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

REACTIONS OF CYCLO-OCTATETRAENE TETRAMER AND OF THE DIMER HEPTACYCLO[8.6.0.$0^{2,6}$.$0^{3,9}$.$0^{7,15}$.$0^{8,12}$.$0^{11,16}$]HEXADECA-4,13-DIENE

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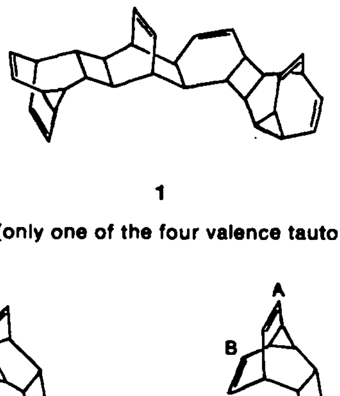
Abstract—Supplementary evidence has been obtained for the formulation of the cyclo-octatetraene tetramer as **1**. Thus tetracyano-ethylene gives a 2:1 adduct **7**, and at *ca* 310° the tetramer fragments cleanly to afford the cyclo-octatetraene dimer **9**. Additions to dimer **9** may be effected selectively at the 4,5-double bond, and occur in the *exo*-mode. The generation of tetrachlorobenzyne from 3,4,5,6-tetrachlorobenzenediazonium carboxylate in tetrahydrofuran results in the ether-ester **22**.

Structure **1** for the tetramer obtained by thermal oligomerisation of cyclo-octatetraene has been proposed by Hoesch *et al.*[2] Our own investigations,[3] leading to the same conclusion, gathered the following additional evidence in support of this formulation.

As reported,[2] the temperature-dependent ^{1}H NMR spectrum of the tetramer revealed the presence of two fluxional 3,4-homotropilidene systems. Comparison with the spectrum of compound **2**[4] was instructive. In this molecule, the two protons H^A and H^B, which retain their vinylic character when rearrangement of the homotropilidene system occurs, give rise to two apparent triplets (actually double doublets,† *J* 9 and 9 Hz‡ at τ 4.07 (1H) and 4.33 (1H). The spectrum of the tetramer (under the same conditions) included similar signals as follows: τ 4.10 (2H, two coincidental dds,† *J* values *ca* 9 Hz), 4.32 (1H, dd, *J* 9 and 9.5 Hz), and 4.35 (1H, dd, *J* 9 and 9 Hz).

The bridged homotropilidene systems of e.g. barbaralane **3**,[6,7] barbaralone **4**,[8] and dihydrobullvalene **5**[7] undergo formal [2+2+2] cycloadditions with tetracyanoethylene to give products of structure **6**. Analogously, reaction of the tetramer with tetracyanoethylene afforded a 2:1 adduct, the PMR spectrum of which showed that homtropilidene systems were no longer present, indicating structure 7. (An attempted reaction of the tetramer with tetrachlorobenzyne is described later).

The tetramer can be produced by heating the cyclo-octatetraene dimer of structure **8**,[2,9] which is known to be highly reactive as a conjugated diene in the Diels–Alder reaction (see Ref. 10), and has been assigned the dienophilic role in its addition to cyclopentadiene.[11] Some supporting evidence for the formulation of the tetramer as a Diels–Alder dimer of compound **8** was obtained from thermolysis experiments, in which the tetramer was found to fragment cleanly above 300° to give high yields of the caged compound **9**. This is thermodynamically the most stable of the cyclo-octatetraene dimers and results[12,13] from dimer **8**, via dimer **10**, at temperatures much lower than that required for the thermolysis of the tetramer.



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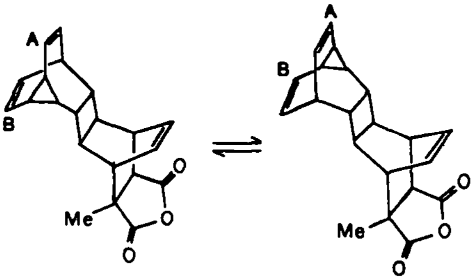
(only one of the four valence tautomers is shown)



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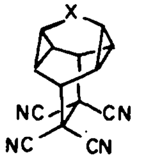
3: $X = CH_2$
4: $X = CO$
5: $X = CH_2CH_2$



