical appraisal of the new results is very desirable†. This is all the more important in that in this field new methods of investigation (especially NMR spectroscopy and gas–liquid chromatography, or GLC) have disclosed significant departures from the known stereochemical rules, and also to the observation of interesting free-radical rearrangements. In the present review we used the results of investigations in which the radical nature of the process has been rigorously proved and the stereochemistry of the products reliably established.

† When the present review had almost been completed, we learnt that a review by Davies [2] dealing with free-radical reactions in the bicycloheptane series had appeared in 1970 in a Chemical Society Special Publication. However, it examines the published information from a somewhat different aspect.

2. FREE RADICAL ADDITION TO NORBORNENES

Since it is known that most of the reagents concerned react with alkenes by a free-radical chain mechanism [3,4], the stereochemistry of the products of addition to norbornene (NB) (I) will be determined mainly by the stereochemistry of two stages: (A) the addition of the free radical X$^{\cdot}$, and (B) chain transfer (scheme 1).

Scheme 1



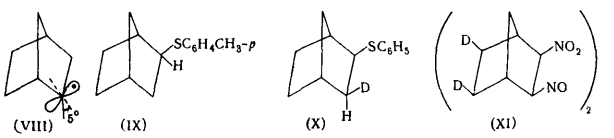
Even the first investigations in this field led to the conclusion of the participation in the reaction of classical free radicals of type (II) as opposed to a non-classical radical of type (VI), analogous to a non-classical carbocation [5]. The absence of addition products of the Wagner–Meerwein rearrangement type during the course of the free radical reactions also evidently agreed with this conclusion.

The *exo*-direction is evidently the most accessible for attack by a free radical in the NB molecule and therefore *exo*-radical attack was considered the rule until recently [6]. The greater accessibility of the *exo*-side of molecule (VII) is evidently due to its lesser steric blocking by the methylene bridge in comparison with the obstacles at the side of the dimethylene bridge in the *endo*-approach of the radical. A second factor favouring the formation of radical (II), and not (III), is the absence in transition state (II) of shielding of the $C_{(5)}$ and $C_{(4)}$ hydrogens, shown in an increase in the torsional strain effect [7].

A theoretical calculation of the structure of the 6-norbornyl radical appeared recently [8]. It was shown

that its most stable configuration has the deformed sp^2 planar structure (VIII) ($H_{(6)}$ emerges from the $C_{(1)}-C_{(6)}-C_{(5)}$ plane at an angle of ~5°), and the orbital with an unpaired electron has maximum extension in the *exo*-direction from $C_{(6)}$. This should also be apparent on assuming the *exo*-approach of the reagent to the norbornyl radical.

Hence both at the stage of initial attack and also at the stage of chain transfer with participation of the norbornyl radical *exo*-approach of the reagents, leading to *cis*-*exo*-addition, is postulated.

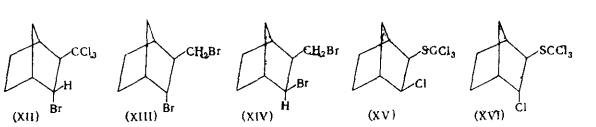


Actually, stereospecific *exo*-addition was observed in the reaction of NB with thiols [*p*-thiocresol[5], methanethiol, 2-methylpropane-2-thiol, thioacetic acid (TAA), and thiophenol[9]], acetone and acetaldehyde[10,11], formamide[12,13], in the free-radical chloroalkylation by chloroalkanes of the RCH_2Cl type[14]. In every instance exclusively *exo*-products of type (IX) were formed. The nature of the addition products did not allow any differences between the *cis*- and *trans*-addition to be distinguished. However, in an investigation specially made for this purpose, Davies and coworkers showed[9] that *S*-deuteriothiophenol adds to NB with the formation exclusively of the *cis*-*exo*-addition product (X). The reaction of N_2O_3 with *exo*-*exo*-2,3-dideuterionorbornene (XI) proceeds in an analogous manner[15].

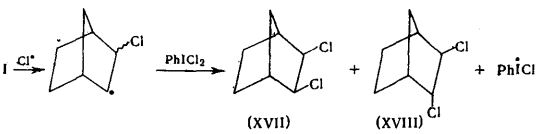
When an attacking radical has a sufficiently large steric volume, the initial addition from the less inconvenient *exo*-side in every instance (with participation of NB) without exception. However, chain transfer can be effected from various sides of the intermediate radical (II), depending on the nature of the reagent and substituent already present in the NB molecule. In this instance the stereoelectronic interaction between group X of Scheme 1, p. 516, and the molecule of the carrier can bring about *trans*-addition, despite the unfavourable effect of the torsion strain. Thus bromotrichloromethane[16-19], *p*-toluenesulphonyl chloride[20], and perfluoroiodopropane[21] give products of the *trans*-addition type (XII) with NB. CCl_4 adds similarly[16]. True, a recent repeat investigation[22] showed that for CCl_4 the ratio of *cis*-*exo*- and *trans*-addition products is 1 : 18.2.

In addition to the above reagents, which give predominantly *cis*-*exo*- or *trans*-products, there are also others for which the stereoelectronic interaction is intermediate. Then a mixture of *cis*-*exo*- and *trans*-addition products is obtained.

Thus a mixture of products of type (XIII) and (XIV) was obtained on the addition to NB of methylene dibromide, methyl bromoacetate[9], t-butyl hypochlorite[23], *N*-chlorourethane[24], N_2O_4,[25] ethyl chloroglyoxalate[26], and bromodicyanomethane[27].



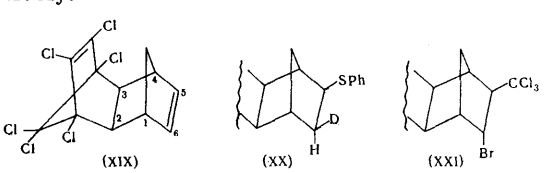
A similar intermediate example is evidently the addition to NB of trichloromethanesulphenyl chloride with the formation of a mixture of the products (XV) and (XVI) in 40 : 60 ratio[28].



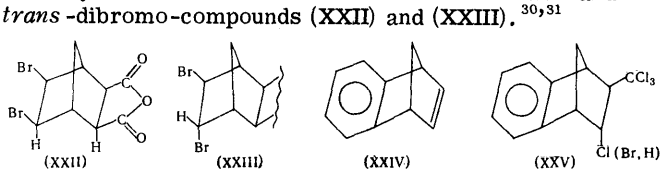
The radical chlorination of NB is yet another example. In the thermal or photochemical generation of chlorine radicals from phenyl iododichloride at 0–80°C, a mixture of the *cis*-*exo*- and *trans*-dichloro-compounds is formed; (XVIII) : (XVII) = 2.4.[29]

During photoinitiated halogenation‡ with chlorine[29], when a less bulky reagent participates in chain transfer, approximately equal amounts of the *cis*-*exo*- and *trans*-dichloro-compounds are formed.

Chain transfer from the endo-side of the intermediately formed radical can probably favour the electronic interactions of group X with the end of the carrier molecule. For example, with CCl_3Br and CCl_4 the repulsive forces that arise act together with the steric factors, leading exceptionally to *trans*-addition. How does the presence of substituents in the norbornene ring affect the stereochemistry of the addition? Evidently, 2,3-*exo*-substituents do not affect the direction of either the initial attack by the radical, or the chain transfer stage. Actually, the reactions of aldrin (XIX) and NB take place analogously: *S*-deuteriothiophenol[1] adds in the *cis*-*exo*-position but bromotrichloromethane, CCl_4,[17] *p*-toluenesulphonyl chloride[20], and perfluoroiodopropane[21] in the *trans*-position with the formation of products of type (XX) or (XXI) respectively:

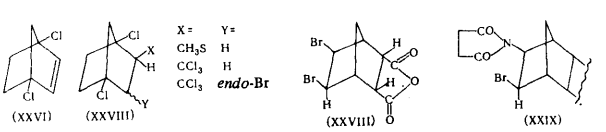


Bromination of the *exo*-anhydride of norbornenedicarboxylic acid leads to a mixture of the *cis*-*exo*- and *trans*-dibromo-compounds (XXII) and (XXIII).[30,31]



The addition of chloroform, CCl_4, or CCl_3Br, to benzonorbornadiene (XXIV),[32] just as for NB itself, leads to *trans*-products of the (XXV) type.

