Stereochemistry of the 2:1 [4 + 2] Adducts of Tetrachlorocyclopentadienone Acetals with Cyclohepta-1,3,5-triene, Tropone, Cyclohexa-1,4-diene, and *p*-Benzoquinone

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The 2:1 [4 + 2] adducts of tetrachloropentadienone acetals with cycloheptatriene and cyclohexa-1,4-diene have *endo,syn,endo*-structures [(III) and (XI)], whereas those with tropone and *p*-benzoquinone possess *endo,-anti,endo*-geometry [(IV) and (XIII)]. The 2:1 adducts derived from cycloheptatriene and cyclohexa-1,4-diene have 'fixed' conformations, the central ring systems being sterically incapable of conformational inversion. Variable-temperature n.m.r. studies indicate that conformational rigidity also exists in the 2:1 adduct of tropone, although the cyclohept-4-enone ring could in principle undergo a degenerate conformational change [(IVa) ⇌ (IVb)].

DIELS–ALDER addition of tetrachlorocyclopentadienone acetals to cyclohepta-1,3,5-triene results in 1:1 and 2:1 adducts.[1] The initial product from 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene and cycloheptatriene is known to be the *endo*-1:1 adduct (I),† since this can be made to undergo an intramolecular [4 + 2] cycloaddition *via* the conformer (Ib) to afford the caged isomer (II).[2] The 2:1 adduct may now be formulated as the *endo,syn,endo*-compound (III; X = $\overline{\text{C·O·[CH}_2\text{]}_2\text{·O}}$) on the following grounds. Its n.m.r. spectrum showed the presence of two vinylic protons (H-1 and H-2) [for numbering see structure (III)], which resonated as a singlet (τ 4·51); one pair of methine protons (H-3 and H-4) produced a doublet (centred at τ 6·66), and the other pair (H-5 and H-6) a more complex yet symmetrical signal (τ 7·15—7·5); one methylene proton (H-7) gave rise to a double triplet (centred at τ 8·02), and another (H-8) to an apparent quartet which was actually two overlapping triplets (centred at τ 9·19).‡ A similar spectrum was obtained for the analogous product [III; X = $C(OMe)_2$][1] from 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (see Experimental section). The approximate geminal and vicinal coupling constants are listed in Table 1.

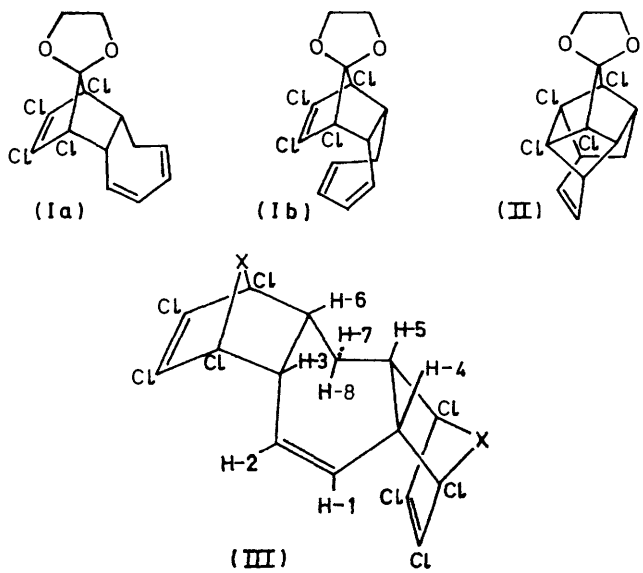
TABLE 1

Approximate coupling constants (Hz) for adduct {III; X = $\overline{\text{C·O·[CH}_2\text{]}_2\text{·O}}$ or $C(OMe)_2$} (from 100 MHz spectrum; sweep-width 1000 Hz)

$J_{1,4}$ (= $J_{2,3}$)	$J_{3,6}$ (= $J_{4,5}$)	$J_{5,7}$ (= $J_{6,7}$)	$J_{5,8}$ (= $J_{6,8}$)	$J_{7,8}$
0 [a]	9	2	13	−13 [b]

[a] The dihedral angles must be close to 90°. [b] The negative sign is assumed.

