

## Dibenz[*a,j*]anthracene via Photo-cyclodehydrogenation of 9,10-Dihydro-2-styrylphenanthrene

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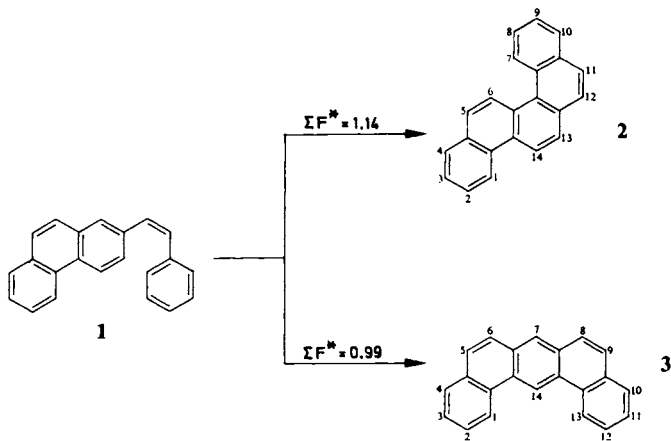
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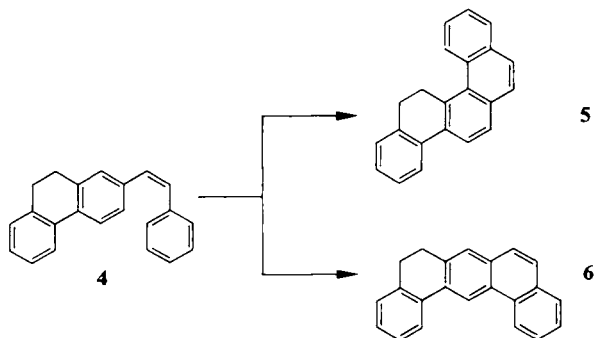
### Dibenz[*a,j*]anthracen durch Photocyclodehydrierung von 9,10-Dihydro-2-styrylphenanthren

Während aus 2-Styrylphenanthren (1) durch Photocyclodehydrierung Benzo[*c*]chrysen (2) entsteht, läßt sich unter Ausnutzung der „ $\Sigma F^*$ -Regel“<sup>5)</sup> aus 9,10-Dihydro-2-styrylphenanthren (4) durch Photocyclodehydrierung zu 6 und anschließende Dehydrierung Dibenz[*a,j*]anthracen (3) erhalten.

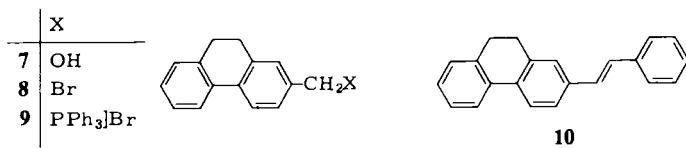
In connection with the synthesis of kekulene<sup>1)</sup> we were looking for an alternative synthetic route to dibenz[*a,j*]anthracenes. Considering the wide application which photo-cyclodehydrogenation reactions of 1,2-diarylethenes found for the synthesis of polycyclic aromatic systems<sup>2)</sup>, a photochemical formation of the dibenz[*a,j*]anthracene skeleton was of special interest. Photo-cyclodehydrogenation of 1,3-distyrylbenzene<sup>3)</sup> as well as of 2-styrylphenanthrene (1)<sup>4)</sup>, however, led to benzo[*c*]chrysene (2) almost exclusively besides only trace amounts of dibenz[*a,j*]anthracene (3). This result is in accordance with the rule that in the case of competing cyclisations the product formed predominantly is the one for which the sum of free valence indices in the excited state  $\Sigma F^*$  of the two atoms involved in the cyclisation is highest<sup>5)</sup>.



Starting from 9,10-dihydro-2-styrylphenanthrene (4), however, photoconversion should result in the formation of 5,6-dihydrobenzo[*c*]chrysene (5) and 5,6-dihydrodibenz[*a,j*]anthracene (6) in about equal amounts since for both cyclisations in first approximation the same  $\Sigma F^*$  value (1.007) was calculated<sup>6)</sup>.



