Perchloro Cage Compounds. I. Structural Studies¹

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A convenient method for the preparation of hitherto inaccessible ketals of perchloro cage ketones is reported. N.m.r. studies of several dimethyl ketals prepared by this technique have confirmed the symmetry properties previously assumed for these systems.

A variety of perchlorinated systems derived from hexachlorocyclopentadiene (and/or its derivatives) have been reported in the literature. Cage-like, carbon skeletal structures such as 1 and 2 have been assigned to a number of these compounds.^{2,3}



The formal similarity of 1 and 2 to the unknown hydrocarbon 3a (cubane) prompted us to consider these pentacyclic systems as potential precursors for the latter.^{3a} Compound 3a is of interest in view of the reported synthesis of its octaphenyl derivative 3b,⁴ despite the fact that the results of an *a priori* theoretical calculation of the strain energy for 3a precludes its existence at room temperature.⁵ Several examples of gas phase photochemical decarbonylations of bicyclic ketones to highly strained bicyclic hydrocarbons have been reported recently.⁶ It is hoped that this

(1) Taken in part from the Ph.D. Dissertation of A. K. Price, Yale University, 1964; National Science Foundation Cooperative Fellow, 1960-1961; National Institutes of Health Predoctoral Fellow, 1962-1963 (G.P.M.-14,407-RI).

(2) (a) E. T. McBee, C. W. Roberts, J. D. Idol, Jr., and R. H. Earle, Jr., J. Am. Chem. Soc., **78**, 1511 (1956); (b) H. E. Ungnade and E. T. McBee, Chem. Rev., **58**, 249 (1958); (c) P. Yates and P. E. Eaton, Tetrahedron Letters, **No. 11**, 5 (1960); (d) P. E. Eaton, Ph.D. Dissertation, Harvard University, 1960; (e) E. T. McBee, W. L. Dilling, and H. P. Braendlin, J. Org. Chem., **27**, 2704 (1962).

(3) We are indebted to the General Chemical Division of Allied Chemical Corporation and the Hooker Chemical Corporation for generous samples of the starting materials employed in these studies.

(3a) NOTE ADDED IN PROOF.—An elegant synthesis of cubane has recently been reported. See, P. E. Eaton and T. W. Cole, Jr., J. Am. Chem. Soc., 86, 962 (1964); 3157 (1964).

(4) E. H. Braye, W. Hübel, and I. Caplier, *ibid.*, **83**, 4406 (1961); H. H. Freedman and D. R. Petersen, *ibid.*, **84**, 2837 (1962); P. M. Maitlis and F. G. A. Stone, *Proc. Chem. Soc.*, 330 (1962); M. Tsutsui, *Chem. Ind.* (London), 780 (1962): G. Büchi, C. W. Perry, and E. W. Robb, J. Org. Chem., **27**, 4106 (1962). The structure of **3b**, has been challenged [R. C. Cookson and D. W. Jones, *Proc. Chem. Soc.*, 115 (1963)]; however, the alternative structure suggested was excluded on the basis of mass spectral fragmentation data [H. H. Freedman and R. S. Gohlke, *ibid.*, 249 (1963)]

(5) The predicted strain energy for 3a is 120-130 kcal./mole; see W. Weltner, Jr., J. Am. Chem. Soc., 76, 4224 (1953). Presumably the intrinsic strain associated with 3a would not differ significantly from that of 3b. In fact, in view of comparatively adverse steric effects and the potential for benzylic stabilization of incipient radicals in 3b it would appear that the propensity for valence isomerization might be promoted by phenyl substitution. It is tacitly assumed, of course, that the nonbonded interactions in the potential valence tautomers of 3b are not so excessive that they represent the product-determining factor.

(6) W. A. Noyes, G. S. Hammond, and J. N. Pitts, "Advances in Photochemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p. 83. technique may be extended to pentacyclic diketones, thus rendering cubane and its perchloro derivative **3c** accessible.

It has been reported that hexachlorocyclopentadiene reacts with sulfur trioxide, chlorosulfonic acid, or fuming sulfuric acid to give sulfur-containing products which may be hydrolyzed to a perchloro ketone assigned structure $4^{2a,b,7}$ (known commercially as Kepone or H-1).



