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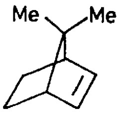
Some Addition Reactions of 1,2,3,4,7,7-Hexachloronorborna-2,5-diene, 1,4,5,6,7,7-Hexachloronorborn-5-en-2-one, and Related Compounds

By **D. I. Davies,* Patricia Mason,** and **M. J. Parrott,** Department of Chemistry, King's College, Strand, London WC2R 2LS

The structures and stereochemistry have been elucidated of the products formed in the addition of methanol and of hydrogen to methyl 1,4,5,6,7,7-hexachloronorborna-2,5-diene-2-carboxylate; the epoxidation, the hydroboration–oxidation, and the addition of diazomethane to 1,2,3,4,7,7-hexachloronorborna-2,5-diene; and the lithium aluminium hydride reduction and the reaction of Grignard reagents with 1,4,5,6,7,7-hexachloronorborn-5-en-2-one. The results, when compared with published results of additions to 1,2,3,4,7,7-hexachloronorborna-2,5-diene and to 7,7-dimethylnorborn-2-ene, suggest that steric factors may not be entirely responsible for the direction of reagent attack.

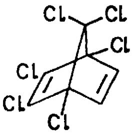
A SYSTEMATIC comparative study of the addition reactions of norbornene (I) and 7,7-dimethylnorborn-2-ene (II) was undertaken by Brown.[1-4] He demonstrated that the 7-methyl substituents exercise steric control over addition reactions involving hydrogenation, hydroboration, epoxidation, and silver ion complexation, but not over oxymercuration, hydrochlorination, and free-radical addition of benzenethiol. These results were rationalised by Brown with the proposal that reactions of the first class proceed through essentially one-stage additions, involving cyclic transition states, which place the adding species in the immediate environment of the 7-methyl substituents. On the other hand, in reactions which proceed in two stages, involving reaction intermediates of small or moderate steric requirements, he suggested that attack occurs at the corners of the bicyclic structure, and is not seriously influenced sterically by the 7-methyl substituents.

(I)



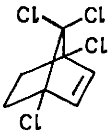
(II)

The work described here is concerned with additions to norbornenes and norbornadienes containing bridge chloro-substituents. One would anticipate from Brown's work that two-stage additions to hexachloronorbornadiene (III) should lead to products derived from *exo*-attack, since the size of a halogeno-substituent is little different from that of methyl. This expectation is not however realised; only trichloromethyl radicals have so far been found to attack hexachloronorbornadiene (III) predominantly from the *exo*-direction,[5] as also occurs with norbornene (I)[6] and norbornadiene (IV).[7] Thiyl radicals, which attack norbornene (I),[8,9] norbornadiene (IV),[10] and 7,7-dimethylnorborn-2-ene (II)[1] predominantly from the *exo*-direction, have been found to give rise to products derived from *endo*-attack on hexachloronorbornadiene (III).[11] Similarly *endo*-attack of thiyl radicals occurs with 1,4,7,7-tetrachloronorborn-2-ene (V),[5] which implies that it is the bridge chlorine atoms in (III), rather than any overlap of double bond orbitals on the *endo*-side of the molecule, that directs attack to the *endo*-side of (III). Bromine atom attack, in the free-radical addition of hydrogen bromide to hexachloronorbornadiene (III), also occurs from the *endo*-direction.[12] The sodium methoxide-catalysed addition of methanol to methyl 1,4,5,6,7,7-hexachloronorborna-2,5-diene-2-carboxylate (VI) is now found to afford the *endo,cis*-addition product (VII) derived from *endo*-attack by methoxide ions. This preference for virtually exclusive *exo*-attack by trichloromethyl radicals, and virtually exclusive *endo*-attack by thiyl radicals and by methoxide ions may be contrasted with the observation [13] that the addition of halogens to hexachloronorbornadiene (III) leads to products derived from both *exo*- and *endo*-



(III)

(IV)



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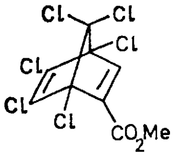

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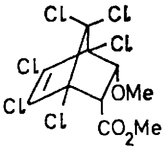

(VII)

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[1] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 201.

[2] H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, 1970, **92**, 1990.

[3] H. C. Brown and Kwang-Ting Liu, *J. Amer. Chem. Soc.*, 1970, **92**, 3502.

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[5] D. I. Davies and P. J. Rowley, *J. Chem. Soc.* (*C*), 1969, 424.

[6] E. Tobler and D. J. Foster, *J. Org. Chem.*, 1964, **29**, 2839.

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

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[10] S. J. Cristol, G. D. Brindell, and J. A. Reeder, *J. Amer. Chem. Soc.*, 1958, **80**, 635.

[11] J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc.* (*C*), 1966, 1498; C. K. Alden, J. A. Claisse, and D. I. Davies, *J. Chem. Soc.* (*C*), 1966, 1540.

[12] E. N. Prilezhaeva, V. A. Azovskaya, and N. P. Petukhova, *Russ. J. Org. Chem.*, 1968, **4**, 606.

[13] D. I. Davies and M. J. Parrott, *J. Chem. Soc.* (*C*), 1970, 659.

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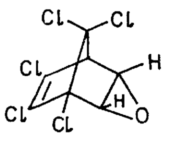
attack by the reacting species. The proportion of *exo*-attack increases with rise in temperature.

By analogy with additions to 7,7-dimethylnorborn-2-ene (I), one-stage additions to hexachloronorbornadiene (III), involving cyclic transition states, would be expected to lead to products of *endo*-attack. Consistent with this expectation is our current demonstration that epoxidation[14] and hydroboration–oxidation[15] of hexachloronorbornadiene (III) give the products (VIII) and (IX) respectively as a result of *endo*-addition. The addition of diazomethane is also found to take place from the *endo*-direction to give the cycloaddition product (X), that is isomerised in the presence of acetic acid at 40°, into structure (XI). Catalytic hydrogenation, in the absence of double bond migration, or isomerisation, is known to be a cyclic *cis*-addition process,[16] particularly for norbornene derivatives.[17] However, in contradiction to a steric effect of bridge chlorine atoms preventing *exo*-cycloadditions, the catalytic hydrogenation of the diene ester (VI) took place from the *exo*-direction to afford the *endo*-ester (XII). This may be compared with the addition of carbene to tetrachlorodimethoxynorbornadiene (XIII), which is reported[18] to give, in very low yield, the product (XIV) derived from *exo*-addition of carbene.



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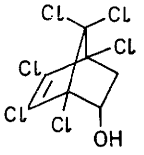

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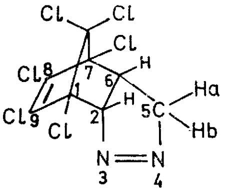
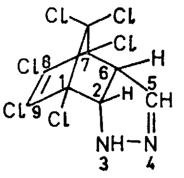


(X)



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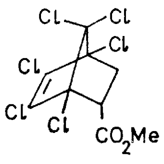

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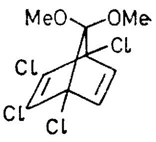

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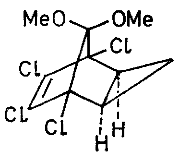
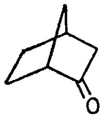


(XIV)

It is thus clear that the proposals of Brown,[1–4] which explain the differences and similarities in certain selected addition reactions of norbornene (I) and 7,7-dimethylnorborn-2-ene (II), cannot be considered sufficient to explain directional orientation in additions to hexachloronorbornadiene (III). Factors other than purely steric must be involved, and account should probably be taken of the electrostatic interaction between attacking species and chloro-substituents as proposed by Davies and Rowley.[5] Oxymercuration,[19] addition of benzyne (generated by the reaction of pentyl nitrite with anthranilic acid),[20] and the addition of 1-chlorobenzotriazole[21] all failed with hexachloronorbornadiene (III). Also maleic anhydride[22] and dimethyl acetylenedicarboxylate,[23] which form cycloaddition products with norbornadiene (IV), failed to react with hexachloronorbornadiene (III). It is possible that these reagents are electrostatically attracted to the *exo*-side of hexachloronorbornadiene (III), but are too large to get near enough to the double bond system for reaction to occur.

