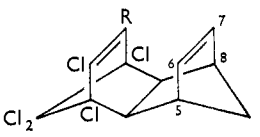
863. *Isodrin in the Diels–Alder Reaction*

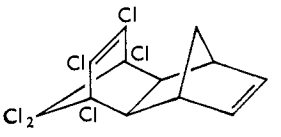
By K. Mackenzie

Polychloro-*endo*-*endo*-*exo*-1,4:5,8-dimethano-octahydroanthracenes readily isomerise to polychloro-*endo*-*endo*-6,7-benzo-1,4:5,8-dimethano-octahydronaphthalenes by a novel transannular hydrogen transfer.

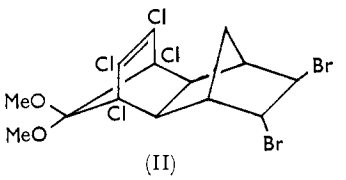
The facility with which norbornadiene and its derivatives undergo Diels–Alder reaction with arylated cyclopentadienones and tetrachlorocyclopentadienone ketals has been described in connexion with retro-Diels–Alder reactions.[1] The *exo*-norbornene derivative aldrin (Id) also reacts moderately easily with these dienes, and the products behave as expected, simply losing carbon monoxide on further treatment as appropriate, a reaction typical of the norborn-2-en-7-one moiety.[2] In fact tetrachlorocyclopentadienone ketals are unusually reactive and Diels–Alder addition occurs with relatively unreactive olefins such as cyclopentene and cyclohexene [1-3] although forcing conditions are required, and it is therefore perhaps a little surprising that the *endo*-*endo*-isomer of aldrin, isodrin (Ia), reacts only slowly with this diene, presumably on account of the steric requirements of the 6,7-hydrogens during the reaction, for they must approach the 2,3-double bond quite closely.[4] A further consequence of this becomes clear in the following.

(Ia : R = Cl)
(Ib : R = OEt)
(Ic : R = OMe)

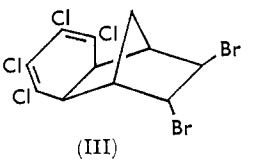




(Id)



(II)



(III)

Hydrolysis of adducts formed from tetrachlorodimethoxycyclopentadiene, *e.g.*, (II), followed by mild thermal decarbonylation gives compounds such as (III) * which exhibit

* The stereochemical assignments are made by the firmly established *exo*-addition mode for norbornenes in reaction with dienes,[5] and on the absence of properties characteristic of the *endo*-*endo*-fused ring series such as conjugate addition of electrophilic reagents.[6] Other modes of addition to simple norbornenes and norbornadienes are unlikely on steric grounds.

[1] K. Mackenzie, *J.*, 1960, 473.
[2] K. Mackenzie, unpublished results. Cf. C. H. F. Allen, *Chem. Rev.*, 1945, **37**, 209; 1962, **62**, 653; I. Bengiat and E. I. Becker, *J. Org. Chem.*, 1958, **23**, 885, and earlier Papers.
[3] P. Eaton and P. Yates, *Tetrahedron*, 1961, **12**, 13.
[4] Cf. J. K. Stille and D. R. Witherell, *J. Amer. Chem. Soc.*, 1964, **86**, 2188.
[5] B. S. Soloway, *J. Amer. Chem. Soc.*, 1952, **74**, 1027; K. Alder, J. Mönch, and H. Wirtz, *Annalen*, 1959, **627**, 47; J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, 1959, **81**, 4273; C. W. Bird, R. C. Cookson, and E. Crundwell, *J.*, 1961, 4809.
[6] B. S. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Amer. Chem. Soc.*, 1960, **82**, 5377. See also refs. 5 and 7.

five characteristic ultraviolet light absorption maxima in the 260—320 mμ range due to the tetrachlorocyclohexa-1,3-diene chromophore.[1,3]

