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THE THERMAL REARRANGEMENT OF TETRA-ARYLATED DIHYDROSEMIBULLVALENE DERIVATIVES, AND $^1H/^{13}C$ NMR-STRUCTURE CORRELATIONS

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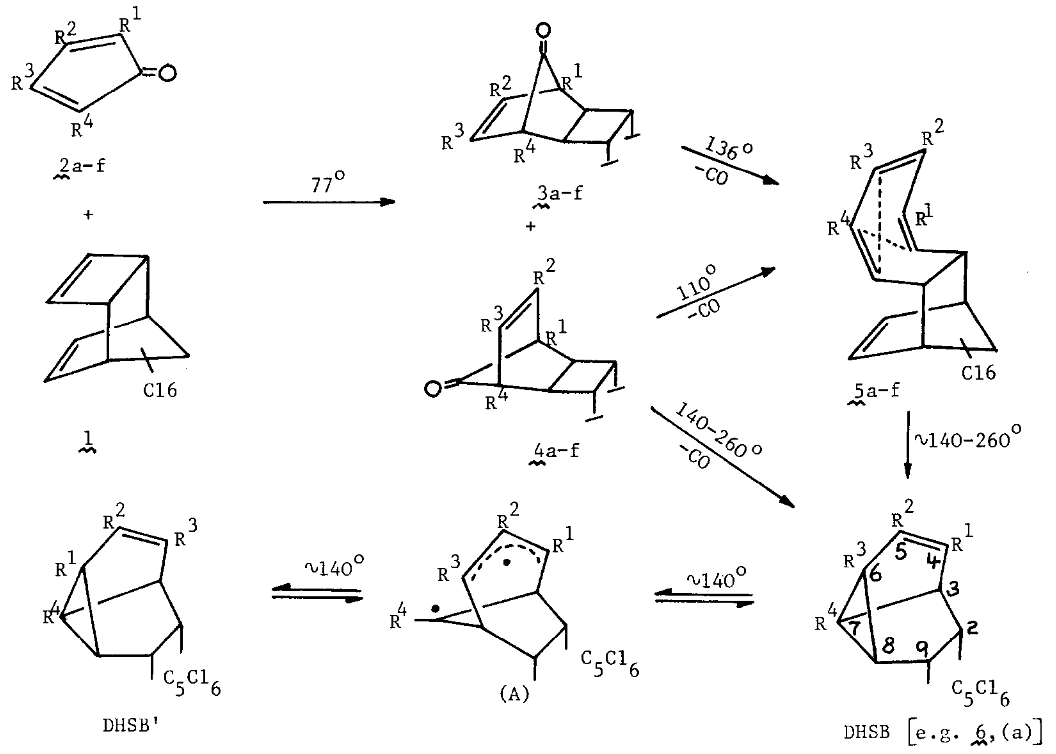
Summary: A systematic study of the thermal cyclisation of isomeric di-p-anisyl-diphenylcyclooctatriene derivatives, and of the facile isomerisation of the resulting dihydrosemibullvalenes, with $^1H/^{13}C$ nmr-structure correlations, supports earlier proposals for rearrangement mechanism.

In earlier papers[1,2,3] we described the reaction sequence illustrated in Scheme 1[4] (e.g. 3,4a → 5a → 6a) and proposed that the facile thermal rearrangement of dihydrosemibullvalene ("DHSB") 7 (Scheme 2) into an isomeric dihydrosemibullvalene (DHSB′), 8 probably involves an intermediate of general type A in Scheme 1. The 4,7-dimethyl-5,6-diphenyl analogue



