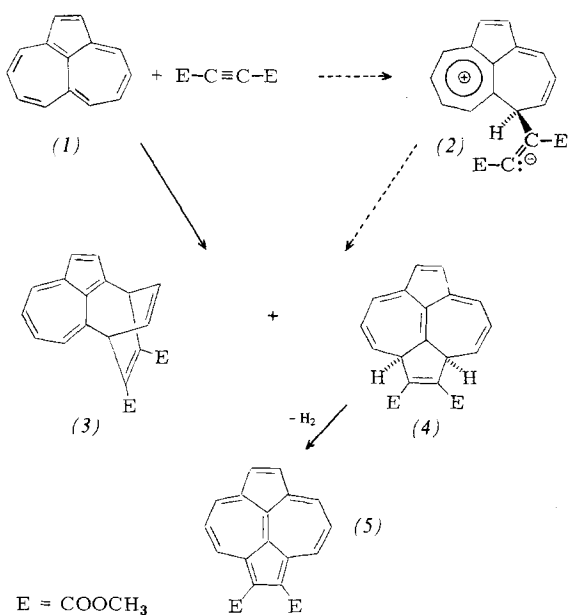


- [2] K. Hafner, K.-P. Meinhardt, and W. Richarz, *Angew. Chem.* 86, 235 (1974); *Angew. Chem. Int. Ed. Engl.* 13, 204 (1974).
- [3] Structures of all compounds described were confirmed by elemental analysis, UV, NMR, and MS spectra.
- [4] K. Hafner and R. Fleischer, *Angew. Chem.* 82, 217 (1970); *Angew. Chem. Int. Ed. Engl.* 9, 247 (1970); K. Hafner, *Pure Appl. Chem.* 28, 153 (1971).
- [5] H. Diehl, Dissertation, Technische Hochschule Darmstadt, 1976.
- [6] (9) and (10) can be obtained in 27 and 12% yield together with 1-aceptylenecarbaldehyde (55%) by direct Vilsmeier formylation of aceptylene with dimethylformamide/phosphoryl chloride.
- [7] The compound (13), R = H, arising from (1), R = H, rapidly undergoes further cycloaddition with the ynamine to form 3-diethylamino-4,10-dimethylbenzo[*a*]cyclopent[*cd*]azulene (green leaflets, m. p. 97 °C); cf. K. Hafner, H. Diehl, and W. Richarz, *Angew. Chem.* 88, 125 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 108 (1976).

## Cycloadditions of Aceptylene— A Facile Synthesis of Dicyclopenta[*ef,kl*]heptalenes<sup>[\*\*]</sup>

By Klaus Hafner, Herbert Diehl, and Winfried Richarz<sup>[\*]</sup>

Similarly to pentalene, azulene<sup>[1]</sup>, and cyclopent[*cd*]azulene<sup>[2]</sup>, the readily accessible aceptylene (1)<sup>[3]</sup> undergoes



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

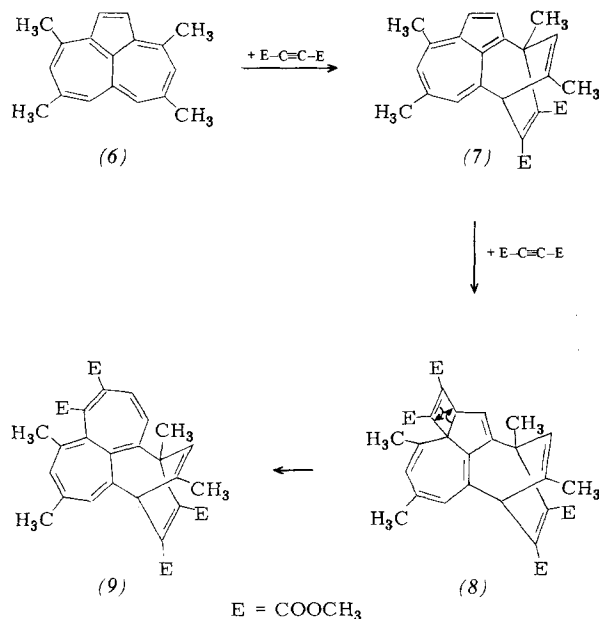
Heating of (1) with dimethyl acetylenedicarboxylate in the molar ratio 1:1 in boiling tetralin for 1 h affords 25% of dimethyl 1,2-dicyclopenta[*ef,kl*]heptalenedicarboxylate (5) (yellowish brown needles, m. p. 172–173 °C) along with 1% of the Diels-Alder adduct (3) (blue-green crystals, m. p. 100–101 °C)<sup>[4, 5]</sup>. 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-<sup>[4]</sup> and 3,5,8,10-tetramethylaceptylene (6)<sup>[6]</sup> also react with the acetylenic ester in a manner analogous to (1), although formation of the Diels-Alder adducts of type (3) predominates. The