The reduction of norcamphor (XV) with complex metal hydrides affords an *endo*-alcohol *via exo*-attack of metal hydride. This is reversed in the presence of 7-methyl substituents, so that the reduction of apocamphor (XVI) affords the *exo*-alcohol as a result of *endo*-attack of metal hydride.[24] Whether or not this is the result of steric control by the bridge methyl groups is not clear since, as Brown has pointed out,[4,25] little is known about the relative steric requirements for the reaction of complex hydrides with ketones. Consistent with this reversal in the direction of attack, in the presence of bridge methyl groups, is the observation that lithium aluminium hydride reduction of 1,4,5,6,7,7-hexachloronorborn-5-en-2-one (XVII) affords the *exo*-alcohol (XVIII) (85%), with only a little of the *endo*-alcohol (IX) (15%). The reaction of methylmagnesium iodide with the ketone (XVII) affords the tertiary alcohol (XIX). Thus in both of these reactions the presence of the bridge chlorine atoms leads to products derived from *endo*-attack.



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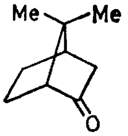

(XVI)

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[14] M. Kleiman, U.S.P. 2,736,730/1956 (*Chem. Abs.*, 1956, **50**, 10,780).

[15] G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 1.

[16] S. Siegel, *Adv. Catalysis*, 1966, **16**, 124.

[17] S. J. Cristol and R. T. LaLonde, *J. Amer. Chem. Soc.*, 1959, **81**, 1655.

[18] S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, 1969, **25**, 1265.

[19] H. C. Brown and P. Geoghegan, jun., *J. Amer. Chem. Soc.*, 1967, **89**, 1522.

[20] L. Friedman and F. M. Logullo, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

[21] C. W. Rees and R. C. Storr, *J. Chem. Soc.* (*C*), 1969, 1474, 1478.

[22] F. Ullmann, *Chem. and Ind.*, 1958, **11**, 73.

[23] C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1966, 1185.

[24] S. Beckmann and R. Mezger, *Chem. Ber.*, 1956, **89**, 2738.

[25] H. C. Brown, *Chem. in Brit.*, 1966, **2**, 199.

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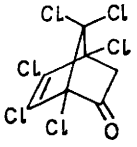
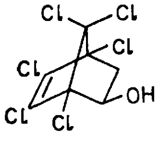
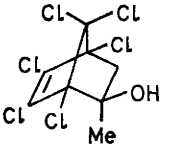
The reactions of the ketone (XVII) with isopropylmagnesium chloride and with ethylmagnesium bromide gave no tertiary alcohols analogous to (XIX). Instead a mixture of the alcohols (IX), (XVIII), and (XX) was formed in the proportions indicated in the Table.



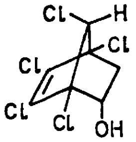
(XVII)



(XVIII)



(XIX)

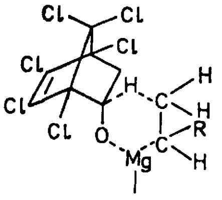


(XX)

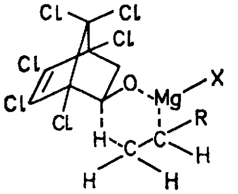
Product proportions from reaction of Grignard reagents with the ketone (XVII)

Grignard	Molar ratio of ketone to Grignard	Ketone reacted (%)	Products (%)		
			(IX)	(XVIII)	(XX)
Pr^{i}MgCl	1 : 2	100	50	16	34
Pr^{i}MgCl	1 : 1	75	48	22	30
EtMgBr	1 : 2	100	41	51	8
EtMgBr	1 : 1	96	42	54	4

The reduction of ketones to alcohols by Grignard reagents is well known, particularly for sterically hindered ketones,[26] and the transition states for formation of alcohols (IX) and (XVIII) along the lines of the mechanistic proposals of Whitmore[27] are represented by structures (XXI) and (XXII), in which R = H and X = Br for ethylmagnesium bromide, and R = Me and X = Cl for isopropylmagnesium chloride. There appears to be no steric barrier to the formation of either transition state, suggesting that comparable amounts of *endo*- and *exo*-alcohols should be formed. Change in Grignard would not be expected to have much effect on product ratio, whereas, particularly when the Grignard is isopropylmagnesium chloride, *endo*-alcohols are found to be favoured.



(XXI)

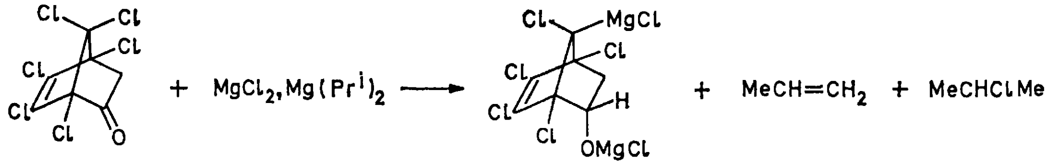


(XXII)

The composition of a Grignard reagent may be described by the equilibrium:

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

Ashby[28] has shown that, in diethyl ether, organomagnesium bromides are monomeric at low concentrations, whereas organomagnesium chlorides are associated even at low concentration. Therefore in the reaction with the ketone (XVII) isopropylmagnesium chloride probably exists largely as $(Pr^i)_2Mg + MgCl_2$. If, in the diagrams (XXI) and (XXII) for the transition states, X = Pr^i, there may be appreciable steric interaction between X and the 7-*anti*-chlorine atom in the transition state (XXII) for the formation of the *exo*-alcohol (XVIII). No similar interaction is present in the transition state (XXI), X = Pr^i, for formation of the *endo*-alcohol (IX) Thus with isopropylmagnesium chloride the transition state (XXI) may well be favoured, leading to *endo*-alcohols (IX) and (XX) as major products. Much more of the *endo*-pentachloro-alcohol (XX) is formed with isopropylmagnesium chloride than when ethylmagnesium bromide is used. The amount is little changed with variation in the amounts of isopropylmagnesium chloride used. It is possible that the stoicheiometry of the reaction with isopropylmagnesium chloride is indicated by the Scheme, suggesting that the formation of (XX) can occur in one stage from the Grignard in the dimeric form. Ethylmagnesium bromide is largely monomeric, and its reaction with (XVII) to afford (XX) would presumably need to take place in two stages. Therefore it is not surprising that the proportion of (XX) is low with ethylmagnesium bromide. However the yield of (XX), although low, doubles when the proportion of reacting ethylmagnesium bromide is doubled, and this may indicate that the formation of (XX) occurs *via* the small amount of ethylmagnesium bromide present in the dimeric form.



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The *endo*-alcohol (IX) was identical with an authentic specimen[29] and had the expected n.m.r. spectrum.[30]

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[26] M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances,' Prentice–Hall, New York, 1954.

[27] F. C. Whitmore, paper presented to the American Chemical Society, April 1943, quoted by H. S. Mosher and E. La Combe, *J. Amer. Chem. Soc.*, 1950, **72**, 3994.

[28] E. C. Ashby and M. B. Smith, *J. Amer. Chem. Soc.*, 1964, **86**, 4363.

[29] E. K. Fields, *J. Amer. Chem. Soc.*, 1956, **78**, 5821.

[30] K. L. Williamson, *J. Amer. Chem. Soc.*, 1963, **85**, 516.

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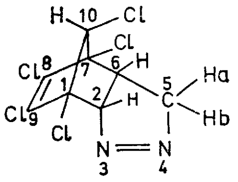
Since it is synthesised by the hydrolysis of the Diels–Alder adduct of vinyl acetate and hexachlorocyclopentadiene, there is no doubt, on the basis of the work of Williamson on Diels–Alder additions of hexachlorocyclopentadiene[30] and pentachlorocyclopentadiene,[31] that the hydroxy-group is *endo*. The *exo*-alcohol (XVIII) characteristically[32] has the 5-*endo* proton signal at higher field than that of the 5-*exo*-proton in (IX).

Although at least two syntheses of the epoxide (VIII) have been reported,[14,33] the stereochemistry of the epoxide group has not been determined until now. It was established as *endo* by reduction with lithium aluminium hydride, and with hydrogen and a platinum catalyst; both methods afforded the known[29,30] *endo*-alcohol (IX).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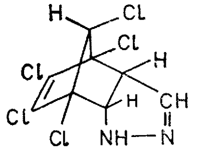
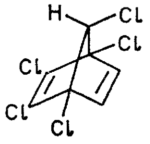

(XXV)

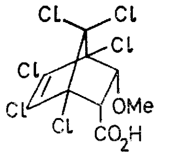

(XXIII)

The product (X) of addition of diazomethane to hexachloronorbornadiene (III), and the rearrangement product (XI) are assumed to have the *endo*-configurations shown, since the comparable compounds, derived from the addition of diazomethane to 1,2,3,4,7-*anti*-pentachloronorborna-2,5-diene (XXIII), in which, as with (III), there is present a 7-*anti*-chlorine atom over the double bond, have the *endo*-structures (XXIV) and (XXV), which may be assigned unambiguously from n.m.r. data (see Experimental section). If these compounds had had the opposite, *exo*-structures, then the 7-*syn*-proton would have shown coupling with the 5-*endo*- and 6-*endo*-protons (norbornane numbering).

