The Cyclic Acetals from 1,4,5,6,7,7-Hexachloronorborn-5-en-2-*endo*-ylalkanols

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The reaction of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethanol with sodium ethoxide to afford the cyclic acetal 5-*endo*,6,7,7,8-pentachloro-4-*exo*-ethoxy-3-oxatricyclo[4.2.1.$0^{4,8}$]nonane is found to involve the intermediacy of 1,4,5,7,7-pentachloro-6-ethoxynorborn-5-en-2-*endo*-ylmethanol and 4-*exo*,5-*endo*,6,7,7,8-hexachloro-3-oxatricyclo[4.2.1.$0^{4,8}$]nonane. 6-*endo*,7,8,8,9-Pentachloro-5-*exo*-ethoxy- and methoxy-4-oxatricyclo-[5.2.1.$0^{5,9}$]decane are formed from the reactions of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylethanol with sodium ethoxide and methoxide, respectively. N.m.r. studies suggest that in these product cyclic acetals the conformation of the pyran ring tends towards a boat rather than a chair form.

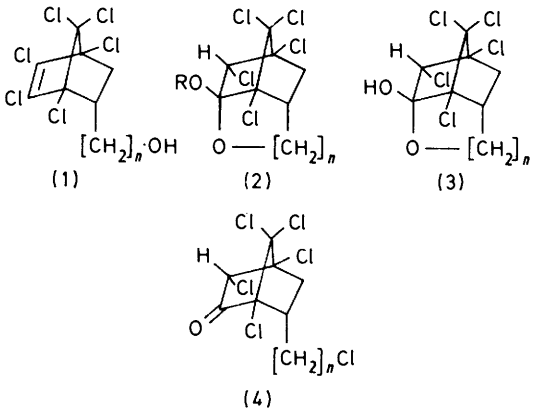
THE reaction of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethanol (1A) with sodium ethoxide in ethanolic solution gives the cyclic acetal (2A), which on treatment with acid affords the hemiacetal (3A); the reaction of (3A) with phosphorus pentachloride produces the chloroketone (4A).[1] This series of reactions is well documented, and a variety of cyclic acetals related to (2A) can be formed by reactions of (1A) with other sodium alkoxides.[1,2] It was subsequently reported [3] that (1A) on treatment with sodium methoxide afforded the cyclic acetal (2B). Surprisingly these authors did not mention the work of Hoch, who had investigated the above reaction and established the structure of (2B) some four years earlier.[1] No reaction pathways for the conversion of (1) to (2) had been proposed, and it seemed to us that

[1] P. E. Hoch, G. B. Stratton, and J. G. Colson, *J. Org. Chem.*, 1969, **34**, 1912.

[2] P. E. Hoch and G. B. Stratton, U.S.P. 3,346,596 (*Chem. Abs.*, 1968, **68**, 39199a); U.S.P. 3,419,380 (*Chem. Abs.*, 1969, **70**, 67761n); P. E. Hoch, U.S.P. 3,661,998 (*Chem. Abs.*, 1972, **77**, 87982h); U.S.P. 3,821,307 (*Chem. Abs.*, 1974, **81**, 120111f).

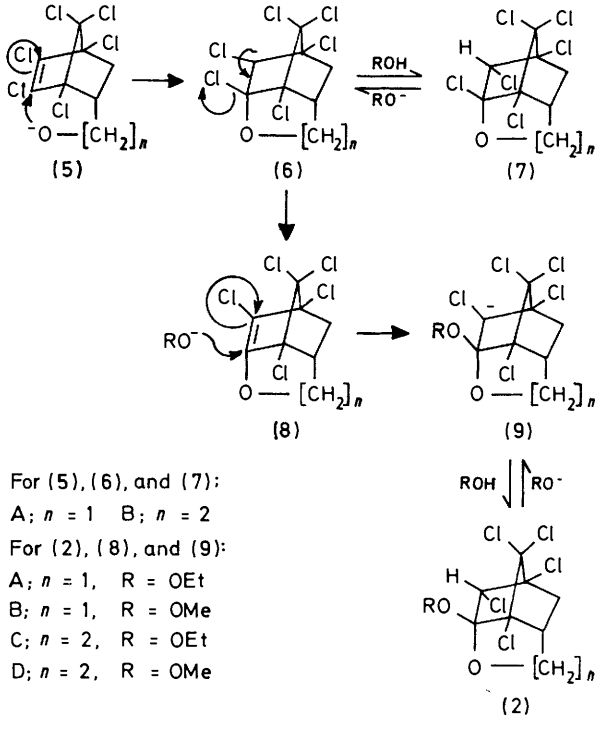
[3] M. Perscheid and K. Ballschmiter, *Z. Naturforsch.*, 1973, **28***b*, 549.

