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THE REARRANGEMENT OF 4,5,6,7-TETRACHLORO-3a,4,7,7a-TETRAHYDRO-4,7-METHANOIDEN-8-ONE[1]

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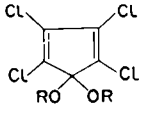
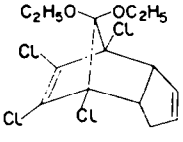
Abstract—4,5,6,7-Tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-8-one (IV) has been prepared by the hydrolysis of the adduct of cyclopentadiene and 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene. It has been shown to undergo quantitative thermal isomerization to 2,3, 3a, 7a-tetrachloro-3a, 4,7,7a-tetrahydro-4,7-methanoinden-1-one (XV), whose structure has been established by its degradation to 2,3-dichloro-bicyclo[2.2.1] heptane-2,3-dicarboxylic acid anhydride (XXI). Aluminum chloride has been found to exercise a remarkably strong accelerating effect on the isomerization reaction. The pathway of the isomerization reaction is interpreted in terms of views recently advanced by Woodward and Katz. Stereochemical assignments are suggested and are corroborated, in part, by the observation that XV undergoes photoisomerization to give a cage compound (XXXI).

THE Diels–Alder reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (I) and its diethoxy analogue (II) with dienophiles is well-known[3] and provides a convenient route for the preparation of bicyclo[2.2.1]hepten-7-one derivatives.[3b] The work here described is concerned with the preparation and isomerization of the ketone of this type derived from the adduct of II[4] and cyclopentadiene.

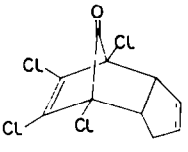


I, R = CH_3

II, R = C_2H_5



III



IV

The major product obtained in the reaction of cyclopentadiene with II was a 1:1 adduct[5] which is assigned structure III on the basis of its mode of formation, infrared spectrum, and conversion to the corresponding ketone, 4,5,6,7-tetrachloro-3a,4,7,7a-tetrahydro-4,7-methanoinden-8-one (IV), on treatment with concentrated sulfuric acid. The assignment of structure IV to the hydrolysis product is based on its infrared

[1] Part of this work has been treated in a preliminary report: P. Yates and P. Eaton, *Tetrahedron Letters* No. 11, 5 (1960).

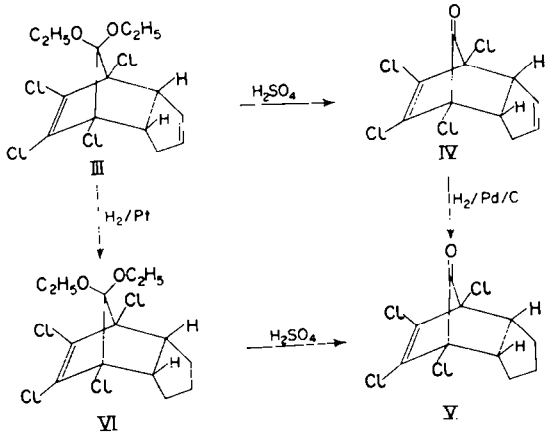
[2] Present address: Department of Chemistry, University of Toronto.

[3a] J. S. Newcomer and E. T. McBee, *J. Amer. Chem. Soc.* **71**, 946 (1949); J. W. Dawson and W. J. Croxall, U.S. Pat. 2,562,893 (1951); cf. *Chem. Abstr.* **46**, 1587 (1952); [b] E. T. McBee, W. R. Diveley and J. E. Burch, *J. Amer. Chem. Soc.* **77**, 385 (1955); H. E. Ungnade and E. T. McBee, *Chem. Rev.* **58**, 249 (1958); [c] C. A. Peri, *Gazz. Chim. Ital.* **85**, 1118 (1955).

[4] J. A. Krynitsky and R. W. Bost, *J. Amer. Chem. Soc.* **69**, 1918 (1947).

[5] This product has been obtained previously by Peri[3c] and by E. P. Ordas, U.S. Pat. 2,697,103 (1954), cf. *Chem. Abstr.* **49**, 15956 (1955).

spectrum, which shows bands at 3·34, 5·48 and 6·33 μ, attributable to vinylic hydrogen, carbonyl, and ethylenic stretching vibrations, respectively. The unusually low wave length of the carbonyl band is characteristic of the bridge carbonyl group of polychlorobicyclo[2.2.1]heptan-7-one systems,[6,7] while the unusually high wave length of the ethylenic double bond stretching band is characteristic of *cis*-1,2-dichloroethylenic systems.[6,8] On hydrogenation over palladium-charcoal in methanol IV was converted to the dihydro compound V, whose infrared spectrum also shows bands at 5·48 and 6·33 μ, but lacks the vinylic hydrogen band of IV at 3·34 μ.



Attempts to hydrolyse the ketal III under milder conditions were unsuccessful; thus, it was recovered unchanged after treatment with 80 per cent sulfuric acid at room temperature.[9] Because of the severity of the conditions under which IV was formed it was considered possible that the reaction might have proceeded with rearrangement, and that the ketone might not be so simply related to its precursor as represented by the expressions III and IV. This relationship was confirmed, however, by the preparation of the dihydro compound VI from III by hydrogenation over platinum in methanol, and the hydrolysis of this product to a ketone identical in all respects to V, the product obtained by hydrogenation of IV. The *endo*-configuration is assigned to the adduct III by analogy;[10] the *endo* configurations for its transformation products IV–VI then follow.

