Nucleophilic Addition and Substitution Reactions of Polyhalogenated Norbornadienes with Alkoxide and Alkenoxide Anions. A Novel Claisen Rearrangement of Allyl Norbornadienyl Ethers

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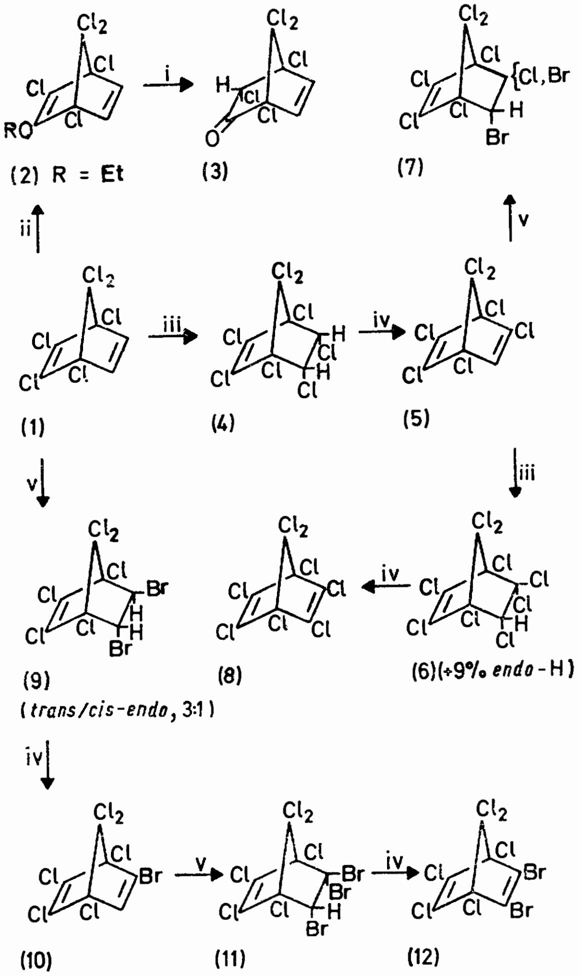
Rational syntheses of polyhalogenonorbornadienes (including the hepta- and octa-chloro-compounds and their bromo- and dibromo-hexachloro-analogues) and their reactions with alkoxide and alkenoxide anions in the presence (or otherwise) of dipolar aprotic solvents are described. Vinylic chlorine or bromine substitution, together with addition of alcohols appear to be the more important of their reactions with these bases. Hydrolysis of the resulting divinylic ethers gives polyhalogenonorbornane-2,5-diones exhibiting unusual long-range n.m.r. spin couplings. Mild thermolysis of the derived allyl vinyl ethers results in Claisen [3.3] sigmatropic rearrangements new to the norbornadienes. Comment is made on the stereochemistry of this rearrangement and on addition reactions of norbornenes.

An earlier paper[1] described the reaction of hexachloronorbornadiene (1) with boiling ethanolic potassium hydroxide; contrary to other reports[2] the major, distilled product was shown to be the vinyl ether (2) whose structure was deduced from its i.r. light absorption, hydrolysis to a thermally stable norbornenone (3) and from the typical but enhanced reactivity towards electrophilic reagents of its isodrin-like[3] *endo-endo* fused tetracyclic cyclopentadiene adduct.

Nucleophilic substitution can be effected to advantage in dipolar aprotic media[4] and we have therefore explored the use of *e.g.* dimethyl sulphoxide as a co-solvent for reactions of (1) and related compounds with alkoxide and alkenoxide anions. From the earlier study it was suggested that factors such as homoallylic stabilisation and dispersion of negative charge by the electronegative environment influenced the stability of the intermediate carbanion formed in the first step of an addition–elimination mechanism for vinylic chlorine substitution; we have therefore also explored the effect on general reactivity towards alkoxides of varying both degree and kind of halogenation in representative norbornadienes, some of which are novel.

In Section A of the following, the synthesis of the various halogenated norbornadienes is described, and in Section B their reactions with alkoxide anions leading to vinylic ethers and alcohol addition products is discussed. In Section C hydrolytic behaviour of the derived vinylic ethers and diethers is described and novel long-range n.m.r. spin couplings in the hydrolysis products are reported. Finally in Section D similar reactions of halogenated norbornadienes with alkenoxide anions is disclosed, together with the unusually easy Claisen rearrangement of the derived allyl vinyl ethers.

Section A. Heptachloro- and Octachloro-norbornadiene: Bromohexachloro- and Dibromohexachloro-norbornadiene.—Rational preparative scale syntheses of the various polyhalogenated norbornenes and norbornadienes used in this work † are outlined in the Scheme. Most of the observations here are apparently unexceptional but there are points of interest. For example the com-



SCHEME Reagents: i, H^+–H_2O; ii, RO^-–ROH–DMSO; iii, Cl_2–CCl_4 or –$CHCl_3$; iv, Bu^tO^-–Bu^tOH–50°; v, Br_2–CCl_4 or –$CHCl_3$

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† During the course of this work, interesting small-scale syntheses of several polyhalogenated norbornadienes *via* Diels–Alder adducts of hexachlorocyclopentadiene with stannylated acetylenes were reported (D. Seyferth and A. B. Evnin, *J. Amer. Chem. Soc.*, 1967, **89**, 1468).

[1] K. Mackenzie, *J. Chem. Soc.*, 1957, 457.

[2] H. M. Molotsky, U.S.P. 2,897,240/1959 (*Chem. Abs.*, 1960, **54**, 1364*a*); U.S.P. 2,995,606/1962; 3,031,464/1962 (*Chem. Abs.*, 1962, **56**, 2351*g*; 1962, **57**, 9695*b*).

[3] S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377; C. W. Bird, R. C. Cookson, and E. Crundwell, *J. Chem. Soc.*, 1961, 4809.

[4] A. J. Parker, *Quart. Rev.*, 1962, **16**, 163; J. F. Bunnett, *Ann. Rev. Phys. Chem.*, 1963, **14**, 271.

position of the product of cycloaddition of hexachlorocyclopentadiene and *trans*-dichloroethylene is temperature dependent; higher temperatures (*e.g.* 165°) favour exclusively *endo-cis* adduct (4); this is probably due to *cis-trans* pre-equilibration of the olefin [5] rather than stereomutation of the adduct.[6] At lower temperatures substantial amounts of the *trans*-dichloro-adduct are also obtained. The *cis-endo* adduct (4) is identical to that formed by chlorination of hexachloronorbornadiene (1). If the chlorination is carried out in methanol little or no methoxy-incorporation occurs in the product; *endo*-approach by molecular chlorine must therefore be accompanied by very rapid anion capture after the initial electrophilic addition, and if a carbonium ion species is formed it must be very short lived. Bromine addition to hexa- and hepta-chloronorbornadiene on the other hand occurs both *cis-endo* and *trans*; in the case of bromohexachloronorbornadiene (10) consideration of mainly steric factors [7] indicates that both these modes of addition can quite reasonably be expected to give the same *cis-endo*-dibromo-compound (11). The *exo*-symmetrical bridged halogenonium ions characteristic of electrophilic halogen addition to olefins are clearly mitigated by the size of the bridge substituents here and whilst there are considerable torsional effects [8] to be overcome in *endo*-addition, especially with bridgehead chlorine substituents, this stereochemical course is followed in part, and provides an interesting measure of the preference for cyclic halogenonium ion formation (whenever possible) for bromination in contrast to the face-edge additions which occur almost exclusively *exo* with certain other reagents in similar steric circumstances [9] when a cyclic three-membered ion is not strongly preferred. An intriguing possibility however is that such *cis-endo*-additions to norbornenes might be examples of thermal symmetry allowed concerted group transfer reactions [10] [*e.g.* structure (13)] in analogy to the dehydrogenations of dihydroaromatic ring compounds by bromine.[11] This could be a realistic possibility since the reactions are carried out in relatively non-polar solvents with poorly nucleophilic olefins; clearly kinetic information would be of value here. The stereochemical features of the various halogen adducts can be deduced with some confidence from n.m.r. chemical shifts and spin-coupling constants; [12,13] this information is largely described in the Experimental section.

The quality and yields of the various polyhalogenonorbornadienes shown in the Scheme noticeably improve with greater halogen content of the substrate for dehydrohalogenation, perhaps a manifestation of the increased *E*1cB character in the elimination transition state [14] and the steric exclusion of other bimolecular nucleophilic processes when using t-butanol as solvent. It is possible also that the product norbornadienes are sterically [15] and electronically more stable than their precursor norbornenes especially when large groups such as bromide anion can be ejected; *e.g.* solutions of tribromohexachloronorbornene (11) spontaneously lose hydrogen bromide.

The photochemical halogenations of diene (1) not surprisingly follow a different course; usefully bromination in u.v. light gives the rearranged product (14) (23%) resulting from [1,2] shift, presumably *via* a classical radical species.[16,17*]

Other products formed in the photochemical bromination are the known *trans*-dibromo- and a novel *cis-exo*-isomer of *cis-endo* adduct (9), (44, 11, and 22% respectively) which are recognizable from their ^{1}H n.m.r. signals. The formation of the sterically very crowded *cis-exo*-dibromo-adduct of olefin (1) is interesting. Recent e.s.r. studies of β-halogenated free radicals show that other factors being equal, the halogen atom (Cl, Br, or I) prefers a conformation parallel to the singly occupied adjacent orbital,[18] suggesting, other things being equal, that *trans*-addition of halogens to olefins should be characteristic of radical processes. The formation of a significant proportion of *cis-exo*-dibromo-adduct once again reflects the strong preference for *exo*-addition at the norbornene double bond when a favourable reaction course is open; rationally, in this case face-edge approach is involved, circumventing steric factors. Photochlorination of diene (1) follows a very similar course, but the proportions of rearranged and *cis-exo*-addition products are increased.

