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THE 18-ELECTRON ELECTROCYCLISATION OF VINYLOGOUS FIDECENE. 1) **)
AN UNUSUAL SEQUENCE OF PERICYCLIC PROCESSES

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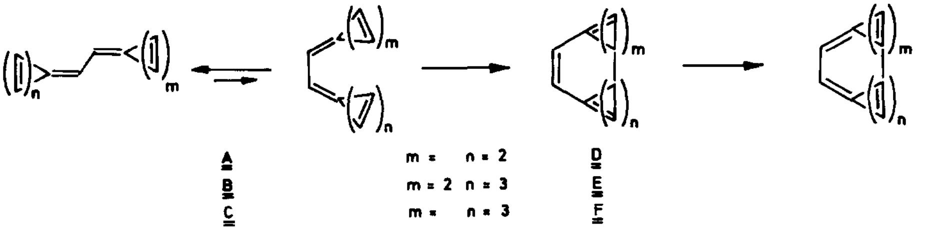
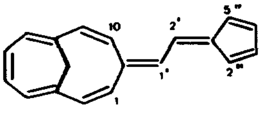
Upon thermal activation the vinylogous fidecene 1 is isomerised into the pentacyclic indenoid hydrocarbon 13 (benzene, $t_{1/2}$ (150°C) ca. 5 min), the formation of which is explained by an initial conrotatory ("symmetry-forbidden") 18-electron electrocyclisation followed by two fast hydrogen migrations ([1.9],[1.5]) and a 14π-electrocyclisation.

The thermal α,ω-electrocyclisation of the vinylogous fulvalenes A 2), B 1) and C 3) (to give D,E and F) is remarkable in view of the unusually large number of π-electrons involved (12,14,16) and the exclusively antarafacial bond formation 4). An extension to systems with even more (18,20,24) π-electrons participating in [4N]- and [4N+2]-pericyclic transition states is offered by the fulvadiens 1-3 5), in which the hendecafulvene unit functions as a 12-electron component. Synthesis and electrocyclisation of 1 ("Vinylogous fidecene", "Pentahendecafulvadiene") 6) are presented in this communication.





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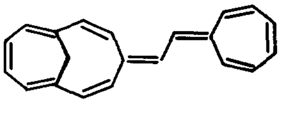

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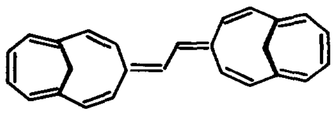

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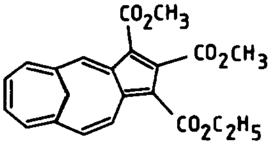
Starting material is the ketone 4 reported by Vogel et al. 7). After Wittig-Horner-condensation ($(C_2H_5O)_2P(O)CH_2CO_2C_2H_5$, NaH, xylene, 140°C) to 5 (m.p. 65°C, 62%, λ_{max} (ethanol)= 388nm (ε=8600)), reduction (LAH, ether, -30°C) to 6 (65%, λ_{max}(ethanol)= 332 nm (ε=3400)) and oxidation (MnO_2, acetone, -20°C) the aldehyde 7 (m.p. 118°C, 48%, λ_{max} (isooctane)= 420 nm (ε= 11300) is obtained. Condensation of 7 with cyclopentadiene under proven conditions (methanol, KOH, 0°C) [1] yields 1 (red-violet crystals, m.p. 114°C, 41%). 1, like most fulvalenes, is only stable in the dark, under an inert atmosphere and at low temperature. Its electronic absorption spectrum (λ_{max}= 430 nm (ε=33500)) compared with that of 3,8-methanofidecene (λ_{max} (cyclohexane)= 415 nm) [6] reflects the expected bathochromic shift. The "fulvenoid" character is typically manifested by the NMR-comparison (^{1}H, ^{13}C) [5,8] with the delocalised 14π-system 8 [9]. $J_{1',2'}$=12.5 Hz (30-150°C) demonstrates the preference for the s-trans-conformation. Since 2"-H is significantly deshielded with respect to 5"-H (Δδ= 0.32 ppm) but 1-H with respect to 10-H (Δδ= 0.07 ppm) is not, it is concluded that C11 is deplaced from the C1C2C9C10-plane (syn or anti) to an extent which excludes a sizable anisotropic influence of the C1"=C2 ' double bond upon the 1(10)-hydrogens.