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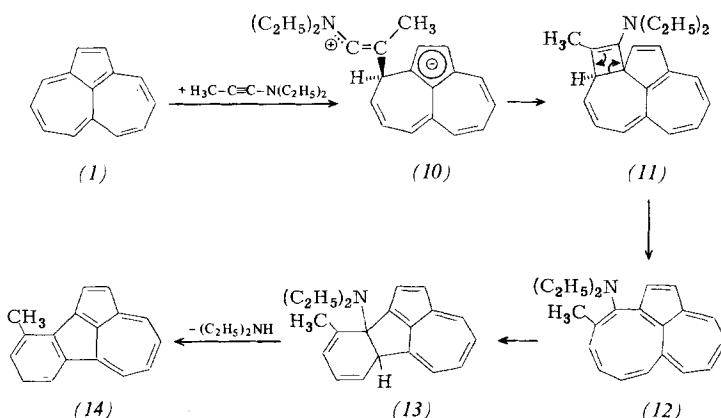
parent tetracyclic system of (5) was hitherto accessible in only very low overall yield by multistep syntheses<sup>[7]</sup>. The spectroscopic properties of (5) resemble those of the unsubstituted tetracyclic hydrocarbon as far as comparison is at all justified.

Like azulene, the azulenoid Diels-Alder adducts of type (3) undergo a dipolar cycloaddition across positions 1,8a of the azulenoid partial structure on treatment with dimethyl acetylenedicarboxylate. Thus 3,5,8,10-tetramethylaceptylene (6)<sup>[6]</sup>, an electron-rich derivative of (1), reacts with

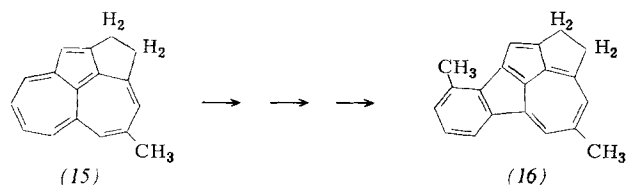


the acetylenic ester in the molar ratio 1:2 to give 3% of the 3,5,8,10-tetramethyl derivative of (5) (light brown needles, m. p. 222 °C), 26% of the Diels-Alder adduct (7) (blue green crystals, m. p. 142–143 °C), and 12% of the thermally stable diene adduct of the unknown cyclohepta[*ef*]heptalene (9) (orange needles, m. p. 205–206 °C; UV spectrum (dioxane):  $\lambda_{\text{max}} = 280$  (log  $\epsilon = 4.16$ ), 292 (4.17), 347 (3.53), 426 (3.15)). The primary formation of the 1:1 adduct (7) is followed by a second cycloaddition to give the adduct (8), valence isomerization of which, *via* cyclobutene ring opening, yields (9).

