Further Reactions of Nucleophiles with Some Chlorine-substituted Norbornadienes

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The reaction of 1,2,3,4,7-*syn*-pentachloronorborna-2,5-diene with ethoxide ions results in a 3:5 mixture of products derived from replacement of a vinylic chlorine atom and from addition to the unsubstituted double bond. The 7-*anti*-isomer and 1,2,3,4-tetrachloronorborna-2,5-diene afford only products of reaction at the chlorine-substituted double bond. The 5-phenyl derivatives of these dienes react with sodium methoxide in methanol to afford the products of the addition of methanol to the phenyl-substituted double bond. Reaction occurs at both double bonds when hexachloronorbornadiene is treated with sodium methanethiolate in ethanol. 5-Methylhexachloronorbornadiene is isomerised to hexachloromethylenenorbornene on treatment with sodium methoxide in methanol; with dimethylformamide as solvent further reaction occurs at the chlorine-substituted double bond of the isomerised diene. The results are interpreted in terms of a series of finely balanced factors controlling product formation.

It has been demonstrated previously [1,2] that the factors which control the site of attack by a nucleophile on a chlorine-substituted norbornadiene are very finely balanced. For example, in the case of hexachloronorbornadiene (1), sodium methanethiolate, in dimethylformamide, replaces one or both vinylic chlorine atoms with a methylthio-group; [2] in contrast sodium ethoxide in ethanol reacts both by addition of ethanol to the unsubstituted double bond and by replacement of a vinylic chlorine atom.[1b] 5-Phenylhexachloronorbornadiene (14) reacts with sodium methoxide in methanol to give exclusively the products (17) and (18) of addition of methanol to the phenyl-substituted double bond.[1b]

The work has now been extended to include the reactions of sodium ethoxide in ethanol with the dienes (2)—(4), sodium methoxide in methanol with the dienes (15), (16), and (25), sodium methoxide in dimethylformamide with the diene (25), and sodium methanethiolate in ethanol with the diene (1). The results are recorded in Tables 1—3, which also contain, for comparative purposes, our earlier [1b] results. Spectral data of products are given in Tables 4—6, and were used as the main basis of structural assignment by comparison with the spectral data [3] already in the literature. Compounds (22), (24), and (26) had properties identical with those already reported.[2,3a,4] Compounds (7) and (8) were identical with samples prepared by the Diels–Alder addition of ethyl vinyl ether to pentachlorocyclopentadiene. Compound (19) was one of the products of Diels–Alder addition of *cis*-β-methoxystyrene to pentachlorocyclopentadiene. The structures of compounds (11) and (13) were confirmed by hydrogenation to afford (29) and (30), respectively. The n.m.r. spectra of (29) and (30) exhibit a long-range W-coupling [5] [J(2-*exo*,6-*exo*); see Table 4], which confirms the *endo*-orientation of the C-2 chlorine substituent in these compounds and hence also in (11) and (13). The identification of compound (21) is based on its hydrogenolysis [6] to give compound (31), the spectral parameters of which are in Table 5.

Comparison of the reaction of hexachloronorbornadiene (1) with sodium ethoxide in ethanol [1b] with the corresponding reaction of the 7-*syn*-pentachloronorbornadiene (2) † shows that for the latter diene the percentage of product of type (C), derived from substitution of a vinylic chlorine atom, is almost half that for the former. Attack on the unsubstituted double bond in (2) leading to addition products (7) and (8) is correspondingly increased

† Throughout this paper the terms *syn* and *anti* are used to describe the orientation of C-7 substituents with respect to the chlorine-substituted double bond or the former site of this double bond, which is always numbered 2,3 to facilitate comparisons.

[1] (*a*) K. Mackenzie, *J. Chem. Soc.*, 1962, 457; C. H. M. Adams, K. Mackenzie, and P. R. Young, *J.C.S. Perkin II*, 1972, 1856; (*b*) D. R. Adams and D. I. Davies, *J.C.S. Perkin I*, 1972, 1237.

[2] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1969, 288.

[3] (*a*) J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.* (*C*), 1966, 1498, and references cited therein; (*b*) A. P. Marchand and N. W. Marchand, *Tetrahedron Letters*, 1969, 5207.

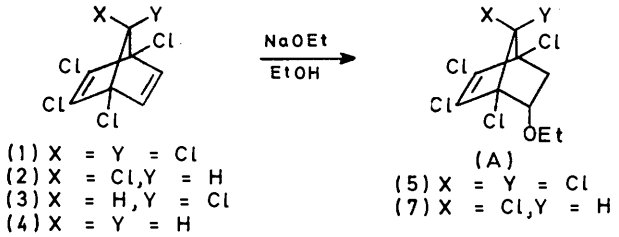
[4] C. K. Alden and D. I. Davies, *J. Chem. Soc.*, 1967, 1017.

[5] M. Barfield and B. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757.

[6] C. K. Alden and D. I. Davies, *J. Chem. Soc.* (*C*), 1968, 700.

TABLE 1

Ratios of products from the reactions of sodium ethoxide in ethanol with 1,2,3,4,7,7-hexachloronorborna-2,5-diene (1), 1,2,3,4,7-*syn*-pentachloronorborna-2,5-diene (2), 1,2,3,4,7-*anti*-pentachloronorborna-2,5-diene (3), and 1,2,3,4-tetrachloronorborna-2,5-diene (4)

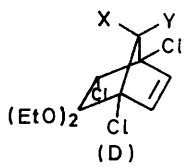


(1) X = Y = Cl
(2) X = Cl,Y = H
(3) X = H,Y = Cl
(4) X = Y = H

(A)
(5) X = Y = Cl
(7) X = Cl,Y = H

(B)
(8) X = Cl,Y = H

(C)
(6) X = Y = Cl
(9) X = Cl,Y = H
(10) X = H,Y = Cl
(12) X = Y = H



(D)

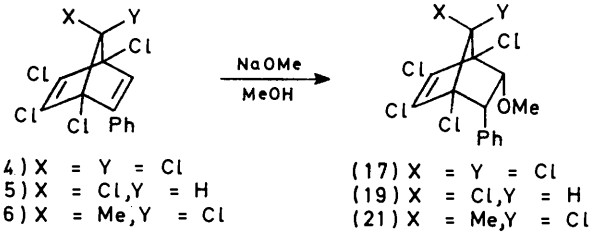
+

(11) X = H,Y = Cl
(13) X = Y = H

Starting compound	Product ratios (%) (A)	(B)	(C)	(D)
(1) [1]	26	0	74	0
(2)	24	38	38	0
(3)	0	0	45	55
(4)	0	0	43	57