These results are consistent only with structure (III), in which the two vinylic protons (H-1 and H-2) are in identical environments, as are the methine pairs H-3 and H-4, and H-5 and H-6, but in which the two methylene protons (H-7 and H-8) are non-identical. In this structure the cycloheptane ring is sterically incapable of conformational inversion.



Hence, in the formation of the 2:1 adduct (III; X = $\overline{\text{C·O·[CH}_2\text{]}_2\text{·O}}$), the Diels–Alder reaction must involve an *endo*-addition to conformer (Ia) of the 1:1 adduct, on the least hindered side of the cyclohepta-2,4-diene ring. Although the geometry of the 2:1 adduct cannot provide information concerning the relative energies of the conformers (Ia) and (Ib), it is evident that conformer (Ia) is subject to less severe steric interactions than is the more compressed form (Ib), and should therefore predominate.

In contrast with the above, the n.m.r. spectrum of the analogous 2:1 adduct [5] of tropone exhibited a double doublet centred at τ 3·82 (H-1) [for numbering see

† In the reactions of cycloheptatriene with hexachlorocyclopentadiene and tetrachlorocyclopentadienone acetals, the formation of 1:1 adducts resulting from exclusive *endo*-[4 + 2] cycloaddition [2] is presumably controlled by the steric effects of the groups in the 5-position of the cyclopentadiene ring; an *exo*-[6 + 4] mode (*cf.* ref. 3) would be inhibited by such effects. An *endo*-[6 + 4] cycloaddition might be sterically possible, but would involve unfavourable secondary orbital interactions in the transition state.[4]

‡ The protons of the ethylenedioxy-groups gave a complex signal at τ 5·7—6·0 (8H).

[1] K. H. Büchel and A. Conte, *Chem. Ber.*, 1967, **100**, 863.
[2] I. A. Akhtar, D. M. Bratby, and G. I. Fray, *J. Chem. Soc.* (*C*), 1969, 2716.
[3] K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, 1970, **92**, 4143.
[4] R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, 1965, **87**, 4388.
[5] R. G. Saxton, B.Sc. Thesis, Bristol University, 1969.

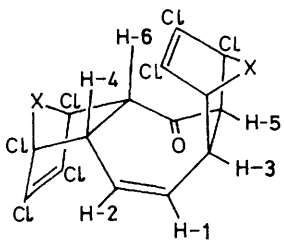
structure (IVa)] and a doublet τ 4·05 (H-2) for the two vinylic protons; the four methine protons gave overlapping signals (τ 6·35—6·75), which could however be analysed as a double doublet (H-3) and three individual doublets (H-4, H-5, and H-6).* These splittings, and the values of the vicinal coupling constants given in Table 2, are entirely in accord with the *endo,anti,endo*-structure (IV; X = C·O·[CH_2]$_2$·O). This system could conceivably undergo the degenerate conformational change (IVa) ⇌ (IVb); however, even at 180° (solution in [$^2H_6$]dimethyl sulphoxide) the n.m.r. spectrum showed no alteration in the pattern of the signals due to the vinylic protons, which would appear equivalent if such a change were rapid on the n.m.r. time scale.

TABLE 2

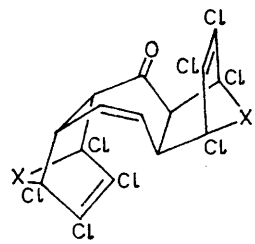
Approximate coupling constants (Hz) for adduct (IV; X = C·O·[CH_2]$_2$·O) (from 100 MHz spectrum; sweep-width 250 Hz)

$J_{1,2}$	$J_{1,3}$	$J_{2,4}$	$J_{3,5}$	$J_{4,6}$
12·5	5·5	0 [a]	9·5	10

[a] The dihedral angle must be close to 90°.



