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Molecular Rearrangements in the Homoisodrin Series

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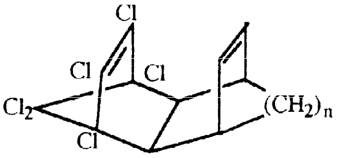
Abstract: Some chemical transformations of homodrin and its epoxide are reported. In particular the products resulting from acid catalysed addition of acetic acid to homodrin have been characterised and the structures established by X-ray crystallography. Some unusual features of the ^{1}H nmr spectra of these compounds are discussed.

INTRODUCTION

Although the insecticidal properties of isodrin **1** and aldrin **3** and the derived epoxides endrin **4** and dieldrin **6** have formerly resulted in their wide usage, the biochemical basis of their mode of action has remained obscure.[1] Biological activity in this area is very sensitive to structural changes; thus the isodrin homologue, homoisodrin **2** and its epoxide, homoendrin, **5** display only very low toxicity towards the common house fly.[2] This prompted us to investigate the chemistry of these compounds for comparison with the results of our earlier studies.[3-7] Mention should be made of some related work[8] which appeared at the same time as our initial publication.[9] The intervention of molecular rearrangements, *vide infra*, necessitated the unambiguous establishment of the structures of some of the products by X-ray crystallography.



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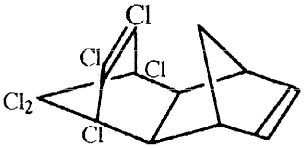

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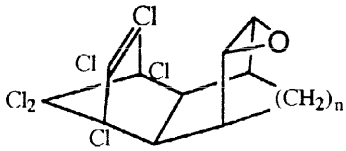

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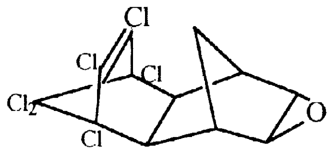

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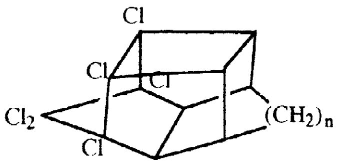

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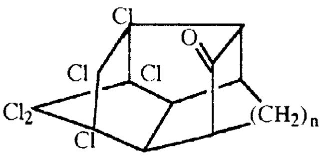

9 n = 1
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RESULTS AND DISCUSSION

Homoisodrin **2** is obtained[2] by cycloaddition of 1,3-cyclohexadiene to hexachlorobicycloheptadiene and the assigned stereochemistry confirmed by X-ray crystallography,[10,11] which also confirms[10] the structure of the cage compound **8** obtained[8,9] by photochemical ring closure and conveniently referred to as photohomoisodrin. Homoisodrin **2** is readily converted[2] to the epoxide, homoendrin **5** whose structure has also been confirmed[11]

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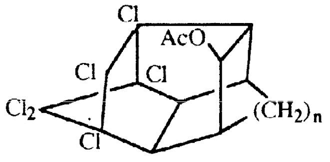
by X-ray crystallography. On treatment with boron trifluoride etherate we find that this epoxide is cleanly converted into the half-cage ketone **10**; an analogous conversion is well established for endrin **4** to **9**.[3] As expected **9** lacks the characteristic infrared absorption at 1600 cm^{-1} for the dichloroethylene moiety, and the ^1H nmr spectrum displays a singlet at δ4.69 for the isolated >CHCl proton. Reducton of this ketone with sodium borohydride and subsequent acetylation provided the acetate **12** which we had expected to encounter as a product of later transformations.



