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REACTIONS OF CYCLO-OCTATETRAENE AND ITS DERIVATIVES—VIII[1]

1,2,3,8- AND 1,2,3,4-TETRACHLOROCYCLO-OCTATETRAENE

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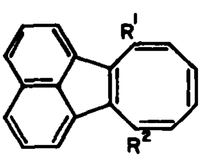
Abstract—Earlier attempts to synthesize 1,2,3,8-tetrachlorocyclo-octatetraene 4 are described. A *ca.* 2:1 mixture of 1,2,3,8- and 1,2,3,4-tetrachlorocyclo-octatetraene was finally obtained by hydrolysis (using 96% trifluoroacetic acid) of the ketal 15 followed by thermal decarbonylation of the product. Reaction of the mixture of cyclo-octatetraenes with bromine gave the (separable) dibromo-derivatives 17 and 18. On attempted debromination with zinc, the dibromodiene 17 formed the benzocyclobutadiene dimer 12, together with the benzobiphenylene 13; these compounds were also produced directly from the cyclo-octatetraene mixture by the action of zinc. In contrast, similar treatment of the dibromodiene 18 led to the *E*-bromostyrene 22. The mixture of cyclo-octatetraenes reacted with maleic anhydride to give the adduct 27, whereas with acenaphthylene the adduct 28 was obtained.

The synthesis of 1,2-acenaphtho-3,8-disubstituted derivatives of cyclo-octatetraene, 1, from the cyclo-octatetraene-dimethyl acetylenedicarboxylate adduct 2 by reaction with acecyclone and related cyclopentadienones 3 has been reported.[2] Earlier, studies[3,4] of an essentially analogous route to 1,2,3,8-tetrachlorocyclo-octatetraene 4 had been made as follows.

Compound 5, available[3-6] from the [4+2] cycloaddition of 1,2,3,4 - tetrachloro - 5,5 - dimethoxycyclopentadiene to 2, was converted into the tetraene-dimethyl ester 6 by hydrolysis of the ketal function with concentrated sulphuric acid and subsequent decarbonylation at 110–120°. Extrusion of dimethyl phthalate by [4+2] cycloreversion was then effected in refluxing xylene, but at least six other products were formed (tlc). In contrast, similar thermolysis of the ketal-bridged compound 5 is a clean reaction leading to the cyclobutene 7, of proved stereochemistry,[4-7] and the proposed route to the cyclo-octatetraene 4 was modified accordingly. Protection of the cyclobutene double bond by (light-catalysed) bromination gave the *cis*-dibromoketal 8 (see Ref. 7), which was hydrolysed and decarbonylated in the usual way to afford the *cis*-dibromodiene 9. A *cis*-configuration for the Br atoms was indicated by the PMR spectra of 8 and 9, and confirmed by the spectrum of the N-phenyltriazolinedione adduct 10 [*cf* that of the



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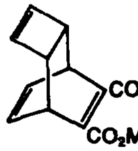

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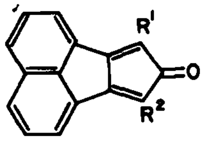

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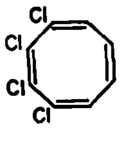

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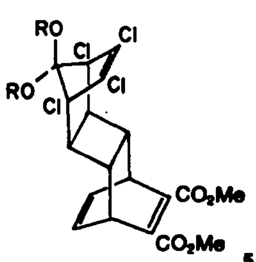

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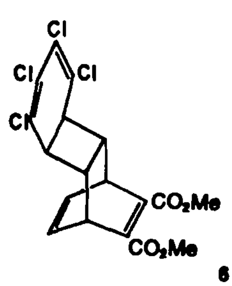

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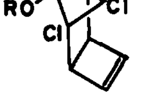

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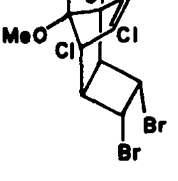

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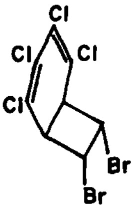

