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Skeletal Rearrangements in Reactions of Isodrin and Endrin

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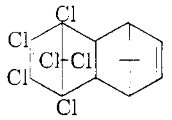
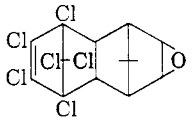
Isodrin and endrin are chlorine-containing insecticides which have the 1,4,5,8-dimethanonaphthalene nucleus and undergo unusual skeletal rearrangements in their reactions. For example, isodrin in the presence of bromine or hydrogen bromide is converted in part to a compound having a hexacyclic, bird-cage skeleton, 1,8,9,10,11,11-hexachlorohexacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]dodecane (VI). In the presence of acid, endrin is transformed to a pentacyclic ketone, 1,8,*exo*-9,10,11,11-hexachloropentacyclo[6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$]dodecan-5-one (XVII). These and other similar changes are described; they suggest that the skeletons of isodrin and endrin have the *endo,endo* configuration.

Isodrin[1] and its epoxide endrin[2] are potent insecticides which have structures identical with those of aldrin and dieldrin, respectively. Evidently the difference between these pairs lies in the configuration of their 1,4,5,8-dimethanonaphthalene nuclei.



Isodrin
Aldrin



Endrin
Dieldrin

This difference manifests itself in the divergent chemical properties of these compounds. Aldrin reacts to give normal products of addition with both neutral and acidic agents, while dieldrin with the latter reacts, though much less readily than the usual epoxides, to give products of simple ring opening.[3] With some reagents isodrin also gives normal products. Simple addition occurs upon epoxidation,[2] hydrogenation, hydroxylation with permanganate, and in reactions with phenyl azide and mercuric acetate. The products isolated from these reactions are endrin and compounds I, II (characterized as the *cis*-diol by the formation of its cyclic ketal of acetone III), IV and V, respectively, described in the Experimental. In the first four reactions the realization of such products is to be expected. With mercuric acetate a product was obtained in which the dichloroethylene grouping was intact (see below). Although addition with rearrangement is possible as in the reactions with bicyclo[2.2.1]hepta-2,5-diene,[4] normal addition is suggested in analogy to other products discussed below.

In other reactions, however, isodrin also gives normal products, but in addition co-products having an altered carbon skeleton. The principal reactions of endrin also involve a skeletal rearrangement. These and other transformations, the subject of this paper, are an unusual characteristic of the stereochemically unique isodrin family of compounds. On the basis of the structures represented for the products of isodrin and endrin, the *endo,endo* configuration[5] can be assigned to them.

The basis for the *endo, endo* concept for isodrin and the notion that its reactions produce products of rearrangement are as follows. When one molecule of addend reacts with isodrin it is found that in many cases the product no longer possesses a double bond. Since isodrin has two double bonds, it would appear that some sort of conjugate addition has occurred with the concomitant formation of a new carbon–carbon bond. Such a process is closely akin to that observed in reactions with bicyclo[2.2.1]hepta-2,5-diene.[4,6,7] Evidence for the disappearance of the two double bonds of isodrin is provided by infrared spectral data. It is recognized that an ethylenic bond bearing one or two chlorines has a stretching vibration which produces an absorption at a wave length of 6.25 μ.[8] This absorption is exhibited by compounds such as vinyl chloride and *cis*-1,2-dichloroethylene and has been noted for all adducts of hexachlorocyclopentadiene which have been examined by us. Thus, the absence of this absorption from the infrared spectrum of a Diels–Alder adduct derived from hexachlorocyclopentadiene is taken to mean that the chlorinated double bond is no longer present. This, together with the fact that only one molecule of addend is consumed, suggests that conjugate addition has occurred. On the basis that such addition was taking place with isodrin, it appeared very likely that its two double bonds were favorably situated for ring closure. This idea is further supported by two examples of isomerization discussed below. Of the four possible configurations which can be visualized for the isodrin structure,[9] two of them, *exo,exo* and *exo,endo* (chlorinated moiety *exo*), do not offer any ready means by which the two olefinic centers can be joined. This joining is possible with the *endo,endo* and *endo,exo* (chlorinated moiety *endo*) forms. However, the latter configuration has been established for aldrin.[10] In the *endo,endo* form there exists the closest approach of the two double bonds, an examination of a ball and spring model of this form indicating that the opposing carbons of the double bonds are at a distance about one-fourth greater than that of a normal carbon–carbon bond. On the basis of this favorable arrangement of double bonds and the above considera-

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[1] R. E. Lidov, U. S. Patent 2,717,851 (to Shell Development Co.), September 13, 1955.

[2] H. Bluestone, U. S. Patent 2,676,132 (to Shell Development Co.), April 20, 1954.

[3] R. E. Lidov, H. Bluestone, S. B. Soloway and C. W. Kearns, *Adv. in Chem. Series*, No. 1, 175 (1950).

[4] S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

[5] See ref. 7 of S. B. Soloway, THIS JOURNAL, **74**, 1027 (1958), for discussion of nomenclature designating geometrical isomerism.

[6] H. Bluestone, S. B. Soloway, J. Hyman and R. E. Lidov, U. S. Patent 2,730,548 (to Shell Development Co.), January 10, 1956.

[7] S. B. Soloway, R. E. Lidov, H. Bluestone and J. Hyman, U. S. Patent 2,738,356 (to Shell Development Co.), March 13, 1956.

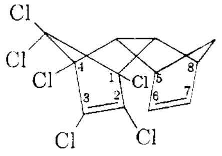
[8] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 330.

[9] K. Alder and G. Stein, *Angew. Chem.*, **47**, 837 (1934).

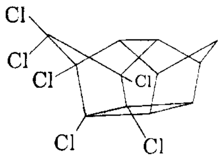
[10] S. B. Soloway, Ph.D. Thesis, Univ. of Colorado, January, 1955.

tions, the *endo,endo* form has been taken for the skeletal configuration of isodrin.

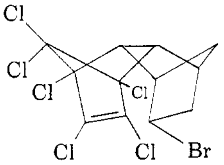
One of the more interesting products derived from isodrin is its hexacyclic isomer VI, m.p. 294–295°[11]. This compound has no double bonds, but rather a cyclobutane ring formed from the two double bonds of isodrin. The resulting carbon skeleton resembles a bird-cage and the structure of this hexacyclic system has been so designated. Isomer VI was obtained when isodrin was treated with either hydrogen bromide (24% yield) or bromine (22% yield). Evidence for the structure of the isomer VI of isodrin is based on the lack of a peak at 6.25 μ in the infrared absorption spectrum, as discussed above, elemental analysis, and the fact that it does not add hydrogen, chlorine or phenyl azide, and does not react with peroxyacetic acid, potassium permanganate or chromic acid. The production of VI from isodrin is seemingly due to polarization, possibly molecular, of the π-electrons of its two double bonds so as to lead to the formation of a four-membered ring. This process leading to a bird-cage skeleton in VI argues for the closeness in space of the two double bonds of isodrin as visualized in the *endo,endo* configuration. This conclusion is supported by the fact that ultraviolet irradiation of isodrin also yields VI.[12]



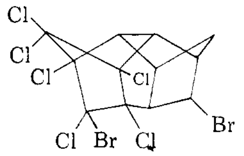
isodrin



VI



VII



VIII

From the reaction of isodrin with hydrogen bromide there was obtained, in addition to VI, the hydrobromide VII in 13% yield. The infrared absorption spectrum of VII showed the presence of the chlorinated double bond and, therefore, that VII is not a product of conjugate addition. Such products from hydrogen bromide may have formed, since the total yield of pure VI and VII was only 37%. It is to be noted that VII is represented as having the *endo,endo* configuration. The possibility was considered that addition might have occurred with Wagner–Meerwein rearrangement without involvement of the chlorinated double bond. This process would lead, however, to the *endo,exo* configuration and the product should then be the same as that which results from the addition of hydrogen bromide to aldrin. However, since the two hydrobromides, VII and VIIa, are different, the unrearranged *endo,endo* configuration is considered to exist in VII. This line of reasoning was used in assigning the *endo,endo* configuration to the products of simple addition to isodrin, as for V above and others discussed below.

