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Diels-Alder Reaction of 3,3',4,4'-Tetrahydro-1,1'-Binaphthalene. One-Pot Synthesis of a Pentahelicenebenzoquinone

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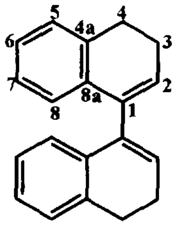
Abstract. The Diels-Alder cycloaddition of the 3,3',4,4'-tetrahydro-1,1'-binaphthalene with 1,4-benzoquinone and N-phenylmaleimide has been studied. The one-pot synthesis of the pentahelicenebenzoquinone is reported and structure analysis of the reaction products by ^{1}H- and ^{13}C-NMR spectroscopy is presented. © 1997 Elsevier Science Ltd.

Until recently, the photocyclodehydrogenation of 1,2-diarylethylenes followed by in situ oxidation (I_2, O_2, TCNE) has been the only easy route leading to helicenes[1]. This procedure, however, is problematic because it normally requires very dilute solutions to prevent photodimerization and can proceed to give isomers. In view of the increasing interest in helicenes, it is necessary to develop synthetic methods to supply helicenes with useful functionality and on a reasonable scale.

Recently Katz et al.[2] reported a synthetic approach to penta- and hexahelicenes based on the multiple Diels-Alder reactions of 1,4-divinylbenzene and 2,7-divinylnaphthalenes with 1,4-benzoquinone.

We have undertaken a broad study to develop synthetic methods for helicenes using the Diels-Alder methodology in an alternate synthetic strategy. We report here a "one-pot" synthesis of pentahelicenebenzoquinone (**5**) by Diels-Alder reaction of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (**1**) with 1,4-benzoquinone (**2**) followed by in situ aromatization. Diene **1** was prepared by coupling α-tetralone[3]; treatment of this compound with zinc in protic chlorotrimethylsilane afforded **1** in 70% yield[4]. Previously[3b] cycloaddition between diene **1** and 1,4-benzoquinone (**2**) was reported to give only one compound as reaction product, the structure of which was tentatively assigned as **3**. We reexamined this reaction and found that when **1** and **2** were subjected to the conditions described in the literature (125-150°C) a 3:2:1 mixture of compounds **3**, **4** and **5**, respectively, was obtained (50%).



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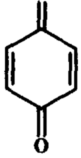

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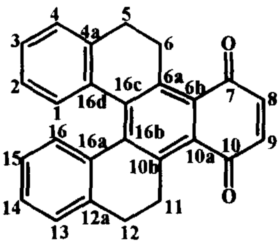

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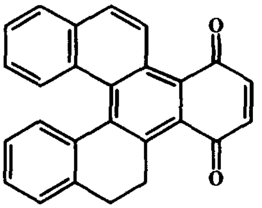

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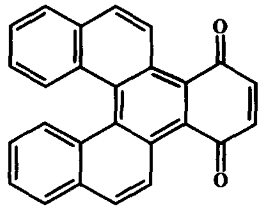

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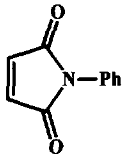

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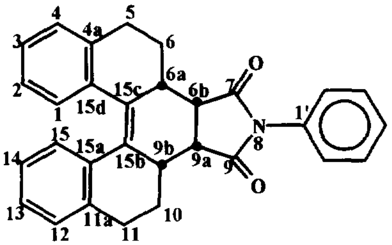

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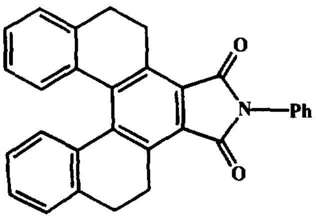

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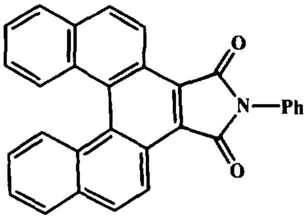

