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THE "VINYLOGOUS SESQUIFULVALENE" 1)
SYNTHESIS, CYCLOADDITION-REACTIONS

Horst Babsch and Horst Prinzbach*

Chemisches Laboratorium der Universität, 78 Freiburg, BRD

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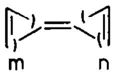
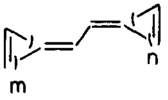
Our interest in cyclic cross-conjugated polyenes of the type (1) has been renewed in view of the preparative and theoretical aspects of the electrocyclisation reactions of their vinylogues (2) and (3). In the series (2) the "vinylogous pentafulvalene" (2a)2) and the "vinylogous heptafulvalene" (2b)3) are known; synthesis and electrocyclisation resp. of the "vinylogous sesquifulvalene" (2c)4) are subject of this and the following communication 5).



(1)



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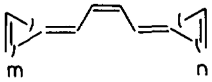


(3)

(a), m = n = 2 (b), m = n = 3 (c), m = 2 n = 3

The synthesis consists of the reaction sequence (4) ⟶ (7) ⟶ (8) ⟶ (9) ⟶ (2c) and was patterned after a model study leading to the highly reactive (1c), in which advantage was taken of the recently discovered isomerisation (4) ⟶ (5) 6). (5), in contrast to its valence isomer tropone, selectively undergoes 1,2-additions to the carbonyl group. Condensation with cyclopentadiene in 5% KOH/methanol (0°C, 12 h) yields the fulvene (6) (orange crystals, m.p. 86°C (dec.), λ_{max}(pentane)=396 nm (ϵ=340), 351 (sh, 12500), 337 (25600), 325 (27300), 312 (sh, 20300)), which is quantitatively isomerised to (1c) under standard conditions ($AgBF_4$/ether/0°C or $\lambda > 280$ nm). The transformation (4) ⟶ (7) (m.p. 52°C), which is difficult because of the pronounced acid-sensitivity of the tetracyclic skeleton, is achieved in 65% yield by addition of lithiumethylidenecyclohexylamine 7) (ether, 20°C, 4 h), careful dehydration over molecular sieves (20°C, 3 d) and hydrolysis on filtration through silica gel. The thermal step (7) ⟶ (8) (CH_3CN, $t_{1/2}$(130°C) ca. 30 min) proceeds faster and more uniformly than in the case of (4), resulting in a mixture of 55-60 % 8-formylmethylenetricyclo[$4.1.0.0^{2,7}$]heptene(8) (E/Z ca. 1:1, b.p. 67-70°C/0.05 torr), 1-3 % 8-formylheptafulvene (10)8) and 5-10 % 8-formylmethylenebicyclo[3.2.0]hepta-3,6-diene. After separation on silica gel (ether/pentane 7:3), (8) is condensed with cyclopentadiene (5 % KOH/methanol, 0°C) to give an E/Z-mixture of (9) (Al_2O_3(bas.),80-85 % , orange crystals, m.p. 50-60°C, λ_{max}(pentane)=378 nm (sh),370, 355, 330), which is quantitatively opened to (2c) (violet crystals (pentane -70°C)) by treatment with $AgBF_4$(0°C). As expected, the analogous reactions of (10) (conveniently obtained from (7) and $AgBF_4$) with cyclopentadiene produces only small quantities of (2c) (at best 10%). Another alternative approach to (2c)-catalytic ($PdI_2[(C_6H_5)_3Sb]_2$) opening of (7) to give (11), conversion into (12) (m.p. 64°C(dec.)) and photochemical isomerisation9) of (12)-fails completely in the last step.

