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THE X-RAY CRYSTAL STRUCTURE OF 2,3-DICHLORO-2,6,8-TRI-t-BUTYL-1-H-BENZ[e]INDENONE - THE PRODUCT OF AN UNUSUAL THERMAL HYDROLYTIC TRANSFORMATION OF A CYCLOOCTATRIENE-ANNELATED HEXACHLORONORBORNENE

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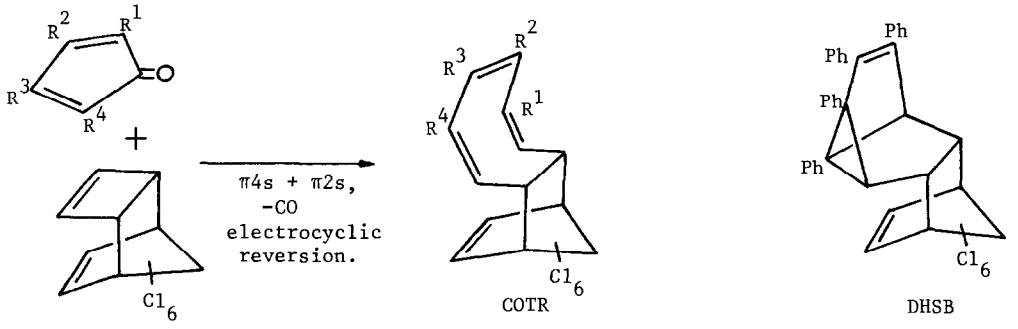
Summary: Brief thermolysis of the hexachlorinated bridged tricyclotriadecatetraenes 2 and 3 in air gives unexpectedly, 2,3-dichlorobenz[e]indenones 6 and 7, as shown by the X-ray crystal structure of benzindenone 6; a rational pathway for this transformation is suggested.

The reaction sequence of Scheme 1, affording convenient access to tri-t-butyl- and triphenylcyclooctatriene derivatives ("COTR") 2 and 3, prompted a study of their thermal behaviour for comparison with that of analogous tetra-aryl (and aryl-alkyl analogues). Tetra-aryl COTR's analogous to 2 and 3, e.g. 4, readily cyclise into dihydrosemibullvalenes, viz 4 → 5[1] (and their vinyl cyclopropane rearrangement isomers[2,3]) under surprisingly mild conditions (e.g. at ∿140°) and rationalization of such facile cyclisation includes relief of non-bonded steric effects, and/or stabilised allylic bi-radicals as cyclisation intermediates rather than a concerted intramolecular ($4\pi a + 2\pi a$) cycloaddition pathway. Whichever of various possibilities more closely resembles the true mechanism for DHSB formation, a reduction in number (as well as changes in type) of COTR substituents can be expected to



1

COTR

DHSB

2 R^2 = H $R^{1,3,4}$ = t-Bu
3 R^2 = H $R^{1,3,4}$ = Ph
4 R^{1-4} = Ph

5 R^{1-4} = Ph

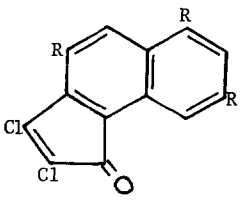
SCHEME 1

have a considerable effect and perhaps give mechanistic insight, especially as it is known that quite different results obtain in the absence of cyclooctatriene substituents.[1]