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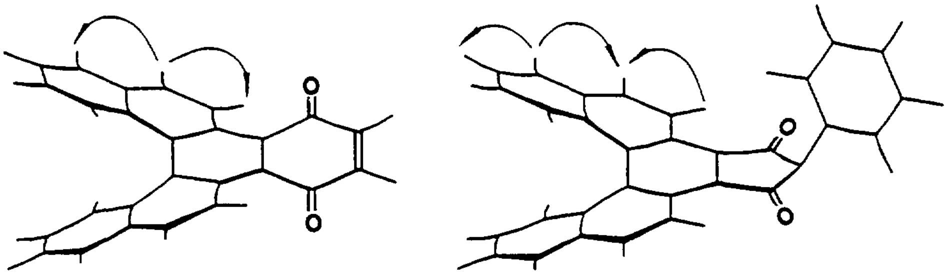
Clearly 1,4-benzoquinone acts not only as dienophile in the Diels-Alder reaction[5] but also as oxidant of the cycloadduct(s) as previously observed[2]. This reaction was then extensively studied in order to change the composition of the reaction mixture in favour of the desired compound **5**[6]. When **1** and **2** interacted at 150 °C for 2h, a 1.5:1 mixture of **4** and **5** was obtained (42 %); with a reaction time of 7 h, the ratio of **4**/**5** was 1:2.3 (35 %). When **1** and **2** interacted at 150 °C for 22 h pentahelicene (**5**) alone was obtained (25 % yield). This, therefore,represents a "one-pot" synthesis of pentahelicenebenzoquinone (**5**). While the yield is only reasonable, the procedure is noteworthy because it is simple, short and permits large quantities of product to be prepared starting from readily available and cheap compounds. Alternatively, compound **5** can be obtained by DDQ oxidation[7] of the mixture of compounds **3**-**5** in 90 % yield. The total yield of **5** in this two-step synthesis is 45 %.

The reaction of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (**1**) with N-phenylmaleimide (**6**) was also studied. When **1** and **6** were heated together at 150 °C, endo-cycloadduct **7** was obtained in 40 % yield. DDQ oxidation of **7** in triglyme at reflux temperature gave a complex mixture, from which compounds **8** and **9** were isolated in low yield (25 % and 6 %, respectively). Attempts to improve the conversion of 7 to the desired pentahelicene **9** failed. The reason why aromatization is difficult seems to be that the fully aromatized compound **9** is highly strained as a consequence of the fusion with the five membered heterocyclic ring.

In conclusion, a new approach to pentahelicenes based on the Diels-Alder reaction of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (**1**) is discussed and the one-pot synthesis of the pentahelicenebenzoquinone (**5**) is reported. Further demonstration of the utility of this synthetic strategy will be reported in due course.

The structures of the reaction products were assigned by analysis of their high-field ^1H and ^{13}C-NMR spectra. The pertinent data are reported in the Experimental Section. Proton and carbon shift assignments were based on COSY, ^1H-{^1H} NOE and HETCOR experiments; some of the quaternary carbons were assigned by 2D long-range heterocorrelated experiments (FLOCK and selective INEPT). The strongly deshielded shift of H(6) proton for compounds 4, **5** and **9** (δ = 9.05-9.24) which is the consequence of the anisotropy effect of the carbonyl function, was diagnostic for their identification. The NOE effect observed between H(4), H(5) and H(6) of pentahelicenes **5** and **9** (see figure) confirmed the structure of both compounds and defined the shift assignments of all protons. The identification of quaternary carbons of compound **5** was made by means of selective 2D INEPT experiments. Selective irradiation of H(2) and H(3) protons gave long-range correlation with C(16d) and C(4a) respectively, while in the same experiment H(5) showed connectivities with C(6a) and C(16d), and H(6) with C(4a) and C(16c).

Finally the cis-relationship between H(6a) and H(6b) protons for the cycloadduct 7 was revealed by ^1H-{^1H} NOE experiments which showed their spatial proximity and by the interproton coupling constant value ($J_{6a,6b}$ = 4.2 Hz).



5 9

Figure. Minimized energy conformations of [5]helicenes 5 and 9; the arrows indicate observed n.O.e's.

EXPERIMENTAL SECTION

All m.ps. were determined on a Buchi 510 melting point apparatus and are uncorrected. IR spectra were recorded in $CHCl_3$ solution on a Perkin Elmer 983 spectrophotometer. Mass spectra were observed on a Hewlett Packard 5970 GC-Ms instrument, calibrated with perfluorotributylamine for 70 eV operations. NMR spectra were run at room temperature on a Varian Associates VXR-400 multinuclear instrument.

