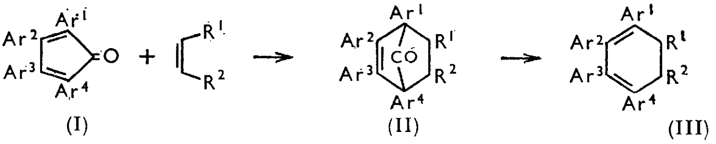
98. *Bicyclo*[2,2,1]*heptadiene in the Diels–Alder Reaction.*

By K. Mackenzie.

5,6,7,8-Tetrasubstituted 1,4,4a,8a-tetrahydro-1,4-methanonaphthalenes and their 2,3-disubstitution products undergo retrogressive Diels–Alder reaction to give aromatic ring compounds and cyclopentadiene or its derivatives.

As is well known,[1] tetraphenylcyclopentadienone and its analogues (I) undergo Diels–Alder addition with ethylenic dienophiles to give carbonyl-bridged adducts (II) or the derived dihydroaromatic compounds (III) resulting from elimination of carbon monoxide, depending on the reaction temperature. The dihydroaromatic compounds may be dehydrogenated merely by heat or by treatment with bromine.[2]



The isolation of unexpected products in the reaction of tetraphenylcyclopentadienone (tetracyclone) with certain bicyclo[2,2,1]heptene derivatives (unpublished work) prompted an examination of the reaction of tetra-arylcyclopentadienones with bicyclo[2,2,1]hepta-2,5-diene. In the following, the course of reaction of cyclopentadienones with bicycloheptadiene is rationalised within a more general reaction sequence.

When tetracyclone and an excess of bicycloheptadiene are heated together at 80—140° in an inert solvent, the crystalline product shows no infrared carbonyl absorption and is stable to heat and mild oxidising agents. Together with the intense ultraviolet-light absorption, these facts characterise the product as a highly conjugated aromatic compound. In a similar reaction with the dimer of 2,5-dimethyl-3,4-diphenylcyclopentadienone the product is again a fully aromatic compound which shows a single intense ultraviolet maximum (216 mμ, ε 24,720) and yields a dibromide when treated with *N*-bromosuccinimide, indicating that the methyl groups derived from the dienone are attached to the aromatic rings.

However, when the more reactive analogue (IV) (phencyclone) is used in a similar reaction the product is certainly the adduct (VI) for it shows intense infrared absorption at 1770 cm.$^{-1}$ (C=O in a strained-ring), rapidly absorbs hydrogen, and decomposes with gas evolution when heated. Moreover this product forms further adducts with dienes (unpublished work).

Heating the adduct (VI) does not, however, give the dihydroaromatic compound (VII): it gives a product which is saturated towards bromine and hydrogen and has an ultraviolet spectrum different from that of the adduct (VI) or phenanthrene.

These three aromatic compounds are 1,2,3,4-tetraphenylbenzene,[1b] 3′,6′-dimethyl-*o*-terphenyl,[2] and 1,4-diphenyltriphenylene (VIII), and have arisen by a retrogressive Diels–Alder reaction of the intermediate dihydroaromatic compounds derived by decarbonylation of the initial adducts,* and in confirmation of this reaction scheme the cyclopentadiene evolved in the reaction of tetracyclone with bicycloheptadiene or when the adduct (VI) is heated may be isolated as the maleic anhydride adduct. Prior

---

* The enhanced stability of phencyclone adducts is well known.[1c, 3]

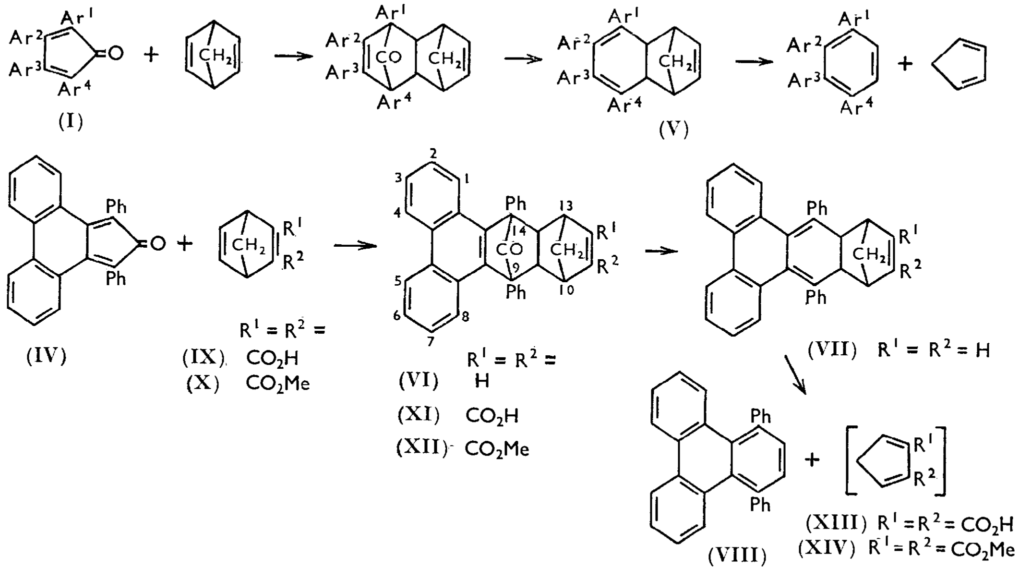
[1] (*a*) Allen, *Chem. Rev.*, 1945, **37**, 209; (*b*) Dilthey, Schommer, and Trösken, *Ber.*, 1933, **66**, 1627; (*c*) Dilthey, Horst, and Scheafer, *J. prakt. Chem.*, 1937, **148**, 53.

[2] Allen and Van Allen, *J. Amer. Chem. Soc.*, 1942, **64**, 1260.

[3] Abramov, *Doklady Akad. Nauk S.S.S.R.*, 1948, **62**, 637.

decomposition of bicycloheptadiene to acetylene and cyclopentadiene in the former case is precluded by the fact that acetylene does not react appreciably with tetracyclone at the reaction temperatures used; retrograde reaction of bicycloheptadiene occurs only at much higher temperatures.[4]

Simple analogues of tetracyclone undergo a similar reaction with bicycloheptadiene, which provides a convenient method of preparing 1,2,3,4-tetra-arylbenzenes and 1,4-diphenyltriphenylenes, especially those having sensitive substituents, and a few examples have been prepared. All the 1,2,3,4-tetra-arylbenzenes show a medium-to-strong band in the infrared spectrum near to 800 cm.$^{-1}$, whilst in the ultraviolet region there are generally two intense maxima near 225 and 250 mμ (ε 30,000—60,000). Both the intensities and the wavelengths of these absorption maxima are rather lower than might be expected and must be determined by the non-planarity of the benzene rings in these crowded molecules.