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[*] Even on the very crude analogy with simple Huckel theory for a three-carbon cyclically delocalized system little stabilisation for a non-classical *radical* would be expected; see, for example, A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, 1961, p. 381; concerted [1,2] sigmatropic shift is unlikely on steric grounds, *cf* R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.

[5] B. S. Rabinowitch and M. J. Hulatt, *J. Chem. Phys.*, 1957, **27**, 592.

[6] *Cf.* P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473; *Science*, 1968, **159**, 833.

[7] D. I. Davies, P. M. Mason, and M. J. Parrott, *J. Chem. Soc.* (*C*), 1971, 3428; W. C. Baird, B. Franzus, and J. H. Surridge *J. Amer. Chem. Soc.*, 1967, **89**, 410; G. W. Klumpp, A. H. Veefkind, W. L. de Graaf, and F. Bickelhaupt, *Annalen*, 1967, **706**, 47, 57; T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2614; see also ref. 9.

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

[9] H. C. Brown and Kwang Ting Liu, *J. Amer. Chem. Soc.*, 1971, **93**, 7335.

[10] S. I. Miller, *Adv. Phys. Org. Chem.*, 1968, **6**, 185.

[11] J. S. Littler, *Tetrahedron Letters*, 1971, 81.

[12] J. C. Davis and T. V. Van Auken, *J. Amer. Chem. Soc.*, 1965, **87**, 3900; P. M. Subramanian, M. T. Emerson, and N. A. LeBel, *J. Org. Chem.*, 1965, **30**, 2624; E. D. Weil, J. G. Colson, P. E. Hoch, and R. H. Gruber, *J. Heterocyclic Chem.*, 1969, **6**, 643.

[13] K. L. Williamson, Yuen-Fang Li Hsu, R. Lacko, and Cheng He Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 6129; K. L. Williamson, *ibid.*, 1963, **85**, 516; see also C. K. Alden and D. I. Davies, *J. Chem. Soc.* (*C*), 1968, 700; D. I. Davies and P. J. Rowley, *ibid.*, 1970, 705.

[14] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965; J. F. Burnett, *Progr. Chem.*, 1969, **5**, 70.

[15] G. Dan Sargent, *Quart. Rev.*, 1966, **20**, 301.

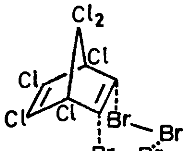
[16] V. F. Bystrov, A. V. Azovskya, N. P. Petukhova, A. U. Stepanyants, and E. N. Prilezhaeva, *Izvest. Akad. Nauk S.S.S.R.*, Ser. khim., 1966, 381.

[17] J. A. Claisse and D. I. Davies, *J. Chem. Soc.* (*C*), 1966, 1045; D. I. Davies, *Chem. Soc. Special Publ.*, 1970, **24**, 201.

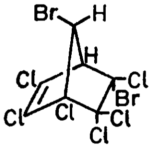
[18] A. R. Lyons and M. C. R. Symons, *J. Amer. Chem. Soc.* 1971, **93**, 7330.

The structures of the various dibromohexachloronorbornenes follow unambiguously from the products of their treatment with base; *e.g.* compound (14) gives diene (15) whilst the *cis-exo*-isomer of (9) gives bromohexachloronorbornadiene (10).

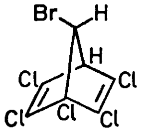
Section B. Addition and Substitution Reactions of Polyhalogenonorbornadienes with Sodium and Potassium Alkoxides.—The mechanism of vinyl halogen substitution in chlorinated norbornadienes [1] reasonably implies either a rate-determining alkoxide anion addition or else halide ion ejection from the alkoxide adduct as the rate-limiting step. The former seems much more likely to be the case in alcohols, and factors which stabilise the relevant intermediate carbanion and/or increase its rate of formation should therefore accelerate the reaction. This is qualitatively observed for heptachloronorbornadiene (5) and especially for octachloronorbornadiene (8), both of which react very readily [compared to (1)] with methoxide ion in warm methanol, giving high yields of predominantly monovinylic ethers. Specifically diene (5) appears to give only one of the possible vinylic monomethoxy-substituted products, namely (17) with *e.g.* no diene (16) being isolated. A considerable amount of a methanol adduct (18b) [$\nu_{\text{max.}}$ 1607vs cm^{-1} (ClC=CCl), τ 5·85(d) and 6·20(d) (J 2·8 Hz, *endo*-5- and *exo*-6-H)] is also formed, and appears to arise from *cis-exo* methanol addition; the adduct survives heating with 0·3M-potassium t-butoxide, and is thus very probably (18b) rather than (18a) since the latter would be expected to be more easily dehydrohalogenated, the preferred mode of vicinal elimination in norbornane compounds being *cis-exo* rather than *trans* or *cis-endo*.[19] Octachlorodiene (8) forms largely a single monoether (19) with potassium methoxide together with a mixture of β- and γ-divinylic ethers (20), (21) (7%), and another compound (3%) which on the basis of its n.m.r. spectrum [τ 6·5(s) and 6·62(s) (2 OMe, non-vinylic) and 5·33 (s, *exo*-5-H)] and mass spectrum [m/e 392 ($C_9H_7Cl_7O_2^{+\cdot}$) and 122 (intense retrodiene fragment $CHCl{=}C(OMe)_2^{+\cdot}$)] appears to be the acetal (22), the product of methanolysis of the first formed α-chloro-ether resulting from addition of methanol to diene (8). Room temperature exposure of diene (8) to methoxide ion in 50% methanolic dimethylformamide also gives mainly the monoether (19). This increased reactivity of polyhalogenated norbornadienes with increasing halogenation parallels that observed with the chloroperfluorocyclobutene and cyclopentene systems, although the gradation in properties is not so marked as with the perfluoro-compounds where the differential effect of α- and β-fluorine substituents plays a critical role.[20] The increase in reactivity shown by dienes (5) and (8) may also be compared with the fact that no divinylic ethers can be isolated from diene (1) under the most vigorous conditions tried, in contrast to its reactivity towards methanethiolate ion [21] where neighbouring α-S(3*d*) orbital participation in the carbanion formed by methanethiolate ion addition to the first formed monothioether accounts nicely for the formation of bisthioethers.



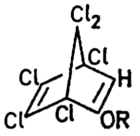
(13)



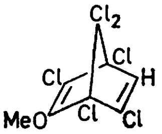
(14)



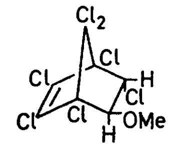
(15)



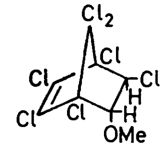
(16) R = Me
(25) R = Et



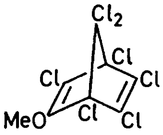
(17)



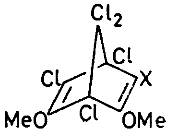
(18b)



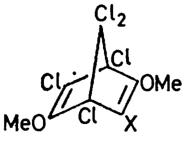
(18a)



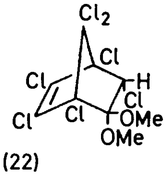
(19)



(20) X = Cl
(27) X = Br



(21) X = Cl
(28) X = Br



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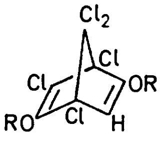
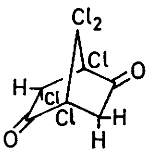
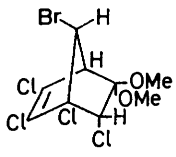


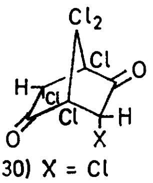
(23) R = Me
(26) R = Et



(24)



(29)



(30) X = Cl
(31) X = Br

Turning to the effect of added dimethyl sulphoxide (DMSO) on product composition, hexachlorodiene (1) is converted to monovinylic ethers even at 25° by the action of alkoxide ions in alcoholic DMSO, the yields in these reactions being increased by mild heating. At molar ratios of base : substrate >2 : 1, addition at the unsubstituted double bond becomes a more important secondary process in these solvent mixtures, and under similar conditions even the rather unreactive norbornene,

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[19] J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *J. Amer. Chem. Soc.*, 1966, **88**, 4922; H. Kwart and J. L. Nyce, *ibid.*, 1964, **86**, 2601.

[20] J. D. Park, G. Groppelli, and J. H. Adams, *Tetrahedron Letters*, 1967, 103; J. D. Park, R. Sullivan, and R. J. McMurty, *ibid.*, p. 173; J. D. Park and W. C. Frank, *J. Org. Chem.*, 1967, **32**, 1333.

[21] A. J. Fry, *J. Org. Chem.*, 1966, **31**, 1863.

dihydro-(1)[1] forms good yields of vinyl ethers. Clearly homoallylic participation cannot be invoked in the latter substitution. Similarly the polychlorodienes (5) and (8) are rapidly converted principally into divinylic ethers by mild warming with potassium hydroxide in 50% methanolic DMSO. However the proportion of methanol adduct (18) formed from diene (5) is increased in the presence of the aprotic solvent under otherwise identical conditions (diether : adduct, 10 : 7) at the expense of the single diether (23) formed. Structure (23) is confirmed by its hydrolysis to the pentachloronorbornane-2,5-dione (24) [$\nu_{max.}$ 1795vs cm^{-1} (α-chloro-CO), τ 5·25 (d, *exo*-3-H), 6·81 (q, *exo*-6-H), and 7·09 (d, *endo*-6-H, $J_{exo\text{-}3\text{-H}/exo\text{-}6\text{-H}}$ 0·6, J_{gem} 19·6 Hz)]. Somewhat similar results are found in the reaction of diene (8) with methoxide ion in MeOH–DMSO, but here it is the proportion of acetal (22) which is increased under partially aprotic conditions at the expense of the mixed β- and γ-diethers (20) and (21). For the octachlorodiene (8) however the reaction is very exothermic and considerably more dilute solutions must be used, making useful qualitative comparison with purely methanolic media more difficult.