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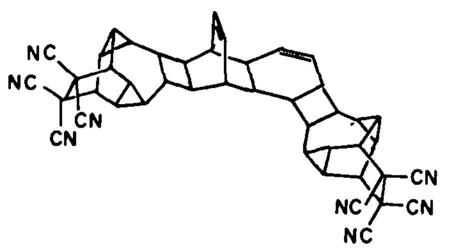

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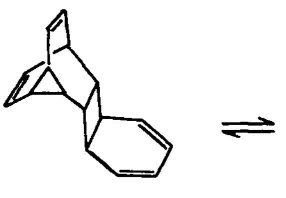
†Revealed by double irradiation experiments.

‡*J* values of *ca* 9 Hz are typical of such protons (cf. Ref. 5).



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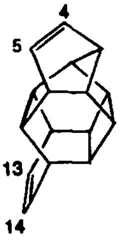

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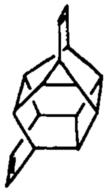

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Table 1. NMR splitting patterns of H-4 and H-5 in addition products of dimer **9** (from 110 MHz spectra; sweep-width 1000 Hz)

	Signal ($\underline{J}$ values in Hz)	
Compound	H-4	H-5
11	d(3)	dd(6 and 3)
12	d(5)	dd(5 and 5)
13	d^a(7)	s^a
17	d(3)	d(3)
18	d(8)	d(8)
19	d(5)	d(5)
20	d(8)	d(8)
21	d(8)	d(8)

[a] With further fine splitting.

The chemistry of the cyclo-octatetraene dimer **9** is little known,[10] and its ready formation from the tetramer **1** provided a stimulus for the investigations described below.

Inspection of a model of structure **9** indicated that the 4,5-olefinic bond might be expected to show some resemblance to the strained C=C of norbornene, while the 13,14-double bond should have a much lower reactivity, commensurate with that of a bicyclo[2.2.2]octene system. Selective attack at the 4,5-double bond could therefore be prognosticated, and was indeed realised in addition reactions, using the reagents listed below, in which the non-involvement of the 13,14-double bond was evident from the presence, in the PMR spectra of the products, of the characteristic signals of its vinylic protons. Moreover, the stereochemistry of the products could be inferred from the splitting patterns of the protons in positions 4 and 5. Examination of molecular models indicated that when H-4 or H-5 possesses *endo*§ stereochemistry, very small couplings with the vicinal bridgehead protons would be expected (*cf.* the norbornane system[14]); furthermore, $J_{4(exo),5(endo)}$ should also be very small.

Bromine. The addition of bromine in dichlormethane at *ca.* − 15° yielded a dibromide which could be assigned structure **11** on the basis of the spectral evidence (Table 1). Debromination of the product, using zinc in acetic acid, regenerated the starting material **9**.

Acetyl hypobromite. This reagent, generated *in situ* from N-bromoacetamide and lithium acetate in acetic acid,[15] produced a mixture of two bromoacetates, which could be formulated as **12** (minor product) and **13** (major product) (Table 1). The illustrated stereochemistry was confirmed by the following results.

Treatment of the bromo-acetates **12** and **13** with aqueous sodium hydroxide was expected to lead to the same *endo*-epoxide **14**, but initial experiments in which the reaction products were chromatographed on silica resulted in a mixture of two ketones.

Observation of the relative shifts of the vinylic protons induced by Pr(fod)$_3$[16] enabled the major and minor components of this mixture to be assigned structures **15** and **16** respectively; no skeletal change accompanied the formation of these products, as shown by their conversion via sodium borohydride reduction, tosylation, and elimination into the parent hydrocarbon **9**. The *endo*-epoxide **14** was eventually secured by employing alkali-treated silica for its chromatographic purification.

m-*Chloroperbenzoic acid.* Direct epoxidation of the dimer **9** with this reagent gave the *exo*-epoxide **17** (Table 1). This product was much more stable than its *endo*-isomer **14**, and was unchanged by chromatography on "untreated" silica.

Dichlorocarbene. Addition of dichlorocarbene, generated from chloroform and aqueous sodium hydroxide in the presence of a phase transfer catalyst,[17] yielded the *exo*-adduct **18** (Table 1).