(IVa)



(IVb)

An attempt to confirm the anticipated stereochemistry of the initial diene addition, by examination of the 1 : 1 adduct, was thwarted by the failure to isolate any of this product, even when a large excess of tropone was used. Nevertheless, the presence of at least one *endo*-fusion in the 2 : 1 adduct was revealed when the compound was treated with concentrated sulphuric acid. Under these conditions hydrolysis of one acetal grouping was followed by a Cope-type rearrangement, with the formation of a product having i.r. ($\nu_{max.}$ 1748, 1713, and 1593 cm^{-1}) and u.v. [$\lambda_{max.}$ 252·5 nm (ε 8700)] spectra in agreement with structure (V; X = C·O·[CH_2]$_2$·O) (*cf.* ref. 6); an *endo*-arrangement of the interacting systems is of course obligatory for the intramolecular rearrangement step.

No such rearrangement took place with the cycloheptatriene 2 : 1 adduct (III; X = C·O·[CH_2]$_2$·O); the more readily hydrolysed analogue [III; X = $C(OMe)_2$][1] afforded the bis-carbonyl-bridged derivative (III; X = CO) ($\nu_{max.}$ 1823 cm^{-1}), the stereochemistry of which precludes the adoption of the transition state required for rearrangement.

For the 2 : 1 adduct of tropone, the above evidence cannot be accommodated by any structure in which there is a *syn*-arrangement of the norbornene systems, and it has already been demonstrated that one of these systems must have the *endo*-configuration. The only possible alternative to structure (IV; X = C·O·[CH_2]$_2$·O) was therefore the *endo,anti,exo*-formulation (VIa or b) (non-degenerate conformers), but this was considered unlikely on steric grounds. Support for this view was obtained on treatment of the analogous 2 : 1 adduct [IV; X = $C(O{\cdot}CH_2Ph)_2$] (prepared from tropone and 1,2,3,4-tetrachloro-5,5-dibenzyloxycyclopentadiene) with trifluoroacetic acid, which effected hydrolysis of both acetal groups to yield the rearranged triketone (V; X = CO), $\nu_{max.}$ 1826, 1753, and 1719 cm^{-1}. In the n.m.r. spectrum of this product, the chemical shifts of the vinylic protons were almost identical with those displayed by the vinylic protons of the acetal diketone (V; X = C·O[CH_2]$_2$·O). While this observation is understandable if the proposed stereochemistry is correct, it would not be expected for structures (VII; X = C·O·[CH_2]$_2$·O) and (VII; X = CO), in which the vinylic protons would be close to the group X. We therefore conclude that the above 2 : 1 adducts of tropone must be represented as *endo,anti,endo*-compounds (IV).

The stereochemistry of the 2 : 1 adducts (IV) derived from tropone is thus different from that of the corresponding cycloheptatriene derivatives (III), addition to the respective 1 : 1 adducts occurring on opposite sides of the dienophilic double bond. A ready explanation of this result emerges if the dienone system in a 1 : 1 adduct of tropone is essentially planar, as shown in (VIII); addition of the diene component in the *endo*-mode and on the exposed side of the dienophilic grouping, would then furnish the required stereochemistry (IV). For the cyclohepta-2,4-dienone ring to achieve planarity, the stabilisation gained by substantial conjugation, in terms of orbital overlap, must be sufficient to overcome the ring strain inherent in such a system. Since a 1 : 1 adduct (VIII) could not be prepared, no direct supporting evidence for planarity of the seven-membered ring could be obtained. However, the carbonyl stretching frequency of 2,4,4-trimethylcyclohepta-2,4-dienone [$\nu_{max.}$ (liquid) 1661 cm^{-1}] [7] seems to indicate a much greater degree of conjugation than would be anticipated if the seven-membered ring were highly puckered and n.m.r. evidence indicates an almost planar π-system in this compound and in cyclohepta-2,4-dienone.[8]

* The protons of the ethylenedioxy-groups gave a complex resonance at τ 5·6—6·0 (8H).

[6] G. I. Fray and D. P. S. Smith, *J. Chem. Soc.* (*C*), 1969, 2710.

[7] G. P. Scott and D. S. Tarbell, *J. Amer. Chem. Soc.*, 1950, **72**, 240.

