Chemistry of Octachlorofulvalene. Diels–Alder Reactions

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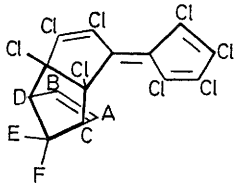
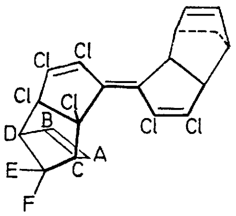
Summary Octachorofulvalene reacted readily as a dienophile with conjugated olefins to afford (2 + 4) mono- and di-adducts, but it reacted as the diene component with norbornadiene; in contrast, decachloro-2,5-dihydrofulvalene and hexachlorofulvene reacted predominantly as dienic partners with cyclopentadiene.

Following its synthesis,[1] we began investigating the chemistry of octachlorofulvalene (**1**). In this communication we report on the Diels–Alder chemistry of (**1**) and related chlorocarbons.

Although (**1**) did not react with cyclohexene, indene, or dicyclopentadiene at 80—95°, it reacted readily at room temperature with cyclopentadiene (**2**) and other conjugated hydrocarbons. The addition of (**2**) at 22° to a stirred slurry of equimolar amount of (**1**) in CH_2Cl_2 yielded deep blue crystals (**3**), m.p. 172—174°, whose elemental analysis indicated a 1:1 adduct composition, $C_{15}H_6Cl_8$; λ_{max} (cyclohexane) 384, 534 nm (log ϵ 4·40, 2·41). Proton n.m.r. revealed that (**3**) is a Diels–Alder adduct formed from (**1**) acting as the dienophile, δ ($CDCl_3$) H_A 6·23 (m), H_B 6·11 (m, J_{AB} 5·9 Hz), H_C 4·45 (m), H_D 3·35 (m), H_E 2·53[dt[2], J_{EF} 10·6, $J_{E(C,D)}$ 1·9, $J_{E(A,B)}$ *ca.* 0·6 Hz], H_F 2·07 [dt, J_{FE} 10·6, $J_{F(C,D)}$ 1·9 Hz]. The more extensive fine splitting of H_B and H_C than of their counterparts (H_A and H_D) indicates a more effective ^4J allylic coupling. The close similarity of the H_E and H_F δ's with those of the equivalent hexachlorofulvene–cyclopentadiene adduct[2] suggests the *endo*-stereochemistry, as shown.



(3)



(4)

When (**1**) was added, with stirring, at room temperature to a large excess of (**2**), an exothermal reaction ensued and the resultant dark slurry soon deposited white crystals. These, after recrystallization from benzene, yielded colourless prisms (**4**), m.p. 244—245° (decomp.), whose elemental analysis indicated the 1:2 adduct, $C_{20}H_{12}Cl_8$, composition. The proton n.m.r. of (**4**) is simple and very similar to that of (**3**), indicating a symmetrical structure in which both cyclopentadiene-derived moieties are identical. Except for the δ's, the spectral features of (**3**) and (**4**) are essentially superposable, thus suggesting the structure shown for (**4**);† λ_{max} (cyclohexane) 340 nm (log ϵ 4·40).

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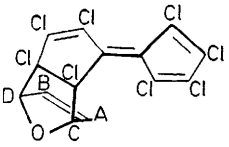
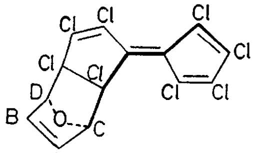
† Considering only alternatives with *endo* ring fusions, there are four symmetrical stereoisomers of (4)‡: *E-E′ E–Z′*, *Z–E′*, and *Z–Z′*, where *E* and *Z* designate positional, and *E′* and *Z′* designated stereochemical relations. In coplanar *Z* arrangements the inter-ring crowding of chlorines found for (**1**)[3] is not alleviated, while in the *E–Z′* arrangement there is more steric interference between *A*,*A′* hydrogens than in the proposed *E–E′* model shown (**4**).