In the presence of a dipolar aprotic solvent, counterion stabilisation of the intermediate carbanions produced in these reactions is expected to be reduced, and their decomposition to products either by anion ejection (leading to vinylic ethers) or by protonation leading to base-stable adducts may be accelerated. A complicating factor however is the increased nucleophilicity of halide anions in aprotic dipolar media;[4] the possibility that this effect could explain the observed product composition *i.e.* an increased proportion of alcohol adduct (by re-addition of chloride ion to the vinylic ether) is negated by the fact that (*a*) vinyl ether (2) is recovered essentially unchanged from hot concentrated solutions of ammonium or lithium chloride in neat DMSO *i.e.* halide ion ejection is clearly irreversible and (*b*) re-addition of chloride anion would occur *exo*. Diversion of dienes (5) and (8) into stable methanol adducts would thus appear to be a kinetic effect.

The general behaviour of bromohexachlorodiene (10) in ethanol–DMSO is similar to that of diene (5) in methanolic media; depending on the conditions either the monoethoxyhexachloro-compound (25) or the single diethoxypentachlorodiene (26) can be isolated. This result can be understood in terms of fast removal of bromide anion ensuring that the product is determined by the sterically more accessible intermediate anion than by the more stable α-chloro-anion resulting from alkoxide addition to the chlorinated olefin (which would lead to a bromopentachloro-monovinylic ether as one of the primary end products). Further substitution then leads to the diether (28). For the dibromohexachlorodiene (12), again an exothermic reaction ensues with potassium hydroxide in 50% methanolic DMSO, and a mixture containing mostly the diethers (27) and (28) together with smaller amounts of monoethers and acetal (addition) products is obtained, in parallel with the reactions of the octachlorodiene (8). Like the perchloro-compounds the diethers are not easily separated by column chromatography, nor by preparative t.l.c.; g.l.c. under a variety of conditions results in extensive decomposition. However the mixture is characterised by its spectral properties.

Finally bromopentachlorodiene (15) gives an excellent yield of the acetal (29) when treated with base, the acetal being characterised by its hydrolysis to the corresponding norbornenone [$\nu_{max.}$ 1602vs and 1785vs cm^{-1} (ClC=CCl, α-chloro-CO)].*

Section C. Hydrolysis of Alkoxypolyhalogenonorbornadienes.—As disclosed above physical methods of separation of the various β- and γ-dialkoxypolyhalogenonorbornadiene mixtures [(20) and (21), (27) and (28)] are not particularly successful. However hydrolysis of these mixtures with concentrated acid gives in each case a single ketone assigned structure (30) and (31) respectively on the basis of general stability and light absorption properties [diketone (30), $\nu_{max.}$ 1803vs cm^{-1} (α-chloro-CO), τ 5·21(s); diketone (31), $\nu_{max.}$ 1813vs cm^{-1}, τ 5·10(d) and 5·28 (d, *J* 0·6 Hz), *m*/*e* 372 ($C_7H_2BrCl_5O_2^{+\cdot}$)]. The diethers (20) and (27) are easily destroyed in the hydrolysis medium presumably *via* an intermediate such as (32) for which no analogue exists in the case of the γ-diketones; the unstable products formed from the β-diethers can actually be extracted from the hydrolysis liquors remaining after the precipitation of the γ-diketones and their relatively low frequency i.r. carbonyl absorption ($\nu_{max.}$ 1750vs and 1765vs cm^{-1}) and deep red colour suggests ring scission–elimination reactions leading to polyhalocyclopentadienones.† The relationship between the diketones (24), (30), and (31) is established by their reduction to the parent diketone (33).

An interesting feature of the n.m.r. spectrum of the 3-bromo-6-chloronorbornane-2,5-dione (31) is the appearance of a long-range spin coupling between the pair of

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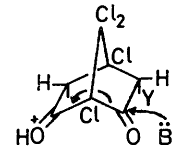
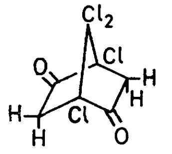
* During the course of this work we also investigated the preparation and reactivity of 2,3-dichloronorbornadiene, which proved surprisingly inert towards nucleophiles; from experiments with this diene, 1,2,3,4-tetrachloro-5-phenylnorbornadiene and the *syn*- and *anti*-1,2,3,4,7-pentachloronorbornadienes we concluded that bridge chlorination was important in determining overall reactivity. D. I. Davies and R. J. Rowley [*J. Chem. Soc.* (*C*), 1969, 288] investigating the reactions of *syn*- and *anti*-pentachlorodienes with the more reactive methanethiolate ion found that the *anti*-isomer reacted faster by a factor of 2 compared to the *syn*-7-chloro-isomer and concluded that this was due to the dipole associated with the C–Cl bond being more favourably orientated to stabilise the intermediate carbanion. However their data for 1,2,3,4-tetrachloronorbornadiene, the *syn*- and *anti*-pentachloro-isomers and hexachloronorbornadiene give the relative rates 0·2 : 0·3 : 0·6 : 1·0 showing that the second bridge chlorine atom is equally important.

† Use is made of this differential stability of the two diethers (20) and (21) in acidic media in assigning the relevant methoxy n.m.r. signals and vinylic ether i.r. frequencies; depending on the conditions the decline of either one or the other of the pair of vinylic ether i.r. bands is observed as the compound is removed, with the appearance during hydrolysis of a typically intense carbonyl absorption, and a characteristic methylene singlet *e.g.* for diketone (30). In acidic methanol β-diether (20) is preferentially removed apparently as methanol adducts, γ-diether being recovered under these conditions (see Experimental section).

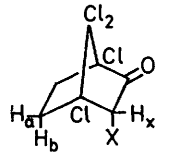
exo-orientated protons; if the transmission of spin coupling between protons separated by intervening carbonyl groups can be neglected, then the observed effect may be another example of ^6J coupling uniquely found in norbornane ring systems; the value of the coupling constant is of the same order of magnitude as those found for ^6J couplings in earlier work (*ca.* 1 Hz).[22,23] A further example of this effect is found in the n.m.r. spectrum of the product of photochemical bromination of the ketone (3)[1] derived by hydrolysis of vinyl ether (2), *i.e.* ketone (36) [τ 4·85 (q, *exo*-3-H), 5·85 (q, *endo*-5-H), and 5·23 (q, *exo*-6-H, $J_{exo\text{-}3\text{-H}/endo\text{-}5\text{-H}}$ 0·35, $J_{exo\text{-}3\text{-H}/exo\text{-}6\text{-H}}$ 0·5, $J_{endo\text{-}5\text{-H}/exo\text{-}6\text{-H}}$ 4·8 Hz)]. In this connexion the norbornenone (3) does not add bromine in the dark at all rapidly, and its photochemical chlorination yields the decachloroketone (38) as well as the nonachloroketone (37).



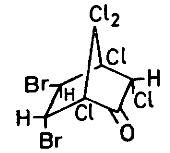
(32)



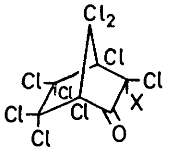
(33)



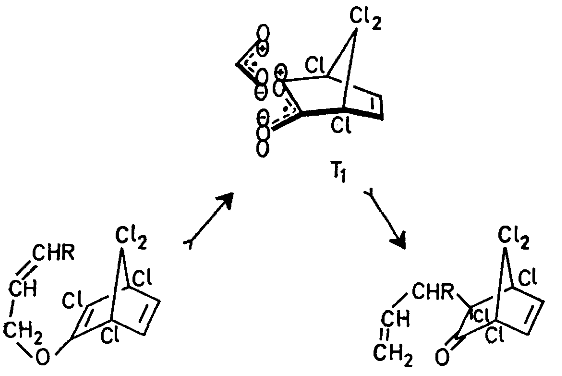
(34) X = Cl
(35) X = Hy



(36)

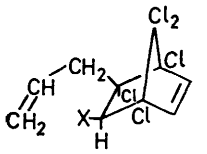


(37) X = H
(38) X = Cl

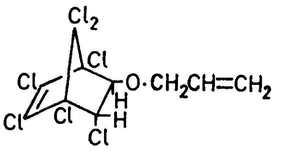


(39) R = H
(43) R = Me

(40) R = H
(44) R = Me



(41) X = OH
(42) X = O·SO$_2$Me



(45)