The ester (XII) is identical with the product of Diels-Alder addition of acrylic acid to hexachlorocyclopentadiene followed by esterification, and with the product of Diels-Alder addition of methyl acrylate to hexachlorocyclopentadiene. The work of Williamson on the Diels-Alder reactions of hexachlorocyclopentadiene[30] and pentachlorocyclopentadiene[31] makes the *endo*-orientation for the methoxycarbonyl group certain.

The product of the sodium methoxide-catalysed addition of methanol to the diene ester (VI) must have the methoxy- and methoxycarbonyl groups *cis* to each other, since $J_{2.3}$ has a value of 8·5 Hz, which is consistent only with a *cis*- and not a *trans*-arrangement for H-5 and H-6.[30] The *endo,cis*-structure (VII), as opposed to *exo,cis*-, is based on the following observations.

When the ester (VII) is heated overnight with potassium hydroxide in methanol, hydrolysis occurs, without epimerisation of the carboxy-group, to give the *endo,cis*-methoxy-acid (XXVI). Such non-epimerisation is consistent with the structure (XXVI) (*cf.* the work of Williamson[31]). The *cis*-acid (XXVI), when treated with mercury(II) oxide and bromine under the conditions of the Cristol–Firth reaction afforded, as major product, the lactone (XXVII), clearly demonstrating the *endo* positioning of the carboxy-group and hence also of the methoxy-group in (XXVI). This may be contrasted with the Cristol–Firth reaction with most chloronorbornenecarboxylic acids, when bromides are the major products, and lactones may only be inferred as products on the basis of i.r. spectral evidence.[34] Treatment of the *endo,cis*-ester (VII) with hydrogen in the presence of palladium–charcoal and triethylamine (the hydrogenolysis conditions devised by Williamson[35]), or alternatively treatment with zinc and acetic acid, gave the *cis*-pentachloro-methoxy-ester (XXVIII). This ester (XXVIII), when kept at reflux overnight with potassium hydroxide in methanol, was hydrolysed and epimerised to afford the *trans*-methoxy-acid (XXIX). Such an epimerisation is in accordance with investigations of Williamson on related compounds.[31]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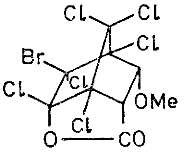
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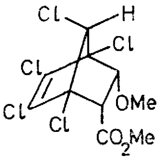
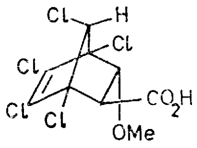
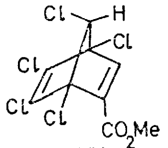
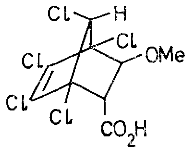

(XXVIII)


(XXIX)


(XXX)


(XXXI)

The *syn*-pentachlorodiene ester (XXX) was prepared as the major product of the Diels–Alder addition of methyl propiolate to pentachlorocyclopentadiene. When the diene ester (XXX) was heated under reflux with molar quantities of sodium methoxide in methanol, the *trans*-methoxy-acids (XXIX) and (XXXI) were formed in the ratio 3 : 7. These were distinguished on the

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

[32] R. R. Fraser, *Canad. J. Chem.*, 1962, **40**, 78; E. W. C. Wong and C. C. Lee, *ibid.*, 1964, **42**, 1245.

[33] H. M. Molotsky and E. G. Ballweber, U.S.P. 2,829,147/1958 (*Chem. Abs.*, 1958, **52**, 12,903); Velsicol Chem. Corp., B.P. 827,435/1960 (*Chem. Abs.*, 1960, **54**, 18,392).

[34] D. I. Davies and P. Mason, *J. Chem. Soc.* (*C*), 1971, 288.

[35] K. L. Williamson, Y. Fang Li Hsu, and E. I. Young, *Tetrahedron*, 1968, **24**, 6007.

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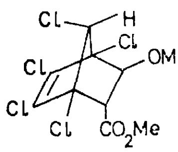
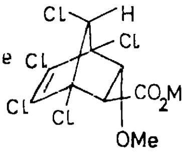
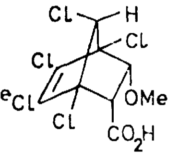
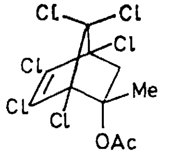
basis[32] of their n.m.r. spectra, which showed the proton next to –OMe in (XXXI) at higher field than the proton next to –OMe in (XXIX), indicating that the methoxy-group is *exo* in (XXXI) and *endo* in (XXIX). Since the stereochemistry of the methoxy-group should not change in the conversion (VII) ⟶ (XXVIII) ⟶ (XXIX) it must be *endo* in all three compounds, including (VII). Since $-CO_2Me$ is *cis* to –OMe in (VII), this is further proof of the *endo,cis*-structure for (VII). The sodium methoxide-catalysed addition of methanol to compound (XXX), in the cold, gave the methoxy-esters (XXXII), (XXXIII), and (XXVIII) in the ratio 70 : 23 : 7. Treatment with potassium hydroxide in refluxing methanol converted the *trans*-methoxy-esters (XXXII) and (XXXIII) into the respective *trans*-methoxy-acids (XXXI) and (XXIX); the reactions were reversed on addition of diazomethane. The *cis*-methoxy-ester (XXVIII) underwent hydrolysis together with epimerisation leading to the *trans*-methoxy-acid (XXIX), a result to be expected on the basis of Williamson's work[31] and which explains the non-isolation of the *cis*-methoxy acid (XXXIV) in the sodium methoxide-catalysed reaction of methanol with the pentachlorodiene ester (XXX) at higher temperatures.

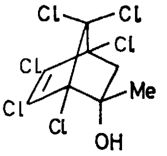

(XXXII)


(XXXIII)

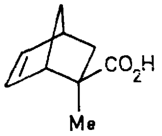

(XXXIV)

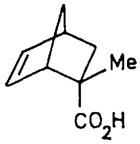
The structure (XIX) of the product of the addition of methylmagnesium iodide to the hexachloro-ketone (XVII) was assigned on the assumption that, like the major product (XVIII), of lithium aluminium hydride reduction, it would be derived from *endo*-attack.


(XXXV)


(XXXVI)

The Diels–Alder addition of isopropenyl acetate to hexachlorocyclopentadiene affords the product (XXXV), which under the mild conditions necessary to effect hydrolysis to (XXXVI) without subsequent dehydration to hexachloromethylenenorbornene, gave a 70 : 30 mixture of (XXXV) and product alcohol (XXXVI). The tertiary alcohols (XIX) and (XXXVI) are distinguished on the basis of their n.m.r. spectra, which show the methyl signal of (XIX) at higher field than that of (XXXVI) allowing the methyl groups to be assigned to *endo*- and *exo*-positions, respectively, on the basis of literature compilations.[36] Consistent with this deduction is our observation that the n.m.r. spectra of the Diels–Alder adducts of cyclopentadiene and methacrylic acid[37] show the methyl signal of (XXXVII) at higher field than that of (XXXVIII).


(XXXVII)


(XXXVIII)

EXPERIMENTAL

N.m.r. spectra at 60 MHz were recorded on a Perkin-Elmer R10 instrument; spectra at 100 MHz were obtained by the PCMU service at Harwell. I.r. spectra were recorded with a Perkin-Elmer 257 grating spectrometer. G.l.c. analysis was carried out with a Griffin D6 Density Balance Chromatograph fitted with a 6 ft. × ¼ in. column of 20% silicone oil SE 30 on Chromosorb W (80—100 mesh). Light petroleum had b.p. 40—60°.

