

Scheme 1. Generation of the vinylcarbene (3) and its reactions. (2), m.p. 199–200°C (dec.), IR (KBr): 1642, 1574, 1395, 1282  $\text{cm}^{-1}$ ,  $^1\text{H-NMR}$  ( $\text{CDCl}_3/[\text{D}_6]-\text{EtOH}$ ):  $\delta = 3.15$  (s, 3H), 3.21 (s, 3H), 3.36 (s, 6H), 5.0 (d, 1H), 7.75 (d, 1H); (4), m.p. 118°C (120°C [2]); (5), m.p. 182°C; (6), b.p. 150°C/0.15 mbar; (7), m.p. 150–151°C.

Cyclization of (3) to give 1,2-bis(dimethylamino)cyclopropene has not yet been observed, which is hardly surprising in view of the pronounced tendency of 1-dimethylamino-2,3-diphenylcyclopropene<sup>[6]</sup> and of dicarbonyl(cyclopentadienyl)(1,2,3-triphenylcyclopropenyl)iron<sup>[7]</sup> to undergo ring cleavage in the presence of acids.

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(1a), 67750-75-8; (1b), 67761-16-4; (2), 67761-17-5; (3), 67761-18-6; (4), 1611-78-5; (5), 67761-20-0; (6), 67761-21-1; (7), 67761-22-2; tetraethylallene-tetracarboxylate, 67761-23-3

- [1] The Allopolarization Principle and Its Applications, Part 2. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.—Part 1: R. Gompper, R. Sobotta, *Angew. Chem.* 90, 808 (1978); *Angew. Chem. Int. Ed. Engl.* 17, 760 (1978).  
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## Synthesis of Penta- and Hexacyclic Conjugated Hydrocarbons by Cycloaddition Reactions<sup>[\*\*]</sup>

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Cycloaddition reactions of bi- and tricyclically conjugated hydrocarbons such as pentalenes, azulenes, and aceheptylenes

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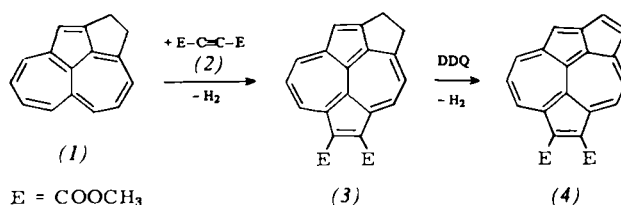
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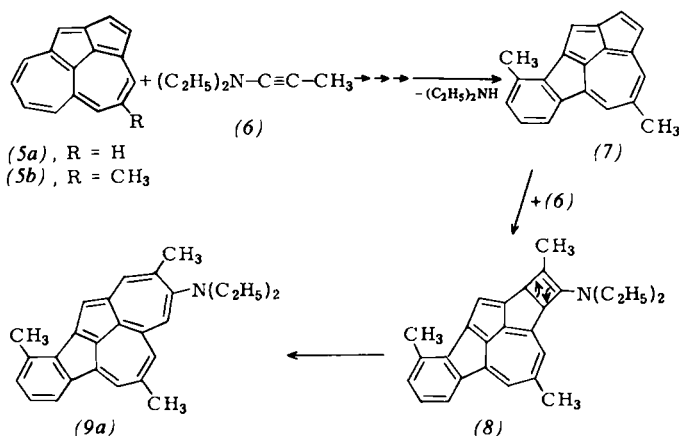
with electron-poor and electron-rich alkynes recently opened up an unexpectedly facile entry to cyclically conjugated systems<sup>[1]</sup>. On examining the scope and limitations of this synthetic approach we obtained, among other compounds, for the first time, the penta- and hexacyclic polyenes (4), (9a), and (10).

By analogy with the dipolar cycloaddition of dimethyl acetylenedicarboxylate and aceheptylene leading to dimethyl 1,2-dicyclopenta[*ef,kl*]heptalenedicarboxylate<sup>[1c]</sup>, the 2,3-ethano-bridged derivative of aceheptylene, 1,2-dihydropentaleno[6.1.2-*def*]heptalene (1)<sup>[2]</sup>, also reacts with the electron-poor alkyne (2) via *peri*-annulation of a five-membered ring to give 30% of the dihydropentaleno[6.1.2-*fgh*]aceheptylene derivative (3)<sup>[3]</sup> (yellow-brown rods, m.p. 176°C). On dehydrogenation with 2,3-dichloro-5,6-dicyanoquinone (DDQ), (3) yields the first completely conjugated nonbenzenoid pentacyclic compound having an 18 $\pi$ -electron system, the ester (4),



in 92% yield as brown rods of m.p. 164–165°C. All attempts to synthesize (4) directly by cycloaddition of (2) and pentaleno[6.1.2-*def*]heptalene (5a)<sup>[2]</sup> have been unsuccessful so far.