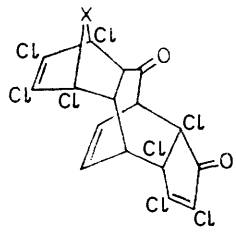
[8] D. J. Bertelli, T. G. Andrews, and P. O. Crews, *J. Amer. Chem. Soc.*, 1969, **91**, 5286.

A second example of the above phenomenon was found with cyclohexa-1,4-diene and *p*-benzoquinone as dienophiles. An *endo,syn,endo*-stereochemistry for the 2 : 1 adduct [9] of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and cyclohexa-1,4-diene was proved as follows.

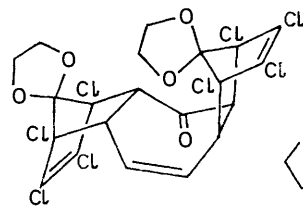
An initial *endo*-addition of the reactants to give the 1 : 1 adduct [IX; X = $C(OMe)_2$] [9] may be inferred by analogy with the closely related compound (IX; X = $\dot{C}\cdot O\cdot[CH_2]_2\cdot\dot{O}$), which on u.v. irradiation yields the cyclised product (X; X = $\dot{C}\cdot O[CH_2]_2\cdot\dot{O}$, Y = CH_2, R = Cl).[10] In the n.m.r. spectrum of the 2 : 1 adduct, the four methine protons gave a complex but symmetrical signal at τ 7·3—7·7; one pair of methylene protons resonated as a double triplet centred at τ 8·15 (*J ca.* −13 * and 4 Hz), and the other pair as a symmetrical complex at τ 9·3—9·7.† The equivalence of the four methine protons, together with the non-equivalence of the two pairs of methylene protons, enables the *endo,syn,endo*-structure (XI) to be assigned unequivocally.‡ Like structure (III), structure (XI) has a 'fixed' conformation, in the sense that complete inversion of the central ring is sterically prevented. As might have been predicted, the more stable conformer [IXa; X = $C(OMe)_2$] of the 1 : 1 adduct is evidently involved in the second cycloaddition.

The mode of this addition contrasts with that adopted by cyclopentadiene in its reaction with the *endo*-1 : 1 adduct (XII; X = CH_2, R = H),[11] since the resulting 2 : 1 adduct has been shown to possess an *endo,anti,endo*-geometry (XIII; X = CH_2, R = H).[12,13] As in the case of tropone, planarity of the dienophilic system in the 1 : 1 adduct provides a rationale for this result. It may be noted that, in *endo*-additions to the dienophiles (IX) and (XII), secondary orbital interactions [4] are possible only with the ene-1,4-dione (XII), and only in a transition state in which the enedione system is planar. For the dienophile (XII), the formation of an *endo,syn,endo*-product would, for obvious steric reasons, require a non-planar enedione grouping, both initially and in the transition state.

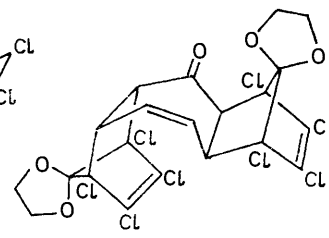
Addition of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene to *p*-benzoquinone affords a 1 : 1 adduct [XII; X = $C(OMe)_2$, R = Cl],[14] $\nu_{max.}$ (CCl_4) 1686 cm^{-1}, the *endo*-configuration of which has been proved by its photoisomerisation to the cage-like structure [X; X = $C(OMe)_2$, Y = CO, R = Cl].[15] By further reaction there was obtained a 2 : 1 adduct, which could be assigned structure [XIII; X = $C(OMe)_2$, R = Cl] by analogy with the cyclopentadiene product (XIII; X = CH_2, R = H). An attempt was made to elucidate the conformation of the cyclohexanedione ring by



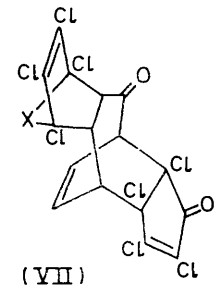
(V)