When the adduct III was heated with 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene (II) in boiling xylene a second Diels–Alder reaction occurred giving a bis-adduct.

[6] E. T. McBee, D. K. Smith and H. E. Ungnade, *J. Amer. Chem. Soc.* **77**, 559 (1955).

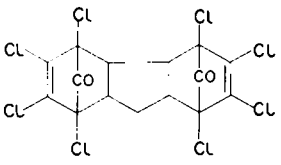
[7] This shift must be due to both the angle deformation (J. O. Halford, *J. Chem. Phys.* **24**, 830 (1956)) at this carbonyl group (cf. Ref. 9) and the presence of the electronegative chlorine atoms; thus, in the absence of the latter, the bridge carbonyl band occurs at ca. 5·6 μ; cf. for example, P. Wilder, Jr. and A. Winston, *J. Amer. Chem. Soc.* **78**, 868 (1956); C. H. DePuy and B. W. Ponder, *Ibid.* **81**, 4629 (1959).

[8] Cf. the ethylenic stretching band of *cis*-1,2-dichloroethylene itself, which falls at 6·29 μ: T.-Y. Wu, *Phys. Rev.* **46**, 465 (1934).

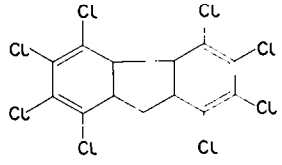
[9] The need for more stringent conditions must reflect the difficulty of converting the single carbon bridge atom from its sp^3 hybridization state in III to the sp^2 hybridization state in the grouping $\rangle C{=}\overset{\oplus}{O}C_2H_5 \leftrightarrow \rangle \overset{\oplus}{C}{-}OC_2H_5$, engendered by the abnormally small C—C—C bond angle at this carbon atom (cf. W. G. Woods, R. A. Carboni and J. D. Roberts, *J. Amer. Chem. Soc.* **78**, 5653 (1956)).

[10] M. C. Kloetzel, *Organic Reactions* Vol. IV, p. 11. John Wiley, New York (1948); K. Alder and M. Schumacher, *Fortschr. Chem. Naturstoffe* **10**, 17 (1953).

This was converted by concentrated sulfuric acid to a diketone, formulated as VII on the following grounds. Its infrared spectrum, with bands at 5·49 and 6·35 μ, is in

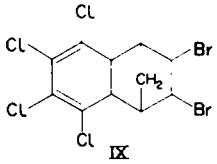


VII

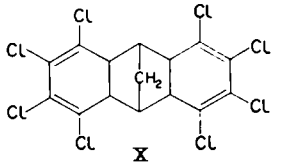


VIII

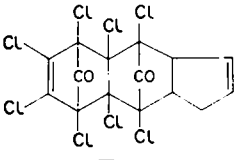
accord with the postulated structure, but excludes the possibility that the second Diels–Alder reaction is preceded by rearrangement of III (*vide infra*). When pyrolyzed at 210° it lost carbon monoxide and gave a product, $C_{13}H_6Cl_8$, which can be formulated as VIII on the basis of the relationship of its ultraviolet spectrum (see Experimental) to that of IX and of X;[11] this result permits the rejection of the alternative formulation XI for the diketone. The assignment of structure VII to the diketone leads to the assignment of structure XII to the bis-adduct itself.[12]



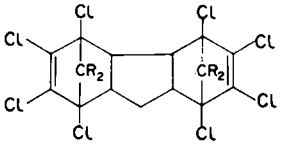
IX



X



XI



XII (R = OC_2H_5)

In contrast to the usual behaviour of bicyclo[2,2,1]hepten-7-one derivatives,[3b,11,13] the ketone IV did not lose carbon monoxide on being heated at 135° for one hour but was converted in quantitative yield to an isomer. The infrared spectrum of the rearrangement product, with bands at 3·23, 5·73 and 6·30 μ, shows that, while the *cis*-1,2-dichloroethylenic system is probably retained, the carbonyl group is no longer at the single carbon bridge of a bicyclo[2,2,1]heptene system. Its ultraviolet spectrum, λ_{max}^{EtOH} 255 mμ (ε 9100), indicates the presence of a conjugated ketonic carbonyl group. On the basis of these spectral data structure XV is assigned to the isomer; they may be compared with those of XIII,[6] $\lambda_{max}^{CCl_4}$ 5·75 and 6·39 μ, λ_{max}^{EtOH} 258 mμ (ε 9000), and of XIV,[14] $\lambda_{max}^{CCl_4}$ 5·70, 6·17 and 6·34 μ, λ_{max}^{EtOH} 258 mμ (ε 6700).

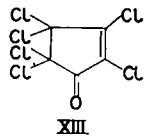
Confirmation of this structural assignment was obtained in the following way. Hydrogenation of XV over platinum in methanol gave a dihydro compound, XVI, with infrared bands at 5·74 and 6·30 μ, but lacking the vinylic hydrogen band of XV at 3·23 μ. This product was highly resistant to oxidation, failing to react with ozone,

[11] K. MacKenzie, *J. Chem. Soc.* 473 (1960).