Bromination of isodrin gave, in addition to the isomer VI, an 11% yield of a dibromide. In contrast to the hydrobromide VII, the dibromide does not possess a double bond, as evidenced by its infrared absorption spectrum, and therefore must have resulted from conjugate addition. Two possibilities for such addition can be visualized: (1) bromine adding to carbons 3 and 6 and a bond forming between carbons 2 and 7; and (2) bromine adding to carbons 3 and 7 and a bond forming between carbons 2 and 6. A choice between these alternatives may be made on the basis of conformational analysis of the products using molecular models. In the first case the product would have a symmetrical valence-bridged hydrocarbon structure, thus causing atoms on carbons 3 and 6 to be directed toward each other in *endo* orientation. Since one of these atoms must be halogen, and, as discussed above, carbons 3 and 6 are almost at bonding distance, serious overlap would result. This situation would not exist in the second case (VIII). Here the valence-bridged hydrocarbon structure would be unsymmetrical, being twisted so that non-bonded interactions are greatly reduced relative to those in the first case. On this basis it is suggested that the dibromide has structure VIII, with the two bromines oriented away from neighboring chlorines and toward the less bulky hydrogens. It is worth noting that the hydrocarbon skeleton of VIII, as well as related ones, are portrayed in the elegant work of Winstein and deVries[13] for products obtained from other reactions. The related structures, resulting from more deep-seated rearrangement discussed by these workers, are probably not applicable to the above dibromide, since such analogous structures would involve excessive non-bonded interactions in the form of a tetrahaloethyl grouping.

In one bromination experiment of isodrin, the only product which was obtained analyzed for $C_{12}H_7BrCl_6$. This constitution suggested that a replacement of hydrogen by a bromine atom had occurred together with the formation of the hexacyclic structure of VI. A postulated structure for the monobromide is IX. A mechanism accommodating the formation of IX may involve attack on carbon-6 of isodrin by a positive bromide and shift of a pair of electrons from the chlorinated double bond to form a new bond between carbons 2 and 7. The resulting charge on carbon 3 is then neutralized by ejection of the proton joined to carbon 6 and bond formation between carbons 3 and 6. The latter sequence is similar to mechanistic interpretations postulated for other transformations, described below, whose products appear clear.

The behavior of isodrin toward bromine was paralleled in part by chlorine. With the latter, however, the product was a complex mixture from which only very small amounts of pure compounds were isolated. One of them was the dichloride X. Its structure is presumed as for the corresponding dibromide VIII, on the basis of analysis and is supported by the absence of the absorption for a

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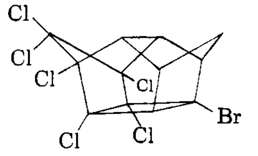
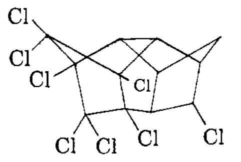
(11) R. E. Lidov and H. Bluestone, U. S. Patent 2,714,617 (to Shell Development Co.), October 2, 1955.

(12) R. C. Cookson and E. Crundwell, *Chemistry & Industry*, 1004 (1958).

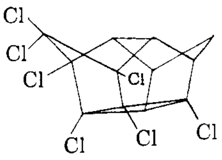
(13) L. de Vriesand, and S. Winstein THIS JOURNAL, **82**, 5363 (1960).



IX



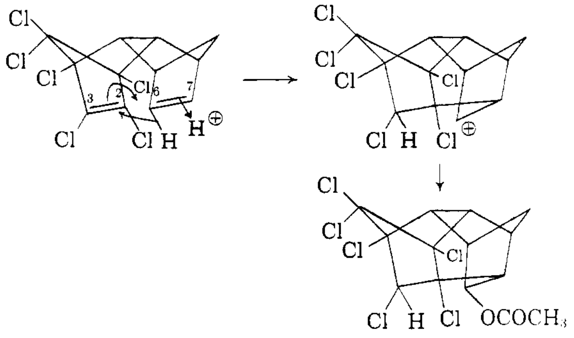
X



XI

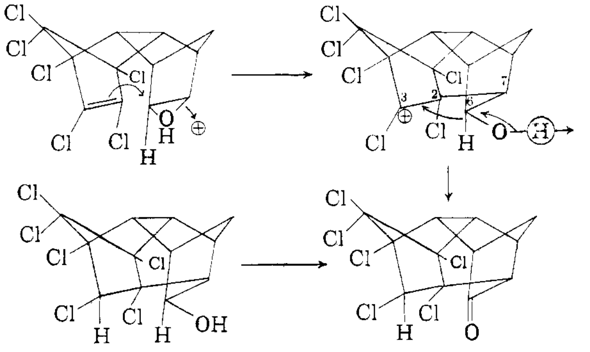
chlorinated double bond from its infrared spectrum. The only other product obtained was a heptachloro compound, $C_{12}H_7Cl_7$. Its structure is presumed to be XI, being similar to that of the bromide IX, and is also supported by infrared spectral data which show the absence of a chlorinated double bond.

A somewhat more complicated case of conjugate addition occurred with the acid-catalyzed addition of organic acids to isodrin. With acetic acid a mixture of products was obtained which consisted mostly of the rearranged acetate XII and the normal acetate XIII. Mixtures of this sort have been observed with bicyclo[2.2.1]hepta-2,5-diene.[4,6,7] With formic acid only the rearranged formate XIV, analogous with XII, was isolated. Both the acetate XII and the formate XIV yielded the pentacyclic alcohol XV upon hydrolysis. The structure of this alcohol was established by its oxidization to a ketone, XVII (see below), whose structure appears clear.



XII

The formation of the precursor acetate XII having an oxygen function introduced on carbon 6 of isodrin can be rationalized as follows. As commonly postulated a proton, or its mechanistic equivalent, may be said to join to carbon 6 of isodrin to give a carbonium ion with the charge on carbon 7. A shift of a pair of electrons from the chlorinated double bond leads to the formation of a bond between C-2 and C-7 with the appearance of the positive center at carbon 3. A hydride shift then occurs from carbon 6 to carbon 3 and the newly formed positive center at carbon 6, the site attacked by a proton at first, reacts with acetate ion, or its equivalent. The resulting product XII thus has a pentacyclic structure formed by a conjugate type of addition which also involved a hydride shift. The acetoxy group is assigned *exo* on the basis of the *exo*-addition rule of Alder.[14] Since a hydride shift is presumed to have occurred from C-6 to C-3, it is very plausible that this occurred by the shortest intramolecular path so as to cause a shift of the chlorine on carbon-3 to the *exo* orientation. Structure XII depicts these orientations. It will be recognized that in the absence of a hydride shift the entering acetoxy group would become bonded to a carbon already bearing chlorine. In that event, hydrolysis would result in the loss of a chlorine. The fact that chlorine was not lost on hydrolysis supports the above conclusions as to the structure of XII.



XV XVII

One of the more significant products of rearrangement encountered in this work is the pentacyclic ketone XVII obtained from endrin. This rearrangement of endrin occurs rather easily under both thermal and acid-catalyzed conditions. It appears that the driving force for isomerization is the concomitant skeletal rearrangement leading to the pentacyclic structure. The evidence for this structure is again based upon analysis and infrared spectral data. In ketone XVII there is only one site of stereoisomerism, that at the carbon (C-9) which bears both a chlorine and a hydrogen atom. As for the acetate XII, the chlorine on C-9 is assigned the *exo* configuration on the basis of mechanistic interpretation. In the acid-catalyzed rearrangement the conjugate acid of endrin may be said to undergo ring-opening of the oxirane group and the formation of a bond between carbons 2 and 7. This leaves the charge on carbon 3, a situation which is stabilized by a hydride shift from C-6 and a loss of a proton from oxygen to give ketone XVII. This hydride shift should proceed in the same way as in the formation of the acetate XII, which indeed it does as shown by the fact that the alcohol XV is oxidized to ketone XVII. These arguments, together with the chemical and physical data, leave little doubt as to the nature of XVII. A recent report is in agreement with the interpretations of the nature of ketone XVII and alcohol XV and of their manner of formation.[15]

Additional support for the structure of ketone XVII is derived from some of its transformations. When XVII was reduced in a number of trials with lithium aluminum hydride an alcohol, XVIII, m.p. 258–260° dec., was obtained. This alcohol is

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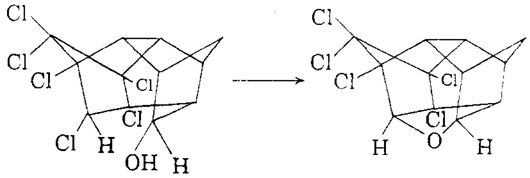
[14] K. Alder, H. Wirtz and H. Koppelberg, *Ann.*, **601**, 138 (1956).

