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THE DIELS-ALDER DIMERISATION OF 2,3-DICHLOROCYCLOPENTADIENONE AND OF 2,3,8,9-TETRACHLOROBICYCLO[4.3.0]NONA-2,4,8-TRIEN-7-ONE

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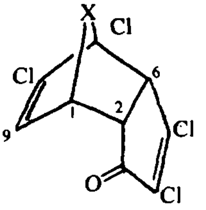
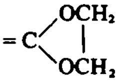
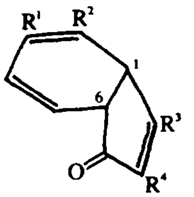
Abstract—The Diels-Alder dimer of 2,3-dichlorocyclopentadienone, shown to be endo-4,5,7,8-tetrachlorotricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3,10-dione **1**, forms 2,3,8,9-tetrachlorobicyclo[4.3.0]nona-2,4,8-trien-7-one **3** on thermal extrusion of carbon monoxide. The trienone **3** itself dimerises at *ca.* 160°, with loss of hydrogen chloride, affording two stereoisomeric aromatic derivatives **8** and **9**.



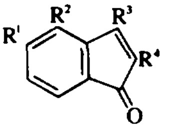
1: X = CO



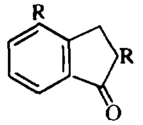
2: $X = C\begin{matrix} OCH_2 \\ | \\ OCH_2 \end{matrix}$



3: $R^1 = R^2 = R^3 = R^4 = Cl$
6: $R^1 = R^2 = R^3 = R^4 = H$
12: $R^1 = R^3 = H$, $R^2 = R^4 = Br$
13: $R^1 = R^3 = H$, $R^2 = R^4 = Cl$



4: $R^1 = R^2 = R^3 = R^4 = Cl$
5: $R^1 = R^3 = R^4 = Cl$, $R^2 = H$



7: R = H
14: R = Br
15: R = Cl

The Diels-Alder dimerisation of 2,3-dichlorocyclopentadienone, which like that of many other cyclopentadienones occurs spontaneously at room temperature,[1] was originally reported by McBee and Myers.[2] Interest in the highly selective orientation of the diene and dienophile components in such dimerisations prompted us to re-examine the product of this reaction, and led to the conclusion that the dimer possesses structure **1**. The spectral evidence for this structure included support for an endo configuration* [from the value of the coupling constant $J_{1,2}$ (4.5 Hz)], but did not distinguish between the two possible orientations of the cyclopent-2-enone ring; the particular orientation depicted in **1** was eventually proved as described below.

McBee and Myers[2] reported that thermolysis of the dimer **1** gave CO, HCl and a compound $C_{18}H_7Cl_7O_2$. However, we found that when the dimer was heated briefly at 170° in *o*-dichlorobenzene, an intermediate decarbonylated product $C_9H_4Cl_4O$ could be isolated (cf ref. 3), and structure **3** could be assigned unequivocally from the observed NMR shifts induced by $Eu(fod)_3$.[4] The bicyclic trienone **3** reacted slowly with bromine, with evolution of HBr, to give the dehydrogenated derivative **4** (cf, e.g. ref. 5), while treatment with acid afforded the dehydrochlorinated product **5**. The latter reaction may be contrasted with that of the unsubstituted trienone **6**, which on similar treatment yields indan-1-one **7**.[6]

When the trienone **3** was heated at ca 160° in the absence of solvent, an exothermic reaction ensued with the evolution of HCl and the formation of the product $C_{18}H_7Cl_7O_2$, m.p. 264·5–266·5°, reported by McBee and Myers;[2] preparative TLC showed that this was accompanied by a minor amount of an isomer, m.p. 284–285° (isomer ratio *ca.* 12:1). The NMR spectra of these isomeric products revealed that each contained two aromatic protons, and the coupling patterns of the remaining protons enabled their relative positions to be assigned. The evidence was not completely unambiguous, but the isomers could be formulated as **8** (major product) and **9** after consideration of the probable mechanism of their formation. The two possible Diels-Alder addition modes of the conjugated diene system of **3** to the cyclopentenone double bond of a second molecule, on the less hindered face of each component and in the endo-manner, would lead to the two stereoisomeric dimers **10** and **11**, which by 1,2-elimination of HCl and subsequent aromatisation would yield **8** and **9** respectively.

