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[4+2] CYCLOADDITION REACTIONS OF HEXACHLOROTROPONE

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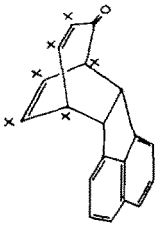
Abstract—The cycloaddition of hexachlorotropone to selected olefins, including 1,3-dienes, has been examined. Unlike tropone, which undergoes [6+4] cycloadditions with 1,3-dienes, only [4+2] processes were observed with hexachlorotropone. Its apparent preference for *exo*-addition (contrast tetrachlorocyclopentadienone) probably results from thermodynamic control of the *endo* : *exo* product ratios.

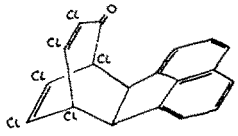
Although hexachlorotropone has been known since 1968,[1] no cycloaddition reactions of this interesting cyclic trienone have been reported. For comparison with the corresponding reactions of tropone, we have investigated the cycloaddition of hexachlorotropone to a number of olefins and 1,3-dienes, as follows.

Tropone reacts with acenaphthylene at 130° to give the



1 : X = H

2 : X = Cl



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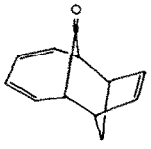

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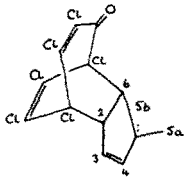

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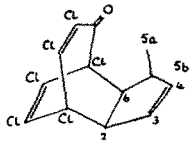

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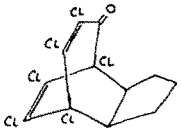

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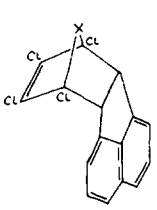
endo-[4+2] adduct **1** (78.5% yield).[2] Hexachlorotropone (in refluxing xylene), however, produced a *ca.* 1:2 mixture of *endo*- and *exo*-adducts, **2** and **3** respectively. The *endo*-isomer **2** was clearly identified by its NMR spectrum, which showed additional shielding of one of the methine protons, presumably by the CO group in the enone bridge.

With cyclopentadiene, tropone gives the [6+4] adduct **4** exclusively[3] (in the absence of acid[4]). Hexachlorotropone and cyclopentadiene (in refluxing benzene) yielded no [6+4] product, but gave a *ca.* 1:1.7 mixture of the *endo*- and *exo*-[4+2] adducts **5** (m.p. 141–142°) and **6** (m.p. 158–160°) respectively. The presence of a fused cyclopentene ring in each of these adducts was evident from their NMR spectra. Moreover, the observed shielding of one of the methylene protons (H-5a) in the higher-melting isomer indicated the *exo*-configuration **6**, and the proximity of this proton to the CO group was confirmed with the aid of $Pr(fod)_3$,[5] the use of which also provided support for the designation of the lower-melting isomer as the *endo*-compound **5**. The specific orientation of the diene relative to the dienophile component in the formation of both the *endo*- and *exo*-adducts is noteworthy. Only one adduct was isolated (46%) after reaction of hexachlorotropone with cyclopentene at 100°; this was the *exo*-isomer **7**, since it was identical with the product obtained by catalytic hydrogenation of **6**.

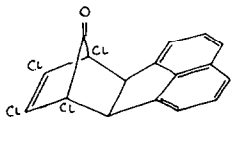
In view of the unusual *endo* : *exo* ratios observed in the above cycloadditions, it was of interest to examine some analogous reactions of tetrachlorocyclopentadienone.[6] Acenaphthylene (at 50°) afforded *endo*- and *exo*-adducts, **8** and **9** respectively, in a ratio of *ca.* 4.2:1; the *endo*-isomer **8** was shown to be identical with a sample obtained by hydrolysis of the acetal **10**.[7] With cyclopentadiene (at room temp.) the predominant product was a mixture of the *endo*-adduct **11**[6] and its Cope-rearranged derivative **12**;[8] only a very small proportion of the *exo*-isomer **13** was isolated (*endo* : *exo* ratio *ca.* 170:1).