two possibilities were those outlined in Schemes 1 and 2. They differ as to whether the initial reaction involves an



For (1), (3), and (4): A; n = 1 B; n = 2
For (2): A; n = 1, R = OEt B; n = 1, R = OMe
C; n = 2, R = OEt D; n = 2, R = OMe

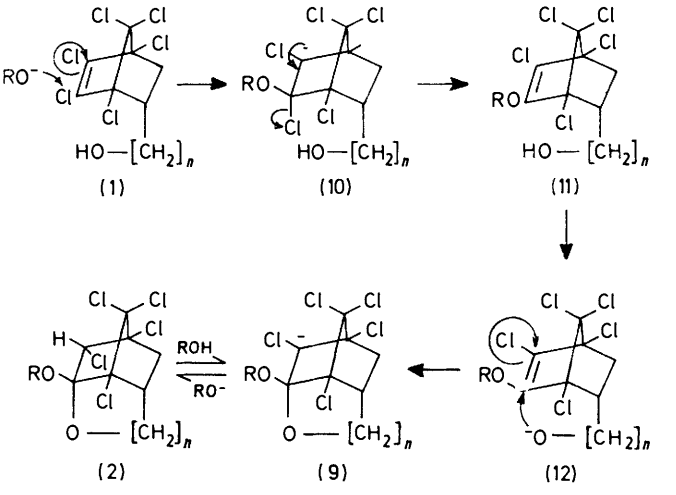
intramolecular alkoxide ion cyclisation (Scheme 1) or whether attack of alkoxide ions occurs on the chlorine-substituted double bond prior to intramolecular cyclisation (Scheme 2). A convenient procedure for the formation of (2A) is to add, during 1 h, a solution of (1A) in ethanol to a solution of sodium ethoxide in refluxing



For (5), (6), and (7):
A; n = 1 B; n = 2
For (2), (8), and (9):
A; n = 1, R = OEt
B; n = 1, R = OMe
C; n = 2, R = OEt
D; n = 2, R = OMe

SCHEME 1

ethanol, and then to boil the mixture at reflux for a further 2 h. However when the addition is carried out at room temperature and stirring is continued for 48 h at room temperature, equally good yields of (2A) result. If under these conditions the reaction is worked up after 16 h, the i.r. spectrum of the crude product contains a band at 1 645 cm^{-1} due to a substituted double bond in addition to that at 1 603 cm^{-1} due to the chlorine-substituted double bond in (1A). Both these double bond absorptions were absent from the i.r. spectrum of the product, effectively pure (2A), obtained after 48 h. The cyclic acetal (2A) exhibits an n.m.r. doublet at τ 5.43 due to >C*H*Cl. The n.m.r. spectrum of the crude product obtained after 16 h, however, showed a more complex pattern in the τ 5.3—5.5 region, of which the τ 5.43 doublet was a part, suggesting that, in addition to (2A), another compound containing the structural unit >CHCl



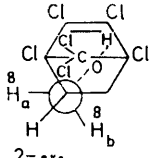
For (1): A; n = 1 B; n = 2
For (2), (9), (10), (11), and (12):
A; n = 1, R = OEt B; n = 1, R = OMe
C; n = 2, R = OEt D; n = 2, R = OMe

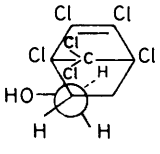
SCHEME 2

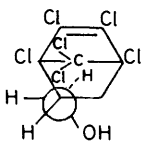
was present. Work-up after 16 h of a large-scale reaction at room temperature allowed isolation of the intermediates (7A) and (11A). These were recognised from their n.m.r. spectral parameters (see Experimental section), and additionally in the case of (7A) by its identity with material synthesised by the oxidation of (1A) with lead tetra-acetate or the reaction of (1A) with a suspension of potassium hydroxide in benzene. The isolation of (7A) and (11A) in the conversion of (1A) into (2A), and the observation that they are not present at the end of the reaction when (2A) is isolated in high yield, strongly support the proposal that they are intermediates in the formation of (2A) from (1A) *via* Schemes 1 and 2. Intermediate (8A) in Scheme 1 is an anti-Bredt compound containing a *transoid* double bond in a seven-membered ring. This does not, however, invalidate Scheme 1, since recent work [4] on the enolate of brendan-2-one has demonstrated the existence of such structures.

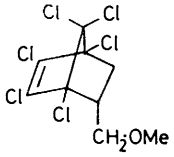
[4] A. Nickon, D. F. Covey, Fu-chih Huang, and Yu-Neng Kuo, *J. Amer. Chem. Soc.*, 1975, **97**, 904.