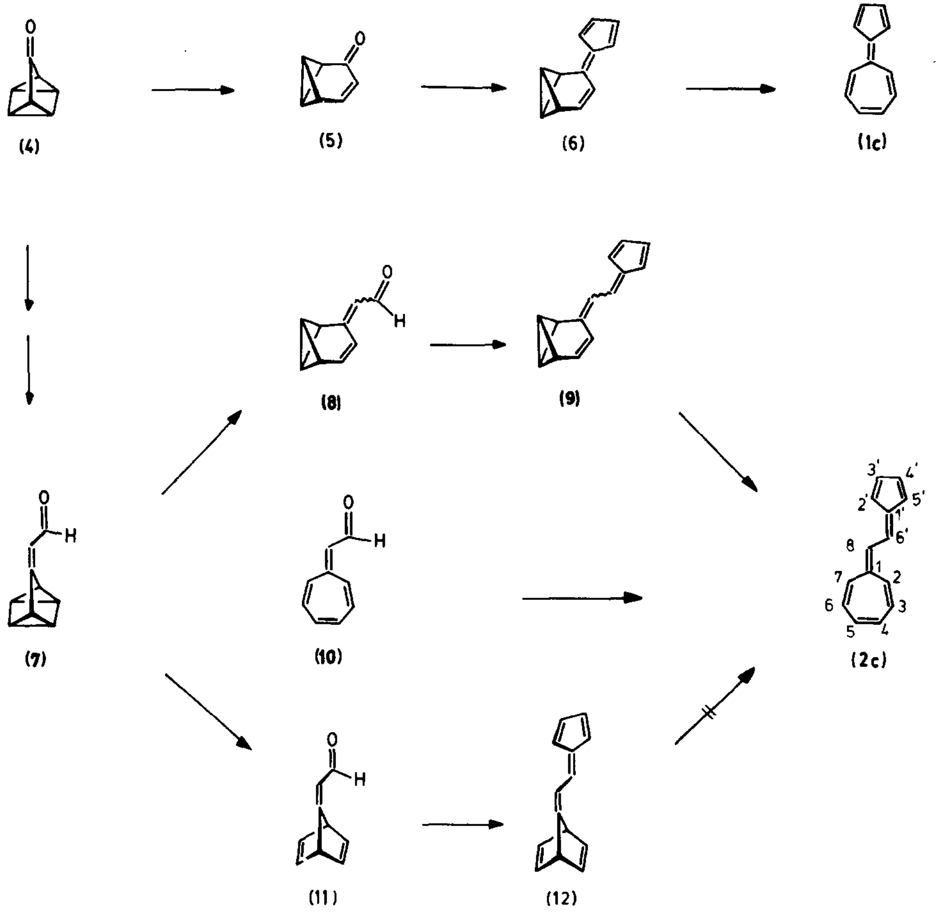
table: ^1H (τ) and ^{13}C NMR data(δ) of compounds (2c), (7) - (9) and (12).

(2c)[a]	3.23, 3.35, 3.38, 3.46, 3.67, 3.89, 3.97, 4.37, 4.7-4.9(4H); 147.2, 144.9, 142.6, 134.6, 133.6, 133.6, 132.9, 132.3, 132.1, 131.2, 130.2, 125.8, 123.0, 118.3 ppm.
(7)[b]	0.22, 3.72, 7.71, 7.82(2H), 7.88(2H), 8.27; $J_{4,8}$=0.7, $J_{8,9}$=8.0 Hz; 191.4, 177.4, 121.1, 27.4, 21.8(2C), 21.5, 20.4(2C) ppm.
(8E)[c]	0.09, 3.80, 4.18, 4.35, 7.79, 7.84(2H), 8.23; $J_{1,2}=J_{2,7}=2.3$, $J_{1,6}=J_{6,7}$ = 2.3, $J_{2,4}=1.2$, $J_{2,6}=4.0$, $J_{4,5}=9.5$, $J_{4,6}=1.2$, $J_{4,5}=1.2$, $J_{5,6}=4.9$, $J_{5,8}$ = 1.4 Hz.
(8Z)[c]	0.14, 4.19, 4.35, 4.69, 6.67, 7.79(2H), 8.16; $J_{1,2}=J_{2,7}=2.3$, $J_{1,6}=J_{6,7}$ = 2.3, $J_{2,4}=1.4$, $J_{2,6}=4.0$, $J_{2,8}=1.3$, $J_{4,5}=9.8$, $J_{4,6}=1.4$, $J_{5,6}=4.9$ Hz.
(9E)[b]	2.87, 3.4-3.6(5H), 3.71, 3.83, 7.11, 7.37(2H), 7.5-7.6; $J_{1,2}=J_{2,7}=2.4$, $J_{1,6}=J_{6,7}=2.4$, $J_{2,4}=1.5$, $J_{2,6}=4.0$, $J_{4,5}=9.0$, $J_{4,6}=1.5$, $J_{4,8}=1.0$, $J_{5,6}$ = 4.5, $J_{5,8}=1.5$, $J_{8,6'}=12.5$ Hz.
(9Z)[b]	2.87, 3.4-3.6(5H), 3.90, 4.24, 6.58, 7.39(2H), 7.5-7.6; $J_{1,2}=J_{2,7}=2.4$, $J_{1,6}=J_{6,7}=2.4$, $J_{2,4}=1.5$, $J_{2,6}=4.0$, $J_{2,8}=1.0$, $J_{4,5}=9.0$, $J_{4,6}=1.5$, $J_{5,6}$ = 4.5 Hz.
(12)[b]	3.0-3.1(4H), 3.17, 3.52(2H), 3.58, 3.80, 4.54, 5.70, 6.09; $J_{8,6'}=11.9$ Hz.