(I)

(V)

(IV)

$R^1 = R^2 =$
(IX) CO_2H
(X) CO_2Me

$R^1 = R^2 =$
(VI) H
(XI) CO_2H
(XII) CO_2Me

(VII) $R^1 = R^2 = H$

(VIII)

(XIII) $R^1 = R^2 = CO_2H$
(XIV) $R^1 = R^2 = CO_2Me$

Under more vigorous conditions, bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (IX) and its dimethyl ester (X) also react with tetracyclone, to give, as the only isolated product 1,2,3,4-tetraphenylbenzene; presumably the cyclopentadiene derivatives eliminated, namely, (XIII) and (XIV), are decomposed or polymerised at the reaction temperature, and attempts to trap these dienes by heating the phencyclone adducts (XI) and (XII) with maleic anhydride gave 1,4-diphenyltriphenylene as the only crystalline product.

These observations necessitated an examination of other tetrahydromethanonaphthalenes analogous to (V) having substituents other than alkyl or aryl, and one approach is outlined in scheme *A*.

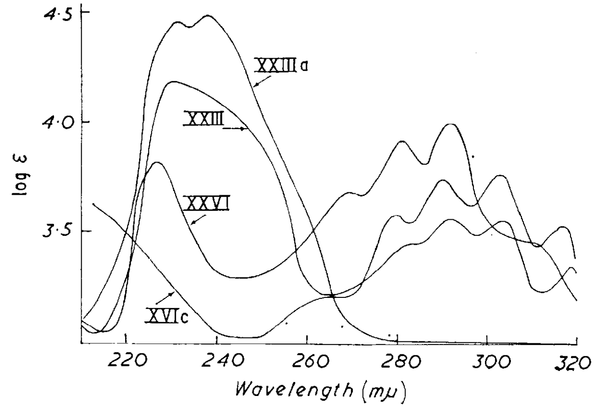
Addition of 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene (XV) to bicycloheptadiene gives the adduct (XVI). Addition of bromine to the adduct occurs without Wagner–Meerwein rearrangement, debromination regenerating the starting material. Hydrolysis of the dibromo-adduct (XVIa) with warm sulphuric acid gives the carbonyl-bridged compound (XVIb), but with boiling acetic–hydrobromic acid mixtures hydrolysis of (XVIa) occurs with concomitant elimination of carbon monoxide to give compound (XVIc), which is also obtained from (XVIb) by mild heating.

---

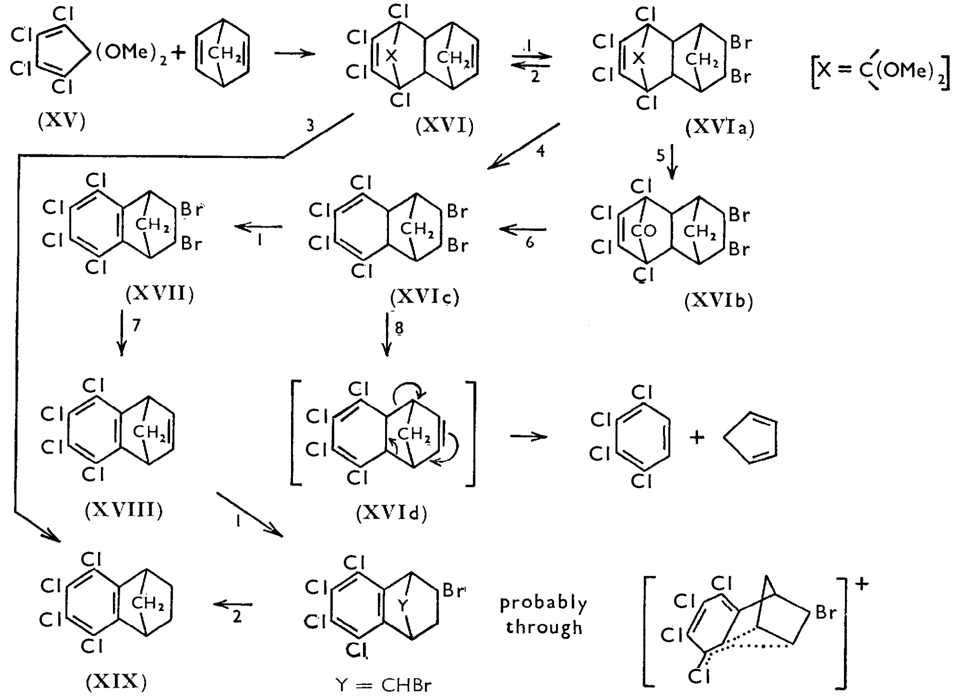
[4] Woods, *J. Org. Chem.*, 1958, **23**, 110.

The compound (XVIc) shows unusual ultraviolet light absorption (Fig.); the band group around 300 mμ represents a bathochromic shift of 44 mμ compared with that of cyclohexa-1,3-diene, whilst the splitting is attributable to the conjugative effects of the chlorine atoms. A similar bathochromic shift (31 mμ) occurs in 1,2,3,4-tetrachlorobuta-1,3-diene.

Ultraviolet spectra of solutions in ethanol containing 4% *of chloroform.*



Debromination of compound (XVIc) under very mild conditions (35—80° with zinc) gives pure 1,2,3,4-tetrachlorobenzene in high yield, and cyclopentadiene can be distilled from the reaction mixture. On a moderate scale the reaction is noticeably exothermic and



Scheme A.

Reagents: 1, Br_2. 2, Zn. 3, H_2–Pd; H_2SO_4; heat; Br_2. 4, HBr–AcOH. 5, H_2SO_4. 6, Heat. 7, Zn–EtOH. 8, Zn–Et_2O or -EtOH.

the ease with which the reaction takes place parallels the decomposition of the 5,6,7,8-tetra-aryl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalenes (V). The driving force of the reaction must therefore be determined by the dissipation of energy in forming the resonance-stabilised product, irrespective of the ring substituents.

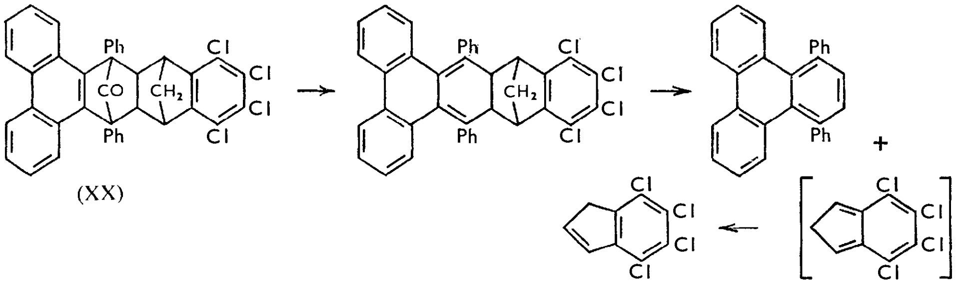
As a dihydrobenzene derivative, (XVIc) is smoothly dehydrogenated with bromine to give 2,3-dibromo-5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-1,4-methanonaphthalene (XVII), which has typical aromatic ultraviolet light absorption. Debromination of this product (XVII) gives the dihydro-compound (XVIII) which has similar spectral properties, rapidly absorbs 1 mol. of hydrogen catalytically, and readily forms an epoxide.