Treatment of 4 with phosphorus pentachloride,^{8a} or alternatively hexachlorocyclopentadiene or 1,1,2,-3,3,4,5,5-octachloropentene-1 with aluminum chloride,^{2a,7,9} affords the perchlorocarbon that is assigned structure 5 (also known as Mirex and Dechlorane). The ketone 4 was chosen as a model substrate for experiments designed to establish the feasibility of the decarbonylation step in the proposed synthetic route to cubane. However, in view of the absence of what we considered definitive evidence for the proposed structures, we decided to confirm that the assignments 4 and 5 were correct before proceeding with the photochemical experiments.

N.m.r. data on 4, while potentially the most convenient and promising source of convincing information on its symmetry properties, were inaccessible because of the perchlorinated character of the ketone.¹⁰ Attention was then turned to methods of introducing hydrogen atoms into 4 (and related cage compounds) in an oriented fashion such that n.m.r. analysis could reveal the symmetry properties of the molecule. Furthermore, the conditions must be sufficiently mild to preclude rearrangement.

It has been recognized that 4 and similar ketones display a marked tendency to form hydrates such as

(7) J. S. Newcomer and E. T. McBee, J. Am. Chem. Soc., 71, 946 (1949).

(8) (a) E. E. Gilbert and S. L. Giolito, U. S. Reissue Patent 24,435 (1958); (b) E. E. Gilbert and P. Lombardo, Belgian Patent 624,290 (1962);
(c) E. E. Gilbert and P. Lombardo, French Patent 1,340,382 (1963); (d) E. E. Gilbert, private communications.

(9) H. J. Prins, Rec. trav. chim., 65, 455 (1946).

(10) While our work was in progress McBee and co-workers^{2e} reported that **5** could be completely dechlorinated and the reduction product was assigned the skeletal structure **1**. However, the published n.m.r. spectrum of the product is not without complexities which render unequivocal interpretation correspondingly difficult. Assuming, however, that no rearrangement occurs during the relatively severe dechlorination step and that the n.m.r. has been correctly interpreted, one would still be ill-advised to infer that **4** possesses a kindred skeletal structure simply on the basis of the known conversion of **4** to **5** with phosphorus pentachloride since at least one rearrangement is reported to occur with a related system under analogous conditions (*vide in tra*).

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6a. A variety of hemiketals also have been prepared by treatment of the ketone with alcohols.^{2a,b,8b-d} It was found that the ketones could be regenerated conveniently by sublimation of hydrates or hemiketals *in vacuo*. However, attempts to prepare ketals of **4** and related ketones by conventional techniques proved unrewarding. For example, treatment of **4** with ethyl orthoformate gave the hemiketal **6d** and reaction with ethylene glycol did not proceed beyond the hemiketal



stage **6e**; the dioxolane could not be obtained directly. Undoubtedly, the reluctance on the part of **4** to form ketals is a reflection of several factors. These probably include steric hindrance and destabilization of a potential carbonium ion at the methylene bridge by negative inductive effects as well as unfavorable geometry.

Fortunately, advantage could be taken of the pronounced acidity exhibited by **6a-c** to prepare their corresponding ketals. For example, treatment of either **6a** or **6b** with diazomethane in ether provides the dimethyl ketal **6f**. The introduction of the gemdimethoxyl groups and attendant protons provided a derivative of **4** which permitted a hitherto impossible n.m.r. study to be made on a compound directly related to **4**. The methoxyl protons in the n.m.r. spectrum of **6f** appear as a clearly defined singlet at τ 6.45 just as anticipated for the dimethyl ketal of a symmetrical ketone such as **4**. The remaining alternative structures **9** and **10** are excluded from consideration by these data.¹¹



The ketal **6f**, once formed, was found to be remarkably stable. Hydrolysis could not be effected even on prolonged heating with hydrochloric or sulfuric acid. Cleavage to **6a** was finally achieved (albeit in low yield) by employing a mixture of hydriodic and acetic acids.

Dechlorination of 6f was achieved with sodium and t-butyl alcohol in tetrahydrofuran, and afforded a ketal assigned structure 7.¹² As anticipated 7 showed

a sharp singlet methoxyl peak at τ 6.93 and, in contrast to 6, hydrolyzed under mild conditions (dilute hydrochloric acid in tetrahydrofuran) to the previously unknown parent ketone 8 [ν 1730 cm.⁻¹ (C=O), m.p. 123°].