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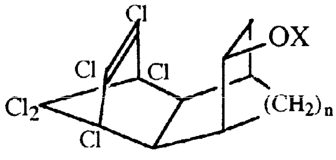
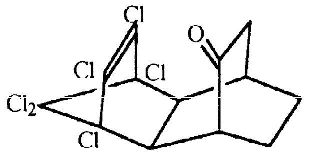


13 n = 1; X = Ms
14 n = 1; X= OAc
15 n = 2; X= H
16 n = 2; X = Ac
17 n = 2; X = Ms



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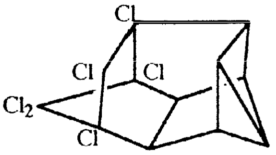
Hydroboration of homoisodrin **2** gave the alcohol **15** which was oxidised with chromic acid to the ketone **18**. The alcohol was also converted into the acetate **16** and the mesylate **17**. Acetolysis of the latter gave a mixture of homoisodrin **2** (87%), photohomoisodrin **8** (7%) and the acetate **16** (12%). These results may be contrasted to the behaviour of the analogous mesylate **13** in the isodrin series[3] which produced a mixture of isodrin **1**, the chlorohydrocarbon **19** (21%), the uncyclised acetate **14** (7%), and the half-cage acetates **20** (8%) and **11** (25%) under comparable conditions. The failure to observe any appreciable amounts of products resulting from transannular bond formation in the solvolysis of **17** may be attributable to the slightly greater separation[10,11] of the reaction site and the carbon-carbon double bond here compared to the situation in **13**.



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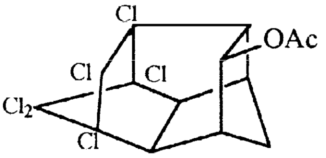

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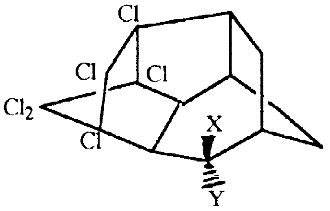
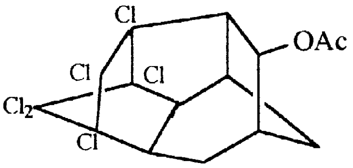


21 X = OAc; Y = H
22 X,Y = O



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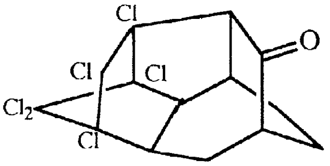

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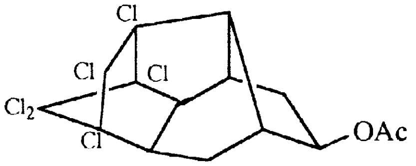