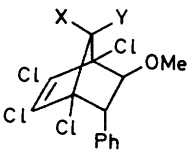
TABLE 2

Ratios of products from the reactions of sodium methoxide with 1,2,3,4,7,7-hexachloro-5-phenylnorborna-2,5-diene (14), 1,2,3,4,7-*syn*-pentachloro-5-phenylnorborna-2,5-diene (15), and 1,2,3,4,7-*anti*-pentachloro-7-*syn*-methyl-5-phenylnorborna-2,5-diene (16)



(14) X = Y = Cl
(15) X = Cl,Y = H
(16) X = Me,Y = Cl

(17) X = Y = Cl
(19) X = Cl,Y = H
(21) X = Me,Y = Cl



(18) X = Y = Cl
(20) X = Cl,Y = H

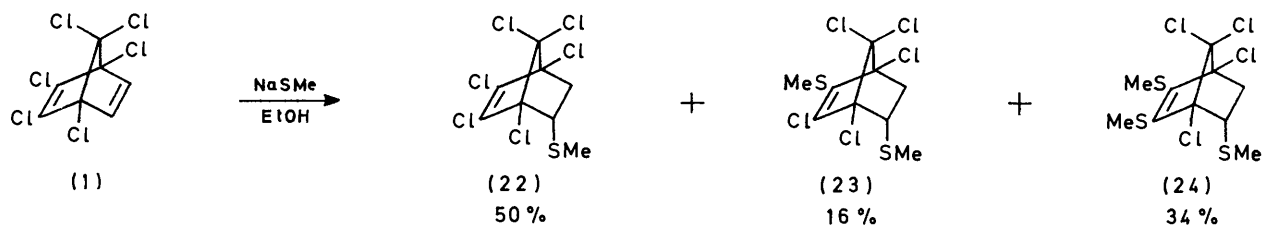
Starting compound	Product ratios (%) *cis,endo*	*trans*
(14) [1]	58	42
(15)	10	90
(16)	100	0

since in (2) there is no 7-*anti*-chlorine atom to combine with the bridgehead chlorine atoms to shield this double-bond from *exo*-approach of an ethoxide ion. *exo*-Attack on the unsubstituted double bond is favoured over *endo*-attack for this reason, and also because it involves no disadvantageous torsional strain.[7] Brown [8] has suggested, on the basis of a consideration of steric effects, that attack on a norbornene double bond should

[7] P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1967, **89**, 699, 701.
[8] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 201.

TABLE 3

Ratios of products from the reactions of sodium methanethiolate in ethanol with 1,2,3,4,7,7-hexachloronorborna-2,5-diene (1), sodium methoxide in methanol with 1,2,3,4,7,7-hexachloro-5-methylnorborna-2,5-diene (25) and sodium methoxide in dimethylformamide with the diene (25)

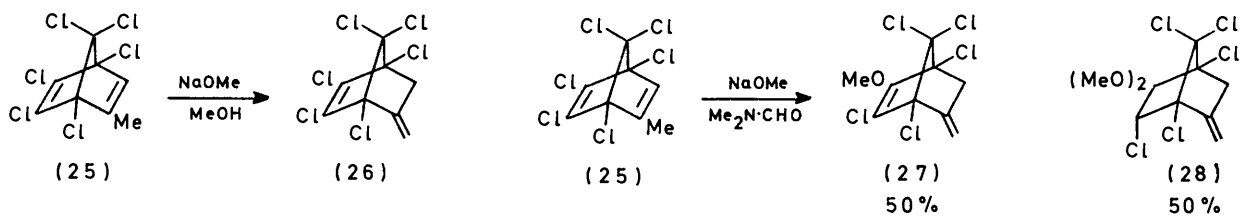


(1)

(22) 50 %

(23) 16 %

(24) 34 %



(25)

(26)

(25)

(27) 50 %

(28) 50 %

TABLE 4

N.m.r. and i.r. data for the products of the reactions of ethoxide ions with the dienes (2)—(4) and methanethiolate ions with the diene (1); details for the products of hydrogenation of (11) and (13) are included

	Chemical shifts (τ) *										Coupling constants (Hz)									
Product	5-*x*	5-*n*	6-*x*	6-*n*	7-*a*	7-*s*	2-*x*	5	6	OCH_2CH_3	OCH_2CH_3	5-*n*, 6-*n*	5-*x*, 6-*n*	6-*x*, 6-*x*	7-*a*, 7-*n*	7-*s*, 7-*n*	7-*s*, 6-*n*	2-*x*, 5-*x*	5,6	OCH_2CH_3	$\nu_{max.}$/cm^{-1} (*cis*-ClC=CX)
(7)	5·81 (q)		7·52 (q)	8·02 (q)	5·94 (s)					6·28 (m)	8·84 (t)	7·8	2·9	12·6						7·0	1603 (X = Cl)
(8) †[b]		6·30 (q)	7·41 (q)	7·96 (q)	5·36 (s)					6·30 (m)	8·78 (t)			2·6	12·4					7·0	1605 (X = Cl)
(9) †					5·46 (s)			3·19 (d)	3·35 (d)	5·60 (q)	8·62 (t)								5·5	7·0	1645 (X = OEt)
(10) ‡						5·59 (d)		3·50 (q)	3·68 (q)	5·63 (q)	8·64 (t)						(0·8)		5·0	6·8	1650 (X = OEt)
(11) ‡						5·63 (t)	5·90 (s)	4·06 (d)		6·33 (m)	8·75 (q)						(1·1)		0	7·2	
(12) †					7·03 (d)	7·23 (d)		3·24 (d)	3·41 (d)	5·62 (q)	7·62 (t)				5·0				5·0	7·0	1635 (X = OEt)
(13) †					7·45 (d)	7·58 (d)	5·91 (s)	3·92 (d)		6·36 (m)	8·78 (m)				8·5	(0·5)		0		7·25	
(22) ‡[c]	6·27 (q)		7·12 (q)	8·26 (q)								8·6	4·0	13·0							
(23) ‡[d]	6·30 (q)		7·13 (q)	8·32 (q)								8·6	4·0	12·5							1600 (X = SMe)
(24) ‡[e]	6·37 (q)		7·13 (q)	8·38 (q)								9·1	4·1	12·8							
(29) †[f]						5·86 (d)	5·94 (d)	7·46—8·02 (m)		6·16—6·59 (m)	8·76 (m)						1·0	1·8		7·0	
(30) †[f]			7·47—8·18m				5·98 (d)			6·21—6·71 (m)	8·78 (m)							1·9		7·0	

[b] $J(5n,6n)$ 7·5 Hz. [c] SMe 7·78 (s). [d] SMe 7·48 (s) and 7·70 (s). [e] SMe 7·47 (s), 7·56, and 7·43 (s). [f] In C_6D_6.
* *x* = *exo*, *n* = *endo*, *a* = *anti*, *s* = *syn*. † 100 MHz N.m.r. ‡ 60 MHz N.m.r.