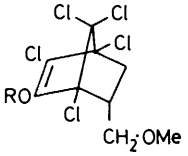
The conditions under which compound (1A) reacts with alkoxide ions do not afford any reaction with 1,2,3,4,7,7-hexachloronorborn-2-ene.[1] Therefore the 2-*endo*-hydroxymethyl group in (1A) must activate the chlorine-substituted double bond towards reaction with alkoxide ions. The hydroxy-group is inductively electron-attracting, and if (1A) were to adopt a conformation in which the hydroxy-group is directed towards the chlorine-substituted double bond, interaction between the lone pair electrons on oxygen and the π-electrons of the double bond could lead to an intramolecular OH · · · π-bonded system.[5] This would reduce the electron density at the carbon atoms of the double bond, and make them more susceptible towards nucleophilic attack. The orientation (13) in which the hydroxy-group is directed towards the chlorine-substituted double bond is supported by the n.m.r. spectral data for (1A) and related compounds (Table 1). The results suggest that in (1A) the 8-protons H_a and H_b have similar environments. Any alternative

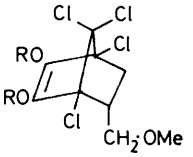

2-*exo* (13)


(14)

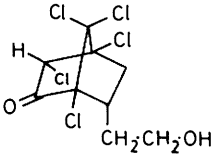

(15)


(17)


(18)


(19)

For (18) and (19):
A; R = OEt B; R = OMe

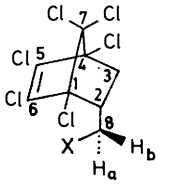

(20)

arrangements, *e.g.* (14) or (15), would result in one of the C-8 protons being underneath the ring system and hence in a different environment from the other. The coupling constants J(2-*exo*, 8a) and J(2-*exo*, 8b) do not differ markedly (7.2 and 5.6 Hz) from the values (6.8 Hz) for (16; X = Me). This also supports the conformation (13), since in either (14) or (15) the values for J(2-*exo*, 8a) and J(2-*exo*, 8b) would differ substantially. This appears to be the case (see Table 1) in (16; X = Cl, Br, or I), which suggests that these molecules prefer conformations related to either (14) or (15) in which the carbon–halogen bond points away from the ring system.

1,4,5,6,7,7-Hexachloronorborn-5-en-2-*endo*-ylmethyl methyl ether (17), on the basis of its n.m.r. spectral data (Table 1), may also have an oxygen atom relatively close to the chlorine-substituted double bond. As the methoxy-group attracts electrons inductively, it was expected that it would activate the chlorine-substituted double bond for attack by a nucleophile. This was borne out experimentally when the reactions of (17) with eth-

TABLE 1

N.m.r. spectral data (90 MHz), for 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethane derivatives (16)


(16)

τ Values

X	H-3-*endo*	H-3-*exo*	H-2-*exo*	H_a-8	H_b-8
H	8.37	7.35	7.10	8.95	8.95
Cl	8.04	7.27	6.79	6.90	6.20
Br	8.07	7.27	6.73	7.15	6.39
I	8.17	7.28	6.70	7.41	6.53
OH	8.11	7.38	6.97	6.58	6.20
OMe *	8.26	7.65	7.34	7.21	6.84

J/Hz

X	3-*endo*, 3-*exo*	3-*endo*, 2-*exo*	3-*exo*, 2-*exo*	2-*exo*, 8a	2-*exo*, 8b	8a, 8b
H	−11.8	3.5	8.6	6.8	6.8	6.8
Cl	−12.8	3.7	8.5	1.0	1.5	−7.7
Br	−13.0	4.1	8.5	11.3	3.2	−9.7
I	−13.0	4.3	9.0	11.3	3.3	−9.0
OH	−12.4	3.9	8.7	7.2	5.6	−10.9
OMe	−11.3	3.5	8.2	7.8	7.0	−13.0

* OCH_3, 7.04 (s).

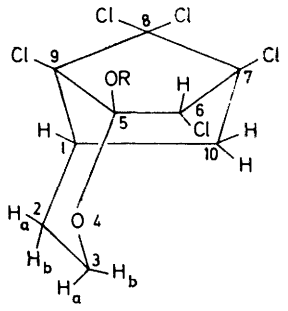
oxide and methoxide ions afforded compounds (18A) and (19A), and (18B) and (19B), respectively, identified by their spectral data (see Experimental section).

