Novel Intramolecular Cyclizations of Diels–Alder Adducts Derived from Hexachlorocyclopentadiene and Allylic Alcohols

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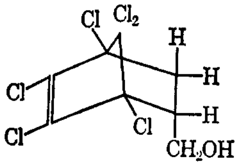
Treatment of 1,4,5,6,7,7-hexachloro-5-norbornene-*endo*-2-methanol (1) with excess alcoholic base results in the formation of a tricyclic ketal, 3a,4,4,5,6-pentachlorohexahydro-6a-methoxy-3,5-methano-2H-cyclopenta[*b*]-furan (2).[2] The ring closure has been shown to take place with sodium or potassium alkoxide, phenoxide, and mercaptide as participating nucleophiles. Bicyclic alcohols 1,4,5,6,7,7-hexachloro-5-norbornene-*endo-cis*-2,3-dimethanol, 1,4,5,6-tetrachloro-7,7-dimethoxy-5-norbornene-*endo*-2-methanol, and 1,4,5,6,7,7-hexachloro-*endo*-2-(epoxyethyl)-5-norbornene (**8**) have also been shown to cyclize in a similar manner.

We have observed an unexpected ring closure involving nucleophilic addition to an isolated double bond[3] while studying the chemistry of various unsaturated alcohol–Diels–Alder adducts of hexachlorocyclopentadiene. Refluxing of **1** with a large excess of sodium methoxide results in the loss of 1 mol equiv of chloride ion and the disappearance of the alcohol group and dichloroethylene unsaturation. The compound resulting is believed to be tricyclic ketal **2**. Cyclization has also been demonstrated with **1** and alcoholic solutions of sodium ethoxide, sodium ethylmercaptide, sodium allyloxide, sodium 4-chlorophenoxide and sodium 2,4-dichlorophenoxide to yield, respectively, **3**, **4**, **5**, **6**, and **7**.



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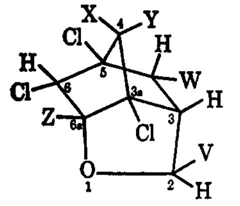
Other bicyclic adducts have been used. The epoxide 1,4,5,6,7,7-hexachloro-*endo*-2-(epoxyethyl)-5-norbornene[4] (**8**) opens up to give an alcohol and when treated with sodium ethoxide yields the ketal **9**. Diol 1,4,5,6,7,7-hexachloro-5-norbornene-*endo-cis*-2,3-methanol[5] was cyclized with sodium methoxide to give **10** and with sodium ethoxide to give the corresponding ethoxy ketal.

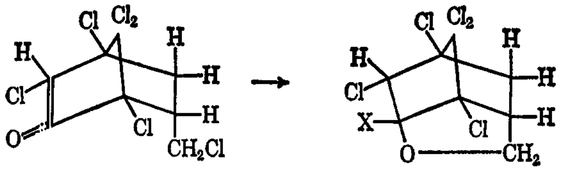
Bicyclic alcohols derived from 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene undergo ring closure also. Ketal **11** results from the reaction of 1,4,5,6-tetrachloro-7,7-dimethoxy-*endo*-5-norbornene-2-methanol[6] (**12**) and sodium ethoxide.

Cyclization of the alcohols occurs most smoothly and in the highest yield when the alkoxides are used in 3–4 molar excess and when they are prepared in the anhydrous form. The cyclization could not be effected with alcoholic potassium cyanide or sodium acetate in acetic acid or with triethylamine in ethanol.



2, V, W = H; Z = OCH_3; X, Y = Cl
3, V, W = H; Z = OCH_2CH_3; X, Y = Cl
4, V, W = H; Z = SCH_2CH_3; X, Y = Cl
5, V, W = H; Z = $OCH_2CH = CH_2$; X, Y = Cl
6, V, W = H; Z = 4-ClC.H$_4$O; X, Y = Cl
7, V, W = H; Z = 2,4-Cl$_2$C.H$_3$O–; X, Y = Cl
9, V = $CH_2OCH_2CH_3$; W = H; Z = OCH_2CH_3; X, Y = Cl
10, V = H; W = CH_2OH; Z = OCH_3; X, Y = Cl
11, V, W = H; Z = OCH_2CH_3; X, Y = OCH_3
13, V, W = H; Z = OH; X, Y = Cl
14, V = H; W = CH_2OH; Z = OH; X, Y = Cl
16, V, W = H; Z = CN; X, Y = Cl
17, V, W = H; Z = COOH; X, Y = Cl