The reason for these contrasting results may be that the reactions of hexachlorotropone described above were subject to some thermodynamic control. The addition of cyclo-octa-1,3,6-triene to hexachlorotropone (in refluxing xylene) gave a product of structure **14**, which must have resulted from *endo*-addition to the 6,7-double bond of the cyclo-octatriene, followed by an intramolecular [4+2] process (cf. Ref. 9). No *exo*-adduct (or caged derivative of



8 : X = CO

10 : X = C(OMe)$_2$



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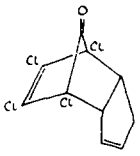

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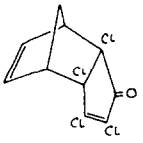

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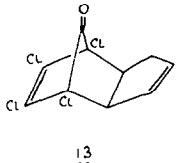

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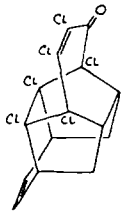

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the *exo*-adduct) was detected, and it is therefore evident that in this case at least the initial Diels–Alder reaction produced only *endo*-adduct.

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; UV spectral data refer to solutions in $CHCl_3$. The reactions with hexachlorotropone were carried out in an atmosphere of N_2.

Reactions of hexachlorotropone[10]

(a) *With acenaphthylene.* Hexachlorotropone (1.2 g) and acenaphthylene (0.60 g) were heated in xylene (25 ml) under reflux for 18 hr, and then the solvent was removed under reduced pressure. [An NMR spectrum (60 MHz) of the residual oil was recorded, and when the spectra of pure samples of the *endo*- and *exo*-adducts had been obtained (see below), the integration showed that these were present in the crude reaction product in a ratio of *ca.* 1:2]. The residue was chromatographed on silica, and elution with light petroleum–benzene (4:) afforded pure *exo*-adduct **3** (150 mg), m.p. *ca.* 233° (dec.) (from $CHCl_3$–MeOH) (Found: C, 49.2; H, 1.65; Cl, 45.7. $C_{19}H_8Cl_6O$ requires: C, 49.1; H, 1.7; Cl, 45.8%); IR ν_{max} 1710, 1600 cm^{-1}; NMR (60 MHz) τ 1.95 – 2.7 (6H), 4.92 (1H, d, *J* 9.5 Hz), 5.08 (1H, d, *J* 9.5 Hz).

Continued elution with an increasing concentration of benzene in the light petroleum produced mixtures of the *exo*- and *endo*-adducts; finally, using a 1:1 ratio of the solvents, a fraction containing a high proportion of the *endo*-isomer **2** was obtained, and repeated crystallisation from $CHCl_3$–MeOH then gave a pure sample (30 mg), m.p. *ca.* 263° (dec.) (Found: C, 49.0; H, 1.65; Cl, 45.7%). IR ν_{max} 1715, 1596 cm^{-1}; NMR (60 MHz) τ 1.95 – 2.7 (6H), 5.13 (1H, d, *J* 8 Hz), 5.53 (1H, d, *J* 8 Hz).

(b) *With cyclopentadiene.* A mixture of hexachlorotropone (5.0 g), cyclopentadiene (15 ml) was benzene (30 ml) was heated under reflux for 18 hr. The soln was evaporated under reduced pressure, and the residue was chromatographed on silica; elution with light petroleum–benzene (3:1) gave a semi-solid mixture (4.9 g). TLC indicated that this material contained three components, pure samples of which were then obtained by using preparative plates [silica; light petroleum (b.p. 60–80°)—EtOAc (75:1)]:

(i) hexachlorotropone-dicyclopentadiene adduct (11%), m.p. 192–194.5° [from light petroleum (b.p. 60–80°)], identical with the product obtained from hexachlorotropone and dicyclopentadiene in refluxing benzene;[11]

(ii) *exo*-adduct **6** (56%), m.p. 158–160° [from light petroleum (b.p. 60–80°)] (Found: C, 38.3; H, 1.7; Cl, 55.8. $C_{12}H_6Cl_6O$ requires: C, 38.05; H, 1.6; Cl, 56.1%); IR ν_{max} 1705, 1595 cm^{-1}; UV λ_{max} 252 nm (ϵ 5425); NMR τ 3.8 – 4.55 (H-3 and H-4), 5.9 – 6.6 (H-2 and H-6), 6.9 – 7.5 (H-5b), 7.7 – 8.1(H-5a) ($J_{2,6}$ 11, $J_{3,4}$ 8, $J_{5a,5b}$ – 18.5,† $J_{5a,6}$ 6, $J_{5b,6}$ 10 Hz);