TABLE 5

N.m.r. (60 MHz) and i.r. data for the products of the reactions of methoxide ions with the dienes (15) and (16) and the product (31) of hydrogenolysis of (21)

	Chemical shifts (τ)								Coupling constants (Hz)				
Product	Ph	OMe	5-*x*	6-*x*	6-*n*	7-*a*	2,3	7-Me	5-*x*, 6-*x*	5-*x*, 6-*n*	2-*x*, 6-*x*	3-*x*, 5-*x*	$\nu_{max.}$/cm^{-1} (*cis*-ClC=CCl)
(19)	2·67 (m)	6·85 (s)	5·64 (d)	6·46 (d)		5·73 (s)			7·8				1599
(20)	2·78 (m)	6·51 (s)	6·05 (d)		6·64 (d)	5·15 (s)				3·2			1603
(21)	2·76br (s)	6·88 (s)	5·77 (d)	6·41 (d)				8·24 (s)	7·6				1603
(31)	2·77br (s)	6·97 (s)	6·17br (d)	6·64br(d)		7·29—8·39br (m)		8·79br (d)					

x = *exo*, *n* = *endo*, *a* = *anti*.

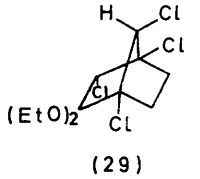
TABLE 6

N.m.r. (100 MHz) and i.r. data for the products from the reactions of methoxide ions with the diene (25)

	Chemical shifts (τ)						Coupling constants (Hz)						$\nu_{max.}$/cm^{-1} (*cis*-ClC=CX)
Product	8-*t*	8-*c*	6-*x*	6-*n*	3-*x*	OMe	6-*x*, 6-*n*	6-*x*, 8-*c*	6-*x*, 8-*t*	6-*n*, 8-*c*	6-*n*, 8-*t*	8-*c*, 8-*t*	
(26)	4·44 (sextet)	4·78 (sextet)	6·9 (octet)	7·28 (octet)			14·6	1·8	2·1	1·8	2·1	1·2	
(27)	4·56 br (t)	4·83 br (t)	7·01 (sextet)	7·31 (sextet)		5·92 (s)	14·7	2·2	1·8	2·2	1·8		1646 (X = OMe)
(28)	4·57 br (t)	4·77 br (t)	7·09 (m)		5·45 (s)	6·58 (s), 6·71 (s)		1·8	2·5	1·8	2·5		

Exocyclic $=CH_2$ is numbered 8; *x* = *exo*, *n* = *endo*, *t* = transoid, *c* = cisoid.

take place at the corner of the molecule and predominantly from the *exo* direction. The results reported here, which mirror those of thiol addition,[9] cannot be explained by an extension of Brown's theory to include



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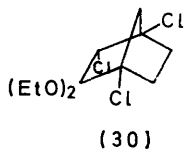

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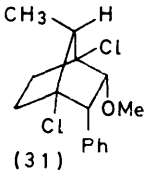
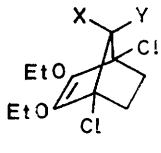


(31)

chlorine-substituted norbornadienes. The appreciable *endo*-attack observed is likely to be due to a combination of steric and electrostatic hindrance to *exo*-attack occasioned by the presence of the bridgehead chlorine atoms. With the 7-*anti*-pentachloronorbornadiene (3) and tetrachloronorbornadiene (4) products of types (A) or (B), derived by addition of ethanol to the unsubstituted double bond, are not formed on reaction with sodium ethoxide in ethanol; reaction occurs solely at the chlorine-substituted double bond to give products of type (C) and (D). As attack by ethoxide ions can occur at both double bonds in (1) and (2) these results indicate that the absence of a 7-*syn*-chlorine substituent makes the chlorine-substituted double bond much more reactive than the unsubstituted double bond. The formation of products (C) from (3) and (4) is readily explained by a 1,2-addition–elimination sequence.[2,10] Products of type (D) are presumably formed as a result of subsequent reaction of (C); this mode of reaction is initially surpris-

[9] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1967, 2249.
[10] W. E. Truce, 'Organic Sulphur Compounds,' ed. N. Kharasch, vol. 1, Pergamon, Oxford, 1961, pp. 112—120.

ing since the product (32) would have been expected in view of the formation of (33) when the dienes (3) and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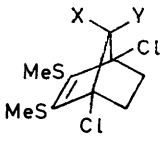
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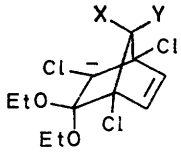
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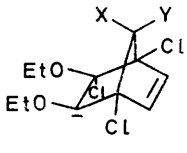
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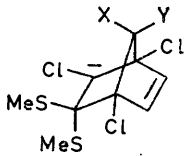
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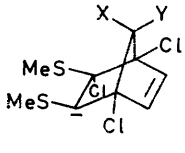
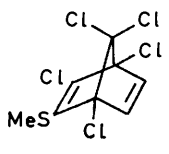

(37)

