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THE 16-ELECTRON ELECTROCYCLISATION OF VINYLOGOUS HEPTAFULVALENE [1)]

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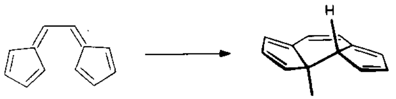
Abstract: The vinylogous heptafulvalene ("heptafulvadiene") (5) cleanly undergoes the antarafacial 16-electron electrocyclisation to (11) upon thermal activation (benzene, E_a = 22.1 kcal/mol; log A = 10.8).

The intention to synthesise potential precursors of angularly annelated π-perimeter molecules by α,ω-electrocyclisation of vinylogous fulvadienes was successfully followed up in the case of the vinylogous pentafulvalene (1) and the vinylogous sesquifulvalene (3); both fulvalenes cyclise regio- and stereospecifically (antarafacial) with participation of all 12π- or 14π-electrons to the 5,6,5-(2)[2)] or 5,6,7-system (4)[1)] resp. Similarly the 7,6,7-system (11) should be accessible by 16-electron electrocyclisation of the vinylogous heptafulvalene ("heptafulvadiene") (5), synthesised by Kitahara et al. [3)]. In addition to α,ω-cyclisation (16π, disrotatory via (7) to (10) or conrotatory via (8) to (11)), cyclisation with participation of 10π-electrons (via (6) to (9)), as realised in the case of vinylogous heptafulvenes [4)], was a possible competing process. From models with a flattened boat for the 7-membered rings, it becomes evident however, that the s-cis-conformation of (5) is helically twisted in such a way, that sterically the best prerequisites exist for efficient antarafacial orbital interaction at the centres C-1 and C-16. According to PPP-calculations carried out by Jensen and Michl [5)], the process (5) → (6) → (9) is symmetry-forbidden for the sterically plausible antarafacial pathway; whereas, in the case of α,ω-cyclisation, the sterically favoured pathway via (8) is symmetry-allowed.



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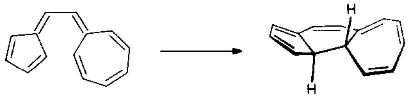
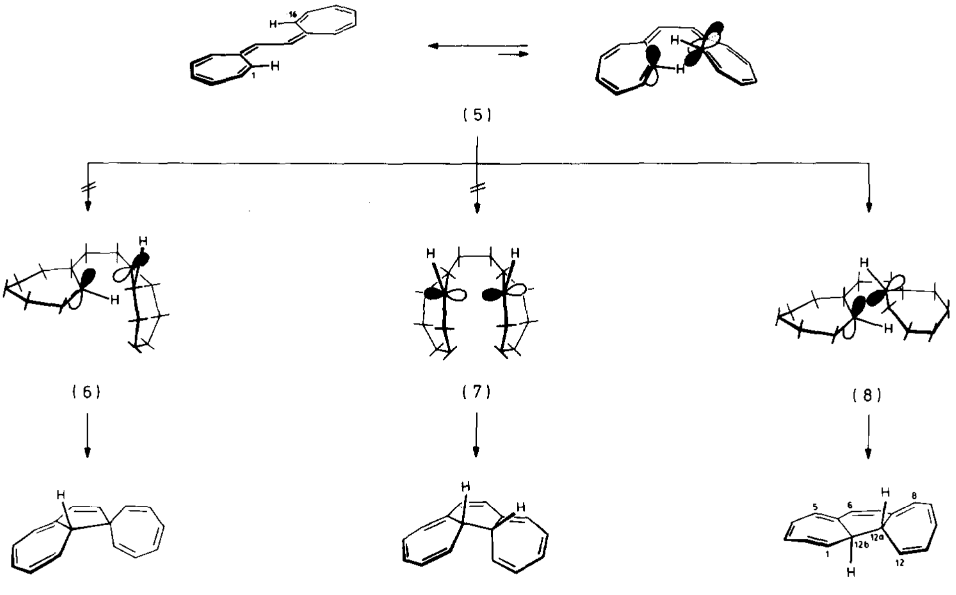


(3) (4)