For the preparation of **4** (and its *trans*-isomer **10**, respectively) 2-acetyl-9,10-dihydrophenanthrene<sup>7)</sup> was converted by an Ortoleva-King reaction<sup>8)</sup> into 9,10-dihydro-2-phenanthrenecarboxylic acid which by lithium aluminum hydride reduction yielded **7**. From **7** via the bromomethyl compound **8** 9,10-dihydro-2-[(triphenylphosphonio)methyl]phenanthrene bromide (**9**) was obtained which by Wittig reaction with benzaldehyde gave a mixture of *cis-trans* isomers **4** and **10** (ratio approx. 55:45).



Irradiation of the **4/10**-mixture as well as of isolated **10** in the presence of iodine (in benzene, Hg-high-pressure lamp) resulted in a mixture of **5** and **6** from which by dehydrogenation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) a mixture of **2** and **3** was obtained (yield 67%, referred to **4/10**). The **2/3**-ratio was determined by integrating characteristic signals in the down-field part of the aromatic range [ $\delta = 8.96-9.04$  (m, 2H), 8.74 ('d',  $J = 8.6$  Hz, 2H), assigned to 6,7-H and 1,14-H, resp., of **2**;  $\delta = 9.93$  (s, 1H), 8.24 (s, 1H), 8.92 (d,  $J = 8.1$  Hz, 2H), assigned to 14-H, 7-H and 1,13-H, resp., of **3**; 360 MHz, CDCl<sub>3</sub>]. From three different photoconversions with subsequent dehydrogenations a **2/3**-ratio of approximately 10:6 was derived. This ratio was confirmed by HPLC by which a separation of **2** and **3** was possible. Thus, by using  $\Sigma F^*$  values as guiding principle the ratio of cyclisation products was in fact shifted into the direction wanted as compared to the photo-cyclodehydrogenation of **1**<sup>9)</sup>.

## Experimental Part

**9,10-Dihydro-2-phenanthrenecarboxylic Acid:** A solution of 42.5 g (0.19 mol) of 2-acetyl-9,10-dihydrophenanthrene in 100 ml of pyridine was added to a solution of 48.5 g (0.19 mol) of iodine in 200 ml of pyridine, and the mixture was heated 1.5 h under reflux. 1-[2-(9,10-Dihydro-2-phenanthryl)-2-oxoethyl]pyridinium iodide, precipitated on standing 12 h at 20°C, was filtered off and washed with acetone: 75.0 g (85%), after recrystallisation from water yellow needles, mp 232°C (dec.).

C<sub>21</sub>H<sub>18</sub>INO (427.3) Calcd. C 59.03 H 4.25 I 29.70 N 3.28  
 Found C 59.45 H 4.31 I 29.59 N 3.32

The suspension of 75.0 g (0.175 mol) of the pyridinium salt in 2.5 l of water and 900 ml of ethanol, after addition of 150 ml of a 40% sodium hydroxide solution, was heated under reflux

for 2 h. The solution was cooled in an ice-bath and acidified with 250 ml of concentrated hydrochloric acid. The precipitate was isolated by filtration, washed with water and crystallised from ethanol: 26 g (66%), colourless needles, mp 211–212°C (lit.<sup>10</sup> 211–213°C).

*9,10-Dihydro-2-(hydroxymethyl)phenanthrene* (**7**): 11.2 g (50 mmol) of 9,10-dihydro-2-phenanthrenecarboxylic acid was added via Soxhlet extraction within 24 h to a refluxing solution of 1.57 g (41 mmol) of lithium aluminum hydride in 500 ml of ether. Working up in the usual way resulted in an oil which crystallised upon addition of toluene and was recrystallised from ligroin (40–80°C)/ether (2:1): 8.6 g (82%) of **7**, colourless needles, mp 78°C (lit.<sup>10</sup> 77–78°C).