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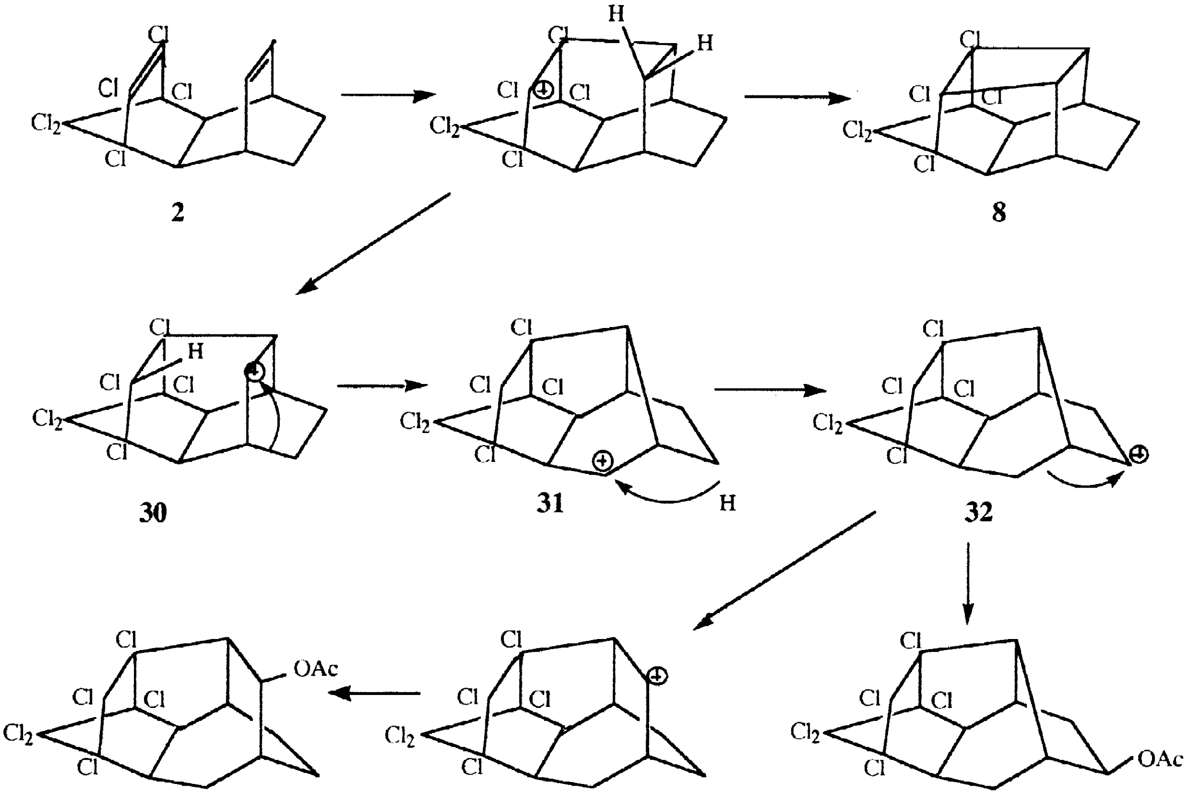
A somewhat different situation was observed when homoisodrin **2** was subjected to sulfuric acid mediated reaction with acetic acid. Apart from some photohomoisodrin **8** (12%), the other products isolated were two isomeric acetates in yields of 47% and 4%. The infrared spectra of both compounds showed the absence of the dichloroethylene moiety and their ^1H nmr spectra displayed singlets *ca.*4.8 δ characteristic of the >CHCl grouping. The major acetate was hydrolysed to the corresponding alcohol, and then oxidised to the ketone which was not identical with the ketone **10**. Originally, analysis of the ^{1}H nmr spectra of this ketone and the precursor acetate led us to suggest[9] the structures **21** and **22** for these compounds. However a subsequent X-ray structural analysis[11] demonstrated the major acetate to have the structure **23**. A major problem in interpreting ^{1}H nmr spectra of these compounds is the very small coupling constants observed for interactions between the bridgehead protons, and the occurrence of comparably sized long range W-type couplings. The structure of the minor acetate has now been established unambiguously as **25** by X-ray crystallography.



Scheme 1

The resulting ORTEP-diagram is shown in Figure 1, and the principal bond lengths and angles in Tables 1 and 2 respectively. As indicated in Scheme 1 the initial steps leading to the cage compound **8** and the cation **30** are analogous to those accounting for the observed product formation in the isodrin series. However **30** then undergoes the well precedented[12] rearrangement of a bicyclo[2.2.2]octanyl cation to a bicyclo[3.2.1]octanyl cation forming **31**, which presumably results in some release of repulsion between carbons. A subsequent 1,3-hydrogen shift then converts **31** into the cation **32**, a minor proportion of which is intercepted by acetate attack forming **25**. However the major portion undergoes a further rearrangement to the cation **33** and capture as the principal acetate **23**.

Attempts to access compounds resulting from capture of the cation **26** such as **21** by cycloaddition of hexachlorocyclopentadiene to **25**[13] or the corresponding ketone were unsuccessful in spite of plentiful literature analogy[14]. It was anticipated that the resulting adducts **26** would undergo photochemically initiated cyclisation to give **21/22** parallel to those well established[6] in the aldrin series.