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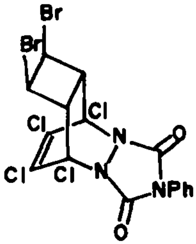

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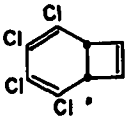

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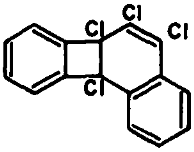

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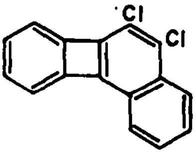

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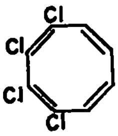

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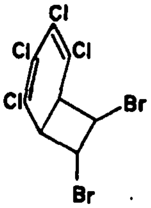

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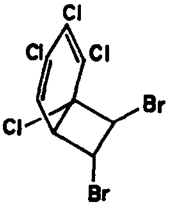

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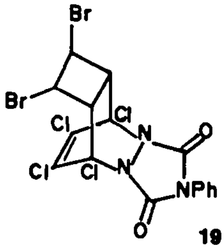
similar adduct derived from the corresponding *trans*-dibromodiene (see below)]. Debromination of the *cis*-dibromodiene 9 was expected to furnish the tetrachlorocyclo-octatetraene 4 via *retro*-6π electrocyclisation of its valence tautomer 11. Treatment of 9 with zinc dust in refluxing ethanol, however, resulted in a mixture of the benzocyclobutadiene dimer 12 and the benzobiphenylene 13 (see below).

Finally, the bromination-debromination procedure was avoided by working with the dibenzyloxy-compound 14 (prepared from 2 and 1,2,3,4-tetrachloro-5,5-dibenzyloxycyclopentadiene), which cleaved at *ca.* 150° to yield the cyclobutene 15. Hydrolysis of the dibenzyloxy-group in 15 was accomplished with 96% trifluoroacetic acid,[8] without prior protection of the cyclobutene double bond, and thermal decarbonylation of the resulting carbonyl-bridged compound then gave a product which was identified as a *ca.* 2:1 mixture of 1,2,3,8-tetrachlorocyclo-octatetraene 4 and its bond-shift isomer, 1,2,3,4-tetrachlorocyclo-octatetraene 16. During the course of this work, Warrener *et al.*[9] reported the preparation of the bicyclic triene 11 and its conversion at 60° into the monocyclic tetraene 4; at a higher temperature (150°), this equilibrated with its bond-shift 16, but it was not found possible to obtain a pure sample of the latter.

The mixture of the two tetrachlorocyclo-octatetraenes



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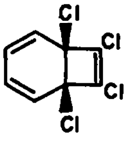

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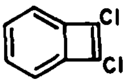

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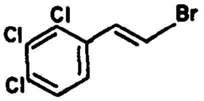

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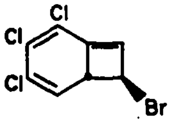

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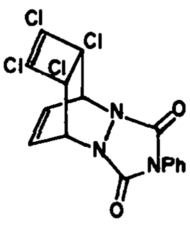

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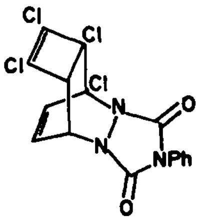

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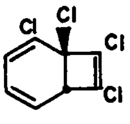

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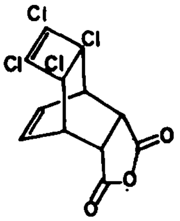

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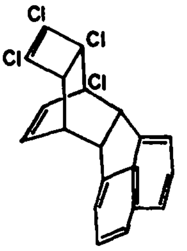

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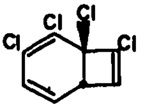

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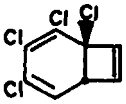