Evidently, 1,4-substituents also do not affect the stereochemistry of the process. The addition of methanethiol, bromotrichloromethane, and chloroform to 1,4-dichloronorborn-5-ene (XXVI) leads to products (XXVII) analogous to those obtained from NB itself[33]:

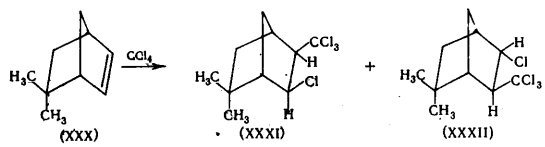


‡ In parallel with the homolytic processes in the above reaction ionic addition also occurs, but the investigators were able to extrapolate the "pure" radical halogenation from the experimental results for the products.

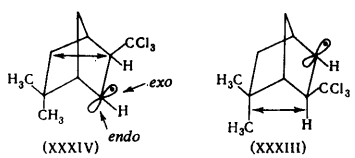
When the substituent occupies the 2- and/or 3-*endo*-positions or is at the double bond of the norbornenyl ring then when *exo*-selectivity is retained in the first stage this can significantly affect the stereochemical results of the reaction.

The exclusive formation of *cis*-*exo*-products occurs in the bromination [30,31] and reaction with *N*-bromosuccinimide [34] of the *endo*-anhydride of norbornenedicarboxylic acid, compounds (XXVIII) and (XXIX). Screening of the *endo*-side of the norbornene ring by the anhydride ring makes *cis*-*exo*-addition the only possibility.

In the reaction of CCl_4 with 2,2-dimethylnorborn-5-ene (XXX) a mixture of the *cis*- and *trans*-products (XXXI) and (XXXII) in the ratio 1.2 : 1 is formed [22]:



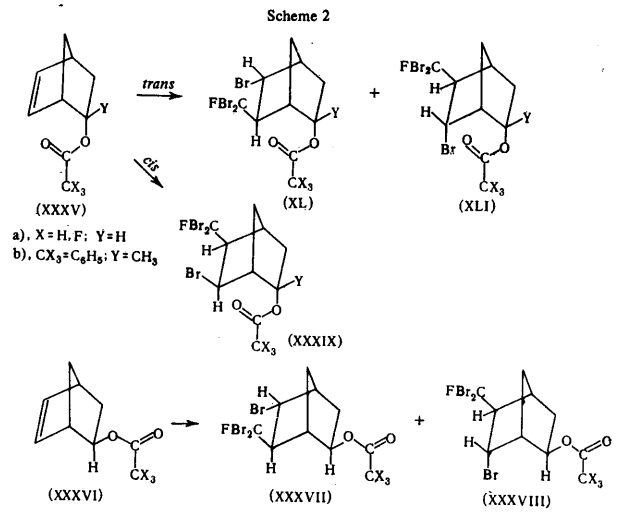
Since the quantities of *cis*- and *trans*-products are approximately equal, clearly the 2-methyl groups have an insignificant effect on the entering CCl_3 radical. As follows from the structure of the products obtained, the influence of the 2-*endo*-methyl group is especially pronounced at the chain transfer stage. Whereas for the radical (XXXIII) *trans*-addition takes place (as for unsubstituted NB), in the radical (XXXIV) the *endo*-methyl group exerts a greater steric barrier than the *exo*-CCl_3 group, which leads to the *cis*-product (XXXI):



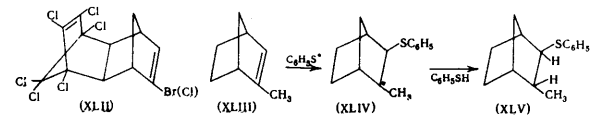
Osborn and coworkers assume [22] that the 2-*endo*-methyl group is situated closer to the line of formation of the new bond than the CCl_3 group and this is evidently also connected with the more rigid steric control of the 2-*endo*-substituent. It is noteworthy that the decrease in steric strain in *exo*-attack at the radical (XXXIV) evidently here plays a more important part than electronic interactions (the forces of repulsion of the two electron-withdrawing substituents in *exo*-attack, and conversely, the attraction of two different substituents in *endo*-attack at the chain transfer stage).

An analogous conclusion about the influence of 2,3-*endo*-substituents was drawn by Ludwick and Martin [35]. In studying the addition of tribromofluoromethane to norborn-5-ene-*endo*-2,3-dicarboxylic anhydride and to norborn-5-ene-2-*endo*- and 2-*exo*-acetate (or -benzoate) (XXXV) or (XXXVI), they found that the ratio of *exo*-*cis*- and -*trans*-addition products is determined by steric requirements produced by the 2-*endo*-substituent. Thus whereas the reaction with NB itself or with the 2-*exo*-acetate (XXXVI) leads to the formation of only the *trans*-products (XXXVII) and (XXXVIII), the 2-*endo*-substituted compounds (XXXV) always form a mixture of the *cis*-*exo*- and *trans*-addition products (XXXIX)–(XLV), and on going from the acetate (XXXVa) to the benzoate (XXXVb) the *trans*-product of type (XLI) almost disappears from the reaction mixture (see Scheme 2):

Scheme 2

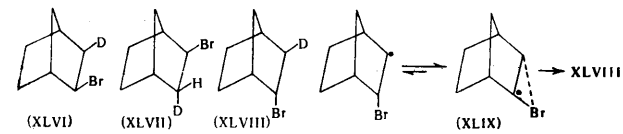


The addition of chloroform to 6-bromoaldrin (XLII) [17] or of *p*-thiocresol to 6-chloroaldrin [36], and also of thiophenol to 6-methylnorbornene (XLIII) [9] proceeds by a *cis*-*exo*-process with the formation of products of the type (XLV):



This is evidently connected with the decrease in the torsion strain in the transition state during chain transfer from the *exo*-direction, and also the existence of a steric barrier for *cis*-distribution of two bulky substituents.

Hence in the norbornene series the rule of initial *exo*-radical attack would seem to be strictly obeyed. However, in 1964, in studying the deuteriobromination of NB, Kwart and Nyce [37] obtained a mixture of three bromo-compounds containing 60% of the product of *exo*-*cis*-addition (XLVI) together with 40% of a mixture of approximately equal amounts of the *trans*-bromo-compounds (XLVII) and (XLVIII)§:



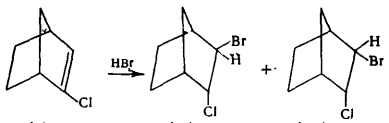
Here *exo*-attack is no longer exceptional, although it remains preferential (4 : 1). Kwart and Nyce assume the possibility of the formation of *trans*-bromo-compounds

§ Kwart and Nyce did not isolate the bromo-compounds (XLVII) and (XLVIII) and the assignment of the corresponding structures was made on the basis of a degradation analysis of the dehydrobromination products. In this it was assumed that in every instance *cis*-elimination takes place preferentially. Later investigations showed that in a series of norbornene halogeno-derivatives *trans*-elimination is six times more preferable than *endo*-*cis*-elimination [30]. Hence the true ratio of the bromides in the complementary investigation may be different.

through a bridged radical of type (XLIX). The greater stability of the latter also evidently brings about a decrease in the steric barrier for *endo*-attack.

The intermediate formation of bridged radicals owing to the possible extension of the valence cloud of the sulphur and halogen atoms was demonstrated earlier in additions to alkenes [39,40] and suggested to explain the comparatively ready 1,2-radical migration of halogen and alkanethio- or arylthio-groups [41]. The existence of such radicals was also confirmed by the EPR method [42].

The hydrobromination of 6-bromo- or 6-chloro-norbornene (L) also leads to a mixture of dihalogeno-compounds owing to both *exo*-attack (LI) and *endo*-attack (LII) by the bromine atom (ratio ≃ 7 : 3). [42-45]



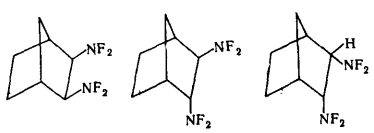
(L) (LI) (LII)

However, the assumption of the possibility of the existence of bridged radicals cannot explain the hypothetical formation of *cis*-*exo*-halogeno-compounds in all the above examples.

The observed instances of *endo*-attack can evidently also be explained without involving the concept of bridged radicals.