(iii) *endo*-adduct **5** (33%), m.p. 141–142° [from light petroleum (b.p. 60–80°)] (Found: C, 38.2; H, 1.7; Cl, 55.6%); IR ν_{max} 1707, 1600 cm^{-1}; UV λ_{max} 256 nm (ϵ 5970); NMR τ 4.0 – 4.2 (H-3 and H-4), 6.0 – 6.2 (H-2), 6.5 – 6.75 (H-6), 7.1 – 7.25 (H-5a and H-5b) ($J_{2,6}$ 9.5, $J_{5a,6}$ 8, $J_{5b,6}$ 7 Hz).

Catalytic hydrogenation of the *exo*-adduct **6**, using pre-reduced Adam's catalyst in EtOH, followed by chromatography of the product on silica [elution with light petroleum–benzene (1:)], afforded **7**, m.p. 167–168° (from ether–light petroleum) (Found: C, 38.3; H, 2.1; Cl, 55.4. $C_{12}H_8Cl_6O$ requires: C, 37.8; H, 2.1; Cl, 55.8%); IR ν_{max} 1710, 1598 cm^{-1}; UV λ_{max} 259 nm (ϵ 6110); NMR τ 6.6 – 6.9 (2H), 7.6 – 9.0 (6H).

(c) *With cyclopentene.* A mixture of hexachlorotropone (0.50 g) and cyclopentene (1.0 ml) was kept at 100° (sealed tube) for 15 hr. The excess of cyclopentene was removed under reduced pressure, and the residue was chromatographed on silica. Elution with light petroluem–benzene (1:1) gave the *exo*-adduct **7** (0.28 g, 46%), m.p. 168–169° [from light petroleum (b.p. 60–80°)], identical with the product obtained by catalytic hydrogenation of the *exo*-cyclopentadiene-adduct **6** (see above).

(d) *With cyclo-octa-1,3,6-triene.* Hexachlorotropone (1.0 g) and cyclo-octa-1,3,6-triene[12] (0.68 g) were heated in xylene (10 ml) under reflux for 39 hr. Volatile material was then removed under reduced pressure, and the residue was chromatographed on silica. Elution with light petroleum–EtOAc (49:1) afforded a fraction which on treatment with light petroleum gave the caged adduct **14** (0.30 g), m.p. 170–172° [from light petroleum (b.p. 60–80°)] (Found: C, 43.1; H, 2.5; Cl, 51.0. $C_{15}H_{12}Cl_6O$ requires: C, 43.0, H, 2.4; Cl, 50.8%); IR ν_{max} 1711, 1602 cm^{-1}; UV λ_{max} 255 nm (ϵ 6200); NMR τ 3.91 (2H, apparent s), 6.3 – 6.55 (1H), 6.95 – 7.3 (2H), 7.45 – 7.75 (1H), 7.75 – 8.25 (3H), 8.5 – 8.7 (1H).

The mother-liquors from the crystallisation of **14** were subjected to preparative TLC [silica; light petroleum (b.p. 60–80°)—ethyl acetate (99:1)] to give a further quantity of **14** (0.13 g; total yield 33%). The only other product which was detected proved to be an adduct of hexachlorotropone and cyclo-octa-1,3,5-triene‡ (reacting *via* its bicyclic valence tautomer; cf. Ref. 14) (95 mg), m.p. 185–186° [from light petroleum (b.p. 60–80°)].[11]

†Negative sign assumed.