X = H, Y = H or Cl

(4) react with sodium methanethiolate. Clearly the intermediate (34) is favoured over (35) because Cl is better than EtO at α-stabilisation of a carbanion.[11] In the case of methanethiolate ions in dimethylformamide product formation only occurs from (37) and never from (36) in spite of the fact that α-stabilisation of a carbanion centre [in (36)] by Cl is likely to be greater than that by MeS [in (37)]. Lack of products from (36) is not due to the aprotic nature of dimethylformamide, since products related to (D) are not formed by reaction of (1) with sodium methanethiolate in ethanol. Therefore product formation from (37) must be due either to instability of (37) causing ready loss of Cl^-, or to a large energy barrier to the formation of the thioacetal system in (36) due to unfavourable steric interaction of this system with the bridgehead chlorine atom. Sodium methanethiolate in ethanol reacts with hexachloronorbornadiene (1) to form the product (22), derived by addition of methanethiol to the unsubstituted double bond, as well as (23) and (24) which are derived by reaction at both double bonds in (1). Experiment shows that (22) cannot be converted into (23) and (24) under the reaction conditions. Therefore (23) and (24) must have their origin in the addition of methanethiol to the unsubstituted double bonds in the initially formed products (38) and (39).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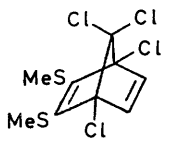
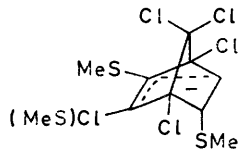

(39)

Previous work [2] has suggested that the unsubstituted double bond greatly activates the chlorine-substituted double bond in (1) towards reaction with methanethiolate anions; thus when nucleophilic addition of methanethiol has removed the unsubstituted double bond in (1) to give (22) the chlorine-substituted double bond will be greatly deactivated towards further reaction. However since Cl probably stabilises a carbanion rather better than MeS, the initial products [(38) and (39)] of reaction at the chlorine-substituted double bond in (1) will be very reactive towards nucleophilic addition to the unsubstituted double bond, owing to the great stability of the intermediate carbanions (40). The assumption that (23) rather than (41) is the addition/monosubstitution product is made because in the potential intermediates (42) and (43) the presumed greater ability of Cl to stabilise a carbanion will result in a greater stability of (43). It has been shown earlier [2] that products (22) and (23) are not formed in the reaction of the diene (1) with sodium methanethiolate in dimethylformamide. The aprotic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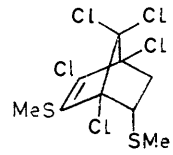
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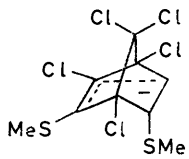
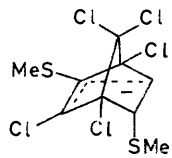
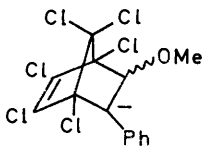
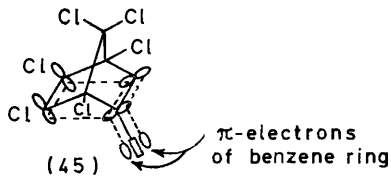

(42)


(43)

nature of dimethylformamide will effectively preclude the nucleophilic addition of methanethiol to the unsubstituted double bonds in (1), (38), and (39).

It has already been reported [1b] that sodium methoxide in methanol reacts with 5-phenylhexachloronorbornadiene (14) to afford (17) and (18), the respective products of *trans*- and *exo,cis*-addition of methanol to the phenyl-substituted double bond. Intermediate (44) is


(44)



(45)

clearly able to accept a proton from solvent only from the *exo*-direction, owing to the disadvantageous torsional strain [7] and steric compression in the product that would result from attack on (44) from the *endo*-direction. However the observation of attack on (14) by methoxide ions from both *exo*- and *endo*-directions is intriguing since in thiol addition,[3a,12] and alkoxide anion addition to (1),[1b] virtually stereospecific *endo*-attack is observed. In the diene (14) extended overlap will occur between the π-electrons of the phenyl group and both lobes of the two *p* orbitals of the 5,6-double bond. The 'lower' halves of these *p* orbitals will also interact with the

[11] J. Hine, N. W. Burske, M. Hine, and P. B. Langford, *J. Amer. Chem. Soc.*, 1957, **79**, 1406; J. D. Park, J. R. Lacher, and J. R. Dick, *J. Org. Chem.*, 1966, **31**, 1116.

[12] C. K. Alden, J. A. Claisse, and D. I. Davies, *J. Chem. Soc.* (*C*), 1966, 1540.

'lower' halves of the two p orbitals of the 2,3-double bond. The phenyl group should be largely coplanar with the 5,6-double double bond and in that orientation will have little effect on the direction of nucleophilic attack at position 6. Formula (45) indicates that overlap will be greatest on the *endo*-side of the molecule and since the p orbital at position 6 is involved on the *endo*-side in both styryl and homallyl systems, it is not so readily available to interact with a nucleophile approaching from the *endo*-direction as is the comparable orbital in the diene (1). Thus *exo*-attack is relatively more favoured in (14) than in (1), any disadvantageous steric and electrostatic effects are insufficient to prevent it, and it takes place in a comparable degree to *endo*-attack. When the 7-*anti*-chlorine substituent is absent, as in the diene (15), methoxide attack takes place almost entirely from the *exo*-direction. However when the 7-*syn*-chlorine substituent of (14) is replaced by a methyl group we find that the resultant diene (16) gives, on reaction with methoxide ion, exclusively the product (21) of *endo*-attack. This difference in direction of attack between (14) and (16) cannot be due to a major steric effect since both dienes are likely to have comparable stereochemistry at the site of attack. For the diene (16) a 6-day reaction time is necessary for a 90% consumption of diene, whereas (14) reacts completely within 30 h. This greater reactivity of the diene (14) may be due to the stabilisation of the intermediate carbanion (44) by the inductive effect of the 7-*syn*-chlorine substituent in addition to delocalisation of the carbanion centre over the 2,3-double bond and the phenyl ring. Such stabilisation is consistent with results of relative rate studies of the reaction of chlorine-substituted norbornadienes with sodium methanethiolate in dimethylformamide.[2] The exclusive formation of the product (21) from *endo*-attack on (16) may be caused by the $+I$ effect of the 7-*syn*-methyl group in the diene (16). This leads to the 7-*anti*-chlorine atom acquiring a more electron-rich character than the 7-*anti*-chlorine atom in the diene (14). Thus, in addition to the steric repulsion of a nucleophile attacking from the *exo*-direction, there will be increased electrostatic repulsion of the incoming nucleophile by the bridge chlorine atom, making *exo*-attack more unfavourable. It is also possible that, as a consequence of the presence of the 7-*syn*-methyl group in (16), the structure is less symmetrical and could be deformed relative to (14). Even small changes in bond angle could make *exo*-attack more difficult than *endo*-attack.