The methanonaphthalene (XVIII) yields a dibromide quite different from the parent compound (XVII) and debrominated only with difficulty to give a poor yield of the dihydro-derivative (XIX) of the starting material (XVIII); Wagner–Meerwein rearrangement must have intervened and is perhaps facilitated by formation of a mesomeric bridged carbonium ion (Ar$_1$-3 type participation [5]), followed by addition of a bromine cation with rearrangement. In this connexion 5,8-diacetoxy-1,4-dihydro-1,4-methanonaphthalene is probably brominated with rearrangement.[6]

Hydrogenation of the adduct (XVI) followed by hydrolysis, heating, and dehydrogenation of the product provides an independent route to compound (XIX).

The dienophile (XVIII) reacts only slowly with tetracyclone to give as the major product 1,2,3,4-tetraphenylbenzene; retrogressive reaction of the intermediate 5,6,7,8-tetrachloro-4a,9,10,10a-tetrahydro-1,2,3,4-tetraphenyl-9,10-methanoanthracene must have given rise to the tetraphenylbenzene, although the second product has not been isolated in this reaction. Heating the compound (XVIII) with phencyclone, however, gives the highly insoluble adduct (XX) which decomposes at a moderate temperature into 1,4-diphenyltriphenylene and 4,5,6,7-tetrachloroindene (XXI).

The structure of the tetrachloroindene (XXI) follows from its ultraviolet light absorption ($\lambda_{\text{max.}}$ 223, 228, and 264 mμ; ε 28,330, 27,030, and 13,950), the formation of a dihydro-derivative in which the ultraviolet light absorption indicates the disappearance of a conjugated double bond ($\lambda_{\text{max.}}$ 216, 281, and 290 mμ; ε 20,640, 438, and 407) and closely resembles that of 1,2,3,4-tetrachlorobenzene, the formation of a furfurylidene derivative (a mixed product is obtained in a similar reaction with benzaldehyde [7]), and by the identity of the dihydro-derivative with authentic 4,5,6,7-tetrachloroindane prepared by addition of the unusually reactive 2,3,4,5-tetrachloro-1,1-dimethoxycyclopentadiene [8] to cyclopentene followed by hydrolysis, heating, and dehydrogenation.



(XX)

(XXI)

(XXIa)

The vigorous conditions required for the decomposition of compound (XX) preclude isolation of the intermediate, but the possibility of synthesising a compound having a

---

[5] See Bethell and Gold, *Quart. Rev.*, 1958, **12**, 173.

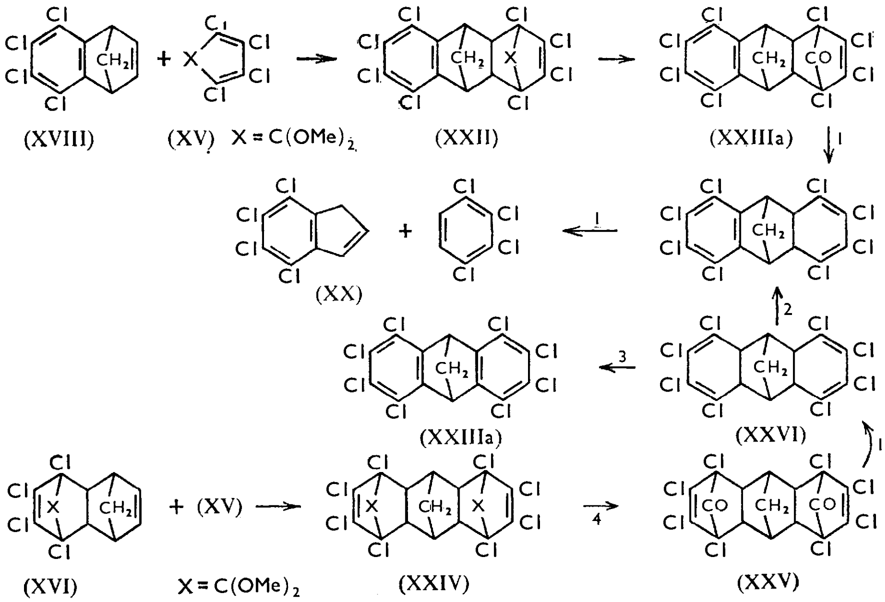
[6] Meinwald and Wiley, *J. Amer. Chem. Soc.*, 1958, **80**, 3667.

[7] Cf. Thiele, *Ber.*, 1900, **33**, 3395; Thiele and Buhner, *Annalen*, 1906, **347**, 249.

[8] Peri, *Gazzetta*, 1955, **85**, 1118.

similar unsaturated system (XXIII) is afforded by the mild conditions involved in scheme *B*. Moderate heating of this compound (XXIII) results in decomposition to 1,2,3,4-tetrachlorobenzene and 4,5,6,7-tetrachloroindene, and the stability of (XXIII) compared with (XVId) is in accord with the view that decomposition of (XXIII) and the dihydroaromatic compound derived from (XX) proceeds through the benzocyclopentadiene structure (XXIa). The more vigorous conditions required for reaction of tetracyclone with bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (and diester) is similarly a result of the necessity of breaking the conjugation of the carboxyl groups during retrogressive reaction.

It is of interest to compare the spectroscopic properties of the intermediates in schemes *A* and *B*. The infrared spectra of (XXIIa, XXV) and (XXIII, XXVI) correspond with those of (XVIb and c) in having strong maxima at 1818 and 1600 cm.$^{-1}$, respectively ($\alpha\alpha'$-dihalogeno-carbonyl, strained ring, and conjugated C=C); the band at 1600 cm.$^{-1}$ is absent from the spectra of (XVII), (XVIII), and (XXIIIa). In the ultraviolet range the absorptions of (XXIII) and (XVIc) closely correspond in the 280—320 mμ region, but that of (XXVI) is shifted to shorter wavelengths, consistently with steric strain which is relieved to some extent in (XXIII) by the planarity of the benzene ring. Internal strain in (XXIII) must contribute to its rate of decomposition.



Scheme B.

Reagents: 1, Heat. 2, Br_2 (1 mol.). 3, Br_2 (2 mols.). 4, H_2SO_4.

Compared with 1,2,3,4-tetrachlorobenzene, the tetracyclic compound (XXIIIa) shows a large bathochromic shift, which seems best explained in terms of aromatic ring strain, although there may be some interaction across the bridged ring.

There remain to be decided the precise stereochemical features of the bridged compounds (XVI) and (XXIV), and this is receiving attention.

EXPERIMENTAL

Ultraviolet light absorptions were measured with a Unicam manual intrument (by Mr. L. T. Heaysman), for solutions in ethanol unless otherwise indicated (those marked * refer to ethanol solutions containg 2% of chloroform); infrared spectral determinations were made on a Grubb–Parsons double-beam grating instrument for paraffin mulls (by Mr. P. J. Cooper and Mr. D. W. Radford).