Phenyl azide. This reagent was found to give rise to two products separable by TLC, but extraction of the silica on which these products were absorbed, using boiling ethyl acetate, gave a single compound. It was evident that the two isomeric triazolines expected to be formed by an initial 1,3-dipolar addition had undergone thermal extrusion of nitrogen to give an N-phenylaziridine, having the *exo*-configuration **19** (Table 1).

1,2,3,4 - *Tetrachloro - 5,5 - ethylenedioxycyclopentadiene.* Cycloaddition of this electron-deficient diene to dimer **9** at 100° in the absence of a solvent yielded two isomeric 1:1 adducts, of m.p. 243–245° (minor product) and 157–159° (major product) respectively. It was apparent that these both resulted from *exo*-addition to the 4,5-double bond of **9** (Table 1). They could therefore be assigned the two structures **20** and **21**, but it was not possible to tell which was which.

To summarise, the strained 4,5-olefinic bond in the cyclo-octatetraene dimer **9** shows a reactivity reminiscent of norbornene, and this resemblance extends to a similar preference for *exo*-addition.

As mentioned above, an attempt was made to effect a reaction between the tetramer **1** and tetrachlorobenzyne. When the latter was generated via tetrachlorobenzenediazonium carboxylate from tetrachloroanthranilic acid and iso-amyl nitrite in tetrahydrofuran, the major product was a compound $C_{17}H_{10}Cl_8O_3$. It was soon realised that this was also formed in the absence of the tetramer, and the spectroscopic evidence indicated

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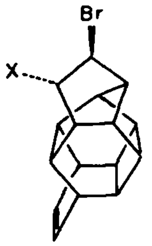
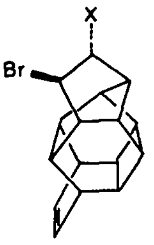
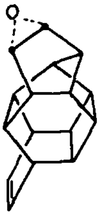
§By analogy with the norbornane system, the terms *endo* and *exo* are used here for convenient denotation of the stereochemistry at position 4 and 5.



11: X = Br
12: X = OAc



13: X = OAc



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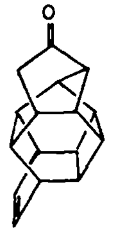

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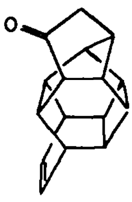

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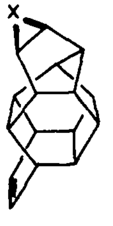
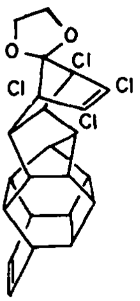


17: X = O
18: X = CCl₂
19: X = NPh



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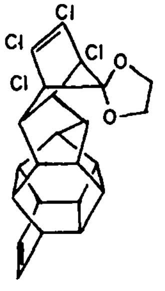

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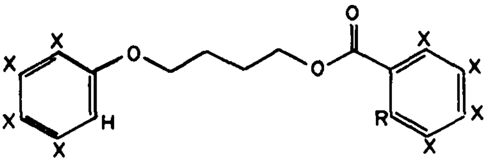
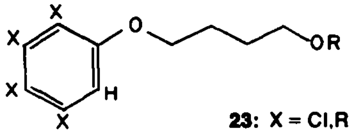
structure **22**. This was confirmed by alkaline hydrolysis, which gave the known[18] 2,3,4,5-tetrachlorobenzoic acid and an alcohol whose elemental composition and spectral properties were consistent with structure **23**. Cleavage of tetrahydrofuran by benzyne (from benzenediazonium carboxylate) has been observed by Wolthuis *et al.*,[19] although this reaction took a somewhat different course and resulted in the products **24** and **25**, or, in the presence of water, **25** and **26**.

EXPERIMENTAL

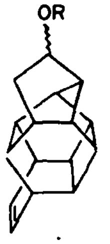
Light petroleum means the fraction of b.p. 40–60°. IR spectra were determined for Nujol mulls; PMR spectra were measured at 100 MHz using solns in $CDCl_3$.