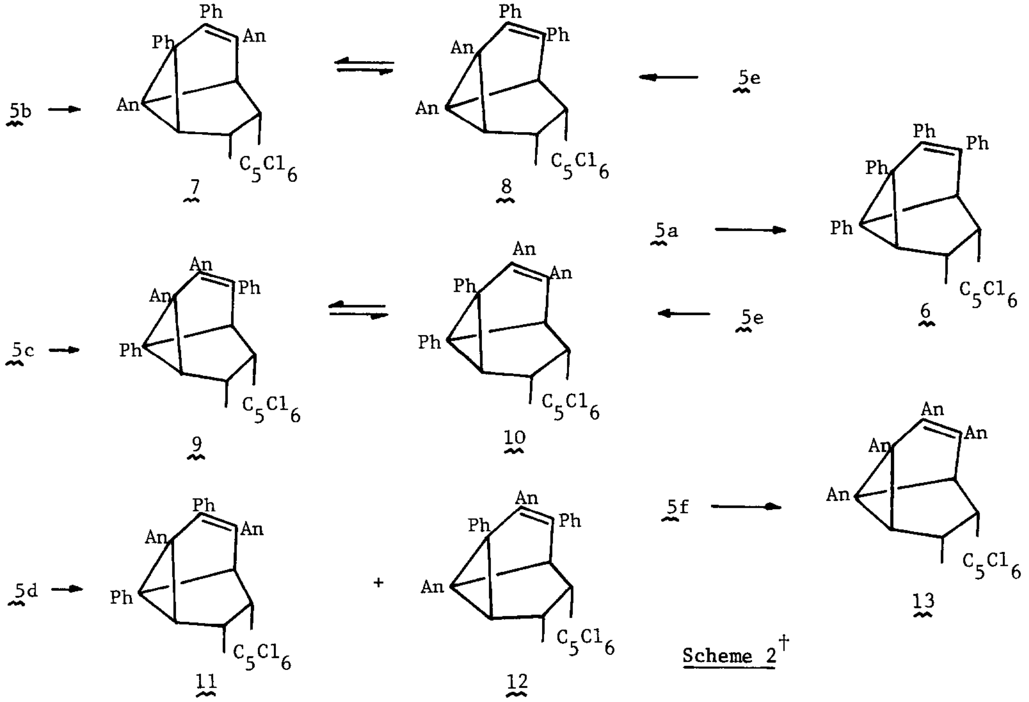
Scheme 1

a) R^{1-4} = Ph
b) $R^{1,4}$ = An $R^{2,3}$ = Ph
c) $R^{1,4}$ = Ph $R^{2,3}$ = An
d) $R^{1,3}$ = Ph $R^{2,4}$ = An
e) $R^{1,2}$ = An $R^{3,4}$ = Ph
f) R^{1-4} = An (An = p-$CH_3OC_6H_4$)

of 6 however fails to exhibit any isomerisation under similar mild conditions.[5] In order to substantiate the course of rearrangement of the tetra-arylated compound 7, in parallel with an investigation of the partly alkylated compounds, we have made a systematic study of the cyclisation of a series of isomeric di-p-anisyldiphenyl analogues (5b-e) of cyclooctatriene ("COTR") 5a and the subsequent rearrangement of the derived DHSB's 7-12 where it was expected that the ^{1}H nmr CH_3O signals would be especially useful for structural correlation. As expected,[1,6] cycloaddition of the relevant cyclopentadienones 2a-f with tricyclononadiene 1 (CCl_4, 77°) gives mixtures of *exo* (3) and *endo* (4) adducts, distinguishable by $^{13}C/^{1}H$ ^{4}J coupling at bridge C=O in e.g. 4b;[7] significantly the *endo* compounds (4) also decarbonylate more readily[8] giving here COTR's (5). Consonent with this, higher temperature cycloadditions (C_6H_5Me, 110°) give essentially only *exo* adducts (3, 74-78%), together with COTR's (5, 21-22%) presumed to derive mainly from the *endo* adducts (4). The COTR's (5) are in practise most readily isolated by thermolysis of the adducts (3 and 4) in boiling xylene (136-8°) the resulting mixtures of COTR's (5) and relevant DHSB's being easily separated by preparative TLC ($AgNO_3$-silica gel). Heating crystals of the stereoisomeric adducts 3a-f and/or 4a-f, or of the derived COTR's 5a-f, near or above the m.p. conveniently affords good yields of the appropriate DHSB's 7-12 and their isomeric rearrangement products, readily recognised by their characteristic ^{1}H nmr spectra.[1]