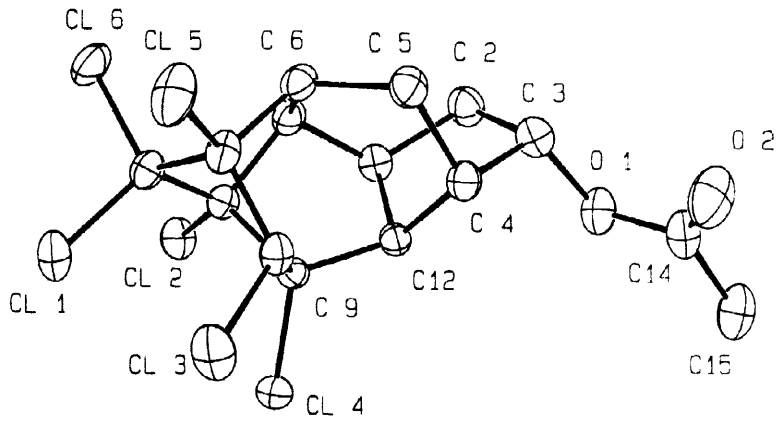


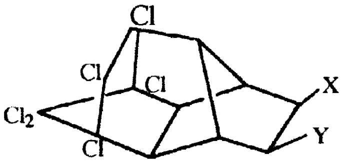
Figure 1. ORTEP diagram for compound 24.

Table 1. Bond lengths (Å) for compound 24.

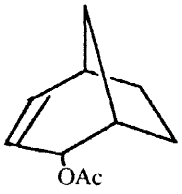
C1-C2	1.543(6)	C1-C11	1.539(7)	C1-C12	1.540(6)
C2-C3	1.540(7)	C3-C4	1.529(7)	C4-C5	1.588(7)
C4-C12	1.561(6)	C5-C6	1.536(6)	C6-C7	1.574(7)
C6-C11	1.595(6)	C7-C8	1.536(7)	C7-C13	1.538(6)
C8-C9	1.579(6)	C9-C10	1.602(6)	C9-C12	1.568(6)
C10-C11	1.547(6)	C10-C13	1.539(6)	C14-C15	1.488(8)
Cl5-C7	1.784(4)	Cl3-C8	1.782(5)	Cl4-C9	1.789(4)
Cl2-C10	1.759(4)	Cl1-C13	1.770(5)	Cl6-C13	1.790(5)
O1-C3	1.472(6)	O1-C14	1.341(6)	O2-C14	1.199(7)

Table 2. Bond angles (°) for compound 24.

C2-C1-C11	119.2(4)	C2-C1-C12	106.7(4)	C11-C1-C12	99.1(3)
C1-C2-C3	104.6(4)	C2-C3-C4	103.6(4)	C2-C3-O1	108.1(4)
O1-C3-C4	110.3(4)	C3-C4-C5	104.6(4)	C3-C4-C12	101.3(3)
C5-C4-C12	112.4(3)	C4-C5-C6	112.7(3)	C5-C6-C7	113.0(4)
C5-C6-C11	113.1(4)	C7-C6-C11	104.3(3)	C6-C7-C8	106.6(3)
C6-C7-C13	102.1(4)	C8-C7-C13	105.3(3)	Cl5-C7-C6	112.4(3)
Cl5-C7-C8	114.1(3)	Cl5-C7-C13	115.2(3)	C7-C8-C9	98.6(3)
Cl3-C8-C7	117.1(3)	Cl3-C8-C9	118.8(3)	C8-C9-C10	103.8(3)
C8-C9-C12	110.1(3)	C10-C9-C12	105.2(3)	Cl4-C9-C8	113.5(3)
Cl4-C9-C10	113.4(3)	Cl4-C9-C12	110.3(3)	C9-C10-C11	98.4(3)
C9-C10-C13	105.8(3)	C11-C10-C13	104.0(3)	Cl2-C10-C9	117.4(3)
Cl2-C10-C11	115.0(3)	Cl2-C10-C13	114.3(3)	C1-C11-C6	114.5(3)
C1-C11-C10	102.2(3)	C6-C11-C10	99.2(3)	C1-C12-C4	98.5(3)
C1-C12-C9	105.4(3)	C4-C12-C9	118.6(3)	C7-C13-C10	93.3(3)
Cl6-C13-C7	112.5(3)	Cl1-C13-C7	117.5(3)	Cl1-C13-C10	114.5(3)
Cl6-C13-C10	112.3(3)	Cl1-C13-Cl6	106.5(2)	O1-C14-C15	110.7(4)
O2-C14-C15	125.7(5)	O1-C14-O2	123.5(5)	C3-O1-C14	115.7