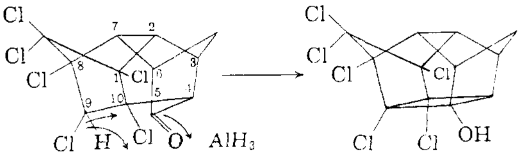
[15] R. C. Cookson and E. Crundwell, *Chemistry & Industry*, 703 (1959).

plainly different from alcohol XV, m.p. 196–197°. Since the latter alcohol afforded upon oxidation ketone XVII, the precursor of alcohol XVIII, these two alcohols are evidently stereoisomers. Further, because the hydroxyl group of XV is indicated on mechanistic grounds to be *exo*, the orientation for the hydroxyl in XVIII remains to be *endo*. This assignment of configuration is consistent with the known course of reduction of ketones in bridged systems by lithium aluminum hydride.[16] Inasmuch as the structure of these alcohols is that of a pentacyclic system, it appeared that dehydration should lead to the hexacyclic isomer VI of isodrin.



XVIII XXIII

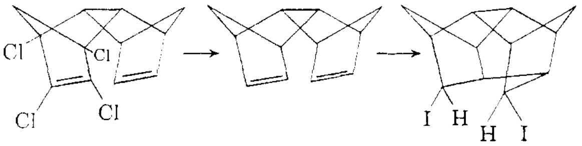
Indeed, when the *endo*-alcohol XVIII was heated with phosphorus pentoxide the only product isolated, though in low yield, was the hexacyclic compound VI, identified by its melting point and infrared spectrum. Dehydration was also attempted with activated alumina at 185°, but in this case a fair yield of a new product was obtained which still contained oxygen, though only five chlorine atoms. A plausible interpretation of the nature of this product is that it is an ether, XXIII, formed by an internal displacement of a chlorine by hydroxyl. The infrared spectrum of XXIII shows a C–O–C absorption in agreement with the structure assigned. The formation of the ether XXIII does suggest that the hydroxyl group in XVIII is oriented *endo*, as postulated above, in a favorable position for displacement of a chlorine atom from the opposite side of the molecule. Since such displacements generally occur by backside attack on carbon, *i.e.*, on the side opposite chlorine, the formation of XXIII argues for an *exo* orientation for the displaced chlorine. This conclusion is in agreement with that reached on the mechanistic grounds discussed above.



XXIV

In those experiments wherein the ketone XVII was reduced to the *endo*-alcohol XVIII, the reducing agent, lithium aluminum hydride, was used in very large excess. In one particular experiment, where about an equivalent of lithium aluminum hydride was employed, a new alcohol, dec. 330°, was obtained. Because the two possible alcohols having a pentacyclic structure XV and XVIII were known, the acetates of all three alcohols were different, and elemental analysis did not indicate an actual reduction, a hexacyclic structure, XXIV, is presumed for this new alcohol. Since the alcohol XXIV is an isomer of the ketone from which it was obtained, it may be said to be an enol of the latter. Its formation may be imagined as occurring by attack on oxygen by aluminum hydride and withdrawal of the pair of electrons bonding carbon 9 to hydrogen to form a bond between carbon 9 and carbon 5. The hydrogen atom joined to carbon 9 is likely lost as a proton and the resulting aluminum derivative affords XXIV upon hydrolysis. This process may be termed "transannular enolization." Its postulated occurrence here indicates again the favorable geometry of the molecule leading to bird-cage skeletons.

In view of the unusual transformations exhibited by isodrin it became of interest to see whether similar changes would occur with its hydrocarbon analog. This analog XXVII, was obtained by reducing isodrin in two stages; first with zinc in acetic acid to replace the two bridge chlorines by hydrogen to give XXVI, and then with sodium in *n*-amyl alcohol to replace the remaining four chlorines. Although XXVII was characterized by its formation of a mono and a bis-(dihydrophenyltriazole), its purity was not established. The presence of saturated hydrocarbons is conceivable.



XXVI XXVII XXX

The only reaction attempted with hydrocarbon XXVII which might give a product of skeletal rearrangement was iodination. The 1,2-addition of iodine to a double bond does not occur generally. Thus, this reagent would be expected to provide a favorable case for rearrangement with XXVII as was observed with bicyclo[2.2.1]hepta-2,5-diene.[4] When 2–5 g. of XXVII was treated with iodine in carbon tetrachloride, a 12–20% yield of a solid diiodine (m.p. 134.5–136°) was realized. On the assumption that only conjugate addition could have occurred, structure XXX was assigned to it. This was verified when the solid diiodide XXX was treated with zinc in methanol and a saturated hydrocarbon analyzing for $C_{12}H_{14}$ was obtained. Because the diiodide XXX is presumed to have the same pentacyclic structure as formed in reactions of isodrin, and its product of deiodination has the same number of hydrogen atoms as its precursor, it appears very likely that the new hydrocarbon is XXXI, which is the unsubstituted bird-cage skeleton of the hexacyclic isomer of isodrin, VI. This interpretation was proved to be correct when VI was dechlorinated by means of sodium in *n*-amyl alcohol and the same hydrocarbon, XXXI, was obtained. The product of the latter reaction did not depress the melting point, 154–156°, of the hydrocarbon obtained from the diiodide and the infrared spectra of these two specimens were identical. It is of interest that the spectrum of hydrocarbon XXXI is practically identical with that of a hydrocarbon of formula $C_{12}H_{14}$ which Winstein and

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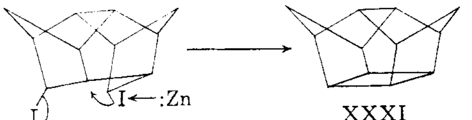
(16) D. S. Noyce and D. B. Denney, This Journal, **72**, 5743 (1950).

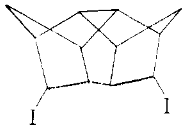
de Vries[13] obtained by a different reaction. Though their specimen melts at 165.5–167.5°, a mixed melting point with XXXI did not show a depression. It is well known that bicyclic compounds of this type have high melting point depression constants. Accordingly, a small amount of impurity in XXXI would account for its low melting point.



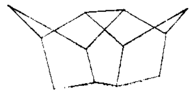
XXXI

A plausible assignment of configuration to the solid diiodide XXX is one where the two iodines are oriented *exo*. This arrangement makes for symmetry in the molecule, a factor which is often responsible for high melting points. It can be rationalized on the basis of mechanistic interpretations of its formation and of its conversion to the bird-cage hydrocarbon XXXI. In the formation of XXX the *exo*-addition rule simply requires both iodine atoms to be so oriented. As depicted, zinc can readily attack an *exo*-oriented iodine and the second iodine atom (*exo*) is then favorably placed for backside displacement by electrons from the first iodine atom.