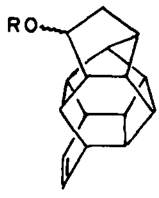


22: X = Cl, R = H
24: X = H, R = NHPh



23: X = Cl, R = H
25: X = H, R = Ph
26: X = H, R = H





27: R = H
29: R = Ts

28: R = H
30: R = Ts

The cyclo-octatetraene tetramer-tetracyanoethylene 1:2 *adduct* **7**. A mixture of **1** (200 mg) and tetracyanoethylene (125 mg) in toluene (20 ml) was heated under reflux for 22 h. Some adduct **7** separated, and more was obtained by concentration of the mother-liquors (total yield 174 mg, 54%). An analytical sample was prepared by recrystallisation from EtOAc (dec. above 300° without melting) (Found: C, 78.1; H, 4.8; N, 16.9. $C_{44}H_{32}N_8$ requires: C, 78.5; H, 4.8; N, 16.7%); IR ν_{max} 1638 cm^{-1}; PMR τ 3.65–3.85 (2H), 4.33 (2H, br s), 6.1–6.3 (2H), 6.3–6.5 (2H), 7.15–7.85 (12H), 8.15–8.9 (12H).

Thermolysis of the cyclo-octatetraene tetramer **1**. The tetramer (3.75 g) was heated under N_2 with a free flame until, at *ca.* 310°, an exothermic reaction commenced, when heating was discontinued. After the reaction had subsided, the product was cooled rapidly and then chromatographed on silica. Elution with light petroleum afforded the dimer **9** (2.91 g, 78%), identical with an authentic sample;[20] PMR τ 3.55–3.75 (1H), 3.85–4.3 (3H), 6.95–8.05 (10H), 8.1–8.4 (1H), 8.6–8.85 (1H).

The silver nitrate complex had m.p. 197–198° (lit.[20] 196°).

The dibromide **11**. Bromine (340 mg) in CH_2Cl_2 (15 ml) was added during 0.5 hr to a soln of dimer **9** (440 mg) in the same solvent (25 ml) at −15° (ice-salt bath). The solvent was removed and the residue was chromatographed on silica. Elution with hexane yielded **11** (170 mg, 22%), m.p. 124–125° from hexane. (Found: C, 52.1; H, 4.4; Br, 43.9. $C_{16}H_{16}Br_2$ requires: C, 52.2; H, 4.4; Br, 43.4%); IR ν_{max} 1608 cm^{-1}; PMR τ 3.55–4.05 (2H), 5.32 (1H, dd, *J* 6 and 3 Hz), 5.59 (1H, d, *J* 3 Hz), 6.8–8.1 (11H), 8.3–8.65 (1H).

Debromination of the product with Zn dust in glacial AcOH at room temp. gave the dimer **9** (78%), identical with an authentic specimen.[19]

The bromo-acetates **12** *and* **13**. A mixture of dimer **9** (243 mg), N-bromo acetamide (164 mg), and lithium acetate (1.6 g) in glacial AcOH (16 ml) was stirred at room temp. for 44 hr, and then poured into water. The product was collected in light petroleum, and chromatographed on preparative silica plates (1:1 benzene-light petroleum) to give two isomeric bromo-acetates.

(i) Bromo-acetate **13** (125 mg, 30%), m.p. 139–140° (from hexane) (Found: C, 61.9; H, 5.6; Br, 22.9. $C_{18}H_{19}O_2Br$ requires: C, 62.2; H, 5.5; Br, 23.0%); IR ν_{max} 1741, 1616 cm^{-1}; PMR τ 3.55–4.05 (2H), 4.55 (1H, d. [with further fine splitting], *J* 7 Hz), 5.82 (1H, s [with fine splitting]), 6.8–8.65 (15H).

(ii) Bromo-acetate **12** (25 mg, 6%), m.p. 124–125° from hexane. (Found: C, 62.2; H, 5.7; Br, 22.6%); IR ν_{max} 1745, 1617 cm^{-1}; PMR τ 3.6–4.1 (2H), 4.47 (1H, dd, J 5 and 5 Hz), 5.67 (1H, d, J 5 and 1 Hz), 7.05–8.9 (15H).

When the reaction was carried out on a larger scale, the major isomer **13** could be obtained simply by fractional crystallisation.

