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THERMAL REARRANGEMENT OF ALKYLARYLDIHYDROSEMIBULLVALENE DERIVATIVES: HYDROGEN ATOM TRANSFER PROCESSES

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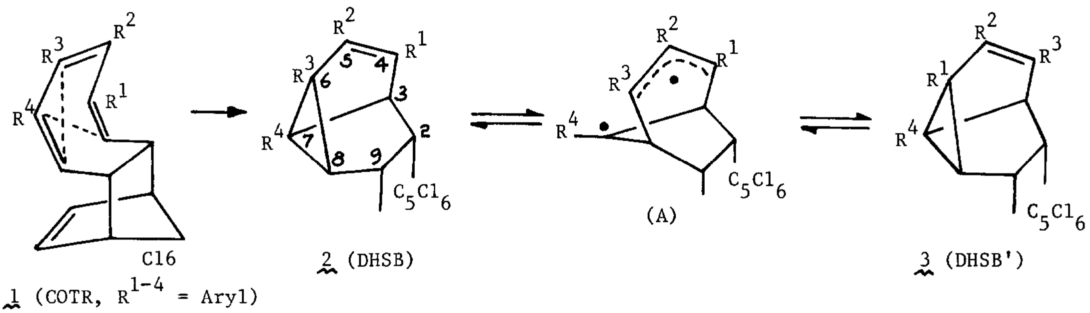
Summary. Alkylaryldihydrosemibullvalene derivatives, besides exhibiting vinylcyclopropane type rearrangements typical of tetraarylated analogues, also undergo H· atom transfer from methyl groups, most easily understood in terms of biradical intermediates resulting from alternative modes of cyclopropane ring scission.

In the preceding[1] and earlier papers[2,3] we described the thermal cyclisation of several tetraarylated cyclooctatriene derivatives (COTR's) e.g. **1** into dihydrosemibullvalenes (DHSB's) e.g. **2** and the thermal equilibrium **2** ⇌ **3**, (Scheme 1). The relative aryl substituent patterns in the primary cyclisation DHSB products **2** and their equilibrating isomers (DHSB's) **3** is entirely consistent with the intermediacy of biradical A.