Compound (1) and its derivatives also react with ynamines in unexpectedly high yields *via* cycloaddition; however, the electron-rich alkyne initially attacks the position of lowest electron density. Reaction of (1) with *N,N*-diethyl-1-propynylamine leads presumably *via* the dipolar intermediate (10)



and the cycloadduct (11) to the thermally unstable cyclonona[*cd*]azulene derivative (12) resulting in cyclobutene ring opening; renewed valence isomerization of (12) to (13) and subsequent elimination of diethylamine affords a 75% yield of the hitherto inaccessible 10-methylbenzo[*a*]cyclopent[*cd*]azulene (14) (yellow-brown platelets, m. p. 136—



137°C)<sup>[8]</sup>. In analogous manner, the tetracyclic hydrocarbon (15) can be transformed in 21% yield into 4,9-dimethyl-1,2-dihydrobenzo[1,2]dicyclopent[*cd,ij*]azulene (16) (bronze colored needles, m. p. 144°C).

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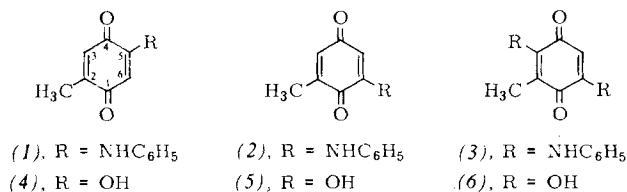
(1), 209-42-7; (3), 58150-65-5; (4), 58150-66-6; (5), 58150-67-7; (5), 3,5,8,10-tetramethyl derivative, 58150-68-8; (6), 17597-70-5; (7), 58150-69-9; (8), 58150-70-2; (9), 58150-71-3; (11), 58150-72-4; (12), 58150-73-5; (13), 58150-74-6; (14), 58150-75-7; (15), 1143-34-6; (16), 58150-76-8; dimethyl acetylenedicarboxylate, 762-42-5; *N,N*-diethyl-1-propynylamine, 4079-68-9

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[2] H. Diehl and K. Hafner, *Angew. Chem.* 88, 124 (1976); *Angew. Chem. Int. Ed. Engl.* 15, 107 (1976).  
[3] K. Hafner, *Pure Appl. Chem.* 28, 153 (1971).  
[4] (1) and its alkyl derivatives also undergo Diels-Alder reaction with maleic anhydride and tetracyanoethylene; K. Hafner and J. Schneider, *Justus Liebigs Ann. Chem.* 624, 37 (1959); K. Hafner and G. Schneider, *ibid.* 672, 194 (1964).  
[5] Correct elemental analyses, UV, NMR, and MS spectra were obtained for all compounds described.  
[6] Cf. [3] and K. Hafner, G. Hafner-Schneider, and F. Bauer, *Angew. Chem.* 80, 801 (1968); *Angew. Chem. Int. Ed. Engl.* 7, 808 (1968).  
[7] A. G. Anderson, Jr., A. F. Montana, A. A. MacDonald, and G. M. Masada, *J. Org. Chem.* 38, 1445 (1973); Ch. Jutz and E. Schweiger, *Synthesis* 1974, 193.  
[8] 3,5-Dimethyl- [4] and 3,5,8,10-tetramethylaceheptylene (6) [6] react with *N,N*-diethyl-1-propynylamine to give 68% of 3,5-dimethyl- and 92% of the 3,5,7,9-tetramethyl derivative, respectively, of (14).

## Oxidative Amination of Toluhydroquinone<sup>[\*\*]</sup>

By Suresh C. Srivastava and Ulfert Hornemann<sup>[\*]</sup>

Schäfer and Aguado<sup>[1]</sup> have reported that the interaction of a variety of hydroquinones with arylamines and sodium iodate constitutes a facile route for the preparation of bis(aryl-amino)-1,4-benzoquinones including (3), for which they gave



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a decomposition point of 147°C but no data to prove its structure. During our attempts to prepare 3,6-dianilintoluquinone (3) by this route using 10 mmol of toluhydroquinone, 20 mmol of aniline (each dissolved in 75 ml of methanol) and 30 mmol of sodium iodate (dissolved in 75 ml of water) and stirring the mixture for 24 h at room temperature, we observed that the predominant reaction product is 5-anilintoluquinone (1) (50% yield), that (3) is obtained in only 26% yield, and that the novel 6-anilintoluquinone (2) is formed in 10% yield.