The potential value of the diazomethane ketalization reaction for the protection of the keto group of 4and similar compounds was recognized and could prove extremely useful provided a convenient means of regenerating the ketone could be devised. This objective was realized in the following manner. Treatment of the benzyl hemiketal **6c** with diazomethane afforded the mixed ketal **6g**. This ketal can be hydrogenolyzed under mild conditions to the hemiketal **6b** which in turn is readily converted to **4** on vacuum sublimation. That unexpected skeletal rearrangement occurs under the exceptionally mild conditions required to generate **6f** and **6g** appears unlikely, and this assumption is corroborated by the observed hydrogenolysis and hydrolysis experiments on **6g** and **6f**, respectively.

The tricyclic diketone 11 (Zincke diketone),¹³ prepared by dimerization of tetrachlorocyclopentadienone generated *in situ*, undergoes photoisomerization to another potentially promising cubane precursor, namely 12.^{2d}



The product was assigned structure 12 largely on the basis of infrared evidence and mode of formation. It is noteworthy that treatment of 12 with phosphorus pentachloride unexpectedly afforded the chlorocarbon 5. It was assumed that the requisite rearrangement occurred in the course of the reaction of 12 with phosphorus pentachloride and not during the photochemical step.^{2d} That this assumption is indeed correct was established unequivocally by again taking advantage of the propensity of cage carbonyl groups to react with nucleophiles. The bishemiketal 14a, formed by allowing the diketone 12 to react with methanol,





⁽¹¹⁾ Assurance that the methoxyl groups in 9 and 10 would have significantly different chemical shifts will be provided later.

⁽¹²⁾ P. G. Gassman and P. G. Pape [J. Org. Chem., 29, 160 (1964); Tetrahedron Letters, No. 1, 9 (1963)] have employed this modification of the Winstein dehalogenation technique and found sodium to be superior to lithium. See. P. Bruck, D. Thompson, and S. Winstein, Chem. Ind. (London), 405 (1960).

was treated with a limited amount of diazomethane which provided a mixture of the bisketal 14c and the ketal-hemiketal 14b. The latter compound on sublimation in vacuo gives the ketone 13.¹⁴ The n.m.r. spectrum of bisketal 14c exhibits two equal-intensity bands at τ 6.40 and 6.53, consistent with the proposed unsymmetrical structure and resulting nonequivalent methoxyl groups. These data, however, do not exclude the alternative structure 15. Additional evidence in support of structure 12 was obtained in the following manner. Treatment of 12 with phosphorus tribromide and bromine gave a keto dibromide, assigned structure 16.15 Ketalization of 16 was effected in the usual manner to give 17. That 17 (and thus presumably 16) retains an unsymmetrical skeletal structure was apparent from its n.m.r. spectrum which shows two



peaks of equal intensity at τ 6.34 and 6.49.¹⁵ Furthermore, dehalogenation of 17 using the previously described technique provides a ketal 18, different from 7. whose n.m.r. spectrum possesses two peaks of equal intensity at τ 6.80 and 6.93. Thus, rearrangement of 12 to a symmetrical structure during the course of its conversion to the bromo ketone 16 and subsequent ketalization appears unlikely. Upon hydrolytić work-up of 18 with dilute hydrochloric acid and subsequent purification by v.p.c. the ketone 19 was obtained. As expected, the infrared spectrum of 19 proved to be identical with that of the saturated photoproduct obtained by Cookson and co-workers from the unsaturated ketone 20 which further supports the structural assignments 12 and 16.¹⁶ Although a deepseated photochemical rearrangement of 20 leading to the formation of an alternate unsymmetrical compound cannot be excluded rigorously, this appears unlikely since ample analogy exists for uncomplicated closures of this type. A variety of closely related systems are known to cyclize without structural reorganization.¹⁷

(14) The keto-ketal **13** has been prepared independently by P. G. Gassman (private communication) by photochemical closure of the dimethyl ketal of **11** in which the conjugated carbonyl group is retained and acts as the chromophore.

(17) See ref. 6, pp. 360, 361.

In summary our n.m.r. data on 14c and 18 exclude symmetrical structures for the compounds in the series related to the diketone 12. This fact coupled with the internal consistency of the conversions among members of the series strongly suggests that 12-14 and 16-19 are correctly represented. In contrast the data on Kepone exclude an unsymmetrical carbon skeleton and are consistent with the proposed structure 4.

The results of our studies on the decarbonylation of 4 and the dechlorination of the product will be reported in a subsequent communication.