In an extension of the conversion of (1A) into (2A) and (2B) the reaction of 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylethanol (1B) with ethoxide and methoxide ions was investigated. The six-membered ring cyclic acetals (2C) and (2D), respectively, were formed under conditions comparable to those required for the formation of (2A) and (2B) from (1A). Acidic hydrolysis of (2C) and (2D) gave the hemiacetal (3B), often contaminated with the hydroxy-ketone (20). It was possible to isolate (3B) by crystallisation. Acidic hydrolysis for a prolonged period gave substantial quantities of (20). The hemiacetal (3B) could be converted into the chloroketone (4B) by treatment with phosphorus pentachloride, a reaction analogous to the formation of (4A) from (3A).

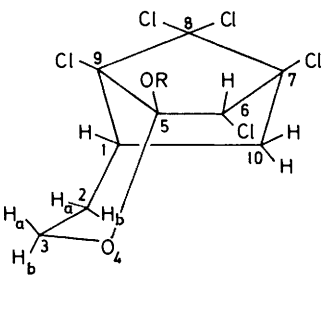
A point of interest in the structures of compounds (2C and D) and (3B) is the conformation of the pyran ring, which could approach either a boat (22) or a chair (21) structure. Information as to the conformation is provided by J(1-*exo*, 2a) and J(1-*exo*, 2b), which

[5] S. Ueji and T. Kinugasa, *Tetrahedron Letters*, 1976, 2037.

should vary with dihedral angle. In the chair form (21), H-1-*exo* bisects the angle between the 2-protons H_a and



(21)



(22)

H_b, and J(1-*exo*, 2a) and J(1-*exo*, 2b) should be equal or at least similar. In the boat form (22), H-1-*exo* and H-2a are eclipsed, whereas H-1-*exo* and H-2b are at the tetrahedral bond angle, which should result in markedly different values for the coupling constants. The observed values (Table 2) are in fact substantially different which makes the boat conformation (22) or something approaching it, much more probable than the chair conformation (21). This may be rationalised by the observation, from molecular models, that the 3-proton H_b in the chair conformation (21) is closer to the 6-*endo*-chlorine atom than is the 3-proton H_a to the 9-chlorine atom in the boat conformation (22). A distorted version of the boat conformation (22), possibly of the twist boat type, would reduce this latter non-bonded interaction still further.

EXPERIMENTAL

N.m.r. spectral measurements at 90 MHz were obtained by using a Bruker HFX 90 instrument.

The following compounds were made by literature procedures: 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethanol (1A),[6] 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethyl chloride (16; X = Cl),[6] 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethyl bromide (16; X = Br),[6] and 1,4,5,6,7,7-hexachloronorborn-5-en-2-*endo*-ylmethyl iodide (16; X = I).[7]

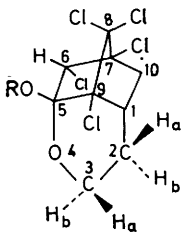
1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-endo-*ylmethane* (16; X = H).[8]—Hexachlorocyclopentadiene (22.0 g, 0.08 mol) and propene (5.0 g, 0.12 mol) were heated in a sealed tube under nitrogen at 180 °C for 6 h. The tube was then cooled and opened, and the excess of propene allowed to evaporate. The residue was treated with charcoal and recrystallised from methanol to afford 1,4,5,6,7,7-*hexachloronorborn*-5-*en*-2-endo-*ylmethane* (16; X = H) (15.5 g), m.p. 140—141 °C (Found: C, 31.3; H, 2.1. $C_8H_6Cl_6$ requires C, 31.2; H, 1.9%); for n.m.r. data see Table 1; $\nu_{max.}$ 1 607 cm^{-1} (*cis*-ClC=CCl).

1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-endo-*ylmethyl Methyl Ether* (17).—Allyl bromide (10 g, 0.082 mol) was added dropwise, with stirring, to a solution of iodine (2.2 g, 0.096 mol) in dry methanol (74 ml). This solution was boiled at reflux for 1 h. Careful fractionation afforded allyl methyl ether (5.2 g), b.p. 46–47° (lit.,[9] 45.5—47°). This ether (5.2 g, 0.072 mol) and hexachlorocyclopentadiene (14.5 g, 0.053 mol) were heated in a Carius tube at 120 °C for 24 h. Fractional distillation afforded the *methyl ether* (17) (14.4 g), b.p. 92—94° at 0.3 mmHg; for n.m.r. data see Table 1; $\nu_{max.}$ 1 610 cm^{-1} (*cis*-ClC=CCl).