For this we must consider the other side of the question: the steric compactness of the attacking radical, which evidently markedly reduces the steric interactions of the entering substituent with the 2,3-*endo*-hydrogen atoms of the NB molecule.

Thus it was recently observed that a mixture of *cis*-*exo*-, *trans*-, and *cis*-*endo*-5,6-difluoroamines, (LIII)–(LV), is formed in the radical addition of tetrafluorohydrazine to NB. [46] In this instance the addition is no longer *exo*-stereospecific, although it still remains *cis*-*exo*-stereoselective.



(L III) (LIV) (LV)

Evidently this also applies to the radical halogenation of NB (see p. 522) in which the formation of *trans*-dihalogeno-compounds is probably partly linked with the initial *endo*-attack.

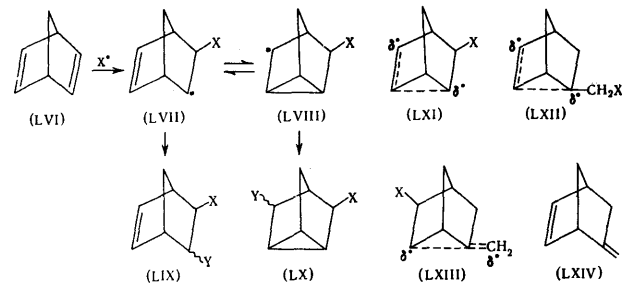
Even more significant changes in the stereochemical rules of radical attack are observed for norbornadienes with 7,7-substituents, especially well screened at the *exo*-side of the molecule. Examples of this series will be examined below.

3. FREE RADICAL ADDITION TO NORBORNADIENE (NBD)

The main feature of the reactions of NBD (LVI) is participation of the second double bond in the process, with the formation of substituted nortricyclene compounds of type (LX) owing to homoallyl interaction (see Scheme 3).

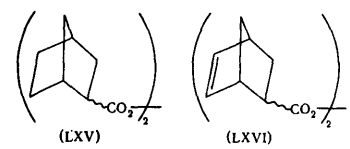
Just as in the NB series, the many investigators have not presented convincing arguments in support of the successive formation of classical intermediate radicals of type (LVII) and (LVIII) and against the existence of a non-classical radical to the type (LXI).

Scheme 3



It is now certain that neither the $C_{(1)}-C_{(2)}$ σ-bond in NB, nor the $C_{(2)}-C_{(3)}$ π-bond in NBD participates significantly in the delocalisation of the radical centre in these systems¶. The investigation of the competing addition of the trichloromethyl radical to a mixture of NB and NBD showed [48] that the effect of the second double bond is strictly additive: NBD is twice as reactive as NB. There is therefore no basis for assuming the existence of a transition state with lower energy, leading to a non-classical radical of type (LXI). The relative rates of addition of the methyl radical† to NB and NBD are 50 and 115 respectively [49]. The ratio of these quantities for NB and NBD probably also shows the absence of significant homoallyl strain. Similar results against the non-classical radicals of the (LXII) and (LXIII) type were obtained in studies [50,51] of the reactions of 5-methyl-norborn-2-ene (LXIV).

The activation parameters for the homolysis of *endo*- and *exo*-bonds of t-butylnorbornyl- and norbornenyl percarboxylates have been compared [52]. The results also rule out the probability of the formation of non-classical radicals at the rate-determining stage of the reaction. Similar results were also obtained in studying the thermal decomposition of diacyl peroxides of the (LXV) and (LXVI) type [53]. The participation of classical free radicals has also been confirmed in many other studies [5,6,36,37,51,54]:



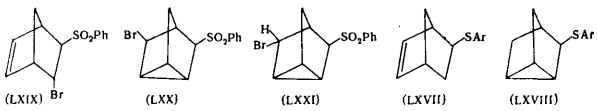
(LXV) (LXVI)

A convincing proof in support of the existence of discrete radicals (LVII) and (LVIII) is, for example, the change in the ratio of the reaction products (Scheme 3) with the concentration of the ligand and its reactivity. For example, *p*-toluenesulphonyl chloride [20], mercapto-acetic acid [55], perfluoroiodopropane [21], chloroform, butanal, heptanal, diethyl phosphite [48], and CCl_4 [56]—reagents with a relatively low transport constant—lead only to the corresponding nortricyclenes. On the other hand *p*-thiocresol and thiophenol [57] give a mixture of 5-*exo*-arylthionorborn-2-enes of type (LXVII) and the nortricyclene thioethers of type (LXVIII). An analogous

¶ True, the participation of the $C_{(2)}-C_{(3)}$ π-bond in the delocalisation of the radical centre at $C_{(7)}$ in the generation of C–7-radicals by the decarbonylation of the corresponding aldehydes is accepted [47], but this is not an addition reaction.

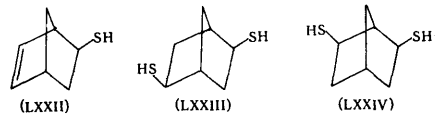
† In relation to the rate of withdrawal of hydrogen from iso-octane by the methyl radical.

mixture of products is formed in the reaction of NBD with CCl_3Br.[56] Phenylsulphonyl bromide forms the *trans*-addition compound (LXIX) and a mixture of the nortricyclene bromides (LXX) and (LXXI) in the ratio 4 : 3:[58]



(LXIX) (LXX) (LXXI) (LXVII) (LXVIII)

However, under the action of ultraviolet radiation H_2S gives only 5-mercaptonorborn-2-ene (LXXII) and the 2,5- and 3,5-dimercaptonorbornanes (LXXIII) and (LXXIV):[59]

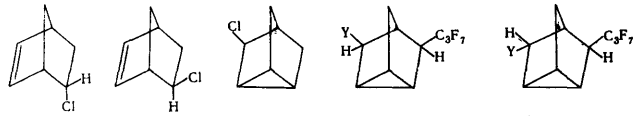


(LXXII) (LXXIII) (LXXIV)

In the reaction of phenylsulphonyl halides with NBD the relative amounts of nortricyclene products of type (LXX) and (LXXI) increase as the ligand activity in halogen transfer is reduced in the sequence: sulphonyl chloride > bromide > chloride[60].

The results of a series of recently published investigations can be explained satisfactorily by considering not only the existence of discrete radicals of structures (LVII) and (LVIII), but also the mobile equilibrium between them. For example, in the reduction of norbornenyl and nortricyclyl bromides and chlorides by tri-n-butyltin hydride the composition of the resulting mixture of NB and nortricyclene did not depend on the initial bromide (or chloride)[61]. In other words, the equilibrium between the norbornene and nortricyclene radicals was established more rapidly than their stabilisation. In the reduction of nortricyclyl bromide with triphenyltin hydride the relative amount of nortricyclene hydrocarbon was increased when the hydride concentration was raised, which agreed completely with the existence of an equilibrium pair of classical radicals. Similar results were also obtained in other methods of regenerating the radicals: by heating di-t-butylpercarboxylates of NB,[52] by decarboxylation of the corresponding aldehydes in chlorobenzene in the presence of peroxides[47], from the corresponding bromides in the presence of cobalt chloride and Grignard reagent in ether[61].

Other interesting examples of homoallyl–cyclopropylcarbinyl rearrangement have been published. For example, Cristol and Glason[62] found that in the reduction of *endo*- and *exo*-norbornenyl and nortricyclyl chlorides (LXXV)–(LXXVII) with sodium diphenyl at room temperature the composition of the reaction products (NB : nortricyclene = 1 : 3) did not depend on the initial chloride, that is, the equilibrium of the radicals was established more rapidly than the capture of an electron from the diphenyl radical-anion. However, at −58°C (LXXV) and (LXXVI) gave a mixture in which there was only 30% nortricyclene, but (LXXVII) a mixture in which there was up to 90% of the latter. Hence the reaction proceeds through classical radicals and the activation energy for their rearrangement is greater than for the capture of electrons from the radical-anion.