Hexachloronorbornadiene (III) (Aldrich; technical grade), shipped under water to prevent oxidation by atmospheric oxygen, was shown by g.l.c. analysis at 180°, and by its n.m.r. spectrum, to contain 5—20% of 1,2,3,4,5-*endo*,7,7-heptachloronorborn-2-ene. It was therefore purified in the following way. Crude diene (III) (13 g.) was dissolved in ether (50 ml.), the water layer was separated, and the remaining ether layer was dried ($MgSO_4$). The ether was removed, and the residue was added to a solution of sodium t-butoxide (1·5 g.) in t-butyl alcohol (50 g.). The mixture was then heated under reflux for 4 hr., cooled, and poured into water (20 ml.). Most of the alcohol was evaporated off and the resultant aqueous suspension of the diene (III) was extracted with methylene chloride (2 × 100 ml.). The extracts were dried ($MgSO_4$), filtered, and evaporated. The crude product (12·2 g.) was distilled to afford pure hexachloronorbornadiene (III) (10 g.), b.p. 95—96°/0·7 mm. (lit.,[38] 75°/0·4 mm.), which was stored under water in the refrigerator.

Methyl 1,4,5,6,7,7-*Hexachloronorborna*-2,5-*diene*-2-*carboxylate* (VI).—A mixture of methyl propiolate (5·3 g.) and hexachlorocyclopentadiene (15·75 g.) was heated at 140° for 24 hr. The product mixture was distilled to give a viscous oil (11·7 g.), b.p. 126—138°/0·2 mm., which on crystallisation from absolute ethanol afforded white crystals of the *ester* (VI) (10·5 g.), m.p. 79—80° (Found: C, 30·8; H, 1·15; Cl, 60·25. $C_9H_4Cl_6O_2$ requires C, 30·4; H, 1·15; Cl, 60·0%), τ (60 MHz) 2·65 (s, H-3) and 6·20 (s, OMe), $\nu_{max.}$ 1730 (C=O), 1610 (*cis*-ClC=CCl), and 1590 ($-CH=C\cdot CO_2Me$) cm.$^{-1}$.

Methyl 1,4,5,6,7,7-*Hexachloronorborn*-5-*ene*-2-endo-*carboxylate* (XII).—A mixture of methyl acrylate (15 g.), hexachlorocyclopentadiene (33·5 g.), and quinol (0·25 g.) was heated at 100° for 48 hr. The product was distilled to give a viscous oil (34·5 g.), b.p. 154—164°/2—3 mm., which on

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[36] W. L. Dilling, R. D. Kroening, and J. C. Little, *J. Amer. Chem. Soc.*, 1970, **92**, 928.

[37] S. Beckman, R. Schaber, and R. Bamberger, *Chem. Ber.*, 1954, **87**, 997.

[38] H. Bluestone, U.S.P. 2,925,445/1960, (*Chem. Abs.*, 1960, **54**, 10,900h).

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crystallisation from methylene chloride–light petroleum gave white crystals of the *ester* (XII) (28·5 g.), m.p. 40·5—41·5° (Found: C, 30·25; H, 1·6; Cl, 58·2. $C_9H_6Cl_6O_2$ requires C, 30·15; H, 1·65; Cl, 59·0%), τ (100 MHz) 6·25 (s, OMe), 6·35 (q, H-2-*exo*), 7·30 (q, H-3-*exo*), and 7·45 (q, H-3-*endo*), *J* (2-*exo*,3-*exo*) 8, *J* (2-*exo*,3-*endo*) 5, *J* (3-*exo*,3-*endo*) 12·5 Hz, $\nu_{max.}$ 1740 (C=O) and 1610 (*cis*-ClC=CCl) cm.$^{-1}$, identical with the product of the reaction with diazomethane of an authentic specimen[30] of 1,4,5,6,7,7-hexachloronorborn-5-ene-2-*endo*-carboxylic acid.

1,2,3,4,7,7-*Hexachloro*-5-endo,6-endo-*epoxynorborn*-2-*ene* (VIII).—(*cf.* ref. 14) An 80% solution (10 g.) of peracetic acid in glacial acetic acid was added dropwise during 2 hr. to a solution of hexachloronorbornadiene (III) (7·5 g.) and sodium acetate (0·1 g.) in glacial acetic acid (4 ml.) at 40—45°. The mixture was stirred at 40—45° for 24 hr., cooled, and then poured into water (20 ml.). It was then extracted with ether (4 × 20 ml.), and the extracts were washed with saturated aqueous sodium hydrogen carbonate (8 × 50 ml.) and water (2 × 50 ml.), dried, ($MgSO_4$), filtered, and evaporated to afford a residue (7·2 g.). On distillation this gave a colourless liquid (7·0 g.), b.p. 106—110°/2·5 mm. G.l.c. analysis of this liquid at 180° showed that it contained unchanged diene (III) (85%) and epoxide (VIII) (15%). Increased reaction time and the use of more peracetic acid had no effect on product proportions. The mixture of (III) and (VIII) (7 g.) was added to a mixture of thioglycollic acid (2·3 g.) and azobisisobutyronitrile (0·1 g.) and heated at 83° for 18 hr. The cooled mixture was dissolved in ether (50 ml.) and washed with saturated aqueous sodium hydrogen carbonate (4 × 50 ml.) to remove the addition product of the diene (IV) and thioglycollic acid. The ethereal solution was washed with water, dried ($MgSO_4$), filtered, and evaporated to give a crude product, which was chromatographed on acid alumina (light petroleum as eluant) to give white crystals of the epoxide (VIII) (0·1 g.), m.p. 115—116° (lit.,[14] 111—112°) (Found: C, 26·55; H, 0·65. Calc. for $C_7H_2Cl_6O$: C, 26·8; H, 0·75%), τ (60 MHz) 6·1 (s, H-5-*exo* and H-6-*exo*), $\nu_{max.}$ 1604 (*cis*-ClC=CCl) and 1250 (epoxide) cm.$^{-1}$.

1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-*one* (XVII).—Chlorine gas was bubbled into a carbon tetrachloride solution of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ol (IX) (prepared by the hydrolysis of the Diels–Alder adduct of vinyl acetate and hexachlorocyclopentadiene[29]) adjacent to a 100 W light bulb, which served to both heat and to irradiate the mixture (procedure described by Johnson and Mark[39]). The reaction was stopped when 2 mol. of hydrogen chloride had been evolved. After removal of the solvent, the residue was distilled to afford 1,4,5,6,7,7-hexachloronorborn-5-en-2-one (XVII) m.p. 67—68°, b.p. 80—90°/0·1 mm. (lit.,[39] m.p. 67—68°, b.p. 105—114/1·1—1·3 mm.), τ (60 MHz) 6·88 (d, H-3-*exo*) and 7·22 (d, H-3-*endo*), *J* (3-*exo*,3-*endo*) 16 Hz, $\nu_{max.}$ 1602 (*cis*-ClC=CCl) and 1790br (C=O) cm.$^{-1}$, identical with a specimen provided by Dr. V. Mark. Johnson and Mark[39] also reported that when the alcohol was added to a stirred mixture of sodium dichromate, water, glacial acetic acid, and benzene, a mild exothermic reaction resulted and the ketone (XVII) was formed in good yield. In our hands a repetition of the procedure gave no exothermic reaction, and no ketone (XVII) resulted.

Diels–Alder Addition of Isopropenyl Acetate to Hexachlorocyclopentadiene.—A mixture of isopropenyl acetate (20 g.) and hexachlorocyclopentadiene (54·6 g.) was heated at 140—150° for 6 days. Distillation of the product gave unchanged hexachlorocyclopentadiene (35 g.), b.p. 79—80°/0·05 mm., and a yellow oil (17·6 g.), b.p. 140°/0·05 mm. The oil was sublimed at 100°/0·1 mm. and slowly yielded waxy crystals of 5-endo-*acetoxy*-1,2,3,4,7,7-*hexachloro*-5-exo-*methylnorborn*-2-*ene* (XXXV), m.p. 53—54° (Found: C, 32·56; H, 2·2; Cl, 57·45. $C_{10}H_8Cl_6O_2$ requires C, 32·2; H, 2·15; Cl, 57·05%), τ (100 MHz) 8·05 (s, Me), 8·10 (s, Me), and 7·2 (s, H-6-*exo* and H-6-*endo*), $\nu_{max.}$ 1615 (*cis*-ClC=CCl) and 1750 (C=O) cm.$^{-1}$.