Accordingly, heating COTR 5c (20 sec/260°) gives, in 60% conversion, approximately equal amounts of two compounds (I), m.p. 203-204.5° and (II), m.p. 186.5-188° each isomer, separately heated, giving the same equilibrium mixture. Under milder conditions ($C_6H_4Cl_2$, 137°, 6h) the rate of conversion is sufficiently slow that compound II is clearly observed (^{1}H nmr) before its isomer I appears, still exceeding the equilibrium concentrated after 400 mins. Compound II is therefore DHSB 9 and I is the rearrangement product 10. Similar experiments with COTR 5b to determine which of DHSB's 7 and 8 appears first are inconclusive due to ^{1}H signal overlap, but there are slight indications that III (m.p. 185°) actually appears before IV (m.p. 234°), and this requires that III be assigned structure 7 and IV is the higher m.p. rearrangement product, DHSB 8 the opposite assignment to that made earlier[2] on the basis of limited data (*vide infra*). Altering the substituent order to an alternating sequence as in COTR 5d should provide further mechanistic insight since theoretically, two alternative intramolecular cyclisation routes are possible giving as primary products DHSB's 11 and 12; each of these should exhibit degenerate rearrangement because of the symmetry of the appropriate biradical intermediate A. Concordantly, thermolysis of COTR 5d and repetitive prep. TLC gives only two isomeric difficultly separable compounds V and VI,[9] different from 7/8 and 9/10; thermolysis of the precursor of 5d, adduct 3d, significantly always gives a product fraction containing an excess of V over VI (ratio 2:1). Here, isomer V (containing 10% VI) is thermally stable at 136-138°/5h, consistent with the isomers V and VI being the expected DHSB products 11 and 12 (see Tables 1 and 2), with no easily accessible interconversion pathway.

As a further test of the proposed reaction sequence of Scheme 1, attention is next directed to COTR 5e; this might also be expected to yield two compounds as immediate cyclisation products (DHSB's 8 and 10) but here each primary product might easily rearrange into DHSB's 7 and 9 respectively. Accordingly thermolysis of COTR 5e (60 sec/250°) and separation as before gives a fraction with a ^1H nmr spectrum identical to that of an artificial mixture of DHSB's 7, 8, 9 and 10, fully confirming expectation.



Scheme 2†

The difficulties inherent in the identification of the primary cyclisation product(s) in a mixture of two or more equilibrating DHSB's (e.g. $7 \rightleftharpoons 8$) can be circumvented by ^1H and ^{13}C structure correlations. For isomer-pairs I/II, III/IV and V/VI the p-anisyl CH_3O group and cyclopropane (H-8) ^1H signals show the largest chemical shift variations between isomers, other signals changing little; comparison of these signals for the three isomer-pairs with those for the analogous tetra-p-anisyl- and tetraphenyl DHSB's, 6, 13, taken with the chemical evidence, then leads to the structural assignments illustrated in Tables 1 and 2.

Table 1

Compound	^1H nmr δ, $CH_3O(CDCl_3/TMS)$			
(13)	3.60	3.67	3.72	3.79
I (10)		3.68(5)*		3.83(4)
II (9)	3.62(6)	3.69(5)		
III (7)			3.72(7)	3.80(4)
IV (8)	3.59(6)		3.72(7)	
V (11)	3.59(6)			3.80(4)
VI (12)		3.68(5)	3.73(7)	

Table 2

Compound	^1H nmr δ H-8	R^3	R^4
(6)	3.22	Ph	Ph
I (10)	3.22	Ph	Ph
II (9)	3.16	An	Ph
III (7)	3.13	Ph	An
V (11)	3.12	An	Ph
VI (12)	3.12	Ph	An
IV (8)	3.08	An	An
(13)	3.03	An	An

*Bracketed figures indicate skeletal positions of $p-CH_3OC_6H_4-$ ("An") groups.