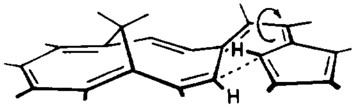
4

5 : R=$CO_2C_2H_5$
6 : R=CH_2OH
7 : R=CHO

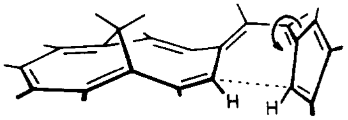
8



For the α,ω-electrocyclisation in 1 two conrotatory and two disrotatory pathways can be distinguished. The conrotatory ("symmetry-forbidden") modes start from the syn-/anti-s-cis-conformations, which are helically twisted around the C1 '-C2 '-single bond. If the hendecafulvene-part in 1 accepts the geometry known for 4 [10], the syn, con pathway 1^* is sterically favorable. The disrotatory ("symmetry-allowed") modes (e.g. 1^{**}) need - as was stressed for A, B and C - a drastic distortion around the exocyclic double bonds and are hampered by steric compressions.



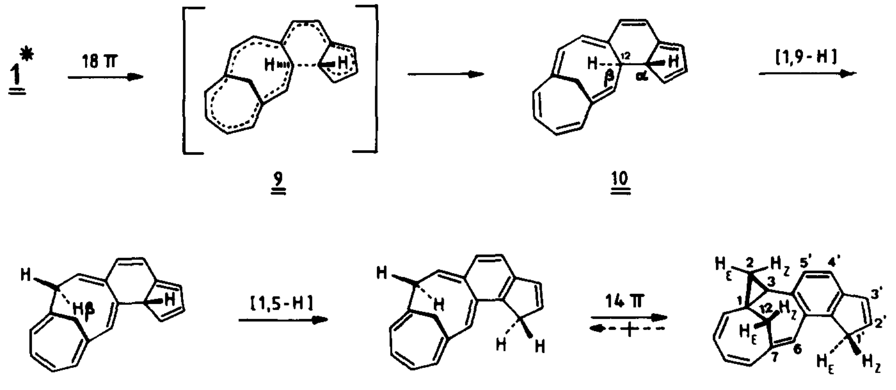
1^* (syn, con)



1^{**} (syn, dis)

On heating in ca. 10^{-2}M degassed benzene solution, 1 remains unaltered up to ca. 120°C. At higher temperatures ($t_{1/2}$(150°C) ca. 5 min, ΔG‡ ca.30 kcal/mole) a single product - besides polymeric material - is observed (TLC, ^{1}H-NMR) and isolated in up to 55% yield. This colourless crystalline isomer (m.p. 72°C) is identified (MS, UV, IR, ^{1}H-, ^{13}C-NMR) as the pentacyclic indenoid hydrocarbon 13; the relative orientation of the three CH_2-groups is confirmed by NO-experiments [11]. Irradiation of 1 in a 10^{-2}M acetone solution (Q 81 lamp, 4 h) does not cause a measurable transformation.

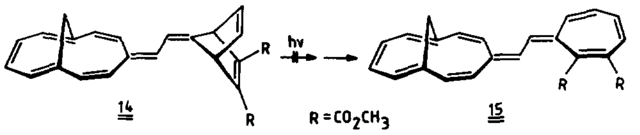
Structure and selectivity in the formation of 13 are plausibly explained by assuming the indermediacy of compounds 10 - 12. In view of the disadvantages of 1^{**}, the 12β-configuration in 10, and hence the "forbidden" conrotatory cyclisation in 1 via the 18-electron transition state 9 [12] is demanded by the fact that only from this β-configuration can the sigmatropic [1,9]-hydrogen migration take place. It is unknown which of the two hydrogen migrations ([1,9],[1,5]) directly follows the initial rate-determining cyclisation. The [1,9]-migration is given preference because of the unusually fast rate in a case which is stereoelectronically very similar [6]. The driving force for the 14-electron electrocyclisation in the 11-membered ring (12 → 13) is obviously the aromatisation in the indene part.