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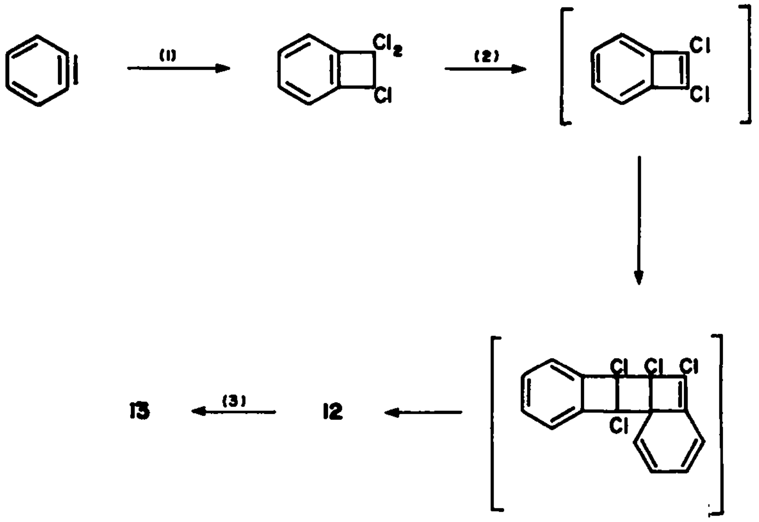
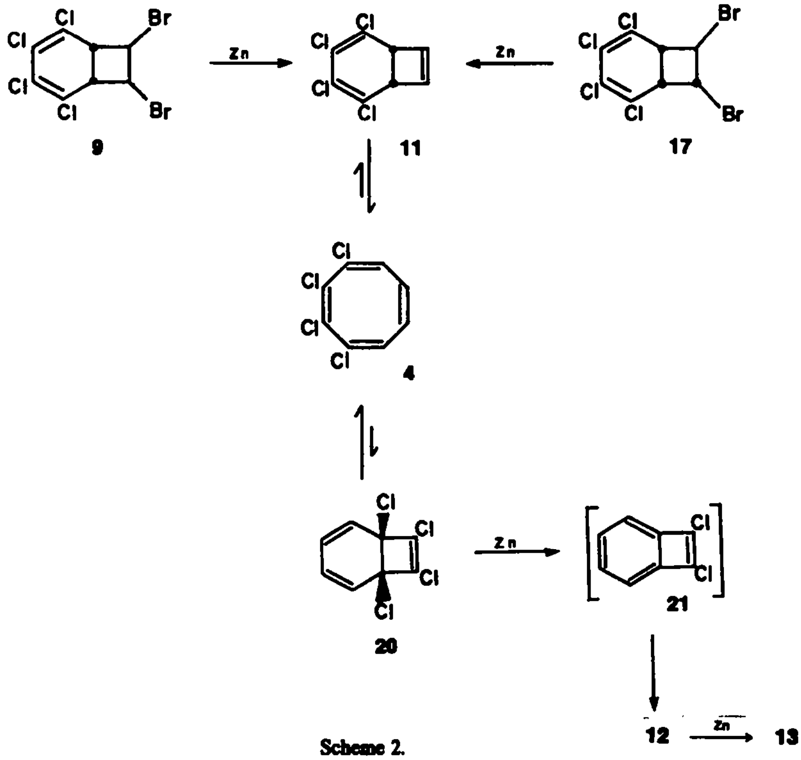
4 and 16 obtained in the present work reacted slowly with bromine under the influence of UV light to yield a separable mixture of two dibromides, formulated as 17 and 18 (PMR spectra). Further evidence for the *trans*-configuration of the Br atoms in 17 was provided by the PMR spectrum of its adduct 19 with N-phenyl-triazolinedione. As with the *cis*-dibromodiene 9, reaction of the *trans*-dibromodiene 17 with zinc led to the products 12 and 13, identical with samples synthesised[10] in this Department by the route outlined in Scheme 1.[11] It is reasonable to suppose that the dibromodienes 9 and 17 gave the bicyclic triene 11 on zinc debromination, but that the initial product equilibrated with the isomer 20 via the cyclo-octatetraene 4; in the presence of an excess of zinc, the triene 20 then suffered dechlorination to give the benzocyclobutadiene 21, which dimerised to afford 12, further dechlorination of which resulted in the benzobiphenylene 13 (Scheme 2). Support for this view was obtained by treatment of the tetrachlorocyclo-octatetraene mixture (4+16) with zinc, which again provided 12 and 13.

