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NOVEL REARRANGEMENT AND CRYSTAL STRUCTURE OF TETRAARYLATED DIHYDROSEMIBULLVALENE DERIVATIVES

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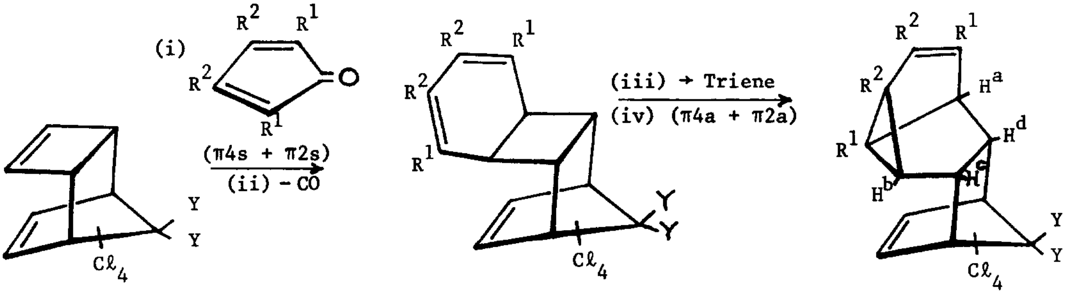
Summary: The structure of a dihydrosemibullvalene, **3**, previously deduced from nmr and mass spectrometry and from chemical transformation of an analogue - is confirmed by X-ray analysis. The thermal rearrangement of other analogous arylated dihydrosemibullvalenes is disclosed.

Reaction schemes postulating transitory intermediates formed by intramolecular (4 + 2)π cycloaddition in thermal reactions of cycloalka-1,3,5-trienes and related compounds have occasionally been advanced to account for unexpected experimental observations.[1] Very recently, however, stable products isolated in thermal reactions otherwise expected to give bicyclic tautomers of heavily substituted cycloocta-1,3,5-trienes, have instead been characterised as novel dihydrosemibullvalene ("DHSB") derivatives on the basis of nmr and mass spectrometry; additionally - in one instance - structural evidence derives from solvolytic rearrangement to a crystalline derivative for which X-ray analysis provides a definitive structure logically related to its DHSB precursor.[2] All these compounds rationally derive from intramolecular (π4a + π2a) cycloaddition in the immediate cycloocta-1,3,5-triene precursor. Concurrently, we have reported the formation of apparently analogous DHSB's **3** - **5** by thermal decarbonylation at 140-240° of relevant cyclopentadienone 1:1 adducts of halogenated tricyclo[4,2,1,$0^{2,5}$]nona-3,7-trienes **1** and/or **2**;[3] compound **6** is similarly derived.[4]



1 Y = Cℓ
2 Y = OMe

BCOD

3 $R^{1,2}$ = Ph, Y = OMe
4 R^1 = p-Anisyl, R^2 = Ph, Y = Cℓ
5 R^1 = Me, R^2 = Ph, Y = Cℓ
6 R^1 = Ph, R^2 = 2'-Pyridyl,Y=Cℓ

The thermal fate of the tetrasubstituted bicyclo[4,2,0]octadiene component ("BCOD") derived in step (ii) contrasts with other pericyclic reactions occurring in diene-unsubstituted analogues.[3]

After extensive purification, compound 3 (M=670) crystallises (poorly) from C_6H_6/MeOH (m.p. 188-190°). Crystals are monoclinic, a = 40.733(7), b = 9.693(12), c = 37.537(6) Å, β = 125.4(2)°, U = 12081(3) Å^3, Z = 16, F(000) = 5500, space group C2/c (2 molecules/asymmetric unit), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.71069 Å, μ(Mo-K_α) = 4.3 cm^{-1}. Application of SHELXTL direct methods routine to the rather poor data[5,6] gave structural fragments; subsequent partial structure expansion allowed location of all non-hydrogen atoms. Refinement by cascade least squares, with anisotropic thermal parameters for only the chlorine and oxygen atoms and with phenyl groups as rigid hexagons (C—C 1.395, C—H 0.960 Å) gave R 0.12.