Experimental¹⁸

Preparation of the Methyl Hemiketal 6b of Decachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{6,9}]decan-3-one (4).^{2a,b,8b-d}—A 0.5-g. (1.0 mmole) sample of decachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one (4) was added to 15 ml. of methanol which previously had been dried over magnesium and distilled. After heating under reflux for 1 hr., the solution was cooled and excess methanol was removed on a rotary evaporator. The resulting white solid was dried under vacuum at 56° to afford a quantitative yield of the hemiketal 6b (0.53 g.). Reversion to starting material may be effected by recrystallization from benzene or sublimation at 150° at 0.3 mm. The hemiketal 6b does not melt below 300°, although partial conversion to the ketone 4 undoubtedly occurs at this temperature.

Anal. Caled. for C₁₁H₄Cl₁₀O₂: C, 25.27; H, 0.77; Cl, 67.83. Found: C, 25.52; H, 0.88; Cl, 66.86.

Preparation of the Benzyl Hemiketal 6c of Decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4).—A 1.70-g. sample of decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4, 3.47 mmoles) was added to a stirred solution of 0.54 g. (5.0 mmoles) of benzyl alcohol in 25 ml. of anhydrous ether. After stirring the solution briefly at room temperature, it was diluted with hexane. The volatile solvents were then removed on a rotatory evaporator and the residual oil crystallized upon standing. This material was then purified by repeated recrystallization from hexane to afford 1.48 g. (71%) of the colorless hemiketal 6c, m.p. 134.5-135.5°. Upon sublimation at 150° and 0.3 mm., the hemiketal reverted to starting material.

Anal. Calcd. for $C_{17}H_8Cl_{10}O_2$: C, 34.10; H, 1.35; Cl, 59.21. Found: C, 34.10; H, 1.24; Cl, 59.51.

Preparation of the Ethyl Hemiketal 6d of Decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4).^{8a,19}—Ethyl orthoformate (2.96 g., 0.02 mole) was added to 5 ml. of ethanol that had previously been saturated with anhydrous hydrogen chloride. To the resulting solution was added slowly with stirring 5.0 g. (0.01 mole) of decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3one (4). After stirring for an additional 4 days at 35°, the mixture was neutralized with a few drops of alcoholic sodium ethoxide and evaporated to dryness on a rotary evaporator. The residue was finally dried at 56° under reduced pressure and 5.2 g. (97%) of the crude product was obtained. Sublimation of a sample of this material resulted in regeneration of starting material. Partial reversion to starting material also occurred upon recrystallization from xylene. Analytical data were therefore obtained without further purification of the product.

Anal. Calcd. for $C_{12}H_6Cl_{10}O_2$: C, 26.85; H, 1.13; Cl, 66.06. Found: C, 26.50; H, 0.92; Cl, 66.14.

This substance does not melt even upon heating to 300° . Decomposition probably occurs to some extent below that point to give ethanol and the ketone 4. The latter has a melting point of 350° .

Preparation of the 2-Hydroxyethyl Hemiketal 6e of Decachioropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4).—Five grams (10.2 mmoles) of decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4), 24 g. (0.39 mole) of ethylene glycol, and 0.01 g. (0.05 mmole) of *p*-toluenesulfonic acid monohydrate were added to 50 ml. of xylene, and the resulting mixture was heated under

(19) E. E. Gilbert and P. Lombardo, private communication.

⁽¹⁵⁾ The ketone 4 reacts under similar conditions to give a dibromide. See E. E. Gilbert and P. Lombardo, U. S. Patent 3,037,906 (1962). That rearrangement of 12 might occur under these conditions has not escaped our attention. The observed unsymmetrical character of 16 could be rationalized in terms of an isomeric rearranged product of gross structure 1 in which only one bromine atom occupies a position on the methylene bridge and the other a bridgehead position. This possibility appears unlikely, however.

⁽¹⁶⁾ R. C. Cookson, J. Hudec, and R. O. Williams, Tetrahedron Letters, No. 22, 29 (1960).

⁽¹⁸⁾ Melting points, where possible, were determined on a Thomas-Hoover capillary melting point apparatus and have not been corrected. Proton n.m.r. spectra were obtained on a Varian A-60 spectrometer. All infrared spectra were determined in potassium bromide. The precise molecular weight of 7 was determined on a high-resolution Associated Electrical Industries M59 instrument employing triisopropylbenzene as a standard.

reflux for a period of 8 hr. Water and excess ethylene glycol were removed by azeotropic distillation. During this process the mixture was kept at constant volume by addition of xylene. After neutralization with alcoholic sodium ethoxide, the reaction mixture was concentrated by removal of excess xylene by distillation. Upon cooling, 4.0 g. of solid was deposited which after recrystallization from benzene afforded 3.6 g. (64%) of the colorless product.