However, hydrolysis of the adduct (IV) formed by heating isodrin with tetrachlorodimethoxycyclopentadiene in sealed tubes, followed by decarbonylation of the derived carbonyl-bridge compound (VII) at 110°, gives only traces of the expected product (X) as characterised by ultraviolet and infrared light absorption. The main product is a compound which exhibits only intense aromatic-type absorption in the ultraviolet range similar to that of tetrachlorodihydromethanonaphthalenes,[1] the absorption near 1600 cm.$^{-1}$ in the infrared range due to the ClC=CCl chromophore also being absent. Proton magnetic resonance data also indicate that no hydrogen is lost from the assumed primary product (X), and that the isolated product is an isomer, $C_{16}H_8Cl_{10}$. On the other hand, the same reaction sequence with the isodrin analogue (Ib) [7] certainly gives compound (XI) ($\nu_{max.}$ 1600, 1640vs cm.$^{-1}$ conj. ClC=CCl and ClC=COEt, $\lambda_{max.}$ 265, 276, 287, 299, 313, near 216 mμ, ε 2433, 3461, 5130, 5862, 3542, ~7900), the vinyl ether group in compounds (V) and (VIII) surviving the concentrated acid conditions used for hydrolysis on account of the combined steric effects of the adjacent dichloromethano-bridge and the transannular hydrogens, in accord with the expected stereochemical features of the molecules. The vinyl ether (XI) also appears to be inert to powerful electrophilic reagents, but its structure is confirmed by lithium reduction to the vinyl ether (XVI) ($\nu_{max.}$ 1620vs cm.$^{-1}$ C=COEt) which is readily hydrolysed by dilute acid to the unsaturated ketone (XIX) ($\nu_{max.}$ 1730vs, near 690ms and 3020ms cm.$^{-1}$ C=O in a strained ring, and *cis*-HC=CH) which absorbs hydrogen (1 mol.) over a catalyst.

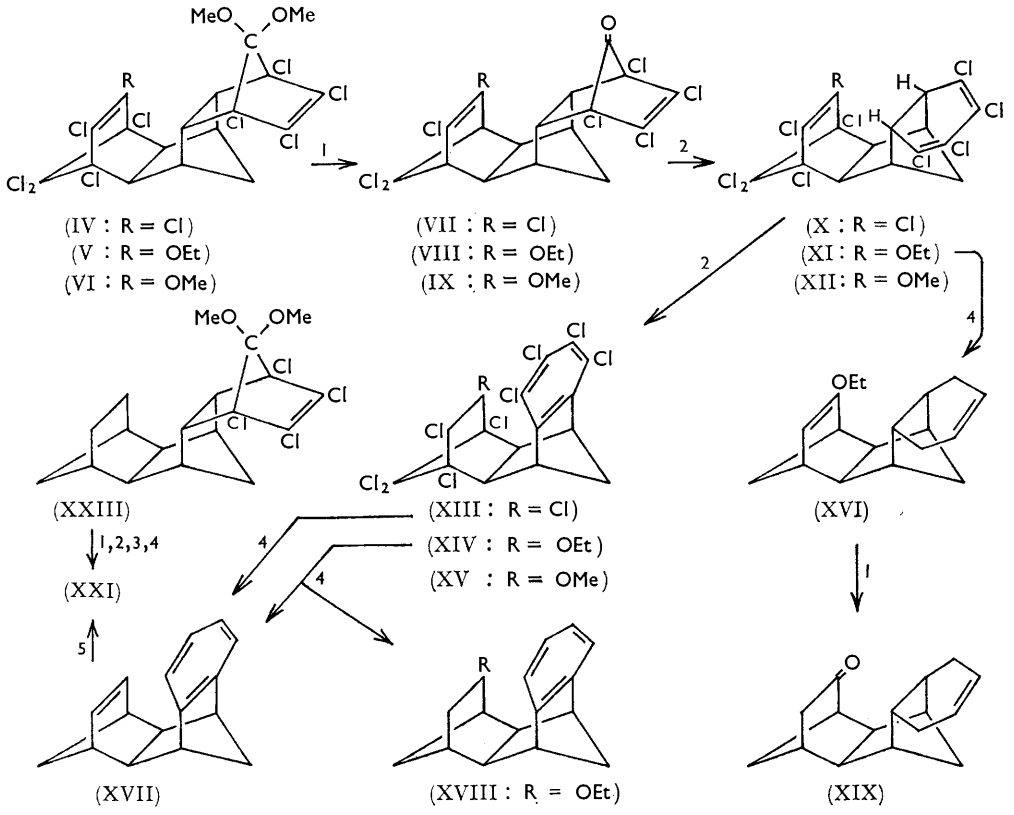
Pure crystalline compound (XI) undergoes a remarkable and complete exothermic transformation when heated, melting near 180° and resolidifying to an isomer which must have structure (XIV) on the basis of its infrared and ultraviolet spectra (1600 cm.$^{-1}$ band missing or v. weak; $\lambda_{max.}$ 215, sh 219·5, 242, 287, 297 mμ, ε 46,170, 43,010, 11,250, 160, 160, aromatic short-wave absorption bathochromically shifted). Proton magnetic resonance data are also consistent with structure (XIV), using isodrin as a model compound to facilitate structural assignments (p. 4650). In addition, dehalogenation of compound (XIV) with lithium gives a mixture of olefin (XVII) and the ethyl ether (XVIII), both clearly *o*-disubstituted benzenes from their spectral properties, the mixture arising from competition between protonation of the carbanion derived by metallation, and expulsion of ethoxide ion from the adjacent carbon.[8] The dihydro-derivative of compound (XVII) is identical with hydrocarbon (XXI) independently synthesised by an unambiguous route, precluding rearrangement of the carbon skeleton in compound (XI) during isomerisation (see Scheme). The isomerisation product of compound (X) is therefore compound (XIII) and this is similarly confirmed by its dehalogenation, principally to compound (XVII), loss of chloride ion being more important than protonation in this case.