Besides the solid diiodide obtained from the isodrin hydrocarbon XXVII there was obtained a crude liquid diiodide which could not be crystallized. This occurred when the iodination was carried out on a large scale. When the crude liquid diiodide was treated with zinc, a hydrocarbon was obtained as a liquid by distillation. It could not be crystallized and its infrared spectrum was different from that of the solid bird-cage hydrocarbon XXXI. The liquid hydrocarbon analyzed for $C_{12}H_{16}$, and was saturated to phenyl azide and catalytic hydrogenation. Both of these products could well have been mixtures, but no attempts were made at separation. Although structures cannot be assigned definitely to these products, speculation is possible in line with those formulated by Winstein and de Vries[13] and with VIII above. Since the liquid hydrocarbon contained two hydrogens more than the bird-cage hydrocarbon XXXI, it is likely a reduction product of a diiodide where the iodines are too far removed from each other so as to allow ring closure. One of a number of possibilities that can be suggested is a structure like that of the dibromide VIII, *viz.*, XXXII; the corresponding hydrocarbon may then be XXXIII, octahydro-2,6-cyclo-1,4,5,8-dimethanonaphthalene.[17] Other structures following those of Winstein and de Vries can also be formulated. Howsoever, the possibility exists, as indicated above, that the products obtained were mixtures of the various valence-bridged structures of Winstein and de Vries.[13]



XXXII



XXXIII

Acknowledgment.—The authors are deeply grateful to Mr. Glenn E. Pollard for the infrared spectral data and to Mr. Paul M. Saliman for the elemental and functional group analyses. We are also most pleased to acknowledge the helpful discussions of Professors Saul Winstein and Stanley J. Cristol during the progress of this work dating back to 1950 and the constructive comments on this manuscript prior to publication by the former.

Experimental[18]

5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (I).—A solution of 18.3 g (0.05 mole) of isodrin in 200 ml. of hexane was hydrogenated over Raney nickel until the uptake of hydrogen had ceased. The catalyst was removed by filtration. Evaporation of the filtrate gave a crude solid which was recrystallized from acetone–methanol to yield 17 g. (95%) of I, m.p. 218–219°; absorbance of 10.0% w./v. solution in carbon tetrachloride at 6.25 μ (C=CCl), 0.222; absorbance of 10.0% w./v. solution of isodrin in carbon disulfide at 6.25 μ, 0.257.

Anal. Calcd. for $C_{12}H_{10}Cl_6$: C, 39.2; H, 2.73. Found: C, 39.4; H, 2.70.

5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene-*exo*-2-*exo*-3-diol (II).—A solution of 19 g. (0.12 mole) of potassium permanganate in 1000 ml. of water was added dropwise to a stirred mixture of 54.8 g. (0.15 mole) of isodrin, 7.2 g. of magnesium sulfate and 2500 ml. of acetone at 5° over a period of 4.5 hours. The salts were filtered and washed with acetone and water, and the filtrate was concentrated to remove the acetone and extracted with ethyl ether. The combined ether extracts were washed with 10% sodium hydroxide solution and then water, dried over anhydrous sodium sulfate and evaporated to leave 52 g. of a dark brown oil. This oil was crystallized from heptane (charcoal) to give 44.5 g. of solid which after two recrystallizations yielded 20.6 g. (35%) of II, m.p. 199–201°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.715; at 3.05 μ (O-H), 1.000.

Anal. Calcd. for $C_{12}H_{10}Cl_6O_2$: C, 36.2; H, 2.51; Cl, 53.4. Found: C, 35.8; H, 2.61; Cl, 53.0.

5,6,7,8,9,9-Hexachloro-*exo*-2,3-(dimethylmethylenedioxy)-1,2,3,4,4a,5,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene (III).—A mixture of 30 g. (0.075 mole) of II and 15 g. of ferric chloride hexahydrate in 225 ml. of acetone was refluxed for 18 hours, cooled, and poured into water. The organics were extracted with ether, and the combined ether extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated. The residue was recrystallized from a mixture of benzene and heptane (charcoal) to yield 29 g. (88%) of III, m.p. 138–139°; absorbance of 10.5% w./v. solution in carbon tetrachloride at 6.25 μ (C=CCl), 0.254; 11.6% w./v. solution in carbon disulfide at 9.52 μ (C—O—C), 1.170.

Anal. Calcd. for $C_{15}H_{14}Cl_6O_3$: C, 41.0; H, 3.19; Cl, 48.5. Found: C, 41.0; H, 3.29; Cl, 48.2.

5.6,7,8,11,11-Hexachloro-3a,4,4a,5,8,8a,9,9a-octahydro-1-phenyl-4,9-*endo,endo*-5,8-dimethano-1H-naphtho(2,3)-triazole (IV) was prepared from isodrin and phenyl azide in boiling benzene and recrystallized from hexane, m.p. 185° dec., absorbance in potassium bromide disk at 6.25 μ, 0.250; at 13.32 μ (phenyl), 0.208.

Anal. Calcd. for $C_{18}H_{15}Cl_6N_3$: N, 8.67. Found: N, 8.22.

3-(Acetoxymercuri)-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,-5,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalen-2-ol Acetate (V).—To a solution of 18.3 g. (0.05 mole) of

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(17) The nomenclature of XXXIII is suggested in analogy to the practice of "Chemical Abstracts" for cyclosteroids. Thus, the prefix 2,6-cyclo means that a valence bridge joins carbons 2 and 6 in the 1,4,5,8-dimethanonaphthalene system. Although the two norbornane units of XXXIII are oriented *endo,endo*, this designation is omitted since the 2,7-valence bridge allows only the *endo,endo* configuration for the system. In like manner the bird-cage hydrocarbon can be named 2,7:3,6-dicyclo-1,4,5,8-dimethanonaphthalene. These suggestions on nomenclature have been submitted to "Chemical Abstracts" for review.

(18) Melting points are uncorrected.

isodrin in 300 ml. of acetic acid, 31.8 g. (0.1 mole) of mercuric acetate was added and the mixture was heated on the steam-bath for 18 hours. On cooling, the homogeneous reaction mixture deposited 26 g. (76% yield) of V, m.p. 175°; recrystallization from benzene did not change the melting point; absorbance in Nujol mull at 6.25 μ (C=CCl), 0.256; at 5.78 μ (C=O), 0.546.

Anal. Calcd. for $C_{16}H_{14}Cl_6HgO_4$: C, 28.1; H, 2.05. Found: C, 28.1; H, 2.06.

1,8,9,10,11,11-Hexachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}-.0^{5,9}]-dodecane (VI). Method A.—Dry hydrogen bromide was passed into a solution of 36.5 g. (0.1 mole) of isodrin in 300 ml. of dry ether at 20° for 2 hours. Water was then added dropwise and the mixture was poured onto cracked ice and neutralized with sodium bicarbonate. Work-up of the product by ether extraction afforded 44.6 g. of an oil which was crystallized in an acetone–hexane mixture. Four drops of crystals were obtained: (1) 3.3 g., m.p. 285°; (2) 8.4 g., m.p. 270°; (3) 15.6 g., m.p. 104–108°; (4) 7.6 g., m.p. 100–145°. The first two crops were combined and recrystallized from acetone–methanol to yield 8.6 g. (24%) of VI, m.p. 287–289°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.90 μ, 0.398; at 13.45 μ, 0.736.

Anal. Calcd. for $C_{12}H_8Cl_6$: C, 39.5; H, 2.21; Cl, 58.3. Found: C, 39.75; H, 2.32; Cl, 58.3.

The recrystallization afforded an additional crop of VI, 1.9 g., m.p. 280–287°. When 13.7 g. of crop 3 was recrystallized from methanol, three crops of crystals were obtained: (a) 5.1 g., m.p. 110–111°; (b) 6.3 g., m.p. 103–108°; (c) 1.5 g., m.p. 109–150°. Crop a was the unrearranged bromide VII, ***exo*-6-bromo-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalene** (13% yield) as evidenced by its elemental composition and infrared spectrum; absorbance of 8.46% w./v. solution in carbon tetrachloride at 6.25 μ (C=CCl), 0.234; at 12.1 μ, 0.00; at 13.97 μ, 0.451.

Anal. Calcd. for $C_{12}H_9BrCl_6$: C, 32.3; H, 2.03; Br + Cl as Cl, 55.7. Found: C, 32.5; H, 2.06; Br + Cl as Cl, 55.6.

Isodrin was also treated with hydrogen bromide in anhydrous acetic acid and in butyl ether; the results were similar.

Method B.—One hundred and forty grams (0.384 mole) of isodrin was brought into solution in 250 ml. of carbon tetrachloride by warming to 65°. Bromine was added in portions so that the exothermic reaction maintained the temperature at 70–75°. The addition of bromine was stopped when no further exothermicity could be noted and the color of bromine did not disappear. The amount of bromine added was 39 g. (0.244 mole). A slightly tan material which separated on cooling of the reaction mixture was filtered and washed with hexane; 60 g., softening at 180° and melting at 285° to a black liquid. This solid was decolorized with charcoal in benzene, and hexane was added to yield 30.2 g. (22%) of VI, m.p. 294–295°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.90 μ, 0.450; at 13.45 μ, 0.790.

