1,4-Dipolar Cycloadditions of Cyclopent[cd]azulene

By Herbert Diehl and Klaus Hafner

Cycloadditions of nonbenzenoid carbo- and hetero cyclic conjugated $n$-electron systems with suitable reactants provide a facile entry to ring systems that were hitherto difficult to prepare, if at all[1]. For instance, cyclopent[cd]azulene (1)[2] which is now readily accessible reacts with dimethyl acetylene dicarboxylate even at room temperature to give 75% of the 1:1 adduct (2) (blue-green leaflets, m. p. 104—105°C[3]; thermal valence isomerization thereof in boiling xylene yields 95% of dimethyl 4,5-acetylenedicarboxylate (4) (brown crystals, m. p. 97—98°C). Formation of small amounts of the isomeric 5,6-diesters (5) together with (2) is in agreement with results of our earlier studies[4]. Compound (5) presumably arises from the primary adduct (3) which appears to be unstable at as low a temperature as 20°C. The formation of (2) and (5) suggests that cycloaddition of (1) with alkynes proceeds via a two-step mechanism involving a resonance-stabilized 1,4-dipole. The solvent dependence[5] of this cycloaddition and orientation phenomena observed in the reactions of (1) with electron-poor and electron-rich alkynes do corroborate this suggestion.

Compound (1) rapidly reacts with propiolaldehyde in dichloromethane at 20°C via the primarily formed dipolar intermediate (6) to give the adducts (7) (yield 76%, blue oil) and (8), which as a result of pronounced ring strain immediately undergoes valence isomerization to 3% of 6-acetylenecarbaldehyde (10)[6] (reddish brown needles, m. p. 65—66°C). In contrast, (7) is only converted into the isomeric 4-carbaldehyde (9)[7] (90% yield, yellowish brown crystals, m. p. 75—76°C on heating to 140°C (boiling xylene, 1 h).

\[ \text{E} = \text{COOCH}_3 \]

However, (1) and its 5,7-dimethyl derivative (R = CH₃) combine with N,N-diethyl-1-propynylamine, according to the resonance structure (1b) via the dipolar intermediate (11) (R = H or CH₃) to give exclusively the adduct (12) which immediately affords the acetylene derivative (13) (R = CH₃; yellowish brown oil, m. p. of the 1,3,5-trinitrobenzene derivative 173—174°C) by cleavage of the cyclobutene ring[8].

Received: December 11, 1975 [Z. 363c IE]

German version: Angew. Chem. 88, 124 (1976)

CAS Registry numbers:

(1) 209-86-9; (2) 58150-77-9; (3) 58150-78-0; (4) 58150-79-1; (5) 58150-80-4; (6) 58150-81-5; (7) 58150-82-6; (8) 58150-83-7; (9) 58150-84-8; (10) 58150-85-9; (11) 58150-86-0; (12) 58150-87-1


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[3] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.
Cycloadditions of Aceheptylene—
A Facile Synthesis of Dicyclopenta[ef,k]heptalenes [**]

By Klaus Hafner, Herbert Diehl, and Winfried Richarz[*]

Similarly to pentalene, azulene**, and cyclopent[cd]azulene**, the readily accessible aceheptylene **(I)** undergos

cycloaddition with activated alkenes to form novel polycyclic systems in a surprisingly simple manner.

**Heating of (I) with dimethyl acetylenedicarboxylate in the molar ratio 1:1 in boiling tetralin for 1 h affords 25% of dimethyl 1,2-dicyclopenta[ef,k]heptalenedicarboxylate **(5)** (yellowish brown needles, m. p. 172-173 °C) along with 1% of the Diels-Alder adduct **(3)** (blue-green crystals, m. p. 100-101 °C)**. Compound **(5)** presumably results from the primary adduct **(4)**, which like **(3)** can be formed from the dipolar intermediate **(2)** produced on attack by the electron-poor alkyne at the position of highest electron density in **(1)**, or by synchronous cycloaddition. 3,5-Dimethyl[**]** and 3,5,8,10-tetramethylaceheptylene **(6)**** also react with the acetylenic ester in a manner analogous to **(I)**, although formation of the Diels-Alder adducts of type **(3)** predominates. The

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**This work was supported by the Deutsche Forschungsgemeinschaft
and the Fonds der Chemischen Industrie.