The chemistry of the ketals was explored. For example, hot sulfuric acid converts ketals **2** or **10** into hemiketals **13** and **14**, respectively. An attempt was made to convert hemiketal **13** into the chloro ether with phosphorus pentachloride. However, chloro methyl ketone **15** resulted instead. Ketone **15** upon reaction with 1 mol equiv of methanolic potassium hydroxide at reflux yields ether **2** in excellent yield. Ketone **15** treated with 1 mol equiv of sodium bicarbonate in a tetrahydrofuran–water mixture at reflux yields hemiketal **13**. These transformations shown quite conclusively prove that **13** is a hemiketal.



15 **2**

Ketone **15** reacts quantitatively with potassium cyanide in refluxing ethanol to give cyano ether **16**. The cyano ether as noted earlier cannot be formed from **1** directly. Compound **16** is hydrolyzed with difficulty at elevated temperatures in sulfuric acid to acid **17**.

The structure of **2** is supported by elemental, infrared (ir), and nuclear magnetic resonance (nmr) analysis. The known alcohol **1** shows the characteristic hydroxyl

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[1] Address inquiries and requests for reprints to this author.

[2] Nomenclature based on 3,5-methano-2H-cyclopenta[*b*]furan: A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd ed, American Chemical Society, Washington, D. C., 1960, RR I 2253.

[3] S. Patai and Z. Rappoport "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, New York, N. Y., 1964, Chapter 8.

[4] E. K. Fields, *J. Amer. Chem. Soc.*, **76**, 2709 (1954).

[5] H. E. Ungrade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).

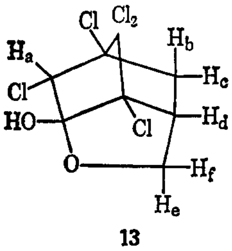
[6] E. T. McBee, W. R. Diveley, and J. C. Burch, *J. Amer. Chem. Soc.*, **77**, 385 (1955).

stretching absorption at 3350 cm^{-1} and the dichloroethylene absorption at 1620 cm^{-1}. Ketal **2** spectrum lacks these absorptions.

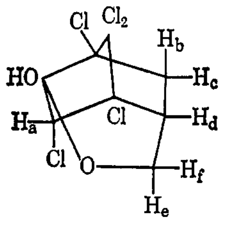
Evidence for the fact that **2** is indeed a ketal was cited earlier in that ketone **15** was readily converted back into **2** and hemiketal **13**. There are many related intramolecular cyclizations reported in the literature.[7-9]

One interesting problem with the assignment of structure **2** was whether a five- or six-membered ring was formed. We initially assumed a five-membered ring on the basis of favored geometry. There are other examples in bicyclic systems of preferred five-membered ring closures, *e.g.*, iodo and bromo lactonization.[10] The decomposition of acid peroxides from *endo*-norbornene-2-carboxylic acid gave essentially all five-membered lactone.[11] The nmr spectrum gave us rather conclusive proof that the five-membered ring closure was the correct configuration in the present work.

The nmr spectrum of **13** is shown in Figure 1. The two structures possible are **13** and **13a**. Proton H_a should show a W[12,13] coupling to H_b if **13** is the correct structure or to H_d if **13a** is correct. The latter proposed coupling between H_d to H_a is not as likely on the basis of inspection of models but cannot be excluded *a priori*. Proton H_a appears as a doublet (J = 1.2 Hz) centered at δ 4.70. Proton H_b is assigned to a skewed quartet centered at δ 2.66. Decoupling of H_a caused this multiplet to collapse to a doublet. This locates the position of the other W-coupled proton. Its identity in the structure must still be designated. Proton H_f was assigned to a quartet centered at δ 4.23 and H_e to a doublet at δ 3.74. Inspection of a molecular model verifies this interpretation in that one is at 90° dihedral angle to H_d and should show little or no coupling to this proton. The other is at about 60° and a 2-4-Hz coupling is expected. Decoupling of H_f causes the doublet assigned to H_e at δ 3.74 to collapse to a singlet. This decoupling of H_f also simplifies the multiplet assigned to H_d at δ 2.88, but does not effect the multiplet assigned to H_b at δ 2.66. We can conclude then that H_b is not coupled to the methylene protons H_e and H_f and is W coupled to H_a. Therefore, we are confident **13** is the correct structure for the ketal. We tacitly assume that all the ketals and derivatives have this same configuration.