The isomerisation of compound (XI) also occurs at much lower temperatures in solution and is fairly rapid above 110°. In the solid phase the reaction does not appear to be influenced by traces of catalysts such as boron trifluoride, palladium on carbon, or chloranil as expected if the reaction is purely intramolecular. The thermal dehydrogenation of tetrachlorocyclohexa-1,3-diene rings in compounds of this type requires much higher temperatures [1,3] and it is clear that the transformations of compounds (X) and (XI) represent a novel type of transannular hydrogen-transfer, probably assisted by the energy release on aromatisation of the diene ring, together with the small overall reduction in steric strain in the system on saturation of the ClC=CR group.

A similar isomerisation occurs with methyl ether (XII), and the order of stability lies in the sequence (XII) > (XI) > (X), suggesting that the polarity of the ClC=CR group may be important in determining the rate of reaction, the fact that the compound (X) [isolated from compound (VII) by cautious heating at 77°] is the least stable perhaps meaning that

[7] K. Mackenzie, *J.*, 1962, 457.
[8] I. T. Miller and H. Heaney, *Quart. Rev.*, 1957, **11**, 109.

the reaction resembles in some ways the dehydrogenation of cyclic dienes by quinones [9] (where, after the prior formation of a charge-transfer complex, hydride transfer is the key step). On a similar basis the vinyl ethers (XI) and (XII) might be expected to be less reactive if the phase which initiated reaction involved partial hydride shift with almost simultaneous intramolecular protonation. The alternative explanation is that the reaction is fully concerted, passing through a hydrogen bridged transition state, the small steric



effect on substituting alkoxyl for chlorine making hydrogen-transfer less favourable by increasing the distance between allylic hydrogens and the double bond. However, the ultraviolet absorption bands of compounds (X), (XI), and (XII) are identical in location, all these maxima being shifted to slightly lower wavelength than the corresponding bands in the spectrum of compound (III) ($\Delta\lambda = 3$ mμ) owing to greater steric strain.

The ultraviolet spectra of the compounds (XIII), (XIV), and (XV) are also closely similar, ε falling to ~160 in the 260—320 mμ range, and it is interesting that the hydrocarbon (XVII) shows more pronounced absorption in this range (ε 500—700) compared with the ether (XVIII) (ε at 270 mμ 285), which suggests that there may be some transannular interaction between the double-bond and the aromatic ring in (XVII).[10]

The proton magnetic resonance spectra of compounds (XIII), (XIV), and (XV) are all closely similar, the band groups corresponding to bridgehead, bridge-methylene, and ring-junction protons being shifted to lower field compared with the relevant bands in the spectrum of isodrin owing to the effect of the aromatic ring.

[9] L. M. Jackman, *Adv. Org. Chem.*, 1960, **2**, 329.

[10] C. F. Wilcox, S. Winstein, and W. G. McMillan, *J. Amer. Chem. Soc.*, 1960, **82**, 5450; S. Winstein, L. de Vries, and R. Orloski, *ibid.*, 1961, **83**, 2020.

Experimental

Infrared light absorption measurements were made on a Unicam S.P. 200 instrument for thin liquid films or Nujol mulls where appropriate; ultraviolet spectra were determined on a Unicam S.P. 800 recording instrument for solutions in ethanol. Proton magnetic resonance data were obtained with a Varian 60 Mc./sec. instrument using tetramethylsilane as internal standard, for solutions in deuterochloroform; data are recorded in the form: chemical shift (τ), multiplicity, integrated peak area, positional assignment by skeletal numbering.

Reaction of Isodrin with Tetrachlorodimethoxycyclopentadiene.—Isodrin (Ia) (36·5 g., 0·1 mole) was heated with tetrachlorodimethoxycyclopentadiene (29·1 g., 0·11 mole) in sealed tubes at 105—110° for 36 hr. The colourless product which had solidified in the tubes was eluted with chloroform (160 ml.) and the hot solution was then diluted with methanol (450 ml.); on cooling the solution the adduct crystallised to give endo-endo-exo-endo-1,2,3,4,5,6,7,8,11,11-*decachloro*-1,4,4a,5,8,8a,9,9a-10,10a-*decahydro*-13,13-*dimethoxy*-1,4:5,8:9,10-*trimethanoanthracene* (IV) (56 g., 89%), m. p. 189° (from ethanol), $\nu_{max.}$ 1601vs; 1158vs, 1210vs cm.$^{-1}$ [ClC=CCl; C(OMe)$_2$] (Found: C, 36·6; H, 2·4. $C_{19}H_{14}Cl_{10}O_2$ requires C, 36·4; H, 2·25%). The adduct was also slowly formed when the reactants were heated under reflux in toluene or chlorobenzene but the yields were smaller in spite of prolonged heating.