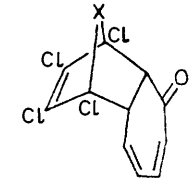
(VIa)



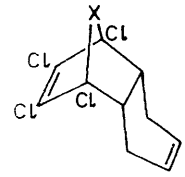
(VIb)



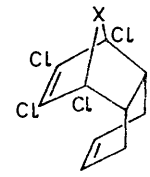
(VII)



(VIII)



(IXa)



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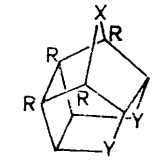
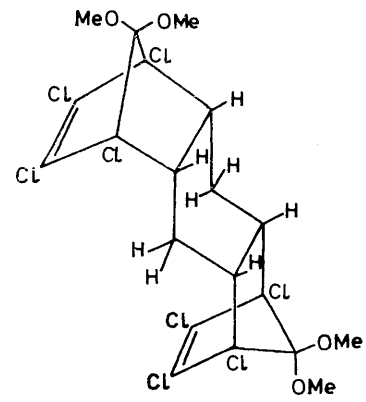
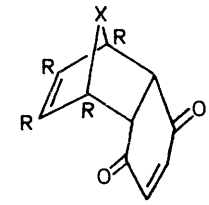


(X)



(XI)



(XII)

* The negative sign is assumed.

† The protons of the methoxy-groups gave two singlets at τ 6·50 (6H) and 6·55 (6H).

‡ The resonance of one pair of methylene protons at very high field may be attributable to anisotropic shielding by the π-bonds.

[9] I. A. Akhtar and G. I. Fray, *J. Chem. Soc.* (*C*), 1971, 2802.

[10] R. J. Stedham, L. S. Miller, and J. R. E. Hoover, *Tetrahedron Letters*, 1966, 2721.

[11] R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 1964, 3062.

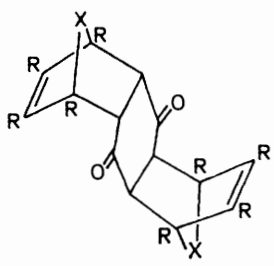
[12] L. deVries, R. Heck, R. Piccolini, and S. Winstein, *Chem. and Ind.*, 1959, 1416.

[13] R. C. Cookson, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, **1964**, 3043.

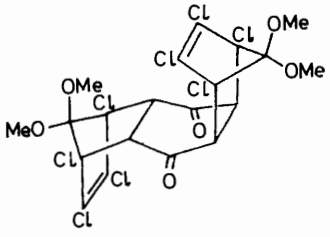
[14] E. T. McBee, W. R. Dively, and J. E. Burch, *J. Amer. Chem. Soc.*, 1955, **77**, 385.

[15] E. M. Bessell, B.Sc. Thesis, Bristol University, 1967; M. Akhtar, Ph.D. Thesis, Bristol University, 1970.

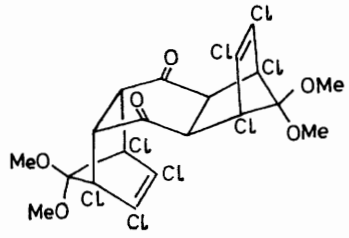
variable-temperature n.m.r. spectroscopy. At room temperature, the four methine protons of the 2 : 1 adduct [XIII; X = $C(OMe)_2$, R = Cl] produced a singlet (τ 6·37),* and the appearance of the signal was unchanged at −100° (solution in dichloromethane); † the cyclohexanedione ring could therefore by planar (*cf.* ref. 13). The adoption of a planar conformation would necessitate the acceptance of a strained dione ring, but on the other hand would minimise non-bonded repulsions in the molecule. However, the evidence would also be consistent with a boat-shaped cyclohexanedione ring which was undergoing a degenerate conformational change, (XIVa) ⇌ (XIVb), still rapid at −100°.



(XIII)



(XIVa)



(XIVb)

EXPERIMENTAL

Light petroleum means the fraction of b.p. 40—60°; i.r. spectra were determined for Nujol mulls; n.m.r. spectra were measured at 100 MHz for solutions in deuteriochloroform.