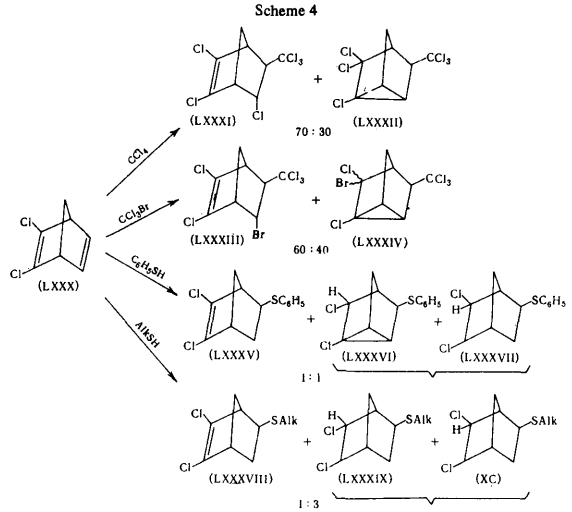
(LXXV) (LXXVI) (LXXVII) (LXXVIII) (LXXIX)

As regards the stereochemistry of addition to unsubstituted NBD, until recently it was always observed that initially there is *exo*-attack by the radical. Chain transfer for the nortricyclene radical (LVIII) evidently proceeds equally readily from both sides of the molecule, as a result of which in every instance mixtures of products of the type (LXXVIII) and (LXXIX) are formed[48,56,58].

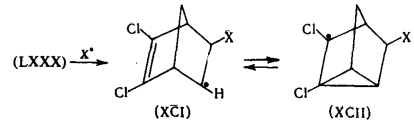
Just as in the NB series, substituents can significantly affect the stereochemical result of additions to NBD and the position of the nortricyclyl–norbornenyl equilibrium.

Thus it has been shown that free-radical addition to 2,3-dichloronorborna-2,5-diene (LXXX)[63] gives products represented in Scheme 4:

Scheme 4



In comparison with the corresponding reactions for unsubstituted NBD, the quantity of nortricyclene derivatives is less in the present instance. Actually, a norbornene derivative of type (LXXXV) is completely absent in the reactions of NBD with, for example, CCl_4, and with thiophenol only 19% of the norbornene addition product (LXXXV) is formed in comparison with 50% of the thioether (LXVII). This is shown by the decrease in reactivity of the 2,3-chloro-substituted double bond of the intermediate radical (XCI) towards intramolecular radical attack, leading to the formation of (XCII), which extends the lifetime of (XCI) in the non-isomerised state:

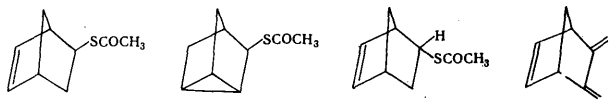


(XCI) (XCII)

The product ratios (LXXXI) : (LXXXII) and (LXXXIII) : (LXXXIV) are evidently regulated in this instance not only by the rate with which the molecule of the attacking agent transfers the chain (dissociation energy of the C–Br bond in $CBrCl_3$ 49.5 kcal mole^{-1}, compared with 67.9 kcal mole^{-1} for C–Cl in CCl_4), but also by steric factors at the chain transfer stage. Finally, we note the formation of *trans*-products with bulky ligands and the absence of appreciable steric differences for chain transfer by the radical (XCII) with *endo*- and *exo*-sides of the molecules.

In all the above examples in the NBD series, *exo*-radical attack is observed initially. However, exceptions have been observed very recently. It has been found that *endo*-addition products are formed in this instance not only with

large addends (for example, N_2F_2 [46]), but also in the addition of thiols [64]. Thus in the reaction with thioacetic acid in addition to 35% *exo*- (XCIII) and 37% nortricyclene (XCIV) thioacetates, 17% of the *endo*-thioacetate (XCV) was observed:



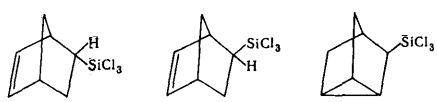
(XCIII) (XCIV) (XCV) (XCVI)

Interestingly, when thiophenol is used the proportion of the *endo*-isomer is reduced‡.

Another example is that of the *endo*-attack by the SPh radical on the intracyclic double bond of the triene (XCVI). [65]

Evidently, the absence of 2,3-*endo*-substituents in the NBD series allows even large ligands to overcome the relatively less availability of the *endo*-side of the diene molecule than is observed in the NB series.

The *endo*-isomer (XCVII) was also observed, together with *exo*- and nortricyclene derivatives (XCVIII) and (XCIX), in the reaction of NBD with trichlorosilane (in 7 : 28 : 53 ratio respectively), which was explained by the coordination of the system of double bonds of NBD with the *d*-orbitals of the silyl radicals participating in the reaction [66]:



(XCVII) (XCVIII) (XCIX)

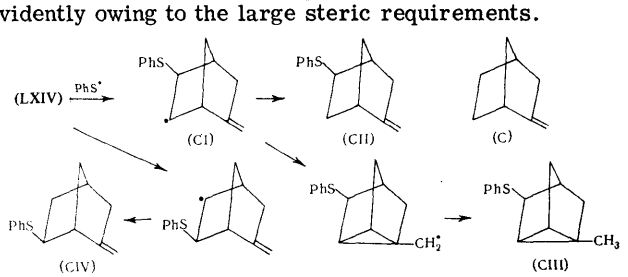
In the radical chlorination of benzonorbornadiene (XXIV) with nitrile chloride, *trans*-dichlorides, formed as a result of initial *endo*-attack by the chlorine atoms, were also isolated [67].

4. ADDITION TO NORBORNANE AND NORBORNENE SYSTEMS WITH HEPTACYCLIC (EXOCYCLIC) DOUBLE BONDS

The presence of a heptacyclic bond significantly affects the reactivity of the bicycloheptene system in homolytic reactions and the stereochemistry of the addition products.

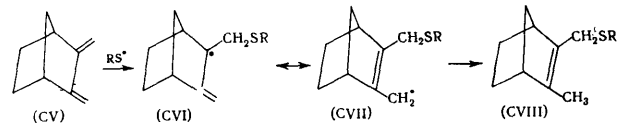
It must first be noted that the heptacyclic double bond is less reactive than an intracyclic one, which follows, for example, from the results on the competitive addition of thiols to NB and methylenenorbornane (C) [65,68] (ratio of reaction rates C/NB = 0.027 for thiophenol [65]).

From the reaction of 6-methylenenorbornene (LXIV) with thiophenol [69], three thioethers, (CII)–(CIV), were isolated, formed by the addition to the more reactive intracyclic double bond. The existence of three discrete radicals—precursors of the thioethers which are formed—was proved. However, the trichloromethyl radical is thought to be added at the heptacyclic double bond [50], evidently owing to the large steric requirements.



‡ In earlier studies the *endo*-thioether was never observed in this instance [57].

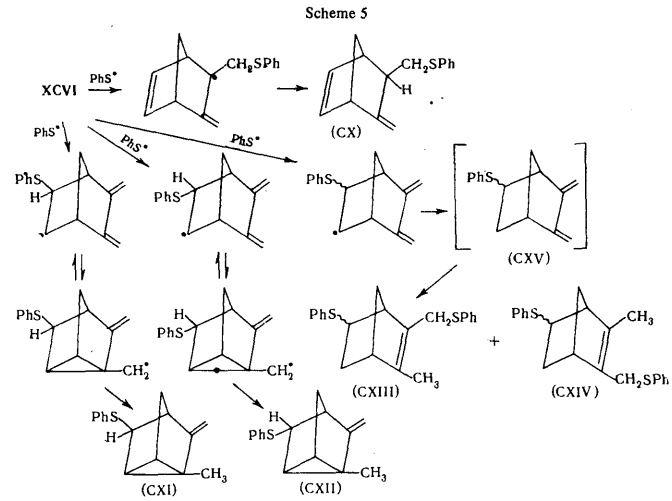
The reaction of *p*-thiocresol [70] and thiophenol [65] with 5,6-dimethylenenorbornane (CV) leads to a 1,4-addition product (CVIII). The formation of the latter is evidently favoured by the greater steric accessibility of the radical centre in (CVII) in comparison with that in (CVI):



(CV) (CVI) (CVII) (CVIII)

On reaction with thiophenol the triene (XCVI) gives a mixture of five thioethers (CX)–(CXIV), see Scheme 5.

Scheme 5



Here, judging from the ratio of the products, attack at the intracyclic double bond—thioethers (CXI)–(CXIV)—and at the 5,6-diene system—thioether (CX)—proceed to approximately the same extent. The diene (CXV) is more active and under the reaction conditions only the products of the addition to it of a second thiol molecule could be isolated. Interestingly, in this instance *endo*-attack by the thiyl radical on the *endo*-cyclic double bond occurred—ratio of thioethers (CXI) : (CXII) = 7 : 3.