Section D. The Reaction of Hexachloronorbornadiene (1) *with Sodium Allyloxide and Related Unsaturated Bases.*—Experiments in which hexachlorodiene (1) was treated with a solution of sodium allyloxide in allyl alcohol with and without various aprotic dipolar cosolvents indicated that besides the expected vinyl ether product a ketone had also formed.[24] In similar experiments with 2 : 1 DMSO–allyl alcohol at 20—25°, column chromatography of the crude product gives a liquid fraction, vinyl ether (39) [$\nu_{max.}$ 1640vs cm^{-1} (ROC=CCl)] and crystalline pentachloropropenylnorbornenone (40) [$\nu_{max.}$ 1780vs cm^{-1} (α-chloro-CO), τ 3·59 (q, HC=CH), 4·15 (m, =CH), 4·82 (m, =CH$_2$), and 7·28 (m, CH$_2$CH=)]. The structure of the vinyl ether (39) follows from its rapid hydrolysis to the known[1] pentachloronorbornenone (3) in sulphuric acid. Hexachloronorbornene undergoes similar vinylic chlorine substitution giving 5,6-dihydro-(39) which however rearranges rapidly only on heating at *ca.* 120° to give a propenylnorbornanone, dihydro-(40), indicating that at least one factor in the unusually ready rearrangement of allyl vinyl ether (39) is the ring strain inherent in the norbornadiene. The stereochemistry[25] of ketone (40) is assigned on the basis of the strong preference for *exo*-face-edge approach in additions to norbornenes,[7,9] in reactions which do not require the intermediacy of a small-ring bridged species; the reduced torsional[8] requirements expected for *exo*-rearrangement also point to structure (40) as being the most likely of the two alternatives. In addition the mesylate of the *exo*-alcohol presumed on the basis of analogy to be formed in the reduction of the ketone with lithium aluminium hydride, shows no tendency to form cyclised products with this same reducing reagent, whereas the *endo*-propenyl isomer might be expected on the grounds of precedent to participate in reductive ring closure.[26,27] The mesylate of the *exo*-alcohol is also rather inert under solvolytic conditions. Further evidence for the stereochemistry of ketone (40) comes from the greater reluctance of γ-substituted analogues of vinyl ether (39) to rearrange into ketones. In the successful cases studied, such as reaction of diene (1) with but-2-enyloxy anion the yield of the initial vinyl ethers themselves is also much reduced (5—20%) compared to the reaction with

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[22] C. H. M. Adams and K. Mackenzie, *J. Chem. Soc.* (*C*), 1969, 480.

[23] J. E. Baldwin and R. K. Pinschmidt, *J. Amer. Chem. Soc.*, 1970, **92**, 5247. For other unusual long-range and virtual couplings in this system see M. E. Freeburger, R. E. Buckles, and J. K. Stille, *Tetrahedron Letters*, 1968, 431; for a summary of ^4J and ^5J couplings see K. Tori and M. Ohtsuru, *Chem. Comm.*, 1966, 886.

[24] K. Mackenzie, unpublished work; *cf.* K. Brack and H. Schinz, *Helv. Chim. Acta*, 1951, **34**, 2006.

[25] E. N. Marvell, J. L. Stephenson, and J. Ong, *J. Amer. Chem. Soc.*, 1965, **87**, 1267; R. Hoffmann and R. B. Woodward, *ibid.*, p. 4389; *cf.* W. von E. Doering and W. R. Roth, *Angew. Chew. Internat. Edn.*, 1963, **2**, 115; A. Jefferson and F. Scheinmann, *Quart. Rev.*, 1968, **22**, 391.

[26] *Cf.* L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 1675; D. S. Noyce and D. B. Denny, *ibid.*, 1950, **72**, 5743. For a discussion on this point see ref. 15.

[27] See, for example, M. Eakin, J. Martin, and N. Parker, *Chem. Comm.*, 1965, 206.

allyloxy anion (estimated initial yield of vinyl ether *ca.* 65%) and significantly higher temperatures are required to initiate rapid Claisen rearrangement (70—80°). Completing the γ-methylated allyloxy series, by extreme contrast 3,3-dimethylallyloxy anion appears to be completely inert in reactions with diene (1), reflecting inhibition to nucleophilic attack with increased bulk of the nucleophile.

Relatively few low temperature [3,3] sigmatropic rearrangements of the Claisen type are known [28] signalling ground-state ring strain, as already evident, and a lowered transition state energy, on account of terminal chlorination of the biradical-like transition complex, thus providing a particularly favourable energy profile for the reaction. The preference for exocyclic rather than endocyclic double bonds sometimes evident in norbornane compounds [29] could also be invoked as an additional factor lowering the energy barrier to be traversed *via* transition state T_1.

In a brief examination of the reactions of hepta- and octa-chlorodienes (5) and (8) with allylic alkenoxides, we find that the former gives mainly the product of *exo-cis* addition of allyl alcohol, compound (45), [*trans* ring protons, τ 5·39 (d, *exo*-5-H) and 6·10 (d, *endo*-6-H, *J* 3 Hz)] and this observation serves to show that any steric inhibition to the *exo*-rearrangement of compound (39) as implied in transition state T_1 is likely to be unimportant. Diene (10) also reacts with allyloxy anion to give small yields of divinylic ethers which quickly transform into carbonyl compounds at ambient temperature, but the products have not been investigated.*

EXPERIMENTAL

^{1}H N.m.r. data for solutions in deuteriochloroform or carbon tetrachloride with tetramethylsilane as internal standard were obtained with a Varian HA100 or A60 instrument. I.r. data were obtained with Unicam SP 200 or Perkin-Elmer 257 instruments for thin films or solutions in carbon tetrachloride or chloroform. Mass spectra were obtained with an AEI-GEC MS 902 mass spectrometer; all ions mentioned had the correct halogen isotopic abundances. Alumina for chromatography refers to 'Woelm' activity grade 1 neutral alumina; silicic acid refers to 'SilicaR' grade CC4 phase, and silica gel refers to Davison preparation. M.p.s are not corrected.

Section A. Halogenonorborndienes.—1,2,3,4,7,7-*Hexachloronorbornadiene* (1). Hexachlorocyclopentadiene (273 g, 1 mol) was heated at 165—175° whilst vinyl chloride was bubbled through the liquid until the correct increase in weight had occurred (18 h). The crude product was cooled at 0—5° overnight and then pressed dry on a sinter funnel to give 1,2,3,4,*endo*-5,7,7-heptachloronorbornene (236 g, 70%). The product (167·7 g, 0·5 mol) was added to a solution of potassium hydroxide (84 g, 1·5 mol) in isopropanol (500 ml) and the mixture was stirred and heated at 75° for 6 h, evaporated to one-third bulk and tipped into water (500 ml). The organic phase was extracted with ether, the extracts were washed, dried, and evaporated, and the oily product was distilled to give hexachloronorbornadiene (1) (93 g, 62%), b.p. 118—120° at 0·1 mmHg, n_D^{20} 1·5512, $\nu_{max.}$ 1609vs, 1093vs, and 753vs cm^{-1}. In a similar experiment using ethanol as solvent pure 2-ethoxy-1,3,4,7,7-pentachloronorbornadiene (2) [1] (*ca.* 10%) appeared in the later fractions after cutting lower boiling material as pure (1) (*ca.* 70%). Use of t-butanol as solvent did not give vinylic ether by-product but resulted in lower yields of diene (1) (*cf.* ref. 30).

1,2,3,4,cis-endo-5,6,7,7-*Octachloronorborn*-2-*ene* (4). Hexachlorocyclopentadiene (27·3 g, 0·1 mol) was heated in a sealed tube with *trans*-dichloroethylene (29·1 g, 0·3 mol) at 165° for 48 h. Excess of dichloroethylene was distilled off and the residual oil was left at 0—5° for 24 h giving crystalline adduct (4) (24 g, 65%), m.p. 177—180°, $\nu_{max.}$ 1610vs, 1273vs, 728vs, and 680vs cm^{-1}, τ 5·07(s). In a similar experiment using molar proportions of diene and olefin heated at *ca.* 140° the product was a mixture of adduct (4), and the *trans*-isomer, τ 5·20(d) and 5·80 (d, *exo*-5- and *endo*-6-H), in the ratio 2 : 1.

In an alternative preparation, hexachloronorbornadiene (1) (50 g, 0·167 mol) was dissolved in carbon tetrachloride (350 ml) and chlorine was bubbled through the solution for 3 h. Vacuum evaporation of solvent gave a quantitative yield (61 g) of the crystalline octachloronorbornene (4), m.p. 178—180° (Found: C, 22·95; H, 0·6. Calc. for $C_7H_2Cl_8$: C, 22·75; H, 0·55%).

1,2,3,4,5,7,7-*Heptachloronorbornadiene* (5). Octachloronorbornene (4) (370 g, 1 mol) was dissolved in t-butanol (1 l) containing potassium hydroxide (168 g, 3·0 mol) and the solution was heated and stirred at 60° for 5 h. The mixture was tipped into water and the organic product was extracted with n-pentane (3 × 500 ml); the extracts were washed, dried, and evaporated and the crude oily product was chromatographed on alumina in light petroleum (b.p. 40—60°) to give 1,2,3,4,5,7,7-*heptachloronorbornadiene* (5) (211 g, 63%), b.p. 74—77° at 0·3 mmHg, n_D^{16} 1·5640, $\nu_{max.}$ 1608vs, 1580vs (ClC=CCl and ClC=CH) 1148vs, 1102vs, and 707vs cm^{-1}, τ 3·43 (s, HC=CCl) (Found: C, 25·05; H, 0·15. C_7HCl_7 requires C, 25·2; H, 0·3%).

Addition of sulphur trioxide to heptachloronorbornadiene (5). The heptachlorodiene (3·84 g, 11·5 mmol) was added to a mixture of 30% oleum (6 ml), sulpholan (6 ml), and methanol (1 ml); the solution turned deep red and after *ca.* 30 min solid separated; this, filtered off and recrystallised from methanol gave 1,2,4,5,6,7,7-*heptachlorotricyclo*-[2,2,1,$0^{2,6}$]*heptane*-endo-3,5-*sultone* (4·16 g, 87%), m.p. 195—196°, $\nu_{max.}$ 1415vs (O·SO·O), 1237vs, and 873vs cm^{-1}, τ 5·43(s) (Found: C, 20·35; H, 0·25. $C_7HCl_7O_3S$ requires C, 20·35; H, 0·25%) [hexachlorodiene (1) had previously been shown to react with oleum [31]].