(1) is also the predominant or a major reaction product when the relative amounts of the reactants are varied. With 10 instead of 20 mmol of aniline the yields of (1), (2) and (3) are 70%, 15% and 10%, respectively, while when 30 mmol instead of 10 mmol of toluhydroquinone is used the yields of (1) and (2) are 40% and 50%, respectively, and no (3) can be detected. In contrast to these observations, but presumably in accord with results obtained by Zincke<sup>[2]</sup>, it was found that a reaction mixture containing 30 mmol toluquinone and 20 mmol aniline in ethanol yielded (1) and (3) in 60% and 30% yield, respectively, and no detectable quantity of (2).

The composition of the reaction mixtures in most cases is 50–70% of (1) versus 30–50% of (2) plus (3). This may be explained as follows: Assuming that it is the sole function of the iodate to generate toluquinone, the product ratio reflects the difference in the reactivity of position 5 versus 6 of toluquinone towards attack by the nucleophilic aniline. Moreover, once any (2) has formed it can give rise to (3) and the extent of this conversion is dependent on the amount of aniline and the amount of oxidizing agent present in the reaction mixture. This explanation holds for most of the reaction mixtures except for that in which toluhydroquinone and sodium iodate were used in excess of aniline. The observed increase in the amount of (2) formed in this case is reproducible but is not readily explained. We suggest that partial formation of a quinhydrone, which would be expected to have the methyl groups oriented in a "para" arrangement, may lead to increased accessibility of the 6 position.

Table 1. Physical data for compounds (1) to (6). All compounds gave the molecular ion in the mass spectrum.

Cpd.	M. p. [°C] (dec.)	<sup>1</sup> H-NMR (δ values, in CDCl <sub>3</sub> )
(1)	150–151	2.05 (d, 3H, <i>J</i> <sub>23</sub> = 1.5 Hz), 6.13 (s, 1H), 6.52 (br., 1H), 7.24 (br., 5H)
(2)	155–156	2.12 (d, 3H, <i>J</i> <sub>23</sub> = 2.0 Hz), 6.18 (d, 1H, <i>J</i> <sub>35</sub> = 2.5 Hz), 6.58 (m, 1H), 7.32 (br., 5H)
(3)	240–242	1.59 (s, 3H), 6.03 (s, 1H), 7.30 (br., 10H)
(4)	127–141	2.03 (d, 3H, <i>J</i> <sub>23</sub> = 1.5 Hz), 6.05 (s, 1H), 6.60 (br., 1H)
(5)	110–120 [a]	2.10 (d, 3H, <i>J</i> <sub>23</sub> = 1.5 Hz), 6.20 (d, 1H, <i>J</i> <sub>35</sub> = 2.0 Hz), 6.60 (m, 1H)
(6)	166–171 [b]	1.97 (s, 3H), 7.24 (s, 1H)

[a] M. p. 117–127°C (dec.) [5]; [b] M. p. 173–175°C [6].

3,6-Dianilintoluquinone (3) (Table 1) precipitated from the reaction mixture as a yellow brown powder and was recrystallized from chloroform; the compound is presumably identical with the dianilintoluquinone (m. p. 232–233°C) prepared by Zincke<sup>[2]</sup>. The filtrate obtained after removal of (3) was evaporated to dryness, the residue extracted with methanol and the extract concentrated to yield (1) (Table 1) as red crystals; this material is presumably identical with the reaction product obtained by Schäfer and Aguado<sup>[1]</sup> and with Zincke's monoanilintoluquinone, (m. p. 144–145°C). (2) (Table 1) was obtained as red crystals after chromatography of the mother liquor on a silica gel column which was