3,3',4,4'-Tetrahydro-1,1'-Binaphthalene (1). To zinc dust (0.5 g) in THF (75 mL) at -50 °C were added α-tetralone (2 g, 13.7 mmol), chlorotrimethylsilane (3.8 mL, 29.9 mmol) and 37 % HCl (2 mL)[4]. The mixture was left under stirring at 20 °C for 14 h and then at 30 °C for 3 h. Then the reaction mixture was diluted with water and extracted with ether. The combined organic layers were washed with aqueous bicarbonate solution and water, dried (Na_2SO_4) and concentrated under reduced pressure. Chromatography of the residue on silica gel (hexane) provided the bisdialine **1** (1.23 g, 70 % yield); m.p. 141 °C (methanol) [Lit.[3] 141 °C]; ^1H-NMR ($CDCl_3$) δ 2.36 (dd, 2H, J = 9.0, 4.5 Hz, Hs-3), 2.86 (dd, 2H, J= 9.0, 2.0 Hz, Hs-4), 6.06 (d, 1H, J = 4.5 Hz, H-2), 6.90 (dd, 1H, J = 8.0, 1.2 Hz, H-8), 6.97 (ddd, 1H, J = 8.0, 7.7, 1.3 Hz, H-7), 7.05 (ddd, 1H, J = 7.9, 7.7, 1.2 Hz, H-6), 7.12 (dd, 1H, J = 7.9, 1.3 Hz, H-5); ^{13}C-NMR ($CDCl_3$) δ 23.27 (C-3), 28.19 (C-4), 125.13(C-8), 126.31 (C-7), 127.73 (C-6), 127.34 (C-5), 127.94 (C-2), 134.70 (C-8a), 135.79 (C-4a), 138.35 (C-1); MS, m/e (rel.intensity) 258 (M+, base), 215 (32), 202 (12), 128 (83), 115 (30), 91 (15), 51 (11).

Diels-Alder reaction of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (1) with 1,4-benzoquinone (2).

a) The diene **1** (5.2 g, 19.9 mmol) and 1,4-benzoquinone (**2**) (22 g, 0.2 mol) were heated together at 150 °C for 2 h. The excess benzoquinone was removed by steam distillation and the residue extracted by $CHCl_3$. The combined extracts were washed with water, dried (Na_2SO_4) and evaporated under reduced pressure to afford a 1.5:1 mixture of compounds **4** and **5** which was chromatographed on column. Elution with toluene gave 1.82 g (25 %) of **4** and 1.21 g (17%) of **5**.

(4): m.p 237-238°C (3:1 hexane-ethylacetate); IR 1652 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 2.81 (ddd, 1H, J = 17.8, 12.2, 8.5 Hz, H-11A)[8], 2.95-3.07 (m, 2H, Hs-12), 4.20 (ddd, 1H, J = 17.8, 4.5, 2.5 Hz, H-11B)[8], 6.85 (d, 1H, J = 10.0 Hz, H-9), 6.94 (d, 1H, J = 10.0 Hz, H-8), 6.99 (dd, 1H, J = 7.4, 7.3 Hz, H-15), 7.06 (d, 1H, J = 7.4 Hz, H-16), 7.12 (dd, 1H, J = 8.5, 7.0 Hz, H-2), 7.25 (dd, 1H, J = 7.4, 7.3 Hz, H-14), 7.39 (d, 1H, J = 7.4 Hz, H-13), 7.47 (dd, 1H, J = 7.9, 7.0 Hz, H-3), 7.79 (d, 1H, J = 7.9 Hz, H-4), 7.86 (d, 1H, J = 9.4 Hz, H-5), 8.05 (d, 1H, J = 8.5 Hz, H-1), 9.18 (d, 1H, J = 9.4 Hz, H-6); ^{13}C-NMR ($CDCl_3$) δ 27.03 (C-11), 29.02 (C-12), 123.67 (C-6), 124.72 (C-2), 126.22 (C-15), 127.24 (C-13), 127.62 (C-4), 127.96 (C-3), 128.58 (C-14), 129.04 (C-16b), 129.04 (C-16b), 129.07 (C-10d), 130.22 (C-2), 130.26 (C-16), 130.41 (C-6a), 130.52 (C-5), 132.63 (C-10c), 133.20 (C-4a), 136.27 (C-16a), 137.60 (C-12a), 138.03 (C-9), 139.00 (C-6b, C-8), 139.93 (C-10b), 142.87 (C-10a), 188.23 (C-7), 188.43 (C-10);MS, m/e (rel. intensity) 360 (M$^+$, base), 313 (33), 207 (6), 157 (28). Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47. Found: C, 86.51; H, 4.41.

