have predominantly *ap* conformations and whose rotational barriers should even be higher.

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(4a), 69224-93-7; *(4b)*, 69224-94-8; *(5a)*, 69224-95-9; *(5b)*, 69224-96-0; *(6a)*, 69224-97-1; *(6b)*, 69224-98-2

[1] a) *G. Binsch*, Top. Stereochem. *3*, 97 (1968); b) *F. Vögtle, H. Förster*, Angew. Chem. *89*, 443 (1977); Angew. Chem. Int. Ed. Engl. *16*, 429 (1977); c) *S. Patai*: The Chemistry of the Carbon-Carbon Triple Bond. Interscience, London 1978.

[2] *(5a)* appears to have been prepared from 9-formyltriptycenetosylhydrazone: *I. I. Brunovlenskaya, T. A. Gudasheva, V. R. Skvarchenko*, Zh. Org. Khim. *10*, 1495 (1974); but the melting point (388 °C) and ^{1}H-NMR data [δ = 7.4 (m, 12H), 7.0 (m, 14H), 5.4 (s, 2H), in thionyl chloride], are not in agreement with those found by us (Table 1, $CDCl_3$), nor those recorded in thionyl chloride for comparison.

[3] We synthesized *(4)*—*(6)* by reaction of the corresponding anthracenes with benzyne and 3,6-dimethylbenzyne respectively. Elemental analyses and spectroscopic data are consistent with the given structures.

[4] The outer CH_3 groups appear as a sharp singlet; the absorption of H-8, 11-13, however, is likewise broadened at room temperature; cooling leads to a sharp multiplet.

[5] *H. Shanan-Atidi, K. H. Bar-Eli*, J. Phys. Chem. *74*, 961 (1970).

[6] According to Stuart-Briegleb space-filling models such marked steric interactions are not to be expected, while CPK models suggest a very rigid structure. Present-day space-filling models are thus of limited use for predicting such steric interactions in large molecules.

[7] For the spatial requirements of methyl groups cf. [1b] and *Ch. Rüchardt, H.-D. Beckhaus, G. Hellmann, S. Weiner, R. Winiker*, Angew. Chem. *89*, 913 (1977); Angew. Chem. Int. Ed. Engl. *16*, 875 (1977); and references cited therein.

[8] Cf. *e.g.* a) *Yu. K. Grishin, N. M. Sergeyev, O. A. Subbotin, Yu. A. Ustynyuk*, Mol. Phys. *25*, 297 (1973); b) *F. Vögtle, P. Koo Tze Mew*, Angew. Chem. *90*, 58 (1978); Angew. Chem. Int. Ed. Engl. *17*, 60 (1978).

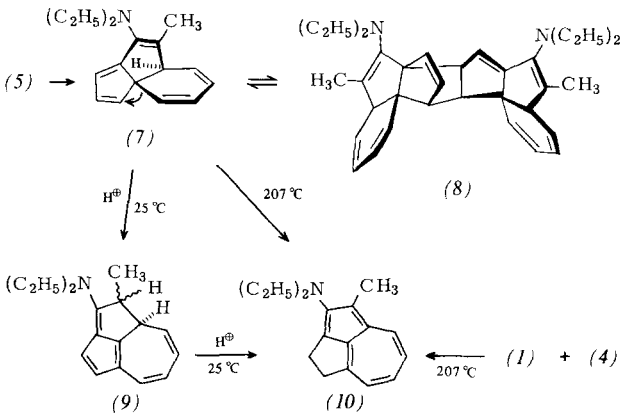
[9] "Temperature of stereochemical rigidity"; *N. M. Sergeyev, K. F. Abdulla, V. R. Skvarchenko*, J. Chem. Soc. Chem. Commun. *1972*, 368.

Surprising Transformation of Azulene by Cycloaddition with 1-(Diethylamino)propyne[**]

By *Klaus Hafner, Hans Jörg Lindner*, and *Werner Ude*[*]

Azulene *(1)* reacts as the prototype of nonbenzenoid "aromatic" hydrocarbons[1] with electrophiles and nucleophiles *via* substitution at positions 1(≡3) and 4(≡8), respectively, or 6. With electron-poor alkynes such as dimethyl acetylenedicarboxylate, *(1)* can undergo not only additive substitution[2a] but—like electron-rich alkenes[2b] also thermally induced dipolar cycloaddition at the five-membered ring; subsequent valence isomerization of the primary adduct *(2)* yields the next-higher homologue of *(1)*, *viz.* the heptalene derivative *(3)*[2c]. We have now attempted reaction of *(1)* with electron-rich alkynes such as 1-(diethylamino)propyne *(4)* in order to obtain the adduct *(5)* *via* (presumably also dipolar) cycloaddition to the seven-membered ring. Valence isomerization of *(5)* could lead to the hitherto unknown cyclopentacyclononene system *(6)*[3].

