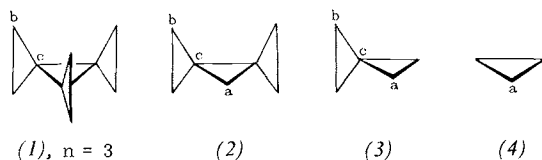


the spectroscopic data for (4), (3), (2), and (1),  $n=3$  (see Table 1).



Whilst the approximate agreement of the C—H stretching frequencies and  $^{13}\text{C}$ —H coupling constants is not surprising and is no argument for or against the existence of conjugative interaction of the cyclopropane rings in (1),  $n=3$ , the almost identical UV spectra of (1),  $n=3$ , and (2) can be regarded as evidence that (1),  $n=3$ , represents no exception in the series (4), (3), (2), (1),  $n=3$ .

This is shown still more clearly by comparison of the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR data. As would be expected if only inductive effects were operative, the  $^1\text{H}$ - and  $^{13}\text{C}$ -resonance signals are shifted by almost constant amounts along the series (4), (3), (2), (1),  $n=3$ :  $\tau(\text{CH}_2)_a$  and  $\delta(^{13}\text{C})_a$  consecutively by about 0.5 and 9 ppm, respectively, downfield, and  $\tau(\text{CH}_2)_b$  and  $\delta(^{13}\text{C})_b$ , consecutively by about 0.05 and 0.6 ppm, respectively, upfield<sup>[19]</sup>. Only the  $^{13}\text{C}$ -resonance signals of the quaternary carbon atoms that would be intimately concerned in delocalization of the C-1, C-2 and C-1, C-3 hybrid orbitals deviate slightly from the additivity observed elsewhere for the shifts; thus the difference [ $\Delta\delta(^{13}\text{C})_c$ ] found on passing from (3) to (2) is 2.5 ppm but increases to 3.9 ppm on passing to (1),  $n=3$ ; yet this deviation is too small to suggest delocalization of the cyclopropane hybrid orbitals in (1),  $n=3$ .

We therefore expect that the strain energy of (1),  $n=3$ , will not fall much below the value 135.1 kcal/mol calculated from the strain energies of cyclopropane (27.15 kcal/mol<sup>[20]</sup>) and spiropentane (63.13 kcal/mol)<sup>[20, 21]</sup>.

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German version: Angew. Chem. 85, 349 (1973)

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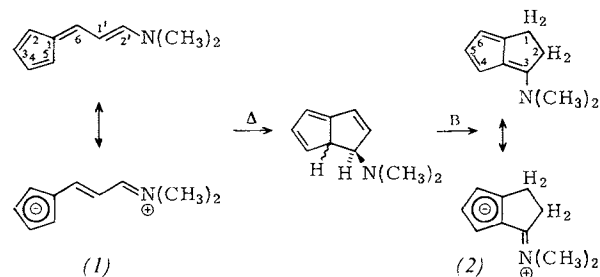
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## A Simple Synthesis of 1,5-Dihydropentalenes<sup>[\*\*]</sup>

By Reinhard Kaiser and Klaus Hafner<sup>[\*]</sup>

Dedicated to Professor B. Eistert on the occasion of his 70th birthday

Dihydropentalenes are important as precursors for a synthesis of pentalene and its derivatives<sup>[1]</sup>. We recently reported a simple synthesis of 1,2-dihydropentalenes (2) by thermolysis of 6-(2'-dimethylaminovinyl)fulvenes (1) in the presence of bases<sup>[2]</sup>. The reaction extends the general principle previously reported by us for the preparation of bi- and poly-cyclic conjugated  $\pi$ -electron systems<sup>[3]</sup>.