1,2,3,4,5,5,endo-6,7,7-*Nonachloronorborn*-2-*ene* (6). Heptachloronorbornadiene (5) (49·7 g, 0·148 mol) was dissolved in carbon tetrachloride (200 ml) and chlorine was bubbled through the solution for 3 h. Removal of the solvent *in vacuo* left a crystalline solid containing 1,2,3,4,5,5,*endo*-6,7,7-nonachloronorborn-2-ene (6) and the *exo*-6-chloro-isomer in the ratio 10 : 1, m.p. 190—200°, $\nu_{max.}$ 1618vs (ClC=CCl) 1170vs, 782vs, and 642vs cm^{-1},

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* An ion-pair mechanism has been suggested for certain instances of the Claisen–Cope rearrangement (D. C. Wigfield, S. Feiner, and K. Taymaz, *Tetrahedron Letters*, 1972, 891): this possibility is clearly relevant in the present cases.

[28] S. F. Reed, *J. Org. Chem.*, 1965, **30**, 1663.

[29] W. B. Lawson and W. J. Baily, *J. Amer. Chem. Soc.*, 1955, **77**, 1606; K. Alder and R. Grell, *Ber.*, 1956, **89**, 2198; H. Krieger, K. Manninen, and J. Paasivirta, *Soumen Kem.*, 1966, **39***B*, 8; M. J. Maskurnik, *Tetrahedron Letters*, 1972, 1797.

[30] H. Bluestone, U.S.P. 2,676,132/1954; 2,925,445/1960.

[31] E. D. Weil, *J. Org. Chem.*, 1964, **29**, 1110.

τ 4·74 (s, *exo*-6-H) and 5·15 (s, *endo*-6-H) (Found: C, 21·1; H, 0·15. Calc. for C_7HCl_9: C, 20·8; H, 0·25%). The mixed product was used in the following experiment.

1,2,3,4,5,6,7,7-*Octachloronorbornadiene* (8). The mixed product from the previous experiment (59 g, 0·146 mol) was dehydrohalogenated as for octachloronorbornene (4) (above). The brown crystalline product, chromatographed on alumina (250 g) in light petroleum (b.p. 30—40°) gave pure 1,2,3,4,5,6,7,7-octachloronorbornadiene (8) (43 g, 89%), m.p. 90—91° (lit., 88·5°), $\nu_{max.}$ 1608vs, 1586vs (ClC=CCl, coupled oscillator?), 1143vs, 1096vs, 902vs, and 704vs cm^{-1}, *m/e* 364 ($C_7Cl_8^{+\cdot}$) (Found: C, 22·9; H, 0·0. Calc. for C_7Cl_8: C, 22·85; H, 0·0%).

Bromination of hexachloronorbornadiene (1). Hexachlorodiene (1) (100 g, 0·33 mol) was dissolved in chloroform (600 ml) and bromine (20 ml, 0·375 mol) was added, the solution stirred for 3 h and then evaporated to give a 3 : 1 mixture of the *trans*-dibromo- and *cis*-dibromo-adducts (9) (151 g, 98%), $\nu_{max.}$ 1605vs, 1236vs, and 1201vs cm^{-1}, τ 5·06 (s, *cis-endo*-dibromo-adduct), 5·15 (d, 1H), and 5·72 (d, 1H, *J* 4·1 Hz, *exo*- and *endo*-H of *trans*-adduct). The *cis-endo*-dibromo-adduct was also prepared by heating hexachlorocyclopentadiene (82 g, 0·3 mol) with *cis*-dibromoethylene (144 g, 0·9 mol) in sealed tubes at 165° for 48 h. Evaporation of the mixture and cooling of the dark oily product gave *cis-endo*-5,6-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene (9) (85 g, 65%), m.p. 209—210°, $\nu_{max.}$ 1605vs, 1236vs, 855vs, 710vs, and 675vs cm^{-1}, τ 5·06 (s, *cis-exo*-5,6-H) (Found: C, 18·1; H, 0·4. Calc. for $C_7H_2Br_2Cl_6$: C, 18·35; H, 0·4%).

Bromination of heptachloronorbornadiene (5). Heptachlorodiene (5) (3·33 g, 0·01 mol) was dissolved in carbon tetrachloride (25 ml) to which bromine (2·4 g, 0·015 mol) had been added; the solution was stood in the dark for 24 h. Solvent and excess of bromine were stripped off *in vacuo* leaving a white solid consisting of *cis-endo*- and *trans*-5,6-dibromo-1,2,3,4,5,7,7-heptachloronorborn-2-ene (4·68 g, 95%), m.p. 260—264°, $\nu_{max.}$ 1609vs (ClC=CCl) 1236vs, 1168vs, 921vs, and 662vs cm^{-1}, τ 4·57 (s, *exo*-6-H) and 4·77 (s, *endo*-6-H) (Found: C, 17·1; H, 0·2. Calc. for $C_7HBr_2Cl_7$: C, 17·05, H, 0·25%).

Bromohexachloronorbornadiene (10). *cis-endo*-Dibromohexachloronorbornene (9) (62·0 g, 0·135 mol) was dehydrobrominated at 50° as for *e.g.* (4). The product was isolated in the usual manner and chromatographed on alumina in light petroleum (b.p. 40—60°) to give after distillation 5-*bromo*-1,2,3,4,7,7-*hexachloronorbornadiene* (10) (38 g, 74%), b.p. 90° at 0·2 mmHg, $\nu_{max.}$ 1606vs (ClC=CCl), 1567vs (BrC=CH), 1210vs, 1150vs, 994vs, and 703vs cm^{-1}, τ 3·25 (s, HC=CBr) (Found: C, 22·45; H, 0·45. C_7HBrCl_6 requires C, 22·25; H, 0·2%).

Tribromohexachloronorbornene (11). Bromohexachloronorbornadiene (10) (5 g, 0·013 mol) was treated with bromine (4·6 g, 0·03 mol) in carbon tetrachloride (50 ml) during 12 h. Removal of the solvent *in vacuo* left 5,5,endo-6-*tribromo*-1,2,3,4,7,7-*hexachloronorborn*-2-*ene* (11) (7 g, *ca.* 100%), m.p. 234—236°, $\nu_{max.}$ 1608vs (ClC=CCl), 1255vs, 1164vs, 1063vs, 674vs, and 642 cm^{-1}, τ 4·64 (s, *exo*-6-H) (Found: C, 15·75; H, 0·2. $C_7HBr_3Cl_6$ requires C, 15·65; H, 0·2%).

Dibromohexachloronorbornadiene (12). The product of the previous experiment (5·38 g, 0·01 mol) was dehydrohalogenated in t-butanol as above. The solution was filtered and the filtrate cooled; 2,3-dibromo-1,4,5,6,7,7-hexachloronorbornadiene (12) crystallised and was filtered off (4·2 g, 89%), m.p. 99—100° (lit., 100·5°), $\nu_{max.}$ 1608vs (ClC=CCl), 1576vs (BrC=CBr), 1098vs, 901vs, and 702vs cm^{-1} (Found: C, 18·45; H, 0·0. Calc. for $C_7Br_2Cl_6$: C, 18·4; H, 0·0%).

Photochemical halogenation of hexachloronorbornadiene (1). Chlorine was bubbled through a solution of the hexachlorodiene (1) (12 g, 0·04 mol) in methylene chloride (180 ml) contained in a silica vessel, irradiated meanwhile for 5 h with light from a high pressure mercury arc. Solvent was evaporated and a portion (1 g) of the resulting crystalline product (14·5 g, 98%) was chromatographed over silicic acid in light petroleum (b.p. 30—40°) giving separation of 1,2,3,4,*endo*-5,6,6,7,7-nonachloronorborn-2-ene (35%), $\nu_{max.}$ 1617vs (ClC=CCl), 1122vs, 1100vs, 686vs, and 644vs cm^{-1}, τ 4·76 (s, *exo*-5-H) but not of the other products, *viz.* 1,2,3,4,*cis-exo*-5,6,7,7-octachloronorborn-2-ene, τ 5·89(s), (15%) and 2,3,4,5,5,6,6,*syn*-7-octachloronorborn-2-ene, τ 5·26 (d, 1H, *anti*-7-H) and 6·18 (d, 1H, 1-H, *J* 2·3 Hz), (50%).