Reaction of Compounds (Ib) *and* (Ic) *with Tetrachlorodimethoxycyclopentadiene.*—*endo-endo*-1,3,4,10,10-Pentachloro-2-ethoxy-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene (Ib), prepared as previously described [7] (26·2 g., 0·07 mole), was heated with tetrachlorodimethoxycyclopentadiene (20·3 g., 0·077 mole) at 115—120° for *ca.* 14 hr. in sealed tubes and the product isolated as before to give endo-endo-exo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*ethoxy*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-13,13-*dimethoxy*-1,4:5,8:9,10-*trimethanoanthracene* (V) (32 g., 71·6%), m. p. 162—164° (from ethanol), $\nu_{max.}$ 1597vs, 1634vs cm.$^{-1}$ (ClC=CCl, ClC=COEt) (Found: C, 39·8; H, 3·2. $C_{21}H_{19}Cl_9O_3$ requires C, 39·5; H, 3·0%).

The methoxy-compound (Ic), prepared by the method described in ref. 7 (56%, b. p. 150—152°/0·2 mm.), was heated with tetrachlorodimethoxycyclopentadiene and the product isolated as described above to give endo-endo-exo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*methoxy*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-13,13-*dimethoxy*-1,4:5,8:9,10-*trimethanoanthracene* (VI) (72%) m. p. 241—242° (from chloroform–methanol), infrared spectrum similar to that of compound (V) (Found: C, 38·35; H, 2·75. $C_{20}H_{17}Cl_9O_3$ requires C, 38·45; H, 2·75%).

Hydrolysis of the Adducts (IV), (V), *and* (VI).—Each of the adducts was slowly hydrolysed by concentrated sulphuric acid at 20—25°, or more rapidly at 80—90° (slight decomposition). In typical experiments the adduct (IV) (20 g.) was ground to a fine powder and suspended in concentrated sulphuric acid (200 ml.) and the suspension magnetically stirred for 3 days and then poured on to crushed ice (*ca.* 1 kg.). The crude carbonyl-bridge compound was collected at the pump (sintered-glass funnel), thoroughly washed with water, sucked as dry as possible and then *in vacuo* at 45°, to give endo-endo-exo-endo-1,2,3,4,5,6,7,8,11,11-*decachloro*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8:9,10-*trimethano*-13-*oxoanthracene* (VII) (15 g., 81%), carefully recrystallised from chloroform–light petroleum (40—60°), m. p. 150° (gas evolution), $\nu_{max.}$ 1813vs, shoulder at 1830ms cm.$^{-1}$ ($\alpha\alpha'$-dichloro C=O in a strained ring) (Found: C, 34·85; H, 1·45. $C_{17}H_8Cl_{10}O$ requires C, 35·05; H, 1·4%).

The alternative method of hydrolysis is illustrated for compound (V); the finely powdered adduct (4·8 g.) was stirred with concentrated sulphuric acid (20 ml.) at 80—90° for 1 hr. and then worked up as described above to give endo-endo-exo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*ethoxy*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8:9,10-*trimethano*-13-*oxoanthracene* (VIII) (3·2 g., 72%), recrystallised as above, m. p. 140° (gas evolution), $\nu_{max.}$ 1810vs, sh at 1830ms cm.$^{-1}$ (Found: C, 38·5; H, 2·15. $C_{19}H_{13}Cl_9O_2$ requires C, 38·5; H, 2·2%). Hydrolysis of the adduct (VI) similarly gave in high yield endo-endo-exo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*methoxy*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8:9,10-*trimethano*-13-*oxoanthracene* (IX), recrystallised as above, m. p. 145—150° (gas evolution) (Found: C, 36·8; H, 1·85. $C_{18}H_{11}Cl_9O_2$ requires C, 37·4; H, 1·9%).