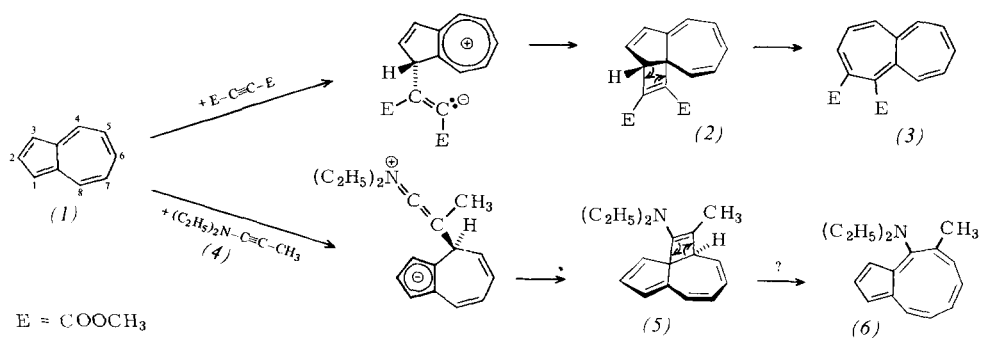
Surprisingly, *(1)* and *(4)* give a colorless crystalline 1:1 adduct *(7)*, m.p. 76 °C, even at room temperature. Compound *(7)* was isolated after 20 d in 83 % yield (based on reacted azulene)[4]. The constitution of the bridged spiro[4.5]decatetraene *(7)* has been confirmed by X-ray structure analysis[5] and ^{1}H- and ^{13}C-NMR spectra (Table 1). Thus *(7)* exists in the crystal as a dimer *(8)* formed by [4+2] cycloaddition of its cyclopentadiene moiety whereas a rapid retro-Diels-



Alder raction to give *(7)* occurs in solution (benzene, trichloromethane). This indicates only low activation energy for dimerization of *(7)* and for the cycloreversion of *(8)* (E_a < 25 kcal/mol)[6].

Formation of *(7)* probably involves the primary adduct *(5)* containing the structural unit of a spiro[3.4]octa-1,5,7-triene, which has been shown by *R. D. Miller et al.*[7] to resist isolation at −10 °C, partly due to a presumably 1,5 sigmatropic ring expansion to form a dihydropentalene. Analogous rearrangement of the 1,3-diene-bridged derivative *(5)* should lead to *(7)*.

In the presence of catalytic amounts of glacial acetic acid at room temperature, *(7)* undergoes fast isomerization in solution (CH_3OH)—possibly by renewed 1,5 sigmatropic alkyl shift—to give 20 % of the 1,8a-dihydrocyclopent[*c,d*]azulene derivative *(9)* (lemon yellow needles, m.p. 87 °C; see Table 1), which is transformed under the same reaction conditions



within *ca.* 3 h to give 2-(diethylamino)-1-methyl-3,4-dihydrocyclopent[*cd*]azulene *(10)* (brown platelets, m.p. 52 °C, yield 80 %; see Table 1). In boiling tetralin, on the other hand, *(7)* gives *(10)* directly in 30 % yield. The same tricyclic com-

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pound also results from reaction of *(1)* with *(4)* in boiling tetralin (yield 17%), probably also *via (7)* as intermediate.

In contrast to *(1)*, 4,6,8-trimethylazulene *(11)* reacts with *(4)* only in boiling tetralin; cycloaddition is hindered by the alkyl groups in positions 4 and 8.

The major product isolated was found to be 15% of the dihydrocyclopentaindene derivative *(14)* (yellow platelets,

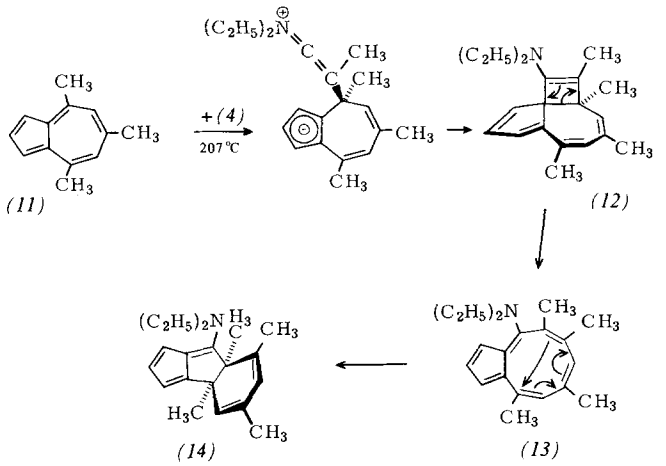

Table 1. Spectroscopic data of *(7)*, *(9)*, *(10)*, and *(14)*.