26 X=H,Y=OAc
27 X=OAc,Y=H



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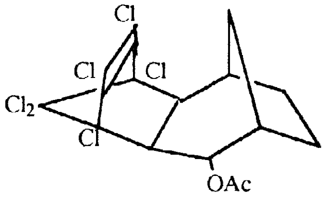

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An interesting structural feature of these half-cage compounds is the close proximity imposed on the inner atoms and the consequent effects on their ^{1}H nmr spectra[15,16]. For example a low temperature neutron diffraction study[17] on the benzoate corresponding to **20** has established a nonbonded H···H distance of only 1.617Å between the >CHCl and >CHO- protons. Comparison of the chemical shifts observed for these protons during the present study are listed in Table 3 and reveal some interesting features.In the case of the ketones **23a**, **10** and **9** progressively increasing deshielding of the >CHCl proton is observed as the proton becomes closer to the carbonyl group. The very marked deshielding of the same proton in the acetates **12** and **11** comes as no surprise in view of the extremely close proximity of the proton to the acetoxy oxygen atom. Comparison of the spectra of the acetate **20** with that of closely related compounds **23b**, **23c** and **24** shows that both the >CHCl and >CHO- protons experience a substantial down field shift due to their very close proximity. As expected the effect is very much reduced in acetate **23**, where the separation is much larger.

Table 3. Chemical shifts (δ) for selected protons.

	Compound	>CHO-	>CHCl
1.	**24**	-	4.47
2.	**10**	-	4.69
3.	**9**	-	5.01
4.	**12**	5.07	6.20
5.	**11**	4.91	6.56
6.	**26**	4.71	4.86
7.	**27**	4.94	4.92
8.	**24**	4.89	4.87
9.	**20**	5.78	5.48
10.	**23**	5.15	4.81

EXPERIMENTAL

Infrared spectra were recorded as nujol mulls, and ^{1}H NMR spectra were recorded at 250 MHz for $CDCl_3$ solutions with TMS as internal standard.

Hydroboration of homodrin. Homodrin **2** (5.5g, 14.5 mmol) was dissolved with stirring in dry diglyme (40ml) under nitrogen and sodium borohydride (0.6g, 15.9 mmol) added. Then boron trifluoride etherate (2.5ml, 19.9 mmol) in diglyme (5ml) was added dropwise over 30 minutes, and the resulting reaction mixture stirred for a further hour. Then water (3ml) was added dropwise followed firstly by aq. sodium hydroxide (0.7g in 6ml water), and subsequently hydrogen peroxide (30%, 6ml). Stirring was continued overnight and the mixture was then poured into excess water and the product collected by chloroform extraction. The dried (Na_2SO_4) extracts were then evaporated *in vacuo* and the residue crystallised from methanol to give *1α,2α, 4α,4aα,5β,8β,8aα-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-ethano-5,8-methano-naphthalen-2-ol* **15** (3.7g, 64%) , mp 197-198°C. (Found: C, 39.82; H, 3.65. $C_{13}H_{12}Cl_6O$ requires: C, 39.32; H, 3.02%); IR (nujol) 3050-3400, 1600 cm^{-1}. Treatment with acetic anhydride in pyridine gave the *acetate* **16**. mp 193-4°C from ethanol. (Found: C, 41.16; H, 3.23. $C_{15}H_{14}Cl_6O_2$ requires: C, 41.04; H, 3.21%); IR (nujol) 1715, 1600 cm^{-1}; ^{1}H NMR 1.23 (1H, ddd,J=15.4, 2.3, 2.3Hz), 1.3-1.4 (1H,m, J≈15Hz), 1.45-1.8 (3H,m), 2.0-2.09 (4H, m including CH_3 singlet at 2.03), 2.12 (1H, ddd, J=2.9, 2.9, 9.6 Hz), 2.2 (1H, ddd, J=3.3, 3.3, 5.9 Hz), 2.83 (1H, dd, J=10.7, 1.7 Hz), 2.97 (1H, dd, J=10.7, 2.6 Hz), 4.93 (1H, ddd, J= 3.3, 5.2, 8.8 Hz).

