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THERMAL TRANSFORMATIONS OF $[_{\pi}4_{s} + _{\pi}2_{s}]$CYCLOADDUCTS OF TETRACYCLONE AND TRICYCLO$[4.2.2.0^{2,5}]$ DECA-3,7-DIENES: SEQUENTIAL DECARBONYLATION, RETRO-6π ELECTROCYCLISATION, AND INTRAMOLECULAR $[_{\pi}4_{a} + _{\pi}2_{a}]$CYCLOADDITION

G.I. Fray,* W.P. Lay, K. Mackenzie,* and A.S. Miller
(School of Chemistry, The University, Bristol BS8 1TS, England)

Dihydrosemibullvalenes result from heating cyclopentadienones with tricyclo$[4.2.2.0^{2,5}]$ decadienes; intramolecular [π4a + π2a]cycloaddition of intermediate tricyclo$[8.2.2.0^{2,9}]$ tetradeca-3,5,7,11-tetraenes provides a rationale.

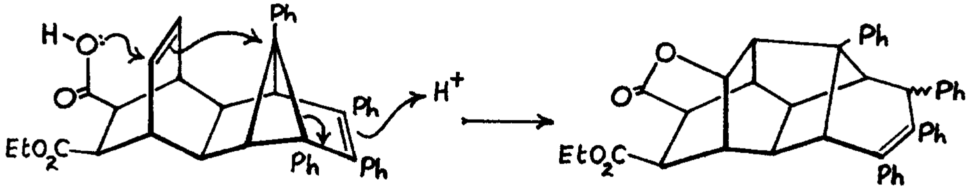
Thermal $[_{\pi}4_{s} + _{\pi}2_{s}]$cycloadditions of hemicyclone 1 at the cyclobutene moiety of carbocyclic systems of type 2 have been reported.[1-4] We have observed similar reactions of tetracyclone 3 with anhydride 2a and with hydrazo-diester 2b, but also find that further transformations follow the well-known decarbonylation process when the adducts are heated. Dauben et al.[1] have shown that hemicyclone 1 and anhydride 2a afford a product formulated as 4;[5] we find that tetracyclone 3 gives a similar adduct 5[5] [m.p. ca. 255° (decomp.); ν_{max} 1859, 1780 sh, 1773 cm.$^{-1}$; ^{1}H n.m.r.† $\tau[(CD_3)_2SO]$ 2.5-3.45 (22H), 6.4-6.6 (2H), 6.7-6.85 (2H), 7.05-7.2 (2H), 7.85-8.06 (2H)], and analogously, hemicyclone 1 and tetracyclone 3 with ester 2b yield 6[5] [m.p. 120-122°, ν_{max} 1770 cm.$^{-}$ ^{1}H n.m.r.† τ 2.8-3.6 (12H), 5.0-5.2 (2H), 5.7-6.1 (4H), 7.6-7.7 (2H), 7.9-8.2 (2H), 8.76 (6H), 8.8 (6H, s)] and 7[5] [m.p. 213-214° (decomp.); ν_{max} 1785 cm^{-1}; ^{1}H n.m.r.† τ 2.7-3.4 (22H), 4.85-4.98 (2H), 5.8-6.12 (4H), 7.30 (2H), 7.52 (2H), 8.71-9.04 (6H)] respectively.[6]

Alkaline hydrolysis of adducts 6 and 7 in air give (via oxidative decarboxylation and deazetation) the cyclohexadienes 8 [m.p. 139-141°; ν_{max} 1770 cm.$^{-1}$; ^{1}H n.m.r.† τ 2.7-3.0 (10H), 4.1-4.5 (4H), 7.3 (4H), 8.75 (6H, s); ^{13}C n.m.r.‡ δ 7.89, 28.76, 53.81, 56.73 (saturated C), 121.04-142.21 (7 signals resolved, = C<), 208.65 (C=O)] and 9 [m.p. 212-213° (decomp.); ν_{max} 1780 cm.$^{-1}$; ^{1}H n.m.r.† τ 2.79-3.33 (20H), 4.22 (4H), 6.70 (2H), 7.30 (2H); ^{13}C n.m.r.‡ δ 30.09, 50.96, 67.22 (saturated C), 121.65-142.33 (11 signals resolved, = C<), 202.83 (C=O)] respectively; in each case subsequent thermal decarbonylation is accompanied by fragmentation, with the formation of the expected tetrasubstituted benzene.[7]

