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THE "VINYLOGOUS SESQUIFULVALENE" [1] 14-ELECTRON-ELECTROCYCLISATION REACTION

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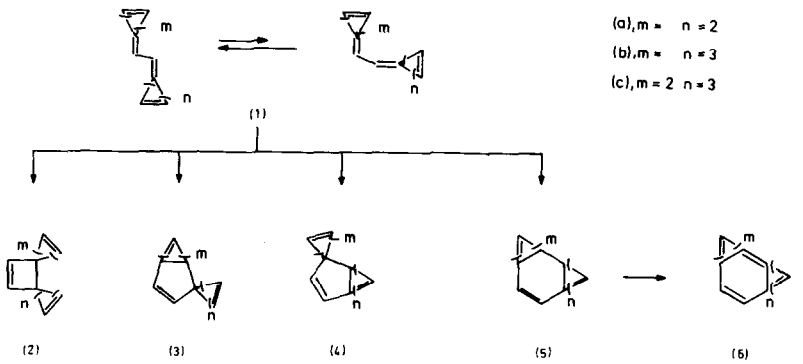
Several modes of electrocyclisation are open to the "vinylogous fulvalenes" ("fulvadienes") upon thermal or photochemical activation. From a preparative aspect, the cyclisation with participation of all π-electrons via six-membered transition states ((1) ⟶ (5), α, ω) is of value insofar, as the products (5) can serve as intermediates on the route to the still unknown angularly anellated, nonbenzenoid π-perimeter molecules (6) [2]. From a mechanistic aspect, the stereochemistry in the cyclisation step (1) ⟶ (5) as a function of the number of participating π-electrons is of special interest [3].



For (1a) we had already shown, that, thermally, it undergoes rapidly and exclusively the symmetry-allowed conrotatory 12-electron-cyclisation to trans- (5a) [4]. The additional attraction with (1c) lies in the fact, that the thermally symmetry-allowed disrotatory process (1c) ⟶ (7) ⟶ (9) for steric reasons is clearly disadvantaged compared with the symmetry-forbidden conrotatory process (1c) ⟶ (8) ⟶ (10). Obviously, the "transoid" transition state (8) resembles closely the helical s-cis conformation of (1c), whilst the "cisoid" transition state (7) needs rather drastic distortions around the C-1/C-8- and C-1'/C-6'-double bonds, in order to avoid severe H/H-compression.

(1c) is indeed thermally labile [1]. Very slowly at 20°C ($t_{1/2}(C_6H_6)$ ca. 215 h), rapidly at 80°C ($t_{1/2}$ ca. 12 min), the deeply coloured (1c) is converted into a colourless product (isosbestic point at 325 nm (acetonitrile)), which, by complete spectral analysis, is established as 1,8-dihydrocyclohept[e]indene (14) (containing (at 80°C)

ca. 5% of its 3,8-dihydro-isomer). In ca. 10^{-2} mol. solution the yield is practically quantitative; detectable competition by any of the alternative, thermally reasonable modes of electrocyclisation ((3), (4)), therefore, is excluded. From the half-lives of the disappearance of (1c) and the appearance of (14), as measured by ^{1}H NMR spectroscopy between 80.0°C and 89.0°C, an E_a value for the cyclisation of 24.4 ± 0.1 kcal/mole (log A = 12.0, $\Delta H^{\ddagger}$ = 23.3 ± 0.5 kcal/mole; $\Delta S^{\ddagger}$ = 6.3 ± 1.3 e.u.) is calculated. It thus becomes clear, why, in contrast to the cyclisation of (1a) (E_a=20.0 ± 0.4 kcal/mole, log A=11.3±0.3)[4], the primary products (9)/(10) or further thermodynamically less stable 1,5-hydrogen migration products (e.g. (11)) cannot be detected (thin layer chromatography, ^{1}H, ^{13}C NMR [5]. It was possible to decide between (9) and (10) by taking advantage of the high reactivity of their cyclopentadiene moiety towards dimethyl acetylenedicarboxylate. With ca. a 300 fold excess of dienophile, besides some polymeric material (probably arising from the unstable addi-