The tendency to polymerisation is much less for (5) than for (1) or (3) and more concentrated solutions of the former can be employed without considerable intermolecular reactions taking place. According to TLC, UV and ^{1}H-NMR control, at temperatures above 60 C^o($t_{1/2}$ = 65 min) (5) undergoes a regio- and streospecific isomerisation;

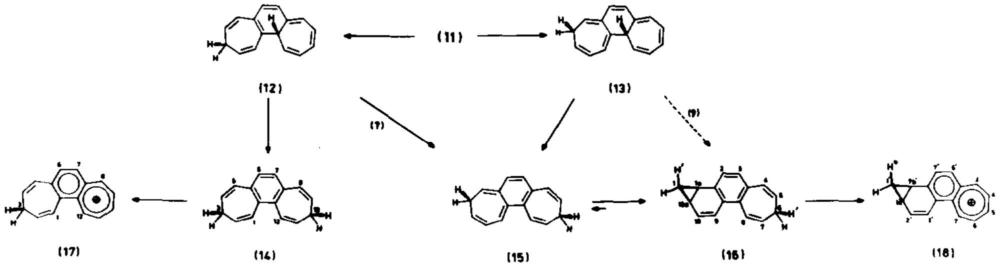
the trans- 12a,12b-dihydrobenzo[1,2:3,4]dicycloheptene structure of the pale yellow (λ_{max}(isooctane) = 366 nm (ε=6300)), crystalline product (m.p. 41°C) is spectroscopically (MS, ^{1}H-, ^{13}C-NMR) established [6]. Without the criteria, decisive in the case of (2) and (4), the decision in favour of C_2-symmetrical (11) rather than σ-symmetrical (10) was initially made on grounds of the $^3J_{12a,12b}$ coupling constant of ≤ 2 Hz (determined from the ^{1}H-(^{13}C-satellite) and partially decoupled ^{13}C-NMR spectra. This coupling is more consistent with the 110° H-C(12a)-C(12b)-H interplanar angle est-

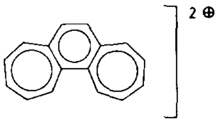


	^{1}H-NMR-data (τ,J(Hz)) of the compounds (11), (14), (16), (17) and (18)
(11)	3.37(dd,4-,9-H),3.52(dd,3-,10-H),3.85(d,5-,8-H),3.99(dd,2-,11-H),4.02(s,6-,7-H),5.07(dd,1-,12-H), 7.74(d,12a-,12b-H);$J_{1,2}$=$J_{11,12}$=9.0,$J_{2,3}$=$J_{10,11}$=5.7,$J_{3,4}$=$J_{9,10}$=11.0,$J_{4,5}$=$J_{8,9}$=6.0.
(14)	2.70(s,6-,7-H),3.30(d),3.32(d)(1-,12-H;5-,8-H),3.92(dt),3.96(dt)(2-,11-H;4-,9-H),7.62(dd,3-,10-H); $J_{1,2}$=$J_{11,12}$=10.0,$J_{2,3}$=$J_{10,11}$=7.0,$J_{3,4}$=$J_{9,10}$=7.0,$J_{4,5}$=$J_{8,9}$=10.0.
(16)	2.67(d),2.79(d)(2-,3-H),3.24(d,8(4)-H),3.33(d,9-H),3.37(d,4(8)-H),3.61(dd,10-H),4.07(ddd,7(5)-H), 4.07(ddd,5(7)-H),7.50(m,1a-H),7.55(ddd,6(6')-H),7.73(ddd,6'(6)-H),7.95(m,10a-H),8.39(m,1-H),10.26 (m,1'-H);$J_{1,1'}$=3.5,$J_{1,1a}$=9.0,$J_{1,10a}$=9.0,$J_{1',1a}$=5.0,$J_{1',10a}$=4.8,$J_{1a,10a}$=7.5,$J_{2,3}$=8.0,$J_{4,5}$=10.0,$J_{5,6}$ =7.0,$J_{5,6'}$=7.0,$J_{6,6'}$=13.5,$J_{6,7}$=7.0,$J_{6',7}$=7.0,$J_{7,8}$=10.0,$J_{9,10}$=10.0,$J_{10,10a}$=5.2.
(17)	-0.08(sd,12-H),0.28(sd,8-H),0.79(sdd,10-H),1.04(sdd,11-H),1.06(sdd,9-H),1.30(d,6(7)-H),1.46(d,7(6)-H), 2.66(d,1-H),2.80(d,5-H),3.33(dt,4-H),3.61(dt,2-H),7.45(t,3-H);$J_{1,2}$=10.0,$J_{2,3}$=7.0,$J_{3,4}$=7.0,$J_{4,5}$=10.0, $J_{6,7}$=8.5,$J_{8,9}$=10.5,$J_{9,10}$=9.5,$J_{10,11}$=9.5,$J_{11,12}$=11.0.
(18)	-0.03(sd,7-H),0.39(sd,3-H),0.92(sdd,5-H),1.21(sdd,6-H),1.26(sdd,4-H),1.28(d,6'(7')-H),1.35(d,7'(6')-H), 2.53(sd,3'-H),2.93(sdd,2'-H),6.89(m,7b'-H),7.33(m,1a'-H),7.44(m,1'-H),10.25(m ,1^{*}'-H);$J_{3,4}$=10.5, $J_{4,5}$ =9.5,$J_{5,6}$=9.5,$J_{6,7}$=11.0,$J_{1',1*'}$=3.7,$J_{1',1a'}$=9.0,$J_{1',7b'}$=9.0,$J_{1*,7b'}$=5.0,$J_{1a',1*'}$=5.0,$J_{1a',2'}$=5.5, $J_{1a',7b'}$=7.0,$J_{2',3'}$=10.0,$J_{6',7'}$=8.5.