Thermal decarbonylation (at ca. 210°) of the tetracyclone adducts 5 and 7, however, leads to products (A) and (B) which are not the expected cyclohexadienes 10 and 11; the n.m.r. spectra of both compounds clearly indicate the absence of a symmetry plane. (A) (m.p. 271-272°): ^{1}H n.m.r.† τ 2.8-3.4 (20H), 3.81 (1H, 't'), 4.08 (1H, 't'), 6.00 (1H, s), 6.25-6.45 (1H), 6.8-7.2 (4H), 7.27 (1H, s), 7.7-7.85 (1H); ^{13}C n.m.r.‡ δ 36.64, 37.68, 42.77, 43.62, 44.41, 45.56, 55.76, 56.24, 59.03, 63.16 (all saturated C), 125.35-142.28 (18 signals resolved, =C<), 171.82 and 172.43 (2 C=O). (B) (m.p. 230-231°): ^{1}H n.m.r.† τ 2.7-3.3 (20H), 3.60 (1H, 't'), 3.80 (1H, 't'), 4.68 (1H), 5.52 (1H), 5.92-5.95 (4H), 6.06 (1H, s), 6.53 (1H), 7.36 (1H, s), 7.40 (1H), 8.87 (6H).

Hydrolysis and concomitant deazetation of (B) gives a hydrocarbon $C_{36}H_{28}$ (m.p. 154-155°), which with maleic anhydride readily forms an adduct identical with (A). The n.m.r. spectra of the hydrocarbon (together with its thermal stability) are clearly inconsistent with structure 12: ^{1}H n.m.r.[†] τ 2.8-3.3 (20H), 3.8-4.8 (4H), 6.10 (1H, s), 6.75-7.0 (2H), 7.11 (1H s); ^{13}C n.m.r.[‡] δ 36.04, 40.77, 52.60, 57.70, 57.94, 66.68 (saturated C), 123.16-142.03 (17 signals resolved, =C<). Four tertiary and two quaternary (δ 57.70 and 57.94) saturated carbon atoms are present in this product, as indicated by offset proton decoupling.

Furthermore, when (A) is heated in ethanolic sulphuric acid an ester-lactone results, possessing structure 13 on the basis of a preliminary X-ray crystallographic examination.[8] This, together with the spectral evidence, enables (A) to be formulated as the dihydrosemibullvalene 14; 1H singlet signals in the ^{1}H n.m.r. spectrum can be assigned to H^{A} and H^{B}, the dihedral angles with H^{D} and H^{C} respectively being ∿90°, and the acid-catalysed rearrangement can readily be envisaged as follows.



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Compound (B) and the derived hydrocarbon may then be represented by 15 and 16 respectively.

The dihydrosemibullvalene system in these compounds may be rationalised as the product of an intramolecular $[_{\pi}4_{a} + _{\pi}2_{a}]$cycloaddition[9] in the valence tautomer 17 of the precursor cyclohexadiene 10 or 11. Possible precedents for a $[_{\pi}4_{a} + _{\pi}2_{a}]$cycloaddition within an eight-carbon framework include the formation of semibullvalenes from polymethyl-[10,11] and benzo-fused[12] cyclo-octatetraenes in thermal reactions, and from cyclo-octatetraene itself[11] in a photochemical process; the only known examples of the cyclo-octa-1,3,5-triene → dihydrosemibullvalene conversion are photochemical.[13,14] There are indications, however, that thermal cross-cyclisation of the cyclo-octatetraene π-framework to an intermediate bicyclo[3.3.0]octadienyl (bis-allylic) diradical can occur.[15] Whilst it is possible that a diradical intermediate might be involved in the conversion of e.g. 10 into 14 (cf. ref. 13) such an intermediate would contain one non-allylic radical centre, although the transannular π-bond might play a stabilising role; discussion of this point is deferred until later, when this and related work will be published in full.[16,17]