Hydrolysis of 5-endo-*Acetoxy*-1,2,3,4,7,7-*hexachloro*-5-exo-*methylnorborn*-2-*ene* (XXXV).—A solution of the acetate (XXXV) (0·3 g.) in ethanol (2 ml.) and concentrated hydrochloric acid (1·5 ml.) was heated under reflux for 18 hr. The cooled mixture was poured into water (20 ml.), and extracted with carbon tetrachloride (4 × 20 ml.). The extracts were dried ($MgSO_4$), filtered, and evaporated to give a crude product (0·25 g.), $\nu_{max.}$ 1750 (C=O of acetate) and *ca.* 3400 cm.$^{-1}$ [OH of the product of the hydrolysis of (XXXV)]. N.m.r. and g.l.c. analysis showed that the crude product contained 70% starting acetate (XXXV) and 30% of 1,4,5,6,7,7-*hexachloro*-2-exo-*methylnorborn*-5-*en*-2-endo-*ol* (XXXVI), τ (60 MHz) 7·43 (d, H-3-*exo*), 7·86 (d, H-3-*endo*), and 8·27 (s, Me), *J* (3-*exo*,3-*endo*) 13 Hz, $\nu_{max.}$ 3100—3600br (OH) and 1605 (*cis*-ClC=CCl) cm.$^{-1}$. No further hydrolysis could be achieved by use of a longer reaction time; the product mixture could not be separated into its components by distillation or crystallisation. Column chromatography on alumina afforded hexachloromethylenenorbornene. Hydrolysis under more vigorous conditions resulted in dehydration of (XXXVI) to give hexachloromethylenenorbornene and tar.

Hydroboration–Oxidation[40] *of Hexachloronorbornadiene* (III).—A solution (1M; 9 ml.) of sodium borohydride in bis-(2-methoxyethyl) ether was added to a solution of hexachloronorbornadiene (III) (5·98 g.) in the same solvent (5 ml.) under nitrogen. The flask was immersed in a water-bath at *ca.* 20° and boron trifluoride–ether complex (1·5 ml.) was added dropwise to the stirred mixture during 0·5 hr., while the temperature was maintained at 20—25°. The mixture was then stirred at this temperature for a further 4 hr. Water (3 ml.) was added to destroy the excess of borohydride, and the organoborane was oxidised at 30—35° by addition of aqueous 3N-sodium hydroxide (2·5 ml.) followed by dropwise addition of 30% hydrogen peroxide (2·5 ml.). The mixture was left for 1 hr. at room temperature and then extracted into ether (4 × 25 ml.). The extracts were washed with ice–water (5 × 100 ml.), dried ($MgSO_4$), filtered, and evaporated to afford a crude product (5 g.), shown by n.m.r. and by g.l.c. analysis at 180° to contain 90% of unchanged diene (III) and 10% of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ol (IX). When set aside in light petroleum (10 ml.), the crude product precipitated white crystals of compound (IX) (0·1 g.), m.p. 154—155°, identical with an authentic specimen.[29,30]

Addition of Diazomethane to Hexachloronorbornadiene (III).—An ethereal solution (20 ml.) of diazomethane (0·68 g.)[41] was distilled into an ice-cold solution of hexachloronorbornadiene (III) (2·5 g.) in ether (25 ml.). The mixture was decolourised after 10 min.; it was then concentrated

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[39] W. K. Johnson and V. Mark, *J. Org. Chem.*, 1961, **26**, 4105.

[40] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, 1961, **83**, 2544.

[41] A. I. Vogel, ‘ A Textbook of Practical Organic Chemistry,’ 3rd edn., Longmans, London, 1964.

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to 10 ml., and light petroleum (10 ml.) was added. The crystals which formed were recrystallised from carbon tetrachloride to give 1,7,8,9,10,10-*hexachloro*-2-exo-H,6-exo-H-3,4-*diazatricyclo*[5,2,1,$0^{2,6}$]*deca*-3,8-*diene* (X) as white needles (2·3 g.), which lost their shape at 130—135° and had m.p. 195—196° with evolution of nitrogen (Found: C, 28·0; H, 1·0; N, 8·15. $C_8H_4Cl_6N_2$ requires C, 28·2; H, 1·2; N, 8·2%), τ (100 MHz) 4·3 (sextet, H-2-*exo*), 6·8 (sextet, H-6-*exo*), 5·50 (octet, H-5a), and 5·45 (octet, H-5b) *J* (2-*exo*,6-*exo*) 8, *J* (2-*exo*,5a) 2, *J* (2-*exo*,5b) 2, *J* (6-*exo*,5a) 8, *J* (6-*exo*,5b) 5, *J* (5a,5b) 19·5 Hz, $\nu_{max.}$ 1605 (*cis*-ClC=CCl) and 1550 (N=N) cm.$^{-1}$. An ethereal solution of the derivative (X) was stable when shaken with 6N-hydrochloric acid. A solution of (X) in carbon tetrachloride was stable when maintained at 80° overnight, but with the addition of a drop of acetic acid, complete rearrangement took place in carbon tetrachloride solution at 40° during 4 hr. to afford 1,7,8,9,10,10-*hexachloro*-2-exo-H,6-exo-H,3,4-*diazatricyclo*[5,2,1,$0^{2,6}$]*deca*-4,8-*diene* (XI), m.p. 133—135° (from carbon tetrachloride) (Found: C, 28·15; H, 1·3; N, 8·2%), τ (100 MHz) 5·3br (d, H-2-*exo*), 5·75br (q, H-6-*exo*), 3·4br (d, H-5), and 4·2—4·5br (m, NH), *J* (2-*exo*,6-*exo*) 10, *J* (6-*exo*,5) 1 Hz, $\nu_{max.}$ 1602 (*cis*-ClC=CCl) and 3300—3450 (NH) cm.$^{-1}$. The rearrangement could also be accomplished by irradiating a carbon tetrachloride solution of (X) with a Phillips 300 Watt ' sun-ray ' lamp for 20 min. When compounds (X) or (XI) were heated at their respective m.p.s or at 200°, with or without copper(I) chloride, and with or without a nitrogen atmosphere, decomposition took place to form unidentified aromatic-like black gums. The reaction of ethereal diazomethane with hexachloronorbornadiene (III) in the presence of copper(I) chloride afforded polymethylene as the sole identifiable product.

Addition of Diazomethane to 1,2,3,4,7-anti-*Pentachloronorborna*-2,5-*diene* (XXIII).—A solution of diazomethane (0·68 g.) in ether (20 ml.) was added to a solution of compound (XXIII) (0·7 g.) in ether (10 ml.). The solution was maintained at 35° for 3 hr. to obtain complete reaction. The ether was removed and the residue was taken up in carbon tetrachloride; the solution was filtered to remove polymethylene. Crystallisation from carbon tetrachloride afforded 1,7,8,9,10-anti-*pentachloro*-2-exo-H,6-exo-H-3,4-*diazatricyclo*[5,2,1,$0^{2,6}$]*deca*-3,8-*diene* (XXIV) as white crystals (0·67 g.), m.p. 147—149° (decomp.) (Found: C, 31·4; H, 1·9; N, 9·1. $C_8H_5Cl_5N_2$ requires C, 31·4; H, 1·65; N, 9·15%), τ (100 MHz) 4·3 (sextet, H-2-*exo*), 6·7 (sextet, H-6-*exo*), 5·75 (s, H-10-*syn*), 5·6 (octet, H-5a), and 5·3 (octet, H-5b), *J* (2-*exo*,6-*exo*) 8, *J* (2-*exo*,5a) 2·5, *J* (2-*exo*,5b) 2·5, *J* (6-*exo*,5a) 8, *J* (6-*exo*,5b) 4, *J* (5a,5b) 19·5 Hz, $\nu_{max.}$ 1592 (*cis*-ClC=CCl) and 1545 (N=N) cm.$^{-1}$. A solution of compound (XXIV) in carbon tetrachloride, when warmed at 40° for 4 hr. with a drop of acetic acid, gave 1,7,8,9,10-anti-*pentachloro*-2-exo-H,6-exo-H-3,4-*diazatricyclo*[5,2,1,$0^{2,6}$]-*deca*-4,8-*diene* (XXV), m.p. 124—128° (decomp.) (from carbon tetrachloride) (Found: C, 31·05; H, 1·8; N, 9·1%), τ (100 MHz) 5·25br (d, H-2-*exo*); 5·75br (q, H-6-*exo*), 5·85 (s, H-10-*syn*), 3·4br (d, H-5), and 4·4—4·9br (m, NH), *J* (2-*exo*,6-*exo*) 10, *J* (6-*exo*,5) 1 Hz, $\nu_{max.}$ 1593 (*cis*-ClC=CCl) and 3200—3450 (NH) cm.$^{-1}$.

