the products (light yellow powder in each case; yield 80 to 90%) can be recrystallized from pentane at −40 °C.

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[1] *H. Schumann, O. Stelzer*, and *W. Gick*, Angew. Chem. *81*, 256 (1969); Angew. Chem. internat. Edit. *8*, 271 (1969); *H. Schumann, W. Gick*, and *R. Weis*, Proc. IV Int. Conf. Organometallic Chem., Bristol 1969, U 4.

[2] *I. Ruidisch* and *M. Schmidt*, J. organometallic Chem. *1*, 160 (1963).

[3] *H. Schumann* and *B. Jutzi*, (b.p. 103 °C/0.1 torr).

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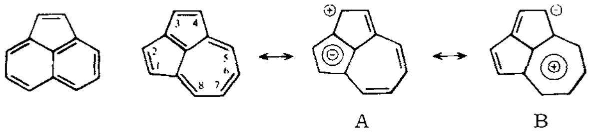
New Synthesis of Aceheptylene

By *Klaus Hafner* and *Rolf Fleischer*[*]

Like acenaphthylene *(1)*, the isomeric compound cyclopent[*cd*]azulene *(2)* can also undergo 1,2-cycloadditions at the double bond of the five-membered ring. In contrast to *(1)*,



(1) *(2)*

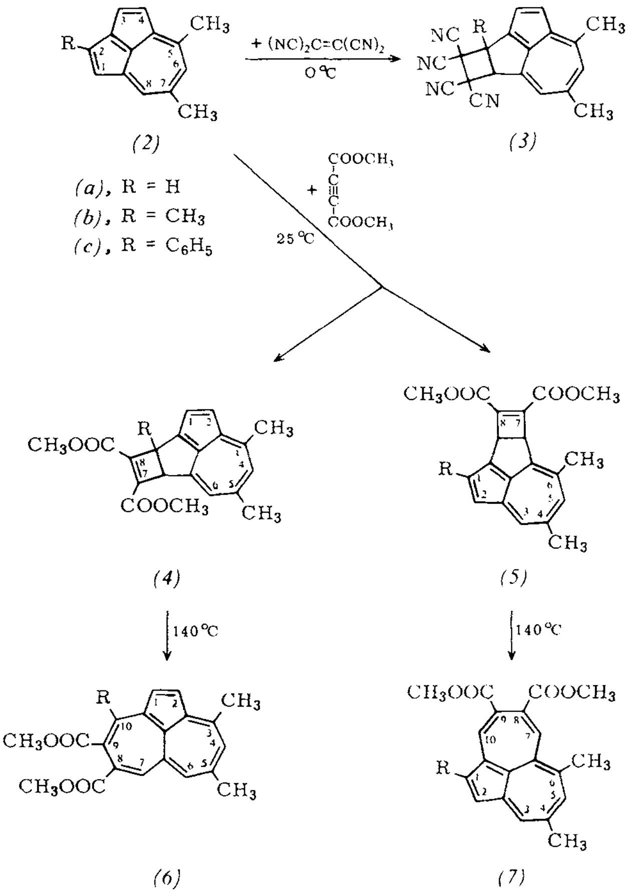
however, *(2)* — like other derivatives of pentalene[1] — combines with multiple-bond systems at 0 °C or at room temperature. The thermally labile 12π-electron system *(2)* is thus converted into stable azulene derivatives.

Reaction of *(2a)* with tetracyanoethylene at 0 °C affords the cyclobutane derivative *(3)* in 60% yield as the sole adduct[2]. Dimethyl acetylenedicarboxylate, however, adds to *(2a)* at 25 °C in methylene chloride (+1% of triethylamine, 15 h) both in the 1,2- and in the 3,4-position to form dimethyl 3,5-dimethyl-6b,8a-dihydrocyclobuta[*a*]cyclopent[*cd*]azulene-7,8-dicarboxylate *(4a)* (m.p. 112 °C, yield 40%) and the corresponding 4,6-dimethyl derivative *(5a)* (m.p. 143–144 °C, yield 10%)[3].

(2b) and *(2c)*[4] combine with dimethyl acetylenedicarboxylate only in the 1,2-position to give *(4b)* (m.p. 141 °C, yield 71%) and a mixture of *(4c)* (m.p. 103–104 °C, yield 53%) and the aceheptylene derivative *(6c)* (m.p. 152 °C, yield 8%), respectively.

X-ray structure analysis[5] and SCF calculations[5,6] indicate a high bond order for the 1,2- and 3,4-linkage in *(2)* and polarization consistent with participation of the resonance structures (2A) and (2B). These findings suggest that reactions of *(2)* with electron-deficient alkenes and alkynes are two-step cycloadditions proceeding *via* resonance-stabilized dipolar intermediates.

Thermal valence isomerization of the adducts *(4a)*, *(4b)*, *(4c)*, and *(5a)* in boiling xylene (1 h) leads to the aceheptylenes *(6a)* (m.p. 150 °C), *(6b)* (m.p. 147 °C), *(6c)* (152 °C), and *(7a)* (m.p. 119–120 °C), respectively, in yields of about 90%. The preparation of *(6)* and *(7)* from the readily accessible cyclopent[*cd*]azulenes supplements the previous syntheses[2,7] of the tricyclic 14π-electron system. The structures



of compounds *(4)*–*(7)* were established by elemental analysis, molecular-weight determination, and UV and NMR spectra.

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[1] 1,3-Bis(dimethylamino)pentalene [*K. Hafner, K. F. Bangert*, and *V. Orfanos*, Angew. Chem. *79*, 414 (1967); Angew. Chem. internat. Edit. *6*, 451 (1967)] reacts with dimethyl acetylenedicarboxylate at 0 °C to give dimethyl 4,8-bis(dimethylamino)azulene-5,6-dicarboxylate [*V. Orfanos*, Dissertation, Technische Hochschule Darmstadt 1968]. In this case, two-step cycloaddition of the enamine system to alkyne giving a cyclobutene derivative is probably followed by valence isomerization of the product to the substituted azulene. A concerted [2 + 8] cycloaddition has been suggested by *R. B. Woodward* [Special Publication No. 21, Chem. Soc. (London) *1967*, 217] as initial step in the formation of diethyl 1,2,3,4,5,8-hexaphenylazulene-6,7-dicarboxylate from hexaphenylpentalene and diethyl acetylenedicarboxylate at 160 °C [*E. LeGoff*, J. Amer. chem. Soc. *84*, 3975 (1962)].

[2] *K. Hafner* and *J. Schneider*, Liebigs Ann. Chem. *624*, 37 (1959).

[3] In addition to *(4a)* and *(5a)*, a 4% yield of dimethyl dimethylaceheptylenedicarboxylate is formed, presumably by addition of the acetylene ester to *(2a)* in the 2,2a- or 2a,3-position.

[4] *K. Hafner* and *K. F. Bangert*, Liebigs Ann. Chem. *650*, 98 (1961).

[5] *H. J. Lindner*, J. chem. Soc. (London), in press.

[6] *U. Müller-Westerhoff*, unpublished; *N. K. DasGupta* and *M. A. Ali*, Theoret. chim. Acta *4*, 101 (1966); *P. Hochmann, R. Zahradnik*, and *V. Kvasnička*, Collect. czechoslov. chem. Commun. *33*, 3478 (1968).

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