13



13a

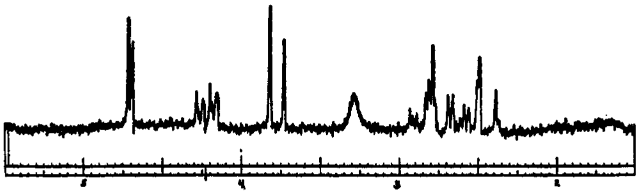
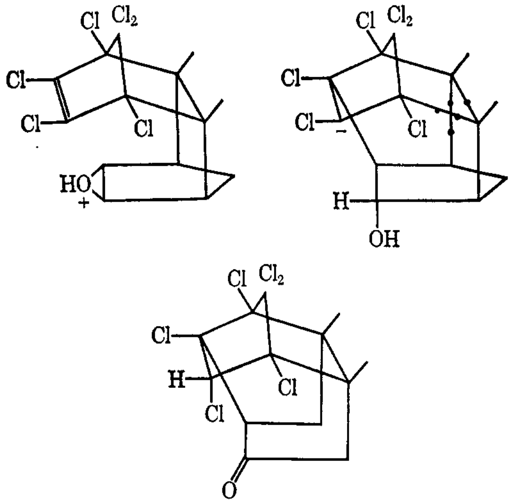


Figure 1.—Nmr spectrum of tricyclic hemiketal **13**.

The formation of these cyclic ketals is unique in the chemistry of hexachlorobicyclic Diels–Alder adducts. Generally the dichloroethylene bond in such adducts is very inert to alkoxide reagents. The reaction of the adduct of hexachlorocyclopentadiene, 1,2,3,4,7,7-hexachloro-2,5-norbornadiene with alcohol base was postulated by Mackensie to result in an addition–elimination to the dichloroethylene bond to form 1,3,4,7,7-pentachloro-2-methoxy-2,5-norbornadiene because of the stabilization of the intermediate carbanion through homoconjugation with the 5,6 double bond.[14] The 5,6-dihydro derivative is inert to alcoholic base under the above conditions. Our own studies have demonstrated the inertness of the dichloroethylene bond in similar adducts of hexachloropentadiene with simple olefins and with 2,5-dihydrofuran.

The relative ease of attack of the dichloroethylene group in the bicyclic alcohols of this study is undoubtedly due to the favored geometry for transannular ring closure of the intermediate *endo* anion formed. Other such transannular reactions have been published. An example is epoxide **18** which upon treatment with acidic reagents also undergoes transannular reactions with the dichloroethylene bond to yield a five-membered ring closed ketone.



The driving force for all these reactions is the formation of the favored pentacyclic structure. The cyclizations in the present study represent the first example of an anion being involved in such reactions.

We did observe that higher yields of the cyclic ketals with less byproducts resulted when an excess of base was used and when the alkoxide was prepared with a minimum of water present. This suggests an unfavorable equilibrium between the alkoxide and the bicyclic alcohol.

Once the bicyclic anion is formed, attack on the electron-deficient ethylene bond should be feasible. This addition of the anion introduces a bridgehead at

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(7) R. T. Arnold, M. Campos, and K. L. Lindsay, *J. Amer. Chem. Soc.*, **75**, 1044 (1953).

(8) J. R. Holium, D. Jerenby, and P. Mathison, *J. Org. Chem.*, **29**, 769 (1964).

(9) D. J. Pasto and M. P. Serve, *J. Amer. Chem. Soc.*, **87**, 1515 (1965).

(10) G. I. Poos and M. Lehman, *J. Org. Chem.*, **26**, 2575 (1961).

(11) H. Hart and F. J. Chloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963).

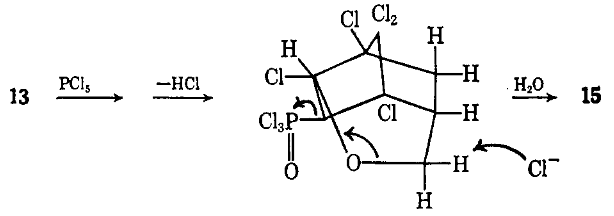
(12) J. Meinwald and A. Lewis, *ibid.*, **83**, 2769 (1961).