Addition of Methanol to Methyl 1,4,5,6,7,7-*Hexachloronorborna*-2,5-*diene*-2-*carboxylate* (VI).—Methyl 1,4,5,6,7,7-hexachloronorborna-2,5-diene-2-carboxylate (VI) (1·19 g.) was dissolved in a solution (15 ml.) of sodium methoxide [from sodium (76 mg.) in methanol (15 ml.)], and the solution was boiled at reflux for 2 hr. On cooling, white crystals separated out, which were filtered off to afford *methyl* 1,4,5,6,7,7-*hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (VII) (1·1 g.), m.p. 111—112° (from carbon tetrachloride) (Found: C, 30·55; H, 2·25; Cl, 54·7. $C_{10}H_8Cl_6O_3$ requires C, 30·95; H, 2·05; Cl, 54·4%), τ (100 MHz) 5·6 (d, H-3-*exo*), 6·5 (d, H-2-*exo*), 6·3 (s, OMe), and 6·5 (s, OMe), *J* (2-*exo*,3-*exo*) 8·5 Hz, $\nu_{max.}$ 1610 (*cis*-ClC=CCl) and 1740 (C=O) cm.$^{-1}$.

Hydrolysis of Methyl 1,4,5,6,7,7-*Hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (VII).—The ester (VII) (3·89 g.) was dissolved in methanol (50 ml.) and potassium hydroxide (1·20 g.) was added. The mixture was boiled at reflux for 16 hr., cooled, diluted with water (150 ml.), and acidified with hydrochloric acid, and the resultant suspension was extracted with methylene chloride (3 × 50 ml.). The methylene chloride solution was dried ($MgSO_4$) and evaporated to afford a residue which gave 1,4,5,6,7,7-*hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylic acid* (XXVI) (2·86 g.), m.p. 198—201° (Found: C, 28·7; H, 1·75. $C_9H_6Cl_6O_3$ requires C, 28·8; H, 1·6%), τ (100 MHz) 5·33 (d, H-3-*exo*), 5·85 (d, H-2-*exo*), 6·35 (s, OMe), and 0·3 (s, CO_2H), *J* (2-*exo*,3-*exo*) 8·4 Hz, $\nu_{max.}$ 1728 (C=O), 1605 (*cis*-ClC=CCl), and 2900—3300 (OH) cm.$^{-1}$.

Hydrogenolysis of Methyl 1,4,5,6,7,7-*Hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (VII) (*Procedure of Williamson* [35]).—The ester (VII) (1·25 g.) was dissolved in ethanol (12·5 ml.) containing triethylamine (1·94 g.). Palladium–charcoal (10%; 0·125 g.) was added and the mixture was shaken under hydrogen for 24 hr. (uptake 83 ml.). It was then filtered and the filtrate was poured into water (100 ml.) and extracted with methylene chloride (3 × 50 ml.). The extract was washed with dilute hydrochloric acid (3 × 50 ml.) and water (3 × 50 ml.), dried ($MgSO_4$), and evaporated. The residue afforded *methyl* 1,4,5,6,7-syn-*pentachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (XXVIII) (1·02 g.), m.p. 158—163° (from ethanol) (Found: C, 34·1; H, 2·3. $C_{10}H_9Cl_5O_3$ requires C, 33·9; H, 2·6%), τ (100 MHz) 5·58 (d, H-3-*exo*), 6·38 (d, H-2-*exo*), 5·80 (s, H-7-*anti*), 6·27 (s, OMe), and 6·42 (s, OMe), *J* (2-*exo*,3-*exo*) 8·7 Hz, $\nu_{max.}$ 1605 (*cis*-ClC=CCl) and 1735 (C=O) cm.$^{-1}$.

Hydrolysis and Epimerisation of Methyl 1,4,5,6,7-syn-*Pentachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (XXVIII).—The ester (XXVIII) (100 mg.) was dissolved in methanol (3 ml.), potassium hydroxide (300 mg.) was added, and the mixture was boiled at reflux for 16 hr., cooled, diluted with water (10 ml.), washed with methylene chloride (10 ml.), acidified with concentrated hydrochloric acid, and extracted with methylene chloride (3 × 10 ml.). The extract was dried ($MgSO_4$) and evaporated to leave a residue, which was recrystallised from carbon tetrachloride to afford 1,4,5,6,7-syn-*pentachloro*-3-endo-*methoxynorborn*-5-*ene*-2-exo-*carboxylic acid* (XXIX) (82 mg.), sublimes 148—155° (Found: C, 31·7; H, 2·3. $C_9H_7Cl_5O_3$ requires C, 31·8; H, 2·1%), τ (100 MHz) 5·68 (d, H-3-*exo*), 7·15 (d, H-2-*endo*), 5·13 (s, H-7-*anti*), 6·45 (s, OMe), and −1·6 (s, CO_2H), *J* (2-*endo*-3-*exo*) 2·9 Hz, $\nu_{max.}$ 1602 (*cis*-ClC=CCl), 1720 (C=O), and 3000—3400 (OH) cm.$^{-1}$.

The acid (XXIX) was also obtained by hydrogenolysis, in the presence of potassium hydroxide, of the ester (VII) (procedure of Alden and Davies [42]).

Reduction with Zinc of Methyl 1,4,5,6,7,7-*Hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (VII).—The

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

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ester (VII) (389 mg.) dissolved in glacial acetic acid (5 ml.) was heated at reflux for 2 hr. with zinc powder (330 mg.). The mixture was filtered, and the filtrate was poured into water (20 ml.) and extracted with methylene chloride (3 × 20 ml.). The extract was washed with saturated sodium hydrogen carbonate solution (3 × 30 ml.), dried ($MgSO_4$), and evaporated to afford methyl 1,4,5,6,7-*syn*-pentachloro-3-*endo*-methoxynorborn-5-ene-2-*endo*-carboxylate (XXVIII) (340 mg.), m.p. and mixed m.p. 158—163° (from carbon tetrachloride), with the expected spectral properties.

Diels–Alder Addition of Methyl Propiolate to 1,2,3,4,5-*Pentachlorocyclopenta*-2,5-*diene*.—Pentachlorocyclopentadiene (20 g.) (prepared by cracking its recrystallised dimer 5*H*,10*H*-decachloropentacyclo[5,2,1,$0^{2,6}$,$0^{3,9}$,$0^{4,8}$]decane) [31] and methyl propiolate (6 g.) were heated in a sealed tube at 140° for 17 hr. The residue was distilled (b.p. 124—128°/0·7 mm.) and fractionally recrystallised from carbon tetrachloride to afford *methyl* 1,4,5,6,7-syn-*pentachloronorborna*-2,5-*diene*-2-*carboxylate* (XXX) (10 g.), m.p. 103—107° (Found: C, 33·3; H, 1·7. $C_9H_5Cl_5O_2$ requires C, 33·5; H, 1·6%), τ (60 MHz) 2·5 (s, H-3), 5·2 (s, H-7-*anti*), and 6·18 (s, OMe), $\nu_{max.}$ 1590 [$CH=C(CO_2Me)$], 1610 (*cis*-ClC=CCl), and 1730 (C=O) cm.$^{-1}$. On the basis of n.m.r. analysis of the crude product, 14% of methyl 1,4,5,6,7-*anti*-pentachloronorborna-2,5-diene-2-carboxylate was present: τ (100 MHz) 2·78 (d, H-3), 5·3 (d, H-7-*syn*), and 6·2 (OMe), *J* (3,7-*syn*) 1·2 Hz.

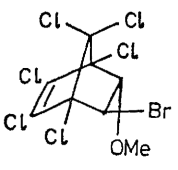
Addition of Methanol to 1,4,5,6,7-syn-*Pentachloronorborna*-2,5-*diene*-2-*carboxylate* (XXX).—(*a*) The diene (XXX) (322 mg.) was dissolved in a solution of sodium (23 mg.) in methanol (5 ml.) and heated at reflux for 2 hr. The solution was cooled, poured into saturated sodium hydrogen carbonate solution (10 ml.), and extracted with methylene chloride (3 × 5 ml.), but no neutral material was obtained. The aqueous solution was acidified and product was extracted with methylene chloride (3 × 5 ml.). The extract was dried ($MgSO_4$) and evaporated to leave a residue shown by n.m.r. to contain acids (XXXI) and (XXIX) in the ratio 7 : 3. The acids were separated by fractional crystallisation from carbon tetrachloride; acid (XXIX) had properties listed previously, whereas 1,4,5,6,7-syn-*pentachloro*-3-exo-*methoxynorborn*-5-*ene*-2-endo-*carboxylic acid* (XXXI) had m.p. 141—142° (sublimes) (Found: C, 31·9; H, 2·3. $C_9H_7Cl_5O_3$ requires C, 31·8; H, 2·1%), τ (100 MHz) 2·6br (s, CO_2H), 5·3 (s, H-7-*anti*), 6·05 (d, H-3-*endo*), 6·8 (d, H-2-*exo*), and 6·4 (s, OMe), *J* (2-*exo*,2-*endo*) 2·7 Hz, $\nu_{max.}$ 1720 (C=O), 1604 (*cis*-ClC=CCl) and 2900—3400 (OH) cm.$^{-1}$.