The molecular structure is in Fig. 1. The essential features of the compound are unambiguously revealed as an endo-norbornene-exo-annellated dihydrosemibullvalene; the mid-field ^{1}H nmr spectrum (as for all compounds 3-6) exhibits two singlets and two doublets in the range 5.7 - 7.7τ due to angular preclusion of significant spin-couplings for Ha, Hb; Hc, Hd therefore appear as well resolved doublets.[7] The abnormally low-field Hb resonance (e.g. τ: 3, 6.93; 4,

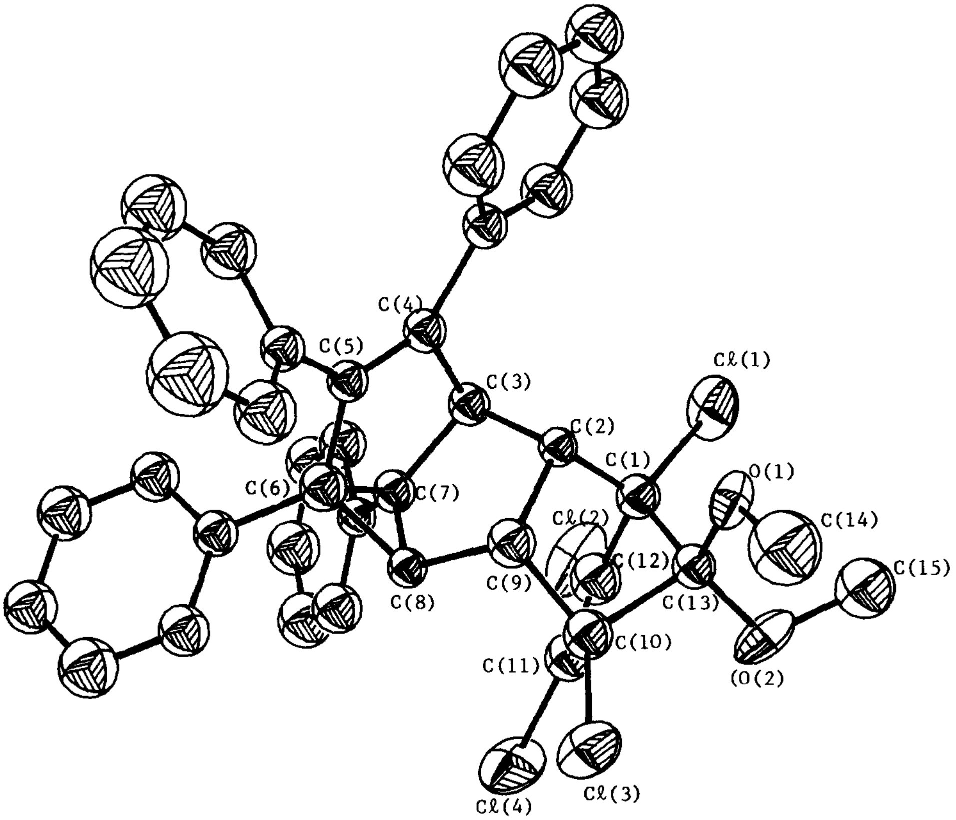
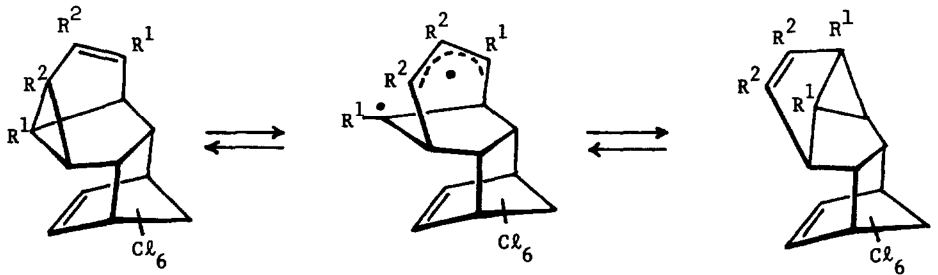