Anal. Calcd. for $C_{12}H_6Cl_{10}O_3$: C, 26.07; H, 1.09; Cl, 64.15. Found: C, 25.45; H, 1.11; Cl, 66.13.

This material resembles the related ethyl hemiketal in that it does not melt below 300°.

Preparation of the Dimethyl Ketal of of Decachloropentacyclo-[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one (4). Method A.—Five grams (10.2 mmoles) of decachloropentacyclo[5.3.0.0^{2,6}0.4¹⁰.0^{5,9}]decan-3-one (4) was finely pulverized and permitted to stand in the air for several hours to achieve complete hydration. To an ethereal solution of the resulting hydrate was added 2.0 g. (48 mmoles) of diazomethane in 72 ml. of ether.²⁰ After standing overnight at room temperature the mixture was filtered and then concentrated on a rotary evaporator. The residue was subsequently recrystallized twice from methanol to give 2.1 g. (38%) of the colorless crystalline ketal, m.p. >310°. The n.m.r. spectrum of 6f consisted of one sharp singlet which appeared at τ 6.45 (OCH₃).

Anal. Calcd. for $C_{12}H_6Cl_{10}O_2$: C, 26.85; H, 1.13; Cl, 66.06. Found: C, 27.39; H, 1.50; Cl, 65.92.

Method B.—A solution of 4.2 g. (0.10 mole) of diazomethane in 150 ml. of ether was added to an ethereal solution of 32.9 g. (63.0 mmoles) of the methyl hemiketal of decachloropentacyclo- $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (6b). The reaction mixture was then treated in essentially the same manner as described above. A total of 25.8 g. (76%) of the ketal 6f was obtained and was identical with that prepared by method A.

Hydrolysis of the Dimethyl Ketal 6f of Decachloropentacyclo-[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one (4).—To a solution of 2.0 ml. of 57% aqueous hydriodic acid in 5.0 ml. of glacial acetic acid was added 0.08 g. (0.15 mmole) of the dimethyl ketal of decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (6f). The resulting solution was stirred at the reflux temperature for 24 hr. Water was then added and the resulting mixture was extracted with methylene chloride. The organic phase was washed in turn with water, aqueous sodium bicarbonate, and finally with concentrated, aqueous sodium iodide. After drying the organic layer over anhydrous sodium sulfate the volatile solvents were removed under vacuum and the residual semisolid was recrystallized from hexane. Repeated sublimation (150° at 0.3 mm.) of the recrystallized product provided 0.015 g. (21%) of decachloropenta $cyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (4) whose structure was confirmed by comparison of its infrared spectrum with that of an authentic sample. The latter determined in KBr shows significant bands at 1810 (s) and 1765 (sh) cm.⁻¹.

Dechlorination of the Dimethyl Ketal 6f of Decachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one (4).¹²—Metallic sodium (20.2 g., 0.88 g.-atom), which had been cut into small pieces, was added to a stirred solution of 10 g. (18.7 mmoles) of the dimethyl ketal 6f of decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one (4) and 33.2 g. (0.448 mole) of t-butyl alcohol in 200 ml. of tetrahydrofuran. The temperature was maintained at 0° during the addition and throughout the course of the reaction which was conducted under a nitrogen atmosphere. With continued stirring the reaction mixture was allowed to warm slowly to room temperature over a period of 2 days and then was maintained at that temperature for an additional 3 days. Unreacted sodium was removed and the remaining mixture was poured onto 1 l. of crushed ice. The resulting mixture was extracted repeatedly with ether. The combined organic phases were subsequently washed thoroughly with water and then dried over magnesium sulfate. The volatile solvent was removed by distillation at 760 mm. and the final fraction was collected by short-path distillation under vacuum (3 mm.). The pot temperature reached a maximum of 160° while the receiver was cooled to -78° . This fraction was gas chromatographed on a Carbowax column and was shown to contain at least three main components in the ratio of approximately 1:2:1 in order of retention times. All three of these products were colorless liquids.