1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-endo-*ylethanol* (1B).—Vinylacetic acid (14.0 g, 0.16 mol) dissolved in anhydrous diethyl ether (30 ml) was added carefully to a suspension of

TABLE 2

N.m.r. spectral data (90 MHz) for 5-*exo*-alkoxy (or hydroxy)-6-*endo*,7,8,8,9-pentachloro-4-oxatricyclo[5.2.1.0^{5,9}]decanes



τ Values

Compound	R	H-1-*exo*	H_a-2	H_b-2	H_a-3	H_b-3	H-6-*exo*	H-10-*endo*	H-10-*exo*
(2C)	Et *	7.04	7.90	8.44	5.66	6.02	5.24	7.57	7.60
(2D)	Me †	7.11	7.93	8.41	5.65	6.03	5.25	7.61	7.64
(3B)	H ‡	6.99	7.89	8.48	5.51	6.12	5.19	7.49	7.53

J/Hz

Compound	R	1-*exo*, 2a	1-*exo*, 2b	1-*exo*, 10-*endo*	1-*exo*, 10-*exo*	2a, 2b	2a, 3a	2a, 3a	2b, 3a	2b, 3b	3a, 3b	10-*endo*, 10-*exo*	10-*exo*, 6-*exo*
(2C)	Et	6.0	3.5	8.2	11.0	14.0	3.5	3.5	11.0	5.5	12.5	0	1.5
(2D)	Me	6.6	3.3	8.3	10.8	13.3	3.3	3.3	10.8	5.8	12.3	0	1.7
(3B)	H	4.6	3.3	8.3	11.6	14.1	1.7	3.3	12.8	5.8	12.2	0	2.0

* O·CH_2·CH_3, 6.29 (q), 8.78 (t). † OCH_3, 6.58 (s). ‡ OH, 6.67 (s).

[6] E. T. McBee, H. Rakoff, and R. K. Meyers, *J. Amer. Chem. Soc.*, 1955, **77**, 4427; E. K. Fields, *ibid.*, 1954, **76**, 2709.

[7] R. Riemschneider and H. J. Kolzsch, *Monatsh.*, 1960, **91**, 41; D. I. Davies and P. Mason, *J. Chem. Soc.* (*C*), 1971, 288.

[8] Prepared by Dr. D. R. Adams, Ph.D. Thesis, London, 1973.

[9] J. C. Irvine, J. L. A. MacDonald, and C. Soutar, *J. Chem. Soc.*, 1915, **107**, 337.

lithium aluminium hydride (7.6 g, 0.2 mol) in anhydrous ether (80 ml). The excess of hydride was then destroyed by careful addition of ethyl acetate and water. The mixture was then extracted with ether (3 × 100 ml); the ether layer was separated, dried ($MgSO_4$), and evaporated. Distillation of the crude product afforded but-3-en-1-ol (8.4 g), b.p. 112—114° (lit.,[10] 112—114°). Hexachlorocyclopentadiene (18 g, 0.066 mol) and but-3-en-1-ol (5 g, 0.069 mol) were heated in a Carius tube at 160 °C for 24 h. Distillation of the crude product afforded the *alcohol* (1B) (21 g), b.p. 124—126° at 0.1 mmHg (Found: C, 31.5; H, 2.45; Cl, 61.4. $C_9H_8Cl_6O$ requires C, 31.3; H, 2.3; Cl, 61.75%); τ 7.03 (m, H-2-*exo*), 8.22 (q, H-3-*endo*), 7.34 (q, H-3-*exo*), 8.76 and 8.07 (CH_2·CH_2·OH), 6.32 (t, CH_2·CH_2·OH), and 7.36 (s, OH); $\nu_{max.}$ 1 610 cm^{-1} (*cis*-ClC=CCl).

Reaction of the Alcohol (1A) *with Potassium Hydroxide in Benzene*.—The alcohol (1A) (5 g, 0.015 mol) was dissolved in a suspension of crushed potassium hydroxide (4.2 g, 0.075 mol) in benzene (100 ml), and the mixture boiled at reflux for 17 h. Water (100 ml) was then added, followed by concentrated hydrochloric acid until pH 7 was reached. The mixture was extracted with ether (3 × 100 ml), and the extract dried ($MgSO_4$) and evaporated; the residue was distilled to afford 4-exo,5-endo,6,7,7,8-*hexachloro*-3-*oxatricyclo*[4.2.1.$0^{4,8}$]*nonane* (7) (2 g), b.p. 89—91° at 0.01 mmHg (Found: C, 28.75; H, 1.8. $C_8H_6Cl_6O$ requires C, 29.0; H, 1.8%); τ 7.31 (m, H-1-*exo*), 5.35 (d, H-5-*exo*), 7.43 (q, H-9-*endo*), 7.37 (oct, H-9-*exo*), and 6.10 (q) and 5.67 (q) (CH_2·O); no double-bond i.r. absorption; M^+ 332.