Reaction of Tetracyclone with Bicyclo[2,2,1]*hepta*-2,5-*diene*.—Tetracyclone [9] (7·7 g., 0·02 mole) was heated with bicycloheptadiene (8·0 g., 0·087 mole) in chloroform (100 ml.) for 48 hr., the colour fading to pale pink; most of the solvent was distilled off and the residue diluted with methanol, whereupon 1,2,3,4-tetraphenylbenzene crystallised as pink needles (7·0 g., 92%), m. p. 191° not depressed on admixture with the authentic compound [1b] (infrared spectra identical). The product was decolorised with the aid of charcoal and had $\lambda_{max.}$ * 225, 245 mμ (ε 28,650, 36,600); $\nu_{max.}$ 800 s cm.$^{-1}$ (1,2,3,4-substituted benzene). An experiment on a larger scale gave also a small quantity of a higher-melting *substance*, m. p. ~250° (Found: C, 93·4; H, 6·4. $C_{61}H_{48}$ requires C, 93·8; H, 6·2%), possibly the diadduct of tetracyclone with bicycloheptadiene.

Isolation of Cyclopentadiene in the Reaction of Tetracyclone with Bicycloheptadiene.—Tetracyclone (1·92 g., 0·005 mol.) was heated with redistilled bicycloheptadiene (1 ml.) in sodium-dried xylene (10 ml.); nitrogen was bubbled through the boiling mixture and then into a solution of maleic anhydride (0·5 g.) in ether (15 ml.). At the end of the reaction (almost colourless mixture after 3·5 hr.), the ethereal solution was evaporated until crystals began to separate; the crystals were filtered off. These (300 mg., 33%) had m. p. 164—165° not depressed on admixture with bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride prepared by addition of cyclopentadiene to maleic anhydride at 10°.

Reaction of 2,5-*Dimethyl*-3,4-*diphenylcyclopentadienone Dimer with Bicycloheptadiene*.—This dimer [10] (13 g., 0·052 mole) and bicycloheptadiene (10 g., 0·11 mole) were heated in chlorobenzene (150 ml.) under reflux for 2 hr. and the solvent then distilled off. The residual oil was boiled with methanol, insoluble material (2 g.) was filtered off, and the filtrate concentrated and allowed to crystallise. 3′,6′-Dimethyl-*o*-terphenyl separated as plates (7·0 g., 53%), m. p. 113° not depressed on admixture with a specimen prepared [2] by passing acetylene into a solution of the dienone dimer in boiling *o*-dichlorobenzene, and having $\lambda_{max.}$ 216 mμ (ε 24,720), $\nu_{max.}$ 806 s cm.$^{-1}$.

3′,6′-Dimethyl-*o*-terphenyl (324 mg., 1 mol.) was heated with *N*-bromosuccinimide (445 mg., 2 mol.) in carbon tetrachloride (15 ml.) until the reaction had subsided; the cooled mixture was filtered from succinimide, the filtrate concentrated and diluted with methanol, and the solid product isolated, to give 3′,6′-bisbromomethyl-*o*-terphenyl (450 mg., 86%), m. p. 135—136° (Found: C, 57·9; H, 4·1. Calc. for $C_{20}H_{16}Br_2$: C, 57·7; H, 3·9%).

Reaction of Phencyclone with Bicycloheptadiene.—Phencyclone [11] (5·0 g., 0·013 mole) was heated with bicycloheptadiene (3 g., 0·33 mole) in chlorobenzene (50 ml.) until the deep-green colour had faded to a light yellow (1—2 hr.); the solvent was distilled off and the residue diluted with methanol, the adduct separating as a buff powder. The product recrystallised from ethyl acetate–methanol to give 9,14-*carbonyl*-9,9a,10,13,13a,14-*hexahydro*-9,14-*diphenyl*-10,13-*methanodibenz*[a,c]*anthracene* (VI) (6 g., 96%), m. p. 224—226° (decomp.) (Found: C, 91·9; H, 5·9. $C_{36}H_{26}O$ requires C, 91·1; H, 5·5%), $\nu_{max.}$ 1770 vs cm.$^{-1}$ (strained-ring CO), principal $\lambda_{max.}$* 225, 262, 273, 300, 312 mμ (ε 30,260, 38,080, 24,140, 11,220, 9521).

The adduct (VI) (950 mg., 0·002 mol.) rapidly absorbed 1 mol. of hydrogen over 5% palladium on chalk, to give the 9,9a,10,11,12,13,13a,14-*octahydro-compound* (700 mg.), m. p. 234—237° (decomp.) (from ethyl acetate–methanol) (Found: C, 90·0; H, 5·85. $C_{36}H_{28}O$ requires C, 90·2; H, 5·9%).

Pyrolysis of the Adduct (VI).—The adduct (1·7 g.) was heated at 200° in a hard-glass flask for 20 min. and the effluent vapour passed into maleic anhydride (400 mg.) in ether (8 ml.); needles of bicyclo[2,2,1]hept-5-ene-2,3-dicarboxylic anhydride (150 mg.) quickly separated, having m. p. and mixed m. p. 164—165°.

The pyrolysis residue, recrystallised from benzene–methanol, gave 1,4-*diphenyltriphenylene* (1·3 g.), m. p. 224—226° not depressed on admixture with a specimen prepared as follows. Acetylene was passed through a solution of phencyclone (500 mg.) in boiling *o*-dichlorobenzene (7 ml.) for 3 hr. The light yellow mixture was cooled and diluted with methanol, and the precipitate recrystallised from benzene–methanol [m. p. 224—226° (300 mg.), $\lambda_{max.}$* 235, 270, 280 mμ (ε 35,460, 44,015, 46,070) (Found: C, 94·7; H, 5·2. $C_{30}H_{20}$ requires C, 95·2; H, 4·8%)].

---

[9] Dilthey and Quint, *J. prakt. Chem.*, 1930, **128**, 139.

[10] Japp and Meldrum, *J.*, 1901, **79**, 1024; Gray, *J.*, 1909, **95**, 2131.

[11] Dilthey, Horst, and Schommer, *J. prakt. Chem.*, 1935, **143**, 189.

Tetra-arylbenzenes.—In a typical experiment, 3,4-di-(*p*-methoxyphenyl)-2,5-diphenylcyclopentadienone [12] (1·5 g.) was heated with bicycloheptadiene (5 ml.) in *o*-dichlorobenzene (20 ml.) under reflux for 6—10 hr., the solvent evaporated *in vacuo*, and the residue recrystallised from benzene–methanol to give 2,3-di-(*p*-methoxyphenyl)-1,4-diphenylbenzene (1·4 g.), m. p. 185—186°, $\lambda_{\max.}$* 232, 255 mμ (ε 33,500, 35,100), $\nu_{\max.}$ 800 s cm.$^{-1}$. A specimen, prepared by passing acetylene into a melt of the cyclone until the mixture was colourless and recrystallised from benzene–methanol, had m. p., mixed m. p., and infrared spectrum identical with those of the above specimen. Abramov and Shapshinskaya [13] report m. p. 181°.