In studying the reactions in the competing addition of thiophenol, methyl mercaptoacetate [65], and methyl and trichloromethyl radicals [48] to alkenes with various combinations of intra- and hepta-cyclic double bonds, results were obtained which mainly agreed with the order of reactivity of these systems. For example, the relative rates of addition for methyl mercaptoacetate are:

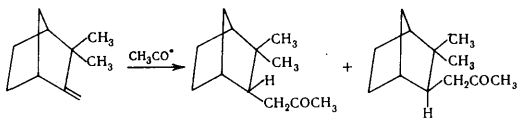
(I)	(LXIV)	(CV)	(XCVI)	(LVI)
1.00	1.44	3.55	1.72	1.83

The slight increase in the reactivity of (LXIV) in comparison with that of NB can be attributed to the somewhat greater strain of the molecule owing to the introduction of the heptacyclic double bond. The diene (CV) is the most active, that is, the intracyclic double bond in the triene (XCVI) decreases the activity of its diene system. According to Trecker and Henry [48] the reason for this is that the transition state for the sterically more favourable 1,4-addition leads to a strained NBD system. In the transition state itself, 1,2-addition evidently destroys the allyl stabilisation of the radical centre owing to conjugation with the π-electrons of the 2,3-double bond and consequently a general reduction in the reactivity of the

triene is observed. Furthermore, from these results it is clear that the intracyclic double bond and the diene system have comparable activities in homolytic reactions.

5. ADDITION TO 1,4,7-SUBSTITUTED NORBORNENES AND NORBORNADIENES

The above examples of *endo*-radical attack with participation mainly of comparatively small addends would appear to be only a few exceptions to the general rule of *exo*-addition. However, even the direction of approach of the addend in stage B (Scheme 1, p. 516) depends on the nature of the substituent present in the alkene molecule or introduced into it in the attack stage. In a recent paper [11] on the addition of various carbonyl compounds to camphene (CXVII) it was shown that even with acetaldehyde 7% of the product formed (CXIX) is due to chain transfer from the *endo*-side of the intermediate radical:



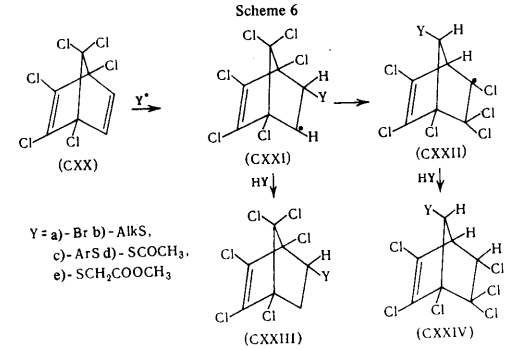
(CXVII) (CXVIII) (CXIX)

It can therefore be assumed that the accumulation of bulky substituents, especially in position 7, can significantly affect the stereochemical results of the reaction. Actually, in studying the addition of ethanethiol to 1,2,3,4-7,7-hexachloronorborna-2,5-diene (HCNBD) (CXX), we observed for the first time the formation of considerable amounts (up to 50%) of an *endo*-addition product (CXXIII).[71]

Subsequent study of the reactions of polysubstituted NBD, undertaken in parallel by Soviet and English chemists (Davies and coworkers, King's College, London), also led to extremely interesting results.

Thus, it was found that the hydrobromination [72-81] and thiylation of HCNBD by various thiols [72,82,83] (alkylthiols, arylthiols, thioacetic acid, methyl thioglycollate) proceed with a high degree of *endo*-stereoselectivity (Scheme 6):

Scheme 6

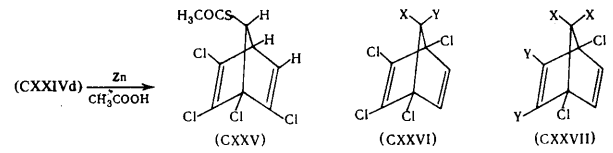


(CXX) (CXXI) (CXXII) (CXXIII) (CXXIV)

In addition to the *endo*-addition products (CXXIII), their isomers with substituents in the 7-*syn*-position (CXXIV) were observed, which showed that the reaction was accompanied by a free radical isomerisation which takes place under mild conditions and which is analogous formally to the well known Wagner–Meerwein cationic rearrangement (the mechanism of this rearrangement is discussed in more detail below). The 7-*syn*-structure of the isomers (CXXIV) was proved by the *endo*-position of the substituent in the corresponding intermediate radical (CXXI), and consequently by the *endo*-stereospecificality of the initial radical attack.

For some time the structure of products of type (CXXIV) was questioned§ in view of the fact that there is some difficulty in proving it rigorously. However, the *syn*-configuration of the substituent was established reliably on the basis of an analysis of the NMR spectrum of the dechlorination products from the 7-*syn*-thioacetate (CXXV) [73,75-78] and by a comparison of the NMR spectra of corresponding sulphides of the HCNBD and 1,2,3,4,7-*anti*-pentachloronorbornadiene (CXXVIb) series [84].

The complete reversal of the direction of radical attack observable in additions to HCNBD was explained [73,74,82,83] mainly by steric screening of the *exo*-side of the molecule of the diene by bulky electronegative 1,4,7-substituents:



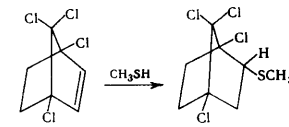
(CXXV) (CXXVI) (CXXVII)

a), X = Cl; Y = H
b), X = H; Y = Cl

a), X = Cl; Y = SMe
b), X = OCH3; Y = Cl

Actually, 1,4,7,7-tetrachloro-2,3-methylthionorborna-2,5-diene (CXXVIIa) and 1,2,3,4-tetrachloro-7,7-dimethoxynorborna-2,5-diene (CXXVIIb), which also contain bulky electronegative substituents at the bridge and alkylthiols mainly in the same manner as HCNBD.[85]

Even in the presence of 2,3-*endo*-hydrogen atoms, 1,4,7,7-tetrachloronorborn-3-ene (CXXVIII) adds ethanethiol *endo*-stereospecifically [86]:



(CXXVIII) (CXXIX)

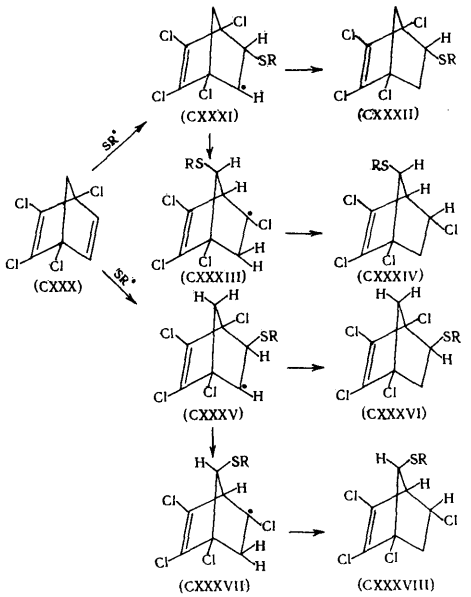
However, the substituent at the bridge is not the only steric barrier against *exo*-attack by a radical. The thiylation of 1,2,3,4-tetrachloronorborna-2,5-diene (TCNBD) (CXXX) with thioacetic acid [72-74] or ethanethiol [84] proceeds nonstereospecifically with the formation of a mixture of *endo*- and *exo*-epimers (CXXXII) and (CXXXVI) and the corresponding products of their rearrangement—7-*syn*- and 7-*anti*-epimers (CXXXIV) and (CXXXVIII) (Scheme 7). About 30% of the products are due to *endo*-radical attack.

Evidently, the absence of bridging chlorine atoms in TCNBD, as compared with HCNBD, greatly facilitates the *exo*-approach of the radical to the multiple bond. The latter also appears in the experimental conditions under which the reaction is effected: heating for 48 h at 60°C for HCNBD and by an exothermic reaction for TCNBD.[73]

Hence the direction of radical attack on the polychloro-substituted NB and NBD is controlled both by the bridge $C_{(7)}$ and also, although to a lesser degree, by the bridge-terminal $C_{(1)}$ and $C_{(4)}$ chlorine atoms. However, the introduction of 1,4-substituents in itself is probably not sufficient condition for the *endo*-approach of a radical, since it has been proved that 1,4-dichloronorbornene (XXVI) forms only *exo*-products with CH_3SH, CCl_3Br, and $CHCl_3$.[33] The absence of 2,3-*endo*-hydrogen atoms in the substituted NBD greatly facilitates *endo*-attack by the

§ Davies and coworkers [82,83] accepted the *cis*-configuration of the substituent on the basis of the absence of the corresponding *exo*-product; the *anti*-configuration has been proposed [72,74] on the basis of analogy with additions to tetrachloronorbornadiene.