In a similar experiment the hexachlorodiene (1) (12 g, 0·04 mol) dissolved in methylene chloride (750 ml) was treated with bromine (7·0 g, 0·044 mol) whilst the solution was irradiated with mercury arc light; similar work up gave endo-6,syn-7-*dibromo*-2,3,4,5,5,exo-6-*hexachloronorborn-2-ene* (14) (4·2 g, 23%), m.p. 198—199°, $\nu_{max.}$ 1621vs (ClC=CCl), 1272vs, 1152vs, and 1056vs cm^{-1}, τ 5·12 (d, 1H, *anti*-7-H) 6·05 (d, 1H, 1-H, *J* 2·2 Hz) (Found: C, 18·0; H, 0·25. $C_7H_2Br_2Cl_6$ requires C, 18·35; H, 0·4%). N.m.r. signals indicated additional products as the known *cis-endo*-5,6-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene (22%), the *trans*-5,6-dibromo-isomer (44%), and also *cis-exo*-5,6-dibromo-1,2,3,4,7,7-hexachloronorborn-2-ene (11%), $\nu_{max.}$ 1606vs (ClC=CCl), 1264vs, 920vs, and 636vs cm^{-1}, τ 5·62(s). The latter *cis-exo*-dibromo-compound isolated in the crude state and treated with potassium t-butoxide in t-butanol gave bromohexachloronorbornadiene (10) identical with the compound described above.

syn-7-*Bromo*-1,2,3,5,6-*pentachloronorbornadiene* (15). *endo*-6,*syn*-7-Dibromo-2,3,4,5,5,*exo*-6-hexachloronorborn-2-ene (14) (920 mg, 2 mmol) was dissolved in ethanol (2 ml) and potassium hydroxide (340 mg, 6 mmol) was added; the solution was heated at 50° for 3 h, and the product was isolated in the usual way. Alumina chromatography of the crude product gave syn-7-*bromo*-1,2,3,5,6-*pentachloronorbornadiene* (15) (410 mg, 60%), m.p. 96—97°, $\nu_{max.}$ 1618vs (ClC=CCl), 1596vs (ClC=CCl, coupled oscillator?), 1240vs, 1159vs, 682vs, and 656vs cm^{-1}, τ 5·16 (d, 1H, 7-H) and 6·38 (d, 1H, 4-H, *J* 2·3 Hz), *m/e* 340 ($C_7H_2Cl_5Br^{+\cdot}$) (Found: C, 24·65; H, 0·45. $C_7H_2BrCl_5$ requires C, 24·5; H, 0·3%).

Sections B and C. Addition and Substitution Reactions of Polyhalogenonorbornadienes and the Hydrolysis of Derived Alkyl Vinyl Ethers.—Numerous experiments were carried out in which hexachlorodiene (1) was treated with ethanolic sodium ethoxide in the presence of dimethylformamide, dimethyl sulphoxide, or hexamethylphosphoramide as dipolar aprotic solvent additive. The following method gave excellent yields of ethyl vinyl ether (2).

Sodium (2·3 g, 0·1 g-atom) was dissolved in ethanol (15 ml) and the solution was added to a solution of hexachlorodiene (1) (15 g, 0·05 mol) in DMSO (30 ml) with stirring during 0·5 h. A mildly exothermic reaction ensued and when this had subsided (temperature kept below 50°) the mixture was heated to 60° for 6 h and then quenched in brine. The dark tarry suspension was filtered through a Kieselguhr pad to remove flocculent decomposition products, the filtrate was extracted with pentane, and the extracts were bulked with ethereal washings of the filter pad. Removal of solvents and distillation of the dark brown oil gave 2-ethoxy-1,3,4,7,7-pentachloronorbornadiene (2)[1] (13·2 g, 86%), b.p. 110—112° at 0·1 mmHg. Under similar conditions of time and temperature comparable yields of vinyl ether (2) were obtained (even with potassium hydroxide as base if the proportion of aprotic dipolar solvent was increased) but the yield of vinyl ether was halved if dimethylformamide was substituted for DMSO. Increasing the proportion of the latter solvent and lengthening the reaction time to *ca.* 100 h allowed modest yields of vinyl ether (2) to be obtained at 20—25° (*e.g.* up to 60%). The still residues were not investigated, but probably contained alcohol addition products (see below).

In a similar experiment hexachlorodiene (1) (9 g, 0·03 mol) was dissolved in DMSO (15 ml) and to the solution was added potassium hydroxide (5 g, 0·09 mol) in methanol (15 ml) at 15° during 0·5 h and the solution heated at 60° for 3·5 h. The product (5·3 g) was isolated in the usual way and chromatographed on silicic acid (30 g) in light petroleum (b.p. 40—60°) giving a methanol adduct, 1,2,3,4,7,7-hexachloro-*endo*-5-methoxynorborn-2-ene, $\nu_{\text{max.}}$ 1606vs (ClC=CCl), 1097vs, 702vs, and 646vs cm^{-1}, τ 5·61 (q, *endo*-5-H), 7·14 (q, *exo*-6-H), 8·08 (q, *endo*-6-H) $J_{5\text{-H-}exo\text{-6-H}}$ 7·5, J_{gem} 12·8, and $J_{5\text{-H-}endo\text{-6-H}}$ 2·8 Hz. The expected methyl vinyl ether was also formed and had $\nu_{\text{max.}}$ 1656vs cm^{-1} (MeOC=CCl), τ 3·26(d), 3·47 (d, *J* 6·2 Hz, CH=CH), and 5·85 (s, OMe). The relative integration of n.m.r. signals gave the ratio of vinyl ether to methanol addition product as 63 : 37.

Reaction of heptachloronorbornadiene with potassium methoxide in methanol. Substitution of heptachloronorbornadiene (5) (10·2 g, 0·031 mol) in an experiment similar to that immediately preceding and separation of the products by column chromatography on silicic acid gave 1,2,3,4,endo-5,7,7-*heptachloro*-exo-6-*methoxynorborn-2-ene* (18b) (2·2 g, 20%), $\nu_{\text{max.}}$ 1607vs (ClC=CCl), 1100vs, 926vs, and 663vs cm^{-1}, τ 6·20 (d, 1H, *endo*-6-H), 5·58 (d, 1H, *exo*-5-H, *J* 2·8 Hz), and 6·40 (s, 3H, OMe) (Found: C, 26·25; H, 1·45. $C_8H_5Cl_7O$ requires C, 26·3; H, 1·4%) and 1,3,4,7,7-*pentachloro*-2,5-*dimethoxynorbornadiene* (23) (3·2 g, 29%) (ratio adduct : diether 7 : 10), $\nu_{\text{max.}}$ 1656vs (ClC=COMe), 1635vs (HC=COMe), 1301vs, 848vs, and 798vs cm^{-1}, τ 3·64 (s, 1H, HC=COMe), 5·90 (s, 3H, OMe), and 6·24 (s, 3H, OMe) (Found: C, 33·3; H, 2·0. $C_9H_7Cl_5O_2$ requires C, 33·3; H, 2·15%).

In some experiments evidence for the formation of a methanol adduct of the hexachloromonomethyl ether (17) was adduced from the appearance of n.m.r. signals at τ 6·2 (s, OMe, sat. ether), 6·1 (d, CHOMe), 5·4 (d, CHCl), and 5·87 (s, MeOC=CCl).

In a similar experiment to the above but omitting DMSO, a monovinyl ether 1,3,4,5,7,7-*hexachloro*-2-*methoxynorbornadiene* (17) (7·3 g, 80%), $\nu_{\text{max.}}$ 1653vs (MeOC=CCl), 1580vs (HC=CCl), 1275vs, and 768vs cm^{-1}, τ 3·52 (s, 1H, 6-H) and 5·98 (s, 3H, OMe), *m/e* 326 ($C_8H_4Cl_6O$ requires 326), was obtained.

Reaction of octachloronorbornadiene (8) *with potassium methoxide in methanol.* The octachlorodiene (8) (11·0 g, 0·03 mol) dissolved in methanol (10 ml) was treated at 45° with a solution of potassium hydroxide (5 g, 0·091 mol) in methanol (20 ml) for 24 h. Work-up in the usual way gave a mixed product (5·9 g); a portion of the product (2 g) was chromatographed on silicic acid (40 g) in light petroleum (b.p. 40—60°) to give 1,3,4,5,6,7,7-*heptachloro*-2-*methoxynorbornadiene* (19) (1·75 g, 89% of recovered product), m.p. 33—34°, $\nu_{\text{max.}}$ 1656vs (MeOC=CCl), 1610vs (ClC=CCl), 1101vs, and 698vs cm^{-1}, τ 5·85 (s, OMe), *m/e* 360 ($M^{+\cdot}$) (Found: C, 26·6; H, 0·7. $C_8H_3Cl_7O$ requires C, 26·45; H, 0·85%). Other products isolated were a mixture of 1,3,4,5,7,7-hexachloro-2,6-dimethoxy- and 1,3,4,6,7,7-hexachloro-2,5-dimethoxy-norbornadienes (20) and (21) (145 mg, 7·5% of product) and 1,2,3,4,*endo*-5,7,7-heptachloro-6,6-dimethoxynorborn-2-ene (22) (177 mg, 3% of product) (see below).

Hydrolysis of heptachloromethoxynorbornadiene (19). The vinyl ether (19) was further characterised by its hydrolysis. The vinylic ether (500 mg) was dissolved in a little sulphuric acid and the solution was left at 25° for 6 h then poured onto ice and the product was isolated by ether extraction and chromatography on silicic acid to give 1,3,4,5,6,7,7-*heptachloronorborn-5-en-2-one* (200 mg, 42%), m.p. 103—106°, $\nu_{\text{max.}}$ 1801vs (α-chloro-CO), 1601vs (ClC=CCl), 1164vs, and 669vs cm^{-1}, τ 5·20(s) (Found: C, 24·25; H, 0·5. C_7HCl_7O requires C, 24·05; H, 0·3%).