Similarly reaction of the alcohol **15** with methanesulfonyl chloride in pyridine yielded the *methanesulfonate* **17**. mp 124-125°C from ethanol. (Found: C, 35.02; H, 2.98. $C_{14}H_{14}Cl_6O_3S$ requires C, 35.46; H, 2.74%).

Oxidation of the Alcohol 15 to 18. To a stirred solution of the alcohol **15** (1.15g, 2.9 mmol) in acetone (15ml) was added dropwise a solution of chromium trioxide (0.23g, 2.3 mmol) in water (1ml) and conc. sulfuric acid (0.2ml). The stirring was continued overnight and the reaction mixture then diluted with water and extracted with chloroform. The dried (Na_2SO_4) extracts were then evaporated *in vacuo* and the residue crystallised from ethanol to give *1α,4α,4aα,5β,8β,8aα-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-ethano-5,8-methanonaphthalen-2-one* **18** (0.3g, 26%). mp 213-216°C. (Found: C, 39.42; H, 2.71.$C_{13}H_{10}Cl_6O$ requires C, 39.52; H, 2.53%); IR (nujol) 1720, 1600 cm^{-1}; ^{1}H NMR 1.6-2.0 (4H, m), 2.1 (1H, dd, J=20.7, 2.9), 2.47-2.51 (2H, m including ddd at 2.48, J=2.9, 2.9, 20.7 Hz), 3.09 (2H, ddd, J=2.5, 2.5 Hz).

Rearrangement of homoendrin 5. Boron trifluoride etherate (0.25 ml, 1.99 mmol) was added to a solution of homoendrin (4) (1g, 2.5 mmol) in dry benzene (20ml) and the mixture refluxed for 30 minutes. Then aqueous sodium hydroxide (5% w/v, 10ml) was added slowly to the cooled reaction mixture. The benzene layer was separated, washed with water, dried (Na_2SO_4) and evaporated *in vacuo* . The residue was crystallised from ethanol to give *2α,3α,3aα,3bα,5β,7aα,8β,8aα-2,5,8-methenocyclopent[a]inden-4(1H)-one* **10** (0.46g, 46%). mp 174-175°C. (Found: C, 39.74; H, 2.55. $C_{13}H_{10}Cl_6O$ requires C, 39.52; H, 2.53%); IR (nujol) 1720 cm^{-1}; ^{1}H NMR 1.58-1.84 (3H, m), 2.14-2.28 (1H, m), 2.63-2.7 (1H, m), 3.03-3.1 (1H, m), 3.13 (1H, dd, J=2.6, 2.6), 3.19 (1H, dd, J=10.7, 2.9 Hz), 3.25 (1H, ddd, J=6.5, 2.9, 0.7 Hz), 4.69 (1H, s).