‡Cyclo-octa-1,3,5-triene could have been an initial contaminant in the 1,3,6-triene,[12] but in any case the latter is known to isomerise *via* a thermal [1,5]-hydrogen shift.[13]

Reactions with tetrachlorocyclopentadienone[6]

(a) *With acenaphthylene.* 2,3,4,4,5-Pentachlorocyclopent-2-en-1-one[15] (2.0 g) in dry acetonitrile (5 ml) was added dropwise to a stirred mixture of anhyd NaOAc (0.87 g), acenaphthylene (3.0 g), and acetonitrile (10 ml) at 50° (oil-bath); after the addition was complete, stirring was continued for 1 hr at the same temp. The mixture was filtered, the filtrate evaporated, and the residue taken up in ether; the ethereal soln was washed with water, dried ($MgSO_4$), and evaporated to give an oily residue. Treatment with light petroleum then yielded the *endo*-adduct **8** (1.60 g, 57%), m.p. *ca.* 195° (dec.) (lit.[7] 191–192°) (from CH_2Cl–light petroleum) (Found: C, 55.0, H, 2.1; Cl, 39.0. Calc. for $C_{17}H_8Cl_4O$: C, 55.2; H, 2.2; Cl, 38.3%); IR ν_{max} 1813, 1589 cm^{-1}; NMR τ 2.15 – 2.6 (6H), 5.51(2H, s). This product was identical with a sample prepared from the dimethyl acetal **10** by treatment with concentrated H_2SO_4.[7]

The mother-liquors from the crystallisation of **8** were chromatographed on silica. Elution with light petroleum–EtOAc (97:3) gave the *exo*-adduct **9** (0.38 g, 13%), m.p. *ca.* 205° (dec.) (from CH_2Cl_2-light petroleum) (Found: C, 55.1; H, 2.2; Cl, 38.7%); IR ν_{max} 1828, 1588 cm^{-1}; NMR τ 2.15 – 2.6 (6H), 5.65 (2H, s).

(b) *With cyclopentadiene.* The reaction was carried out at room temp as described by Diesche,[6] using 4.0 g of 2,3,4,4,5-pentachlorocyclopent-2-en-1-one. Chromatography of the product on silica, and elution with light petroleum–EtOAc (24:1) gave a number of fractions from which the known *endo*-adduct **11** (1.75 g), m.p. *ca.* 125° (dec.) [lit. 123–123.5°,[8] 126–128° (dec.)[6]], and its Cope-rearranged derivative **12** (2.13 g), m.p. 78–80° (lit.[8] 82–83°), were obtained by fractional crystallisation from light petroleum.

Preparative TLC [silica; light petroleum–CH_2Cl_2 (9:1)] of the mother-liquors yielded the *exo*-adduct **13** (23 mg), m.p. 99–100° (dec.) (from light petroleum) (Found: C, 42.4; H, 2.0; Cl, 50.2. $C_{10}H_6ClO$ requires: C, 42.3; H, 2.1; Cl, 49.9%); IR ν_{max} 1824, 1592 cm^{-1}; NMR τ 4.0 – 4.2 (1H), 4.3 – 4.5 (1H) – 6.55 (1H), 6.75 – 7.05 (1H), 7.3 – 7.5 (2H).

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REFERENCES

[1]R. West and K. Kusuda, *J. Am. Chem. Soc.* **90**, 7354 (1968).
[2]T. Uyehara and T. Tsushima, *Chem. and Ind.* 354 (1971).
[3]R. C. Cookson, B. V. Drake, J. Hudec and A. Morrison, *Chem. Comm.* 15 (1966); S. Ito, Y. Fujise, T. Okuda and Y. Inoue, *Bull. Chem. Soc. Japan* **39**, 1351 (1966).
[4]S. Ito, K. Sakan and Y. Fujise, *Tetrahedron Letters* 2873 (1970).
[5]R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.* **93**, 1525 (1971).
[6]W. H. Dietsche, *Tetrahedron Letters* 201 (1966).
[7]L. S. Besford, R. C. Cookson and J. Cooper, *J. Chem. Soc.* (C), 1385 (1967).
[8]P. Yates and P. Eaton, *Tetrahedron* **12**, 13 (1961).
[9]I. A. Akhtar and G. I. Fray, *J. Chem. Soc.* (C), 2802 (1971).
[10]K. Kusuda, R. West and V. N. Rao, *J. Am. Chem. Soc.* **93**, 3627 (1971).
[11]J. C. Chadwick, Ph.D. Thesis, University of Bristol (1974).
[12]W. O. Jones, *J. Chem. Soc.* 1808 (1954).
[13]W. R. Roth, *Liebigs Ann.* **671**, 25 (1964).
[14]I. A. Akhtar and G. I. Fray, *J. Chem. Soc.* (C), 2800 (1971).
[15]J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.* **71**, 946 (1949).