

**HELICAL PHENANTHRENES, PART 5. SYNTHESIS OF PENTAHELICENE-7,8-DIONE *via* INTRAMOLECULAR BENZOIN CONDENSATION<sup>+</sup>**Anja MODLER-SPREITZER, Rainer FRITSCH and Albrecht MANNSCHRECK<sup>1,\*</sup>*Institut für Organische Chemie, Universität Regensburg, D-93040 Regensburg, Germany;**e-mail: <sup>1</sup> albrecht.mannschreck@chemie.uni-regensburg.de*

Received February 16, 2000

Accepted March 21, 2000

*Dedicated to Professor Otakar Červinka on the occasion of his 75th birthday.*

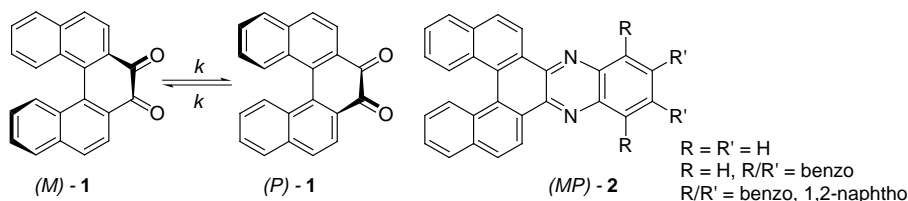
The intramolecular benzoin condensation of [1,1'-binaphthyl]-2,2'-dicarbaldehyde (**5**), followed by oxidation with air, provides a new synthesis of (*MP*)-pentahelicene-7,8-dione (**1**). With reference to the original preparation of this quinone *via* acyloin condensation, its present yield (73% for the ring-closing step) is considerably increased.

**Key words:** Benzoin condensation; Helicenediones; Pentahelicene-7,8-dione; Helicenes; Quinones; Binaphthyls; Helicity.

Phenanthrene-9,10-quinones can be rendered non-planar by substitution. If the steric hindrance is sufficiently severe, the enantiomers, *e.g.* (*M*)- and (*P*)-**1**, are stable at room temperature<sup>2</sup>. Barriers to helix inversion can be determined at temperatures above ambient and compared with the barriers of helicene hydrocarbons<sup>2</sup>. The quinone functionality has the advantage relative to the hydrocarbons that derivatives, *e.g.*, phenazines<sup>3</sup> (*MP*)-**2**, can be prepared which might be included into the above comparisons. For such a project, at least one non-planar quinone should be accessible in satisfactory yield for the subsequent synthesis of racemic derivatives, separation of their stereoisomers and measurement of the barriers to thermal stereoisomerizations. (*MP*)-Pentahelicene-7,8-dione (**1**) would be a good candidate because of its chromophore and because its *C*<sub>2</sub> symmetry avoids further unwanted isomerism. However, the access to **1** requires a multistep synthesis<sup>2</sup>, the last steps being an Ullmann coupling with 25% and an acyloin condensation with 47% yield. Therefore, the present work aims at a

+ Part 4 see ref.<sup>1</sup>

better preparation of **1**, mainly for the purpose of the study of its derivatives with respect to their stereoisomerizations.



4,5-Disubstituted phenanthrene hydrocarbons have been oxidized<sup>1,2</sup> in one or two steps yielding 30% or less of the corresponding 9,10-quinones. Oxidation<sup>4</sup> of hexahelicene with  $\text{CrO}_3$  resulted in 37% of one of its ortho-quinones. No oxidation of pentahelicene to possible quinones has been published, probably because, contrary to hexahelicene, difficulties<sup>5</sup> have been encountered in the preparation of pentahelicene *via* the usual route, the photocyclodehydrogenation of stilbenes.

In addition, the intramolecular acyloin condensation of sterically hindered dimethyl biphenyl-2,2'-dicarboxylates and the subsequent oxidation with air served for the preparation of the corresponding phenanthrene-9,10-quinones<sup>1,2</sup> in yields from 30 to 75%. Similarly, 47% of the desired pentahelicenequinone **1** was obtained<sup>2</sup> from dimethyl [1,1'-binaphthyl]-2,2'-carboxylate. In all cases, however, access to the dimethyl carboxylates was by multistep syntheses.

The intramolecular formation of benzoin (benzoin condensation) from biphenyl-2,2'-dicarbaldehydes in the presence of cyanide anion may result in phenanthrene-9,10-quinones after oxidation with air. This was described<sup>6,7</sup> for a few examples, but in only one case, a tetraalkoxy substituted quinone<sup>7</sup>, the yield (65%) was given. Therefore, we intended to synthesize pentahelicene-7,8-dione (**1**) *via* intramolecular benzoin formation.