1,2,3,4-*Tetrachloro*-5,5-*ethylenedioxycyclopentadiene–Cycloheptatriene* 2 : 1 *Adduct* (III; X = $\overline{C{\cdot}O{\cdot}[CH_2]_2{\cdot}O}$).—A mixture of 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene [16] (15·7 g), cycloheptatriene (2·8 g), and xylene (25 ml) was heated under reflux for 17 h. The solvent was removed under reduced pressure, and the residue was chromatographed on silica. The product was eluted with 50% benzene–light petroleum, and afforded the 2 : 1 *adduct* (3·1 g, 17%), m.p. 276—278° (from chloroform–methanol) (Found: C, 40·9; H, 2·4; Cl, 46·3. $C_{21}H_{16}Cl_8O_4$ requires C, 40·9; H, 2·6; Cl, 46·05%); $\nu_{max.}$ 1597 cm^{-1}; for n.m.r. spectrum see Discussion section.

1,2,3,4-*Tetrachloro*-5,5-*dimethoxycyclopentadiene–Cycloheptatriene* 2 : 1 *Adduct* [III; X = $C(OMe)_2$].—This was prepared as described by Büchel and Conte; [1] τ 4·52 (2H, s), 6·46 (3H, s), 6·52 (3H, s), 6·67 (2H, d, *J ca.* 9 Hz), 7·15—7·5 (2H), 8·02 (1H, dt, *J ca.* −13 and 2 Hz), and 9·28 (1H, dt, *J ca.* −13 and 13 Hz).

1,2,3,4-*Tetrachloro*-5,5-*ethylenedioxycyclopentadiene–Tropone* 2 : 1 *Adduct* (IV; X = $\overline{C{\cdot}O{\cdot}[CH_2]{\cdot}O}$) (with R. G. Saxton).—The cyclopentadienone acetal (5·2 g) was heated with tropone [17] (2·1 g) in refluxing toluene (100 ml) for 22 h. Removal of the solvent, followed by extraction of the residue with boiling ethanol and recrystallisation of the ethanol-insoluble material from chloroform–ethanol, gave the 2 : 1 *adduct* (5·0 g, 79·5%), m.p. 246·5—247·5° (rapid heating) (Found: C, 40·0; H, 2·2; Cl, 45·1. $C_{21}H_{14}Cl_8O_5$ requires C, 40·1; H, 2·2; Cl, 45·1%); $\nu_{max.}$ 1679 and 1579 cm^{-1}; for n.m.r. spectrum see Discussion section.

1,2,3,4-*Tetrachloro*-5,5-*dibenzyloxycyclopentadiene–Tropone* 2 : 1 *Adduct* [IV; X = $C(O{\cdot}CH_2Ph)_2$].—A mixture of 1,2,3,4-tetrachloro-5,5-dibenzyloxycyclopentadiene [18] (7·0 g), tropone (2·0 g), and toluene (20 ml) was heated under reflux for 20 h. Removal of the solvent and chromatography of the residue on silica gave a fraction (eluted with 50% benzene–light petroleum) which afforded the 2 : 1 *adduct* (1·8 g, 23%), m.p. 142·5—143·5° (from chloroform–light petroleum) (Found: C, 57·4; H, 3·6; Cl, 30·3. $C_{45}H_{34}Cl_8O_5$ requires C, 57·6; H, 3·7; Cl, 30·2%); $\nu_{max.}$ 1668 and 1598 cm^{-1}; τ 2·65—2·95 (20H), 3·7—4·2 (2H), 4·9—5·3 (8H), and 6·25—6·65 (4H).