(*b*) The diene (XXX) (322 mg.) was dissolved in a solution of sodium (23 mg.) in methanol (5 ml.) at room temperature. After 5 min. the solution was poured into saturated sodium hydrogen carbonate solution (10 ml.) and extracted with methylene chloride (3 × 5 ml.). The extract was dried ($MgSO_4$) and evaporated, and the residue was shown by analysis (100 MHz n.m.r. spectrum) to contain compounds (XXXII), (XXXIII), and (XXVIII) in the ratio 70 : 23 : 7. Column chromatography on silica gel (2% ether–light petroleum as eluant) afforded successively *methyl* 1,4,5,6,7 syn-*pentachloro*-3-exo-*methoxynorborn*-5-*ene*-2-endo-*carboxylate* (XXXII), m.p. 67—70° (Found: C, 33·8; H, 2·8. $C_{10}H_9Cl_5O_3$ requires C, 33·9; H, 2·6%), τ (100 MHz) 6·05 (d, H-3-*endo*), 6·85 (d, H-2-*exo*), 5·3 (s, H-7-*anti*), 6·20 (s, OMe), and 6·45 (s, OMe), *J* (2-*exo*,3-*endo*) 2·5 Hz, $\nu_{max.}$ 1603 (*cis*-ClC=CCl) and 1735 (C=O) cm.$^{-1}$; *methyl* 1,4,5,6,7-syn-*pentachloro*-3-endo-*methoxynorborn*-5-*ene*-2-exo-*carboxylate* (XXXIII), m.p. 76—79° (Found: C, 33·9; H, 2·9. $C_{10}H_9Cl_5O_3$ requires C, 33·9; H, 2·6%), τ (100 MHz) 5·65 (d, H-3-*exo*), 7·10 (d, H-2-*endo*), 5·0 (s, H-7-*anti*), 6·20 (s, OMe), and 6·50 (s, OMe), *J* (2-*endo*,3-*exo*) 2·8 Hz, $\nu_{max.}$ 1602 (*cis*-ClC=CCl) and 1730 (C=O) cm.$^{-1}$; and compound (XXVIII), identical with the product of zinc–acetic acid reduction or catalytic hydrogenolysis of the ester (VII).

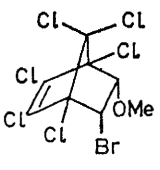
The reaction was also performed on the same scale but with 1 mmole of *N*-methylmorpholine in place of sodium methoxide as base. With a reaction time of 15 hr. the three esters were formed in the same ratio to that given above.

The acids (XXIX) and (XXXI) were quantitatively converted, on treatment with diazomethane in ether solution, into the respective methyl esters (XXXIII) and (XXXII).

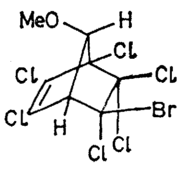
Cristol–Firth Reaction of 1,4,5,6,7,7-*Hexachloro*-3-endo-*methoxynorborn*-5-*ene*-2-endo-*carboxylic Acid* (XXVI).—A solution of bromine (1·12 g.) in carbon tetrachloride (20 ml.) was added during 30 min. to a solution of the acid (XXVI) (2·63 g.) in carbon tetrachloride (200 ml.) in which red mercury(II) oxide (1·52 g.) was suspended. The mixture was kept at reflux in the dark during the addition, and then maintained at reflux for a further 30 min. The mixture was filtered and washed with saturated sodium hydrogen carbonate solution (3 × 100 ml.) and sodium thiosulphate solution (2 × 100 ml.). The solution was dried ($MgSO_4$) and evaporated to afford a residue which was washed with light petroleum and recrystallised from carbon tetrachloride to afford 5-exo-*bromo*-1,4,5-endo,6-exo,7,7-*hexachloro*-3-endo-*methoxy*-6-endo-*hydroxynorbornane*-2-endo-*carboxylic acid lactone* (XXVII) (1·36 g.), m.p. 182—183° with sublimation at 170—180° (Found: C, 24·2; H, 1·1. $C_9H_5BrCl_6O_3$ requires C, 23·8; H, 1·1%), τ (100 MHz) 4·95 (d, H-3-*exo*), 6·35 (d, H-2-*exo*), and 6·30 (s, OMe), *J* (2-*exo*,3-*exo*) 10 Hz, $\nu_{max.}$ 1830 cm.$^{-1}$ (C=O); no absorption near 1610 cm.$^{-1}$ (*cis*-ClC=CCl). The filtrate from the crystallisation was shown by n.m.r. (100 MHz) to contain a mixture (1·56 g.) of the bromides (XXXIX), (XL), and (XLI) in the ratio 57 : 16 : 28. Separation by column chromatography on basic alumina (light petroleum as eluant) afforded successively the following bromides, which were recrystallised from methanol. 5-exo-*Bromo*-1,2,3,4,7,7-*hexachloro*-6-endo-*methoxynorborn*-2-*ene* (XXXIX), b.p. 110°/0·5 mm. (Found: C, 23·5; H, 1·3. $C_8H_5BrCl_6O$ requires C, 23·4; H, 1·2%), τ (100 MHz) 5·45 (d, H-5-*exo*), 6·1 (d, H-6-*endo*), and 6·35 (s, OMe), *J* (5-*endo*,6-*exo*) 2·5 Hz, $\nu_{max.}$ 1602 cm.$^{-1}$ (*cis*-ClC=CCl). 5-endo-*Bromo*-1,2,3,4,7,7-*hexachloro*-6-endo-*methoxynorborn*-2-*ene* (XL), m.p. 62—63° (Found: C, 23·4; H, 1·4%), τ (100 MHz) 5·15 (d, H-5-*exo*), 5·85 (d, H-6-*endo*), and 6·40 (s, OMe), *J* (5-*exo*,6-*exo*) 7 Hz, $\nu_{max.}$ 1605 cm.$^{-1}$ (*cis*-ClC=CCl). 5-exo-*Bromo*-1,2,3,5-endo,6,6-*hexachloro*-7-syn-*methoxynorborn*-2-*ene* (XLI), m.p. 99—103° (Found: C, 23·2; H, 1·4%), τ (100 MHz) 5·6 (d, H-7-*anti*), 6·2 (d, H-4), and 6·43 (s, OMe), *J* (4,7-*anti*) 2 Hz, $\nu_{max.}$ 1620 (*cis*-ClC=CCl).



(XXXIX)



(XL)



(XLI)

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Compound (XL) was also synthesised by the following procedure. 1-Bromo-2-methoxyethylene[43] (2·0 g.; shown by n.m.r. to contain *cis*- and *trans*-isomers in the ratio 2·9 : 1·0), hexachlorocyclopentadiene (2·7 g.), and quinol (0·1 g.) were heated at 150° for 16 hr. in a sealed tube. The tarry product was extracted with chloroform (100 ml.) and after removal of solvent the extract was purified by chromatography on basic alumina (light petroleum as eluant) to afford compound (XL), (450 mg.), m.p. 62—63° (from methanol), as sole isolable product, having properties identical to those already listed.

Addition of Hydrogen to Methyl 1,4,5,6,7,7-*Hexachloronorborna*-2,5-*diene*-2-*carboxylate* (VI).—A solution of the methyl ester (VI) (0·5 g.) in absolute ethanol (50 ml.) was shaken over 10% palladium–charcoal (50 mg.) under hydrogen until 1 mol. had been absorbed (15 min.). The mixture was filtered and evaporated to afford methyl 1,4,5,6,7,7-hexachloronorborn-5-ene-2-*endo*-carboxylate (XII) (0·5 g.), m.p. 40·5—41·5°, identical with an authentic specimen.[30] Adams platinum oxide and Raney nickel[41] were equally effective catalysts.