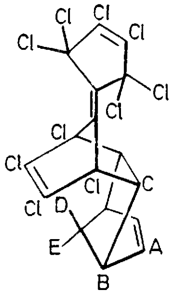
The reaction of (**1**) with furan (**5**) also proceeded smoothly at 22° and gave, regardless of the mole ratios, a single, 1 : 1 adduct, $C_{14}H_4Cl_8O$, (**6**), λ_{max} (cyclohexane) 383 nm (log ϵ 4·42), for which proton n.m.r. suggests structure (**6a**) or (**6b**).



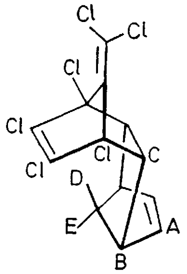
(6a)



(6b)



(10)



(11)

Subsequently we found that (**1**) reacted at room temperature with other conjugated hydrocarbons as well, including butadiene, cyclohexa-1,3-diene, cycloheptatriene, and cyclooctatetraene. It also reacted readily with norbornadiene (**7**), but no clean adduct was isolable, even though the proton n.m.r. of the reaction mixture clearly indicated the presence of several products. To obtain approximate n.m.r. parameters of possible adducts, we investigated the reaction of (**7**) with a close relative of (**1**), decachloro-2,5-dihydrofulvalene (**8**)[4] and with hexachlorofulvene (**9**).[5]

The magenta solution of (**8**) in an excess of (**7**) faded in two days at 22° and deposited white crystals (**10**) m.p. 239—241°, $C_{17}H_8Cl_{10}$, [δ, H_A 6·31 (td), H_B 2·98 (qui), H_C 2·67 (d), H_D 1·45 (dt), and H_E 1·24 (dm) ($J_{AB} \simeq J_{BD} \simeq J_{BE} \simeq$ 1·8—1·9, J_{AD} 0·45, J_{CE} 0·6, and J_{DE} *ca.* 11 Hz; λ_{max} (cyclohexane) 234 nm (log ϵ 4·21), i.r. (KBr) 1658, 1632, 1613, 1601 cm^{-1} (C=C)].

The reaction of (**9**) with (**7**), effected at 93° for 80 h, yielded adduct (**11**), m.p. 137—138°, whose proton n.m.r. was similar to that of (**10**), suggesting the symmetrical structure.§ The *endo–exo* stereochemistry shown is suggested by analogy with the reaction of (**7**) with hexachlorocyclopentadiene and by the n.m.r. parameters of the adduct[6] (*cf.* ref. 2).

Based on the n.m.r. data of (**10**) and (**11**), the spectrum of the reaction product of (**1**) and (**7**) was analysed. Indeed, there were clean, sharp peaks at δ 6·36, 3·02, and 2·68, whose coincidence with those of above, does suggest the equivalent adduct formation between (**1**) and (**7**).

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‡ The loss of the fulvenic chromophore precludes structures in which both cyclopentenylene groups are attached to the same ring.

§ (2 + 4) adducts with cyclopentadiene as the dienic partner were obtained not only with other fulvenes, *e.g.* 1,2,3,4-tetrachloro-6-phenylfulvene, but also with their 6-substituted (-OH, -NH_2, -NHPh) 1,2,3,4-tetrachloro-6-aza analogues. In contrast, in its reactions with (8) and (9), cyclopentadiene readily reacted at room temperature predominantly as the dienophile.

[1] V. Mark, *Tetrahedron Letters*, 1961, **333**; V. Mark, *Org. Synth.*, 1966, **46**, 93.
[2] Which was cyclized on irradiation to the cage isomer, thus confirming the *endo* stereochemistry: E. T. McBee, E. P. Wesseler, D. L. Crain, R. Hurnaus, and T. Hodgins, *J. Org. Chem.*, 1972, **37**, 683.
[3] P. J. Wheatley, *J. Chem. Soc.*, 1961, 4936.
[4] R. M. Smith and R. West, *J. Org. Chem.*, 1970, **35**, 2681.
[5] A. Roedig, *Annalen*, 1950, **569**, 161.
[6] A. P. Marchand and J. E. Rose, *J. Amer. Chem. Soc.*, 1968, **90**, 3724.