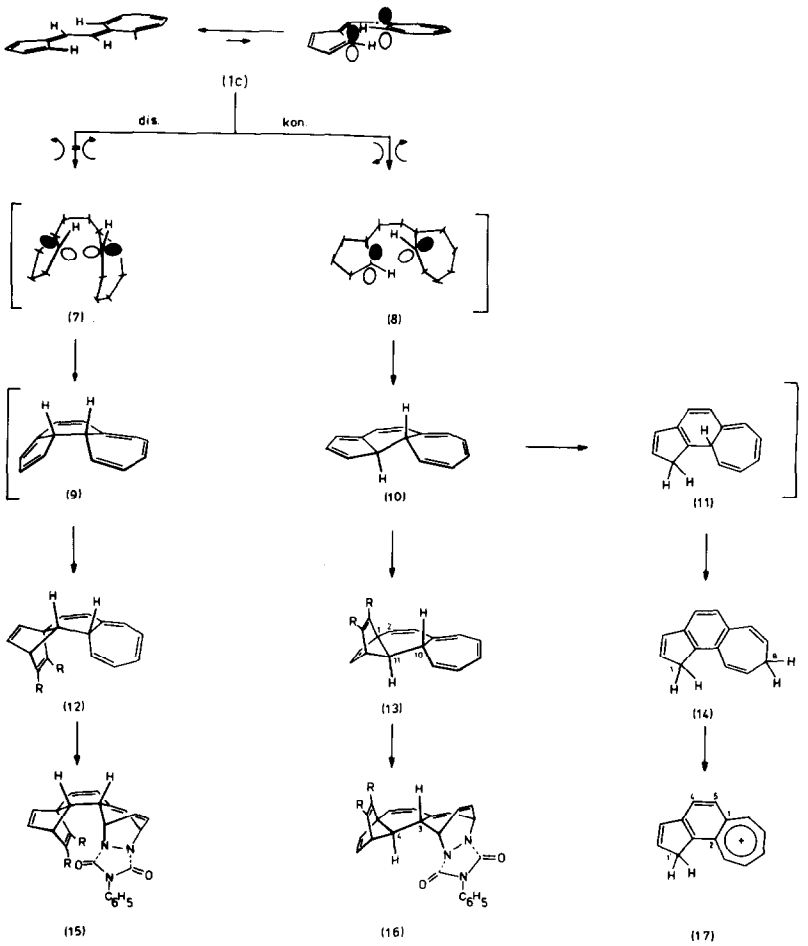
table: ^{1}H NMR data (τ) of compounds (13),(14) and (17) ($CDCl_3$, 180, 360 MHz)

(13)	2.96, 3.07, 3.55(2H), 3.67(2H), 3.88, 3.91, 5.00, 5.95, 6.25[b], 6.28[b], 7.30, 7.65; $J_{5,10}$=2.0, $J_{8,9}$=10.0, $J_{8,10}$=2.0, $J_{9,10}$=4.8, $J_{10,11}$ = 10.0, $J_{11,12}$=1.1, $J_{12,15}$=0.8, $J_{12,16}$=3.2, $J_{15,16}$=5.2 Hz.
(14) (1,8-)	2.68, 2.75, 3.11, 3.31, 3.33, 3.42, 4.04, 4.17, 6.60(2H), 7.49 (2H); $J_{1,2}$=$J_{1,3}$=1.9, $J_{2,3}$=5.6, $J_{4,5}$=8.0, $J_{6,7}$=10.3, $J_{7,8}$=$J_{8,9}$=6.6, $J_{9,10}$=10.3 Hz.
(14) (3,8-)	2.62, 2.81, 2.88, 3.12, 3.31, 3.38, 4.0-4.2(2H), 6.56(2H), 7.54 (2H); $J_{1,2}$=5.6, $J_{1,3}$=$J_{2,3}$=1.9, $J_{4,5}$=8.0, $J_{6,7}$=10.3, $J_{7,8}$=$J_{8,9}$ = 6.6, $J_{9,10}$ = 10.3 Hz.
(17)[a]	0.28, 0.37, 0.99, 1.25, 1.37, 1.3-1.45(2H), 2.53, 2.61, 5.79(2H); $J_{3,4(6,7)}$ = 10.2, $J_{4,5}$=$J_{5,6}$=9.0, $J_{6,7(3,4)}$=10.8, $J_{1',2'}$=$J_{1',3'}$ = 1.8, $J_{2',3'}$=5.6, $J_{4',5'}$=9.0 Hz.