Reduction of 1,2,3,4,7,7-*Hexachloro*-5-endo,6-endo-*epoxynorborn*-2-*ene* (VIII) *with Lithium Aluminium Hydride.*—A solution of epoxide (VIII) (0·1 g.) in anhydrous ether (2·5 ml.) was added to a suspension of lithium aluminium hydride (0·004 g.) in ether (2·5 ml.), and the resulting mixture was stirred for 24 hr. The excess of hydride was destroyed with water (1 ml.), and the mixture was poured into ice-cold dilute sulphuric acid (10 ml.). The ethereal layer was separated, and the aqueous layer extracted with carbon tetrachloride (4 × 10 ml.). The combined extracts were dried ($MgSO_4$), filtered, and evaporated to give 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ol (IX) (0·098 g.), m.p. 154—155°, identical with an authentic specimen.[29]

Addition of Hydrogen to 1,2,3,4,7,7-*Hexachloro*-5-endo,6-endo-*epoxynorborn*-2-*ene* (VIII).—A solution of the epoxide (VIII) (27 mg.) in anhydrous ethanol (10 ml.) was shaken over Adams platinum oxide (10 mg.) in hydrogen until 1 mol. had been absorbed. Filtration and evaporation afforded 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ol (IX) (25 mg.), m.p. 153—154·5°, identical with an authentic specimen.[29]

Reduction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-*one* (XVII) *with Lithium Aluminium Hydride.*—A solution of the hexachloronorbornenone (XVII) (1·05 g.) in ether (50 ml.) was added dropwise during 2 hr. to a stirred suspension of lithium aluminium hydride (0·05 g.) in ether (50 ml.). The mixture was then stirred in the cold for a further 18 hr. The excess of hydride was destroyed with ethyl acetate (1 ml.). The mixture was poured carefully into an excess of ice-cold dilute sulphuric acid (100 ml.). The ethereal layer was separated, and the aqueous layer was washed with carbon tetrachloride (2 × 50 ml.). The organic extracts were combined, dried ($MgSO_4$), filtered, and evaporated. The crude product (0·75 g.) was distilled to afford a mixture (0·6 g.) of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ol,(IX) and its 2-*exo*-isomer (XVIII), b.p. 90—95/0·1 mm., as a waxy solid m.p. 20—30° (Found: C, 26·5; H, 1·3; Cl, 66·9. $C_7H_4Cl_6O$ requires C, 26·55; H, 1·25; Cl, 67·15%).

G.l.c. analysis showed that the crude product contained two compounds in the ratio 15 : 85. The retention time and the n.m.r. spectrum of the minor isomer were identical with those of authentic 2-*endo*-ol (IX).[29] Compound (XVIII) showed τ (100 MHz) 6·0 (q, H-2-*endo*), 7·35 (q, H-3-*exo*), and 7·55 (q, H-3-*endo*), *J* (2-*endo*,3-*endo*) 7·5, *J* (2-*endo*,3-*exo*) 4·5, *J* (3-*endo*,3-*exo*) 12·5 Hz, $\nu_{max.}$ 1610 (*cis*-ClC=CCl) and 3100—3600 (OH) cm.$^{-1}$.

Reaction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-*one* (XVII) *with Methylmagnesium Iodide.*—Methyl iodide (2·84 g.) was added dropwise during 0·5 hr. to a suspension of magnesium turnings (0·48 g.) in ether (15 ml.). When the formation of the Grignard reagent was complete, the mixture was stirred for 0·5 hr., then a solution of the ketone (XVII) (3·15 g.) in ether (20 ml.) was added during 0·5 hr. The mixture was stirred at room temperature for 4 hr., and then crushed ice was added to decompose the unchanged Grignard reagent. After acidification with 6N-hydrochloric acid (20 ml.), the ethereal layer was separated, and the aqueous layer was washed with ether (3 × 20 ml.). The combined ethereal extracts were dried ($MgSO_4$), filtered, and evaporated to give a brown solid (1·8 g.), which afforded white crystals of 1,4,5,6,7,7-*hexachloro*-2-endo-*methylnorborn*-5-*en*-2-exo-*ol* (XIX), m.p. 185—186° (from light petroleum) (Found: C, 28·85; H, 1·8; Cl, 63·9. $C_8H_6Cl_6O$ requires C, 29·05; H, 1·85; Cl, 64·25%), τ (60 MHz) 7·30 (d, H-3-*exo*), 7·73 (d, H-3-*endo*), 8·72 (s, Me), and 7·20 (s, OH), *J* (3-*exo*,3-*endo*) 13 Hz, $\nu_{max.}$ 1612 (*cis*-ClC=CCl) and 3300—3600 (OH) cm.$^{-1}$.

Reaction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-*one* (XVII) *with Isopropylmagnesium Chloride.*—To magnesium turnings (0·48 g.) under nitrogen, a few drops of isopropyl chloride and a crystal of iodine were added. When reaction commenced, the remainder of the isopropyl chloride (1·5 g.) in ether (10 ml.) was added at such a rate (0·5 ml./min.) as to maintain moderate reflux. After the addition, the mixture was stirred for 2 hr. and set aside overnight. A solution of the ketone (XVII) (3·15 g.) in ether (15 ml.) was added dropwise with stirring during 0·5 hr. to the isopropylmagnesium chloride in ether. After 4 hr. stirring at room temperature the mixture was worked up as for the methylmagnesium iodide reaction. The crude product (3·5 g.) on distillation gave a colourless waxy material (2·8 g.), b.p. 132—138°/2·5 mm., which on treatment with light petroleum (5 ml.) slowly deposited white crystals of 1,4,5,6,7-syn-*pentachloronorborn*-5-*en*-2-endo-*ol* (XX) (0·4 g.), m.p. 106—107° (Found: C, 28·85; H, 1·45; Cl, 60·55. $C_7H_5Cl_5O$ requires C, 28·75; H, 1·7; Cl, 60·3%), τ (60 MHz) 5·30 (s, H-7-*anti*), 5·98 (q, H-2-*exo*), 7·39 (q, H-3-*exo*), and 7·94 (q, H-3-*endo*), *J* (3-*exo*,3-*endo*) 13, *J* (3-*exo*,2-*exo*) 7·5, *J* (2-*exo*,3-*endo*) 3 Hz, $\nu_{max.}$ 1610 (*cis*-ClC=CCl) and 3200—3550 (OH) cm.$^{-1}$. G.l.c. analysis of the crude product at 180° showed that it contained compounds (XX) (50%), (XVIII) (16%), and (IX) (34%). The alcohols (IX) and (XVIII) were identified by comparison with the product of the reduction of (XVII) with lithium aluminium hydride.

The reaction was repeated with equimolar quantities of the reagents [ketone (XVII) (3·15 g.), magnesium turnings (0·24 g.), and isopropyl chloride (0·78 g.)]. The crude product (3 g.) contained compounds (XX) (48%), (IX) (30%), and (XVIII) (22%).

Reaction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-*one* (XVII) *with Ethylmagnesium Bromide.*—A solution of ethyl bromide (2·18 g.) in ether (5 ml.) was added dropwise during 0·5 hr. to a suspension of magnesium turnings (0·48 g.) in ether (10 ml.). When the reaction was complete, the mixture was stirred for 0·5 hr., and a solution of the ketone (XVII) (3·15 g.) in ether (20 ml.) was added during 0·5 hr.

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[43] J. F. Arens, *Rec. Trav. chim.*, 1955, **74**, 271.

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The mixture was then stirred at room temperature for a further 5 hr., and was worked up as for the methylmagnesium iodide reaction. The crude product (3·5 g.) was distilled to give a white waxy solid (2·7 g.), m.p. 25—30°, b.p. 139—141°/2·5 mm. G.l.c. analysis of the crude mixture at 180° showed it contained compounds (XX) (8%), (IX) (41%), and (XVIII) (51%).

The reaction was repeated with the ketone (XVII) (3·15 g.), magnesium turnings (0·24 g.), and ethyl bromide (1·09 g.). The crude product contained compounds (XX) (4%), (IX) (42%), and (XVIII) (54%).

Unsuccessful Additions to Hexachloronorbornadiene (III).—The following reagents did not add to hexachloronorbornadiene (III): benzyne generated by reaction of pentyl nitrite with anthranilic acid,[20] 1-chlorobenzotriazole,[21] maleic anhydride under conditions where it adds to norbornadiene,[22] dimethyl acetylenedicarboxylate under conditions where it adds to norbornadiene,[23] oxymercuration–demercuration reagent.[19]

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