a: C_6D_6 bzw. CD_3COCD_3; b: $CDCl_3$; c: C_6D_6

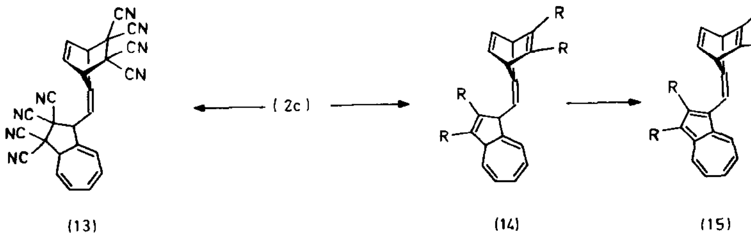
The structure and fulvenoid character of (2c) were established from the spectroscopic data. In the electron spectrum (absorption begins around 800 nm) the longest wavelength maximum (λ_{max}(pentane) = 450 nm (sh, ϵ=21000), 424 (41000), 414 (41000)) loses its fine structure and is slightly bathochromically shifted in polar solvents (λ_{max}(ethanol) = 417 nm (ϵ=43000), λ_{max}(acetonitrile)=430 nm (ϵ = 41500))10). Chemical shifts as well as coupling constants ($J_{2,3}=12.0$, $J_{6,7}=12.0$, $J_{2',4'}=1.8$, $J_{4',5'}=5.0$ Hz) in the ^1H and ^{13}C NMR spectra (table) are in accord with expectation 2,3,11). The sterically plausible, not necessarily planar s-trans-conformation is indicated by anisotropy effects (e.g. upon 2-H, 2'-H) and $J_{6',8}$ = 13.0 Hz. The most intensive peaks in the MS spectrum are m/e = 180 (M^+, 64 %), m/e = 179 (M^+-1,100), and m/e = 178 (M^+-2,73).

(2c) can be stored at -70°C; on standing at 20°C or upon warming slowly it mostly polymerises. When rapidly heated to 130°C, however, it clearly shows melting behaviour and the melt consists of (2c), polymeric material and dihydrocyclohept[e]indenes [5].



The latter arise from electrocyclisation (discussed in the following paper), which sets in, even though very slowly, at 20°C in solution.

To elucidate the stereochemistry of this process knowledge about the reactivity of (2c) towards dienophiles was required. TCNE (2.5 eq.) is added instantaneously at 0°C in a [4+2]- and [8+2]- fashion to the fulvene- and heptafulvene-portions resp. to give



a mixture of isomers of (13). Reaction with dimethyl acetylenedicarboxylate is still slow at 80°C ($t_{1/2}$ electrocyclisation ca. 12 min) but with a 500 fold excess ca. 30 %

of the isomeric species (14) are isolated and can then be oxidised (MnO_2) to yield the azulene-derivative (15) (m.p. 93°C).

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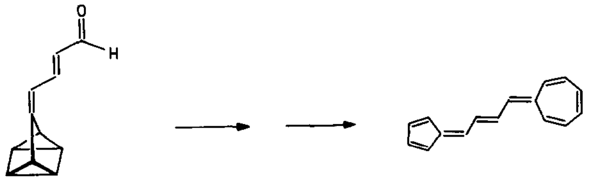
6) H. Prinzbach, H. Babsch, H. Fritz, Tetrahedron Lett. 1976, 2129; very recently we have extended this reaction and synthesised (17) (trans-(3c)) (λ_{max}(acetonitrile) = 458 nm) starting from the aldehyde (16) (m.p. 61°C) (O. Schweikert, H. Prinzbach).

(16)



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10) We thank R. Jensen and Prof. Dr. J. Michl for PPP-calculations, which will be discussed in the full paper.

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