Decarbonylation Experiments with the Carbonyl-bridge Compounds (VII), (VIII), *and* (IX).—(*a*) The ketone (VII), prepared as above but not further purified (5 g.), was heated in toluene (12 ml.) under gentle reflux for 1½ hr., the solution diluted with benzene, filtered, and then concentrated; methanol was added to incipient cloudiness and endo-endo-1,2,3,4,5,6,7,8,11,11-*decachloro*-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (XIII) then crystallised

(3·3 g., 70%), m. p. 298°, after further crystallisation from toluene and drying at 110° *in vacuo* to remove toluene which appeared firmly held (efflorescence). (No absorption near 1600 cm.$^{-1}$ in the infrared, $\lambda_{max.}$ 215, sh, 220, sh 242, 287, 297 mμ, ε 47,020, 12,060, 160, 160; polychloro-aromatic ring, short-wave absorption bathochromically shifted.) Proton magnetic resonance data: 6·33 (triplet) (2H) 4a,9a; 6·08 (sextet) (2H) 9,10; 7·9 (complex quartet) (2H) methylene bridge, 12; 6·23 (singlet) (2H) 2,3 [Isodrin: 6·6 (triplet) (2H) 4a,8a; 6·95 (sextet) (2H) 5,8; 8·33 (complex quartet) (2H) methylene bridge, 9] (Found: C, 34·8; H, 1·8. $C_{16}H_8Cl_{10}$ requires C, 34·65; H, 1·45%).

In further experiments with the ketone (VII) the pure carbonyl compound (0·5—1·0 g.) was decomposed in chloroform, carbon tetrachloride, benzene, and toluene solutions for 2—24 hr. In each case compound (XIII) was isolated but heating compound (VII) (2 g.) in carbon tetrachloride (5 ml.) for 1 hr. under gentle reflux followed by partial removal of solvent and dilution of the residue with light petroleum (b. p. 40—60°) gave compound (XIII) (550 mg.) and a further crop of crystals of impure endo-endo-exo-1,2,3,4,5,6,7,8,11,11-*decachloro*-1,4,4a,8a,9,9a,10,10a-*octahydro*-1,4:9,10-*dimethanoanthracene* (X) (675 mg., 35·5%) which further crystallised from carbon tetrachloride–light petroleum (b. p. 40—60°), gave purer material, m. p. 298° (transparent crystals turned opaque near 180°), $\nu_{max.}$ 1595vs, 1620vs cm.$^{-1}$ (conj. ClC=CCl and ClC=CCl), $\lambda_{max.}$ 216, 265, 276, 287, 299, 313 mμ, ε 20,480, 1092, 1591, 2258, 2469, 1504 (Found: C, 34·8; H, 1·55%).

The compound (X) (130 mg.) was heated in *o*-xylene (5 ml.) for 4 hr. at near reflux temperature; when the solution was cooled crystals of compound (XIII) separated, m. p., mixed m. p., and infrared spectrum identical.

(*b*) The ketone (VIII), prepared as above from the adduct (V) (35 g.) and carefully dried but not further purified, was heated in toluene (200 ml.) under gentle reflux for 2 hr., the solvent partially removed *in vacuo*, and the residual solution cooled and diluted with methanol; endo-endo-exo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*ethoxy*-1,4,4a,8a,9,9a,10,10a-*octahydro*-1,4:9,10-*dimethanoanthracene* (XI) crystallised (20 g., 64% overall); after a further crystallisation from toluene, m. p. 184—185°, resolidifying and melting again at 208—210°, $\nu_{max.}$ 1615vs, 1643vs cm.$^{-1}$ (conj. ClC=CCl; ClC=COEt), $\lambda_{max.}$ 216, 265, 276, 287, 299, 313 mμ, ε 7900, 2433, 3461, 5130, 5862, 3542. Proton magnetic resonance data were also consistent with structure (XI), total peak area integral = 13 protons, with considerable overlapping of signals 6·5—7 τ (Found: C, 38·3; H, 2·1. $C_{18}H_{13}Cl_9O$ requires C, 38·3; H, 2·3%).

On prolonged heating of the ketone (VIII) (9·5 g.) in toluene (50 ml.) and partial evaporation of the solvent, instead of the compound (XI) a further crystalline product was obtained. This recrystallised from toluene–methanol, gave endo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*ethoxy*-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (XIV), m. p. 209—210° (6 g., 66%) (no absorption near 1600 cm.$^{-1}$), $\lambda_{max.}$ 215, sh 219·5, sh 242, 287, 297 mμ, ε 46,170, 43,010, 11,250, 160, 160 [aromatic ring, cf. compound (XIII)]. Proton magnetic resonance: 6·44 (triplet) (2H) 4a,9a; 6·1 (complex) (2H) 9·10; 7·9 (complex quartet) (2H) methylene bridge, 12; 6·35 (doublet) (1H) 3; 7·1 (doublet) (1H) 2; 6·63 (quartet) (2H) OCH_2; 8·97 (triplet) (3H) CH_3 (Found: C, 38·8; H, 2·45%).