*2-(Bromomethyl)-9,10-dihydrophenanthrene* (**8**): 2.10 g (10 mmol) of **7** and 2.297 g (15 mmol) of bromotrimethylsilane in 20 ml of chloroform were stirred under nitrogen for 1 h at 20°C. After 50 ml of chloroform had been added the solution was washed with concentrated sodium hydrogensulfite solution and with water, and was dried over sodium sulfate. The solid residue obtained by evaporation in vacuo was recrystallised from ligroin (40–60°C)/ether (4:1): 2.5 g (92%) of **8**, colourless plates, mp 67–68°C.

$C_{15}H_{13}Br$  (273.2) Calcd. C 65.95 H 4.80 Br 29.25 Found C 66.12 H 4.81 Br 29.17

*9,10-Dihydro-2-[(triphenylphosphonio)methyl]phenanthrene Bromide* (**9**): The mixture of 2.0 g (7.33 mmol) of **8** and 2.2 g (8.39 mmol) of triphenylphosphane in 50 ml of toluene was heated under reflux for 15 h. The precipitate obtained on cooling was collected by filtration, washed with toluene and ether, and dried in vacuo at 100°C: 3.77 g (96%) of **9**, mp 249°C (dec.).

$C_{33}H_{28}BrP$  (535.5) Calcd. C 74.02 H 5.27 Br 14.92 Found C 73.91 H 5.16 Br 14.92

*9,10-Dihydro-2-styrylphenanthrene* (**4/10**): 455 mg (0.85 mmol) of **9** was added under nitrogen to 54 mg (1 mmol) of sodium methoxide in 20 ml of methanol. To this ylide solution 110 mg (1.04 mmol) of benzaldehyde was added slowly. After stirring 1 h at 20°C 20 ml of water was added, and the mixture was extracted with ligroin (40–80°C). The combined extracts were washed with water, dried over sodium sulfate and evaporated in vacuo. Chromatography on silica from tetrachloromethane yielded 230 mg (96%) of a mixture of **4** and **10** (according to <sup>1</sup>H NMR about 55:45) from which by crystallisation from ethanol 90 mg (38%) of pure **10** was obtained: colourless plates, mp 135°C. – <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ = 2.88 (s, 4H), 7.13 (s, 2H), 7.22–7.94 (m, 12H).

$C_{22}H_{18}$  (282.4) Calcd. C 93.57 H 6.42 Found C 93.60 H 6.53

From the **4/10**-mixture **4** was separated by HPLC (LiChrosorb RP 18, Methanol/H<sub>2</sub>O 10:1) as an oil with higher *R<sub>F</sub>* than **10** [<sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>): δ = 2.77 (s, 4H), 6.59 (s, 2H), 7.0–7.85 (m, 12H)].

*Photo-cyclodehydrogenation of 4/10 to 5/6 and Subsequent Dehydrogenation to 2/3*: 500 mg (1.77 mmol) of **10** dissolved in 500 ml of benzene was irradiated in a pyrex-vessel in the presence of iodine for 7 h with a 500 W mercury high-pressure lamp. The oil obtained by evaporation in vacuo was chromatographed from tetrachloromethane on silica: 360 mg (73%) of a colourless solid shown by <sup>1</sup>H NMR to be a mixture of **5** and **6**.

200 mg (0.71 mmol) of this mixture and 200 mg (0.88 mmol) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in 20 ml of benzene were heated under reflux for 14 h under nitrogen. Filtration from chloroform over basic alumina followed by chromatography on silica from tetrachloromethane yielded 185 mg (93%) of a crystalline product shown by <sup>1</sup>H NMR (see above) to be a mixture of **2** and **3** in the ratio 10:6. Three different runs starting either from pure **10** or from the **4/10**-mixture obtained in the Wittig reaction led to the same 2/3-ratio. **2** and **3** were separated by HPLC (column: Spherisorb 10 Alumina, 250 × 4.6 mm; mobile phase: *n*-hexane; pressure:

25 bar; flow rate: 0.5 ml/min; UV detection at 254 nm); **2** (shorter retention time) and **3** were identified with authentic samples (mp,  $^1\text{H}$  NMR)<sup>11</sup>.

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- <sup>8</sup>) Cf. F. Kröhnke, *Angew. Chem.* **75**, 181 (1963); *Angew. Chem., Int. Ed. Engl.* **2**, 225 (1963).
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