All new compounds have been characterised by elemental analysis and/or mass spectra.

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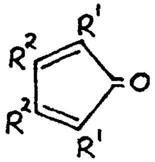
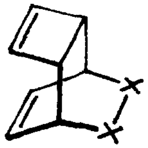


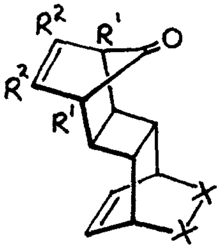
1 : R^1=Me, R^2=Ph

3 : R^1=R^2=Ph



2 a : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{CH.CO}\diagdown\\|\qquad\quad O\\\mathrm{CH.CO}\diagup\end{array}$ (endo)

b : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{N.CO_2Et}\\|\\\mathrm{N.CO_2Et}\end{array}$



4 : R^1=Me, R^2=Ph

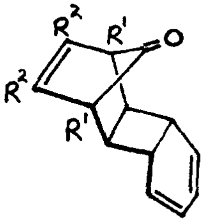
5 : R^1=R^2=Ph

$\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{CH.CO}\diagdown\\|\qquad\quad O\\\mathrm{CH.CO}\diagup\end{array}$

6 : R^1=Me, R^2=Ph

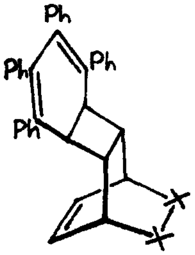
7 : R^1=R^2=Ph

$\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{N.CO_2Et}\\|\\\mathrm{N.CO_2Et}\end{array}$



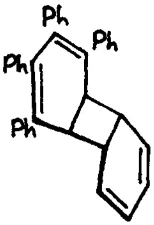
8 : R^1=Me, R^2=Ph

9 : R^1=R^2=Ph



10 : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{CH.CO}\diagdown\\|\qquad\quad O\\\mathrm{CH.CO}\diagup\end{array}$

11 : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{N.CO_2Et}\\|\\\mathrm{N.CO_2Et}\end{array}$



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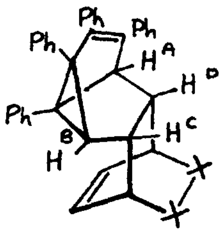
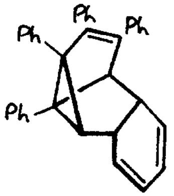


14 : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{CH.CO}\diagdown\\|\qquad\quad O\\\mathrm{CH.CO}\diagup\end{array}$

15 : $\begin{array}{c}X\\|\\X\end{array} = \begin{array}{l}\mathrm{N.CO_2Et}\\|\\\mathrm{N.CO_2Et}\end{array}$



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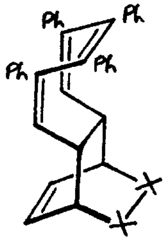

17 : $\begin{array}{c}\mathrm{X}\\ |\\ \mathrm{X}\end{array} = \begin{array}{l}\mathrm{CH.CO}\\ |\\ \mathrm{CH.CO}\end{array}\!>\mathrm{O}$ or $\begin{array}{l}\mathrm{N.CO_2Et}\\ |\\ \mathrm{N.CO_2Et}\end{array}$

References and Footnotes

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† Unless stated otherwise, $CDCl_3$ solution/TMS internal standard.

‡ Ppm downfield from TMS in $CDCl_3$.

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