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SYNTHESIS AND 20π-ELECTROCYCLISATION OF HEPTAHENDECAFULVADIENE 1) - AN UNUSUAL SEQUENCE OF PERICYCLIC PROCESSES

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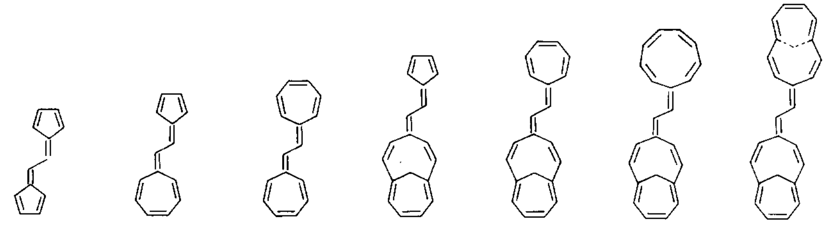
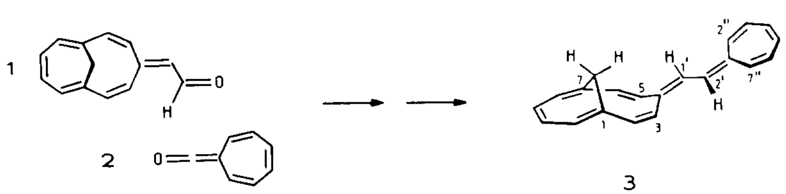
Upon thermal activation the newly synthesised heptahendecafulvadiene E (≡ 3) is isomerised into the pentacyclic hydrocarbons 9/11 (xylene,t$_{1/2}$(150°C) ca.5min), the formation of which is explained by initial conrotatory 20-electron electrocyclisation followed by a cascade of 10π/6π-pericyclic processes.

The fulvadienes A-D - not however G (as dicyano-derivative) - regiospecifically undergo α,ω-electrocyclisation, irrespective of the number of π-electrons involved (12-18) 2-6) in the conrotatory sense 7). Synthesis and 20π-electrocyclisation of the heptahendecafulvadiene E (≡ 3, 4-(2,4,6-cycloheptatrien-1-ylideneethylidene)bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene) are the subject of this communication.



After an unsuccessful attempt to prepare derivatives of E by a pentafulvene → heptafulvene ring enlargement in the pentahendecafulvadiene D 5), the parent molecule 3 became

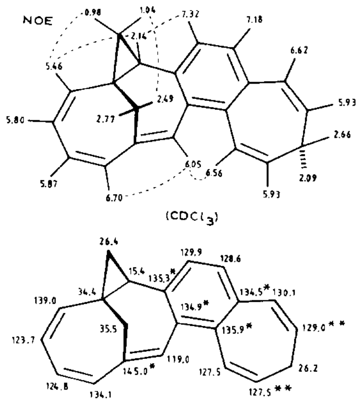


available in modest yield (15-20%, not optimised) through cycloaddition of the ketene 2 8) to the aldehyde 1 5). 3 (red-brown crystals, m.p. 90-95°C, m/e= 270 (M^+, 100%)), like most fulvalenes, is light- and air sensitive, but can be stored in the dark at -30°C. A relatively strong bathochromic shift of 39 nm is exhibited in the UV/VIS spectrum for the longest wavelength absorption (isooctane, 429 nm (ε= 25900)) as compared with the corresponding fulvalene 12 9), while the ^{1}H-nmr data are, as expected, very similar and typically "fulvalenoid" (^{1}H-nmr(400 MHz, $CDCl_3$):δ= 0.99 (d, 12E-H), 4.12 (dt, 12Z-H), 5.44 (mc, 6"-H), 5.60 (mc, 3"-H), 5.66 (mc, 4"-,5"-H), 5.77 (d, 2-,6-H), 5.90 (d, 1'-H)*, 5.97 (d, 7"-H), 6.07 (d, 2'-H)*, 6.25 (d, 2"-H), 6.27 (mc, 11-H)**, 6.30 (mc, 8-H)**, 6.31 (d, 5-H), 6.40 (d, 3-H), 6.79 (mc, 9-,10-H); $J_{2,3}=J_{5,6}=J_{1',2'}=J_{2'',3''}=J_{6'',7''}$= 12, $J_{12E,12Z}$= 11.2, $J_{8,12Z}=J_{11,12Z}$= 1.5Hz)[12]. From the fact that 2"-H is deshielded relative to 7"-H by 0.28 ppm and 3-H with respect to 5-H only by 0.09 ppm it is concluded - as in the case of D - that C-4 is deplaced from the C2C3C5C6 - plane to such an extent that the C4=C1'-double bond exerts the known anisotropic influence upon 2''-H, whilst the C2'=C1''-double bond does not markedly affect 3-H. With $J_{1'2'}$= 12Hz the s-trans-conformation (3) is clearly far preferred to the s-cis-conformation (3'). 3, in contrast to the 'mixed' fulvadiene D, is not selectively protonated in CF_3CO_2H.