(13) E. W. Garbish, Jr., *Chem. Ind.* (London), 1715 (1964).

(14) K. Mackenzie, *J. Chem. Soc.*, 457, (1962).

the point of oxygen attachment. The strained ring system resulting prevents ejection of a chloride ion since this would introduce a double bond at a bridgehead. It is probable that the anion quickly accepts a proton to form the transient chloro ether. However, this chloro ether was never isolated. It is assumed that under the conditions necessary for ring closure, *i.e.*, excess base, protic solvent, elevated temperature, etc., solvolysis of the bridge chlorine occurs resulting in ketal formation. It must be presumed that there is appreciable resonance assistance to chlorine release by the oxygen, normal with α-chloro ethers, in spite of the apparent strain that would result. Such bridgehead halogens are normally rather inert. In fact, the inertness of the other halogens present in this series of derived compounds under these experimental conditions attests to this.

The reaction of phosphorus pentachloride with hemiketal **13** and subsequent hydrolysis yields ketone **15**. We suggest that attack of the phosphorus pentachloride occurs on the hemiketal first to form a phosphonium complex[15] which weakens the oxygen–carbon bond making it more susceptible to chloride attack. However, for steric reasons chloride attacks the oxymethylene group to yield, on hydrolysis, chloro methyl ketone **15**.



Experimental Section

The melting points were obtained in a capillary tube with the Thomas-Hoover Unimelt apparatus and are corrected. The carbon and hydrogen elemental analysis were carried out by Galbraith Laboratories and the chlorine and nitrogen in the Hooker Chemical Corp. Laboratories. The ir spectra were determined using a Beckman IR-9 or IR-12 spectrophotometer, nmr spectra using either a Varian HA-100 or A-60 spectrophotometer.

3a,4,4,5,6-Pentachlorohexahydro-6a-methoxy-3,5-methano-2H-cyclopenta[*b*]furan (2). Preparation A.—To a stirring solution of sodium methoxide at reflux prepared from 6.9 g (0.3 g-atom) of sodium metal and 200 ml of methyl alcohol was added dropwise a solution of 33.1 g (0.1 mol) of **1**. Addition was made in 1.2 hr and the suspension was refluxed 1 additional hr. The reaction mixture was poured into 1.5 l. of water and the solid that precipitated collected on a filter, dried, and recrystallized from hexane to yield 21.3 g (65%) of product, mp 93.5–94.5°.

Anal. Calcd for $C_9H_9Cl_5O_2$: C, 33.11; H, 2.78; Cl, 54.32. Found: C, 33.24; H, 2.95; Cl, 54.50.

Preparation B.—Over a period of a few minutes, 100 g of **15** was added to 1570 ml of a solution prepared from 25 g of sodium in methyl alcohol at reflux. The resulting dark suspension was refluxed for 12 hr. The excess methyl alcohol was distilled from the product under vacuum, and the residue was acidified and filtered. The filter cake was washed with water and 60 g of solid was recovered and recrystallized from heptane to provide a product having a melting point of 93–94°. The melting point and infrared spectrum indicated the product to be the same as 2 above.

3a,4,4,5,6-Pentachlorohexahydro-6a-ethoxy-3 5-methano-2H-cyclopenta[*b*]furan (3).—A solution of sodium ethoxide was prepared by adding 92 g (4.1 g-atom) of sodium metal to 5 l. of absolute ethanol. To this solution was added, with stirring at reflux, a solution of 331 g (1.0 mol) of **1** in 1 l. of absolute ethanol. Addition was made dropwise over 1 hr and the suspension was stirred at reflux an additional 2 hr. Water (4 l.) was added to the reaction mixture and hydrochloric acid added to neutralize the base. The solid product was collected on a filter, washed several times with water and dried under vacuum at 50° overnight to a constant weight of 332 g (97%). Recrystallization from *n*-heptane and a treatment with Darco yielded 325 g (96%) product, mp 110–111.5°.

Anal. Calcd for $C_{10}H_{11}O_2Cl_5$: C, 35.28; H, 3.26; Cl, 52 07. Found: C, 35.40; H, 3.36; Cl, 52.00.