In the event, COTR 2 is remarkably inert to heat, being unchanged after thermolysis at 230-260° (1-2 min), conditions usually effective for high-yield cyclisation of analogous tetraaryl COTR's into DHSB products. Longer heating of COTR 2 in vacuo is also ineffective, but heating the compound in air or under ("O_2 free")N_2 (~250°, 10 mins) results in discolouration, and later, effervescence. Preparative TLC of the combined crude products of several experiments, and recrystallisation of the orange-red product fraction gives a new compound (A) (in 32% conversion based on 2), red plates m.p. 188-189°. Compound(A)is characterised as $C_{25}H_{30}Cl_2O$ (elemental composition and m/e 416 $M^{+\cdot}$ with the correct $^{35}Cl^{37}Cl$ abundance ratio); with IR ν_{max} 1715 s cm^{-1}, UV λ_{max} 423 nm (ε = 3520) and 294 nm (ε = 10,000), and the deep-red colour, a cyclopentadienone derivative suggests itself. The ^1H NMR spectrum exhibits narrow multiplets at δ 8.81, 8.60 and 7.49 (rel. intensity 1:1:1) and three high-field sharp singlets in the 1 - 1.5 ppm range (rel. intensity 9:9:9), consistent with three vinylic protons and three t-Bu groups all environmentally different. ^{13}C nmr indicates that all the =C(H) nuclei are actually aromatic with doublets at 117.1, 123.5 and 131.8 ppm, and apart from high field t-Bu signals all other signals correspond to unsaturated carbon. In addition a weak signal at 188 ppm (C=O) is significantly higher than usually observed for a variety of tetra-arylated cyclopentadienones where this signal appears at 200.4 ± 0.4 ppm,[4] indicative of shielding effects in ketone A.

An analogous red compound (B) m.p. 277-278° forms the sole isolated reaction product from thermolysis of COTR 3, similarly characterised as a cyclopentadienone $C_{31}H_{28}Cl_2O$ (combustion analysis and m/e 476, $M^{+\cdot}$) with λ_{max} 435 nm (ε = 2,700), 294 nm (ε = 11,100) corresponding to bands in A with an additional absorption at 318 nm (ε = 12,600) due to the Ph substituents. In the ^1H NMR range ketone B exhibits only unsaturated proton resonance, of particular note being three signals at δ 9.06, 7.86 and7.66 analogous to signals in compound(A), whilst in the ^{13}C range the corresponding =C(H) signals appear at 120.4 and 135.5, the third signal anticipated being obscured by the Ph group =CH signals at 127.5 - 129.9 ppm.

Speculative schemes can be constructed which account for the conversion of COTR 2 ($C_{25}H_{32}Cl_6$) into a cyclopentadienone ($C_{25}H_{30}Cl_2O$); these involve hydrolytic and thermal loss of HCl, but none of the more obvious candidates for the structure of (A) (or B) accord with the ^1H and ^{13}C nmr evidence. Recourse to single crystal X-ray structure determination therefore shows that (A) is 2,3-dichloro-4,6,8-tri-t-butylbenz[e]indenone 6, and by analogy (B) is most probably the phenylated analogue, 7.