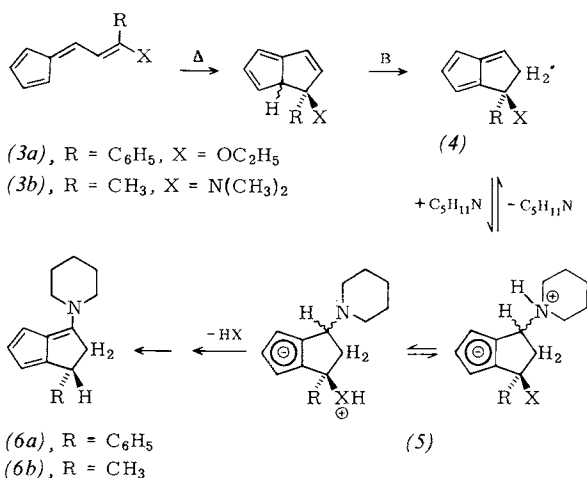
When applying this ring-closure reaction to derivatives of (1) carrying alkyl or aryl substituents in the side chain we observed that the cyclization and subsequent reactions were strongly dependent on the nature, number, and position of the substituents. Whereas fulvenes of type (1) with 6-alkyl or 6-aryl substituents afforded 1-alkyl- or 1-aryl-1,2-dihydro-3-dimethylaminopentalenes<sup>[4]</sup>, the expected 1-alkyl- or 1-aryl-1-dimethylamino- or 1-ethoxy-1,2-dihydropentalenes (4) were not formed from terminally alkylated or arylated 6-(2'-dimethylamino- or -ethoxy-vinyl)fulvenes (3)<sup>[5]</sup> in boiling piperidine; the only products isolated were 1-alkyl- and 1-aryl-1,2-dihydro-3-piperidinopentalenes (6) which are resonance-stabilized and have lower energy than (4).

These products (6) may have been formed in a thermodynamically controlled reaction by nucleophilic attack of the piperidine on the electrophilic center<sup>[6]</sup> of an initially

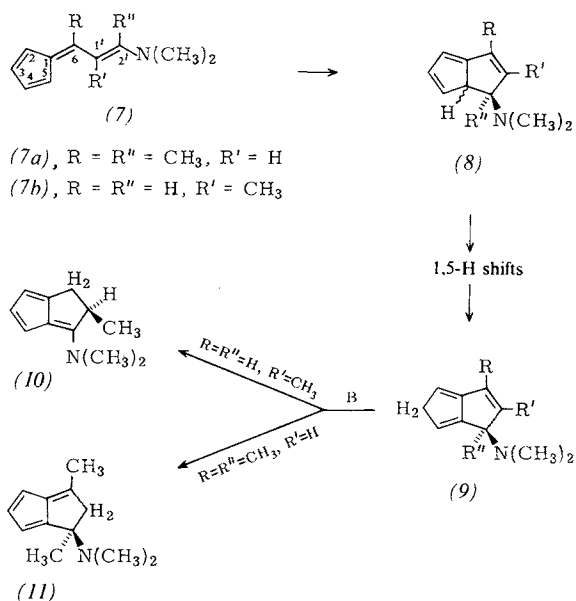
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[\*\*] This work was supported by the Fonds der Chemischen Industrie.

formed intermediate (4) and subsequent loss of dimethylamine or ethanol from (5).

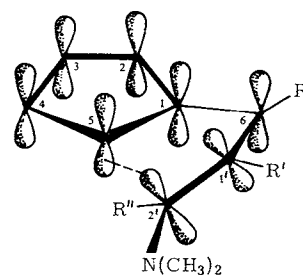


On the other hand, 6-(2'-dimethylaminovinyl)fulvenes (7)<sup>15</sup> alkylated at position 1' or dialkylated at positions 6 and 2' cyclize even below 20°C and in the absence of a base. However, no derivatives of 1,2-dihydropentalene are formed, as by the ring closure of (1) or (3), but instead the reaction yields the thermally rather unstable 1,5-dihydropentalenes (9)<sup>17</sup> which can be isomerized by bases, e.g. by piperidine, to the thermodynamically more stable fulvenoid 1,2-dihydropentalenes (10) or (11). In



the formation of (9) an electrocyclic reaction of (7), giving (8), is probably followed by a double 1,5-H shift characteristic for cyclopentadienes<sup>18</sup>. Consideration of models and UV spectra of (7) show that in (7a) there is steric hindrance between the substituents in positions 6 and 2' and in (7b) between R' on C-1' and the H atom at position 2 or 5; this would be relieved by rotation of the enamine portion around the C(6)—C(1') bond so as to move it out of the plane of the molecule. In the sterically most favored case the p<sub>z</sub>-orbitals of C-6 and C-1' form an angle of 60 to 90°. In this process the p<sub>z</sub>-orbitals of C-2' and C-5 come so close together that an electrocyclic reaction occurs even below 20°C, presumably by a conrotatory 8 π-electron process<sup>19</sup>. These conditions favoring cycliza-

tion do not arise with (1) and (3), for which the transoid conformation of the exocyclic group is favored instead, hence their cyclization requires a higher activation energy. However, under the conditions necessary for this cycliza-