Scheme 7



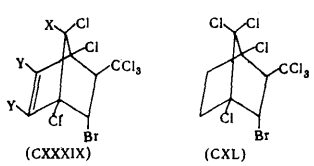
radical. In this the screening effect of the 2,3-*endo*-hydrogen atoms in NB is probably comparable in magnitude with the similar but oppositely directed effect of the 1,4-chlorine atoms in TCNBD: in the addition of thioacetic acid to NBD 17% of an *endo*-thioacetate of type (XCV) is isolated[64], but for TCNBD under comparable conditions the amount of *endo*-epimer (CXXXII) is doubled[73].

Evidently, of the two bridging substituents it is the 7-*anti*-chlorine atom that acts as a steric barrier against *exo*-attack. Thus, it has been proved[84] that in reaction with ethanethiol and thiophenol 1,2,3,4-*syn*-7-pentachloronorborna-2,5-diene (CXXVIa) behaves like TCNBD, and its 7-*anti*-isomer (CXXVIb) like HCNBD.

Even now it can be stated that the "*exo*-addition" rule cannot be considered all-embracing and the direction of attack by the free radical is a function of the degree of substitution of the diene and of the position and nature of the substituents.

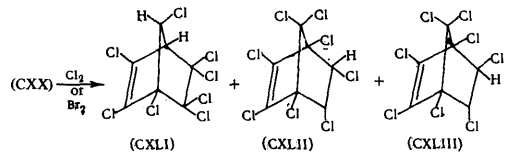
However, all the bicyclic alkenes investigated above contained substituents of similar inductive effect (OCH_3, Cl). It remained uncertain whether the effect of the bulky substituents on the direction of radical attack in polysubstituted NB and NBD is a purely steric effect or whether in this instance an electronic effect is also apparent.

From this point of view it is interesting that the addition of CCl_3Br to HCNBD, TCNBD, 7-*anti*-pentachloronorbornadiene (CXXVIb), 1,4,7,7-tetrachloronorbornene (CXXVIII), and 2,3-dimethylthio-1,4,7,7-tetrachloronorbornadiene (CXXVIIa) leads, just as for NB itself, solely to products of *trans*-addition with the *exo*-disposed trichloromethyl group of the type of (CXXXIX) and (CXL):[86]



where X = Cl or H, Y = Cl; or X = Cl, Y = SCH_3.

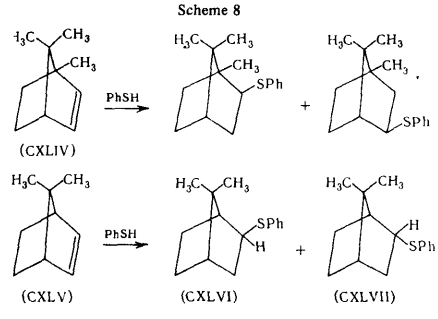
In studying the bromination and chlorination of HCNBD, although they were not able to inhibit the ionic processes, Davies and Parrot[87] also showed that *exo*-radical attack by halogen atoms takes place and a large proportion of the 7-*anti*-isomer (CXLI) is formed as a result of isomerisation of the product of radical *exo*-addition[87]:



Purely radical chlorination of HCNBD was effected by the same investigators by the action of sulphuryl chloride with the formation of the same three isomers but in another ratio. It is notable that whereas the *cis*-*endo*-product (CXLII) is almost absent in the reaction with Cl_2, it amounts to 11% of the isomeric mixture when SO_2Cl_2 is used, which is evidently associated with the greater size of the carrier-addend.

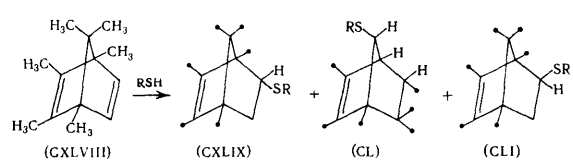
On the basis of the exceptional *exo*-attack by the bulky CCl_3 radical and the analogous behaviour of halogen atoms, Davies and coworkers[9,86] concluded that the direction of radical attack in the series of substituted NB and NBD is controlled mainly by electronic, and not steric, factors. In this, the relatively more electron-deficient $CCl_3^{\cdot}$ and $Br^{\cdot}$ radicals will experience some attraction at the side of the bridge chlorine atoms and the less electrophilic thioradicals $CH_3S^{\cdot}$ are repelled by the same substituents, which facilitates *endo*-radical attack. Davies and Rowley[109] think that this assumption agrees with the exclusive *exo*-addition of thiophenol to bornylene (CXLIV) and apobornylene (CXLV)[109] (Scheme 8).

Scheme 8



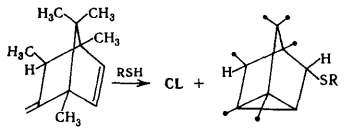
Brown and Kawakami's reinvestigation of the last reaction confirmed the high degree of *exo*-stereoselectivity, but it was found that in this instance up to 5% of the *endo*-thioether (CXLVII) is formed in comparison with 0.5% for NB itself.

On the other hand, it was shown recently[89,90] that the addition of 2-methylpropane-2-thiol to hexamethylnorbornadiene (HMNBD) (CXLVIII) proceeds with a high degree of *endo*-stereoselectivity with the formation of the 5-*endo*-, 7-*syn*-, and 5-*exo*-sulphides (CXLIX)–(CLI) in the ratio 51 : 45 : 4, respectively:



where R = t-C_4H_9.

Stereospecific *endo*-radical attack was also observed in the reaction of 2-methylpropane-2-thiol with methylenepentamethylnorbornene (CLII).[89,90] As a result, nortricyclene and 7-*syn*-sulphides (CL) and (CLIII) were obtained—both by addition of the thiol to the intracyclic double bond of the diene¶:



(CLII) (CLIII)

where R = t-C_4H_9.

Of the two dienes, (CXLVIII) and (CLII), the first was much more reactive in thiylation, but the intracyclic double bond of the diene (CLII) was much more reactive than the heptacyclic, just as was found earlier for unsubstituted alkenes[48,65] (see p. 521).

Taking into account the results of the thiylation of the polymethylated bicyclenes it must be assumed that the stereochemistry of the free radical addition to norbornene and diene systems is probably determined by a complex combination of electronic and steric factors. It seems that there is a definite lower limit for most of the steric and electronic factors under discussion produced by the substituents present either in the norbornyl system or in the molecule of attacking agent. Agents with not very demanding steric requirements (halogens, hydrogen halides, certain thiols, tetrafluorohydrazine, and nitryl chloride) can attack the molecule of unsubstituted NB and NBD from the *exo*- and the *endo*-directions, with preferred *exo*-attack. For 2-*endo*-substituted NB and NBD the ratio of the products depends on the stereoelectronic interrelations of the 2-*endo*-substituent and addend at both stages of the addition. For NB and NBD with 1,4,7-substituents, the 7-substituent, located above the plane of the double bond, and to a lesser extent the under-bridge substituents exhibit considerable steric control. However, the latter cannot appear for addends with low steric requirements (as evidently occurs in the reaction of thiophenol with bornylene and apobornylene).

An analogous proposal was recently made by Brown and Kawakami[88], who investigated the addition of various reagents under polar and radical conditions to NB and apobornene (CXLV) (including radical thiylation). They concluded that the breakdown of *exo*-stereospecificity in the reactions of apobornylene is the consequence of the appearance of steric control at the side of the 7-methyl substituents. However, the latter may not appear, depending on the mechanism of addition of the addend and the steric requirements of the latter.

In this connection it is also relevant to mention two recent papers[91,92], in which it was noted that the relative reactivity of the alkene under radical additions depends mainly on the induction effect of the alkyl substituent for the addition of small radicals, and is determined by the steric requirements in attack by large radicals.