It is of interest that the thermal dimerisation of the trienone **3** is not paralleled by the related compounds **6**, **12**, **13**, which undergo hydrogen-transfer with the formation of the corresponding indan-1-ones **7**,[7] **14**,[8] and

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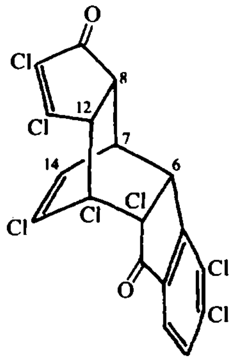
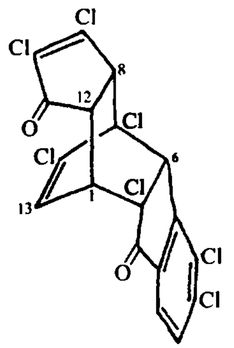
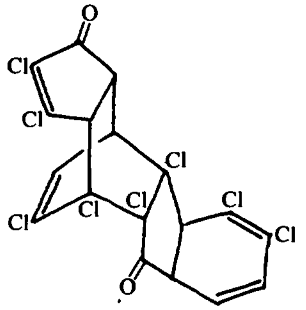
*Attempts to prove an endo-configuration by intramolecular photochemical cycloaddition of the two olefinic bonds in the dimer **1**, or in the derived acetal **2**, failed.



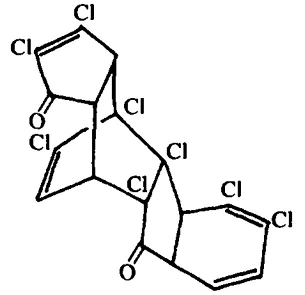
8



9



10



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15[3] severally. The absence of a halogen atom on C_9 of such trienones would in any case prevent their dimers from aromatising via thermal 1,2-dehydrohalogenation.

EXPERIMENTAL

Unless stated otherwise, NMR spectra were measured at 100 MHz for solutions in $CDCl_3$; light petroleum means the fraction of b.p. 40–60°. IR spectra were determined for Nujol mulls.

2,3-*Dichlorocyclopentadienone dimer* **1**. This was prepared as described by McBee and Myers;[2] m.p. 186–188° (decomp.) (lit.[2] 184–185°); IR ν_{max} 1815, 1785 sh, 1720, 1590 cm^{-1}; UV (EtOH) λ_{max} 243 nm (ϵ 8650); NMR τ 3·65 (d, H-9) 6·2–6·45 (m, H-1 and H-6), 6·70 (dd, H-2) ($J_{1,2}$ 4·5, $J_{1,9}$ 4·5, $J_{2,6}$ 6·5 Hz).

[With H. A. Poulton] The acetal **2** was prepared in the usual way from ethylene glycol in the presence of toluene - p - sulphonic acid, using refluxing benzene and a Dean-Stark separator for the continuous removal of water. The product **2** had m.p. 146·5–147·5° (from ether) (Found: C, 42·0; H, 2·3; Cl, 41·9. $C_{12}H_8Cl_4O_3$ requires: C, 42·1; H, 2·4; Cl, 41·5%); IR ν_{max} 1725, 1590 cm^{-1}; NMR τ 3·95 (d, H-9), 5·7–6·1 (m, 4 protons of ethylenedioxy-group), 6·24 (d, H-6), 6·61 (dd, H-2), 6·83 (dd, H-1) ($J_{1,2}$ 5, $J_{1,9}$ 4, $J_{2,6}$ 6 Hz).