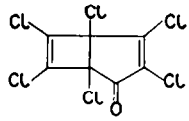
[12] Bis-adducts of I and II with butadiene, furan and thiophene have been obtained previously by Peri[3c], who formulated them as analogues of XII without supporting evidence. Very recently the addition of I to cyclopentene has been described.[11]

[13] C. F. H. Allen, *Chem. Rev.* 37, 209 (1945).

[14] A. Roedig and L. Hörnig, *Liebigs Ann.* **598**, 208 (1956).

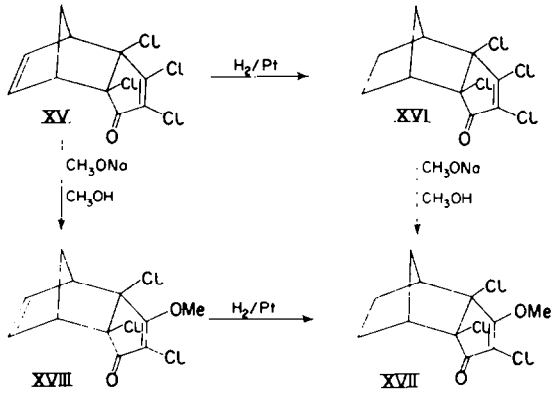


XIII



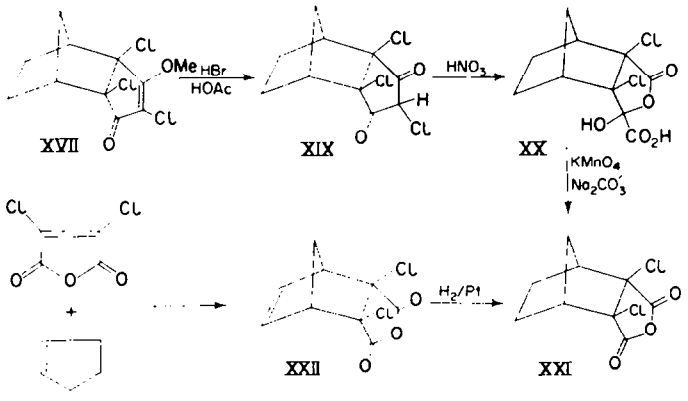
XIV

potassium permanganate or alkaline hydrogen peroxide. On treatment with sodium methoxide in methanol it gave in high yield a product in which one of the chlorine atoms of XVI had been replaced by a methoxyl group. This product is formulated as XVII on the basis of the spectral data: infrared bands at 5·78, 6·24 and 7·73 μ,[15a] ultraviolet maximum at 264 mμ (ε 13,000).[15b] It could also be formed from XV by



XV XVI XVIII XVII

reaction first with sodium methoxide in methanol to give XVIII, followed by hydrogenation. Cleavage of the enol ether XVII was effected with hydrogen bromide in acetic acid giving the β-diketone XIX, with bands in its infrared spectrum at 3·80, 4·05, 5·91 and 6·34 (very broad) μ.[16] Oxidation of this product with fuming nitric acid



XVII XIX XX XXII XXI

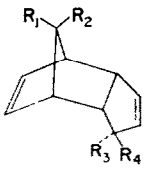
[15a] Cf. the infrared spectrum of 2,3-dimethoxy-2-cyclopentenone which has bands at 5·86, 6·11 and 7·46 μ [P. Yates and C. D. Anderson, unpublished].

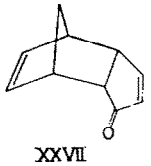
[b] Thus, enol methyl ethers from 2,4- and 4,4-dimethyl-1,3-cyclopentanedione have λ_{max}^{MeOH} 242·5 mμ (ϵ 12,700) and 237 mμ (ϵ 14,500), respectively, [B. Eistert and W. Reiss, *Chem. Ber.* **87**, 108 (1954)], and it has been observed in related β-diketonic systems that substitution by halogen atoms on any of the carbon atoms adjacent to the carbonyl groups brings about appreciable, and cumulative, bathochromic shifts, provided that enolization is still possible [E. R. Blout, V. W. Eager and D. C. Silverman, *J. Amer. Chem. Soc.* **68**, 566 (1946)].

[16] Cf. the infrared spectrum of 1,3-cyclopentanedione which has bands at ca. 6·0 and 6·35 (broad) μ [J. H. Boothe, R. G. Wilkinson, S. Kushner and J. H. Williams, *J. Amer. Chem. Soc.* **75**, 1732 (1953)].

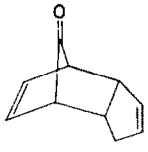
at 90° for five minutes gave an acidic product, $C_{10}H_{10}Cl_2O_5$, with bands in its infrared spectrum at 2·92, 3·4 (very broad), 5·62 and 5·75 μ; this is formulated as the lactol XX. Further oxidation with aqueous basic potassium permanganate gave XXI which was shown to be identical with the product obtained by hydrogenation of XXII, the Diels–Alder adduct from cyclopentadiene and dichloromaleic anhydride.[17] Although the stereochemistry of XVIII has not been established independently, it may be assigned the *endo* configuration with a high degree of certainty;[10] this leads to the *endo* assignment for the other members of this series, including XV. Corroboration of this configurational assignment for XV was obtained by photochemical cyclization (*vide infra*).