The endo-*epoxide* **14**. A mixture of **13** (1.39 g) in benzene (60 ml) and NaOH (1.60 g) in MeOH (170 ml) and water (1 ml) was heated under reflux for 4 hr, and then poured into water. The product was collected in CH_2Cl_2, and chromatographed on silica plates which had been prepared using aqueous 0.4M KOH in place of water. Elution with 1:1 benzene–light petroleum gave the *endo*-**14** as an oil (0.37 g, 41%), which was purified further by distillation [80° (bath)/6 mm] [Found: M (mass spectrum), 224.120. $C_{16}H_{16}O$ requires: M, 224.120]; ν_{max} (liquid film) 1616 cm^{-1}; PMR τ 3.6–4.05 (2H), 6.2–6.5 (2H), 6.75–8.6 (12H).

The ketones **15** *and* **16**. When **13** (1.21 g) was treated as described above, and the product was chromatographed on a silica column, elution with ether–benzene (1:50) afforded **15**, while elution with ether–benzene (4:50) gave an oil which was subjected to preparative tlc on silica. Multiple elution with EtOAc–hexane (1:10) then yielded a further quantity of **15**, and the isomeric ketone **16**.

(i) Ketone **15** (454 mg, 58%), m.p. 77–79° from hexane at −75°. (Found: C, 85.3; H, 7.3. $C_{16}H_{16}O$ requires: C, 85.7; H, 7.4%); IR ν_{max} 1738, 1611 cm^{-1}; PMR τ 3.55–4.05 (2H), 6.9–8.6 (14H). The 2,4-dinitrophenylhydrazone had m.p. 213–214° from EtOH–Me_2CO. (Found: C, 64.8; H, 5.0; N, 13.9. $C_{22}H_{20}N_4O_4$ requires: C, 65.3; H, 5.0; N, 13.9%).

(ii) Ketone **16** (121 mg, 15%), m.p. 76–77° from hexane. (Found: C, 85.2; H, 7.2%). The 2,4-dinitrophenylhydrazone had m.p. 209–211° (from Me_2CO) (Found: C, 65.3; H, 4.9; N, 14.1%).

The ketone **15** was also obtained by treatment of **12** with aqueous alkali, but no **16** was isolated (possibly because of the small scale of the experiment).

The exo-*epoxide* **17**. A soln of *m*-chloroperbenzoic acid (414 mg) in CH_2Cl_2 (5 ml) was added during 20 min to a stirred soln of **9** (496 mg) in the same solvent (5 ml); stirring was then continued for 1.5 hr. The mixture was poured into 2% NaOHaq (50 ml), and the product was collected in light petroleum. The resulting *exo*- **17** (450 mg, 84%) was then purified by preparative tlc, followed by distillation [70° (bath)/0.2 mm]; m.p. 52–54° [Found: M (mass spectrum), 224.119. $C_{16}H_{16}O$ requires: M, 224.120]; IR ν_{max} 1615 cm^{-1}; PMR τ 3.5–4.1 (2H), 6.53 (1H, d, J 3 Hz), 6.61 [1H, d (with further fine splitting), J 3 Hz] 7.0–8.8 (12H).

Reconversion of ketones **1** *and* **16** *into dimer* **9**. (a) Ketone **15** (257 mg) in MeOH (10 ml) was added during 15 min to $NaBH_4$ (87 mg) and NaOH (8 mg) in the same solvent (25 ml). The mixture was stirred for 2 hr, and then 5% HClaq (10 ml) was added, followed by water (100 ml). Collection of the product in CH_2Cl_2 gave **27** (187 mg, 72%), m.p. 112–113° from hexane. (Found: C, 84.7; H, 7.9. $C_{16}H_{18}O$ requires: C, 84.9; H, 8.0%); IR ν_{max} 3355 br, 1617 cm^{-1}; PMR τ 3.5–4.05 (2H), 5.4–5.75 (1H), 7.1–8.7 (15H).

Similar treatment of **16** (196 mg) afforded the isomeric **28** (115 mg, 54%), m.p. 108–109° from hexane. (Found: C, 84.7; H, 8.2%); IR ν_{max} 3330 br, 1615 cm^{-1}; PMR τ 3.5–4.05 (2H), 5.35–5.7 (1H), 7.05–8.85 (15H).