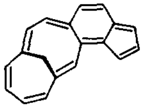
1 9 10

11 12 13

Because of the necessarily rather drastic reaction conditions, the chances of intercepting the primary product 10 were a priori rather poor. After thermolysis of 1 in excess dimethyl acetylenedicarboxylate (150°C) - conditions successfully applied to D and E - only a [4+2]-adduct of the pentafulvene part in 1, probably resulting from anti-attack, is found (14, m.p. 168-170°C, 80%). The latter, in contrast to 5, did not undergo a [12+2]-addition under any of the conditions tried. Efforts to take advantage of 14 for the synthesis of 15, a useful model for the 20π-fulvalene 2, through photochemical methylenenorbornadiene → methylenenorcaradiene isomerisation [13] were unsuccessful. There was no indication that the presumably rather labile [1] 18π-annulene 16 was present, when 1 was thermolysed in the presence of MnO_2 (benzene, cp. 8). Since 12 was a potential equilibrium product of 13, the latter was treated with trityl tetrafluoroborate; yet no hydride elimination yielding the conjugate acid of 16 was observed.



14 $R = CO_2CH_3$ 15



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**) *Dedicated to Prof. Dr. W.v.E. Doering on the occasion of his 65th birthday - as an expression of our good wishes and a mark of our esteem.*

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8) L. Knothe, H. Prinzbach and H. Fritz, Liebigs Ann. Chem. 1977, 687.

9) 1: ^{1}H-NMR(CDCl$_3$):δ=0.69(d,12E-H),3.60(dt,12Z-H),5.99(d,1-H),6.06(d,10-H),6.26(m,5"-H),6.47(m,4"-H),6.50(m,4-,7-H),6.58(m,2"-,3"-H),6.58(d,2-H),6.60(d,1'-H),6.68(d,9-H),6.95(m,5-,6-H),7.25(d,2'-H); $J_{4,12Z}=J_{7,12Z}=1.3, J_{4'',5''}=5.0, J_{5,6}=J_{12E,12Z}=11.0, J_{2,3}=J_{9,10}=12.0, J_{1',2'}=12.5$Hz. The novel 'azulenoid' 14π-annulene 8 (H. Prinzbach, Pure Appl. Chem. 28, 281 (1971)) was obtained by [12+2]-addition of dimethyl acetylenedicarboxylate to 5 followed by oxidation with MnO$_2$ (greenish crystals, m.p. 149-152°C, 25%,λ_{max}(ethanol)=590nm(ε=1 500); ^{1}H-NMR(CDCl$_3$):i.a.δ=-0.81(d,13Z-H)*,-0.49(d,13E-H)*,7.67(t,7-H)**,7.81(t,8-H)**,7.86(d,6-H)***,7.93(d,11-H),8.11(d,9-H)***,9.67(d,12-H),10.17(s,4-H); $J_{6,7}=J_{7,8}=J_{8,9}=9.0, J_{11,12}=10.5$Hz; ^{13}C-NMR(CDCl$_3$):i.a.δ=31.3(13-C),130.7(7-C)*,132.2,132.3(11-,6-C)**,134.3(12-C),135.2(8-C)*,135.8(9-C)**,147.8(4-C). The unsubstituted 8 is approached via 14π-electrocyclisation of vinylogues hendecafulvenes [5].

10) D.W. Hudson and O.S. Mills, Chem. Commun. 1971, 153.

11) 13: MS:m/e=244(M$^+$); UV(ethanol):λ_{max}(ε)=323nm(4500),273(sh,14700),256(26500); ^{1}H-NMR(CDCl$_3$): δ=0.99(dd,2Z-H)*,1.01(dd,2E-H)*,2.14(dd,3-H),2.48(d,12Z-H),2,75(d,12E-H),3.20(d,1'E-H),3.37(d,1'Z-H),5.47(d,11-H),5.80(dd,9-H)**,5.89(dd,10-H)**,6.09(s,6-H),6.54(m,2'-H),6.69(d,8-H),6.85(m,3'-H),7.22(d,4'-H),7.35(d,5'-H); $J_{3,10}=0.3, J_{2',3}=0.4, J_{1'E,5'}=J_{1'Z,5'}=J_{3,6}=J_{5',6}=J_{9,11}=0.5, J_{1'E,6}=0.7, J_{3,12E}=J_{6,12Z}=J_{8,10}=1.0, J_{6,12E}=1.3, J_{6,8}=1.4, J_{8,11}=1.5, J_{1'E,2'}=J_{1'Z,2'}=J_{1'E,3'}=J_{1'Z,3'}=J_{11,12Z}=2.0, J_{2E,2Z}=4.5, J_{2',3'}=J_{2E,3}=5.5, J_{4',5'}=J_{9,10}=7.5, J_{2Z,3}=9.5, J_{8,9}=10.5, J_{10,11}=11.5, J_{12E,12Z}=12.0, J_{1'E,1'Z}=23.5$Hz.

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