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 39.5; H, 2.21; Cl, 58.3. Found: C, 39.4; H, 2.35; Cl, 58.3.

The original filtrate, combined with the hexane washings, precipitated on standing 66 g. of a yellow solid, m.p. 175° dec. This solid was treated as the one above to yield 41.2 g. (21%) of VIII, m.p. 185° dec.

Method C.—A mixture of 17 g. (0.044 mole) of XVIII and 17 g. of phosphorus pentoxide was heated by means of an oil-bath at 145° for 0.5 hour. The resulting black material was treated with water and extracted with benzene. A carbonaceous solid was filtered from the water and benzene phases, and the benzene solution was dried over anhydrous sodium sulfate and evaporated. The residue was recrystallized three times from benzene–hexane (charcoal) to yield 1.0 g. (6%) of VI, m.p. 291–292°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.90 μ, 0.315; at 13.45 μ, 0.597. The entire infrared spectrum was identical with those of the products obtained by methods A and B.

Anal. Calcd. for $C_{12}H_8Cl_6$: C, 39.5; H, 2.21; Cl, 58.3. Found: C, 39.4; H, 2.47; Cl, 58.4.

***exo*-2-Bromo-5,6,7,8,9,9-hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene (VIIa).**—Hydrogen bromide gas was passed into a solution of 36.5 g. (0.1 mole) of aldrin in 200 ml. of ether cooled externally with an ice-bath until the increase in weight was 22.5 g. The mixture was allowed to stand overnight at room temperature. Evaporation of the solvent and addition of water gave 41 g. of solid which was recrystallized from acetone to yield 28.5 g. (64%) of VIa, m.p. 173–174.5°. The analytical specimen was also obtained from acetone and melted at 177–178°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.146; at 12.1 μ, 0.254; at 13.97 μ, 0.00.

Anal. Calcd. for $C_{12}H_9BrCl_6$: C, 32.3; H, 1.80; Br + Cl as Cl, 55.7. Found: C, 32.2; H, 2.10; Br + Cl as Cl, 55.7.

***exo*-5-*endo*-10-Dibromo-1,8,9,10,11,11-hexachloropentacyclo [6.2.1.1^{3,6}.0^{2,7}.0^{4,9}]dodecane (VIII).**—Bromine (8.0 g., 0.05 mole) was added dropwise to a stirred solution of 18.3 g. (0.05 mole) of isodrin in 150 ml. of acetic acid at room temperature and the reaction mixture was refluxed for 2.5 hours. The solvent was distilled and the residual oil was dissolved in hexane. The hexane solution was washed with sodium bicarbonate solution and then water, and dried over anhydrous calcium chloride. Concentration of the hexane solution gave 4.2 g. of material melting at about 150°; further evaporation and the addition of methanol gave 4.3 g. more of solid. These solids were combined and recrystallized from methanol–acetone to yield 2.8 g. (11%) of product presumed to be VIII, m.p. 190° dec.; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.85 μ, 0.495.

Anal. Calcd. for $C_{12}H_8Br_2Cl_6$: C, 27.4; H, 1.52; Br + Cl as Cl, 54.1. Found: C, 27.6; H, 1.57; Br + Cl as Cl, 54.0.

Additional crops melting over wide ranges were obtained, but none were reduced to a pure component.

4-Bromo-1,8,9,10,11,11-hexachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (IX).—Ten grams (0.028 mole) of isodrin was dissolved in 65 ml. of acetic acid by warming to 65°. Bromine (5.2 g., 0.03 mole) was added dropwise to the warm solution producing an exothermic reaction. The reaction mixture was poured into water and the product was extracted with ether. Evaporation of the ether left about 12 g. of a viscous, tan oil which could not be made to crystallize. Distillation of 8 g. of this oil gave 6.0 g. of product, b.p. 197–213° (1.2 mm). The distillate was crystallized from a methanol–acetone mixture to give 1.0 g. of product, m.p. 213–245°, which upon recrystallization yielded 0.3 g. (3.6%) of presumed IX, m.p. 256–257°.

Anal. Calcd. for $C_{12}H_7BrCl_6$: C, 32.4; H, 1.58; Br + Cl as Cl, 56.0. Found: C, 32.6; H, 1.75; Br + Cl as Cl, 56.3.

A second crop of crystals amounted to 0.3 g., m.p. 251–253. Attempts to obtain additional solids from the mother liquor were unsuccessful.

1-*exo*-5,8,9,9,10,11,11-Octachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.-0^{4,10}]dodecane (X).—A solution of 20 g. (0.054 mole) of isodrin in 100 ml. of carbon tetrachloride was cooled by means of an ice–water-bath and chlorine was introduced until a yellow color persisted. The carbon tetrachloride was removed by evaporation and two codistillations with ethyl alcohol. Evaporation of the ethanol and crystallization of the residue from methanol gave 2.0 g. of material, m.p. 194–197°, and 2.0 g. of a second crop, m.p. 197–200°. The addition of a small amount of water to the mother liquor precipitated a tacky solid. Recrystallization of the first crops from methanol yielded 1.3 g. (5%) of product presumed to be X, m.p. 212–213°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.85 μ, 0.322.

Anal. Calcd. for $C_{12}H_8Cl_8$: Cl, 65.1. Found: Cl, 65.0.

1,4,8,9,10,11,11-Heptachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.-0^{4,10}.0^{5,9}]dodecane (XI).—Chlorine was passed rapidly into a solution of 100 g. (0.274 mole) of isodrin in 500 ml. of chloroform at room temperature until a yellow color persisted. The reaction was moderately exothermic. Evaporation of the solvent left a yellow oil which could not be induced to crystallize. When the oil was allowed to stand in 350 ml. of hexane, 11.4 g. of a colorless solid, m.p. 168–174°, separated. Recrystallization of this solid from heptane gave 9.0 g. of product, m.p. 165–171°, which upon recrystallization from isopropyl alcohol yielded 5.5 g. (5%) of presumed XI, m.p. 175–175.5°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 7.90 μ, 0.275.

Anal. Calcd. for $C_{12}H_7Cl_7$: C, 36.1; H, 1.75; Cl, 62.2. Found: C, 36.0; H, 1.72; Cl, 62.2.

The hexane mother liquor was chromatographed on a column of activated alumina and the column was eluted first with hexane and then with benzene. From the hexane eluates there were obtained solids melting over a thirty degree range, about 130–160°. Recrystallization of some of these solids afforded 4.0 g. of X, m.p. 210–211°, and an additional crop of 1.9 g., m.p. 204–206°. One of the benzene fractions was evaporated to give 5.0 g. of crude solid which upon recrystallization from benzene–methanol (1:4) afforded 2.0 g. of impure XI, m.p. 165–167°, m.m.p. with pure XI, 168–172°. Another benzene fraction gave 13 g. of crude solid. This was also recrystallized from benzene–methanol to give 7.6 g. of XI, m.p. 171–174°.

1,8-*exo*-9,10,11,11-Hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-*exo*-5-ol Acetate (XII).—A solution of 50 g. (0.137 mole) of isodrin in 180 ml. of glacial acetic acid was heated to reflux and then 20 ml. of concentrated sulfuric acid was added. Refluxing was continued for 20 minutes. Upon cooling, crystals, 15 g., m.p. 160° dec., precipitated from the reaction mixture. This crop was removed by filtration and was not examined. The filtrate was poured into water, and the mixture was neutralized with sodium bicarbonate solution and extracted with carbon tetrachloride. Evaporation of the solvent gave an oil which was recrystallized from ethanol to yield 35.4 g. of crude product, m.p. 130–170°. The crude product was again recrystallized from ethanol to yield 13.2 g. (23%) of impure XII, m.p. 204–208°; absorbance in Nujol mull at 6.25 μ (C=CCl), 0.019; at 5.80 μ (C=O), 0.583.