(5): m.p. 246-247 °C (3:1 hexane-ethylacetate); IR 1652 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 6.97 (s, 1H, H-8), 7.21 (dd, 1H, J = 8.6, 7.0 Hz, H-2), 7.54 (dd, 1H, J = 8.1, 7.0 Hz, H-3), 7.92 (d, 1H, J = 8.1 Hz, H-4), 8.04 (d, 1H, J = 9.2 Hz, H-5), 8.13 (d, 1H, J = 8.6 Hz, H-1), 9.24 (d, 1H, J = 9.2 Hz, H-6); ^{13}C-NMR

(CDCl$_3$) δ 123.19 (C-6), 125.27 (C-2), 127.53 (C-4), 127.60 (C-8), 128.08 (C-3), 129.15 (C-6b), 130.00 (C-1), 130.06 (C-5), 130.07 (C-16d), 131.63 (C-16c), 132.74 (C-4a), 138.12 (C-8), 188.65 (C-7); MS, m/e (rel. intensity) 358 (M$^+$, 76), 281 (63), 207 (base), 150 (23), 44 (91). Anal. Calcd for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found: C, 87.34; H, 3.95.

b) When the same mixture of diene **1** and benzoquinone (**2**) was heated at 150 °C for 22 h, pentahelicenebenzoquinone (**5**) alone was obtained in 25% yield.

c) Diene **1** (2.6 g, 10.1 mmol), and 1,4-benzoquinone (**2**) (11 g, 0.1 mol) were subjected to Bergman conditions^{3b} (125-150 °C, 3 h); the reaction mixture was worked up as described above to afford a residue which was chromatographed on column (gradient elution from hexane to 9:1 hexane-ethylacetate) to obtain a purified reaction mixture (1.8 g, 50 % yield).

Careful ^{1}H-NMR analysis showed this mixture to be a 3:2:1 mixture of compounds **3**, **4** and **5**, respectively.

(3)^{3b}: ^{1}H-NMR (CDCl$_3$) δ 2.80 (m, 1H, H-6A)^8, 2.85-2.90 (m, 2H, Hs-5), 4.00 (m, 1H, H-6B)^8, 6.83 (s, 1H, H-8), 6.89 (dd, 1H, J = 7.5, 7.4 Hz, H-2), 6.98 (d, 1H, J = 7.5 Hz, H-1), 7.15 (dd, 1H, J = 7.5, 7.4 Hz, H-3), 7.29 (d, 1H, J = 7.5 Hz, H-4); ^{13}C-NMR (CDCl$_3$) δ 27.21 (C-6), 29.04 (C-5), 125.69 (C-2), 127.04 (C-4), 128.25 (C-3), 129.17 (C-16c), 130.69 (C-1), 134.11 (C-16d), 138.84 (C-8), 139.04 (C-6a), 139.55 (C-4a), 140.77 (C-6b), 187.66 (C-7).

DDQ oxidation of compounds 3-5. A solution of the mixture of compounds **3-5** (1.8 g) in benzene (54 mL) was treated with DDQ (10.8 g) and then heated at reflux temperature under nitrogen for 38 h. Then the reaction was worked up as usual to afford pentahelicene benzoquinone (**5**) in 90 % yield.

Diels-Alder cycloaddition of 3,3',4,4'-tetrahydro-1,1'-binaphthalene (1) with N-phenylmaleimide (6). The diene **1** (0.5 g, 1.9 mmol) and N-phenylmaleimide (**6**) (1.5 g, 9.2 mmol) were heated together at 150 °C for 3 h. Then the reaction mixture was worked up according to the procedure described above to give a residue which was purified by column chromatography. Gradient elution (9:1 to 7:3 hexane-ethylacetate) gave 0.32 g of pure cycloadduct 7 (0.32 g, 40 % yield): m.p. 217-218 °C (3:1 hexane-ethylacetate); IR 1707 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ 2.02 (m, 1H, J = 13.5, 8.0, 7.4, 3.5 Hz, H-6A)^8, 2.48 (m, 1H, J = 13.5, 8.3, 6.2, 3.4 Hz, H-6B)^8, 2.64 (ddd, 1H, J = 14.6, 8.0, 3.4 Hz, H-5A)^8, 2.96 (ddd, 1H, J = 14.6, 8.3, 3.5 Hz, H-5B)^8, 3.02 (ddd, 1H, J = 7.4, 6.2, 4.2 Hz, H-6a), 3.41 (dd, 1H, J = 4.2, 2.0 Hz, H-6b), 6.83 (dd, 1H, J = 7.8, 7.7 Hz, H-2), 6.98 (m, 1H, H-2'), 7.04 (dd, 1H, J = 7.7, 7.5 Hz, H-3), 7.12 (d, 1H, J = 7.5 Hz, H-4), 7.20 (d, 1H, J = 7.8 Hz, H-1), 7.28 (m, 1H, H-4'), 7.31 (m, 1H, H-3'); ^{13}C-NMR (CDCl$_3$) δ 25.27 (C-6), 29.70 (C-5), 37.96 (C-6a), 45.16 (C-6b), 125.26 (C-2), 126.42 (C-2'), 127.34 (C-3), 127.70 (C-4), 128.49(C-4'), 129.02 (C-3'), 129.75 (C-1), 133.32 (C-15c), 134.17 (C-1'), 134.20 (C-15d), 144.77 (C-4a), 176.73 (C-7); MS, m/e (rel. intensity), 431 (M$^+$, 38), 281 (23), 257(base), 207 (42), 73 (30). Anal. Calcd for $C_{30}H_{25}O_2N$: C, 83.50; H, 5.84; N, 3.25. Found: C, 83.37; H, 5.82; N, 3.27.