Attempted debromination of the second *trans*-



Reagents: (1) $Cl_2C{=}CHCl$; (2) KOBu^t; (3) Zn, EtOH

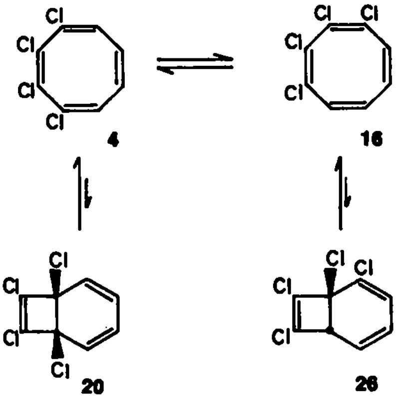
Scheme 1.



Scheme 2.

dibromodiene 18 gave a product which could be formulated as the *E*-bromostyrene 22 (PMR spectrum). This could have been formed by thermally-allowed conrotatory ring-opening of an intermediate 23.[12]

It has been shown[9] that the cyclo-octatetraenes 4 and 16 add N-phenyltriazolinedione to afford the products 24 and 25 respectively, indicating the involvement of the valence tautomers 20 and 26 in these [4+2] cycloadditions. We found that the *ca.* 2:1 mixture of 4 and 16 reacted with maleic anhydride in refluxing xylene to yield the adduct 27† (79%), and with acenaphthylene in the same solvent to give the adduct 28† (60%). Thus, under these reaction conditions, the two cyclo-octatetraenes 4 and 16 and the bicyclic trienes 20 and 26 must all have been in equilibrium (Scheme 3), and while maleic anhydride preferred 20 as a Diels–Alder partner, acenaphthylene reacted faster with 26. The latter reaction has "inverse" electron-demand,[13] and receives a ready explanation in terms of frontier orbital theory[14] (the other possible valence tautomers, 11, 29 and 30, if present, would all offer even more electron-deficient 1,3-diene systems, but steric factors might be expected to intervene).



Scheme 3.

EXPERIMENTAL

Unless stated otherwise, light petroleum refers to the fraction of b.p. 60–80°, and PMR measurements to the 100 MHz spectra of CCl_4 solns. IR spectra were determined for Nujol mulls, and U.V. spectra for solns in EtOH.

The triene-ketal-dimethyl ester 5 [with Kettlewell[3]]. This was prepared (52%) from 2 and 1,2,3,4 - tetrachloro - 5,5 - dimethoxycyclopentadiene[15] in refluxing toluene (16 hr); m.p. 180.5–181.5° (lit. 186°,[5,7] 182.5–185.5°[6]).

The tetraene-dimethyl ester 6 [with Kettlewell[3]]. Finely powdered 5 (8.5 g) in conc H_2SO_4 (50 ml) was kept for several days at room temp. with occasional shaking. The resulting soln was filtered through sintered glass and the filtrate was poured onto ice. The solid product was collected, washed thoroughly with water, and dried, giving the crude carbonyl-bridged product (IR ν_{max} 1814 cm^{-1}). This was then heated in xylene (50 ml) at 110–120° for 45 min. Removal of the solvent and crystallisation of the residue from Me_2CO afforded 6 (4.3 g, 59%), m.p. 198–199°. (Found: C, 49.4; H, 3.0; Cl, 32.8. $C_{18}H_{14}Cl_4O_4$ requires: C, 49.6; H, 3.2; Cl, 32.5%); IR ν_{max} 1723, 1700, 1640, 1610 cm^{-1}; UV λ_{max} 295 nm (ϵ 4360); PMR τ ($CDCl_3$) 3.4–3.6 (2H), 5.75–5.95 (2H), 6.31 (s, 6H), 7.35–7.55 (4H).

The ketal-diene 7 [with Akhtar[4]]. Heating 5 in refluxing xylene overnight gave 7 (93%), m.p. 85–87° (lit. 80–81°,[5,7] 83.5–84.5°[6]).