Similarly prepared in high yield from the relevant cyclone and bicycloheptadiene were the following 1,2,3,4-tetra-arylbenzenes:

From 2-*p*-methoxyphenyl-3,4,5-triphenylcyclopentadienone,† 1-p-*methoxyphenyl*-2,3,4-*triphenylbenzene*, m. p. 178—179°, $\lambda_{\max.}$* 227·5, 250 mμ (ε 28,880, 30,310), $\nu_{\max.}$ 801 ms cm.$^{-1}$ (Found: C, 89·7; H, 6·2. $C_{31}H_{24}O$ requires C, 90·3; H, 5·8%).

From 2,3,4,5-tetra-(*p*-methoxyphenyl)cyclopentadienone [14] (rather slow reaction, the cyclone exhibiting thermochromism, green-black when cold, deep-red when hot), 1,2,3,4-*tetra*-(p-*methoxyphenyl)benzene*, m. p. 192—193°, $\lambda_{\max.}$* 231, 260 mμ (ε 29,060, 32,440), $\nu_{\max.}$ 796 ms cm.$^{-1}$ (Found: C, 80·8; H, 6·0. $C_{34}H_{30}O_4$ requires C, 81·3; H, 6·0%).

From 3-*p*-dimethylaminophenyl-2,4,5-triphenylcyclopentadienone,[12] 2-p-*dimethylaminophenyl*-1,3,4-*triphenylbenzene*, m. p. 196—197°, $\lambda_{\max.}$* 225, 240 mμ (ε 35,110, 34,680), $\nu_{\max.}$ 797 s cm.$^{-1}$ (Found: C, 90·3; H, 6·6. $C_{32}H_{27}N$ requires C, 90·3; H, 6·4%).

From 2,5-diphenyl-3,4-di-*p*-diphenylylcyclopentadienone,[12] 1,4-*diphenyl*-2,3-*di*-p-*diphenylylbenzene*, m. p. 213—214°, $\lambda_{\max.}$ 224, 264 mμ (ε 42,240, 65,240), $\nu_{\max.}$ 800 m cm.$^{-1}$ (Found: C, 94·3; H, 5·6. $C_{24}H_{30}$ requires C, 94·3; H, 5·7%).

Reaction of Tetracyclone with Bicyclo[2,2,1]*hepta*-2,5-*diene*-2,3-*dicarboxylic Acid.*—This acid [15] (2·0 g., 0·01 mol.) was heated with tetracyclone (3·84 g., 0·01 mol.) in *o*-dichlorobenzene (50 ml.) for 14 hr. The solvent was evaporated *in vacuo*, the residue diluted with methanol, and the product filtered off and recrystallised from benzene–methanol, to give 1,2,3,4-tetraphenylbenzene (2·2 g., 58%), m. p. 191°.

Dimethyl bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate also gave tetraphenylbenzene (60%).

Reaction of Phencyclone with Bicyclo[2,2,1]*hepta*-2,5-*diene*-2,3-*dicarboxylic Acid and its Dimethyl Ester.*—Phencyclone (1·91 g., 0·005 mole) was boiled with the acid (900 mg., 0·005 mole) in chlorobenzene (25—30 ml.) until the deep-green colour had faded (30 min.); the cooled solution was diluted with methanol, and the precipitated solid filtered off to give substantially pure adduct (XI) (1·5 g., 54%), m. p. 243—245° (decomp.), insoluble in the usual solvents and decomposing when heated with the higher-boiling solvents.

The adduct (500 mg.) was heated at the m. p. for 2 hr. (until gas evolution ceased), and the residual glass crystallised from benzene–methanol (after removal of a little tar) to give 1,4-diphenyltriphenylene (250 mg., 74%), m. p. and mixed m. p. 224—226°. In a similar experiment on a larger scale in the presence of maleic anhydride no other product was isolated.

Phencyclone (8·0 g., 0·012 mole) was heated with dimethyl bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate (4·31 g., 0·021 mole) in chlorobenzene (50 ml.) for 45 min., cooled, and diluted with methanol, and the precipitate was recrystallised from chloroform–methanol, to give *dimethyl* 9,14-*carbonyl*-9,9a,10,13,13a,14-*hexahydro*-9,14-*diphenyl*-10,13-*methanodibenz*[a,c]-*anthracene*-11,12-*dicarboxylate* (XII) (9·3 g., 75%), m. p. 248—50° (decomp.) (Found: C, 80·7; H, 5·2. $C_{40}H_{30}O_5$ requires C, 81·3; H, 5·1%).

This ester (1·5 g.) was boiled in nitrobenzene (20 ml.) with maleic anhydride (230 mg.) for 1 hr., the solvent was evaporated *in vacuo*, and the residual solid boiled with methanol; the cooled mixture was filtered, concentrated, and allowed to crystallise; *ca.* 5 mg. of diphenyltriphenylene separated. The insoluble residue, recrystallised from benzene–methanol, gave 1,4-diphenyltriphenylene (750 mg., 75%), m. p. 224—226°.

---

† From 1-*p*-methoxyphenyl-3-phenylpropan-2-one by the method of Coan, Trucker, and Becker [14]; cf. ref. 12.

[12] Dilthey, Trosken, Plum, and Schommer, *ibid.*, 1934, **141**, 331.
[13] Abramov and Shapshinskaya, *Zhur. obshchei Khim.*, 1952, **22**, 1450.
[14] Coan, Trucker, and Becker, *J. Amer. Chem. Soc.*, 1953, **75**, 900.
[15] Diels and Alder, *Annalen*, 1931, **490**, 236.

Reaction of Bicyclo[2,2,1]*heptadiene with* 2,3,4,5-*Tetrachloro*-1,1-*dimethoxycyclopentadiene.*—The cyclopentadiene [16] (b. p. 112°/8 mm., n_D^{20} 1·5300; 80 g., 0·303 mole) was heated with bicycloheptadiene (160 g., 1·74 mole) under reflux for 14 hr., the excess of bicycloheptadiene removed under a partial vacuum, the warm residue poured into hot methanol (800 ml.), and the whole boiled and filtered. From the filtrate crystallised 1,2,3,4-*tetrachloro*-1,4,4a,5,8,8a-*hexahydro*-1,4-*dimethoxymethano*-5,8-*methanonaphthalene* (XVI) as needles (100 g., 93%), m. p. 118° after a further crystallisation from methanol (Found: C, 47·5; H, 4·0. $C_{14}H_{14}O_2Cl_4$ requires C, 47·2; H, 3·95%).

When hydrogenated (1 mol.) over 5% palladium on calcium carbonate the adduct gave an *octahydro-derivative*, m. p. 106—107° (Found: C, 47·1; H, 4·45. $C_{14}H_{16}O_2Cl_4$ requires C, 46·9; H, 4·5%).

Bromination of the Adduct (XVI).—The adduct (XVI) (35·6 g.) was treated in chloroform (100 ml.) with bromine (16 g., 0·1 mol) in two equal portions; the solution, which rapidly became warm and colourless, was concentrated and then diluted with methanol. 2,3-*Dibromo*-5,6,7,8-*tetrachloro*-1,2,3,4,4a,5,8,8a-*octahydro*-5,8-*dimethoxymethano*-1,4-*methanonaphthalene* (XVIa) separated almost immediately as prisms (51 g., 99%), m. p. 146—147° (from chloroform–methanol) (Found: C, 33·0; H, 2·5. $C_{14}H_{14}O_2Cl_4Br_2$ requires C, 32·6; H, 2·7%).