The facile thermal isomerization of IV to XV is reminiscent of the rearrangement of the alcohols XXIII and XXIV recently discovered by Woodward and Katz.[18] On being heated at 140° these were converted to their isomers, XXV and XXVI, respectively; in the case of the former an equilibrium mixture of XXIII and XXV was obtained, while in the latter case, although an equilibrium was undoubtedly involved, conversion of XXIV to XXVI was essentially complete. Although these investigators





XXVII



XXVIII

XXIII, $R_1 = R_2 = R_3 = H$, $R_4 = OH$

XXIV, $R_1 = R_2 = R_4 = H$, $R_3 = OH$

XXV, $R_1 = OH$, $R_2 = R_3 = R_4 = H$

XXVI, $R_2 = OH$, $R_1 = R_3 = R_4 = H$

did not observe directly the isomerization of the corresponding ketones in this series, their observation that the alcohol XXV when subjected to Oppenauer oxidation with aluminum t-butoxide and quinone in boiling benzene gave the rearranged ketone XXVII was interpreted in terms of initial oxidation to the ketone XXVIII followed by facile and complete rearrangement to XXVII.[19,20] On the basis of their elegant demonstration of the retention of complete stereochemical integrity in the rearrangement of XXIII and XXIV, Woodward and Katz[18] concluded that the isomerizations proceed not by complete dissociation and recombination but, rather, by the cleavage of *one* of the bonds of the dicyclopentadiene system and the formation of a new bond via a stage XXIX. Although we lack in the case of the isomerization of IV the rigorous stereochemical arguments developed in the cases of the isomerization of XXIII and XXIV, we consider that the facility of the reaction, the absence of other

[17] A. M. Clifford and C. E. Gleim, U.S. Pat. 2,391,226 (1945); cf. *Chem. Abstr.* **40**, 3136 (1946).

[18] R. B. Woodward and T. J. Katz, *Tetrahedron* **5**, 70 (1959); as pointed out by these authors, this type of reaction is a special case of the Cope rearrangement, cf. E. G. Foster, A. C. Cope and F. Daniels, *J. Amer. Chem. Soc.* **69**, 1893 (1947).

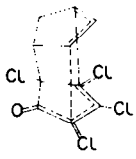
[19] T. J. Katz, Ph. D. Thesis, Harvard (1959).

[20] This interpretation was based on the fact that the alcohol XXV failed to rearrange when heated in boiling benzene alone. However, the possibility that the rearrangement of XXV is catalysed by aluminum t-butoxide (*vide infra*) and precedes oxidation cannot be excluded. *Note added in proof:* R. C. Cookson, J. Hirdec and R. O. Williams, *Tetrahedron Letters* No. 22, 29 (1960), have very recently reported that oxidation of XXV in basic medium affords XXVIII.

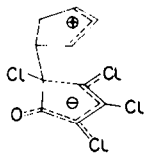
products, and the inherent similarity to the earlier cases make it highly probable that the reaction proceeds by an analogous route, via XXX. The presence of the carbonyl group will undoubtedly lead to an unusually large polarization of the electronic displacements in the sense of XXXa. The observations that IV was completely converted to XV and that no detectable isomerization occurred in the reverse direction are in accord with expectation since the equilibrium IV $\rightleftharpoons$ XV should lie heavily in favor of XV, in which the carbonyl group is directly conjugated and lacks much of the disabling angle deformation peculiar to the bridge carbonyl group of IV.[7,9,21]

It was of considerable interest to find that the conversion of IV to XV took place

XXIX



XXX



XXX a

very rapidly at *room temperature* when a solution of IV in carbon tetrachloride was *treated with aluminium chloride*, in fact, when a large excess of this reagent was used, rearrangement was complete *within three minutes*. Acceleration of the rearrangement by aluminum chloride could also be effected in homogeneous medium by the use of a solution of aluminum chloride in dichloromethane.[22] Similar, but less striking, acceleration was brought about by ferric chloride and by sulfuric acid.[23] The action of these acidic reagents must be related to their ability to coordinate with the carbonyl oxygen atom of IV and thus to facilitate the bond-breaking process symbolized in XXX and XXXa. It may be noted that catalysis of the Diels–Alder reaction by acids has been observed in several instances.[24] This common feature of the Diels–Alder reaction and of the rearrangement here discussed is of interest in the light of the postulated relationship between these two types of reaction.[18] We have been led thereby to the exploration of the efficacy of aluminum chloride in the acceleration of the Diels–Alder reaction; preliminary results indicate that in some cases this reagent serves this purpose in excellent fashion.[25]

We turn finally to some photochemical experiments which shed further light on the stereochemistry of XV. When this compound in solution in carbon tetrachloride was irradiated overnight with a water-cooled Hanovia 450 watt mercury arc source, it was converted in part to a *new isomer*, whose infrared spectrum shows a band at 5·52 μ but lacks the bands of XV at 3·23, 5·73 and 6·30 μ. Its ultraviolet spectrum, unlike that of XV, shows no high intensity absorption, but a weak plateau at ca. 295 mμ (ε 30) and weak end absorption (ε_{210} 630). These spectral data clearly indicate that the photoproduct contains neither vinylic hydrogen atoms nor a *cis*-1,2-dichloroethylenic

[21] A similar situation clearly holds in the case of the equilibrium XXVII $\rightleftharpoons$ XXVIII.[19]

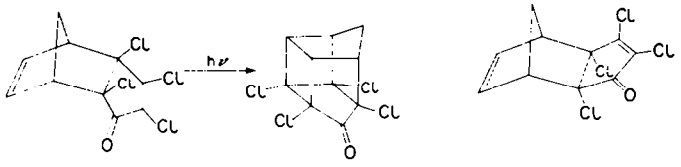
[22] This result eliminates the possibility that the acceleration of the isomerization depends on an interaction with the aluminum chloride surface.