## EXPERIMENTAL

For reactions performed under nitrogen, Schlenk techniques and nitrogen-saturated solvents were used. Column chromatography was carried out on ICN silica gel 60 F<sub>254</sub> (63–200  $\mu\text{m}$ ). Melting points were determined on a Büchi SMP-530 or on a Mikroskop-Heiztisch Reichert THERMOVAR and are not corrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra ( $\delta$ , ppm;  $J$ , Hz) were recorded on Bruker AC-250 or ARX-400 instruments at 24 and 21  $^\circ\text{C}$ , respectively. UV spectra were obtained on a Hitachi U-2000 in MeOH;  $\lambda_{\text{max}}$  in nm (log  $\epsilon$ ). IR diagrams were recorded on a Beckman Acculab 1 in KBr pellets ( $\nu$  in  $\text{cm}^{-1}$ ) and mass spectra on Finnigan MAT 112S/SS200 or MAT 95 spectrometers.

**(MP)-2,2-Dimethyl-1,1'-binaphthyl (3)**

Synthesized from 1-bromo-2-methylnaphthalene according to ref.<sup>8</sup>

**(MP)-2,2'-Bis(dibromomethyl)-1,1'-binaphthyl (4)**

Synthesis performed in a way analogous to ref.<sup>9</sup> with **3** (29.9 g, 106 mmol), NBS (102.6 g, 576 mmol) and dibenzoylperoxide (5 g) in dry CCl<sub>4</sub> (1 l). Purification of crude **4** according to ref.<sup>9</sup> was not successful. Repeated washing with small portions of hot acetone yielded colourless crystals of **4** (39.8 g, 63%), m.p. 215–217 °C (ref.<sup>10</sup> 222 °C). <sup>1</sup>H NMR data are in agreement with ref.<sup>8</sup>.

**(MP)-[1,1'-Binaphthyl]-2,2'-dicarbaldehyde (5)**

Synthesized in a way similar to ref.<sup>10</sup>. Compound **4** (24 g, 0.04 mol) and dry NaOAc (320 g, 3.90 mol) in glacial HOAc (1.2 l) were refluxed for 2 days. Pouring the warm mixture into ice/water (1.2 l) resulted in a precipitate which was sucked off, dried, dissolved in ether (500 ml) and filtered from non-dissolved particles. The solvent of the filtrate was removed and crude **5** (12 g, 97%) was obtained. Purification by chromatography using petroleum ether–diethyl ether–acetone, 4 : 2 : 1, as an eluent yielded (*R<sub>f</sub>* 0.56) slightly yellow crystals of **5** (8.0 g, 64%), m.p. 124–126 °C (ref.<sup>10</sup> 131.5 °C). <sup>1</sup>H NMR, IR and MS data are in agreement with ref.<sup>9</sup>

**(MP)-Pentahelicene-7,8-dione (1)**

Binaphthyl **5** (3.0 g, 9.7 mmol) and NaCN (0.35 g, 7.1 mmol) were stirred in dry DMF (200 ml) at 100 °C for 16 h under nitrogen. The mixture was poured into water (1.5 l) and air was sucked through it for 8–10 h. The colour turned to milky bordeaux red. The mixture was saturated with NaCl and extracted twice with CHCl<sub>3</sub> (approximately 500 ml). The organic layers were collected, dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo*. The dark red residue was purified by chromatography in CH<sub>2</sub>Cl<sub>2</sub> (*R<sub>f</sub>* 0.56), yielding dark red crystals of **1** (2.18 g, 73%), m.p. 235–237 °C (ref.<sup>2</sup> 222–226 °C). For <sup>1</sup>H and <sup>13</sup>C NMR see Table I. UV: 222 (4.87), 239 (4.59), 268 (4.40), 277 (4.37), 307 (4.17), 390 (3.61). IR: 3 050, 1 690, 1 670, 1 630, 1 610, 1 580, 1 420, 1 285.

**(MP)-7,8-Dimethoxypentahelicene (6)**

A general method of ref.<sup>11</sup> was used. Quinone **1** (0.30 g, 1.0 mmol), sodium dithionite (0.40 g, 2.0 mmol) and Adogen 464 (0.34 g, 0.80 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) and water (20 ml) were stirred for 5 min at room temperature under nitrogen. The red colour of the quinone disappeared immediately. NaOH (0.33 g, 8.0 mmol) was added and the mixture was stirred again for 10 min. The solution turned dark red, due to the formation of the dianion of 7,8-dihydroxypentahelicene. After adding MeI (1.8 ml, 29 mmol), the flask was closed in order to prevent the escape of MeI during stirring for another 12 h. The aqueous phase was washed with some CH<sub>2</sub>Cl<sub>2</sub>, the organic one with water. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated, yielding a yellow oil which was purified by chromatography in CH<sub>2</sub>Cl<sub>2</sub>. Slightly yellow solid of **6** (0.27 g, 80%), m.p. 112–114 °C. For C<sub>24</sub>H<sub>18</sub>O<sub>2</sub> (338.4) calculated: 85.18% C, 5.36% H; found: 84.66% C, 5.52% H. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>, 400.1 MHz): 4.14 s, 6 H (OCH<sub>3</sub>); 7.29 ddd, 2 H, <sup>3</sup>*J* = 8.5, <sup>3</sup>*J* = 6.9, <sup>4</sup>*J* = 1.4