The 5-methylhexachloronorbornadiene (25), when treated with sodium methoxide in methanol, was isomerised to the hexachloromethylenenorbornene (26), which did not react further. Such isomerisation is a consequence of the bond and angle strain in the diene (25) which is slightly relieved by isomerisation to (26) in which an sp^3-hybridised carbon atom replaces an sp^2-hybridised atom in the ring system. The failure of methoxide ions to add to (25) under conditions which permit addition to (1) [1] is due to the presence of the methyl group in (25) resulting in an increased electron availability in the homoconjugated diene system. The reaction of the methyl diene (25) with sodium methoxide in dimethylformamide also results in isomerisation [to (26)] but subsequent reaction occurs to give (27) and (28). These are both derived from attack of methoxide anion at C-5 rather than C-6, since only attack at C-5 can lead to a carbanion centre (at C-6) which is stabilised by homoconjugation with the exocyclic double bond. The reason for reaction of (26) with methoxide ions in dimethylformamide, but not in methanol, must be the greater nucleophilicity of methoxide ions in the latter solvent. Methanol is a solvating solvent and the nucleophilicity of the methoxide ions is reduced as a result of dispersal of charge in the solvating solvent ethanol.

It is now clear that a number of competing factors are involved in controlling product formation when nucleophiles react with chlorine-substituted norbornadienes. To rationalise any particular reaction it is necessary to consider (i) the nature of the solvent, (ii) steric and electrostatic effects on the direction of approach by a nucleophile, and (iii) the ability of substituent groups to stabilise carbanions. The conditions necessary for reaction of a chlorine-substituted norbornadiene with a nucleophile are fairly stringent, as they are with related compounds,[13] and it is therefore scarcely surprising that the chloro-diene insecticides persist relatively unchanged for long periods in the soil and in plant and animal systems.[14]

EXPERIMENTAL

N.m.r. spectra were recorded, unless otherwise stated, for 10% solutions in carbon tetrachloride with tetramethylsilane as internal standard (100 MHz by the P.C.M.U., Harwell, and 60 MHz with a Perkin-Elmer R10 or R12B spectrometer). I.r. data were recorded with a Perkin-Elmer 257 grating spectrometer. Column chromatography was carried out with light petroleum (b.p. 40—60°)–ether mixtures and the following adsorbents: (a) basic alumina (activity I), (b) silica gel (B.D.H.; 60—120 mesh), (c) silica gel (Fisons; 100—200 mesh), and (d) neutral alumina (activity I). G.l.c. analysis, unless stated otherwise, was performed on a Perkin-Elmer F11 gas chromatograph fitted with 2 m × $\frac{1}{8}$ in stainless steel columns packed with (A) 15% SE30, 15% PPE, 5% KOH on Chromosorb W (80—100 mesh), and (B) 2·5% silicone gum rubber E 301 on AW–DMCS Chromosorb G (80—100 mesh).

Pentachloronorbornadienes (2) *and* (3).—The mixture from the Diels–Alder reaction [15] of pentachlorocyclopentadiene with vinyl bromide was chromatographed by method (a) to give 5-*endo*-bromo-1,2,3,4,7-*anti*-pentachloronorborn-2-ene, 5-*exo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-ene, and 5-*endo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-ene, with properties identical to those reported.[15,16] 5-*endo*-

[13] K. Mackenzie and C. H. M. Adams, *J. Chem. Soc.* (*C*), 1969, 480 and references cited therein; C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Amer. Chem. Soc.*, 1972, **94**, 8905.

[14] See for example K. Mellanby, 'Pesticides and Pollution,' 2nd edn., Collins, London, 1970.

[15] R. Alexander, D. I. Davies, D. H. Hey, and J. N. Done, *J. Chem. Soc.* (*C*), 1971, 2367.

[16] K. L. Williamson, Yuan-Fang Li Hsu, R. Lacko, and Chung He Youn, *J. Amer. Chem. Soc.*, 1969, **91**, 6129.

Bromo-1,2,3,4,7-*anti*-pentachloronorborn-2-ene (10·0 g, 0·03 mol) was dissolved in t-butyl alcohol (100 ml) containing potassium t-butoxide (14 g), and the solution was stirred and boiled at reflux for 30 h. The t-butyl alcohol was then evaporated off and the residue was mixed with water (100 ml) and extracted with chloroform (3 × 100 ml). The combined extracts were dried ($MgSO_4$) and evaporated and the residue was distilled to afford 1,2,3,4,7-*anti*-pentachloronorborna-2,5-diene (3) (2·2 g), b.p. 56—60° at 0·25 mmHg, n_D^{25} 1·5337 (lit.,[8] b.p. 140—141° at 12 mmHg, n_D^{25} 1·5340). Similar treatment of a mixture (10 g) of 5-*endo*- and 5-*exo*-bromo-1,2,3,4,7-*syn*-pentachloronorborn-2-enes afforded 1,2,3,4,7-*syn*-pentachloronorborna-2,5-diene (2) (1·7 g), b.p. 56—60° at 0·2 mmHg, n_D^{25} 1·5419 (lit.,[9] b.p. 133—135° at 10 mmHg, n_D^{25} 1·5392).

1,2,3,4-*Tetrachloronorborna*-2,5-*diene* (4).—Hexachloronorbornadiene (1) (14·7 g, 0·049 mol) and zinc dust (16·0 g, 0·25 g atom) were added to glacial acetic acid (100 ml) and the mixture was stirred and boiled at reflux for 7 h, filtered, and poured into water (200 ml). The resultant suspension was extracted with light petroleum (3 × 200 ml). The combined extracts were washed with saturated sodium hydrogen carbonate solution (3 × 50 ml), dried ($MgSO_4$), and evaporated and the residue was distilled to afford 1,2,3,4-tetrachloronorborna-2,5-diene (4) (8·2 g), b.p. 48—50° at 0·1 mmHg, n_D^{25} 1·5409 (lit.,[8] b.p. 110—115° at 5 mmHg, n_D^{25} 1·5403).