Anal. Calcd. for $C_{14}H_{12}Cl_6O_2$: C, 39.6; H, 2.83; Cl, 50.1. Found: C, 39.6; H, 2.89; Cl, 50.2.

This experiment was repeated on a threefold scale and fractional recrystallization of the crude product from methanol–acetone finally yielded 10.2 g. (6.6%) of XII as needles, m.p. 215–216°; absorbance in Nujol mull at 6.25 μ (C=CCl), 0.00; at 5.80 μ (C=O), 0.554.

Compound XII was also obtained by the esterification of XV with acetic anhydride. From 1.0 g. of XV there was obtained 0.5 g. of XII, m.p. 206–208°; m.m.p. with the impure XII of above, 202–205°.

1,2,3,4,10,10-Hexachloro-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalen-*exo*-6-ol Acetate (XIII).—A mixture of 11.0 g. (0.03 mole) of isodrin, 15 ml. of water, 100 ml. of acetic acid and 30 ml. of 50% (by volume) of sulfuric acid was refluxed for 20 hours, cooled, and poured into water. The aqueous solution was neutralized with sodium bicarbonate and the organic material was extracted with carbon tetrachloride. Evaporation of the solvent after drying over anhydrous calcium chloride left 19.9 g. of an oil. Treatment of the oil with methanol–acetone gave 2.7 g. of solid, m.p. 171–178°. This solid was twice recrystallized from methanol to yield 1.0 g. (8%) of XIII, m.p. 193–197°; absorbance in Nujol mull at 6.25 μ (C=CCl), 0.136; at 5.80 μ (C=O), 0.444.

Anal. Calcd. for $C_{14}H_{12}Cl_6O_2$: Cl, 50.1; sapon. equiv., 425. Found: Cl, 50.1; sapon. equiv., 427.

Compound XIII was also obtained by esterifying 1.0 g. of XVI with acetic anhydride. The product weighed 0.8 g. (72% yield), m.p. 188–192°; m.m.p. with XIII above, 184–194°.

1,8-exo-9,10,11,11-Hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-*exo*-5-ol Formate (XIV).—A mixture of 50 g. (0.137 mole) of isodrin and 350 ml. of formic acid was heated to reflux and 35 ml. of concentrated sulfuric acid was added. The reaction mixture became homogeneous after 2 hours at reflux and was then allowed to cool. A solid precipitated, 52.2 g., m.p. *ca.* 160° dec. Recrystallization from methanol–acetone yielded 10.2 g. (18%) of XIV, m.p. 216–218°; absorbance in potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 5.78 μ (C=O), 0.567.

Anal. Calcd. for $C_{13}H_{10}Cl_6O_2$: C, 37.95; H, 2.43; Cl, 51.9. Found: C, 37.6; H, 2.19; Cl, 52.0.

The mother liquor was concentrated to yield an additional 11.5 g. of crystals, m.p. 210–213°, which was presumed to be XIV. Further concentration and recrystallization from the same solvent mixture afforded a total of 25.5 g. of material melting in the range of 230–247°. Chlorine analysis (57.8% Cl) and the melting points indicated this material to be isodrin.

1,8-*exo*-9,10,11,11-Hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-*exo*-5-ol (XV).—A solution of 9.0 g. (0.021 mole) of XII in 200 ml. of ethanol containing 5% by weight of hydrogen chloride was refluxed for 17 hours. Distillation of the solvent left a solid which, after washing with sodium bicarbonate solution and water and then drying, weighed 8.1 g., m.p. 185–195°. Recrystallization from benzene gave 4.8 g. of XV, m.p. 196–197°, and a second crop of 2.8 g., m.p. 194–196°; the total yield was 94%. The infrared spectrum of XV in a potassium bromide disk showed zero (0.00) absorbance at 6.25 μ (C=CCl), and 0.285 at 2.92 μ (O—H).

Anal. Calcd. for $C_{12}H_{10}Cl_6O$: C, 37.6; H, 2.60; Cl, 55.6. Found: C, 37.7; H, 2.75; Cl, 56.0.

Compound XV was also obtained by the alcoholysis of XIV. The reaction was effected with the combined crops (21.5 g., 0.052 mole) of XIV described above by refluxing for 16 hours in 750 ml. of isopropyl alcohol containing 5% by weight of hydrogen chloride. After partial evaporation of the solvent a solid which separated was collected on a filter, 2.0 g., m.p. 237–239° dec. The filtrate was taken to dryness and the residue was dissolved in benzene; the benzene solution was washed with water, dried over anhydrous calcium chloride, and concentrated. Four crops of crystals were obtained: (1) 5.0 g., m.p. 185–188°; (2) 3.4 g., m.p. 195–197° (m.m.p. with XV above, 194–196°); (3) 1.2 g., m.p. 195–197°; and (4) 7.9 g., m.p. 235–240°. Crops 2 and 3 represent a 23% yield of XV. The identity of the fourth crop, as well as the initial solid collected, was not established, but both fractions were presumed to be isodrin on the basis of their melting points.

5,6,7,8,9,9-Hexachloro-1,2,3,4,4a,5,8,8a-octahydro-1,4-*endo,endo*-5,8-dimethanonaphthalen-*exo*-2-ol (XVI).—A crude solid product (36.1 g., 0.085 mole) obtained as above from the addition of acetic acid to isodrin and consisting mainly of the isomers XII and XIII, was refluxed for 42 hours in 750 ml. of methanol containing 7% by weight of hydrogen chloride. The solvent was distilled and the residual oil was dissolved in ether. The ether solution was washed with sodium bicarbonate solution and dried over anhydrous calcium chloride. Evaporation of the solvent left 28.4 g. of a waxy solid which was crystallized from hexane to which a small amount of acetone was added to help dissolve the solid. The first crop of crystals was a mixture of alcohols, mainly XV, 18.0 g., m.p. 205–210° dec.; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.018; at 2.92 μ (O—H), 0.420.

Anal. Calcd. for $C_{12}H_{10}Cl_6O$: C, 37.6; H, 2.60; Cl, 55.6. Found: C, 37.7; H, 2.75; Cl, 56.0.

The second crop of crystals amounted to 8.0 g., m.p. 220° dec. Recrystallization from the same solvent mixture yielded 4.8 g. (15%) of XVI, m.p. 222° dec.; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.296; at 3.00 μ (O—H), 0.430.

Anal. Found: C, 37.6; H, 2.68; Cl, 55.5.

1,8-*exo*-9,10,11,11-Hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecan-5-one (XVII). Method A.—A mixture of 25 g. (0.066 mole) of endrin, 100 ml. of butyl ether and 100 g. of concentrated hydrochloric acid was refluxed with vigorous stirring for 23 hours. Fifteen grams (60% yield) of XVII, m.p. 285° dec., was collected directly by filtration; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 5.68 μ (C=O), 0.768.

Anal. Calcd. for $C_{12}H_8Cl_6O$: C, 37.8; H, 2.12; Cl, 55.9. Found: C, 38.0; H, 2.15; Cl, 55.9.

Method B.—Two grams of endrin was heated in a test-tube at 150° when an exothermic reaction occurred and the temperature rose to 278°. Recrystallization of the residue from toluene yielded 1.0 g. of XVII (50%), m.p. 275–285° dec., which caused no depression in m.p. when admixed with XVII of method A.

Method C.—A solution of 4.0 g. of potassium permanganate in 50 ml. of water was added with stirring at 70° to 6.0 g. (0.016 mole) of XV in 150 ml. of acetic acid. About 25 ml. of dilute sulfuric acid was then added and the mixture was heated at 80–85° for 2 hours when all of the oxidizing agent was consumed. The reaction mixture was filtered and the residue of manganese salts was washed with acetone. The filtrates were combined and poured into water to precipitate a white solid. The solid was filtered and washed with water, sodium bicarbonate solution, and water again; 2.4 g., m.p. 270° dec. The filtered manganese salts were again washed with acetone and in the manner indicated above an additional crop, XVII, was realized, 2.2 g., m.p. 280–282° dec.; m.m.p. with XVII of method A, 282–285° dec. The combined yield of XVII was 75%.