The dibromo-adduct (XVIa) (4·24 g.) was heated with zinc powder (1·5 g.) in ethanol (70 ml.) during 2 hr., the hot mixture filtered, and the filtrate concentrated and cooled; the adduct (XVI) separated (1·6 g.; m. p. and mixed m. p.).

Hydrolysis of the Dibromo-adduct (XVIa).—(*a*) A suspension of the dibromo-adduct (3·8 g.), acetic anhydride (17 ml.) and 48% w/v hydrobromic acid (8·5 ml.) was heated just below the b. p. for 16 hr. Effervescence commenced within the first hour. The aqueous acid was distilled off, and the residue filtered off, washed with water, dried *in vacuo*, and recrystallised from benzene–methanol, to give 2,3-*dibromo*-5,6,7,8-*tetrachloro*-1,2,3,4,4a,8a-*hexahydro*-1,4-*methanonaphthalene* (XVIc) (1·7 g., 52%), needles, m. p. 153°, $\lambda_{max.}$ 210, 279, 290, 302, 316 mμ (ε 4134, 4335, 6279, 6766, 3913), $\nu_{max.}$ 1608 s cm.$^{-1}$ (conjugated C=C) (Found: C, 30·0; H, 1·8. $C_{11}H_8Cl_4Br_2$ requires C, 29·9; H, 1·8%).

(*b*) The dibromo-adduct (2 g.) was added to sulphuric acid (20 ml.),[16] warmed at 80—90° for 15 min., and poured on ice. The product was filtered off, washed with sodium hydrogen carbonate solution and water, and dried *in vacuo*. The crude product decomposed on attempted crystallisation from ethanol and had m. p. 145—150° (decomp.), $\nu_{max.}$ 1818 cm.$^{-1}$ (αα′-dihalogeno-CO; strained ring). The crude product (1·8 g.) was heated in chlorobenzene (15 ml.) for 1 hr., the solvent evaporated *in vacuo*, and the residue recrystallised from benzene–methanol, to give the above product (XVIc) (1 g.; m. p., mixed m. p. and infrared spectrum).

The dibromo-adduct was also hydrolysed when suspended in sulphuric acid at room temperature for 3 hr.

Debromination of the Product (XVIc).—The dibromo-compound (15 g.) was heated with zinc dust (12 g.) in ethanol (150 ml.) under reflux; a vigorous reaction appeared complete in 10 min. The mixture was cautiously distilled and the first few drops of distillate were added to an ethereal solution of maleic anhydride, evaporation of which then gave the maleic anhydride cyclopentadiene adduct (*ca.* 300 mg.), m. p. and mixed m. p. 164—165°. The remaining reaction residue was filtered whilst hot, concentrated, and allowed to cool. 1,2,3,4-Tetrachlorobenzene crystallised as needles (7 g., 95%), m. p. 47—48° (Found: C, 34·0; H, 1·0; Cl, 65·1. Calc. for $C_6H_2Cl_4$: C, 33·4; H, 0·9; Cl, 65·7%), having the correct infrared spectrum [mononitro-derivative, m. p. 64—65° (Found: C, 27·6; H, 0·4; N, 4·9. Calc. for $C_6HO_2NCl_4$: C, 27·6; H, 0·4; N, 5·4%)].

Dehydrogenation of the Product (XVIc).—The compound (XVIc) (2·2 g., 0·005 mol.) was heated with bromine (1 g., 0·006 mol.) in chlorobenzene (20 ml.) for 2 hr., the solvent partially evaporated *in vacuo*, and the residue diluted with methanol; the solid product recrystallised from benzene–methanol to give 2,3-*dibromo*-5,6,7,8-*tetrachloro*-1,2,3,4-*tetrahydro*-1,4-*methanonaphthalene* (XVII) (2 g., 92%), m. p. 168—169°, $\lambda_{max.}$ 222, 284, 292 mμ (ε 26,020, 290, 238), no max. near 1600 cm.$^{-1}$ (Found: C, 30·6; H, 1·7. $C_{11}H_6Cl_4Br_2$ requires C, 30·0; H, 1·4%).

Debromination of the Compound (XVII).—The dibromo-compound (1·5 g.) was heated with zinc powder (640 mg., 2 atom-equiv.) in ethanol (30 ml.) for 3 hr. under reflux; the warm mixture was filtered, concentrated, and cooled; 5,6,7,8-*tetrachloro*-1,4-*dihydro*-1,4-*methanonaphthalene*

---

[16] McBee and Newcomer, *J. Amer. Chem. Soc.*, 1949, **71**, 946.

(XVIII) crystallised as needles, m. p. 118° (810 mg., 85%), $\lambda_{max.}$ 222, 285 mμ (ε 26,930, 291) (Found: C, 47·5; H, 2·1. $C_{11}H_6Cl_4$ requires C, 47·2; H, 2·2%). This absorbed 1 mol. of hydrogen over 5% palladium on calcium carbonate, to give the *tetrahydro-compound*, needles (from methanol), m. p. 108—109°, $\lambda_{max.}$ 216, 281 mμ (ε 24,670, 360) (Found: C, 46·8; H, 2·95. $C_{11}H_8Cl_4$ requires C, 46·8; H, 2·9%).

Second Synthesis of 5,6,7,8-*Tetrachloro*-1,2,3,4-*tetrahydro*-1,4-*methanonaphthalene.*—The adduct (XVI) (7·1 g.) was hydrogenated as above, and the product recrystallised from methanol. This product (7·0 g.; m. p. 106—107°) was ground, suspended in sulphuric acid (25 ml.), and kept at room temperature for 1 hr., then poured on ice; the crude carbonyl-bridged compound was filtered off, washed with sodium hydrogen carbonate solution and water, and dried *in vacuo.* This product was heated in chlorobenzene (20 ml.); effervesence commenced at 60° and heating was continued for 1 hr., then solvent was evaporated *in vacuo* and the residue recrystallised from methanol, to give 5,6,7,8-*tetrachloro*-1,2,3,4,4a,8a-*hexahydro*-1,4-*methanonaphthalene* (3 g., 54%), m. p. 101—102°, $\lambda_{max.}$ 279, 290, 302 mμ (ε 4543, 6418, 6645), $\nu_{max.}$ 1600 s cm.$^{-1}$ (conjugated C=C) (Found: C, 46·1; H, 3·45. $C_{11}H_{10}Cl_4$ requires C, 46·5; H, 3·55%).

This product (500 mg.) with bromine (3 drops) in boiling chlorobenzene (10 ml.) for 1 hr. gave after evaporation the product (XIX) (350 mg.), m. p. and mixed m. p. 108—109° (from methanol).