(*c*) Finely powdered adduct (VI) (3·5 g.) was hydrolysed in the usual manner, the carbonyl compound (IX) isolated as before, and carefully dried but not further purified and then decarbonylated by heating in toluene (30 ml.) for 1 hr. at reflux temperature. The solvent was partially removed *in vacuo* and the product which separated was filtered off and recrystallised from chloroform–light petroleum (b. p. 60—80°) to give endo-endo-exo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*methoxy*-1,4,4a,8a,9,9a,10,10a-*octahydro*-1,4:9,10-*dimethanoanthracene* (XII) (1·4 g., 46%), m. p. 183°, resolidifying and melting again at 266—267°, $\nu_{max.}$ 1617vs, 1640vs cm.$^{-1}$ (conj. ClC=CCl, ClC=COMe), $\lambda_{max.}$ 216, 265, 276, 287, 299, 313 mμ, ε 8420, 2247, 3232, 4814, 5391, 3290 (Found: C, 37·15; H, 2·0. $C_{17}H_{11}Cl_9O$ requires C, 37·1; H, 2·1%). The compound (XII) was also isolated when the carbonyl compound (IX) was decomposed in *o*-xylene at the b. p. for 1½ hr. but heating for longer periods gave compound (XV).

The triene (XII) (300 mg.) was heated in *p*-cymene (5 ml.) at reflux temperature for 1½ hr. and the solution then diluted with methanol; endo-endo-1,3,4,5,6,7,8,11,11-*nonachloro*-2-*methoxy*-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (XV) crystallised (200 mg., 67%), m. p. 266—267° (no absorption near 1600 cm.$^{-1}$), $\lambda_{max.}$ 215, sh 219·5, sh 242, 287, 297 mμ ε 47,430, 44,000, 11,570, 150,150. Proton magnetic resonance: 6·45 (triplet) (2H) 4a,9a; 6·08 (complex) (2H) 9,10; 7·88 (complex quartet) (2H) methylene bridge, 12; 6·32 (doublet) (1H) 3; 7·2

(doublet) (1H) 2; 6·75 (singlet) (3H) OCH_3 (Found: C, 36·75; H, 1·8. $C_{17}H_{11}Cl_9O$ requires C, 37·1; H, 2·1%).

Experiments with the Triene (XI).—The pure triene (XI) (500 mg.) was heated in a tared fusion tube supported in a stirred oil-bath, the temperatures of the oil-bath and the sample being separately recorded. Near 180° (oil-bath at 180°), melting of the sample commenced, accompanied by a sudden rapid rise in temperature to 205°, the oil-bath remaining at 180°. The vessel was allowed to cool, and re-weighing showed that no significant loss of matter had occurred. The tube contents were recrystallised to give pure aromatic compound (XIV), m. p. 209—210° (90%), mixed m. p. and infrared spectrum identical with those of a previous specimen. Similar experiments were conducted with the triene (XI) in the presence of traces of boron trifluoride etherate, 5% palladium–charcoal, and also with chloranil, without any noticeable difference in the result. A similar experiment with a solution of the triene (XI) (1 g.) in chlorobenzene (saturated soln.) failed to exhibit any temperature rise near 180° but vacuum-distillation of the solvent and recrystallisation of the residue gave the aromatic compound (XIV) (750 mg.), m. p. 210° (mixed m. p. and infrared spectrum satisfactory).

The pure triene (XI) (1 g.) was ground to a fine powder and suspended in concentrated sulphuric acid (10 ml.), the suspension allowed to stand overnight, and then poured on to ice. Isolated and recrystallised in the usual way the product had m. p. 180°, resolidifying and then melting again at 210°, undepressed on admixture with (XIV).

Dehalogenation Reactions with Lithium.—The general procedure was based on that of Bruck, Thompson, and Winstein [11] using excess of lithium with t-butyl alcohol in dry tetrahydrofuran.

(*a*) *Dehalogenation of the Triene* (XI).—Pure crystalline compound (XI) (11·10 g., 0·02 mole) was dissolved in tetrahydrofuran (96 ml.), t-butyl alcohol (35·5 g., 0·47 mole) was added, and the mixture brought to gentle reflux, whilst chopped lithium ribbon (7·0 g., 1·004 g.-atom) was added through the condenser during 2—2½ hr., the mixture being thoroughly stirred throughout. The reaction proceeded smoothly with gentle heating and, after a further 1 hr., unreacted lithium was separated off and the residual grey slurry poured on to ice. The organic phase was thoroughly extracted with benzene, the combined extracts were washed with brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residual oil was distilled *in vacuo* to give a fraction, b. p. 115—117°/0·2 mm., largely endo-endo-exo-2-*ethoxy*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:9,10-*dimethanoanthracene* (XVI) (3 g., 58·5%), $\nu_{max.}$ 1620vs; 670s, 705w, 3020ms $cm.^{-1}$ (C=COEt; cyclic *cis*-HC=CH) (Found: C, 83·95; H, 9·3. $C_{18}H_{24}O$ requires C, 84·3; H, 9·45%). Hydrogenated over platinic oxide in ethanol, the product absorbed hydrogen (*ca.* 1 mol.); evaporation of the solvent and chromatography of the product on alumina to remove slight ketonic contaminant gave an oil whose infrared spectrum was virtually transparent in the 670—750 $cm.^{-1}$ region and which showed only weak absorption near 3020 $cm.^{-1}$. Vinyl ether group was retained, 1620vs $cm.^{-1}$.