imated for (11) than with the 20°estimate for (10). In the meantime a x-ray crystal structure carried out by <u>Hädicke</u> [5] has confirmed the structure (11).

An E_a-value of 22.1 kcal/mol (benzene) for the cyclisation (5) → (11) emerges from the half-lives determined at five temperatures between 60 and 90°C resp. (log A= 10.8; $\Delta H^{\ddagger}$ = 21.4 kcal/mol, $\Delta S^{\ddagger}$ = -11.5 cal/mol·deg). The activation barrier therefore lies between the values for (1) → (2) (E_a = 20.0 kcal/mol, log A = 11.3) and (3) → (4) (E_a = 24.4 kcal/mol, log A=12.0) [7]. Since H-shifts in the tropilidene rings of (11) are relatively slow [8], the isolation of the product presents no problem here, in contrast to the situation upon thermolysis of (1) and (3). At 160°C (11) is converted into a 7:3 mixture (ca. 90%) of 3,10-dihydrobenzo[1,2:3,4]dicycloheptene (14) and 1,1a,6,10a-tetrahydrocyclohepta[a]cyclopropa[f]naphthalene (16) [9] (together with two minor components) via the probable, non-identified intermediates (12), (13) and (15) [10]. From (14)/(16) one derives the tropylium salts (17)/(18) [11] conventionally (trityl tetrafluorborate, CH_2Cl_2, 20°C). Generation of the 14π-cation (19) by hydride elimination from (17) was not observed with $SbCl_5/AsCl_3$.





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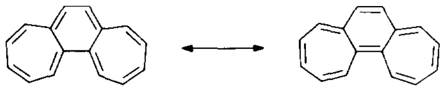

(20)

According to past experience [1-3,11,12] and calculations [13] the 16π-tricyclic (20) (benzo[1,2:3,4]dicycloheptene) should be highly unstable. For its generation, pathways, which do not involve benzenoid intermediates (e.g. based on (11)), appear most promising. Under a variety of dehydrogenating conditions, successfully employed for other labile polyenes, (11) is consumed without any evidence for the formation of deeply coloured (20). Various attempts to deprotonate its conjugate acid (17) led only to rapid decolourisation. For (17) no H/D-exchange is observed in CF_3CO_2D after 48h (20°C).

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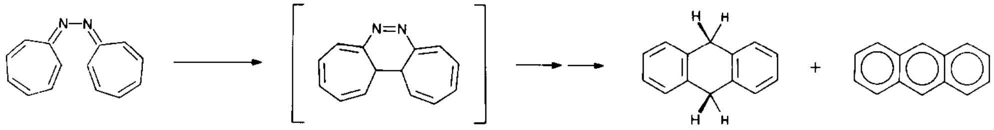

(i) (ii)

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