[23] In the latter case a two-phase system, consisting of sulfuric acid and a solution of IV in carbon tetrachloride was used; this system differed from that used for the preparation of IV by the action of sulfuric acid on III, when no solvent was used. Some rearrangement of IV to XV occurred under these conditions also, however XV was not observed in the product isolated since it, unlike IV, is soluble in sulfuric acid.

[24] W. Rubin, H. Steiner and A. Wassermann, *J. Chem. Soc.* 3046 (1949), and earlier papers; A. Rodgman and G. F. Wright, *J. Org. Chem.* **18**, 465 (1953); L. E. Gast, E. W. Bell and H. M. Teeter, *J. Amer. Oil Chemists Soc.* **33**, 278 (1956).

[25] P. Yates and P. Eaton, *J. Amer. Chem. Soc.* **82**, 4436 (1960).

system and that its carbonyl group occupies a highly strained position and is no longer conjugated. This isomer is therefore assigned the structure XXXI.[26] Such a cage compound can arise only from the *endo* compound XV, and not from its *exo*-stereoisomer, XXXII. The possibility that XXXI was directly derived not from XV, but from IV, formed by initial isomerization of XV under the influence of the ultraviolet



XV XXXI XXXII

radiation (i.e. by reversal of the thermal isomerization process IV → XV) is excluded by the observation that IV was unaffected by such irradiation. Thus, the earlier assignment of the *endo* configuration to the thermal isomerization product, XV, is corroborated by the photochemical experiments.[27] Further, it may be noted that the Woodward–Katz mechanism requires that XV be formed from the *endo* isomer IV, rather than its *exo* analogue, and hence the earlier postulation of *endo* configurations for III and its congeners is consistent with the views subsequently developed.

EXPERIMENTAL[28]

1,2,3,4-*Tetrachloro*-5,5-*diethoxycyclopentadiene* (II)

A freshly prepared ethanolic solution of sodium ethoxide (from 93 g sodium in 1800 ml absolute ethanol) was added slowly with stirring to a solution of hexachlorocyclopentadiene (500 g) in absolute ethanol (1 l.). During the addition the solution temp was maintained at 30–35° by external cooling. After being stirred overnight, the solution was diluted with water (2 l.) and carbon tetrachloride (300 ml) was added to decrease the viscosity of the oil which separated. The organic layer was separated and washed with water, followed by 1% hydrochloric acid until the wash liquids were slightly acid. The organic residue was fractionated *in vacuo* to give 417 g (78%) of a greenish-yellow, sweet-smelling liquid, b.p. 124–127° 11 mm (lit[3a] b.p. 101–103° 5 mm).

4,5,6,7-*Tetrachloro*-8,8-*diethoxy*-3a,4,7,7a-*tetrahydro*-4,7-*methanoindene* (III)

Freshly distilled cyclopentadiene (103 g) was added to II (400 g) in purified hexane (340 ml). A few crystals of hydroquinone were added as a polymerization inhibitor. After the initial exothermic reaction subsided, the solution was boiled under reflux overnight. Distillation through an efficient fractionation column at a 5:1 reflux ratio gave 407 g of slightly yellow liquid, b.p. 100–109° 0·1 mm. This material crystallized from methanol as fine, white needles (398 g, 81%), m.p. 54–55° (lit[3c] m.p. 49–50°); λ_{max} 3·23, 3·32, 3·40, 6·22, 8·48 μ. (Found: C, 47·22; H, 4·28; Cl, 39·38. Calc. for $C_{14}H_{16}Cl_4O_2$: C, 46·95; H, 4·50; Cl, 39·61%).

4,5,6,7-*Tetrachloro*-3a,4,7,7a-*tetrahydro*-4,7-*methanoinden*-8-*one* (IV)

Three hundred grams III were added as a melt to conc sulfuric acid (200 ml) with vigorous agitation. After being stirred for 24 hr, the mixture was filtered through a sintered glass funnel. The brown granular residue was pulverized with chipped ice (100 g). The resulting tan powder was taken up in pet ether; this solution was washed with water, dried, and decolorized with activated charcoal. Five crops of crystals (total, 120 g, 48%) were obtained by repeated concentration of this solution.

[26] Cf. the related photoisomerization reactions observed by R. C. Cookson, E. Crundwell and J. Hudec, *Chem. & Ind.* 1003 (1958).

[27] This argument lacks complete rigor in that it is possible, albeit unlikely, that XXXI might have been derived indirectly from the *exo* isomer XXXII by its initial photoisomerization to the *endo* isomer XV via complete dissociation and recombination.