1,2,3,4,7-syn-*Pentachloro*-5-*phenylnorborna*-2,5-*diene* (15).—Pentachlorocyclopentadiene [15] (8·0 g, 0·03 mol) and phenylacetylene (8·0 g, 0·08 mol) were heated together in a sealed tube under nitrogen for 4 h. The crude product was then distilled, and the distillate (8·0 g; b.p. 132° at 0·1 mmHg) was chromatographed by method (b) to yield successively (i) 1,2,3,4,7-anti-*pentachloro*-5-*phenylnorborna*-2,5-*diene* (0·4 g), m.p. 85—86° (from methanol) (Found: C, 45·5; H, 2·3; Cl 51·2. $C_{13}H_7Cl_5$ requires C, 45·8; H, 2·1; Cl, 52·3%), τ (60 MHz) 2·63 (m, Ph), 3·59 (d, H-6), and 5·28 [d, H-7-*syn*, J(6,7-*syn*) 1·2 Hz], $\nu_{max.}$ 1598 cm^{-1} (*cis*-ClC=CCl); and (ii) 1,2,3,4,7-syn-*pentachloro*-5-*phenylnorborna*-2,5-*diene* (15) (1·5 g), m.p. 81—82° (from methanol) (Found: C, 45·5; H, 1·9%), τ (60 MHz) 2·62 (m, Ph), 3·27 (H-6), and 5·13 (q, H-7-*anti*), $\nu_{max.}$ 1603 cm^{-1} (*cis*-ClC=CCl).

1,2,3,4,7-anti-*Pentachloro*-7-syn-*methyl*-5-*phenylnorborna*-2,5-*diene* (16).—Phenylacetylene (8·0 g, 0·08 mol) and pentachloromethylcyclopentadiene [17,18] (15·0 g, 0·06 mol) were dissolved in toluene (25 ml) and the solution was stirred and boiled at reflux for 64 h. The toluene was evaporated off and a portion of the mixture (10 g) was chromatographed by method (c) to afford 1,2,3,4,7-anti-*pentachloro*-7-syn-*methyl*-5-*phenylnorborna*-2,5-*diene* (16) (1·7 g), m.p. 79—80° (from methanol) (Found: C, 47·3; H, 2·5. $C_{14}H_9Cl_5$ requires C, 47·4; H, 2·6%), τ (60 MHz) 2·68 (s, Ph), 3·48 (s, H-6, and 8·16 (s, Me), $\nu_{max.}$ 1606 cm^{-1} (*cis*-ClC=CCl).

1,2,3,4,7,7-*Hexachloro*-5-*methylnorborna*-2,5-*diene* (25).—Hexachlorocyclopentadiene (10·0 g, 0·04 mol) and propyne (4 g, 0·1 mol) were heated in a sealed tube under nitrogen at 180° for 7 h. The tube was then cooled and opened, and the excess of propyne was allowed to evaporate. Distillation of the residue afforded 1,2,3,4,7,7-hexachloro-5-methylnorborna-2,5-diene (25) (11·1 g), b.p. 50° at 0·01 mmHg, n_D^{25} 1·5460 (lit.,[19] 1·5440) (Found: C, 30·9; H, 1·4. Calc. for $C_8H_4Cl_6$: C, 30·7; H, 1·3%).

Reactions of Dienes with Nucleophiles.—(i) 1,2,3,4,7-syn-*Pentachloronorborna*-2,5-*diene* (2) *with sodium ethoxide in ethanol.* The diene (2) (1·0 g, 0·004 mol) was added to a solution of sodium (0·7 g, 0·03 g atom) in ethanol (18 ml). The mixture was boiled at reflux, with stirring, for 72 h, cooled, and evaporated; the residue was then mixed with water (50 ml) and extracted with chloroform (3 × 50 ml), and the combined extracts were dried ($MgSO_4$), filtered, and evaporated. G.l.c. analysis of the residue on column (A) at 180° showed the presence of starting material and three other components in the ratio 34 : 24 : 38 (in order of increasing retention time). Chromatography by method (d) afforded successively unchanged diene (2) (0·1 g); 1,2,4,7-syn-*tetrachloro*-3-*ethoxynorborna*-2,5-*diene* (9) (0·03 g), b.p. 34° at 0·08 mmHg; 1,2,3,4,7-syn-*pentachloro*-5-endo-*ethoxynorborn*-2-*ene* (7) (0·3 g), b.p. 40° at 0·08 mmHg (Found: C, 35·4; H, 3·1. $C_9H_9Cl_5O$ requires C, 34·8; H, 2·9%); and 1,2,3,4,7-syn-*pentachloro*-5-exo-*ethoxynorborn*-2-*ene* (8) (0·3 g), b.p. 40° at 0·08 mmHg (Found: C, 35·1; H, 3·1. $C_9H_9Cl_5O$ requires C, 34·8; H, 2·9%).

(ii) 1,2,3,4,7-anti-*Pentachloronorborna*-2,5-*diene* (3) *with sodium ethoxide in ethanol.* The diene (3) (1·0 g, 0·004 mol) was added to a solution of sodium (0·7 g, 0·03 g atom) in ethanol (18 ml). The solution was boiled under reflux, with stirring, for 72 h, then evaporated, and the residue was mixed with water (50 ml) and extracted with chloroform (3 × 50 ml). The extracts were dried ($MgSO_4$), filtered, and evaporated. N.m.r. analysis of the residue showed the absence of starting material and the presence of two other components in the ratio 45 : 55 (based on integration of olefinic absorptions). The residue was taken up in methanol, decolourised with charcoal, and crystallised to give 1,2-endo,-4,7-anti-*tetrachloro*-3,3-*diethoxynorborn*-5-*ene* (11) (0·2 g), m.p. 127—129° (Found: C, 41·6; H, 4·3. $C_{11}H_{14}Cl_4O_2$ requires C, 41·3; H, 4·4%). The filtrate from the crystallisation was evaporated and the residue chromatographed by method (d) to afford successively 1,2,4,7-anti-*tetrachloro*-3-*ethoxynorborna*-2,5-*diene* (10) (0·05 g), b.p. 48—50° at 0·2 mmHg (Found: C, 39·4; H, 3·3. $C_9H_8Cl_4O$ requires C, 39·45; H, 2·9%), and the norbornene (11) (0·2 g).