Cpd.	100 MHz-^{1}H-NMR (δ, J) in $CDCl_3$	UV, λ_{max} [nm] (log ε) in *n*-hexane
(7) [a]	6.37 (dd, $J_1=4.5$ Hz, $J_2=2$ Hz; 1H), 6.2–5.6 (m, 5H) 4.9–4.7 (m, 1H), 3.2–2.8 (m, 1H), 2.97, 2.93 (q, $J=7$ Hz; 4H, CH_2—CH_3), 1.70 (d, $J=2$ Hz; 3H, CH_3), 0.98 (t, $J=7$ Hz; 6H, CH_2—CH_3)	328 (3.09) sh, 259 (3.89)
(9)	6.8–6.5 (m, 1H), 6.65, 6.25 (d, $J=4.5$ Hz; 2H), 6.0–5.6 (m, 2H), 5.5–5.4 (m, 1H), 4.9–4.0 (m, 6H), 1.48 (d, $J=7$ Hz; 3H, CH_3), 1.30 (t, $J=7$ Hz; 6H, CH_2—CH_3)	400 (3.62), 336 (4.25), 319 (4.13) sh, 273 (4.08), 267 (4.04) sh, 252 (3.89) sh, 213 (4.16)
(10)	7.61 (d, $J=10$ Hz; 1H), 7.2–6.4 (m, 3H), 3.7–3.2 (m, 4H, CH_2—CH_2), 3.46 (q, $J=7$ Hz; 4H, CH_2—CH_3), 2.52 (s, 3H, CH_3), 1.16 (t, $J=7$ Hz; 6H, CH_2—CH_3)	530 (2.51), 436 (4.06), 429 (3.89) sh, 410 (3.88), 403 (3.75) sh, 392 (3.59) sh, 363 (3.61) sh, 337 (3.83) sh, 316 (4.75), 306 (4.58) sh, 295 (4.26) sh, 256 (4.17), 224 (4.10) sh
(14)	6.55 (dd, $J_1=4$ Hz, $J_2=2.5$ Hz; 1H), 6.16 (dd, $J_1=4$ Hz, $J_2=1$ Hz; 1H), 5.80 (dd, $J_1=2.5$ Hz, $J_2=1$ Hz; 1H), 5.60, 5.44 (mc, 2H), 3.9–3.3 (m, 4H, CH_2—CH_3), 1.93, 1.65 (d, $J=1.5$ Hz; 6H, CH_3), 1.34, 1.16 (s, 6H, CH_3), 1.28 (t, $J=7$ Hz; 6H, CH_2—CH_3)	333 (4.24), 266 (3.84), 217 (3.98) sh

[a] 25.2 MHz-^{13}C-NMR (δ) in $CDCl_3$: 165.8 (quart. C), 140.7 (2 quart. C), 135.3, 135.1, 130.5, 124.3 (1 C—H each), 122.8(2 C—H), 115.6 (C—H), 69.1 (quart. C), 47.4 (2 CH_2—CH_3), 44.2 (C—H), 13.8 (2 CH_2—CH_3), 13.2 (CH_3).

m. p. 123—124 °C; see Table 1)[8], containing a resonance-stabilized aminofulvene moiety whose structure was established by spectroscopy and X-ray studies[9]. This thermally induced reaction should also involve initial formation of the primary adduct *(12)* analogous to *(5)*, which for steric reasons related to its substituents is no longer capable of 1,5 sigmatropic ring expansion but instead undergoes valence isomerization to the likewise unstable cyclopentacyclononene system *(13)*. Valence isomerization in a manner characteristic of cyclononatetraene derivatives[10] ultimately gives the thermally stable systems *(14)*.

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(1), 275-51-4; *(4)*, 4231-35-0; *(5)*, 69258-21-5; *(6)*, 69278-32-6; *(7)*, 69258-22-6; *(8)*, 69258-23-7; *(9)*, 69258-24-8; *(10)*, 69278-31-5; *(11)*, 941-81-1; *(12)*, 69258-25-9; *(14)*, 69258-26-0

[1] *E. Heilbronner* in *D. Ginsburg*: Non-Benzenoid Aromatic Compounds. Wiley-Interscience, New York 1959, pp. 171 ff.; *A. Streitwieser*: Molecular Orbital Theory for Organic Chemists. Wiley, New York 1961, p. 297.