5,6,7,8-*Tetrachloro*-2,3-*epoxy*-1,2,3,4-*tetrahydro*-1,4-*methanonaphthalene.*—The compound (XVIII) (2·85 g.) 0·01 mol.) was treated in benzene (15—20 ml.) with peracetic acid (from 90% hydrogen peroxide and acetic anhydride) (3·0 ml., 4 mol.), kept at 10° overnight, and then extracted with sodium hydroxide solution, washed with water, dried (Na_2SO_4), and evaporated. The residual *epoxide*, recrystallised from benzene–methanol, formed needles (1·76 g., 58%), m. p. 155°, $\nu_{max.}$ 844 s and 1195 ms cm.$^{-1}$ (epoxy-group) (Found: C, 45·0; H, 2·35. $C_{11}H_6OCl_4$ requires C, 44·6; H, 2·0%).

Reaction of the Compound (XVIII) *with Bromine.*—The compound (2·80 g.) was treated in chloroform (25 ml.) with bromine (1·6 g., 1 mol.), then diluted with methanol; the product which separated gave, on recrystallisation from chloroform–methanol, (?)6,9-*dibromo*-5,6,7,8-*tetrachloro*-1,2,3,4-*tetrahydro*-1,4-*methanonaphthalene* (3·56 g.), plates, m. p. 151—152° [mixed m. p. with (XVII) depressed] (Found: C, 30·1; H, 1·6. $C_{11}H_6Cl_4Br_2$ requires C, 30·0; H, 1·4%).

This dibromo-compound (1·1 g.) was heated with zinc dust (240 mg.) in boiling acetic acid (15 ml.) for 5 hr., and the cooled mixture was filtered and poured into water. The flocculent precipitate was filtered off and boiled with methanol, a little insoluble material filtered off, and the filtrate concentrated and allowed to crystallise. The solid which separated (30 mg.) had m. p. 95° raised to 105° by a further crystallisation [mixed m. p. with (XIX) not depressed, infrared spectra identical].

Reaction of Compound (XVIII) *with Tetracyclone.*—Tetracyclone (192 mg.) was heated with compound (XVIII) (280 mg.) in *o*-dichlorobenzene (10 ml.) for 7 hr., after which the deep red colour had faded. The solvent was evaporated *in vacuo* and the residue diluted with methanol. 1,2,3,4-Tetraphenylbenzene separated (*ca.* 200 mg.; m. p. 180—183° raised to 191° after a recrystallisation from benzene–methanol).

Reaction of Compound (XVIII) *with Phencyclone.*—Phencyclone (3·82 g.) was heated with compound (XVIII) (2·80 g., 1 mol.) in chlorobenzene (35 ml.) for 45 min., the deep green colour fading and the adduct separating. The cooled mixture was diluted with methanol, and the precipitated solid filtered off and triturated with chloroform–methanol, to give the adduct (XX) (5·5 g., 83%) which was extremely insoluble in the usual solvents and had m. p. 265—267° (decomp.), $\nu_{max.}$ 1770 vs cm.$^{-1}$ (strained-ring CO).

Pyrolysis of the Adduct (XX).—The adduct (10 g.) was heated at 200° in a hard-glass flask for 2 hr. 4,5,6,7-*Tetrachloroindene* which sublimed on the cooler walls of the flask as needles and was collected at intervals (700 mg., 30%) had m. p. 190—191°, $\lambda_{max.}$ 223, 228, 264, 298 mμ (ε 28,330, 27,030, 13,950, 230) (Found: C, 42·4; H, 1·7; Cl, 55·8. $C_9H_4Cl_4$ requires C, 42·6; H, 1·6; Cl, 55·8%). The residual solid was almost pure diphenyltriphenylene (6·8 g., 98%), m. p. 224—226° (from benzene–methanol).

4,5,6,7-Tetrachloroindene (254 mg.) (0·001 mol.) absorbed 1 mol. of hydrogen over 5% palladium on chalk, to give 4,5,6,7-*tetrachloroindane* (200 mg.), needles (from methanol), m. p. and mixed m. p. (see below), m. p. 154°, $\lambda_{max.}$ 216, 282, 292 mμ (ε 20,640, 438, 407) (Found: C, 42·2; H, 2·3; Cl, 55·8. $C_9H_6Cl_4$ requires C, 42·3; H, 2·4; Cl, 55·4%).

4,5,6,7-Tetrachloroindene (254 mg., 1 mol.) was warmed in ethanol (30—40 ml.) with furfuraldehyde (192 mg., 2 mol.) and a few drops of 5% ethanolic alkali; crystals soon separated; recrystallised from ethanol they gave the *furfurylidene derivative* (150 mg.), orange needles, m. p. 190—191° (Found: C, 51·0; H, 1·85; Cl, 43·4. $C_{14}H_6OCl_4$ requires C, 50·6; H, 1·8; Cl, 42·7%).

4,5,6,7-*Tetrachloroindane*.—Cyclopentene (6·8 g., 1 mol.) was heated with tetrachlorodimethoxycyclopentadiene (26·4 g., 1 mol.) at 150° in sealed tubes for several hours. The product was boiled with methanol and charcoal and the solution was then filtered, concentrated, and allowed to crystallise. 4,5,6,7-*Tetrachloro*-3a,4,7,7a-*tetrahydro*-4,7-*dimethoxymethanoindane* separated as needles (20 g., 60%), m. p. 84—85° (Found: C, 43·8; H, 4·2. $C_{12}H_{14}O_2Cl_4$ requires C, 43·4; H, 4·25%).

This product (20 g.) was warmed as a slurry in sulphuric acid (15 ml.) at 60—70° for 15—20 min., then poured on ice. The product was filtered off, washed with sodium hydrogen carbonate solution and water, and dried *in vacuo* (yield 14 g.). A portion (3 g.) was heated with chloranil (3 g.) in xylene (15 ml.) under reflux overnight, and the cooled mixture then diluted with benzene and extracted with sodium hydroxide solution, washed with water, and dried (Na_2SO_4). The solvents were removed under a partial vacuum and the yellow crystalline solid recrystallised from ethanol (charcoal), to give colourless 4,5,6,7-tetrachloroindane (1 g., 37%) with m. p., mixed m. p., and infrared spectrum identical with those of the product obtained as above.

Alternatively the carbonyl-bridged compound (2 g.) was heated in chlorobenzene (10 ml.) for 1 hr., and the solution treated with bromine (1·12 g.) whilst still hot; hydrogen bromide was evolved and the solution quickly became colourless. The solvent was evaporated *in vacuo* and the residue recrystallised from ethanol to give 4,5,6,7-tetrachloroindane (1 g., 56%).

Reaction of Compound (XVIII) *with Tetrachlorodimethoxycyclopentadiene*.—Compound (XVIII) (2·82 g., 1 mol.) was heated with tetrachlorodimethoxycyclopentadiene (4·0 g., 1·5 mol.) in chlorobenzene (25 ml.) for 5—6 hr., the solvent distilled off, and the residue recrystallised from benzene–methanol to give 1,2,3,4,5,6,7,8-*octachloro*-1,4,4a,9,9a,10-*hexahydro*-1,4-*dimethoxymethano*-9,10-*methanoanthracene* (XXII) (3·5 g., 65%) as needles, m. p. 218° (Found: C, 39·9; H, 2·15. $C_{18}H_{12}O_2Cl_8$ requires C, 39·8; H, 2·2%).