(iii) 1,2,3,4-*Tetrachloronorborna*-2,5-*diene* (4) *with sodium ethoxide in ethanol.* The diene (4) (3·7 g, 0·016 mol) in ethanol (25 ml) was added to a solution of sodium (3·0 g, 0·13 g atom) in ethanol (50 ml) and the mixture was boiled under reflux, with stirring, for 72 h, cooled, and evaporated. The residue was mixed with water (100 ml) and extracted with chloroform (3 × 50 ml), and the extracts were dried ($MgSO_4$), filtered, and evaporated. G.l.c. analysis of the residue on a Griffin D6 density balance chromatograph, fitted with a 6 ft × 0·25 in column of 20% silicone oil on 60—80 mesh Chromosorb W at 180° (nitrogen as carrier gas) showed the presence of starting material (4) and two components in the ratio 43 : 57. Fractional distillation afforded 1,2,4-trichloro-3-ethoxynorborna-2,5-diene (12) (0·5), b.p. 35—37° at 0·1 mmHg (decomp.), M^+ in range 238—244 ($C_9H_9Cl_3O$); and a mixture of (12) and 1,2-endo,4-*trichloro*-3,3-*diethoxynorborn*-5-*ene* (13). Chromatography by method (d) allowed isolation of (13) (1·3 g), m.p. 63—64° (from methanol) (Found: C, 46·0; H, 5·3. $C_{11}H_{12}Cl_3O_2$ requires C, 46·3; H, 5·3%).

(iv) 1,2,3,4,7-syn-*Pentachloro*-5-*phenylnorborna*-2,5-*diene* (15) *with sodium methoxide in methanol.* A solution of the

[17] R. P. Levek, *Diss. Abs.*, 1968, **28***B*, 2775.
[18] S. D. Volodkovich, N. N. Mel'nikov, B. A. Khaskin, and S. I. Shestakova, *J. Org. Chem. U.S.S.R.*, 1967, **3**, 1190.
[19] D. Seyferth and A. B. Evnin, *J. Amer. Chem. Soc.*, 1967, **89**, 1468.

diene (15) (1·0 g, 0·003 mol) in methanol (10 ml) was added to a solution of sodium (0·5 g, 0·022 g atom) in methanol (15 ml). The mixture was boiled at reflux for 30 h, cooled, and poured into water (100 ml), and the resultant aqueous suspension was extracted with carbon tetrachloride (3 × 50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated, and the residue was shown by n.m.r. analysis to contain unchanged diene (*ca.* 10%) and two products in the ratio 9 : 1 (based on integration of two absorptions corresponding to OMe). Chromatography of the residue by method (d) afforded unchanged diene (15) (0·1 g); 1,2,3,4,7-syn-*pentachloro*-6-exo-*methoxy*-5-endo-*phenylnorborn*-2-*ene* (20) (0·3 g), m.p. 98—99° (from methanol) (Found: C, 45·8; H, 2·8. $C_{14}H_{11}Cl_5O$ requires C, 45·3; H, 3·0%); 1,2,3,4,7-syn-*pentachloro*-6-endo-*methoxy*-5-endo-*phenylnorborn*-2-*ene* (19) (0·05 g), m.p. 118—120°, sublimed 90—110° at 0·1 mmHg (Found: C, 44·9; H, 3·0. $C_{14}H_{11}Cl_5O$ requires C, 45·3; H, 3·0%).

(v) 1,2,3,4,7-anti-*Pentachloro*-7-syn-*methyl*-5-*phenylnorborna*-2,5-*diene* (16) *with sodium methoxide in methanol.* A solution of the diene (16) (1·0 g, 0·003 mol) in methanol (10 ml) was added to a solution of sodium (0·52 g, 0·023 g atom) in methanol (5 ml). The mixture was boiled at reflux and the disappearance of starting material was monitored by g.l.c. on column (B) at 180°. After 6 days, when the diene (16) had been 90% consumed, the mixture was cooled, poured into water (50 ml), and extracted with chloroform (3 × 50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to yield a residual oil (1·0 g). G.l.c. analysis showed unchanged diene (16) and one other major component. Chromatography by method (c) gave a mixture (0·1 g) of unchanged diene (16) with traces of unidentifiable components of shorter retention time, a complex mixture (0·25 g) of unidentifiable components, and 1,2,3,4,7-anti-*pentachloro*-7-syn-*methyl*-6-endo-*methoxy*-5-endo-*phenylnorborn*-2-*ene* (21) (0·3 g), m.p. 93·5—94° (from methanol) (Found: C, 46·6; H, 3·4. $C_{15}H_{13}Cl_5O$ requires C, 46·6; H, 3·4%).

(vi) 1,2,3,4,7,7-*Hexachloronorborna*-2,5-*diene* (1) *with sodium methanethiolate in ethanol.* The diene (1) (1·2 g, 0·004 mol) was dissolved in a solution of sodium methanethiolate (2·3 g, 0·033 mol) in ethanol (25 ml), and the solution was boiled at reflux for 72 h. The solvent was then evaporated off and the residue mixed with water (50 ml) and extracted with chloroform (3 × 50 ml); the combined extracts were dried ($MgSO_4$). N.m.r. analysis after removal of solvent showed that 83% of the diene (1) had been consumed to afford three products in the ratio 50 : 16 : 34 (based on integration of SMe absorptions). Repeated chromatography by methods (b) and (d) afforded successively 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-yl methyl sulphide (22) (0·1 g), properties as reported;[12] 1,3,4,7,7-pentachloronorborn-2-ene-2-*endo*,5-diyl bis(methyl sulphide) (23) (0·1 g), b.p. 80° at 0·2 mmHg, M^+, 356 ($C_9H_9{}^{35}Cl_5S_2$); and 1,4,7,7-tetrachloronorborn-2-ene-2-*endo*,3,5-triyl tris(methyl sulphide) (24) (0·1 g), m.p. 56—57° (lit.,[2] 46—47°), M^+, 368 ($C_{10}H_{12}{}^{35}Cl_4S_3$).

Compound (22) (0·05 g, 0·00015 mol) was added to a solution of sodium methanethiolate (0·1 g, 0·0014 mol), in ethanol (2 ml) and the solution was boiled at reflux for 72 h. N.m.r. analysis of the residue after similar work-up indicated that it was mainly unchanged norbornene (22).

(vii) 1,2,3,4,7,7-*Hexachloro*-5-*methylnorborna*-2,5-*diene* (25) *with sodium methoxide in methanol.* The diene (25) (2·5 g, 0·008 mol) was added to a solution of sodium (1·5 g, 0·065 g atom) in methanol (50 ml) and the resultant solution was boiled at reflux for 50 h, then evaporated. The residue was mixed with water (100 ml) and extracted with chloroform (3 × 50 ml), and the extract was dried ($MgSO_4$), filtered, and evaporated. Distillation of the residue [after g.l.c. analysis on column (B) at 120° and 180°] afforded solely 1,2,3,4,7,7-hexachloro-5-methylenenorborn-2-ene (26) (2·0 g), b.p. 80—84° at 0·1 mmHg, n_D^{25} 1·5593 (lit.,[4] b.p. 65—68° at 0·05 mmHg, n_D^{20} 1·5610).