[28] Melting points are uncorrected. Carbon tetrachloride was used as the solvent for infrared spectral determinations, unless otherwise noted. Petroleum ether refers to a fraction with b.p. 30–60°.

The fine, white needles had m.p. 123–123·5°; λ_{max} 3·34, 3·40, 3·48, 5·48, 6·33 μ; λ_{max}^{EtOH} 260 mμ (shoulder, ε 190). (Found: C, 42·32; H, 2·05; Cl, 49·86; M.W., 250. Calc. for $C_{10}H_6Cl_4O$: C, 42·29; H, 2·13; Cl, 49·94%; M.W. 284).

4,5,6,7-*Tetrachloro*-8,8-*diethoxy*-2,3,3a,4,7,7a-*hexahydro*-4,7-*methanoindene* (VI)

A solution of III (5 g, 0·014 mole) in 50 ml methanol was treated with hydrogen at 1 atm over platinum. Hydrogen uptake ceased after the absorption of one molar equivalent. The catalyst was filtered and the solution partially evaporated to give 4·2 g (83%) of the dihydro derivative (VI). Recrystallization from methanol gave colorless crystals, m.p. 76–76·5°; λ_{max} 3·34, 3·42, 6·22, 8·48 μ (Found: C, 46·89; H, 4·76. Calc. for $C_{14}H_{16}Cl_4O_2$: C, 46·69; H, 5·04%).

4,5,6,7-*Tetrachloro*-2,3,3a,4,7,7a-*hexahydro*-4,7-*methanoinden*-8-*one* (V)

(i) *From hydrolysis of* VI. Two grams VI were shaken with conc sulfuric acid (20 ml) for 15 min. The mixture was then poured onto cracked ice. The resultant solid was filtered and twice crystallized from pet ether, giving V as white crystals (0·9 g, 56·5%), m.p. 68·5–69·5°; λ_{max} 3·40, 3·48, 5·48, 6·33 μ. (Found: C, 41·97; H, 3·10. Calc. for $C_{10}H_8Cl_4O$: C, 41·99; H, 2·82%).

(ii) *From hydrogenation of* IV. A solution of IV (2 g, 0·0073 mole) in methanol (30 ml) was treated with hydrogen at atm press over palladium/charcoal. Hydrogen uptake ceased after the absorption of one molar equivalent. The catalyst was filtered and the solution diluted with water (150 ml). The oil which separated was taken up in pet ether. The solution was dried, decolorized, and concentrated to give 1·8 g (89·5%) of a crystalline product identical to the ketone obtained by hydrolysis of VI. A mixture m.p. of the two products showed no depression; their infra-red spectra were identical.

1,2,3,4,5,6,7,8-*Octachloro*-1,4,4a,4b,5,8,8a,9a-*octahydro*-1, 4:5,8-*dimethano-fluoren*-10,11-*dione* (VII)

A solution of III (3·58 g, 0·01 mole) and 1,2,3,4-tetrachloro-5,5-diethoxycyclopentadiene (5 g, 0·017 mole) in xylene (40 ml) containing a few crystals of hydroquinone was boiled under reflux overnight. When the solution was cooled, 6·3 g (97%) of adduct crystallized. Four grams of this product were stirred vigorously with conc sulfuric acid (30 ml) for 6 hr. Dilution of the solution with ice-water precipitated the diketone VII. Repeated crystallization of the crude product from large volumes of carbon tetrachloride gave 2·6 g (84%) of glistening white plates, m.p. 200° (with evolution of carbon monoxide); λ_{max}^{KBr} 5·49, 6·35 μ.

(Found: C, 35·85; H, 1·45; Cl, 57·08. Calc. for $C_{15}Cl_8H_6O_2$: C, 35·90; H, 1·21; Cl, 56·52%).

1,2,3,4,5,6,7,8-*Octachloro*-4a,4b,8a,9a-*tetrahydrofluorene* (VIII)

One gram of the diketone VII was heated in a test tube maintained at 210° by a bath of refluxing nitrobenzene until carbon monoxide evolution ceased (ca. 10 min). The residue crystallized from hot carbon tetrachloride as white needles, m.p. 207–208°; λ_{max} 6·48 μ; $\lambda_{max}^{Et_2O}$ 263 mμ (shoulder, ε 9200), 273 mμ (ε 11,200), 284 mμ (ε 12,800), 295 mμ (ε 11,800), 308 mμ (ε 7400).

(Found: C, 35·34; H, 1·49; Cl, 63·33. Calc. for $C_{13}Cl_8H_6$: C, 35·02; H, 1·36; Cl, 63·62%).

Thermal isomerization of IV: *Formation of* 2,3,3a,7a-*tetrachloro*-3a,4,7,7a-*tetrahydro*-4,7-*methanoinden*-1-*one* (XV)

Two hundred grams IV were heated at 135° for 1 hr. On solidification of the melt a quantitative yield of the rearranged ketone (XV) was obtained. Crystallization from ligroin (b.p. 66–75°) gave large, colorless crystals, m.p. 82–83°; λ_{max} 3·23, 3·31, 3·44, 5·73, 6·30 μ; λ_{max}^{EtOH} 255 mμ (ε 9100).

(Found: C, 42·53; H, 2·14; Cl, 49·86; M.W., 288. Calc. for $C_{10}H_6Cl_4O$: C, 42·29; H, 2·13; Cl, 49·94%; M.W., 284).