a : CD_3CN ; b : OCH_3

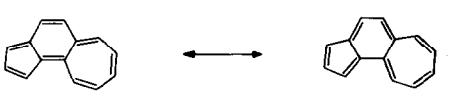
tion products), ca. 20% (14), 5 % of the known bisadduct of (1c) [1] and ca. 25 % of one 1:1 adduct (ethanol, m.p. 74°C) are formed and separated by chromatography (silica gel, benzene/ethyl acetate 9:1); with ca. a 500 fold excess the formation of (14) is almost totally suppressed (ca. 3 %) with 30 % each of the 2:1 and 1:1 adducts forming. On the basis of the ^{1}H and ^{13}C NMR analysis structure (13) is assigned to the 1:1 adduct, whereby it is assumed, in analogy with earlier findings [4], that the addition occurs from the side opposite to 10b-H. With dihedral angles between 10-H and 11-H of 25-40°C in (12) and of 145-160° in (13) the coupling constant $J_{10,11}$=10.0 Hz favours (13). This argument was strengthened, when it was found, that (13), which is resistant towards TCNE at 60°C, instantaneously adds N-phenyltriazolindione at 20°C, giving rise to a ca. 1:1 mixture of monoadducts, to which the exo/endo isomeric struc-

tures (16) have been assigned on spectroscopic (MS, ^{1}H, ^{13}C NMR) grounds. In particular, the trans-arrangement of 3-H and 4-H is convincingly indicated by the $J_{3,4}$-value of 12.0 Hz, when the dihedral angles of ca. 0° in (15) and 170-180° in (16) [6] are considered. Since there is no reason, why (9) should not add dimethyl acetylenedicarboxylate with a rate similar to (10), or why (12) should be much less stable than



(13), the absence of (12) manifests the stereospecificity of the ring closure. In conclusion: under the given steric restraints the 14-electron-electrocyclisation of (1c) follows the symmetry-forbidden conrotatory pathway [7].

Under conventional conditions of hydride elimination (triphenylmethyltetrafluoroborate, CH_2Cl_2, 20°C) (14) yields the very unstable indenotropylium salt (17). Upon



addition of a solution of (17) to DBN a deep blue product is formed ($\lambda_{max}(CH_2Cl_2)$ = 849, 770, 642, 585, 479 nm), which at -60°C survives for several hours, but at 20°C, however, rapidly decomposes. Experiments are in progress to characterise this product, thought to be the 14π-hydrocarbon (6c) ("phenazulene") [8].

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1) Cyclic cross-conjugated bond systems, part 34.- part 33: H. Babsch, H. Prinzbach, preceeding paper. In part in collaboration with cand. rer. nat. A. Beck.

2) H. Sauter, H. Prinzbach, Angew. Chem. 84, 297 (1972); Angew. Chem., Int. Ed. Engl. 11, 296 (1972).

3) R.B. Woodward, R. Hoffmann, Angew. Chem. 81, 797 (1969); Angew. Chem., Int. Ed. Engl. 8, 781 (1969). To a first approximation the vinylogous fulvalenes (1) are considered as perturbed linear polyenes. More information concerning their HOMO's is expected from PE-studies.

4) H. Sauter, B. Gallenkamp, H. Prinzbach, Chem. Ber. 110, 1382 (1977).

5) For sigmatropic H-migrations in alkylcyclopentadienes $\triangle H^{\ddagger}$ values of 18-20 kcal/mole are reported: E. Hedaya, D.W. McNeil, P. Schissel, D.J. McAdoo, J.Am.Chem.Soc. 90, 5284 (1968); S. McLean, P. Haynes, Tetrahedron 21, 2329 (1965).

6) Inspection of models reveals, that after photo[2+2]cycloaddition in the norbornadiene skeleton of (12) or (13) 2-H becomes situated outside the edge or above the plane of the cyclopropane-ring, thereby being exposed to distinctly different anisotropy effects. In the geometrically rather similar situation, discussed in l.c. [4], a diamagnetic shift of 0.7 ppm has been observed for the trans-isomer. So far, however, we have not been able to effect this photocycloaddition in (13).

7) There can be little doubt, that (1b) [1], if it undergoes the 16-electron-cyclisation, does so in the allowed conrotatory fashion.

8) For some stable derivatives of (6c) synthesised via [12+2]cycloadditions to 8,9-dicyanosesquifulvalene see: H. Prinzbach, H.-W. Schneider, Angew. Chem. 85, 1112 (1973); Angew. Chem.,Int. Ed. Engl. 12, 1007 (1973).