In speaking about the electronic effects of the substituents evidently discussion must not be limited to consideration of only their electrostatic interaction with the attacking radical. This point of view, adopted by Davies and Rowley[86] to explain the exclusive *exo*-addition of CCl_3 radicals to polychloro-substituted NB and NBD ascribes relative nucleophilic properties to thiyl radicals, which clearly contradicts known results[93,94]. Evidently, in addition to the electrostatic interaction of the substituents their effect on the double bond of the bicyclene must be considered to a lesser extent. For example, it is known that whereas NB and NBD add various electrophilic reagents very readily[95,96], in the HCNBD molecule the 5,6-double bond has almost lost its nucleophilic nature and the corresponding reactions occur under much more severe conditions and with very small yields[73,83].

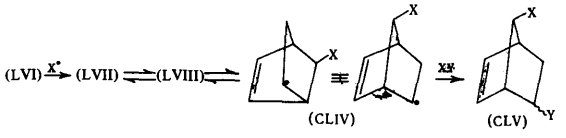
Bearing in mind the magnetic anisotropy of the double bond (for example, the shift of the signals of the 2,3-vinyl protons under the action of 7-*syn*-CH_3 groups[97]) it seems most probable that in these systems the direction of radical attack will be determined by the complex stereoelectronic effects of the substituents in addition to the steric factors.

Undoubtedly further accumulation of experimental results in this field will allow the influence of steric and electronic effects on the stereochemical results of the reactions to be distinguished more sharply.

6. MECHANISM OF ISOMERISATION OF NORBORNENYL RADICALS

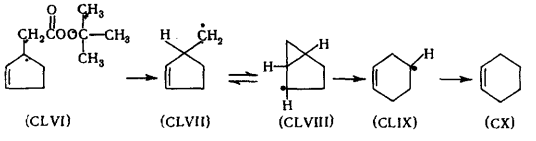
The results described in the preceding section show that addition to NBD is usually accompanied by the rearrangement of intermediate radicals with the formation of nortricyclene structures or compounds with 7-*syn*- or 7-*anti*-substituents. Usually the formation of both isomerised products is not observed in a single reaction. However, it was extremely strange, that the nortricyclyl (cyclopropylcarbinyl) radical (LVIII) found in equilibrium with the norbornyl radical (LVII)[61,62] does not exist in equilibrium with radical (CLIV), apparently because the breaking of the 2,6-bond is equally probable (Scheme 9),

Scheme 9



(CLIV) (CLV)

particularly as in several recent papers the formation of the cyclopropylcarbinyl radical is taken as the intermediate stage of the 1,2-migration of the vinyl groups. Such a mechanism was, for example, proposed for the thermal rearrangement of t-butyl cyclopent-2-enylperoxoacetate (CLVI):[96]

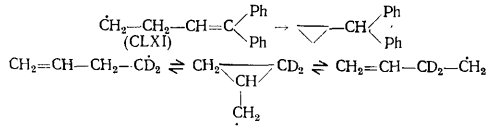


(CLVI) (CLVII) (CLVIII) (CLIX) (CX)

We note that during the rearrangement of ester (CLVI) rearrangement of the primary radical centre (CLVII) into the secondary (CLIX) takes place. Although Slaugh[98] also does not consider this sufficient driving force, nevertheless the reverse isomerisation (from the corresponding cyclohexenyl derivative) does not occur under these conditions.

¶ In this instance, in addition to free-radical isomerisation of the Wagner–Meerwein type already mentioned, 1,3-migration of hydrogen in the intermediate radical was observed, this will be considered in more detail below, p. 525.

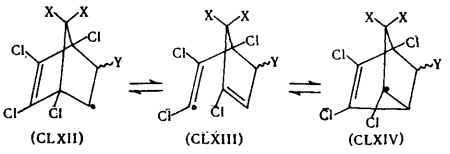
Confirmation of the proposed mechanism is given by the formation of cyclopropyldiphenylmethane in the generation of 4,4-diphenyl-3-butenyl radicals (CLXI) from the corresponding per-esters [98] or the formation of a mixture of but-1-ene-3,3-d_2 and but-1-ene-4,4-d_2, by the radical decarbonylation of 4-pentenal [99]:



Taking into account all the above information, it would be expected that the nortricyclyl radical (LVIII) can also play the part of an intermediate product in the process of 1,2-vinyl migration with the formation of 7-substituted NB (CLV).

Alden and Davies [100] also proposed just such a scheme for the mechanism of the above-mentioned radical rearrangement of the Wagner–Meerwein type, and then confirmed it reliably by a series of experimental facts, and it has now been adopted in the studies of other investigators. It was first assumed that the rearrangement proceeds according to a scheme [10,72,101] analogous to that proposed earlier for the high-temperature isomerisation of bornyl radicals [32]. However, in none of the instances investigated was a substituted allylcyclopentene corresponding to the radical (CLXIV) observed. The formation of an isomerised radical (CLXIV) both directly from (CLXII) and also through the stage of formation of (CLXIII) requires the (relatively unfavourable from the energy point of view) breaking of the $C_{(1)}-C_{(2)}$ vinyl bond (the dissociation energy of this bond is 10 kcal mole^{-1} above the dissociation energy of the C–C bond in alkanes) [102].

Scheme 10

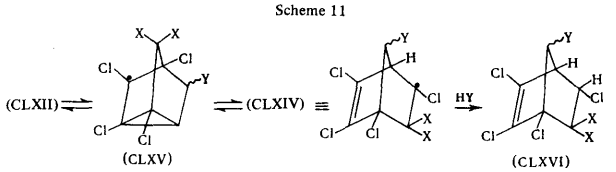


(CLXII) (CLXIII) (CLXIV)

Since until recently in reactions involving NBD itself only the formation of substituted nortricyclenes was observed, evidently an important factor for the occurrence of homolytic isomerisation according to Scheme 9 is the introduction into the molecule of the diene of substituents favourable to β-breaking with the shift of the equilibrium towards the side of formation of the radical (CLIV). This agrees completely with the known general position of free-radical chemistry [103,104].

The driving force for the observed rearrangement is evidently the greater stability of radical (CLXIV) in comparison with radical (CLXII), brought about by stabilisation of the radical centre by the neighbouring chlorine atom. The latter is consistent with the results of Nesmeyanov and coworkers on the isomerisation of acyclic halogen-containing radicals [41,105,106]. In a similar manner, the change from secondary to tertiary radical centre is probably the driving force for rearrangement in reactions involving HMNBD (Scheme 12, p. 526).

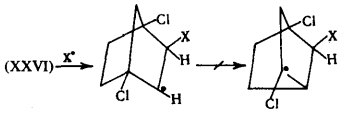
Scheme 11



(CLXII) (CLXIV) (CLXV) (CLXVI)

Here in the reaction with HCNBD the *syn/endo* ratio of the sulphides (CXXIV)/(CXXIII) (Scheme 6, p. 522) was ~3 : 1, [73] and under similar conditions with HMNBD it becomes only ~1 : 1. [90] This is in good agreement with the known greater stabilising effect of the chlorine atom standing at the radical centre in comparison with the corresponding effect of the methyl group [41].

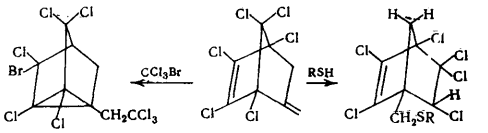
Characteristically, in the absence of a second double bond in the molecule of 1,4-dichloronorbornene (XXVI) even in the presence of a chlorine atom, which should be favourable to the stabilisation of a new radical centre, isomerisation products were not observed [33]:



In accordance with the proposed mechanism, the structure and ratio of the final products of addition to saturated NBD should be determined by the action of steric and electronic factors on the position of the equilibrium (CLXII) ⇌ (CLXV) ⇌ (CLXIV) and the rate of chain transfer of the radicals formed intermediately.

Actually, in the addition of thioacetic acid to TCNBD [73] the decrease of steric strain at the chain transfer stage from the *exo*-radical (CXXXV) to the *endo*-radical (CXXXI) (Scheme 7), evidently leads to an increase in the lifetime of the first. This, in turn, significantly alters the ratio of the products: *exo/anti* (CXXXVI)/(CXXXVIII) ≃ 1 : 1, whereas *endo/syn* (CXXXII)/(CXXXIV) ≃ 18 : 1. The screening of the 7-*anti*-chlorine atom of the *exo*-side of the HCNBD molecule in comparison with TCNBD also appears in the ratio of the thioacetates obtained: *endo/syn* (CXXIIId)/(CXXIVd) ≃ 0.7 : 1, but for *endo/syn* (CXXXII)/(CXXXIV) ≃ 18 : 1.