Reduction and Acetylation of 10. The ketone **10** (0.3g, 0.76 mmol) and sodium borohydride (0.2g, 5.3 mmol) in ethanol (20ml) were stirred overnight at room temperature. Excess water was then added and the products isolated by chloroform extraction. The dried (Na_2SO_4) extracts were then evaporated *in vacuo* and the residue dissolved in dry pyridine (5ml) and acetic anhydride (1ml) added. The reaction mixture was allowed to stand overnight and then water (50ml) was added. The *2α,3α,3aα,3bα,4α,5β,7aα,8β,8aα-2,5,8-metheno-cyclopent[a]inden-4(1H)-yl acetate* **12** (0.22g, 66%) was isolated by chloroform extraction and crystallised from ethanol. mp 185-187 °C . (Found: C, 41.37; H, 3.45. $C_{15}H_{14}Cl_6O_2$ requires: C, 41.04; H, 3.21%); IR (nujol) 1730 cm^{-1}; ^{1}H NMR 1.23-1.46 (2H, m), 1.58-1.74 (1H, m), 1.74-1.94 (1H, m), 2.14-2.3 (4H, m including

3H singlet for CH_3), 2.7-2.85 (2H, m including a dd, J=9.9, 2.5 Hz), 2.92 (1H, dd, J=9.9, 2.6 Hz), 3.04-3.14 (1H,m), 5.07 (1H,d, J=5.5 Hz), 6.2 (1H, s).

Acetolysis of the Mesylate 17. The mesylate **17** (1.2g, 2.4 mmol) was disolved in dry acetic acid (20ml) containing anhydrous sodium acetate (1g) and the solution refluxed for 20 hours. It was then cooled and poured into excess water. The organic products were extracted with chloroform, and the combined extracts washed several times with water to remove all acetic acid. They were then dried (Na_2SO_4) and evaporated *in vacuo* . The residue was chromatographed on silica gel in cyclohexane to give homodrin **2** (0.8g, 87%). Further elution with carbon tetrachloride gave photohomodrin **8** (0.06g, 7%), and with carbon tetrachloride/benzene (2:3) the acetate **16** (0.14g, 12%).

Acid Treatment of Homodrin 2. Homodrin (5g, 13.2 mmol) was added to a mixture of acetic acid (250ml) and conc. sulfuric acid (50ml) and then refluxed for 1 hour. The cooled solution was then poured into a large volume of water and extracted several times with chloroform. The combined chloroform extracts were washed successively with water, aqueous sodium bicarbonate solution and finally with water before drying (Na_2SO_4) and evaporation *in vacuo* . Extraction of the resulting residue with hot carbon tetrachloride left a highly insoluble material identified as *1α,2β,2aβ,4β,4aβ,6α,7aβ,7bβ,8R*,9R*-2,2a,3,3,4,9-hexachloro-1,6:2,4-dimethano-1H-cyclopent[cd]inden-8-yl acetate* **23** (2.75g, 47%).mp 172-173°C (Found: C, 41.37; □H, 3.42. $C_{15}H_{14}Cl_6O_2$ requires: C, 41.04; H, 3.21%); IR (nujol) 1725cm^{-1}; ^{1}H NMR 1.33-1.47 (1H, m), 1.68-1.85 (2H, m), 2.05 (1H, s), 2.09 (3H, s), 2.38 (1H, br.s), 2.82 (1H, d, J=11.4 Hz), 2.94 (1H, ddd, J=11.9, 5.2, 1.7 Hz), 3.09 (1H, ddd, J=8.5, 5.5, 5.5 Hz), 3.23 (1H,dd, J=8.8, 8.8 Hz), 4.8 (1H, s), 5.15 (1H, s).
Chromatography of the carbon tetrachloride extract over silica gel provided photohomodrin **8** (0.6g, 12%). Subsequent elution with carbon tetrachloride containing increasing proportions of benzene gave the *acetate* **24** (4%). mp 207-209°C (Found: C, 41.47; H, 3.52. $C_{15}H_{14}Cl_6O_2$ requires: C, 41.04; H, 3.21%); IR (nujol) 1720 cm^{-1}; ^{1}H NMR 1.46 (1H, ddd, J= 16.6, 7.0, 2.6 Hz), 1.88 (1H, ddd, J=15.8, 8.1, 1.8 Hz), 2.03 (3H, s), 2.06 (1H, d, J=4.0 Hz), 2.18 (1H, d, J=16.2 Hz), 2.22 (1H, d, J=16.9 Hz), 2.72 (1H, br.d, J≈9 Hz), 2.89 (1H, ddd, J= 9.8, 2.6, 2.6 Hz), 2.98 (1H, dd, J=9.8, 6.8 Hz), 3.03-3.2 (1H, m), 4.87 (2H, br.s).