Reaction of octachloronorbornadiene (8) *with potassium methoxide in methanol–dimethyl sulphoxide.* Octachlorodiene (8) (3·68 g, 0·01 mol) was dissolved in DMSO (50 ml) and mixed at 10° during 1 h with a solution of potassium hydroxide (1·96 g, 0·035 mol). The temperature was allowed to rise to 40° and after 2 h the mixture was quenched in water and the organic product isolated in the usual way. A portion of the mixed product (1 g) was chromatographed on silicic acid (40 g) as before giving monoether (19) (60 mg, 6%) and an equimolar mixture of the divinylic ethers (20) and (21) (790 mg, 79%), m.p. 64—66°, $\nu_{\text{max.}}$ 1662vs (MeOC=CCl) (21) and 1645vs (ClC=COMe) (20), 1263vs, 1108vs, and 896vs cm^{-1}, τ 5·86(s) and 5·87(s) respectively (MeO, ratio 1 : 1), *m/e* 356 ($M^{+\cdot}$) (Found: C, 30·4; H, 1·65. Calc. for $C_9H_6Cl_6O_2$: C, 30·1; H, 1·65%). The diethers were correlated with respective i.r. and n.m.r. signals by their selective partial hydrolysis (see below) and by the isolation of hexachloronorbornane-2,5-dione (30) from diether (21). A further chromatographic eluent (150 mg, 15%) contained the acetal (22) 1,2,3,4,*endo*-5,7,7-heptachloro-6,6-dimethoxynorborn-2-ene, τ 6·50(s) and 6·62(s) (2 MeO, non-vinylic) and 5·33 (s, *exo*-5-H), *m/e* 392 ($C_9H_7Cl_7O_2{}^{+\cdot}$), 357 ($C_9H_7Cl_6O_2{}^{+\cdot}$), and 122 [intense, $CHCl{=}C(OMe)_2{}^{+\cdot}$].

Hydrolysis experiments with the diethers (20) *and* (21). 1,3,4,6,7,7-*Hexachloronorbornane*-2,5-*dione* (30). The mixture of diethers (3·5 g) was stirred in conc. sulphuric (*ca.* 20 ml) at 25° for 4·5 h. The mixture was tipped into ice and the products isolated by ether extraction in the usual way, the extracts evaporated and the crude solid product was chromatographed on silicic acid to give 1,3,4,6,7,7-*hexachloronorbornane*-2,5-*dione* (30) (1 g, 31%), m.p. 149—150°, $\nu_{\text{max.}}$ 2960vs, 1803vs (α-chloro-CO), 1068vs, 945vs, 891vs, and 858vs cm^{-1}, τ 5·21(s) (Found: C, 25·4; H, 0·7. $C_7H_2Cl_6O_2$ requires C, 25·4; H, 0·6%). A second eluent from the column comprised a red oil which rapidly decomposed to a tar; initial $\nu_{\text{max.}}$ 1755vs, 1740vs, and 1604vs cm^{-1}. This product was not further characterised.

Differential hydrolysis of the mixed diethers (20) *and* (21). Numerous experiments were carried out to determine if either of the divinyl ethers could be selectively destroyed. In typical experiments the diene mixture (200—500 mg) in carbon tetrachloride (4—8 ml) was stirred with conc. sulphuric acid (4—8 ml) whilst the composition of the organic phase was monitored by i.r. and n.m.r. absorption.

The initially strong i.r. vinyl ether band at 1662 cm^{-1} decreased in intensity as a new intense peak at 1805—1810 cm^{-1} appeared characteristic of diketone (30), together with a sharp band at 2960 cm^{-1}. In the n.m.r. spectrum the vinyl ether methoxy-peak at τ 5·86 declined in intensity and among other peaks a signal at τ 5·20 characteristic of (30) appeared. Chromatography of the mixed products demonstrated that the diketone (30) was separable from the ethers. Similar experiments were carried out using hydrogen bromide in wet ether, and i.r. monitoring indicated that the initially strong band at 1645 cm^{-1} in the mixture of diethers diminished in intensity as a new band appeared at 1770—1780 cm^{-1}. In the n.m.r. the sharp vinylic methoxy-singlet at τ 5·87 declined in intensity as a number of other signals appeared; but if dry methanol was used instead of wet ether in similar experiments, these n.m.r. effects were not accompanied by the appearance of carbonyl absorption. Chromatography of the products of a number of acidic methanolyses gave a crystalline solid which appeared to consist of γ-diether (21) together with a methanol adduct of divinylic ether (20), and smaller amounts of a similar adduct of diether (21). Consistent with this the mass spectra of fractions showing n.m.r. signals attributable to methanol adducts exhibited ions at *m/e* 388 ($C_{10}H_{10}Cl_6O_3$), 353 ($C_{10}H_{10}Cl_5O_3$), 266 (C_5Cl_5OMe, retrodiene fragment), 231 (C_5Cl_4OMe), and 122 [retrodiene fragment, $CHCl{:}C(OMe)_2$]. Sulphuric acid hydrolysis of this mixed product gave a mixture of carbonyl compounds which was shown to contain diketone (30).

T.l.c. experiments had demonstrated the presence of the two vinylic diethers (20) and (21) in crystalline samples of the mixture obtained by cooling crude reaction product from reactions of diene (8) with methoxide ion, but the two spots ran very close together and partially overlapped.

The reaction of monobromohexachloronorbornadiene (10) *with potassium ethoxide in ethanol–dimethyl sulphoxide*. The monobromohexachlorodiene (10) (2·05 g, 5·4 mmol) was dissolved in dimethyl sulphoxide (4·5 ml) and a solution of potassium hydroxide (1·2 g, 21 mmol) in ethanol (4·5 ml) was added with external cooling; the solution was stirred at 60° for 3 h and the product was isolated in the usual way. Distillation gave 1,3,4,7,7-pentachloro-2,5-diethoxynorbornadiene (26) (1·44 g, 75%), b.p. 139—141° at 1·5 mmHg, $\nu_{max.}$ 1650vs (EtOC=CCl), 1624vs (EtOC=CH), 880vs, and 765vs cm^{-1}, τ 3·85 (s, HC=COEt), 6·07 (m, 2 CH_2), and 8·75 (m, 2 CH_3), *m/e* 350 ($C_{11}H_{11}Cl_5O_2^{+\cdot}$). The diether was characterised by its hydrolysis, giving after crystallisation from methanol 1,3,4,7,7-*pentachloronorbornane*-2,5-*dione* (30; X = H), m.p. 122—124°, $\nu_{max.}$ 1795vs (α-chloro-CO), 1410vs ($COCH_2$), 1063vs, and 682vs cm^{-1}, τ 5·25 (d, *exo*-3-H), 6·81 (q, *exo*-6-H, $J_{exo\text{-}3\text{-}H/exo\text{-}6\text{-}H}$ 0·6 Hz), and 7·09 (d, *endo*-6-H, J_{gem} 19·6 Hz), *m/e* 294 ($C_7H_3Cl_5O_2^{+\cdot}$) (Found: C, 28·6; H, 0·95. $C_7H_3Cl_5O_2$ requires C, 28·35; H, 1·0%).

The same diketone (30; X = H) was obtained by similar hydrolysis of pentachlorodimethoxynorbornadiene (23) (above), with identical m.p. and mixed m.p.

1,4,7,7-*Tetrachloronorbornane*-2,5-*dione* (33). Pentachloronorbornane-2,5-dione (30; X = H) (500 mg, 1·7 mmol) was dissolved in acetic acid (5 ml) and zinc dust (300 mg, 4·5 mg-atom) was added; the mixture was heated and stirred for 4 h. The cooled, filtered solution was tipped into water and the crystalline product which precipitated was filtered off; this, recrystallised from methanol gave 1,4,7,7-*tetrachloronorbornane*-2,5-*dione* (33) (200 mg, 45%), m.p. 102—103°, $\nu_{max.}$ 1787vs (α-chloro-CO), 1408vs, 1074vs, and 1018vs cm^{-1}, τ 7·08(d) 6·72(d) [*endo*-2(6)-H, *exo*-2(6)-H, J_{gem} 19·5 Hz] (Found: C, 32·40; H, 1·6. $C_7H_4Cl_4O_2$ requires C. 32·10; H, 1·55%).

Reaction of dibromohexachloronorbornadiene (12) *with potassium methoxide in methanol–dimethyl sulphoxide*. The hexachlorodibromodiene was treated with a solution of potassium hydroxide in methanol–DMSO exactly as for diene (8). From diene (12) (4·75 g) a mixed product (3·5 g) was obtained of which a portion (500 mg) was chromatographed on silicic acid in light petroleum (b.p. 40—60°) as before to give 5-bromo-1,3,4,7,7-pentachloro-2,6-dimethoxynorbornadiene (27) admixed with the isomeric 6-bromo-1,3,4,7,7-pentachloro-2,5-dimethoxynorbornadiene (28), m.p. 67—69°, $\nu_{max.}$ 1662vs (ClC=COMe), 1640vs (BrC=COMe), 1286vs, and 1103vs cm^{-1}, τ 5·95 (poorly resolved q for four different types of vinylic methoxy) (Found: C, 26·75; H, 1·5. Calc. for $C_9H_6BrCl_5O_2$: C, 26·8; H, 1·5%).

3-*Bromo*-1,4,6,7,7-*pentachloronorbornane*-2,5-*dione* (31). The mixed diethers from the previous experiment (1 g) was stirred with conc. sulphuric acid (10 ml) for 3 h and the mixture was poured onto ice; the product was extracted into ether which on evaporation gave a red oil. The crude product was chromatographed on silicic acid in light petroleum (b.p. 30—40°) to give endo-3-*bromo*-1,4,endo-6,7,7-*pentachloronorbornane*-2,5-*dione* (31) (200 mg, 19%), m.p. 142—143°, $\nu_{max.}$ 1813vs (α-chloro-CO), 1805 (1795 in Nujol), 1064vs, 883vs, and 677vs cm^{-1}, τ 5·10(d), 5·28(d) (*exo*-3-H and *exo*-6-H, *J* 0·6 Hz) (Found: C, 22·8; H, 0·7. $C_7H_2BrCl_5O_2$ requires C, 22·4; H, 0·5%).

The bromopentachloronorbornanedione (31) (100 mg, 0·27 mmol), treated with zinc dust as for pentachlorodiketone (30; X = H) gave on work-up by pouring into water, ether extraction, evaporation and recrystallisation of the crude product from methanol, tetrachloronorbornanedione (33) (20 mg, 28%), m.p. and mixed m.p. 102—103°, i.r. spectrum identical to that of the authentic compound.