3a,4,4,5,6-Pentachlorohexahydro-6a-ethylthio-3,5-methano-2H-cyclopenta[*b*]furan (4).—A solution of sodium ethyl mercaptide was prepared from 4.6 g (0.2 g-atom) of metallic sodium, 100 ml of dry ethanol and 12.4 g (0.2 mol) of ethyl mercaptan. To this mercaptide solution heated to 65° was added dropwise with stirring a solution of 16.5 g (0.05 mol) of 1,4,5,6,7,7-hexachloro-5-norbornene-*endo*-2-methanol. The addition was made in 5 min and the reaction mixture was stirred at reflux for 2 hr and then poured into 500 ml of water. The water suspension was made slightly acid with dilute hydrochloric acid and extracted with three 75-ml portions of diethyl ether. The ether solution was washed twice with 50-ml portions of water treated with anhydrous magnesium sulfate and filtered. The dry ether was removed on a Rinco evaporator and the crude brown oil (17.8 g) fractionated.• The major fraction, 8 g (45%), distils at 138–140° (0.1 mm), n^{25}D 1.5721.

Anal. Calcd for $C_{10}H_{11}Cl_5S_0$: C, 33.69; H, 3.11; Cl, 49.74; S, 9.00. Found: C, 33.61; H, 3.05; Cl, 49.9; S, 9.5.

3a,4,4,5,6-Pentachloro-6a-allyloxy-3,5-methano-2H-cyclopenta[*b*]furan (5).—To 250 ml of anhydrous allyl alcohol was added 9.2 g (0.4 g-atom) of metallic sodium. To this solution heated to 100° was added dropwise a solution of 33.1 g (0.1 mol) of **1** over 2 hr. The suspension was stirred at reflux for an additional 4.0 hr, then filtered hot. The alcohol solution was acidified with hydrochloric acid then subjected to a vacuum evaporation. The residue was diluted with excess water and 28.0 g of brown solid was collected on a filter. Recrystallization of the product from heptane treated with Darco gave 22 g (62%) of white crystalline solid, mp 48–49°.

Anal. Calcd for $C_{11}H_{11}Cl_5O_2$: C, 37.48; H, 3.15; Cl, 50.30. Found: C, 37.25; H, 3.09; Cl, 50.40.

3a,4,4,5,6-Pentachlorohexahydro-6a-(4-chlorophenoxy)-3 5-methano-2H-cyclopenta[*b*]furan (6).—A solution of sodium ethoxide was prepared from 9.2 g (0.4 g-atom) sodium metal and 150 ml of anhydrous ethanol. To this solution was added 51.4 g (0.4 mol) of *p*-chlorophenol. A solution of 33.1 g (0.1 m) of **1** in 100 ml of ethanol was added dropwise over 1 hr. The mixture was refluxed 1 hr and passed through a filter. The filtrate was heated to effect solution and adjusted to a pH <1 with 1:1 water–hydrochloric acid. The acid solution was diluted with 500 cc of water and the oil was separated and washed several times with 75-ml portions of water. The oil weighting 28.2 g was taken up in hexane and the solid that formed recrystallized to yield 20 g of white crystals, mp 128.5–129.5°.

Anal. Calcd for $C_{14}H_{10}Cl_6O_2$: C, 39.75; H, 2.38; Cl, 50.30. Found: C, 39.59; H, 2.27; Cl, 50.10.

3a 4,4,5,6-Pentachlorohexahydro-6a-(2,4-dichlorophenoxy)-3,5-methano-2H-cyclopenta[*b*]furan (7).—A solution of sodium alkoxide prepared from 9.2 g (0.4 g-atom) of sodium metal and 200 ml of ethanol was treated with 65.6 g (0.4 mol) of 2,4-dichlorophenol. To this solution at reflux, 32.1 g (0.1 mol) of **1** in 100 ml of ethanol was added dropwise over 0.5 hr. The suspension was stirred at reflux for 3.0 hr. The reaction mixture was evaporated to one-third of its volume and the residue added to a large excess of water. The oil that separated crystallized on standing to yield 32 g of solid which crystallized from hexane to yield 15 g solid, mp 109–129°. The solid was treated with dilute aqueous sodium hydroxide, then recrystallized from heptane to yield 10 g (22%) of a solid, mp 136–138°.

Anal. Calcd for $C_{14}H_9Cl_7O_2$: C, 36.76; H, 1.98; Cl, 54.26. Found: C, 37.00; H, 2.00; Cl, 54.70.