The cis-*dibromoketal* 8 [with Akhtar[4]]. A mixture of 6 (2.9 g) and Br_2 (1.45 g) in CCl_4 (5 ml) was irradiated with a UV lamp at room temp. until the uptake of Br_2 was complete (*ca.* 5 hr). Evaporation of the solvent then gave 8 (4.0 g, 93%), m.p. 119.5–120.5°, from light petroleum, b.p. 40–60°. (Found: C, 27.8; H, 2.1; Br, 32.9; Cl, 30.1. $C_{11}H_{10}Br_2Cl_4O_2$ requires: C, 27.8; H, 2.1; Br, 33.0; Cl, 29.9%); IR ν_{max} 1600 cm^{-1}; PMR τ 5.7–5.9 (2H), 6.45–6.65 (8H).

cis - anti - 7,8 - *Dibromo* - 2,3,4,5 - *tetrachloro* - *bicyclo*[4.2.0]*octa* - 2,4 - *diene* 9 [with Akhtar[4]]. Reaction of finely powdered 8 (6.0 g) with conc H_2SO_4 (50 ml), essentially as described for the preparation of 6, followed by treatment of the resulting (crude) carbonyl-bridged product (IR ν_{max} 1822 cm^{-1}) in refluxing xylene for 8 hr, afforded 9 (3.8 g, 75%), m.p. 118–120°, from light petroleum. (Found: C, 24.2; H, 0.95; Br, 40.1; Cl, 35.0. $C_8H_4Br_2Cl_4$ requires: C, 23.9; H, 1.0; Br, 39.8; Cl, 35.3%); IR ν_{max} 1608 cm^{-1}; PMR τ 4.9–5.2 (2H), 6.0–6.25 (2H). The adduct 10 (prepared in Me_2CO at room temp.) had m.p. 153–155° (dec.) from MeOH. (Found: C, 33.4; H, 1.7; Br, 27.5; Cl, 24.3; N, 7.4. $C_{16}H_9Br_2Cl_4N_3O_2$ requires: C, 33.3; H, 1.6; Br, 27.7; Cl, 24.6; N, 7.3%); IR ν_{max} 1806, 1752 cm^{-1}; PMR τ ($CDCl_3$) 2.3–2.8 (5H), 5.5–5.7 (2H), 6.1–6.3 (2H).

Reaction of the cis-*dibromodiene* 9 *with zinc* [with Akhtar[4]]. A mixture of 9 (2.4 g) and Zn dust (1.25 g) in EtOH (25 ml) was heated under relux for 6 hr and then filtered. Evaporation of the filtrate, and chromatography of the residue on silica, furnished the following products (both eluted with hexane). (a) Compound 13 as orange needles (107 mg, 14%), m.p. 135.5–137°, from hexane. (Found: C, 71.2; H, 3.1; Cl, 26.2% M (mass spectrum), 270. $C_{16}H_8Cl_2$ requires: C, 70.9; H, 3.0; Cl, 26.1%; M (^{35}Cl), 270); UV λ_{max} 229, 266, 291, 303, 386, 404 nm (log ϵ 4.37, 4.66, 4.40, 4.43, 3.55, 3.65); PMR τ ($CDCl_3$) 2.5–2.75 (4H), 3.3–3.4 (4H). (b) Compound 12 (173 mg, 18%), m.p. 209–210°, from light petroleum. (Found: C, 55.5; H, 2.6; Cl, 41.45%; M (mass spectrum), 340. $C_{16}H_8Cl_4$ requires: C, 55.8; H, 2.3; Cl, 41.3%; M (^{35}Cl), 340); IR ν_{max} 1618, 1586, 1560 cm^{-1}; PMR τ ($CDCl_3$) 2.6–2.9 (8H).