(b) A mixture of toluene-*p*-sulphonyl chloride (38 mg), alcohol **27** (21 mg), and dry pyridine (0.2 ml) was kept at 0° for 48 hr, then poured onto ice. The resulting crystalline **29** (25 mg) was dried, and heated in dry collidine (2 ml) under reflux in a N_2 atmos for 16 hr. The mixture was poured into water and acidified with HCl, and the product was collected in light petroleum to yield **9** (12 mg, 88%), identical with an authentic specimen.

Analogously, **28** (57 mg) gave **30** (79 mg, 77%), which in refluxing collidine was also converted into **9** (40 mg, 93%).

The dichlorocarbene-adduct **18**. A mixture of **9** (241 mg), benzyl triethylammonium chloride (90 mg), $CHCl_3$ (2.74 g), and 50% NaOHaq (4.6 ml) was stirred vigorously for 4 hr, then poured into water. Collection of the product in CH_2Cl_2 gave the adduct **18** (175 mg, 52%), m.p. 136–137° from acetone. (Found: C, 70.1; H, 5.6; Cl, 2.4. $C_{17}H_{16}Cl_2$ requires: C, 70.1; H, 5.5; Cl, 24.4%); IR 1612 cm^{-1}; PMR τ 3.55–4.05 (2H), 7.1–8.25 (11H) [including AB q: 7.84 (1H, d, J 8 Hz) and 8.05 (1H, d, J 8 Hz)], 8.45–8.7 (1H).

The N-*phenylaziridine* **19**. A mixture of **9** (332 mg), phenyl azide (286 mg), and ether (0.5 ml) was kept in the dark at room temp. for 4 days. Removal of the solvent followed by preparative tlc of the residue on silica (1:10 EtOAc–hexane) gave two bands which were extracted separately with boiling EtOAc (using a Soxhlet apparatus). In each case evaporation of the extract afforded **19** (total yield 330 mg, 69%), m.p. 136–137° (from Me_2CO) (Found: C, 87.8; H, 7.3; N, 4.6. $C_{22}H_{21}N$ requires: C, 88.2; H, 7.1; N, 4.7%); IR ν_{max} 1616, 1600 cm^{-1}; PMR τ 2.65–3.25 (5H), 3.55–4.05 (2H), 7.05–8.3 (13H) [including AB q: 7.19 (1H, d, J 5 Hz) and 7.31 (1H, d, J 5 Hz)], 8.5–8.75 (1H).

The Diels–Alder adducts **20** *and* **21**. A mixture of **9** (42 mg) and 1,2,3,4-tetrachloro-5,5-ethylenedioxycyclopentadiene[21] (53 mg) was heated at 100° (bath) for 3 hr. Fractional crystallisation of the resulting gum from MeOH then gave the two isomeric **20** and **21**: (i) m.p. 243–245° (21 mg, 22%) (Found: C, 59.2; H, 4.3; Cl, 29.5. $C_{23}H_{20}O_2Cl_4$ requires: C, 58.8; H, 4.3; Cl, 30.2%); IR ν_{max} 1614, 1596 cm^{-1}; PMR τ 3.6–4.0 (2H), 5.65–6.0 (4H), 6.96 (1H, d, J 8 Hz), 7.1–8.2 (13H) [including d, J 8 Hz, at τ 7.30]; (ii) m.p. 157–159° (55 mg, 59%) (Found: C, 58.8; H, 4.4; Cl, 30.2%); IR ν_{max} 1617, 1599 cm^{-1}; PMR τ 3.6–4.1 (2H), 5.6–6.0 (4H), 6.90 (1H, d, J 8 Hz), 7.10 (1H, d, J 8 Hz), 7.15–8.85 (12H).

4 - (2,3,4,5 - *Tetrachlorophenoxy*)*butyl* 2,3,4,5-*tetrachlorobenzoate* **22**. A soln of tetrachloroanthranilic acid (2.65 g) in dry THF (35 ml) was added during 20 min to a stirred soln of iso-amyl nitrite (10 ml) in the same solvent (50 ml) at 45° (bath) under a N_2 atmos. The mixture was stirred at the same temp. for a further 4 hr, and the solvent was removed under reduced pressure. Chromatography of the residue on silica, using 1:1 benzene–light petroleum as eluant, gave **22** (0.75 g, 14%), m.p. 115–116° (from Me_2CO) (Found: C, 37.6; H, 1.9; Cl, 51.8. $C_{17}H_{10}Cl_8O_3$ requires: C, 37.4; H, 1.9; Cl, 52.0%); IR ν_{max} 1734, 1707 cm^{-1}; PMR τ 2.21 (1H, s), 3.05 (1H, s), 5.35–5.6 (2H), 5.75–6.0 (2H), 7.8–8.1 (4H).