Method D.—A solution of 5.0 g. of chromium trioxide in 8 ml. of water was added dropwise to a refluxing solution of 6.1 g. of isodrin in 25 ml. of acetic acid; 20 ml. of 70% by volume of sulfuric acid was added and refluxing was continued for 1 hour. The solution was cooled and poured onto cracked ice to precipitate a solid. Recrystallization from methanol yielded 1.9 g. (30%) of XVII, m.p. 278–283°. Another recrystallization from methanol yielded pure XVII, m.p. 285–286° dec.

Anal. Calcd. for $C_{12}H_8Cl_6O$: C, 37.8; H, 2.10; Cl, 55.9. Found: C, 37.8; H, 2.18; Cl, 55.9.

1,8-*exo*-9,10,11,11-Hexachloropentacyclo[6.2.1.1^{3,6}.0^{2,7}-.0^{4,10}]dodecan-*endo*-5-ol (XVIII).—A mixture of 5.0 g. (0.014 mole) of XVII and 0.5 g. (0.013 mole) of lithium aluminum hydride in 150 ml. of anhydrous butyl ether was refluxed for 9 hours. The reaction mixture was treated with methanol and then with water. The organic material was then extracted into benzene, but 2 g. of solid, insoluble in organic solvents, remained undissolved. The benzene extract was washed once with saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of the solvent left a solid residue which was recrystallized from benzene–cyclohexane to yield 2.0 g. of XVIII (37%), m.p. 258–260° dec.; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 2.98 μ (O—H), 0.270.

Anal. Calcd. for $C_{12}H_{10}Cl_6O$: C, 37.6; H, 2.61; Cl, 55.6. Found: C, 38.5; H, 2.77; Cl, 54.0.

In a repetition of this experiment starting with 114 g. (0.3 mole) of XVII and 11.4 g. (0.3 mole) of lithium aluminum hydride, the product after three recrystallizations from carbon tetrachloride amounted to 45 g. (40% yield), m.p. 259–262° dec.

The acetate of XVIII (XIX) was prepared by refluxing XVIII in acetic anhydride, m.p. 148–150°; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 5.77 μ (C=O), 0.920.

Anal. Calcd. for $C_{14}H_{12}Cl_6O_2$: C, 39.5; H, 2.81; Cl, 50.1. Found: C, 39.4; H, 2.81; Cl, 49.0.

***p*-Nitrobenzoate of XVIII (XX)**, m.p. 196–197°. *Anal.* Calcd. for $C_{19}H_{13}Cl_6NO_4$: C, 43.0; H, 2.45; Cl, 40.0; sapon. equiv., 532. Found: C, 43.4; H, 2.62; Cl, 39.8; sapon. equiv., 523.

3,5-Dinitrobenzoate of XVIII (XXI), m.p. 242–243.5°. *Anal.* Calcd. for $C_{19}H_{12}Cl_6N_2O_6$: C, 39.5; H, 2.08; Cl, 36.9. Found: C, 39.4; H, 1.84; Cl, 36.8.

***p*-Phenylazobenzoate of XVIII (XXII)**, m.p. 220–221°. *Anal.* Calcd. for $C_{25}H_{18}Cl_6N_2O_2$: C, 50.8; H, 3.05; Cl, 36.0. Found: C, 51.0; H, 3.04; Cl, 35.2.

1,8,10,11,11-Pentachloro-5,9-epoxypentacyclo[6.2.1.1^{3,6}, 0^{2,7}.0^{4,10} dodecane (XXIII).—Seven and one-half grams (0.02 mole) of the alcohol XVIII was dried in a suction flask at 200° for 1 hour under 7 mm. pressure. The flask was allowed to cool under vacuum. Ten grams of finely powdered activated alumina was then added and mixed with the alcohol. The flask was stoppered and heated under 7 mm. pressure for 1 hour at 185°. The reaction mixture was then boiled in benzene and filtered. Removal of the solvent from the filtrate afforded a solid residue. Fractional recrystallization from benzene–hexane and then methanol yielded 2.0 g. (26%) of XXIII, m.p. 185–187°; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 9.10 μ (C—O—C), 0.905.

Anal. Calcd. for $C_{12}H_9Cl_5O$: C, 41.6; H, 2.60; Cl, 51.2. Found: C, 41.5; H, 2.62; Cl, 51.5.

1,8,9,10,11,11-Hexachlorohexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}-0^{5,9}[dodecan-5-ol (XXIV).—A mixture of 3 g. (0.08 mole) of lithium aluminum hydride in 800 ml. of anhydrous butyl ether was stirred while 100 g. (0.26 mole) of XVII was added. The mixture became warm and a gas evolved. After the reaction subsided, the mixture was refluxed for 2.5 hours and then cooled. Water and 170 ml. of 10% sulfuric acid were added and the resulting two-phase system was filtered. The ether phase was separated, combined with additional ether extracts of the aqueous phase, and dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the solvent was recrystallized from carbon tetrachloride (charcoal) to yield 84 g. of crude product presumed to be XXIV, decomposing about 320°, but subliming at about 245°; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 2.98 μ (O—H), 0.484; at 5.70 μ (C=O) 0.247. A pure specimen of XXIV, dec. 330°, was obtained after three recrystallizations from acetone–hexane; absorbance in a potassium bromide disk at 6.25 μ, 0.00; at 2.98 μ, 0.350; at 5.70 μ, 0.00.

Anal. Calcd. for $C_{12}H_8Cl_6O$: C, 37.8; H, 2.12; Cl, 55.9. Found: C, 38.3; H, 2.35; Cl, 55.4.

Acetate of XXIV (XXV).—Refluxing of crude XXIV in acetic anhydride for 2 hours gave XXV, m.p. 191–194°, in 59% yield; absorbance in a potassium bromide disk at 6.25 μ (C=CCl), 0.00; at 5.68 μ (C=O), 0.798.

Anal. Calcd. for $C_{14}H_{10}Cl_6O_2$: C, 39.7; H, 2.37. Found: C, 39.6; H, 2.40.

1,2,3,4-Tetrachloro-1,4,4a,5,8,8a-hexahydro-1,4-*endo*, *endo*-5,8-dimethanonaphthalene (XXVI).—In a typical experiment a mixture of 36.5 g. (0.1 mole) of isodrin, 35.6 g. (0.45 mole) of zinc dust and 175 ml. of acetic acid was refluxed with stirring for 5 hours. The zinc and zinc salts were filtered and washed with acetone. The combined filtrates were freed of solvent and the residue was recrystallized from a mixture of acetone and methanol (charcoal) to yield 14.6 g. (50%) of XXVI, m.p. 73–75°; absorbance of 9.83 per cent. w./v. solution in carbon tetrachloride at 6.25 μ (C=CCl), 0.325.

Anal. Calcd. for $C_{12}H_{10}Cl_4$: C, 48.7; H, 3.38; Cl, 48.0. Found: C, 48.5; H, 3.46; Cl, 47.7.

1,4,4a,5,8,8a-Hexahydro-1,4-*endo*,*endo*-5,8-dimethanonaphthalene (XXVII).—To a stirred and refluxing solution of 74 g. (0.25 mole) of XXVI in 1000 ml. of *n*-amyl alcohol (dried over anhydrous sodium sulfate) there was added in portions 115 g. (4.6 moles) of sodium over the course of 68 hours. Methanol was then added to the reaction mixture which was still warm and fluid. The resulting solution was transferred to a separatory funnel containing water and the mixture was extracted several times with benzene. The combined extracts were washed with water and then dried over anhydrous calcium sulfate. Analysis of the combined aqueous solutions for chloride ion indicated that 3.0 atoms of chlorine had been replaced per molecule of XXVI. The solvent was distilled at reduced pressure and the oily residue was distilled to yield 15.6 g. (40%) of crude XXVII contaminated with an alcohol, b.p. 40–42° (0.2 mm.); absorbance of 9.87% w./v. solution in carbon tetrachloride at 2.75 μ (O—H), 0.33; at 3.25 μ (=C—H), 0.285; absorbance of 14.33% w./v. in carbon disulfide at 14.05 μ (*cis*-H—C=C—H), 1.380.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.1; H, 8.86. Found: C, 87.7; H, 10.0.