6 R = t-Bu (=+, Scheme 2)
7 R = Ph

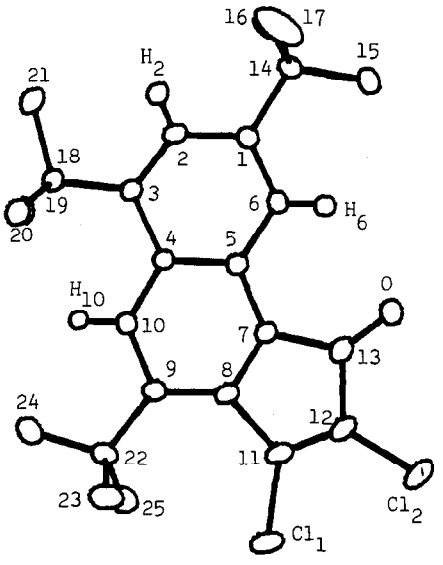
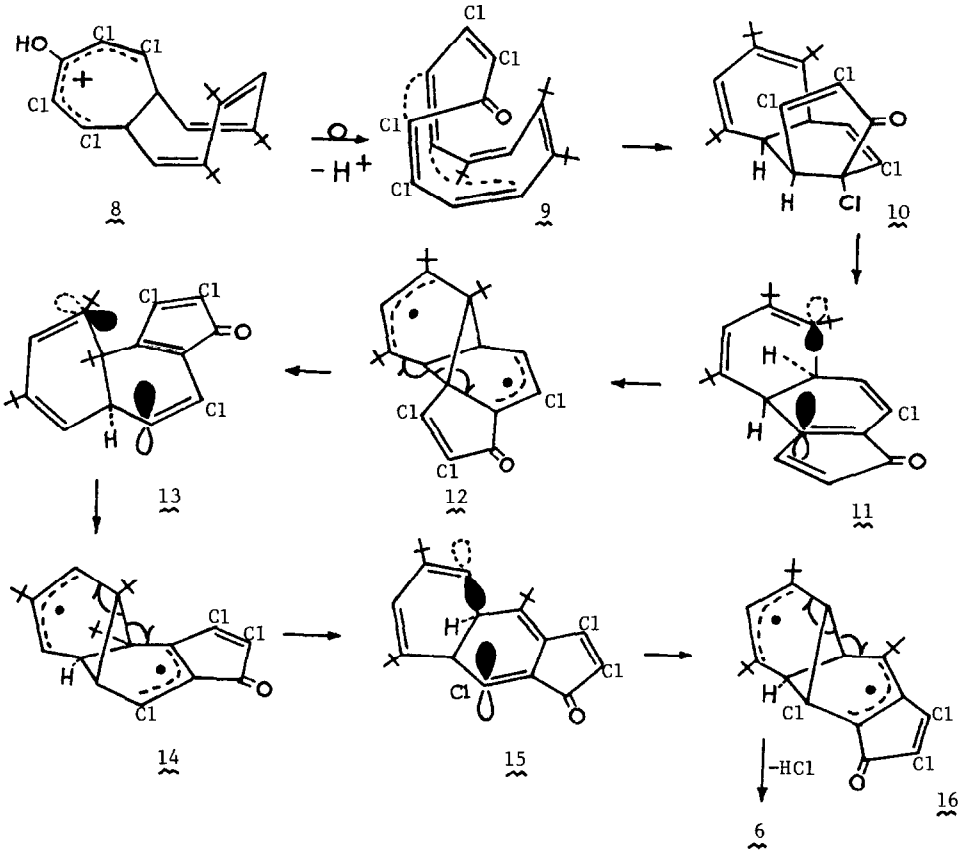


Figure The molecular structure of (A). Methyl hydrogen atoms and the disorder of 15-17 are not shown.

Crystals of (A) are monoclinic, space group $P2_1/c$, $\underline{a}$ = 9.554(1), $\underline{b}$ = 12.144(2), $\underline{c}$ = 19.958(2) Å, β = 100.99(1)°, $\underline{Z}$ = 4. The structure was solved by direct methods and refined by full-matrix least-squares to $\underline{R}$ = 0.060, $\underline{R}'$ = 0.073 for 2939 reflections with $\underline{I} \geq 3\sigma(\underline{I})$. Carbon atoms 15-17 (see Figure) are disordered and the nine methyl hydrogen atoms attached to them were not located. The experimentally-determined molecular geometry is fully consistent with the formulation of (A) as 6: the carbon atoms 1 - 13 are coplanar to ±0.10 Å and there is a localised double bond at 11 - 12 of length 1.332(8) Å.



SCHEME 2

Currently available evidence precludes fully secure rationalization of the transformation of COTR's 2 and 3 into benzindenones 6 and 7; however the isolation of only one major product (besides e.g. COTR 2) suggests a rather specific reaction sequence. One possible pathway is illustrated in abbreviated form in Scheme 2. Ring-expansion of the hexachloronorbornene element (via a chlorinated norcarene[5]) and hydrolysis[6] gives bicyclic cation 8, from which at least three cyclisation routes to tricyclic ketone 10 can be envisaged. The simplest and most specific of these involves the pericyclic ring-opening of protonated ketone 8 to cyclotriadecahexaenone 9 which collapses by $4\pi + 2\pi$ cycloaddition to the relatively unstrained ketone 10; loss of HCℓ from 10 giving dihydrobenzindenone 11 and successive cross cyclisation/ring opening steps via substituent stabilised diaskeuastic biradicals[7] provides a rational route to benzindenone 6.

Consistent with this scheme, the final HCℓ elimination step is not easily available to the isomeric precursor trichlorodihydrobenzindenones or the biradical species connecting them on the reaction co-ordinate; all the biradical and neutral intermediates could therefore be in equilibrium before HCℓ elimination precipitates benzindenone 6 - the most stable of the isomers having an alternating t-Bu substituent pattern.

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