Hydrolysis of the ester **22**. A mixture of the ester (290 mg), NaOH (2.5 g), MeOH (25 ml), water (5 ml), and benzene (10 ml) was heated under reflux for 4 hr. Water was added, and the mixture was extracted repeatedly with ether. Acidification of the aqueous layer with HCl then precipitated 2,3,4,5-tetrachlorobenzoic acid (53 mg, 38%), m.p. 192–194° (lit.[18] 194–195°) from Me_2CO.

The combined ethereal extracts were washed with water, dried ($MgSO_4$), and evaporated, and the residue was chromatographed on silica. Elution with 9:1 benzene-ether gave **23** (92 mg, 56%) as an oil [Found: M (mass spectrum) 301.942 (^{35}Cl) $C_{10}H_{10}Cl_4O_2$ requires: M, 301.943 (^{35}Cl)].

The 3,5-dinitrobenzoate had m.p. 138–139° (dec) from Et_2O–Me_2CO. (Found: C, 40.9; H, 2.7; Cl, 28.3; N, 5.6. $C_{17}H_{12}Cl_4N_2O_7$ requires: C, 41.0; H, 2.4; Cl, 28.5; N, 5.6%).

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REFERENCES

[1] Part VI. R. J. Atkins, G. I. Fray and A. Gilbert, *Tetrahedron Letters* 3087 (1975).
[2] L. Hoesch, A. S. Dreiding and J. F. M. Oth, *Israel J. Chem.* **10**, 439 (1972).
[3] R. G. Saxton, Ph.D. Thesis, University of Bristol (1973).
[4] R. R. Deshpande, A. Gilbert, G. I. Fray and R. G. Saxton, *Tetrahedron Letters* 2163 (1971).
[5] R. Merényi, J. F. M. Oth and G. Schröder, *Chem. Ber.* **97**, 3150 (1964).
[6] H. Musso, *Angew. Chem.* Internat. Edn. 7, 306 (1968).
[7] H.-P. Löfer, T. Martini, H. Musso and G. Schröder, *Chem. Ber.* **103**, 2109 (1970).
[8] K. Kurabayashi and T. Mukai, *Chem. Comm.* 1016 (1972).
[9] G. Schröder, *Cyclooctatetraen* p. 63. Verlag Chemie, Weinheim (1965).

[10] G. I. Fray and R. G. Saxton, *The Chemistry of Cyclo-octatetraene and Its Derivatives*, pp. 373–375. Cambridge University Press, Cambridge (1978).

[11] D. M. Bratby, J. C. Chadwick, G. I. Fray and R. G. Saxton, *Tetrahedron* **33**, 1527 (1977).

[12] G. Schröder and J. F. M. Oth, *Angew. Chem.* Internat. Edn. **6**, 414 (1967).

[13] H. W. Moore, *J. Am. Chem. Soc.* **86**, 3398 (1964).

[14] L. M. Jackman and S. Sternhell, *Applications of NMR Spectroscopy in Organic Chemistry*, 2nd Edn p. 289 Pergamon Press, Oxford (1969).

[15] L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, p. 12. Wiley, New York (1967).

[16] R. F. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.* **93**, 1522 (1971).

[17] E. V. Dehmlow and J. Schönefeld, *Liebig's Ann.* **744**, 42 (1971).

[18] B. W. Nordlander and W. E. Cass, *J. Am. Chem. Soc.* **69**, 2679 (1947).

[19] E. Wolthuis, B. Bouma, J. Modderman and L. Sytsma, *Tetrahedron Letters* 407 (1970).

[20] W. O. Jones, *J. Chem. Soc.* 2036 (1953).

[21] K. Mackenzie, *Ibid.* 5710 (1964).