Fig. I

(50% Probability Thermal Ellipsoids)†

6.99^a; **5**, 7.65) which earlier obscured structural assignment,[8] and similarly unusual ^{13}C cyclopropane t-CH resonance (δ: **3**, 39.33[9], $J_{^{13}C/^{1}H}$ 157 Hz; **4** 40.39; **5** 39.53) find analogy in very recent data for a DHSB derivative having a monoarylated cyclopropane ring[10] (t-CH, ^{1}H, τ: 6.99, 7.45 ^{13}C, δ: 35.01, 52.63; quat C, 47.98).

DHSB's **3** - **6** accumulate slowly in heated solutions of **1** and/or **2** with relevant cyclopentadienones at 140-190°, together with other decarbonylation products, (e.g. BCOD and tautomeric cyclooctatriene derivatives) which when separately heated, give appropriate DHSB's. Melting crystals of the 2,5-di(p-anisyl)-3,4-diphenyldienone adduct of **1** (235°, 1-2 min.) however gives not only **4** (m.p. 234° decomp.) but also an isomer **7** (m.p. 185°), whilst **4** and **7** when separately heated (144°, 24 hr) yield ca. 1:1 mixtures of the two compounds. These have nearly identical m/e and ^{1}H/^{13}C nmr spectra which are closely similar;[11] significantly MeO signals are deshielded in **7** (τ:^{a} 6.24, 6.34; δ: 55.04, 55.15) [and closer than in **4** (τ:^{a} 6.32, 6.45; δ: 54.91, 55.09)] as are vinyl and aromatic quat. ^{13}C signals which converge into pairs and doublets, unlike their more even spacing in the spectrum of **4**. In addition isomer **7** shows broad complex ^{1}H resonance (τ 2.8 - 3.7), but **4** also displays a well separated sharp singlet (τ 2.85, 5H Ph) in this region consistent with the presence of essentially different types of phenyl group. All these relative differences lend support to the suggested structure of **7** as the product of an unusually facile 1,3-allylic (biradical?) rearrangement of apparently novel type:



4 R^1 = p-Anisyl, R^2 = Ph
6 R^1 = Ph, R^2 = 2'-Pyridyl

7 R^1 = p-Anisyl, R^2 = Ph
8 R^1 = Ph, R^2 = 2'-Pyridyl

Similarly congruent, no isomerism has been detected in analogous preparations of **3** (whose rearrangement would be degenerate) nor of **5** (in which appropriate radical centres would be less well stabilised); but in the preparation of DHSB **6** a closely related isomer **8** obtrudes[12] and in the reaction of 2,5-diphenyl-3,4-di(2'-pyridyl)cyclopentadienone with the cyclobutene dienophile in cyclooctatetraene maleic anhydride adduct, the expected[2] DHSB derivative is a mixture of two isomers having appropriate spectroscopic properties.[13] Further work on the thermal reactions of **3**-**8**, their analogues, and precursors is in hand.