The most volatile of the three (~ 0.07 g.) was shown by elemental and spectral analysis to be 2,2'-bitetrahydrofuranyl. The n.m.r. spectrum consists of one multiplet centered at τ 6.32 (3H) and another at 8.18 (4H).

Anal. Calcd. for $C_3H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.43; H, 9.66.

The product of intermediate volatility was characterized as the dimethyl ketal 7 of pentacyclo $[5.3.0.0^{2,6}0^{4,10}.0^{5,9}]$ decan-3-one (8, 0.15 g., 4%). The n.m.r. spectrum shows a sharp singlet at τ 6.93, a broad singlet at 7.2, a multiplet at 7.4, and a reasonably sharp singlet at 8.67. The relative intensities were 6:2:6:2, respectively.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; mol. wt., 192.1150. Found: C, 73.86; H, 8.27; mol. wt., 192.1143.

The final product was shown to be the dimethyl ketal of Δ^3, Δ^8 tricyclo[5.2.1.0^{2,6}]decadien-10-one (0.075 g., 2%). The n.m.r. spectrum exhibits a multiplet at τ 4.12, a multiplet at 4.58, a broad singlet at 6.82, sharp singlets at 6.85 and 6.98, an ill-defined multiplet at 7.23, and a very broad peak from about 7.5 to 8.5. The relative areas of these peaks are approximately 2:2:3: 3:3:5:2.5, respectively.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.75; H, 8.46.

Hydrolysis of the Dimethyl Ketal of Δ^3, Δ^8 -Tricyclo[5.2.1.0^{2,6}]decadien-10-one. —The dimethyl ketal of Δ^3, Δ^8 -tricyclo[5.2.1.0^{2,6}]decadien-10-one (0.027 g., 0.14 mmole) was dissolved in a mixture of 1.0 ml. of tetrahydrofuran and 0.5 ml. of 0.1 N hydrochloric acid. The mixture was warmed briefly and then allowed to stand for several days at 5°. After neutralizing with sodium blearbonate and diluting with water, the organic layer was separated and shaken with a saturated solution of sodium chloride. Final separation and purification of the product, Δ^4, Δ^8 -tricyclo[5.2.1.-0^{2,6}]decadien-3-one (20) was effected by vapor phase chromatography on a Carbowax column to give 0.005 g. (24%) of a colorless liquid which solidified upon standing. The infrared spectrum of the product was identical with that of an authentic sample of 20.²¹

Hydrolysis of the Dimethyl Ketal 7 of Pentacyclo $[5.3.0.0^{2,6}-0^{4,10}.0^{5,9}]$ decan-3-one (8).—The hydrolysis and work-up of the dimethyl ketal 7 of pentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$ decan-3-one (8) was effected in essentially the same manner as described earlier for the dimethyl ketal of Δ^3, Δ^8 -tricyclo $[5.2.1.0^{2,6}]$ decanien-10-one. The resulting ketone 8 was obtained as colorless crystals (0.01 g., 26%), m.p. 123°. The infrared spectrum determined in KBr showed a strong carbonyl band at 1730 cm.⁻¹.

Preparation of the Benzyl Methyl Ketal 6g of Decachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one (4).—An ethereal solution of 0.3 g. (7.1 mmoles) of diazomethane was added to a solution of 1.3 g. (2.2 mmoles) of the benzyl hemiketal of decachloropentacyclo[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one (6c) in 25 ml. of ether. After standing overnight the solution was diluted with methanol and then concentrated on a rotary evaporator. The solid residue (0.98 g.) was purified by recrystallization from methanol (74% yield, m.p. 148.5–149.5°).

Anal. Calcd. for $C_{18}H_{10}Cl_{10}O_2$: C, 35.28; H, 1.64; Cl, 57.86. Found: C, 35.25; H, 1.65; Cl, 57.87.