(viii) 1,2,3,4,7,7-*Hexachloro*-5-*methylnorborna*-2,5-*diene* (25) *with sodium methoxide in dimethylformamide.* The diene (25) (2·5 g, 0·008 mol) was added to a suspension of sodium methoxide (3·0 g, 0·065 mol) in dimethylformamide (50 ml). The mixture was shaken for 7 h, then poured into water (100 ml), and extracted with carbon tetrachloride (5 × 50 ml). The combined extracts were dried ($MgSO_4$), filtered, and evaporated. N.m.r. analysis of the residue showed two products in the ratio 1 : 1 (based on integration of OMe absorptions). Repeated chromatography by method (c) gave 1,3,4,7,7-*pentachloro*-2-*methoxy*-5-*methylenenorborn*-2-*ene* (27) (0·2 g), b.p. 50° at 0·1 mmHg (Found: C, 35·5; H, 2·5. $C_9H_7Cl_5O$ requires C, 35·0; H, 2·3%), and 1,3-endo,-4,7-*pentachloro*-2,2-*dimethoxy*-5-*methylenenorbornane* (28) (0·1 g), m.p. 102—104°, sublimed 120° at 0·2 mmHg (Found: C, 35·8; H, 3·1. $C_{10}H_{11}Cl_5O_2$ requires C, 35·3; H, 3·3%).

Diels–Alder Addition of Ethyl Vinyl Ether to Pentachlorocyclopentadiene.—Pentachlorocyclopentadiene[15] (5·0 g, 0·021 mol) and ethyl vinyl ether (10·0 g, 0·139 mol) were dissolved in xylene (25 ml) and the solution was boiled at reflux for 70 h. The xylene was evaporated off and the residue distilled to afford a mixture (3·5 g), b.p. 80—83° at 0·1 mmHg (Found: C, 35·0; H, 3·0. Calc. for $C_9H_9Cl_5O$: C, 34·8; H, 3·4%), of 1,2,3,4,7-*syn*-pentachloro-5-*endo*-ethoxynorborn-2-ene (7) and its 7-*anti*-epimer. Preparative thick-layer chromatography on silica gel resulted in isolation of (7) and of 1,2,3,4,7-*anti*-pentachloro-5-*endo*-ethoxynorborn-2-ene, identified on the basis of its spectral properties: τ (60 MHz) 5·58 (q, H-5-*exo*), 6·00 (d, H-7-*syn*); 6·36 (m, $OCH_2{\cdot}CH_3$), 7·24 (q, H-6-*exo*), 8·22 (sextet, H-6-*endo*), and 8·83 (t, $OCH_2{\cdot}CH_3$) [J(5-*exo*,6-*exo*) 7·7, J(5-*exo*,-6-*endo*) 2·5, J(6-*exo*,6-*endo*) 12·8, J(7-*syn*,6-*endo*) 2·1 Hz], $\nu_{max.}$ 1600 cm^{-1} (*cis*-ClC=CCl).

Diels–Alder Addition of cis-β-*Methoxystyrene to Pentachlorocyclopentadiene.*—Pentachlorocyclopentadiene[15] (2·4 g, 0·01 mol) and *cis*-β-methoxystyrene[16] (0·9 g, 0·007 mol) were dissolved in xylene (10 ml) and the solution was boiled at reflux for 18 h. The xylene was evaporated off and the residue chromatographed by method (b) to give the dimer of pentachlorocyclopentadiene (0·5 g), m.p. 214—217° (lit.,[16] 221°), and a 57 : 43 mixture (0·2 g), m.p. 145—148° (Found: C, 45·1; H, 3·1. Calc. for $C_{14}H_{11}Cl_5O$: C, 45·3; H, 3·0%), of 1,2,3,4,7-*syn*-pentachloro-6-*endo*-methoxy-5-*endo*-phenylnorborn-2-ene (19) and 1,2,3,4,7-*anti*-pentachloro-6-*endo*-methoxy-5-*endo*-phenylnorborn-2-ene, identified from the n.m.r. (100 MHz) spectrum of the mixture [τ 2·77br (s, Ph), 5·73 (s, H-7-*syn*), 5·75 (d, H-5-*exo*), and 6·46 (d, H-6-*exo*); J(5-*exo*,6-*exo*) 8·0 Hz].

Hydrogenolysis[6] *of* 1,2,3,4,7-anti-*Pentachloro*-6-endo-*methoxy*-7-syn-*methyl*-5-endo-*phenylnorborn*-2-*ene* (21).—The norbornene (21) (50 mg, 0·00026 mol) was dissolved in ethanol (2 ml) to which were then added 10% palladium–charcoal (0·05 g) and potassium hydroxide (0·1 g, 0·018 mol) in ethanol (2 ml). Hydrogenation (uptake *ca.* 15 ml) followed by chromatography [method (a)] afforded 1,4-di-

chloro-6-*endo*-methoxy-7-*syn*-methyl-5-*endo*-phenylnorbornane (31) (7 mg), b.p. 100—110° at 0·1 mmHg, *m/e* 284 (M^+, $C_{15}H_{18}{}^{35}Cl_2O$), 248 (M − HCl), and 134 (retro-Diels–Alder fragment $PhCH{=}CHOCH_3^+$).

Hydrogenation of 1,2-endo,4,7-anti-*Tetrachloronorborn-5-ene* (11).—The norbornene (11) (52 mg) was dissolved in ethanol (2 ml) and 10% palladium–charcoal (10 mg) was added. Hydrogenation (uptake 3·5 ml in 15 min) gave material which was sublimed (70—75° and 0·5 mmHg) to afford 1,2-endo,4,7-anti-*tetrachloro*-3,3-*diethoxynorbornane* (29) (34 mg), m.p. 101—102° (Found: C, 41·5; H, 5·0. $C_{11}H_{16}Cl_4O_2$ requires C, 41·0; H, 5·0%).

Hydrogenation of 1,2-endo,4-*Trichloronorborn-5-ene* (13).—The norbornene (13) (16 mg) was hydrogenated similarly to afford 1,2-endo,4-*trichloro*-3,3-*diethoxynorbornane* (30) (6 mg), b.p. 65—70° at 10·5 mmHg (Found: C, 45·6; H, 5·9. $C_{11}H_{17}Cl_3O_2$ requires C, 45·9; H, 6·0%).

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