In degassed $5 \cdot 10^{-3}$ molar xylene solutions 3 remains practically unchanged up to 100°C for several hours. At 150°C the red-brown colour gradually ($t_{1/2}$ ca. 5 min) becomes yellow-brown. After partial (30%, 50%) as well as after total conversion (in addition to polymeric material) two products are formed in a practically constant 2:1 ratio (40%, not optimised) (DC, ^{1}H-nmr): isomeric with 3 (m/e= 270 (M^+)) they are identified by elaborate ^{1}H- and ^{13}C-nmr analyses (with extensive NOE measurements) as 9 (pentacyclo [$14.4.1.0^{1,3}.0^{4,14}.0^{7,13}$] heneicosa-4,6,8,11,13,15,17,19-octaene, yellowish oil, λ_{max}(ethanol)= 335 nm (ε= 6500) and 11 ((1α,4β)-pentacyclo[$14.4.1.0^{1,3}.0^{4,14}.0^{7,12}$]heneicosa-5,7,9,11,13,15,17,19-octaene, yellow crystals, m.p. = 203-205°C, λ_{max}(ethanol)= 351 nm (ε= 11300)).

^{1}H

^{13}C



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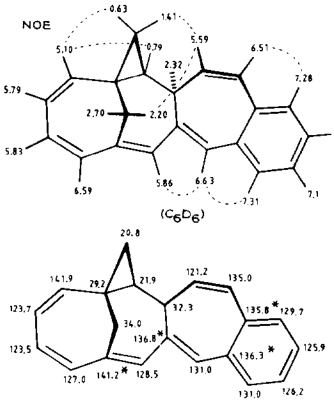

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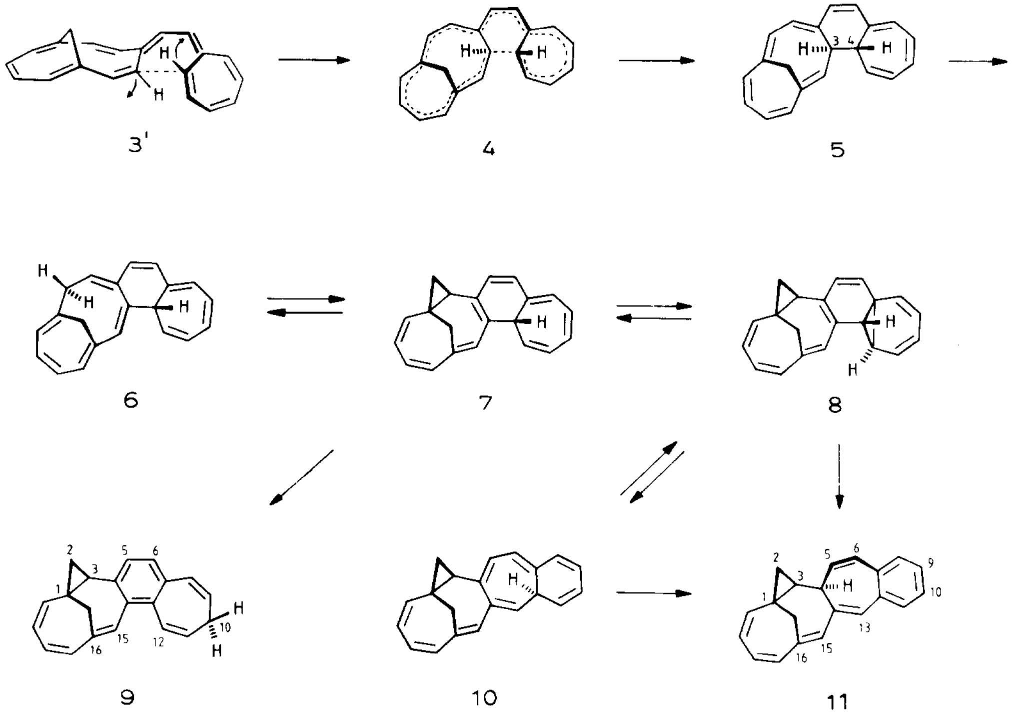
In line with arguments presented for the thermolysis of D [5], the formation of 9/11 is explained with the intervention of the common intermediates 5-7, which result from an initial 20π-electrocyclisation via the syn-conrotational transition state 4 (which sterically profits from the helical 3'-conformation), [1,9]-suprafacial H-migration and 10π-electrocyclisation. [1,5]-H-migration in 7 and homo-[1,5]-H-migration in its "bisnorcaradiene"-tautomer 8 [13] are the final (irreversible) steps (11 could also arise via 10). The 3β,4α-configuration in the kinetically labile 5 and consequently the formally "symmetry-allowed" syn-conrotatory mode of cyclisation in 3 is firmly, albeit indirectly, established: (i) The [1.9]-H-migration in 5 is only possible anti to the CH_2-bridge. (ii) The β-orientation of 4-H in 11 and consequently of the corresponding hydrogen in 8 follows from the NOE-experiments and the two hydrogens in the newly formed cyclopropane ring of 8 must be trans. Obviously, this peri- and stereospecificity 14) is proven only to the limited extent of isolated products. That the 18π-version in D had taken the same syn-con-pathway underlines once more the dominance of steric factors. The cis-fulvatriene vinylogoues of A-C 1) do