Hydrogenolysis of the Benzyl Methyl Ketal 6g of Decachloropentacyclo [5.3.0.0^{2,6}.0^{4,10}.0^{5,9}] decan-3-one (4).²²-A mixture of 0.5 g. of palladium chloride, 80 ml. of distilled water, and 2.7 ml. of concentrated hydrochloric acid were placed in a hydrogenation flask and shaken for 30 min. under a hydrogen atmosphere at a pressure of 30 p.s.i. The aqueous acidic solution was then decanted and the catalyst was rinsed repeatedly with distilled water and finally with absolute alcohol. An alcoholic solution of 0.1 g. (0.16 mmole) of the benzyl methyl ketal of decachloropentacyclo-[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]decan-3-one was added to the flask; the resulting slurry was shaken for 48 hr. under a hydrogen atmosphere (30 p.s.i.). The catalyst was then collected on a filter. Heptane was added to the filtrate and the volatile solvents were removed under vacuum. (The heptane was employed to facilitate the crystallization of the residue.) Recrystallization from hexane followed by sublimation (150° at 0.3 mm.) gave 0.03 g. (38%) of decachloropentacyclo $[5.3.0.0^{2,6}.0^{4,10}.0^{5,8}]$ decan-3-one (4) which was characterized by comparison of its infrared spectrum with that of an authentic sample.

⁽²¹⁾ R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959); R. C. Cookson, J. Hudec, and R. O. Williams, Tetrahedron Letters, No. 22, 29 (1960).

⁽²⁰⁾ W. E. Bachmann and W. S. Struve, Org. Reactions, 1, 50 (1942). (22) H. Gilman and J. W. Morton, Jr., Org. Reactions, 8, 263 (1954).

Preparation of the Mono- and Bisdimethyl Ketals (13 and 14c, Respectively) of Octachloropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{6,9}] decane-4,8-dione (12).—Octachloropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{5,9}] decane-4,8-dione (10.7 g., 0.025 mole) was dissolved in 50 ml. of methanol. After standing for a short time the methanol was evaporated and the residual oil was dissolved in 50 ml. of ether. To this solution was then added an ethereal solution of 2.64 g. (0.063 mole) of diazomethane. After standing overnight, the mixture was diluted with hexane and concentrated on a rotary evaporator. An initial sublimation of the residual oil removed excess starting material from the products. Complete separation was obtained by chromatographing the crude mixture of products on Merck neutral alumina. Elution was effected with carbon tetrachloride, ether, and finally methanol.

Removal of volatile solvents from the eluates which emerged from the column first left a pale yellow solid which was recrystallized from methanol to afford 2.3 g. (18%) of colorless crystals, m.p. > 300°. Infrared analysis suggests that this product is bisdimethyl ketal (14c) of octachloropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{6,9}]decane-4,8-dione (12). The n.m.r. spectrum further supports this view. It consists of two sharp singlets at τ 6.40 and 6.53 in a ratio of 1:1, respectively.

Anal. Caled. for $C_{14}H_{12}Cl_8O_4$: C, 31.85; H, 2.29; Cl, 53.73. Found: C, 31.79; H, 2.33; Cl, 54.01.

Evaporation of the intermediate eluates and subsequent sublimation of the combined residues $(150^{\circ} \text{ at } 0.3 \text{ mm.})$ gave 1.1 g. (9%) of colorless crystals, m.p. 280°. From the infrared spectrum it was apparent that this product was the monodimethyl ketal (13) of octachloropentacyclo[$5.3.0.0^{2,6}.0^{3,10}.0^{5,9}$]decane-4,8dione. The carbonyl absorption band of 13 occurs at 1808 cm.⁻¹. *Anal.* Calcd. for C₁₂H₆Cl₈O₂: C, 29.91; H, 1.26; Cl, 58.87. Found: C, 29.70; H, 1.30; Cl, 58.97.

Preparation of Octachloropentacyclo $[5.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$ decane-4,8-dione $(12).^{2d}$ —A solution of 51.5 g. (0.118 mole) of Δ^4, Δ^{5} -octachlorotricyclo $[5.2.1.0^{2,6}]$ decadiene-3,10-dione (11) in 200 ml. of dichloromethane was irradiated for a period of 35 hr. at 30° in a quartz vessel under nitrogen. A 450-w. Hanovia lamp was employed as a source. Water (2 ml.) was then added slowly with vigorous agitation to precipitate the hydrate of the colorless cage diketone 12. The mother liquor was then treated with activated charcoal and returned to the irradiation flask. After repeating this process three times, a combined yield of 47.8 g. of the hydrate was obtained. The crude product was then sublimed under vacuum at approximately 140° to give 43.1 g. (84%)of pale yellow crystals, m.p. 285° (lit.^{2d} >300°). The sublimed dione 12 was not purified further before proceeding with subsequent conversions.