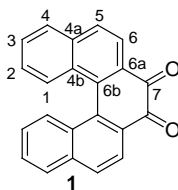
(H-3); 7.55 ddd, 2 H,  $^3J = 8.1$ ,  $^3J = 6.9$ ,  $^4J = 1.1$  (H-2); 8.05 dd, 2 H,  $^3J = 8.1$ ,  $^4J = 1.4$  (H-1); 8.06 AB, 2 H,  $^3J = 8.8$ , br (H-5); 8.30 AB, 2 H,  $^3J = 8.8$  (H-6); 8.34 d, 2 H,  $^3J = 8.5$ , br (H-4). Alternative assignment by exchanging H-1 and H-4 as well as H-2 and H-3 is possible. UV: 206 (4.71), 233 (4.85), 264 (4.48), 270 (4.48), 307 (4.56), 332 (4.19). IR: 3 060, 2 940, 2 860, 1 610, 1 600, 1 580, 1 385, 1 265. EI MS (70 eV),  $m/z$  (%): 338 ( $M^+$ , 100), 323 ( $M^+ - CH_3$ , 28), 307 ( $M^+ - OCH_3$ , 55).

## RESULTS AND DISCUSSION

We prepared [1,1'-binaphthyl]-2,2'-dicarbaldehyde (**5**, Scheme 1), by essentially known<sup>8-10</sup> procedures, in order to synthesize quinone **1** by intramolecular benzoin formation. By this route, **1** was obtained in a yield of 73% for the ring-closing step, which means an overall yield of 21% referring to four steps, starting from commercial 1-bromo-2-methylnaphthalene, required for the preparation<sup>8</sup> of **3**. Besides the  $^1H$  and  $^{13}C$  NMR spectra of **1** with full assignments, the transformation<sup>11</sup> (Scheme 1) into the corresponding hydroquinone dimethyl ether **6** *via* phase-transfer catalysis served to confirm the structure of **1**.

With respect to this new result, (*MP*)-**1** can be considered the best accessible chiral phenanthrene-9,10-quinone. Hence, **1** will be preferred to other

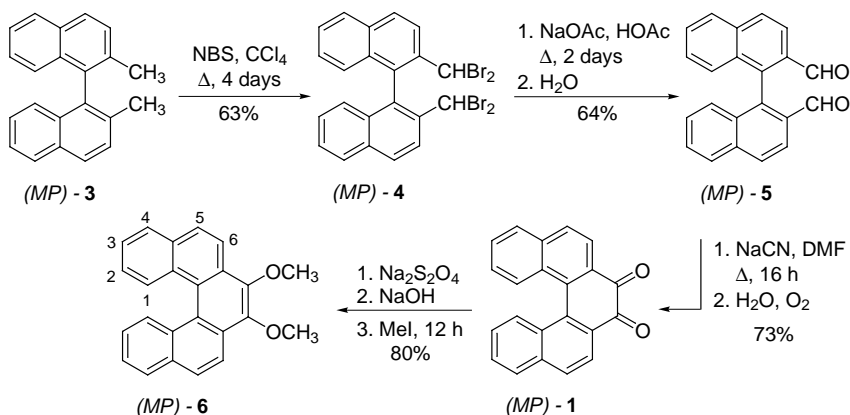
TABLE I  
 $^1H$  NMR (250.1 MHz) and  $^{13}C$  NMR (100.6 MHz) spectra of **1** in  $CDCl_3^a$



Position	1	2	3	4	4a	4b	5	6	6a	6b	7
$\delta(^1H)$	7.42	7.32	7.64	7.94	–	–	7.99	8.15	–	–	–
Multipl.	d,br	ddd	ddd	d,br	–	–	AB	AB	–	–	–
$^3J$ , Hz	8.7	8.7	8.3	8.3	–	–	8.4	8.4	–	–	–
$^3J$ , Hz		6.6	6.6		–	–	–	–	–	–	–
$\delta(^{13}C)$	128.7	126.1	129.2	128.5	137.3	130.0	130.0	123.2	127.9	137.4	183.0

<sup>a</sup> Assigned by a  $^1H/^{13}C$  correlation and a  $^{13}C/^{13}C$  INADEQUATE spectrum. The intensities of all six  $^1H$  absorptions are equal.  $^4J_{13} = ^4J_{24} = 1.3$  Hz

quinones in a future project: The known<sup>3</sup> racemic phenazines (MP)-2 as well as further single- and double-helical phenazines, quinoxalines and 2,3-dihydroquinoxalines<sup>12</sup> can now be prepared more easily than by using



SCHEME 1

the acyloin condensation<sup>2</sup> for the synthesis of **1**. The barriers to the helix inversions of these nitrogen derivatives may then be compared with the known<sup>2</sup> barriers.

*Dr M. Putala (Comenius University, Bratislava) kindly verified the preparation of 1 and contributed substantially to several details of the manuscript. We are grateful to Dipl.-Chem. F. Brandl for his help concerning graphics and to Dr T. Burgemeister and Mr F. Kastner for NMR spectra and their assignment.*

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