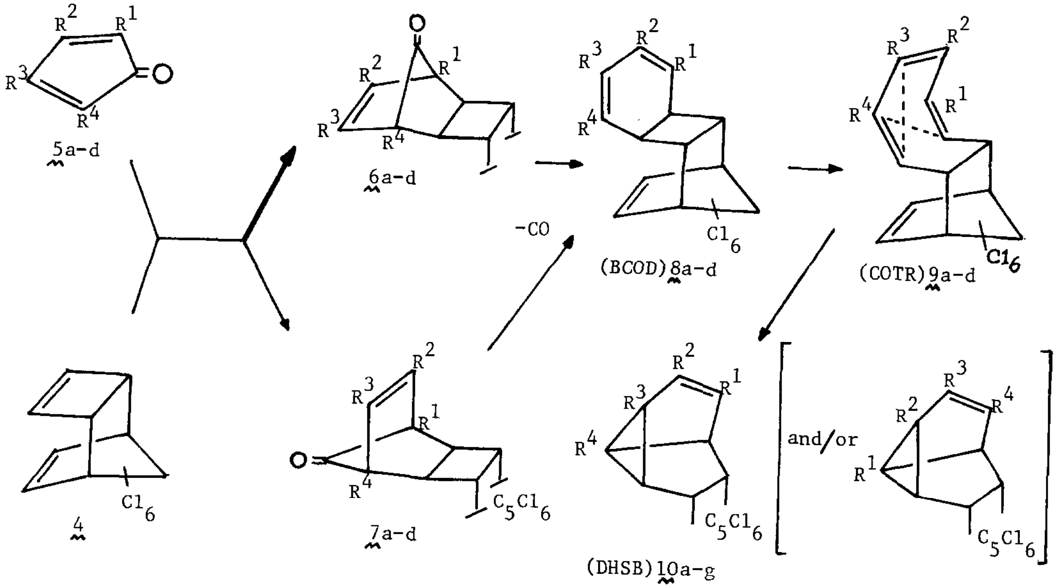


Scheme 1

The COTR's **1** are directly accessible by a sequence depicted in Scheme 2, by decarbonylation of *exo*/*endo* stereoisomeric *tetraaryl*cyclopentadienone adducts of tricyclononadiene **4**, and electrocyclic ring opening of the presumed primary decarbonylation products, tetraaryl bicyclo[4.2.0]octadiene ("BCOD") analogues of e.g. **8**a. However adduction of dimethyldiphenylcyclopentadienone, **5**a, with tricyclononadiene **4** (136-138°) gives a single adduct[2] **6**a (in analogy with **7**c identified by $^1H/^{13}C$ ^4J spin coupling[4]) and also, by contrast with the tetraarylated analogues, decarbonylation product BCOD **8**a, which is more rapidly formed from the *endo* isomer **7**a.[1] Both adduct **6**a and BCOD **8**a give dihydrosemibullvalene **10**a *via* COTR **9**a on stronger heating,[2] with no DHSB isomers, suggesting that an intermediate biradical B analogous to A is less readily formed (as expected) when R^4 is an alkyl group. Varying the number and sequence of alkyl substituents in the intermediate COTR's **9** as well as the thermolysis temperature might be expected to provide insight into the accessibility of biradicals analogous with A and we have therefore made a systematic study of the thermolysis products of the partially alkylated series of COTR's 9a-d[5] (and/or their precursor adducts 6a-d), and their cyclisation and DHSB rearrangement products 10a-f.[5]

Further investigation confirms that only DHSB 10a is formed in the thermolysis of adduct 6a. Whilst analysis of accumulated minor solution thermolysis products gives two isomeric bridged peroxides of BCOD 8a(^{1}H n.m.r., m/e) one of which is identical to the product of ariel photolysis of BCOD 8a,[6] no isomer of DHSB 10a can be detected (^{1}H n.m.r., prep. TLC). Instead, heating crystals of DHSB 10a (250°/120 sec.) gives, after extensive purification, besides recovered 10a, an air-sensitive gum assigned structure 11.[5] Here, the crude product ^{1}H n.m.r. exhibits signals due to DHSB 10a and isomeric triene 11 (1:1 ratio) and a set of signals of variable relative intensity analogous to those of triene 11 but with a lower-field CH_3 singlet (δ 1.72) rather than the high-field CH_3 doublet characteristic of 11 (δ 0.87, J = 7Hz) consistent with the formation of the isomeric triene 12 *(but which is not easily isolated). The fixed stereochemistry of DHSB 10a precludes* 1,5-homodienyl sigmatropic shift as the source of 11 and a biradical B analogous to A seems implicated, 1,4-H· atom transfer to the adjacent allylic radical terminii giving rise to 11 and its isomer 12.[7] Such a ring-strain dissipation pathway is not available in the tetraarylated DHSB systems, and cannot be envisaged either for the isomeric DHSB's 10b and 10e potentially accessible from COTR 9b. Accordingly, solution thermolysis of COTR 9b (172°, 7 hr.) gives as expected DHSB's 10b, 10e distinguishable by the greater separation of the CH_3 ^{1}H n.m.r. singlet resonances in isomer 10b (δ 0.97 and 1.94) compared to those for 10e (δ 1.28 and 1.76); the greater cyclopropyl proton deshielding in DHSB 10e (δ 2.84) compared to that in isomer 10b (δ 2.24), concomitant with two proximate Ph groups in the former, and a similar effect on the bridgehead (H-6) signal (10b δ 3.88, 10e δ 3.52) provides adequate structural confirmation. Heating solutions of either DHSB 10b or 10e (138°, 380 min.) gives an equilibrium mixture (10b:10e = 65:35), rearrangement being relatively fast compared to H· transfer which is slow at 196° for DHSB 10a; briefly heating crystals of DHSB isomer 10b and 10e (230°) however, gives an identical mixed product from each, containing both DHSB's 10b and 10e and a new compound identified as the methylenecyclopentene 13 formed *via* a biradical intermediate C, illustrating an alternative allylic C-3 ring-scission in DHSB 10b. None of the isomeric methylenecyclopentene which could arise from DHSB 10e by this mechanism *via* intermediate D is detectable, probably reflecting steric effects on stability in the biradical, and on the relative ease of H· transfer, which can be seen in models to be more favourable in intermediate C than in its isomer D. (The intermediate C could also arise directly from the COTR 10b; however both DHSB's 10b and 10e accumulate in the similar thermolysis of the cyclo-triene before compound 13 appears).

Thermolysis of COTR 9c (215-230°) on the other hand gives only DHSB 10c of the two possible and at higher temperatures the ring-scission H· transfer product 14 is formed, analogous behaviour to that of DHSB 10a; the rearrangement 10c → 14 *is also effected* catalytically by $AgNO_3$-silica gel at 25°.[8] Similar experiments with COTR 9d more closely follow expectation; besides DHSB 10f, whose rearrangement is degenerate, two other isomeric equilibrating DHSB's, 10d and 10g are produced (ratio 10f:10d:10g - 3:2:1).