Preparation of 8,8-Dibromooctachloropentacyclo[5.3.0.-0^{2,6}.0^{3,10}.0^{5,9}]decan-3-one (16).¹⁵—A mixture of 4.8 g. (0.011 mole) of octachloropentacyclo[5.3.0.0^{2,6}.0^{3,10}.0^{5,9}]decane-4,8-dione (12), 3.28 g. (0.012 mole) of phosphorus tribromide, and 1.94 g. (0.012 mole) of bromine was heated in a sealed tube for 18 hr. at approximately 122°. The orange mixture was then added to crushed ice; the resulting yellow solid was collected on a filter. After being dried at 55° under vacuum the product was purified by chromatography on Merck neutral alumina. Elution was performed with benzene, ether, and methanol. A final purification was effected by sublimation (150° at 0.3 mm.) to afford 1.1 g. (17%) of the crystalline dibromide 16, m.p. > 300°. The infrared spectrum of 16 exhibits a carbonyl band at 1810 cm.⁻¹ (KBr). Preparation of the Dimethyl Ketal 17 of 8,8-Dibromooctachloropentacyclo $[5.3.0.0^{2,6}.0^{3,10}.0^{5,9}]$ decan-4-one (16).—Eight grams (0.014 mole) of 8,8-dibromooctachloropentacyclo $[5.3.-0.0^{2,6}.0^{3,10}.0^{5,9}]$ decan-4-one (16) was dissolved in 50 ml. of methanol. After standing for a short time the excess methanol was removed and the residual semisolid was dissolved in 50 ml. of ether. To this solution was then added an ethereal solution of 1.39 g. (0.033 mole) of diazomethane. After standing overnight the mixture was diluted with methanol and concentrated on a rotary evaporator. Recrystallization of the resulting yellow solid from methanol gave 5.1 g. (58%) of the ketal 17, m.p. > 300°. The n.m.r. spectrum has sharp singlets of equal intensity at τ 6.34 and 6.49.

Anal. Caled. for $C_{12}H_{9}Br_{2}Cl_{8}O_{2}$: C, 23.03; H, 0.97; Br, 25.55; Cl, 45.34. Found: C, 23.13; H, 0.90; Br, 25.65; Cl, 45.65.

Preparation of the Dimethyl Ketal 18 of Pentacyclo-[5.3.0.0.^{2,6}0^{3,10}.0^{6,9}]decan-4-one (19).—The dehalogenation of the dimethyl ketal of 8,8-dibromooctachloropentacyclo-[5.3.0.0^{2,6}.0^{3,10}.0^{6,9}]decan-4-one (17) was carried out in essentially the same manner as that previously described for the dechlorination of the dimethyl ketal 6f of decachloropentacyclo-[5.3.0.0^{2,6}.0^{4,10}.0^{6,9}]decan-3-one (4). The dehalogenated ketal 18, a colorless liquid,²³ was obtained in 12% yield along with a small amount of 2,2'-bitetrahydrofuranyl.

The n.m.r. spectrum exhibits sharp singlets at τ 6.80 and 6.93 and broad multiplets at 7.28 and 7.68. In addition, relatively broad singlets appear at τ 8.52 and 8.65. These peaks have approximate integrated intensities of 3:3:6.8:1.2:1:1, respectively.

Hydrolysis of the Dimethyl Ketal 18 of Pentacyclo[5.3.0.- $0^{2,6}.0^{3,10}.0^{5,9}$] decan-4-one(19).—The hydrolysis and work-up of the dimethyl ketal 18 of pentacyclo[5.3.0. $0^{2,6}.0^{3,10}.0^{5,9}$] decan-3-one was achieved in essentially the same manner as described previously for the dimethyl ketal 7. A total yield of 0.01 g. (32%) of the colorless crystalline ketone was obtained, m.p. 124.5-125.5 (lit.¹⁶ m.p. $124-126^{\circ}$). The carbonyl band in the in-frared spectrum of 19 appears at 1755 cm.⁻¹ (KBr) which is also consistent with that reported by Cookson for the ketone 19.¹⁶ A direct comparison of the infrared spectrum of the product with that of 19 confirmed the assignment.

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⁽²³⁾ The infrared spectrum of the ketal **18** proved to be identical with that of a sample which had been prepared in an independent fashion by ketalization of **19** by Dr. K. V. Scherer, Jr. Dr. Scherer, however, was able to obtain the product in the form of a low-melting solid $(33-34^\circ)$. The combustion analysis reported (private communication) is consistent with the proposed structure.