Oxidation of the Alcohol (1A).—Anhydrous benzene (18 ml), the alcohol (1A) (5 g, 0.015 mol), lead tetra-acetate (7.1 g, 0.016 mol), and calcium carbonate (1.66 g, 0.016 5 mol) were placed in a 100 ml flask equipped with a water separator containing potassium carbonate. The mixture was stirred and heated at reflux for 8 h, then washed with water, dried, and filtered, and evaporated. The residue was distilled to afford 4-*exo*,5-*endo*,6,7,7,8-hexachloro-3-oxatricyclo[4.2.1.$0^{4,8}$]nonane (7) (0.21 g) with properties as above, followed by 1,2,3,4,7,7-hexachloronorborn-2-en-5-*endo*-ylmethyl acetate (5.05 g), b.p. 116—118° at 0.01 mmHg (lit.,[6] 154—155° at 2 mmHg).

Isolation of Intermediates in the Reaction of the Alcohol (1A) *with Sodium Ethoxide*.—The alcohol (1A) (1 g, 0.003 mol) dissolved in absolute ethanol (2.5 ml) was added to a solution of sodium ethoxide [sodium (0.3 g, 0.013 g atom) in ethanol (12 ml)]. The mixture was stirred at room temperature overnight (16 h), water (12 ml) was then added, and the pH was adjusted to 7 with concentrated hydrochloric acid. The precipitated solid cyclic acetal (2A), m.p. 114—115° (lit.,[1] 110—111.5°) was filtered off, and the filtrate extracted with chloroform (3 × 25 ml). The extract was dried ($MgSO_4$), filtered, and evaporated. The residue was separated into three components by preparative plate chromatography (20 cm × 20 cm; Kieselgel GF_{254}) with a 4 : 1 benzene–light petroleum (b.p. 40—60 °C) as eluant: (i) the cyclic acetal (2A), m.p. 112° (lit.,[1] 110—111.5°); (ii) 1,4,5,7,7-*Pentachloro*-6-*ethoxynorborn*-5-*en*-2-endo-*ylmethanol* (11A) (0.1 g), b.p. 80—83° at 0.1 mmHg (Found: C, 35.45; H, 3.3. $C_{10}H_{11}Cl_5O_2$ requires C, 35.25; H, 3.25%); τ 7.0 (m, H-2-*exo*), 8.12 (q, H-3-*endo*), 7.35 (q) H-3-*exo*),6.72 (q) and 6.22 (q) (CH_2·OH), 8.16 (s, OH), 5.62 (q, O·CH_2·CH_3), and 8.61 (t, O·CH_2·CH_3); $\nu_{max.}$ 3 340 and 3 620 (OH) and 1 645 cm^{-1} (*cis*-EtO·C=CCl); M^+ 340; (iii) 4-*exo*,5-*endo*,6,7,7,8-hexachloro-3-oxatricyclo[4.2.1.$0^{4,8}$]nonane (7) (0.1 g); properties as recorded earlier. When the reaction was carried out for 48 h instead of 16 h, only the cyclic acetal (2A) 95% was obtained.

Reaction of the Alcohol (1B) *with Sodium Ethoxide*.—A solution of the alcohol (1B) (5 g, 0.014 5 mol) in ethanol (11 ml) was added over 0.4 h to a solution of sodium ethoxide [sodium (1.334 g, 0.058 g atom) in ethanol (57 ml)] at *ca.* 74 °C. The mixture was then boiled at reflux for a further 2 h. Water (58 ml) was then added, followed by concentrated hydrochloric acid until pH 7 was reached. The mixture was extracted with chloroform (3 × 100 ml) and the extract dried ($MgSO_4$) and evaporated. The residue was distilled to afford 6-endo,7,8,8,9-*pentachloro*-5-exo-*ethoxy*-4-*oxatricyclo*[5.2.1.$0^{5,9}$]*decane* (2C) (4.6 g), b.p. 103—104° at 0.02 mmHg, m.p. 64—65° (from n-pentane) (Found: C, 37.45; H, 3.75. $C_{11}H_{13}Cl_5O_2$ requires C, 37.25; H, 3.65%); for n.m.r. data see Table 2; no double-bond i.r. absorption.

Reaction of the Alcohol (1B) *with Sodium Methoxide*.—The alcohol (1B) (5 g, 0.0145 mol) was dissolved in methanol (11 ml) and added dropwise over 0.5 h to a solution of sodium methoxide [sodium (1.334 g, 0.058 g atom) in methanol (57 ml)] at *ca.* 65 °C. The mixture was then boiled at reflux for a further 17 h. Water (58 ml) was then added, followed by concentrated hydrochloric acid until pH 7 was reached. The mixture was then extracted with chloroform (3 × 100 ml) and the extract dried ($MgSO_4$) and evaporated. The residue was distilled to afford 6-endo,7,8,8,9-*pentachloro*-5-exo-*methoxy*-4-*oxatricyclo*[5.2.1.$0^{5,9}$]*decane* (2D) (4.4 g), b.p. 106—107° at 0.04 mmHg, m.p. 99—100° (from methanol) (Found: C, 35.25; H, 3.15. $C_{10}H_{11}Cl_5O_2$ requires C, 35.25; H, 3.25%); for n.m.r. data see Table 2.