2,3,8,9 - *Tetrachlorobicyclo*[4.3.0]*nona* - 2,4,8 - *trien* - 7 - *one* **3**. Dimer **1** (4·0 g) in *o*-dichlorobenzene (10 ml) was heated rapidly to 170° (internal), this temperature being maintained for 3 min. The solvent was removed under reduced pressure, and the residue was extracted several times with boiling light petroleum. Concentration of the combined extracts yielded the trienone **3** (2·5 g, 69%), m.p. 97–98° [Found: C, 40·4; H, 1·5; Cl, 52·4%; *M* (mass spectrum), 268 (^{35}Cl). $C_9H_4Cl_4O$ requires C, 40·0; H, 1·5; Cl, 52·5%; *M*, 268 (^{35}Cl)]; IR ν_{max} 1725, 1642, 1590 cm^{-1}; UV (EtOH) λ_{max} 239 nm (ϵ 11200); NMR τ (CCl_4) 4·0–4·5 (m, H-4 and H-5), 5·96 (d, H-1), 6·15–6·4 (m, H-6) ($J_{1,6}$ 9·5, $J_{4,5}$ 10, $J_{4,6}$ – 2·5,* $J_{5,6}$ 3·5 Hz). Stepwise addition of Eu(fod)$_3$ to a soln of **3** in $CDCl_3$ resulted in large and progressive down-field shifts of the resonance due to H-6, until the signal eventually appeared at lower field than H-1.

Treatment of **3** with an excess of Br_2 in CCl_4 at room-temp. overnight gave the bright yellow 2,3,4,5-tetrachloroindenone **4**, m.p. 178–179° (from acetone) (Found: C, 40·0; H, 0·75; Cl, 52·4. $C_9H_2Cl_4O$ requires: C, 40·3; H, 0·75; Cl, 52·9%); IR ν_{max} 1730, 1598 cm^{-1}; NMR τ 2·5–2·8 (AB q, 2 aromatic protons, *J* 8 Hz).

Stirring an ethereal soln of **3** with conc HCl at room-temp overnight yielded the orange 2,3,5-trichloroindenone **5**, m.p. 170–171° (from light petroleum) (Found: C, 46·2; H, 1·3; Cl, 45·8. $C_9H_3Cl_3O$ requires: C, 46·3; H, 1·3; Cl, 45·55%); IR ν_{max} 1740, 1600, 1590 cm^{-1}; NMR τ 2·43 (apparent s, 1 aromatic proton), 2·69 (apparent s, 2 aromatic protons). Resolution of the 2-proton signal was achieved by the addition of Pr(fod)$_3$,[4] when it appeared as an AB q, *J* 8 Hz.

The dehydrochlorinated dimers of **3**. The trienone **3** (3·0 g) was melted, and the temp. of the melt was raised cautiously to *ca.* 160°, when an exothermic reaction occurred with the evolution of HCl. Crystallisation of the residue from $CHCl_3$-MeOH furnished the dehydrochlorinated dimer **8** (2·2 g), m.p. 264·5–266·5° (lit.[2] 262–264°) [Found: *M* (mass spectrum), 500 (^{35}Cl). Calc. for $C_{18}H_7Cl_7O_2$: *M*, 500 (^{35}Cl)]; IR ν_{max} 1730, 1603, 1592 cm^{-1}; UV ($CHCl_3$) λ_{max} 262 nm (ϵ 23100): NMR τ 2·25–2·55 (AB q, 2 aromatic protons, *J* 8·5 Hz), 4·25 (d, H-14), 5·75–6·05 (m, H-7 and H-12), 6·12 (d, H-6), 6·75 (dd, H-8) ($J_{6,7}$ 2·5, $J_{7,8}$ 3, $J_{7,14}$ 7, $J_{8,12}$ 6·5 Hz).

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*Negative sign assumed.

Preparative TLC of the mother liquors from the above crystallisation, using Kieselgel and 10% EtoAc in light petroleum (b.p. 60–80°), gave a further 278 mg of **8** (total yield 86%), and in addition the isomeric product **9** (210 mg, 8%), m.p. 284–285° (from CH_2Cl_2-light petroleum) [Found: C, 43·0; H, 1·5; Cl, 49·1%; *M* (mass spectrum), 500 (^{35}Cl). $C_{18}H_7Cl_7O_2$ requires C, 42·9; H, 1·6; Cl, 49·3%; *M*, 500 (^{35}Cl)]; IR ν_{max} 1740, 1615, 1540 cm^{-1}; UV ($CHCl_3$) λ_{max} 258, 278 sh (ϵ 15500, 13200); NMR τ 2·33 (apparent s, 2 aromatic protons), 3·81 (d, H-13), 5·74 (s, H-6), 5·99 (d, H-8), 6·24 (dd, H-1), 6·36 (dd, H-12) ($J_{1,12}$ 2·5, $J_{1,13}$ 7·5, $J_{8,12}$ 6·5 Hz).

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