Cpd.	UV in M. p. [°C] Yield	NMR (τ) [c]
(6a)	315 (4.44) 107–108 75%	5.54 (m, H-1); 6.30 (qd, H-2, J <sub>2,2</sub> ≈ 17 Hz, J <sub>1,2</sub> ≈ 7.5 Hz); 7.04 (qd, H-2, J <sub>1,2</sub> ≈ 2.7 Hz); 3.71 (qd, H-4, J <sub>4,5</sub> ≈ 4.5 Hz, J <sub>4,6</sub> ≈ 1.2 Hz); 3.24 (qd, H-5, J <sub>5,6</sub> ≈ 2.7 Hz); 4.11 (m, H-6); 2.69 (m, C <sub>6</sub> H <sub>5</sub> -1); 6.35 (m, N(CH <sub>2</sub> ) <sub>2</sub> -3); 8.29 (m, (CH <sub>2</sub> ) <sub>3</sub> ) [a]
(6b)	315 (4.46) 82–84 36%	7.69–6.07 (m, H-1, 2H-2, N(CH <sub>2</sub> ) <sub>2</sub> -3); 3.88 (qd, H-4, J <sub>4,5</sub> ≈ 4.5 Hz, J <sub>4,6</sub> ≈ 1 Hz); 3.36 (qd, H-5, J <sub>5,6</sub> ≈ 2.5 Hz); 4.14 (m, H-6); 8.72 (d, CH <sub>3</sub> -1, J ≈ 6.6 Hz); 8.31 (m, (CH <sub>2</sub> ) <sub>3</sub> ) [a]
(9a)	214 — 75%	4.32 (q, H-2, J ≈ 1.5 Hz); 4.04–4.19 (m, H-4, H-6); 6.68 (m, 2H-5); 8.68 (s, CH <sub>3</sub> -1); 7.88 (s, N(CH <sub>3</sub> ) <sub>2</sub> -1); 8.09 (d, CH <sub>3</sub> -3, J ≈ 1.5 Hz) [b]
(9b)	215 — 79%	5.90 (m, H-1); 4.31 (m, H-3); 3.93 (q, H-4, J <sub>4,5</sub> ≈ 1.5 Hz); 6.61 (m, 2H-5); 3.76 (q, H-6, J <sub>5,6</sub> ≈ 1.5 Hz); 8.04 (m, CH <sub>3</sub> -2); 7.78 (s, N(CH <sub>3</sub> ) <sub>2</sub> -1) [a]
(10)	312 (4.39) 74–75 60%	6.41–7.04 (m, H-1, H-2); 7.35–7.71 (m, H-1); 3.84 (qd, H-4, J <sub>4,5</sub> ≈ 4.5 Hz, J <sub>4,6</sub> ≈ 0.8 Hz); 3.33 (qd, H-5, J <sub>5,6</sub> ≈ 2.3 Hz); 4.01–4.20 (m, H-6); 8.65 (d, CH <sub>3</sub> -2, J ≈ 7 Hz); 6.77 (s, N(CH <sub>3</sub> ) <sub>2</sub> -3) [a]
(11)	264 (4.14) — 33%	7.31 (d, H-2, J <sub>2,2</sub> ≈ 20 Hz); 6.80 (d, H-2); 3.90 (qd, H-4, J <sub>4,5</sub> ≈ 5 Hz, J <sub>4,6</sub> ≈ 0.6 Hz); 3.19–3.39 (m, H-5); 4.05 (m, H-6); 8.57 (s, CH <sub>3</sub> -1); 7.80 (s, N(CH <sub>3</sub> ) <sub>2</sub> -1); 7.88 (t, CH <sub>3</sub> -3, J ≈ 1.5 Hz) [a]