The vinyl ether (XVI) was stirred with sulphuric acid (20% w/v, 40 ml.) and dioxan (2 ml.) for 3 hr., the suspension was saturated with salt and extracted with light petroleum, the combined extracts were washed with brine, dried, ($MgSO_4$), and evaporated, and the residue was distilled to give a single fraction, b. p. 124—128°/0·2 mm., which solidified to a wax (900 mg., 50·5%); this was chromatographed on silica gel (20 g.) in 1 : 1 chloroform–light petroleum (b. p. 60—80°), to give a single eluate of endo-endo-exo-1,2,3,4,4a,5,8,8a,9,9a,10,10a-*dodecahydro*-1,4:9,10-*dimethano*-2-*oxoanthracene* (XIX) (850 mg.), b. p. 150°/0·4 mm., solidifying to a wax, m. p. 65—70°, $\nu_{max.}$ 1738vs; 3020ms, 680ms, 695mw, 710w (C=O in a strained ring; cyclic *cis*-HC=CH). The ketone was also unsaturated to bromine and to potassium permanganate in acetone. In addition, proton magnetic resonance indicated olefinic protons (2), but suggested that isomeric material might also be present (position of the double-bond?) (Found: C, 83·55; H, 8·8. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%).

Dehalogenation of the Aromatic Compound (XIII).—The polychloro-compound (XIII) (5·55 g., 0·01 mole) was dissolved in tetrahydrofuran (40 ml.) containing t-butyl alcohol (10 g., 0·13 mole) and the solution brought to reflux temperature. Chopped lithium ribbon (2·37 g., 0·355 g.-atom) was added in small portions through the condenser during *ca.* 1 hr. with vigorous stirring, a vigorous reaction commencing. The mixture was heated and stirred for a further 13 hr., excess of lithium removed, the slurry poured on to crushed ice, and the organic phase

[11] P. Bruck, D. Thompson, and S. Winstein, *Chem. and Ind.*, 1960, 405.

extracted as before and distilled *in vacuo*, to give endo-endo-1,4,4a,9,9a,10-*hexahydro*-1,4:9,10-*dimethanoanthracene* (XVII) (1·6 g., 75%), b. p. 94—96°/0·2 mm., $\nu_{max.}$ 3060ms, 750vs, 765vs and characteristic band group at 1930w, 1885w, and 1770w cm.$^{-1}$ (*o*-disubst. benzene), $\lambda_{max.}$ near 210, 267, 274, 280 mμ, ε 10,100, 521, 676, 610 (Found: C, 91·1; H, 7·75. $C_{16}H_{16}$ requires C, 92·25; H, 7·75. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%). The hydrocarbon was probably contaminated with its dihydro-derivative but the infrared spectrum was almost identical with that of a purer specimen later isolated (see below).

Dehalogenation of the Aromatic Compound (XIV).—The polychloro-compound (XIV) (11·1 g., 0·02 mole) was treated with cut lithium ribbon (7·0 g., 1·004 g.-atom) in tetrahydrofuran (96 ml.) containing t-butyl alcohol (35·5 g., 0·47 mole) in the manner described above for compound (XIII), and the product isolated as before and distilled to give a fraction (2 g.), b. p. 100—110°/0·1—0·2 mm., after a low-b. p. fore-run. The infrared spectrum showed this to be a mixture of hydrocarbon (XVII) and an ethyl ether (intense absorption at 1100 cm.$^{-1}$). A similar mixture was isolated when sodium was used in place of lithium in the reduction (yield 1·5 g.); the two reduction products were combined and chromatographed in light petroleum (b. p. 60—80°) on silica gel to give pure compound (XVII) (800 mg., 10% overall), $\lambda_{max.}$ 209, 259, 266, 272, 280 mμ, ε 11,490, 478, 637, 733, 382 (Found: C, 92·3; H, 7·75%), after distillation.

The second chromatographic fraction, similarly isolated and distilled, gave endo-endo-2-*ethoxy*-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (XVIII) (700 mg., 7% overall), $\nu_{max.}$ 3060ms, 735vs, 745vs, and characteristic bands in the 1700—2000 cm.$^{-1}$ range (*o*-disubst. benzene), $\lambda_{max.}$ near 205, 270, 278 mμ, ε 14,940, 285, 271 (Found: C, 85·15; H, 8·9. $C_{18}H_{22}O$ requires C, 84·95; H, 8·7%).