Treatment of the Cycloheptatriene Adduct [III; X = $C(OMe)_2$] *with Sulphuric Acid.*—A mixture of the 2 : 1 adduct [III; X = $C(OMe)_2$] (3·0 g) and concentrated sulphuric acid (100 ml) was shaken at room temperature for 4 h. The mixture was poured on ice, and the resulting solid was collected, washed with water, and dried. Recrystallisation from benzene then yielded the *diketone* (III; X = CO) (2·2 g, 86%), m.p. *ca.* 210° (decomp.) (rapid heating) (Found: C, 39·0; H, 1·6; Cl, 53·2. $C_{17}H_8Cl_8O_2$ requires C, 38·7; H, 1·5; Cl, 53·7%); $\nu_{max.}$ 1823 and 1585 cm^{-1}.

Treatment of the Tropone Adduct (IV; X = $\overline{C{\cdot}O{\cdot}[CH_2]_2{\cdot}O}$) *with Sulphuric Acid.*—A slurry of the 2 : 1 adduct (IV; X = $\overline{C{\cdot}O{\cdot}[CH_2]_2{\cdot}O}$) (1·25 g) in concentrated sulphuric acid (65 ml) was heated on a steam-bath, with stirring, until a clear solution was obtained (*ca.* 15 min). Work-up in the usual way afforded the rearranged *acetal diketone* (V; X = $\overline{C{\cdot}O{\cdot}[CH_2]_2{\cdot}O}$) (1·05 g, 90%), m.p. *ca.* 285° (decomp.) (rapid heating) (from chloroform–ethanol) (Found: C, 39·1; H, 1·8; Cl, 48·55. $C_{19}H_{10}Cl_8O_4$ requires C, 38·95; H, 1·7; Cl, 48·4%); $\nu_{max.}$ 1748, 1713, and 1593 cm^{-1}; $\lambda_{max.}$ (CH_2Cl_2) 252·5 nm (ε 8700); τ 3·7—3·95 (1H), 4·2—4·45 (1H), 5·6—5·95 (4H), and 6·0—6·55 (4H).

Treatment of the Tropone Adduct [IV; X = $C(O{\cdot}CH_2Ph)_2$] *with Trifluoroacetic Acid.*—The 2 : 1 adduct [IV; X = $C(O{\cdot}CH_2Ph)_2$] (0·5 g) was dissolved in a warm mixture of trifluoroacetic acid (7 ml) and water (0·5 ml), and the

* The protons of the methoxy-groups gave rise to two singlets at τ 6·49 (6H) and 6·53 (6H).

† Examination of the (more complex) signal due to the corresponding methine protons in the cyclopentadiene–*p*-benzoquinone 2 : 1 adduct (XIII; X = CH_2, R = H), at room temperature and at −100°, led to a similar result for this molecule also.

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solution was left at room temperature overnight. Evaporation under reduced pressure and recrystallisation of the residue from benzene then gave the rearranged *triketone* (V; X = CO) (0·2 g, 68%), m.p. *ca.* 230° (decomp.) (rapid heating) (Found: C, 37·7; H, 1·1; Cl, 51·7. $C_{17}H_6Cl_8O_3$ requires C, 37·7; H, 1·1; Cl, 52·3%); $\nu_{max.}$ 1826, 1753, 1719, and 1600 cm^{-1}; τ 3·65—3·9 (1H), 4·1—4·4 (1H), and 5·95—6·7 (4H).

1,2,3,4-*Tetrachloro*-5,5-*dimethoxycyclopentadiene*–p-*Benzoquinone* 2 : 1 *Adduct* [XIII; X = $C(OMe)_2$, R = Cl].—A mixture of the 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene–*p*-benzoquinone 1 : 1 adduct [14] (1·0 g), 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene [19] (2·0 g), and xylene (25 ml) was heated under reflux for 41 h. After removal of the solvent, treatment of the residual oil with ether afforded a crystalline solid, which afforded the 2 : 1 *adduct* (1·1 g, 64·5%), m.p. 258—260° (decomp.) (rapid heating) (from dichloromethane–ether) (Found: C, 38·0; H, 2·5; Cl, 44·85. $C_{20}H_{16}Cl_8O_6$ requires C, 37·8; H, 2·5; Cl, 44·6%); $\nu_{max.}$ 1720 and 1603 cm^{-1}; for n.m.r. spectrum see Discussion section.

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