Scheme 2

a $R^{1,4} = CH_3$ $R^{2,3} = Ph$

b $R^{1,4} = Ph$ $R^{2,3} = CH_3$

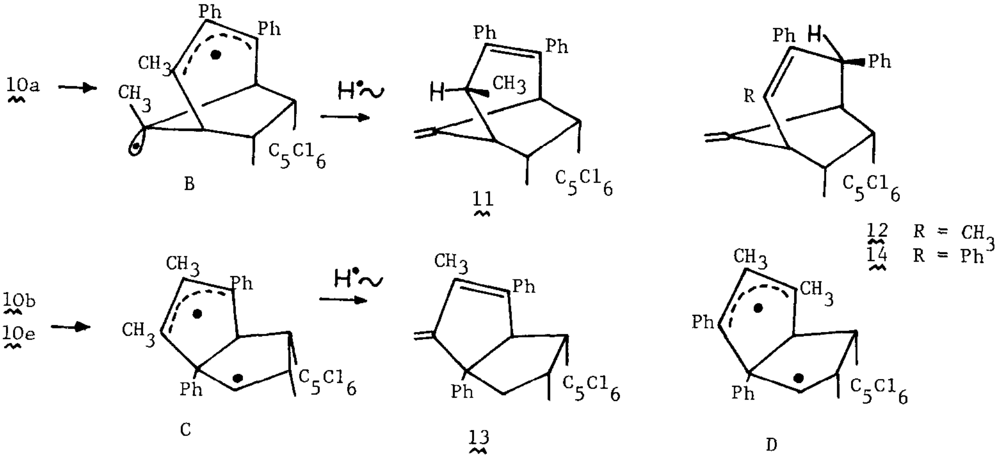
c $R^{1,2,3} = Ph$ $R^4 = CH_3$

d $R^{1,2,4} = Ph$ $R^3 = CH_3$

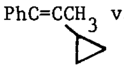
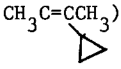
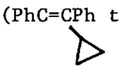
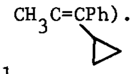
e $R^{1,2} = CH_3$ $R^{3,4} = Ph$

f $R^{1,3,4} = Ph$ $R^2 = CH_3$

g $R^1 = CH_3$ $R^{2,3,4} = Ph$



DHSB's 10d,g are also those theoretically expected but not observed from COTR 9c, the isomers being distinguishable by their differential CH_3 ^1H n.m.r. chemical shifts, as well as by the relative positions of cyclopropyl and bridgehead signals in close analogy to DHSB's 10b,e. The thermodynamically most stable rearrangement product DHSB 10d incorporates a stilbene element (cf. 10b,e 65:35, $PhC=CCH_3$ vs. $CH_3C=CCH_3$) and the primary cyclisation of COTR 9d follows the two alternative pathways equally in complete contrast to COTR 9c where only one of the alternative primary cyclisation products is realised, to that DHSB(10c) with a stilbene element, ($PhC=CPh$ to the exclusion of $CH_3C=CPh$). Prolonged heating of COTR 9d gives difficultly separable mixtures whose ^1H n.m.r. spectra suggest H$\cdot$ shift rearrangement products analogous to that from DHSB 10b (e.g. the triphenyl analogue of methylenecyclopentene derivative 12).

In summary, the four alkylaryl COTR's 9a-d undergo the same cyclisation, and subsequent DHSB vinylcyclopropane rearrangements as the tetraarylated analogues, but methyl substituents at radical centres in the relevant bi-radical intermediates allow alternative H$\cdot$ transfer pathways as ring-strain dissipating mechanisms.

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Footnotes and References

1. S. Greenfield and K. Mackenzie, Tetrahedron Letters, (1984)
2. W.P. Lay, K. Mackenzie, A.S. Miller, and D.L. Williams-Smith, Tetrahedron, (1980), 36, 3021.
3. G.E. Taylor, K. Mackenzie, and G.I. Fray, Tetrahedron Letters, (1980), 4935.
4. R.Y.S. Tan, R.A. Russell, and R.N. Warrener, ibid., (1979), 5031 give related examples.
5. All cyclooctatrienes, dihydrosemibullvalenes and their isomeric rearrangement products have been characterised by elemental composition and/or accurate $M^{+\cdot}$ mass measurement, in addition to ^1H, ^{13}C n.m.r. and m/e for all compounds discussed.
6. D.L. Williams-Smith, Ph.D. Dissertation, University of Bristol (1971).
7. For a discussion of hydrogen transfer mechanism in methyl vinyl cyclopropane rearrangements see J.J. Gajewski "Hydrocarbon Thermal Isomerizations" (Academic Press), 1981, p.81
8. It is well known that Ag^{I} cation may catalyse the rearrangement of strained-ring systems[9] but this example is the only instance found in the present work.
9. cf. L.A. Paquette, Accounts Chem. Research (1971), 4, 280.

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