In studying the reaction of HCNBD with methanethiol and ethanethiol at various temperatures and addend concentrations and also under comparable conditions but with different thiols [73], it was shown that the ratio of the products, and consequently also the position of the equilibrium of the corresponding radicals (Scheme 11, X = Cl), depends significantly on the experimental conditions and rate constants of chain transfer to the addend participating in the reaction. The latter is also confirmed by the example of reactions with participation of hexachloromethylenenorbornene (CLXVII): only the corresponding nortricyclene (CLXVIII) was isolated in the reaction of this diene with CCl_3Br whereas addends with a lesser transfer constant (alkanethiols, thioacetic acid, methyl thioglycollate) give only products of rearrangements of the type (CLXIX): [97]

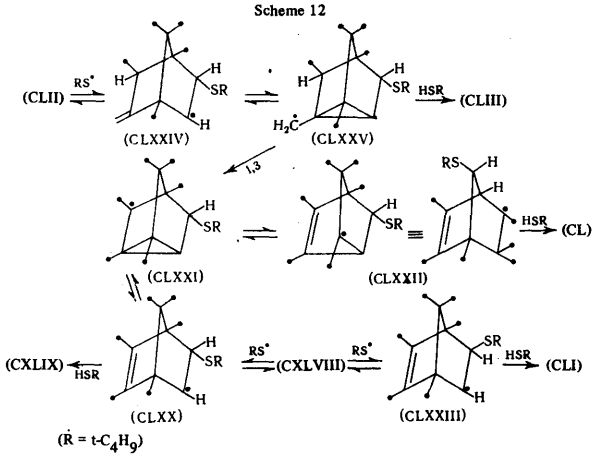


(CLXVIII) (CLXVII) (CLXIX)

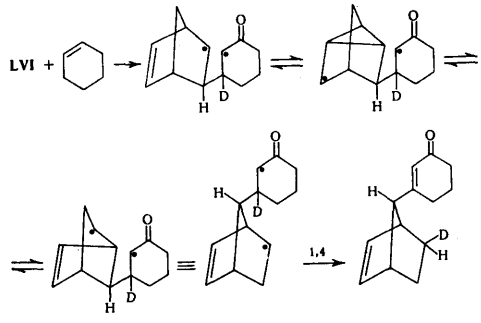
Confirmation of the proposed scheme of rearrangement is also the formation of the same 7-*syn*-sulphide (CL) in the thiylation of HMNBD and methylenepentamethylnorbornene (CLII), which can evidently proceed solely through the

formation of a common intermediate nortricyclene radical (CLXXI) (Scheme 12).[89,90] The presence in the reaction mixture of a nortricyclene product corresponding to radical (CLXXV) and the absence of a sulphide corresponding to the radical (CLXXI) is evidently connected with steric hindrance at the chain transfer stage, with participation of the latter:

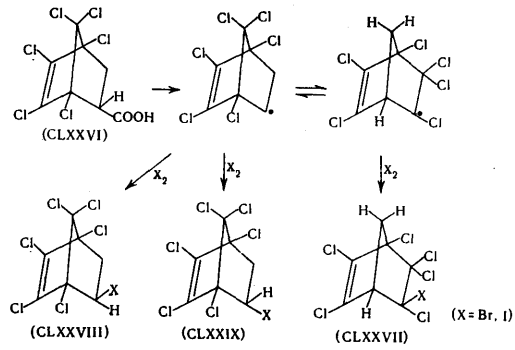
Scheme 12



Interestingly, for the formation of 7-*syn*-sulphide (CL) from the diene (CLII) 1,3-migration of the hydrogen with a corresponding shift of the radical centre in the radical (CLXXV) is postulated. The possibility of such a migration is confirmed, for example, by results obtained by McCullough and Rasmussen[107], who describe the *exo*-stereospecific 1,4-migration of hydrogen in the photochemical reaction of NBD with cyclohexen-2-one or 3-methylcyclohexen-2-one.



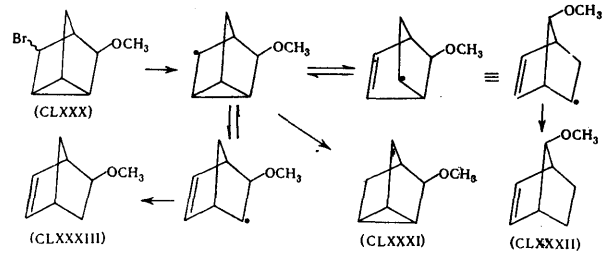
Hence in radical reactions of addition to polysubstituted NBD equilibrium is established between the intermediately formed radicals according to Scheme 9. The position of the equilibrium is determined by the competition between the steric and electronic interactions of the substituents of the reagents and also by the experimental conditions. Another example of this is Davies and Mason's modified Hunsdiecker reaction[2] for 1,4,5,6,7,7-hexachloronorborn-2-ene-5-carboxylic acid (CLXXVI) and its methyl analogue. In both instances when bromine is used the corresponding rearranged products (CLXXVII) are formed. Evidently, participation in the reaction of a slower chain carrier (in comparison with iodine) ensures the possibility of isomerisation:



Interestingly, the ratio of *exo*- to *endo*-halides (CLXXVIII) : (CLXXIX) when iodine is used is higher than for bromine, which also evidently confirms the importance of the electronic factor in this instance.

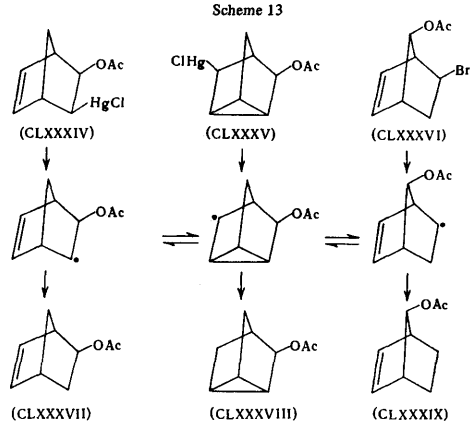
A rearrangement of the Wagner–Meerwein type has been reported very recently in the reaction of unsubstituted NBD with tetrafluorohydrazine[46] and cyclohexen-2-one[107].

In investigating the reaction of Grignard reagents with methoxy-substituted nortricyclyl bromide (CLXXX)†, Davies and coworkers observed both the norbornene ethers (CLXXXII) and (CLXXXIII) in the reaction mixture as well as the corresponding nortricyclene (CLXXXI):[2]



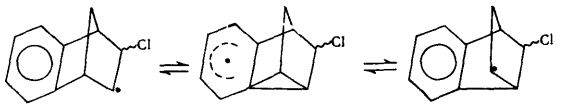
Similar results were obtained in the reduction of acetoxy-substituted mercury chlorides (CLXXXIV), (CLXXXV) or bromides (CLXXXVI) with sodium tetrahydroborate, or tri-n-butyl- or triphenyl-tin hydride or deuteride[108]. Irrespective of the initial acetate an equilibrium mixture of the three products (CLXXXVII)–(CLXXXIX) was obtained (see Scheme 13):

Scheme 13



The radical rearrangement with 1,2-shift of the phenyl group was observed in the reaction of benzonorbornadiene (XXIV) with nitryl chloride[67]:

† $CoCl_2$ catalyst.



Interestingly, in this instance the isomers ratio *endo/syn* ≃ 20 : 1, and *exo/anti* ≃ 1.3 : 1, which also clearly shows steric control in the radicals formed as intermediates.

From the above examples, it becomes evident that under different experimental conditions, in particular when addenda with a low transfer constant participate in the reaction, the lifetime of the intermediate radicals can be sufficient for the establishment of equilibrium according to Scheme 9 (p. 524).

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Hence a rather complex and still extremely contradictory interrelation of the steric and electronic effects of the substituents, which determine the direction of both stages of 1,2-addition and also the position of the equilibrium between the radicals formed, is observed in the reactions examined. Therefore the continuation of investigations in this field using modern methods of characterisation is extremely interesting and useful for finding both general and particular rules in free radical chemistry.

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