not show a comparable propensity for α,ω-cyclisation, what attests to the stereoelectronic advantages of the fulvadienes A-E(F) for these unusual multi-electron electrocyclic processes 7).

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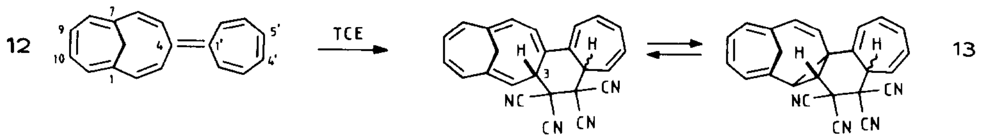
9) The 18π-heptahendecafulvalene 12 is prepared from bicyclo[5.4.1]undeca-2,5,7,9,11-pentaene-4-one 10) and the ketene 2 in 82% yield (red-brown crystals, m.p. 104°C, λ_{max}



(ethanol)= 390 nm (ε= 2300), ^{1}H-nmr(250 MHz, $CDCl_3$):δ= 0.52 (12E-H), 3.78 (12Z-H), 5.34 (d, 3(5)-H), 5.8-6.0 (m, 3'(6')-H), 4'(5')-H), 6.18 (2'(7')-H), 6.40 (m, 8(11)-H), 6.55 (d, 2(6)-H), 6.9 (9(10)-H); $J_{2,3}$= 12.0, $J_{12E,12Z}$= 11.2, $J_{2',3'}$= 10.5 Hz.- ^{13}C-nmr($CDCl_3$) 11):δ= 31.2 (C-12), 119.8 (C-3(5)), 122.0 (C-1(7))*, 123.3 (C-8(11)), 127.3 (C-4)*, 127.6 (C-4'(5'))**, 129.8 (C-9(10)), 131.1 (C-2(6)), 131.8 (C-3'(6'))**, 136.0 (C-1')*. It momentarily (25°C) adds tetracyanoethylene in a probably concerted [18+2]-anti-cis-fashion, the stereochemistry in the 1:1-adduct 13 (which rearranges to two [4+2]-adducts of the heptafulvene-part) is only unambigous at C-3 ($\delta_{3\text{-}H}$= 4.87(C_6D_6), $\delta_{C\text{-}3}$= 45.6($CDCl_3$)) 12).

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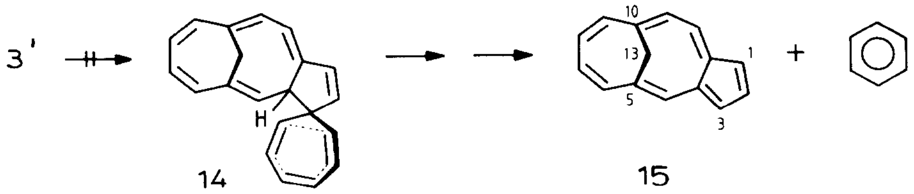
14) The deeply coloured 14π azulenoid annulene 15, a potential product of a competing 14π-electrocyclisation (14) - as observed at 400°C with dicyano-G 6) -, was prepared inde-



pendently and would have been detected in minute quantities (λ_{max}(C_2H_5OH)= 640 nm; ^{1}H-nmr(250 MHz, [D_6]acetone):δ= -0.24 (d, 13E-H), 0.90 (dt, 13Z-H), 7.11 (d, 11-H), 7.23 (dd, 2-H), 7.27 (d, 9-H), 7.38 (dd, 7-H), 7.45-7.51 (m, 1-,3-H), 7.53 (dd, 8-H), 7.60 (d, 6-H), 7.83 (d, 12-H), 8.72 (s, 4-H); $J_{1,2}$=$J_{2,3}$= 5, $J_{6,7}$=$J_{8,9}$= 8.0, $J_{7,8}$= 10.0, $J_{11,12}$= 10.5, $J_{13E,13Z}$= 11.2, $J_{6,13Z}$=$J_{9,13Z}$= 1.5 Hz) 12).

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