In contrast, reaction of the methyl derivative (5b)<sup>[4]</sup> with *N,N*-diethyl-1-propynylamine (6) for 90 min in refluxing xylene affords the thermally stable pentacyclic 1,2-benzopentaleno[6.1.2-*def*]heptalene derivative (9a) in 34% yield (based on conversion of (5b)) as brown needles of m.p. 188°C. Like aceheptylene<sup>[1c]</sup>, (5b) is expected to initially undergo a dipolar cycloaddition with (6). Two consecutive valence isomeriza-



tions and subsequent elimination of diethylamine lead to the pentacyclic hydrocarbon (7). Like cyclopent[*cd*]azulene<sup>[1b]</sup>, this product immediately combines in another formal [2+2] cycloaddition with a further mole of (6) to give (8), which by valence isomerization finally yields (9a). Even on reaction of (5b) with less than one equivalent of (6), compound (7) could not be isolated. In accordance with quantum-chemical calculations<sup>[5]</sup> on the dicyclopent[*cd,ij*]azulene system present in (7), this compound exhibits a pronounced reactivity towards cycloaddition partners, mainly at the double bond in the unsubstituted five-membered ring.

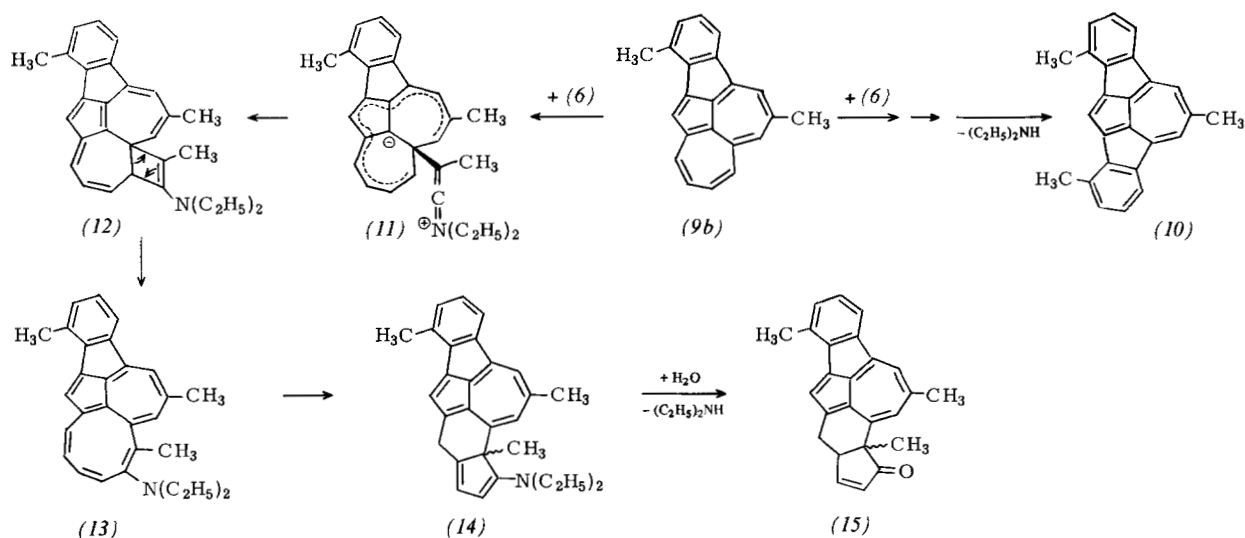


Table 1. Spectroscopic data of (4), (9a), (10), and (15).