Reaction of the Acetal (2D) *with Concentrated Sulphuric Acid*.—The acetal (2D) (6 g, 0.017 mol) mixed with concentrated sulphuric acid (18.39 g) was stirred and warmed at 70 °C for 1 h. The mixture was then added to water (141 g) and the suspension warmed to *ca.* 70 °C and allowed to cool. The mixture was extracted with ether (3 × 100 ml) and the extract dried (Na_2SO_4) and evaporated. The residue was distilled to afford 6-endo,7,8,8,9-*pentachloro*-4-*oxatricyclo*-[5.2.1.$0^{5,9}$]*decan*-5-exo-*ol* (3B) (4 g), b.p. 112—114° at 0.01 mmHg, m.p. 93—94° (from carbon tetrachloride) (Found: C, 33.05; H, 2.65. $C_9H_9Cl_5O_2$ requires C, 33.1; H, 2.75%); for n.m.r. data see Table 2; $\nu_{max.}$ 3 570 cm^{-1} (OH) (crude sample showed >C=O bond at 1 795 cm^{-1}, absent from spectrum of recrystallised product).

The hemiacetal (3B) (71%) could be prepared by a similar procedure from (2C).

Conversion of the Hemiacetal (3B) *into the Chloro-ketone* (4B).—The hemiacetal (3B) (1 g, 0.003 mol) mixed with phosphorus pentachloride (0.8 g, 0.003 6 mol) was stirred and warmed gently. When the temperature reached 55—60 °C an exothermic reaction occurred and hydrogen chloride was evolved. The solution was maintained at a gentle reflux for 3 h and then poured onto crushed ice. The resultant mixture was extracted with n-hexane and the extract dried (Na_2SO_4) and evaporated. The residue was crystallised from n-pentane to afford 1,3-endo,4,7,7-*pentachloro*-6-endo-(2-*chloroethyl*)*norbornan*-2-*one* (4B) (0.75 g), m.p. 85—86° (Found: C, 31.55; H, 2.25. $C_9H_8Cl_6O$ requires C, 31.3; H, 2.3%); τ 7.14 (m, H-6-*exo*), 7.34 (q, H-5-*endo*), 7.26 (q, H-5-*exo*), 5.08 (d, H-3-*exo*), 8.41 (m) and 8.00 (m) (CH_2·CH_2·Cl), and 6.43 (q, CH_2·CH_2Cl), $\nu_{max.}$ 1 795 cm^{-1} (>C=O).

Conversion of the Acetal (2C) *into the Hydroxy-ketone* (20).—The acetal (2C) 2 g, 0.005 6 mol) was mixed with concentrated

[10] E. Grischkevitsch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 880.

sulphuric acid (6.2 g), warmed to *ca.* 80 °C, and kept at this temperature for 5 h with stirring. The mixture was then added to water (50 ml) and the resulting suspension warmed to *ca.* 70 °C and allowed to cool. The mixture was extracted with ether (3 × 50 ml), and the extract dried (Na_2SO_4) and evaporated. Distillation afforded 1,3-endo,4,7,7-*pentachloro*-6-endo-(2-*hydroxyethyl*)*norbornan*-2-*one* (20) (0.55 g), b.p. 123—126° at 0.2 mmHg (Found: C, 32.8; H, 2.8. $C_9H_9Cl_5O_2$ requires C, 33.1, H, 2.75%); τ (60 MHz) 6.92 (m, H-6-*exo*), 7.33 (q, H-5-*endo*), 7.24 (q, H-5-*exo*), 5.09 (d, H-3-*exo*), 8.04 (m) and 8.53 (m) (CH_2·CH_2·OH), 6.74 (t, CH_2·CH_2·OH), and 7.20 (s, OH); $\nu_{max.}$ 3 560 (OH) and 1 796 cm^{-1} (=C=O).