The triene - ketal - dimethyl ester 14. A mixture of 2 (20 g) and 1,2,3,4 - tetrachloro - 5,5 - dibenzyloxycyclopentadiene[16] (24.1 g) was heated in toluene (50 ml) under reflux for 20 hr. Removal of the solvent and crystallisation of the residue from $CHCl_3$-light petroleum gave the adduct 14 (16 g). Evaporation of the mother liquors and further heating of the residue in refluxing toluene (30 ml) for 20 hr yielded an additional quantity (6 g) of 14 (total yield 22 g, 57%), m.p. 170–171°. (Found: C, 59.35; H, 4.2; Cl, 21.1. $C_{33}H_{28}Cl_4O_6$ requires: C, 59.8; H, 4.2; Cl, 21.4%); IR ν_{max} 1727, 1642, 1607 cm^{-1}; PMR τ ($CDCl_3$) 2.6–2.9 (10H), 3.45–3.55 (2H), 5.05 (2H, s), 5.09 (2H, s), 5.85–6.05 (2H), 6.28 (6H, s), 7.55–7.6 (2H), 7.9–8.0 (2H).

The ketal-diene 15. A soln of 14 (21.8 g) in xylene (60 ml) was heated under reflux for 20 hr. After removal of the solvent, the residue was chromatographed on alumina. Elution with hexane gave an oil which crystallised from light petroleum to give the ketal-diene 15 (10.8 g, 70%), m.p. 80–81°. (Found: C, 58.8; H, 3.9; Cl, 29.9. $C_{23}H_{18}Cl_4O_2$ requires: C, 59.0; H, 3.9; Cl, 30.3%); IR ν_{max} 1605 cm^{-1}; PMR τ 2.7–2.85 (10H), 3.93 (2H, s), 5.05 (2H, s), 5.09 (2H, s), 6.48 (2H, s).

Hydrolysis and decarbonylation of the ketal-diene 15. A mixture of 15 (10.8 g), trifluoroacetic acid (25 ml), and water (1 ml) was heated on the steam-bath for 15 min. Water was added, and the product was collected in CH_2Cl_2. The soln was washed with water, dried ($MgSO_4$), and evaporated to give the (crude) carbonyl-bridged product (IR ν_{max} 1818 cm^{-1}), which was then heated in refluxing xylene for 45 min. The solvent was removed, and the residue was chromatographed on silica. Elution with hexane afforded an oil, which crystallised from MeOH to yield a mixture of 4 and 16 (4.75 g, 85%), m.p. 53–55°. (Found: C, 39.7; H, 1.7; Cl, 58.25. Calc. for $C_8H_4Cl_4$: C, 39.7; H, 1.7; Cl, 58.6%); the PMR spectrum was consistent with that of a *ca.* 2:1 mixture of 4 and 16.[9]

trans - 7,8 - *Dibromo* - 2,3,4,5 - *tetrachlorobicyclo*[4.2.0]*octa* - 2,4 - *diene* 17 and trans - 7,8 - *Dibromo* - 1,2,3,4 - *tetrachlorobicyclo*[4.2.0]*octa* - 2,4 - *diene* 18. The *ca.* 2:1 mixture of 4 and 16 (2.5 g) was brominated as in the preparation of 8. Crystallisation of the product from MeOH gave 18 (0.58 g, 14%), m.p. 119–121°. (Found: C, 23.9; H, 1.0; Br, 39.45; Cl, 35.4.

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†The illustrated *endo*-stereochemistry is unproven.

$C_8H_4Br_2Cl_4$ requires: C, 23.9; H, 1.0; Br, 39.8; Cl, 35.3%); IR ν_{max} 1615 cm^{-1}; PMR τ ($CDCl_3$) 3.80 (1H, d, *J* 6 Hz), 5.13 (1H, d, *J*, 9 Hz), 6.01 (1H, dd, *J* 9 and 9 Hz), 6.25 (1H, dd, *J* 9 and 6 Hz).