Cpd.	<sup>1</sup> H-NMR (δ, J) in CDCl <sub>3</sub>	UV, λ <sub>max</sub> [nm] (log ε) in dioxane
(4)	4.14 (s, 3H, OCH <sub>3</sub> ), 4.16 (s, 3H, OCH <sub>3</sub> ), 7.19 (dd, J <sub>1</sub> = 10 Hz, J <sub>2</sub> = 1.5 Hz; 1H), 7.48 (d, J = 4.5 Hz; 1H), 7.58 (d, J = 4.5 Hz; 1H), 8.00 (d, J = 9.5 Hz; 1H), 8.10 (s, 1H, H <sup>10</sup> ), 8.42 (dd, J <sub>1</sub> = 10 Hz, J <sub>2</sub> = 1.5 Hz; 2H), 9.61 (d, J = 9.5 Hz; 1H)	2.31 (4.45), 270 (4.77), 287 (4.69), 323 (4.25), 350 (4.13), 386 (3.87), 401 (3.81), 423 (3.76), 449 (3.64), 493 (3.33), 558 (3.27), 594 (3.52), 661 (2.85), 792 (2.55)
(9a)	1.10 (t, J = 7 Hz; 6H, CH <sub>2</sub> -CH <sub>3</sub> ), 2.34 (s, 3H, CH <sub>3</sub> ), 2.47 (d, J = 1 Hz; 3H, CH <sub>3</sub> ), 2.87 (s, 3H, CH <sub>3</sub> ), 3.05 (q, J = 7 Hz; 4H, CH <sub>2</sub> -CH <sub>3</sub> ), 6.40 (s, 1H), 6.87 (s, 1H), 7.08 (s, 1H), 7.41 (mc, 1H), 7.45 (s, 1H), 7.63 (s, 1H), 7.85 (s, 1H), 8.00 (mc, 1H)	272 (4.52) sh, 300 (4.72) sh, 312 (4.77) sh, 322 (4.80), 352 (4.42) sh, 390 (4.00) sh, 436 (3.91) sh, 454 (4.00), 516 (3.37), 557 (3.19), 647 (2.00) sh, 709 (2.16), 784 (2.21), 880 (2.00) sh, 1042 (1.18) sh
(10)	2.39 (s, 6H, 7-CH <sub>3</sub> , 9-CH <sub>3</sub> ), 3.03 (s, 3H, 2-CH <sub>3</sub> ), 6.72-6.98 (m, 5H), 7.34 (mc, 2H), 7.98 (s, 2H, H <sup>1</sup> , H <sup>3</sup> )	231 (3.79), 245 (3.69) sh, 275 (3.87) sh, 285 (3.99) sh, 309 (4.42), 348 (3.33), 367 (3.27), 388 (3.22), 411 (2.46) sh, 426 (2.45), 464 (1.59), 502 (1.78), 621 (2.25), 833 (1.83), 928 (1.81), 1111 (1.41)
(15)	1.81 (s, 3H, CH <sub>3</sub> ), 2.66 (s, 3H, CH <sub>3</sub> ), 2.85 (s, 3H, CH <sub>3</sub> ), 3.45 (mc, 1H, H <sup>6a</sup> ), 3.72 (dd, J <sub>1</sub> = 18.6 Hz, J <sub>2</sub> = 3.7 Hz; 1H, 7-CH <sub>2</sub> ), 3.99 (dd, J <sub>1</sub> = 18.6 Hz, J <sub>2</sub> = 4.9 Hz; 1H, 7-CH <sub>2</sub> ), 6.13 (dd, J <sub>1</sub> = 7 Hz, J <sub>2</sub> = 3 Hz; 1H, H <sup>6</sup> ), 6.42 (dd, J <sub>1</sub> = 7 Hz, J <sub>2</sub> = 1 Hz; 1H, H <sup>5</sup> ), 7.12 (mc, 2H), 7.56 (s, 1H), 7.64 (s, 1H), 7.78 (mc, 1H), 7.94 (s, 1H)	221 (4.36), 283 (4.84), 356 (3.87), 371 (3.83), 380 (3.68) sh, 461 (3.24), 482 (3.33), 504 (3.23) sh, 650 (2.37) sh, 688 (2.39), 752 (2.29) sh, 860 (1.76) sh

Like (5b), but unlike (9a), the hydrocarbon (9b)<sup>[6]</sup> also reacts with (6) in a dipolar cycloaddition at the unsubstituted seven-membered ring. Thereby trimethyldibenzo[4,5;7,8]dicyclopent[cd,ij]azulene (10) is formed (grayish blue platelets; m. p. 224–225°C; <10% yield) in a reaction sequence analogous to the formation of (7). Compound (10) is the first fully conjugated thermally stable derivative of the hitherto unknown dicyclopent[cd,ij]azulene, which presumably has a high ring strain.

The major product formed besides (10), however, is the ketone (15) (greenish yellow needles, m. p. 290°C; yield 56%), which is only sparingly soluble in organic solvents. This points to a primary attack of (6) on (9b) with formation of the resonance-stabilized dipole (11). Subsequent cyclization gives the cyclobutene derivative (12), and valence isomerization of (12) via the thermally unstable cyclononaazulene derivative (13) forms the enamine (14), which yields (15) on hydrolysis.

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(1), 67745-88-4; (2), 762-42-5; (3), 67745-89-5; (4), 67745-90-8; (5b), 1213-66-7; (6), 4231-35-0; (9a), 67761-63-1; (9b), 67745-91-9; (10), 67745-92-0; (15), 67745-93-1

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