An infrared spectrum of a concentrated solution of the material prior to crystallization showed no band at 5·48 μ, indicating the absence of unreacted IV and the Diels–Alder dimer of tetrachlorocyclopentadienone. The completeness and unidirection of the thermal rearrangement process was further demonstrated by the heating of a small sample of pure IV in a m. p. capillary tube at 135° for 5 min; after cooling and subsequent solidification, the sample had m.p. 82–83°, identical to the m.p. of pure XV.

2,3,3a,7a-*Tetrachloro*-3a,4,5,6,7,7a-*hexahydro*-4,7-*methanoinden*-1-*one* (XVI)

A solution of XV (50 g, 0·176 mole) in warm methanol (300 ml) was treated with hydrogen at atm press over platinum. Hydrogen uptake was very rapid and stopped sharply after the absorption of one molar equivalent. The catalyst was filtered and water (600 ml) was added. The oil which separated was taken up in ether; the solution was dried, decolorized, and diluted with pet ether. Two crops of white crystals were obtained by concentration of this solution. Recrystallization from pet ether gave 44 g (87%) of the dihydro compound XVI, m.p. 65–65·5°; λ_{max} 3·35, 3·45, 5·74, 6·30 μ.

(Found: C, 42·11; H, 3·04. Calc. for $C_{10}H_8Cl_4O$: C, 41·99; H, 2·82%).

2,3a,7a-*Trichloro*-3-*methoxy*-3a,4,5,6,7,7a-*hexahydro*-4,7-*methanoinden*-1-*one* (XVII)

(i) *From* XVI. Freshly prepared methanolic sodium methoxide (from 4·05 g sodium in 50 ml methanol) was added rapidly with stirring to a solution of XVI (40 g) in methanol (300 ml). Sodium chloride was precipitated almost immediately. After 15 min, water (600 ml) was added. The resulting precipitate was crystallized from hot methanol to give a virtually quantitative yield (39·2 g) of white crystals, m.p. 102·5–103·5°; λ_{max} 3·35, 3·45, 5·78, 6·24, 7·73 μ; λ_{max}^{EtOH} 264 mμ (ε 13,000).

(Found: C, 47·12; H, 3·93. Calc. for $C_{11}H_{11}Cl_3O_2$: C, 46·92; H, 3·94%).

(ii) *From hydrogenation of* XVIII. A solution of XVIII (1 g, 0·00358 mole) in methanol (30 ml) was treated with hydrogen at 1 atm over platinum. Hydrogen uptake ceased after the absorption of one molar equivalent. The catalyst was filtered. On concentration the filtrate deposited 0·9 g (88·5%) of crystalline material identical to the product obtained by the action of sodium methoxide on XVI. A mixture m.p. of the two products showed no depression, their infrared spectra were identical.

2,3a,7a-*Trichloro*-3-*methoxy*-3a,4,7,7a-*tetrahydro*-4,7-*methanoinden*-1-*one* (XVIII)

This compound was prepared from XV (0·5 g) and sodium methoxide by the same procedure as that used for the preparation of XVII from XVI. Crystallization of the product from methanol gave a quantitative yield of white plates, m.p. 106–106·5°; λ_{max} 3·30, 3·38, 3·44, 5·82, 6·25, 7·73 μ.

(Found: C, 47·57; H, 3·20; Cl, 37·91. Calc. for $C_{11}H_9Cl_3O_2$: C, 47·26; H, 3·25; Cl, 38·05%).

2,3a,7a-*Trichloro*-3a,4,5,6,7,7a-*hexahydro*-4,7-*methanoinden*-1,3-*dione* (XIX)

A solution of XVII (25 g) in glacial acetic acid (100 ml) and a 30–35% solution of hydrogen bromide in acetic acid (25 g) were heated together on the steam-bath for 4 hr. The container was sealed except for a fine capillary for pressure release. As the reaction proceeded large, tan crystals separated. These were recrystallized from methanol to give 20·4 g (86%) of colorless crystals, m.p. 233° dec; λ_{max}^{KBr} 3·35, 3·80, 4·05, 5·91, 6·34 (v. broad) μ.

(Found: C, 44·83; H, 3·27; Cl, 39·80. Calc. for $C_{10}H_9Cl_3O_2$: C, 44·89; H, 3·39; Cl, 39·76%).

Oxidation of XIX *with nitric acid: Formation of* XX

Ten grams of XIX in a 50 ml round-bottomed flask equipped with a condenser were covered with fuming nitric acid (85%, 30 ml). A vigorous reaction ensued and brown fumes were evolved immediately. Complete reaction was effected by heating the flask on the steam-bath until no further evolution of brown fumes was evident. The solution on cooling in an ice-salt bath deposited fine, white needles. These were freed of nitric acid and dried by prolonged treatment with boiling benzene under a Dean–Stark trap. Dilution of the benzene solution with ligroin (b.p. 100–105°) and concentration gave 5·2 g (50%) of large, colorless cubic crystals of XX, dec 200°; λ_{max}^{KBr} 2·92, 3·4 (v. broad), 5·62, 5·75 μ.