DDQ Oxidation of cycloadduct 7. Treatment of cycloadduct 7 (0.5 g, 1.16 mmol) with DDQ (4 g) in refluxing triglyme (12 mL) for 18 h, gave a mixture of dehydrogenated products (0.290 g). Careful chromatography of the mixture on a silica gel column on elution with toluene gave pure **8** (0.123 g, 25 %) and **9** (0.029 g, 6 %).

(8): m.p. 239-240°C (3:1 hexane-ethylacetate); IR 1712 cm^{-1}; ^{1}H-NMR (DMSO) δ 2.50-4.09 (m, 4H, Hs-5 and Hs-6), 7.03 (dd, 1H, J = 7.8, 7.6 Hz, H-2), 7.17 (d, 1H, J = 7.8 Hz, H-1), 7.29 (dd, 1H, J = 7.7, 7.6 Hz, H-3), 7.46 (d, 1H, J = 7.7 Hz, H-4), 7.50 (m, 1H, H-2'), 7.51 (m, 1H, H-4'), 7.59 (m, 1H, H-3'); ^{13}C-NMR (DMSO) δ 23.82 (C-6), 27.74 (C-5), 125.72 (C-2), 127.92 (C-4), 127.66 (C-2' and C-4'), 128.06 (C-15c), 128.50 (C-3), 128.83 (C-3'), 129.73 (C-1), 132.02 (C-1'), 133.01, 138.12, 138.39 (C-4a, C-15d, C-6b), 139.05 (C-6a), 167.17 (C-7); MS, m/e (rel. intensity) 427 (M^+, base), 276 (20), 263 (10), 154 (5), 77 (88). Anal. Calcd for $C_{30}H_{21}O_2N$: C, 84.29; H, 4.95; N, 3.28. Found: C, 84.49; H, 4.93; N, 3.27.

(9): m.p. 332-334°C (3:1 hexane-ethylacetate); IR 1712 cm^{-1}; ^{1}H-NMR (DMSO) δ 7.39 (dd, 1H, J = 8.0, 7.1 Hz, H-2), 7.49 (m, 1H, H-4'), 7.58 (m, 1H, H-2'), 7.59 (m, 1H, H-3'), 7.70 (dd, 1H, J = 8.1, 7.1 Hz,H-3), 8.16 (d, 1H, J = 8.1 Hz, H-4), 8.31 (d, 1H, J = 8.8 Hz, H-5), 8.37 (d, 1H, J = 8.0 Hz, H-1), 9.04 (d, 1H, J = 8.8 Hz, H-6); ^{13}C-NMR (DMSO) δ 120.28 (C-6), 124.98 (C-2), 125.51, 125.66 (C-6a, C-6b), 126.94 (C-4), 127.40 (C-4'), 127.76 (C-2'), 127.78 (C-3), 127.88 (C-15d), 128.28 (C-1), 128.30 (C-3'), 129.53, 130.44 (C-4a, C-15c), 129.78 (C-5), 132.43 (C-1'); MS, m/e (rel. intensity): 423 (M^+, base), 341 (10), 275 (77), 207 (47), 137 (16), 73 (31). Anal. Calcd for $C_{30}H_{17}O_2N$: C, 85.09; H, 4.05; N, 3.31. Found: C, 85.22; H, 4.05; N, 3.30.

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