Reaction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-endo-*ylmethyl Methyl Ether* (17) *with Sodium Ethoxide.—Method A.* The methyl ether (17) (2 g, 0.005 8 mol) dissolved in ethanol (5 ml) was added to a solution of sodium ethoxide [sodium (0.56 g, 0.024 g atom) in ethanol (24 ml)] and the mixture stirred for 17 h at room temperature. Water (25 ml) was then added followed by dilute hydrochloric acid until pH 7 was reached. The suspension was extracted with ether (3 × 30 ml) and the extract dried ($MgSO_4$) and evaporated. The residue was separated by preparative plate chromatography (20 × 20 cm; Kieselgel GF_{254}) with light petroleum (b.p. 40—60 °C) as eluant to afford the unchanged methyl ether (17) and 1,4,5,7,7-*pentachloro*-6-*ethoxynorborn*-5-*en*-2-endo-*ylmethyl methyl ether* (18A) (0.35 g), b.p. 99—101° at 0.45 mmHg (Found: C, 37.4; H, 3.7. $C_{11}H_{13}Cl_5O_2$ requires C, 37.25; H, 3.65%), τ 7.20 (m, H-2-*exo*), 8.08 (q, H-3-*endo*), 7.46 (q, H-3-*exo*), 6.98 (q) and 6.52 (q) (CH_2·O·CH_3), 6.73 (s, OCH_3), 6.42 (q, O·CH_2·CH_3), and 8.78 (t, O·CH_2·CH_3); $\nu_{max.}$ 1 640 cm^{-1} (*cis*-EtO·C=CCl).

Method B. The methyl ether (17) (2 g, 0.005 8 mol) was dissolved in ethanol (5 ml) and added to a solution of sodium ethoxide [sodium (0.56 g, 0.024 g atom) in ethanol (25 ml)]; the mixture was stirred at room temperature for 60 h. Water (25 ml) was then added, followed by concentrated hydrochloric acid until pH 7 was reached. The mixture was extracted with ether (3 × 50 ml) and the extract dried ($MgSO_4$) and evaporated. The residue was separated by preparative plate chromatography (20 × 60 cm; Kieselgel GF_{254}) with light petroleum (b.p. 40—60 °C) as eluant to afford unchanged (17), (18A) (0.2 g), and 1,4,7,7-*tetrachloro*-5,6-*diethoxynorborn*-5-*en*-2-endo-*ylmethyl methyl ether* (19A) (0.12 g), b.p. 106—108° at 0.4 mmHg (Found: C, 42.55; H, 4.85. $C_{13}H_{18}Cl_4O_3$ requires C, 42.85; H, 4.95%); τ 7.16 (m, H-2-*exo*), 8.03 (q, H-3-*endo*), 7.41 (q, H-3-*exo*), 6.95 (q) and 6.47 (q) (CH_2·O·CH_3), 6.71 (s OCH_3), 6.41 (4 H, q, O·CH_2·CH_3), and 8.77 (6 H, t, O·CH_2·CH_3); $\nu_{max.}$ 1 618 cm^{-1} (*cis*-EtO·C=C·OEt).

Reaction of 1,4,5,6,7,7-*Hexachloronorborn*-5-*en*-2-endo-*ylmethyl Methyl Ether* (17) *with Sodium Methoxide.*—By method B (above) the reaction between the methyl ether (17) (2 g, 0.005 8 mol) and sodium methoxide [from sodium (0.56 g) in methanol (25 ml)] afforded 1,4,5,7,7-*pentachloro*-6-*methoxynorborn*-5-*en*-2-endo-*ylmethyl methyl ether* (18B) (0.34 g) b.p. 60—62° at 0.06 mmHg (Found: C, 35.5; H, 3.3. $C_{10}H_{11}Cl_5O_2$ requires C, 35.25; H, 3.25%); τ 7.15 (m, H-2-*exo*), 8.08 (q, H-3-*endo*), 7.48 (q, H-3-*exo*), 6.96 (q) and 6.52 (q) (CH_2·O·CH_3), 6.74 (s, CH_2·O·CH_3), and 6.65 (s, OCH_3); $\nu_{max.}$ 1 650 cm^{-1} (*cis*-MeO·C=CCl); and 1,4,7,7-*tetrachloro*-5,6-*dimethoxynorborn*-5-*en*-2-endo-*ylmethyl methyl ether* (19B) (0.28 g), b.p. 67—69° at 0.06 mmHg (Found: C, 39.05; H, 4.15. $C_{11}H_{14}Cl_4O_3$ requires C, 39.3; H, 4.15%); τ 7.12 (m, H-2-*exo*), 8.05 (q, H-3-*endo*), 7.46 (q, H-3-*exo*), 6.93 (q) and 6.49 (q) (CH_2·O·CH_3), 6.73 (s, CH_2·O·CH_3), 6.66 (3 H, s, OCH_3), and 6.63 (3 H, s, OCH_3); $\nu_{max.}$ 1 620 cm^{-1} (*cis*-MeO·C=C·OMe).

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