The mother liquors from the crystallisation of 18 yielded, after chromatography on silica (elution with hexane), the isomeric 17 (1.45 g, 35%), m.p. 68–69° (from MeOH), (Found: C, 23.8; H, 1.05; Br, 40.15; Cl, 34.95%); IR ν_{max} 1610 cm^{-1}; PMR τ 5.11 (1H, ddd, *J* 8, 6 and 1.5 Hz), 5.30 (1H, ddd, *J* 6, 6 and 1 Hz), 5.80 (1H, ddd, *J* 12, 8 and 1 Hz), 6.28 (1H, ddd, *J* 12, 6 and 1.5 Hz). The adduct 19 (prepared in Me_2CO at room temp.) had m.p. 166–167° (dec), from MeOH. (Found: C, 33.15; H, 1.6; Br, 27.4; Cl, 24.3; N, 7.1. $C_{16}H_9Br_2Cl_4N_3O_2$ requires: C, 33.3; H, 1.6; Br, 27.7; Cl, 24.6; N, 7.3%); IR ν_{max} 1805, 1750 cm^{-1}; PMR τ ($CDCl_3$) 2.3–2.8 (5H), 5.1–5.4 (1H), 5.75–6.0 (1H), 6.0–6.3 (2H).

Reaction of the trans-*dibromodiene* 17 *with zinc.* Treatment of 17 (0.50 g) with Zn dust (0.25 g) in refluxing EtOH (5 ml) for 6 hr, followed by chromatographic separation of the products (see above), yielded 13 (10 mg) and 12 (40 mg), identical with the specimens obtained previously.

Reaction of the tetrachlorocyclo-octatetraene mixture (4 + 16) *with zinc.* Similar treatment of the *ca.* 2:1 mixture of 4 and 16 (1.0 g) gave 13 (100 mg) and 12 (90 mg), identical with the previous samples.

Reaction of the trans-*dibromodiene* 18 *with zinc.* A mixture of 18 (0.58 g) and Zn dust (0.38 g) in EtOH (5 ml) was heated under reflux for 1 hr. After filtration and evaporation of the filtrate, the residue was chromatographed on silica. Elution with hexane afforded 22 (150 mg, 36%), m.p. 77–79°, from MeOH. (Found: C, 33.65; H, 1.5; Br, 28.0; Cl, 37.45. $C_8H_4BrCl_3$ requires: C, 33.55; H, 1.4; Br, 27.9; Cl, 37.1%); IR ν_{max} 1603 cm^{-1}; UV λ_{max} 224, 269 nm (log ϵ 4.34, 4.27); PMR τ ($CDCl_3$) 2.66 (1H, d, *J* 14 Hz), 2.72 (1H, d, *J* 8 Hz), 2.84 (1H, d, *J* 8 Hz), 3.26 (1H, d, *J* 14 Hz).

The maleic anhydride adduct 27. The *ca.* 2:1 mixture of 4 and 16 (242 mg) was heated with maleic anhydride (98 mg) in refluxing xylene (1.5 ml) for 3 hr. On cooling the soln, crystals of the adduct 27 (270 mg, 79%), separated; m.p. 224–226°, from $CHCl_3$. (Found: C, 42.8; H, 1.7; Cl, 41.4. $C_{12}H_6Cl_4O_3$ requires: C, 42.4; H, 1.8; Cl, 41.7%); IR ν_{max} 1870, 1790 cm^{-1}; PMR τ ($CDCl_3$) 3.6–3.75 (2H), 6.1–6.2 (2H), 6.3–6.5 (2H).

The acenaphthylene adduct 28. A similar experiment in which the mixture of 4 and 16 (242 mg) was heated with acenaphthylene (152 mg) in refluxing xylene (3 ml) for 18 hr gave the adduct 28 (235 mg, 60%), m.p. 258–260° (dec), from $CHCl_3$–MeOH. (Found: C, 60.8; H, 3.2; Cl, 36.3. $C_{20}H_{12}Cl_4$ requires: C, 60.9; H, 3.1; Cl, 36.0%); IR ν_{max} 1630 cm^{-1}; PMR ($CDCl_3$) 2.15–2.8 (6H), 4.17 (1H, d, *J* 8 Hz), 4.45 (1H, dd, *J* 8 and 6 Hz), 5.41 (1H, d, *J* 7 Hz), 5.8–6.0 (1H), 6.42 (1H, d, *J* 3.5 Hz), 6.55–6.75 (1H).

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