The hydrocarbon (XVII) (210 mg., 0·001 mole) slowly absorbed hydrogen (1 mol.) over platinic oxide catalyst in ethanol to give a dihydro-derivative identical with an authentic specimen prepared as follows.

Synthesis of the Hydrocarbon (XXI).—Purified isodrin was dehalogenated with lithium by the method of Bruck, Thompson, and Winstein [11] to give *endo-endo*-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene as a waxy solid (80%). This (8·0 g., 0·00505 mole) was heated with tetrachlorodimethoxycyclopentadiene (13 g., 0·05 mole) in toluene (60 ml.) for 48 hr. at reflux temperature. The solvent was removed *in vacuo* and the residue recrystallised from ethanol to give endo-exo-endo-endo-1,2,3,4-*tetrachloro*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8:9,10-*trimethano*-11,11-*dimethoxyanthracene* (XXII) (10 g., 74%), m. p. 129—130° (from methanol) (Found: C, 54·35; H, 5·2. $C_{19}H_{20}Cl_4O_2$ requires C, 54·05; H, 4·8%).

The adduct (4·22 g., 0·01 mole) very slowly absorbed hydrogen (1 mol.) over palladium on chalk to give endo-exo-endo-endo-1,2,3,4-*tetrachloro*-1,4,4a,5,6,7,8,8a,9,9a,10,10a-*dodecahydro*-1,4:5,8:9,10-*trimethano*-11,11-*dimethoxyanthracene* (XXIII) (3·5 g., 82%), m. p. 162—163° (from ethanol) (Found: C, 54·2; H, 5·5. $C_{19}H_{22}Cl_4O_2$ requires C, 53·8; H, 5·2%).

The dihydro-adduct (XXIII) (3·5 g.) was ground to a fine powder, suspended in concentrated sulphuric acid (30 ml.), the mixture allowed to stand at 20° for 24 hr., poured on to crushed ice, and the precipitated carbonyl compound filtered off, thoroughly washed, and dried *in vacuo* at 45°, and then decarbonylated by heating in dry *o*-xylene under reflux for 1½ hr. The solvent was removed *in vacuo* and the residue dissolved in chloroform, treated with charcoal, filtered, evaporated, and diluted with light petroleum (b. p. 60—80°), to give crystalline exo-endo-endo-1,2,3,4-*tetrachloro*-4a,5,6,7,8,8a,9,9a,10,10a-*decahydro*-5,8:9,10-*dimethanoanthracene* (XXIV) (2·4 g., 83%), m. p. 132—133°, unchanged on further crystallisation from petroleum, $\nu_{max.}$ 1600vs cm.$^{-1}$ (conj. ClC=CCl system), $\lambda_{max.}$ 267, 278, 289, 300, 314·5 mμ, ε 2332, 3731, 4140, 5578, 3365 (Found: C, 54·8; H, 4·6. $C_{16}H_{16}Cl_4$ requires C, 54·9; H, 4·6%).

The diene (XXIV) (2·18 g., 0·0062 mole) was heated with bromine (1·26 g., 0·007 mole) in carefully dried chlorobenzene (20 ml.) for 2 hr. at 120—130°, hydrogen bromide being visibly evolved. The solvent was evaporated *in vacuo* and the powdery residue recrystallised from light petroleum (b. p. 60—80°), to give endo-endo-1,2,3,4-*tetrachloro*-5,6,7,8,8a,9,10,10a-*octahydro*-5,8:9,10-*dimethanoanthracene* (XXV) (1·15 g., 53%), m. p. 137—139° raised to 140—141° after further crystallisation (no absorption near 1600 cm.$^{-1}$ in the infrared; band group characteristic of the precursor in the 260—320 mμ range absent) (Found: C, 55·5; H, 4·1. $C_{16}H_{14}Cl_4$ requires C, 55·2; H, 4·05%).

The tetrachloro-compound (XXV) (1 g.) was dissolved in tetrahydrofuran (10 ml.) containing t-butyl alcohol (2·5 g.); finely chopped lithium ribbon (200 mg.) was added and the mixture was heated under reflux for 2½—3 hr. and then worked up in the manner described above. The

oily product was distilled *in vacuo* to give endo-endo-1,2,3,4,4a,9,9a,10-*octahydro*-1,4:9,10-*dimethanoanthracene* (XXI) (400 mg., 66%) having an infrared spectrum identical with that of dihydro- (XVII) (Found: C, 91·0; H, 8·95. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%).

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