Section D. The Reaction of Hexachloronorbornadiene (1) *with Sodium Allyloxide in Allyl Alcohol–Dimethyl Sulphoxide*. Hexachloronorbornadiene (1) (60 g, 0·2 mol) was dissolved in DMSO (180 ml) and to this a solution of sodium allyloxide, made by dissolving sodium (10 g, 0·42 g-atom) in allyl alcohol (100 ml), was added with stirring during 1 h. The exothermic reaction which ensued was controlled by the rate of mixing, the temperature being kept at *ca.* 50° for a further 4 h. Work-up in the usual manner gave crude product (44 g, 68%), $\nu_{max.}$ 1780vs, 1640vs, and 1603vs cm^{-1} (α-chloro-CO, ClC=COR, and ClC=CCl). Distillation of the product gave the following fractions (b.p. at 0·1—0·5 mmHg, yield): 87—109°, 2 g [mainly (1) and vinylic ether]; 113—116°, 15·2 g [mainly vinyl ether and (1)]; 116—118°, 11·1 g (vinyl ether and carbonyl compound); and 120—124°, 8 g (mostly ketone). The final fraction solidified, and recrystallised from petrol gave 1,3,4,7,7-*pentachloro*-exo-3-*prop*-2-*enylnorborn*-5-*en*-2-*one* (40), m.p. 84—86°, $\nu_{max.}$ 1775vs (α-chloro-CO), 1300vs, 1015vs, and 995vs cm^{-1} ($CH=CH_2$), τ 3·59 (q, 2H, CH=CH), 4·15 (m, 1H, CH=), 4·82 (m, 2H, $=CH_2$), and 7·28 (complex t, 2H, CH_2), $J_{5\text{-}H/6\text{-}H}$ 6 Hz (Found: C, 37·7; H, 2·3. $C_{10}H_7Cl_5O$ requires C, 37·5; H, 2·2%). The ketone very slowly decomposed.

In a similar experiment the crude product was purified at ambient temperature by column chromatography on alumina using light petroleum (b.p. 60—80°)–diethyl ether (ranging from 100% petroleum to 100% ether). After mixed eluents containing diene (1) and vinyl ether, a fraction containing pure propenylnorbornenone (40) was collected which on evaporation gave the crystalline ketone (10·8 g, *ca.* 17%). The mixed vinyl ether fractions were hydrolysed in conc. sulphuric acid to give (from 3·2 g) 1,3,4,7,7-pentachloronorborn-5-en-2-one (1·2 g, 43%), m.p. and mixed m.p.[1] 123—124°. The ketone absorbed hydrogen (1 mol equiv.) to give 1,3,4,7,7-pentachloronorbornan-2-one identical to an authentic specimen [1] m.p. and mixed m.p. 154° (Found: C, 30·0; H, 1·85. Calc. for $C_7H_5Cl_5O$: C, 29·8; H, 1·8%).

Propenylnorbornenone (40) absorbed hydrogen (2 mol. equiv.) over Pd–charcoal in ethanol to give 1,3,4,7,7-*pentachloro*-exo-3-*n-propylnorbornan*-2-*one*, m.p. 94—96° (Found: C, 37·0; H, 3·3. $C_{10}H_{11}Cl_5O$ requires C, 37·0; H, 3·4%).

In similar experiments with diene (1) and sodium allyloxide in which dimethylformamide replaced DMSO, samples of vinyl ether free of carbonyl component were obtained by vacuum evaporation of the crude product. Vinylic ether fractions from these and similar experiments were variously heated at 120—150°; the characteristic vinyl ether i.r. absorption at 1645 cm^{-1} diminished in intensity as an intense carbonyl band due to ketone (40) appeared and increased in intensity at 1775 cm^{-1}. A much slower rearrangement of the vinyl ether occurred at 25°.

1,3,4,7,7-*Pentachloro*-exo-3-*propenylnorborn*-5-*en*-exo-2-*ol*. The ketone (40) (6·4 g, 20 mmol) was dissolved in tetrahydrofuran (100 ml) and lithium aluminium hydride (970 mg, 30 mmol) was added as a slurry in tetrahydrofuran (50 ml) during 1 h at 65°. The mixture was heated and stirred under reflux for 5 h and then moist ether was added and the product was isolated in the usual manner to give 1,3,4,7,7-*pentachloro*-exo-3-*prop*-2-*enylnorborn*-5-*en*-exo-2-*ol* (41) (5·2 g, 81%), m.p. 94—96° (from petroleum), $\nu_{max.}$ 3400vs and 1140vs cm^{-1} (alcohol OH) (Found: C, 37·4; H, 2·75. $C_{10}H_9Cl_5O$ requires C, 37·25; H, 2·8%). Treated with methanesulphonyl chloride in benzene–pyridine solution, the alcohol (41) gave a *mesylate* (60%), m.p. 135—137°, $\nu_{max.}$ 1470vs, 1385vs, and 1360vs (O·SO$_2$), τ 3·63, 3·79 (each d, 1H, *J* 3·1 Hz, CH=CH), 4·82, 4·98 (m, 2H, =CH$_2$), 3·8—4·2 (complex m, 1H, CH=), 7·3 (complex m, 2H, CH$_2$), 5·26 (s, 1H, *endo*-2-H), and 6·88 (s, 3H, SO$_2$Me) (Found: C, 32·9; H, 2·6. $C_{11}H_{11}Cl_5O_3S$ requires C, 33·0; H, 2·7%).

The mesylate derivative of alcohol (41) was reduced with lithium aluminium hydride; the product had spectral properties consistent with it being 1,4,5,7,7-pentachloro-*exo*-5-propenylnorborn-2-ene and neither from this experiment nor from attempted solvolysis of the mesylate in aqueous organic media was any tricyclic product obtained.

1,2,4,7,7-*Pentachloro*-3-*allyloxynorborn*-2-*ene*. 1,2,3,4,7,7-Hexachloronorborn-2-ene (10 g, 0·33 mol) was dissolved in DMSO (100 ml) and a solution of sodium (1·4 g, 67 mg-atom) in allyl alcohol (50 ml) was slowly added, the mixture was stirred and heated at 45° for 24 h, and the product was isolated in the usual manner. The crude vinylic ether (7·23 g, 68%) was chromatographed on alumina in light petroleum (b.p. 40—60°), b.p. 110—112° at 0·5 mmHg, n_D^{25} 1·5371 (Found: C, 37·55; H, 3·0. $C_{10}H_9Cl_5O$ requires C, 37·55; H, 2·8%). This product, heated under nitrogen at *ca.* 120° for 8 h partially rearranged (i.r.) and crystallisation of the crude oily product from petroleum gave 1,3,4,7,7-pentachloro-*exo*-3-propenylnorbornan-2-one, m.p. and mixed m.p. 90—92°, identical to the authentic compound.

Reaction of hexachloronorbornadiene (1) *with sodium* trans-*but*-2-*enyloxide in* trans-*but*-2-*enol*–*DMSO*. In a similar experiment to that above with allyl alcohol save that the proportion of DMSO was increased to 200 ml, the crude product was extracted with n-pentane and then with ether; evaporation of the ethereal extracts and dissolution of the oily product in warm petrol gave crystalline 1,3,4,7,7-*pentachloro*-exo-3-*but*-3-*enylnorborn*-5-*en*-2-*one* (44) (8·1 g, 12%), m.p. 98—100°, $\nu_{max.}$ 1780vs cm^{-1} (Found: C, 39·5; H, 2·7. $C_{11}H_9Cl_5O$ requires C, 39·6; H, 2·7%). The n-pentane extract had $\nu_{max.}$ 1640vs cm^{-1} (ClC=COR) and carefully chromatographed on alumina in pentane gave 1,2,4,7,7-*pentachloro*-2-trans-*but*-2-*enyloxynorbornadiene* (43) (12·2 g, 18%), b.p. 126—130° at 0·1 mmHg (Found: C, 39·4; H, 2·7. $C_{11}H_9Cl_5O$ requires C, 39·6; H, 2·7%). A sample of the vinyl ether (43) heated at *ca.* 70° slowly rearranged into ketone (44), but no rearrangement occurred at 25°.

In a similar experiment to the above using 3,3-dimethylallyl alcohol [24] little or no ketonic or vinyl ether product was found.

Addition of allyl alcohol to heptachloronorbornadiene (5). The heptachlorodiene (5) (5·5 g, 17 mmol) was dissolved in DMSO (15 ml) and a solution of sodium (1 g, 40 mg-atom) in allyl alcohol (10 ml) was added to the solution of diene with external cooling; the mixture was stirred at 25° for 6 h and the product was isolated in the usual way to give an oil (3·1 g), $\nu_{max.}$ 1640vs and 1645vs (ROC=CCl), 1610, and 1585vs cm^{-1} (ClC=CCl?). Chromatography of the mixture however gave only one pure component, 1,2,3,4,endo-5,7,7-*heptachloro*-6-exo-*prop*-2-*enyloxynorborn*-2-*ene* (45) (430 mg, 14%), τ 5·39 (d, 1H, *exo*-5-H), 6·10 (d, 1H, *endo*-6-H, *J* 3·0 Hz), 5·72 (d, 2H, CH$_2$, *J* 5 Hz), 3·84—4·4 (complex m, 1H, CH=), and 4·6 and 4·83 (complex d, 1H each, *cis* and *trans* =CH$_2$) (Found: C, 30·9; H, 1·65. $C_{10}H_7Cl_7O$ requires C, 30·7; H, 1·8%).

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