3a,4,4,5,6-Pentachlorohexahydro-6a-ethoxy-2-ethoxymethyl-3,5-methano-2H-cyclopenta[*b*]furan (9).—To a solution of sodium ethoxide prepared by adding 9.2 g (0.40 g-atom) of metallic sodium to 250 ml of absolute ethanol was added 34.4 g (0.10 mol) of **8**. The solution was heated to reflux with stirring for 9 hr, cooled to room temperature, acidified with dilute hydro-

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(15) G. A. Wiley, B. M. Rein, R. L. Herskowitz, *Tetrahedron Lett.*, 2509 (1964).

chloric acid and filtered. The filtrate was concentrated and the residue taken up in 100 ml of diethyl ether. The ether solution was washed with 50 ml of water then dried over anhydrous magnesium sulfate. After filtration and removal of the ether by evaporation, the oil residue weighing 35 g was subjected to a vacuum distillation to give 28 g (70.2%) of a pale yellow oil distilling at 150–151° (0.15 mm), $n^{25}D$ 1.5164.

Anal. Calcd for $C_{13}H_{17}O_3Cl_5$: C, 39.18; H, 4.30; Cl, 44.48. Found: C, 39.30; H, 4.30; Cl, 44.45.

3a,4,4,5,6-Pentachlorohexahydro-7-hydroxymethyl-6a-methoxy-3,5-methane-2H-cyclopenta[*b*]furan (10).—A solution of sodium methoxide was prepared from 9.2 g (0.4 g-atom) of sodium metal and 200 ml of methanol. To this solution at reflux with stirring was added over 0.75 hr a solution of 36.1 g (0.1 mol) of 1,4,5,6,7,7-hexachloro-5-norbornene-*endo-cis*-2,3-dimethanol in 300 ml of methanol. After addition was complete the suspension was stirred at reflux for 1.0 hr. The mixture was filtered and the filtrate reduced by evaporation to one-fourth its original volume. The residual solution was acidified with hydrochloric acid then diluted with 600 ml of water and chilled. The water was decanted from a semicrystalline solid. The solid was crystallized from toluene then from heptane to yield 14.2 g (40%) of crystalline white solid, mp 157–158.5°.

Anal. Calcd for $C_{10}H_{11}Cl_5O_3$: C, 33.88; H, 3.13; Cl, 50.01. Found: C, 33.78; H, 3.27; Cl, 49.5.

3a,5,6-Trichlorohexahydro-6a-ethoxy-4,4-dimethoxy-3,5-dimethano-2H-cyclopenta[*b*]furan (11).—To 150 ml of anhydrous ethanol was added 10.2 g (0.4 g-atom) of metallic sodium. This solution was warmed with stirring to reflux and a solution of 32.2 g (0.1 mol) of 1,4,5,6-tetrachloro-7,7-dimethoxy-5,5-norbornene-*endo*-2,2-methanol was added in 0.75 hr. The suspension was stirred for 3.0 hr at reflux, filtered, and the solvent removed under vacuum. The residue was treated with excess water, and the suspension acidified with hydrochloric acid. The oil resulting solidified and was crystallized from 150 ml of petroleum ether (immersed in a Dry Ice–acetone cooling bath). The white solid weighing 24.0 g, mp 62–68°, was recrystallized to yield 20.0 g (60%) of product, mp 68.5–69.5°.

Anal. Calcd for $C_{12}H_{17}Cl_3O_4$: C, 43.65; H, 5.17; Cl, 32.07. Found: C, 43.60; H, 5.14; Cl, 32.19.

3a,4,4,5,6-Pentachlorohexahydro-6a-hydroxy-3,5-methano-2H-cyclopenta[*b*]furan (13). Preparation A.—A suspension of 30 g (0.88 mol) of 3 in 50 ml of concentrated sulfuric acid was warmed to 88–100° with stirring and held for 0.75 hr. The hot acid solution was poured into 700 ml of ice and water; the suspension resulting was warmed to 80°, then cooled and filtered. The solid weighing 13.0 g was recrystallized from benzene several times to yield 7.0 g (26%) of white crystals, mp 231–232°.

Anal. Calcd for $C_8H_7Cl_5O_2$: C, 30.76; H, 2.26; Cl, 56.74. Found: C, 30.96; H, 2.20; Cl, 56.90.

The infrared spectrum has an OH band at 2.91 μ but shows no C=O or C=C stretching.