[a] In CDCl<sub>3</sub>; [b] In CCl<sub>4</sub>; [c] TMS as internal standard.

tion neither the cyclization products (8) (R = R' = H, R'' = H, alkyl, or aryl) nor the 1,5-dihydropentalene derivatives (9) (R = R' = H, R'' = H, alkyl, or aryl) expected as a result of 1,5-H shifts are stable; in the thermal cyclization in the presence of bases they are rapidly converted into the more inert, tautomeric, resonance-stabilized, fulvenoid 1,2-dihydropentalenes (2) or (6).

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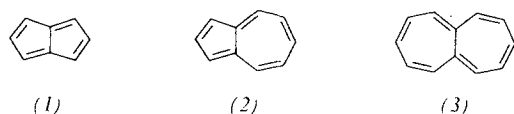
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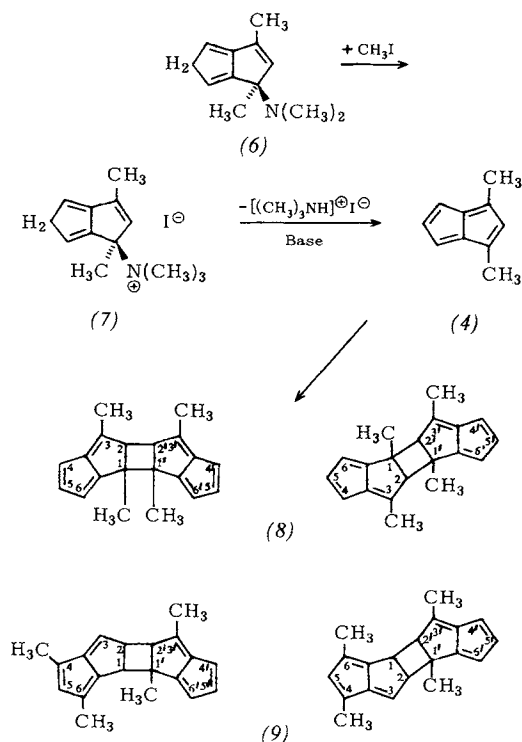
## Concerning Pentalene, 2-Methylpentalene, and 1,3-Dimethylpentalene<sup>[\*\*]</sup>

By Klaus Hafner, Reinhard Dönges, Ernst Goedecke, and Reinhard Kaiser<sup>[\*]</sup>

In the series of non-alternant bicyclic hydrocarbons, pentalene (1) has, unlike azulene (2)<sup>[1]</sup> and heptalene (3)<sup>[2]</sup>,



withstood attempts at synthesis that have extended over decades<sup>[3]</sup>. Each of the three compounds contains a peripheral  $\pi$ -electron system perturbed by a central  $\sigma$ -bond;



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in the case of azulene (2), isomeric with naphthalene and having 10  $\pi$ -electrons, the system has "aromatic" character, whereas heptalene (3) with 12  $\pi$ -electrons behaves as a cyclopolyolefin. According to the Hückel rule, pentalene, with 8  $\pi$ -electrons, should not have "aromatic" properties, but quantum-chemical calculations have given contradictory results<sup>[4]</sup>. Since it is not permissible to draw conclusions about the parent compound from the few known benzo-annulated or highly substituted pentalene derivatives, it is of interest to test the theoretical predictions by synthesis of (1) or its simple alkyl derivatives.

Starting from 1,2- and 1,5-dihydropentalene derivatives, for which we have described a simple method of preparation<sup>[5-7]</sup>, we have now been able to detect pentalene (1),

Table 1. Physical properties of the products (8), (9), (12), and (14).