(Found: C, 42·69; H, 3·69; Cl, 24·68; N.E., 140. Calc. for $C_{10}H_{10}Cl_2O_5$: C, 42·73; H, 3·59; Cl, 25·23%; N.E., 140·5).

2,3-*Dichlorobicyclo*[2,2,1]*heptane*-2,3-*dicarboxylic acid anhydride* (XXI)

(i) *From alkaline permanganate oxidation of* XX. One gram XX was dissolved in distilled water (6 ml) by the addition of sufficient sodium carbonate to maintain the pH at 10. Aqueous potassium permanganate (0·9 g in 20 ml water) was added slowly over ½ hr with constant stirring. After 3 additional hr, the solution was bleached and the precipitated manganese dioxide dissolved by the addition of conc hydrochloric acid and sulfur dioxide. The solution was saturated with ammonium sulfate and extracted with ether. The extract was evaporated to dryness in a sublimation tube; the

tube was then evacuated and heated gently. The colorless sublimate thus obtained was recrystallized from ether to give 7·2 g (87%) of XXI, m.p. 202–203° (sealed cap); λ_{max} 5·28, 5·36, 5·53 μ.

(Found: C, 46·04; H, 3·67; Cl, 29·89. Calc. for $C_9H_8Cl_2O_3$: C, 45·98; H, 3·43; Cl, 30·17%).

(ii) *From hydrogenation of* XXII. A solution of XXII (1 g, 0·0043 mole) in anhydrous ether (50 ml) was treated with hydrogen at 1 atm over platinum. Hydrogen uptake ceased after the absorption of one molar equivalent. The catalyst was filtered and the solution concentrated; white crystals (0·6 g, 59·5%) were deposited. After one sublimation *in vacuo*, these gave a product identical to the product obtained by oxidation of XX. A mixture m.p. of the two products showed no depression; their infrared spectra were identical.

Dichloromaleic anhydride[29]

A solution of mucochloric acid (100 g), in fuming nitric acid (200 ml) was boiled under reflux overnight. On cooling, the solution deposited long, white needles which were filtered and heated over an intense free flame; after removal of nitric acid and water, the product distilled readily and crystallized immediately giving 85 g (86·5%) of flaky, white crystals, m.p. 119–120° (lit[29] m.p. 119–120°); λ_{max} 5·40, 5·50, 5·60, 6·23, 10·8 μ.

2,3-*Dichlorobicyclo*[2,2,1]*hept*-5-*ene*-2,3-*dicarboxylic acid anhydride* (XXII)

A heavy-walled glass pressure bottle was charged with dichloromaleic anhydride (10 g) and freshly distilled cyclopentadiene (5 g), sealed, and heated under autogenous pressure at 150° for 45 min. After cooling, the resulting solid mass was ground up and extracted with a large volume of ether. Decolorization, followed by partial evaporation of the ether extract, gave 8 g (57%) of white crystals, m.p. 189–190° (sealed cap) (lit.[17] m.p. 188–189°); λ_{max} 5·31, 5·38, 5·55, 6·17 μ.

(Found: C, 46·48; H, 2·82. Calc. for $C_9H_6Cl_2O_3$: C, 46·38; H, 2·60%).

Acceleration of the isomerization of IV *to* XV *by aluminum chloride*

Aluminum chloride (0·3 g) was added to a solution of IV (0·10 g) in carbon tetrachloride (5 ml), and the mixture was swirled for 3 min. The reaction was then quenched with ice-water (50 ml). The organic layer was dried over sodium sulfate and stripped of solvent *in vacuo*. The infrared spectrum of the residue showed that complete isomerization to XV had occurred. Similar results were obtained with dichloromethane as solvent, using both heterogeneous and homogeneous systems. Marked acceleration of the isomerization was also observed when solutions of IV in carbon tetrachloride were treated with ferric chloride or concentrated sulfuric acid in large excess, but infrared spectral analysis showed that these reagents were not as effective as aluminum chloride.

2,3,5,6-*Tetrachloropentacyclo*[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]*decan*-4-*one* (XXXI)

A solution of XV (3 g) in carbon tetrachloride (25 ml) contained in a small quartz flask was irradiated overnight with water-cooled Hanovia 450 watt mercury arc. The solution was concentrated *in vacuo* to 6 ml and chromatographed on Davison silica with carbon tetrachloride as eluent. One gram of VI was recovered from the early eluates. Spectral analysis of intermediate fractions showed the presence of XXXI and its hydrate, while later fractions contained photodecomposition products of the solvent. Removal of solvent from the intermediate fractions followed by sublimation of the residue at 60° under high vacuum gave 1·7 g of colorless material; crystallization from dichloromethane–ligroin (b.p. 66–75°) and two sublimations gave 0·48 g (24%, based on starting material consumed) of pure product, m.p. 113·5–114·5°, λ_{max} 5·52 μ, $\lambda_{max}^{Et_2O}$ 295 mμ (plateau, ϵ 30), ϵ_{210} 630.

(Found: C, 42·09; H, 1·82; Cl, 49·76. Calc. for $C_{10}H_6Cl_4O$: C, 42·29; H, 2·13; Cl, 49·94%).

Irradiation of IV under similar conditions returned only starting material.

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[29] Cf. G. L. Ciamician and P. Silber, *Ber. Dtsch. Chem. Ges.* **16**, 2396 (1883).