†An = $p-CH_3OC_6H_4-$

Further complementary validation of these assignments is found in the ^{13}C nmr spectra for the isomer-pairs, the p-anisyl tert. aromatic (= CH) nucleii giving signals well separated from those of the Ph groups; in particular, δ values for the C-3' nucleus in the p-(i.e. 4-') $CH_3OC_6H_4$- groups fall characteristically into two of the four narrow frequency bands exhibited by this nucleus in the tetra-p-anisyl DHSB (13), and a similar pattern to that for the ^{1}H (CH_3O) chemical shifts in Table 1 is clearly apparent. For example isomers III, IV and VI all exhibit a signal at δ 112.8 ± 0.06 corresponding to each having a 7-p-anisyl- substituent. Similarly signals at 113.88, 113.3 and 113.03 ppm can be assigned to the C-3' nucleii for p-anisyl groups at the 4, 5 and 6 positions of the DHSB. Correlations are also evident for the p-anisyl C-2' nucleii which similarly resonate in four narrow frequency bands in the lower field range 127.53 - 131.48 ppm, and in fact the ^{13}C nmr signals for each of the eight equivalent pairs of tert. (= CH) aromatic nucleii in all of the tetraarylated DHSB's discussed here form a completely self-consistent set in which the δ values depend only on the relative position of the aromatic group in the DHSB system, independently of the other aryl substituents, exactly paralleling the CH_3O ^{1}H frequency pattern. However no simple analogous pattern is seen for the CH_3O ^{13}C signals. Finally, the C-3 bridgehead ^{13}C frequencies show a regular upfield shift with increasing p-anisyl substitution.

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References and Footnotes

1. W.P. Lay, K. Mackenzie, A.S. Miller and D.L. Williams-Smith, Tetrahedron, (1980), 36, 3021.

2. G.E. Taylor, K. Mackenzie and G.I. Fray, Tetrahedron Letters, (1980), 4935.

3. cf. G.I. Fray, W.P. Lay, K. Mackenzie and A.S. Miller, ibid., (1979), 2711.

4. Cyclopentadienones 2d (m.p. 217-218°) and 2e (m.p. 171-172°) used in the present work appear to be new compounds (cf. ref. 9 below); the compound identified as 2e by W. Broser, J. Reusch, H. Kurreck and P. Siegle, (Z. Naturforsch B. (1969), 24, 685) may, from the m.p.(212°), actually be ketone 2d. However we have made ketone 2e by the unambiguous method of E.I. Becker, L. Mehr and P.E.Spoerri, J.Amer.Chem.Soc., (1955), 77, 984.

5. At higher temperatures, different types of rearrangement ensue with diakyldiaryl analogues of the tetra-arylated compounds 6 etc.; these involve H· transfer reactions, also most easily accommodated in terms of intermediate bi-radicals analogous with A in Scheme 1. K. Mackenzie and S. Greenfield, Tetrahedron Letters, accompanying paper. In this connexion we also thank J.W. Barton and M. Shepherd for useful information.

6. For related stereochemical differentiation in cycloadditions of cyclopentadienones to cyclobutenes see C.N. Anderson, I.W. McCay and R.N. Warrener, ibid, (1970), 2735.

7. R.Y.S. Tan, R.A. Russell and R.N. Warrener, ibid, (1979), 5031.

8. cf. I.A. Akhtar, R.J. Atkins, G.I. Fray, G.R. Geen and T.J. King, Tetrahedron, (1980), 3033. G.Kretshner, I.W.McCay, M.N.Paddon-Row and R.N.Warrener, Tetrahedron Letters (1975), 1339.

9. All cyclooctatriene derivatives, and derived dihydrosemibullvalenes except compound VI (which is contaminated with ∿5% of its isomer V), have been fully characterised by elemental composition and/or accurate mass, in addition to m/e, ^{1}H and ^{13}C nmr for all compounds discussed.

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