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Footnotes and References

1. R.F. Childs, R. Grigg and A.W. Johnson, J. Chem. Soc. C., 201 (1967).
2. G.I. Fray, W.P. Lay, K. Mackenzie, and A.S. Miller, Tetrahedron Letters, 2711 (1979). (Note: m.p. of compd. designated "6" in this paper is 210-212° not 120-122°); I.A. Akhtar, R.J. Atkins, G.I. Fray, G.R. Green, and T.J. King, Tetrahedron, in press (1980).
3. W.P. Lay, K. Mackenzie, A.S. Miller, and D.L. Williams-Smith, Tetrahedron, in press (1980).
4. **6**, isolated in lower yield than **8** and silica gel TLC resolved with lower R_f (20% Et_2O in $CC\ell_4$/petrol), m.p. 242-243° (decomp.) ^{1}H, τ: 1.70(m), 2.6-3.5(m); 5.66(s), 5.95(s); 6.01 and 6.66 (each d, J ≃ 7Hz) ^{13}C, δ: 38.90, 54.82, 56.94, 62.62 (sat. CH) 58.78, 59.32, 80.50, 82.51, 103.85 (quat. C); 22 signals resolved in the range 120.92-155.75 (aryl and vinylic =C). M/e almost identical to that of compound 6, with intense fragment ions at 679.90, 681.96, 683.97, 685.97, 687.98 and 689.96 ($M^{+\cdot}$, M+2, M+4 etc. with correct $^{35}C\ell$ / $^{37}C\ell$ abundance ratios).
5. Data collected by Syntex $P2_1$ diffractometer at 25°. Of 8911 reflections observed in the range $0° < 2\theta < 50°$, 3332 were deemed observed according to the criterion $I > 3.0\ \sigma(I)$.
6. G.M. Sheldrick, Anorganisch-Chemisches Institut der Universitat, Gottingen, Germany.
7. E.g. **3**, τ: 6.38, 6.94 each d (J = 7.0 Hz) 5.8, 6.9 each s.
8. D.L. Williams-Smith, Ph.D. dissertation, University of Bristol (1971).
9. **3**, other signals: ^{1}H;^{3} ^{13}C, δ: 51.36, 52.39, 63.33 (sat. CH, $J_{^{13}C/^{1}H}$ 144, 144 and 145 Hz); 55.26 (2 MeO); 56.88, 58.02, 108.13, 108.34, 113.87 (sat. quat. C); 125.52-130.45 (10 signals) and 124.76-142.97 (8 weaker signals) (aryl and vinyl =C).
10. 6,7-Benzo-1,4-diphenyltricyclo[3,2,1,$0^{2,8}$]octane: S. Weigl and J. Warkentin, Canadian J. Chem., 58, 210 (1980).
11. Other signals: ^{1}H, τ:[a] **4**, 5.82, 7.02 (each s, bridgehead) 6.28, 6.74 (each d, ring junction, J ≃ 7 Hz); **7**, 5.85, 6.97 (each s, bridgehead) 6.43, 6.77 (each d, J ≃ 7 Hz). ^{13}C, δ: **4**, 55.87, 56.78, 63.62 (sat. CH); 57.25, 80.66, 82.48, 103.93 (sat. quat. C, 1 signal obscure); 112.86-131.54 (8 signals) and 126.73-157.85 (9 weaker signals, 3 signals obscured). **7** 39.76, 55.96, 57.91, 63.76 (sat. CH); 56.34, 80.72, 82.45, 103.96 (sat. quat. C, 1 signal obscured); 112.84-130.51 (10 signals) and 129.10-159.06 (10 weaker signals) (aryl and vinyl =C); **4** and **7** each have m/e 738 ($M^{+\cdot}$) and 703 ($M-C\ell^{+\cdot}$).
12. **8**, m.p. 244-246° (decomp.) ^{1}H, τ: 1.72(m), 2.6-3.3(m); 5.70(s), 5.99(s); 6.04, 6.70 (each d, J ≃ 7.5 Hz) ^{13}C, δ: 38.85, 54.78, 56.85, 62.56 (sat. CH); 58.72, 59.28, 80.49, 82.46, 103.79 (quat. C); 21 signals resolved in range 120.92-155.71 (aryl and vinylic =C, 1 signal obscured). M/e 679.92, 681.94, 683.95, 685.93, 687.95, 689.92 ($M^{+\cdot}$, $M+2^{+\cdot}$ etc. with correct $^{35}C\ell/^{37}C\ell$ abundance ratios).
13. *Actually obtained for the isolated dicarboxylic acids.*

[a] ^{1}H τ data refer to solutions in $CC\ell_4$; all other ^{1}H and ^{13}C data refer to $CDC\ell_3$ with TMS as internal standard, determined on Jeol PS100 or FX90Q instruments. Mass spectra determined using MS902 - VG Micromass facility.

[†] Other data deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Cambridge, CB2 1EW.

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