Preparation B.—To a mixture of 84 g of sodium bicarbonate, 500 g by weight of water and 3925 ml of ethyl alcohol were added 330 g of **15**. The mixture was refluxed for 10 hr and then evaporated on a steam cone. Excess water was added to the product, and an oil formed. The oil was treated with hexane. About 25 g of product that was insoluble in hexane was subjected to infrared analysis and found to have a spectrum identical with that of **13** above.

3a,4,4,5,6-Pentachlorohexahydro-6a-hydroxy-7-hydroxymethyl-3,5-methano-2H-cyclopenta[*b*]furan (14).—A suspension of 120 ml of concentrated sulfuric acid and 24 g (0.65 mol) of **10** was stirred with heating to 90–92° and held at this temperature for 8 min. The solution resulting was poured into ice and the solid resulting collected on a filter. After a thorough washing with water, the solid weighing 15 g was recrystallized three times from a methanol–water solution to yield 10.8 g (67.5%) of solid, mp 236–238° with decomposition.

Anal. Calcd for $C_9H_9Cl_5O_3$: C, 31.56; H, 2.65; Cl, 51.77. Found: C, 31.61; H, 2.61; Cl, 52.00.

The infrared spectrum shows OH absorption at 3540 cm^{-1}.

Preparation of 2-Keto-1,3,4,7,7-pentachloro-6-chloromethylnorbornene (15).—A mixture of 18.74 g (0.06 mol) of **13** and 14.6 g (0.061 mol) of phosphorus pentachloride was carefully warmed with shaking. At 50–55° an exothermic reaction took place with vigorous evolution of hydrogen chloride. The pale yellow solution resulting was stirred at reflux (118–120°) for 2.0 hr, then poured into crushed ice. The white solid obtained was washed several times with water and crystallized from hexane to yield 11.0 g (55%), mp 69.5–71.5°.

Anal. Calcd for $C_8H_6Cl_6O$: C, 29.04; H, 1.83; Cl, 64.30. Found: C, 29.23; H, 1.97; Cl, 63.80.

The infrared spectrum shows C=O absorption at 1790 cm^{-1} (CCl_4) and no OH stretching.

3a,4,4,5,6-Pentachlorohexahydro-6a-cyano-3,5-methano-2H-cyclopenta[*b*]furan (16).—A solution containing 13.2 g (0.04 mol) of **15** in 100 ml of ethanol and 30 ml of water was treated with 5.2 g (0.079 mol) of potassium cyanide. The solution was stirred at reflux for 2.0 hr. The resulting dark suspension was acidified with dilute sulfuric acid and then evaporated to near dryness. The residue was poured into 150 ml of water and the brown solid collected on a filter. The solid was dissolved in hexane, dried over magnesium sulfate (anhydrous), and filtered. The excess hexane was removed, and 6.0 g of crystals separated upon cooling the solution, having mp 226–231°. Recrystallization raised the melting point to 235–236°.

Anal. Calcd for $C_9H_6ONCl_5$: C, 33.63; H, 1.88; N, 4.36; Cl, 55.16. Found: C, 33.70; H, 2.02; N, 4.28; Cl, 33.61.

3a,4,4,5,6-Pentachlorohexahydro-3,5-methano-2H-cyclopenta[*b*]furan-6a-carboxylic Acid (17).—**16** (8 g) was added to 40 ml of 81% sulfuric acid and 100 ml of glacial acetic acid. The solution was stirred at reflux (127°) for 14 hr, cooled and poured into 500 ml of ice water. The resulting solid was collected on a filter, washed thoroughly with water and dried to yield 6 g of white solid, mp 279–281° dec.

Anal. Calcd for $C_9H_7Cl_5O_3$: C, 31.76; H, 2.07; Cl, 52.08; neut equiv, 340.4. Found: C, 31.56; H, 2.07; Cl, 51.8; neut equiv, 341.

Registry No.—Hexachlorocyclopentadiene, 77-47-4; **2**, 17144-77-3; **3**, 17145-53-8; **4**, 17145-58-3; **5**, 17387-24-5; **6**, 19362-33-5; **7**, 17145-56-1; **9**, 19362-35-7; **10**, 17145-51-6; **11**, 17145-54-9; **13**, 17144-71-7; **14**, 17145-62-9; **15**, 17144-74-0; **16**, 17144-75-1; **17**, 17144-76-2.

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