Hydrolysis of the Adduct (XXII).—The pure solid (3 g.) was heated in sulphuric acid (20 ml.) at 80—90° for 4—5 hr. The cooled mixture was poured on ice, and the product washed with water, dried *in vacuo*, and recrystallised from benzene–methanol, to give 1,2,3,4,5,6,7,8-*octachloro*-4a,9,9a,10-*tetrahydro*-9,10-*methanoanthracene* (XXIII) (2·5 g., 89%), needles, m. p. 214°, $\nu_{max.}$ 1600 s cm.$^{-1}$ (conjugated C=C) (cf. Figure) (Found: C, 38·2; H, 1·0. $C_{15}H_6Cl_8$ requires C, 38·3; H, 1·3%).

In a similar experiment the adduct (XXII) (10 g.) was heated with sulphuric acid (70 ml.) for 1 hr. at 70—80° and the product isolated as before (7·5 g., 80%; m. p. 214°). The infrared spectrum of this product showed a strong band at 1818 cm.$^{-1}$ and must have consisted substantially of the carbonyl-bridged compound (XXIIa) which decomposed to (XXIII) with extreme ease.

Pyrolysis of the Anthracene Derivative (XXIII).—The product (XXIII) (7·5 g.) was heated under reflux in *o*-dichlorobenzene (50 ml.) for 6 hr., the solvent evaporated *in vacuo*, the residue boiled with ethanol, a quantity of solid filtered off (3 g. of starting material), and the filtrate concentrated and cooled; needles of 4,5,6,7-tetrachloroindene separated (1·6 g., 43%), having m. p. 175—180° raised to 189—190° (mixed m. p.) by a further crystallisation from ethanol (charcoal).

Reaction of the Adduct (XVI) *with Tetrachlorodimethoxycyclopentadiene*.—The adduct (XVI) (7·12 g., 1 mol.) was heated with tetrachlorodimethoxycyclopentadiene (5·28 g., 1 mol.) in chlorobenzene (70 ml.) under reflux overnight, the solvent removed, and the residue recrystallised from benzene–methanol, to give 1,2,3,4,5,6,7,8-*octachloro*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8-*bisdimethoxymethano*-9,10-*methanoanthracene* (XXIV) (9 g., 74%), needles, m. p. 287° (Found: C, 40·9; H, 3·2; Cl, 45·3. $C_{21}H_{20}O_4Cl_8$ requires C, 40·7; H, 3·25; Cl, 45·7%).

Hydrolysis of the Di-adduct (XXIV).—The product (XXIV) (9 g.), when heated in sulphuric acid (40 ml.) at 90° for 2 hr., became a slightly pink paste. The mixture was poured on ice, and the product filtered off, washed with sodium hydrogen carbonate solution and water, and dried *in vacuo* (6 g., 77%). A small quantity was recrystallised from acetone–light petroleum (b. p. 60—80°), to give 1,2,3,4,5,6,7,8-*octachloro*-1,4,4a,5,8,8a,9,9a,10,10a-*decahydro*-1,4:5,8-*dicarbonyl*-9,10-*methanoanthracene* (XXV), plates, m. p. 258—259° (decomp.), $\nu_{max.}$ 1818 vs cm.$^{-1}$

(αα′-dihalogeno-CO, strained ring) (Found: C, 39·3; H, 1·7; Cl, 54·1. $C_{17}H_8O_2Cl_8$ requires C, 39·4; H, 1·5; Cl, 53·7%).

In a similar experiment the di-adduct (20 g.) was heated with sulphuric acid (60 ml.) for only 10 min. at 80—90°, and the thick paste was worked up as before, to give the crude carbonyl-bridged compound (12 g., 70%). This was heated in *o*-dichlorobenzene (50 ml.), gas evolution commencing at 80° and the rather insoluble product beginning to separate; the mixture was heated under reflux for 1 hr. to complete the reaction, the solvent largely distilled off *in vacuo*, and the residue diluted with methanol; the crystals were filtered off and recrystallised from benzene–methanol, to give 1,2,3,4,5,6,7,8-*octachloro*-4a,8a,9,9a,10,10a-*hexahydro*-9,10-*methanoanthracene* (XXVI) (9 g., 59% overall), needles, m. p. 254°, $\nu_{max.}$ 1600 s cm.$^{-1}$ (conjugated C=C) (cf. Figure) (Found: C, 38·7; H, 1·3. $C_{15}H_8Cl_8$ requires C, 38·2; H, 1·7%).

The compound (XXVI) (31 g., 68%), m. p. 254°, was also prepared by heating the crude carbonyl-bridged compound (XXV) (50 g.) in a beaker at 140—160° for 1 hr.

Semidehydrogenation of Compound (XXVI).—The compound (XXVI) (1·04 g.) was heated in chlorobenzene (25 ml.) with bromine (320 mg., 1 mol.) slowly to the b. p. The solution was evaporated *in vacuo*, and the residue recrystallised from benzene–methanol, to give compound (XXIII) (700 mg., 70%), m. p. 212° raised to 214° by a further crystallisation (mixed m. p. with the previous specimen undepressed, infrared spectra identical).

Pyrolysis of Solid (XXIII).—The pure solid (6 g.) was heated at 180° until all molten; 1,2,3,4-tetrachlorobenzene distilled on to the cooler parts of the vessel and after 1 hour's heating the mixture was cooled and extracted with methanol, the tetrachlorobenzene readily dissolving. The extracts were concentrated and allowed to crystallise, giving 1,2,3,4-tetrachlorobenzene (400 mg., 30%), needles m. p. 43—44° raised to 47—48° (mixed m. p.) by a further crystallisation. The less soluble reaction residue recrystallised from ethanol, to give 4,5,6,7-tetrachloroindene (2 g., 61%), m. p. 187° raised to 190° by a further crystallisation.

Dehydrogenation of Compound (XXVI).—The compound (XXVI) (1·04 g., 1 mol.) was treated with bromine (640 mg., 2 mol.) in chlorobenzene (25 ml.); isolation in the usual way gave 1,2,3,4,5,6,7,8-*octachloro*-9,10-*dihydro*-9,10-*methanoanthracene* (XXIIIa) (400 mg.), m. p. 274—275° (see Figure) (no absorption near 1600 cm.$^{-1}$) (Found: C, 39·0; H, 1·0; Cl, 61·2. $C_{15}H_4Cl_8$ requires C, 38·5; H, 0·9; Cl, 60·6%).

The author expresses his appreciation of the interest and encouragement of The Government Chemist, the late Dr. G. M. Bennett, C.B., F.R.S., during the course of this work; he also thanks the Acting Government Chemist for permission to publish this work, the Civil Service Commissioners for a Research Fellowship, and The Shell Chemical Company for gifts of materials.

THE LABORATORY OF THE GOVERNMENT CHEMIST,
CLEMENT'S INN PASSAGE, LONDON, W.C.2.

[*Received, June* 24*th*, 1959.]