A purer sample of XXVII was prepared by a variation of the above conditions. To a stirred solution of 23 g. (0.08 mole) of XXVI in a mixture of 50 ml. of dry *n*-amyl alcohol and 450 ml. of xylene at reflux, there was added over the course of 5.5 hours 21.3 g. (0.9 mole) of sodium. The reaction was carried out under a nitrogen atmosphere. Work-up of the reaction mixture as above yielded 3.8 g. (31%) of XXVII, b.p. 43–44° (0.1 mm.), n^{25}D 1.5157.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.1; H, 8.86. Found: C, 90.1; H, 8.94.

The mono-(dihydrophenyltriazole) of XXVII (XXVIII) was prepared by treating 1.6 g. (0.01 mole) of the hydrocarbon XXVII with 2.4 g. (0.02 mole) of phenyl azide with cooling at 30° for 0.5 hour. Trituration with pentane yielded 1.3 g. (47%) of product, m.p. 165° dec., which was recrystallized from a mixture of benzene and heptane to yield 1.0 g. (36%) of XXVIII, m.p. 164–165° with gas evolution.

Anal. Calcd. for $C_{18}H_{19}N_3$: N, 15.1. Found: N, 15.8.

The bis-(dihydrophenyltriazole) of XXVII (XXIX) was prepared by refluxing 0.7 g. (2.5 mmoles) of the mono-(dihydrophenyltriazole) XXVIII with 1.0 g. (8.4 mmoles) of phenyl azide in 15 ml. of heptane for 3 hours. The solid which separated on cooling was filtered, washed with pentane, and recrystallized from a mixture of benzene and heptane to give XXIX, m.p. 215–216° with gas evolution.

Anal. Calcd. for $C_{24}H_{24}N_6$: N, 21.2. Found: N, 20.6.

Compound XXIX was obtained directly from a reaction mixture of 3.2 g. of the hydrocarbon XXVII and 3.0 g. of phenyl azide. The addition of pentane yielded 0.25 g. (3%) of XXIX, m.p. 215–217° dec. Recrystallization from benzene raised the melting point to 220.5–221.5° dec.; m.m.p. with the specimen obtained above, 215–217° dec.

Anal. Calcd. for $C_{24}H_{24}N_6$: N, 21.2. Found: N, 21.8.

***exo*-5-*exo*-9-Diiodopentacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}]dodecane (XXX).**—Iodine (2.0 g., 0.008 mole) was added in portions to

2.0 g. (0.013 mole) of XXVII dissolved in 10 ml. of carbon tetrachloride and the mixture was refluxed for 0.5 hour. A small amount of unreacted iodine was removed by filtration and the filtrate was concentrated. The addition of hexane to the residual brown oil yielded about 1 g. (20%) of XXX as crystals having a greenish cast, which on recrystallization from a mixture of benzene and cyclohexane (charcoal) gave XXX as white crystals, m.p. 134.5–136°. This product absorbed only 0.06 molar equivalent of hydrogen when hydrogenated over palladium-on-charcoal.

Anal. Calcd. for $C_{12}H_{14}I_2$: C, 35.0; H, 3.40; I, 61.7. Found: C, 35.6; H, 2.60; I, 61.0.

This experiment was repeated four times starting with 3.5–5.0 g. of XXVII and in each case the solid diiodide XXX was obtained, though in only 12–20% yield.

Iodination of XXVII.—When iodination of XXVII was carried out on a larger scale a crystalline product could not be isolated. Thus, 33 g. (0.13 mole) of iodine was added in portions to a stirred solution of 20 g. (0.13 mole) of XXVII in 100 ml. of carbon tetrachloride over the course of 2 hours. The temperature was maintained at 40° by control of the rate of addition. The mixture was stirred at 50° for 45 minutes and then at room temperature overnight. A large amount of unreacted iodine was separated by filtration. The filtrate was washed with dilute sodium thiosulfate solution to remove dissolved iodine and then water, and dried over anhydrous calcium sulfate. Evaporation of the carbon tetrachloride left an oil which could not be made to crystallize in hexane. Removal of the solvent under vacuum left 34 g. of a dark viscous oil, presumably crude diiodide XXXII.

Zinc Deiodination of XXXII.—A suspension of the above crude diiodide XXXII, 34 g., in 250 ml. of methanol was refluxed for 64 hours with stirring in the presence of 34 g. of powdered zinc. The cooled reaction mixture was filtered and the inorganic zinc salts and unreacted zinc were washed with benzene. The combined filtrate and washings were acidified with 25% sulfuric acid and extracted with benzene. The combined extracts were washed with water, dried over anhydrous calcium sulfate, and evaporated to leave 14 g. of an oil which could not be made to crystallize in the cold from either pentane or a mixture of acetone and methanol. The oil was distilled to yield 5.5 g. (42% based on pure diiodide) of saturated hydrocarbon (A), b.p. 60–66° (2.3 mm.), $n^{31}D$ 1.5202 (see below for infrared data). This product did not react with phenyl azide and absorbed 0.02 molar equivalent of hydrogen when hydrogenated over palladium-on-charcoal.

Anal. Calcd. for $C_{12}H_{16}$: C, 90.0; H, 10.0. Found: C, 89.9; H, 9.65; I, trace.

Hexacyclo[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]dodecane (XXXI).—A mixture of 3.5 g. (8.5 mmoles) of the solid diiodide XXX, m.p. 135°, 3.5 g. (0.054 mole) of powdered zinc and 50 ml. of methanol was refluxed for 89 hours with stirring. The cooled reaction mixture was filtered and the inorganic zinc salts and unreacted zinc were washed with benzene. The combined filtrate and washings were acidified with 25% sulfuric acid and extracted with benzene. The combined extracts were washed with water, dried over anhydrous calcium sulfate, and concentrated to leave 1.4 g. (theory 1.3 g. of XXXI) of an oily solid. This material was recrystallized from methanol (charcoal) to yield XXXI, m.p. 154–156°. The product did not take up hydrogen when hydrogenated over palladium-on-charcoal.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.1; H, 8.86. Found: C, 91.6; H, 8.80.

The hydrocarbon XXXI was also prepared from XI, 1,8,9,10,11,11-hexachlorohexacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9})-dodecane. A solution of 6.0 g. (0.016 mole) of VI in 100 ml. of *n*-amyl alcohol was treated at reflux with 14 g. of sodium added in portions over a period of 2 days. Methanol and then water were added to the cooled reaction mixture and the organic product was extracted with benzene. The benzene solution was washed with water, dried over anhydrous calcium sulfate, and evaporated to leave 4 g. of a dark oil. This oil was dissolved in methanol, but charcoaling and cooling did not afford a solid. When the solvent was removed under vacuum a very small amount of crystals formed in the residual oil. These were filtered and recrystallized from methanol to yield the hydrocarbon XXXI, m.p. 153–155°; m.m.p. with that obtained from the diiodide XXX, m.p. 152–156°.

The hydrocarbon XXXI was compared with a specimen presumably having the same structure which was supplied by S. Winstein (m.p. 165.5–167.5°) and found to be identical. The latter melted in our apparatus at 164–165.5° and a mixture of it with XXXI (m.p. 154–156°) melted at 159–162°. The infrared spectra of these two samples were practically identical. Absorbances for their most prominent peaks are given in the following list together with those for the similarly constituted, unidentified hydrocarbon (A) obtained from the crude liquid diiodide above.

Wave length, μ	Absorbance				
	Hydrocarbon of S. Winstein in KBr disk	XXXI, m.p. 154–156°, in soln.		(A) in soln.	
3.25 (=C—H)	0.00	0.00	6.05% w./v. CCl_4	0.00	12.26% w.v. CCl_4
3.35 (C—H)	1.047 (3.42 μ)	1.595		1.620	
3.50	0.508	0.400		0.920	
7.65	.321	.154	6.90% w./v. CS_2	.410	8.12% w./v. CS_2
7.73	.643	.287		.058	
7.83	.413	.183		.067	
10.83	.250	.107		.023	
12.14	.300	.128		.020	
12.89	.232	.075		.00	
ca. 14 (*cis*-H—C=C—H)	.00	.00		.00	