Hydrolysis and Oxidation of 23. The acetate **23** (0.8g, 1.82 mmol) was refluxed with ethanolic potassium hydroxide solution (0.7M, 20ml) for 2 hours. The cooled solution was then diluted with water and extracted with chloroform to isolate the crude alcohol which was crystallised from ethanol mp 225-228 (0.2g, 27%); IR (nujol) 3400 cm^{-1}. The alcohol (0.15g, 0.38 mmol) was dissolved in acetone (15ml) and a solution of chromium trioxide (0.2g, 2 mmol) in water (1ml) and conc. sulfuric acid (0.2ml) was added slowly with stirring. The reaction mixture was allowed to stand overnight and then was diluted with water and extracted with chloroform. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated *in vacuo.* The residue was crystallised from ethanol to give *1α,2β,2aβ,4β,4aβ,6α,7aβ,7bβ,9R*-2,2a,3,3,4,9-hexachloro-1,6:2,4-dimethano-1H-cyclopent[cd]inden-8-one* **10** (0.1g, 66%). mp 125-126°C. (Found: C, 39.67; H, 2.79. $C_{13}H_{10}Cl_6O$ requires C, 39.52; H, 2.53%); IR (nujol) 1700 cm^{-1}; ^{1}H NMR 1.86 (2H, br.s), 1.99 (1H, ddd, J=15.1, 9.4, 5.0 Hz), 2.18 (1H, d, J= 15.1Hz), 2.9 (1H, br.s), 3.06 (1H, ddd, J=11.2, 5.3, 1.5 Hz), 3.25-3.36 (2H, multiplet including a doublet at 3.31, J=11.0 Hz), 3.48 (1H, t, J=8.8 Hz), 4.47 (1H, s).

X-ray Structure Determination-Crystal Data. Empirical formula $C_{15}H_{14}Cl_6O_2$, formula weight 438.99 Colourless crystal (from chloroform), prismatic habit dimensions (mm) 0.50 x 0.70 x 0.70. Monoclinic, space group $P2_1/C$. Unit cell dimensions a = 8.532(5), b = 12.496(7), c = 16.308 Å, β = 94.90(7)°.
V = 1732.3(20) $Å^3$, Z = 4, D calc.= 1.68 Mg/m^3. $\lambda(MoK\alpha)$ = 0.7107 Å, 2θ range 5-50°. μ = 0.99 mm^{-1}.
F(000) = 891.37

Data collection. Picker diffractometer, Zr-filtered Mo-Kα radiation, temperature 298 °K. A standard reflection was measured every 100 reflections and showed significant deterioration ($\approx$ 20 %) during the data collection. It was not clear whether this was due to sublimation or radiolysis. (The good faces of the crystal were quite unpitted after data collection). Linear extrapolation was used. A Gaussian absorption correction was applied, transmission factors 0.507 to 0.605. These corrections substantially improved the residual. 3052 reflections were collected, of which 2561 had Inet > 2.5σ (Inet).

Structure solution and refinement. The structure was solved by direct methods using the NRCVAX package[18]. All the atoms, including the hydrogen atoms, were located from the Fourier difference map. Non-hydrogen atoms were given anisotropic temperature factors, hydrogen atoms isotropic factors and fixed (theoretical) positions. Refinement was by full-matrix least squares with unit weighting of the F's. The final values of the residual indices were R = 0.048, Rw = 0.049, GoF = 4.64. In the last difference map the lowest and highest densities were -0.54 and 0.46 $eÅ^{-3}$.

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