Cpd.	Yield (%)	M. p. [ C ]	UV $\lambda_{\text{max}}$ (nm) (log $\epsilon$ ) in <i>n</i> -hexane	NMR ( $\tau$ ), $J$ (Hz) in $\text{CCl}_4$ [a]
(8a)	32	110–112	267 (4.38) 379 (3.14)	8.43 ( $\text{CH}_3$ -1/s), 6.91 (H-2/m), 8.00 ( $\text{CH}_3$ -3/s), 4.16 (H-4/dd), 3.45 (H-5/dd), 4.31 (H-6/m), $J_{4,5} = 5.5$ , $J_{4,6} = 0.5$ , $J_{5,6} = 2$
(8b)	1.6	80 (dec.)	261, 389	8.65 ( $\text{CH}_3$ -1/s), 6.53 (H-2/m), 7.95 ( $\text{CH}_3$ -3/s), 4.26 (H-4/dd), 3.50 (H-5/m), 4.59 (H-6/m), $J_{4,5} = 5.5$ , $J_{4,6} = 0.5$ , $J_{5,6} = 2$
(8c)	4	180 (dec.)	259 (4.31) 267 (4.38) 284 (4.08) 404 (3.23)	9.03 ( $\text{CH}_3$ -1/s), 7.30 (H-2/m), 7.81 ( $\text{CH}_3$ -3/s), 3.98 (H-4/dd), 3.30 (H-5/dd), 4.20 (H-6/m), $J_{4,5} = 5$ , $J_{4,6} = 0.5$ , $J_{5,6} = 2$
(9a)	4.5	150 (dec.)	256 (4.22) 262 (4.24) 279 (4.05) 408 (3.21)	7.17 (m), 6.61 (m), 6.92 (m) (H-1, H-2, H-2'), 9.05 ( $\text{CH}_3$ -1'/s), 3.58 (H-3/d), 7.83 ( $\text{CH}_3$ -3'/s), 7.99 ( $\text{CH}_3$ -4/d), 4.00 (H-4'/dd), 3.80 (H-5/m), 3.32 (H-5'/dd), 8.10 ( $\text{CH}_3$ -6/s), 4.25 (H-6'/m), $J_{2,3} = 3$ , $J_{4,5} = 0.5$ , $J_{4,6} = 5$ , $J_{4,6} = 0.5$ , $J_{5,6} = 2$
(9b)	6			6.80 (m), 6.67 (m), 6.50 (m) (H-1, H-2, H-2'), 8.52 ( $\text{CH}_3$ -1'/s), 3.95–4.00 (H-3, H-5/m), 7.99 ( $\text{CH}_3$ -3'/s), 8.13 ( $\text{CH}_3$ -4/d), 4.16 (H-4'/dd), 3.48 (H-5'/dd), 8.23 ( $\text{CH}_3$ -6/s), 4.49 (H-6'/d), $J_{4,5} = 5$ , $J_{4,6} = 1$ , $J_{5,6} = 2$
(12a)	22	103–104 (dec.)	254 (4.16) 387 (3.02)	6.25–6.43 (H-1/dm), 5.69–5.99 (H-2/dm), 3.71 (H-3/m), 4.11 (H-4/dd), 3.33 (H-5/dd), 4.35 (H-6/m), $J_{4,5} = 5$ , $J_{4,6} = 0.8$ , $J_{5,6} = 1.8$
(12b)	10	84 (dec.)	254 (4.21) 259 (4.22) 275 (4.07) 400 (3.17)	7.05 (H-1/dm), 6.39 (H-2/dm), 3.26 (H-3/m), 3.92 (H-4/dd), 3.23 (H-5/dd), 4.01 (H-6/m), $J_{4,5} = 5.1$ , $J_{4,6} = 0.7$ , $J_{5,6} = 1.8$
(14a)	26	106–107 (dec.)	257 (4.20) 272 (4.11) 382 (2.90)	6.35–6.53 (H-1/m), 5.84–6.04 (H-2/m), 3.97 (H-3/m), 4.43 (H-4/m), 8.00 ( $\text{CH}_3$ -5/s), 4.52 (H-6/m)
(14b)	12	140 (dec.)	258 (4.25) 263 (4.28) 276 (4.15) 392 (3.06)	7.00–7.13 (H-1/m), 6.38–6.56 (H-2/m), 3.48 (H-3/m), 4.22 (H-4/m), 7.88 ( $\text{CH}_3$ -5/s), 4.15 (H-6/m)

[a] TMS as internal standard.