[2] a) *W. Treibs*, Naturwissenschaften *52*, 452 (1965); b) *R. Huisgen*, Acc. Chem. Res. *10*, 117 (1977), and references cited therein; c) *K. Hafner, H. Diehl, H. U. Süss*, Angew. Chem. *88*, 121 (1976); Angew. Chem. Int. Ed. Engl. *15*, 104 (1976).

[3] We have observed a corresponding reaction sequence on treatment of the aceheptylene system with the ynamine *(4)*: *K. Hafner, H. Diehl, W. Richarz*, Angew. Chem. *88*, 125 (1976); Angew. Chem. Int. Ed. Engl. *15*, 108 (1976); *K. Hafner, H. D. Diesel, W. Richarz, ibid. 90*, 812 (1978) and *17*, 763 (1978).

[4] All new compounds gave correct elemental analyses and mass spectra.

[5] Triclinic needles $P\bar{1}$. $a=1773(1)$, $b=1231(1)$, $c=680.7(5)$ pm, $\alpha=101.00(5)$, $\beta=85.94(5)$, $\gamma=106.63(5)°$, $Z=2$; 2148 observed reflections with $|F|>2\sigma_F$ (STOE two circle diffractometer, $Cu_{K\alpha}$ radiation $\lambda=154.18$ pm); refined to $R=0.108$ [11].

[6] Dimerization of 1,3-di-*tert*-butylpentalene-5-carbaldehyde, -5-carbonitrile, and -5-carboxylic methyl ester, as well as cycloreversion of the dimers have similarly low activation energies (*M. Suda, K. Hafner*, Tetrahedron Lett. *1977*, 2449).

[7] *R. D. Miller, M. Schneider*, Tetrahedron Lett. *1975*, 1557; cf. also: *R. D. Miller, D. Kaufmann, J. Mayerle*, J. Am. Chem. Soc. *99*, 8511 (1977); *A. de Meijere, L. U. Meyer*, Chem. Ber. *110*, 2561 (1977).

[8] In addition, 9% of an isomer (colorless leaflets, m.p. 86 °C) of *(14)* is isolated, which is probably a diethylamino(tetramethyl)dihydro-*s*-indacene.

[9] Orthorhombic platelets, $P2_12_12_1$, $a=1675(1)$, $b=1331(1)$, $c=754.6(5)$ pm, $Z=4$; 764 observed reflections with $|F|>2\sigma_F$ (STOE two circle diffractometer, $Cu_{K\alpha}$ radiation $\lambda=154.18$ pm); refined to $R=0.070$ [11].

[10] *G. Boche, H. Böhme, D. Martens*, Angew. Chem. *81*, 565 (1969); Angew. Chem. Int. Ed. Engl. *8*, 594 (1969); *G. Boche, H. Weber, D. Martens, A. Bieberbach*, Chem. Ber. *111*, 2480 (1978), and references cited therein.

[11] *G. M. Sheldrick*, SHELX-76, unpublished.

Facile Ring Enlargement of Azulene to Give the Cyclopentacyclononene System by Dipolar Cycloaddition[**]

By *Klaus Hafner, Hans Jörg Lindner*, and *Werner Ude*[*]

Azulene *(1a)* and 4,6,8-trimethylazulene *(1b)* react with 1-(diethylamino)propyne *(2)* to form 1,3-diene-bridged spiro-[3.4]octa-1,5,7-triene derivatives *(3)*, which undergo stabilization by 1,5 sigmatropic ring enlargement to bridged spiro-[4.5]decatetraene *(4)* or by valence isomerization *via* the cyclopentacyclononene *(5)* to give the dihydrocyclopentaindene derivative *(6)*[1a]. Owing to the valence isomerization characteristic of cyclononatetraenes[1b], the azulene-homologous cyclopentacyclononene system could not yet be isolated. This result prompted a study of cycloadditions of *(2)* with azulenes bearing substituents which hinder or rule out valence isomerization of the nine-membered ring in *(5)*. Inspection of models suggested that the readily accessible 1,2-dihydrocyclopent[*cd*]azulene *(7)*[2] should be particularly suitable for this purpose.

The bridged azulene *(7)* reacts like azulene with *(2)* at room temperature to give a brownish red crystalline 1:1

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