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Diels-Alder reactions of arylethenes. Synthesis of some [5]phenacenes and fluorenoanthracenes.

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Abstract. A one-pot high yielding route to 3,4-dihydro-1-(2H)-anthracenone (**9**) based on high pressure Diels-Alder reaction is described. The synthesis of 3,4-dihydro-1-vinylphenanthrene (**1**) and 3,4-dihydro-1-vinylanthracene (**2**) is reported. A new synthetic two-step approach to [5]phenacenes and fluorenoanthracenes has been developed. It is based on the Diels-Alder reaction of arylethenes **1** and **2** with benzyne (**13**), 1,4-benzoquinone (**14**), 1,4-naphthoquinone (**15**) and inden-1-one (**17**) and on the aromatization of the cycloadducts. Structure analysis of the reaction products by ^{1}H and ^{13}C-NMR spectroscopy is presented.

Polycyclic aromatic compounds with condensed benzene rings have received much attention because of their interesting physical and chemical properties[1,2]. The extended aromatic structures considered to date are either linearly annelated (anthracene, naphthalene, pentacene, etc.) or have benzene rings in a phenanthrene-like fusion. The latter compounds have recently been named [n]phenacenes, where n is an integer that indicates the number of fused benzene rings, and can be viewed as graphite ribbons of varying lengths[3]. Such compounds are of theoretical and perhaps practical interest because of their electronic properties. Mallory and coworkers[3] recently reported the synthesis of some [7]phenacenes based on the photocyclodehydrogenation of diarylethenes, a well-known methodology[4] widely used to synthesize Polycyclic aromatic compounds (PACs).

As a part of a broad study[5] on the development of new synthetic methods of PACs based on the Diels-Alder reaction of arylethenes, we now report the synthesis of dienes **1** and **2** and their application to the synthesis of the [5]phenacenes **3-5** and of the fluorenoanthracenes **6-7** (Scheme 1). This synthetic route to PACs involves the cycloaddition of dihydroarylethenes that are more reactive than the corresponding arylethenes[6,7], with appropriate dienophiles followed by the aromatization of the cycloadducts.

Results and discussion

3,4-Dihydro-1-vinylphenanthrene (**1**) was conveniently prepared by adding methyl-magnesiumbromide to 3,4-dihydro-1-(2H)-phenanthrenone[8] (**8**) and subsequently

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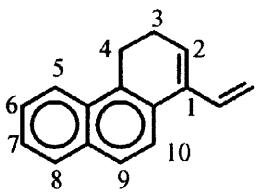
dehydrating the carbinol by treating it with phosphorus tribromide in dichloromethane and then with lithium bromide and lithium carbonate (50% overall yield). The previous procedure[9] for dehydrating, accomplished by heating a benzene solution of the alcohol in presence of quinoline-iodine, afforded diene **1** in lower yield (30%). 3,4-Dihydro-1-vinylanthracene (**2**) was analogously prepared by treating the 3,4-dihydro-1-(2H)-anthracenone (**9**) with vinylmagnesium bromide and by dehydrating the tertiary alcohol in 40% overall yield. 3,4-Dihydro-1-(2H)-anthracenone (**9**) (Scheme 2) was previously prepared[10] by treating 1,2-dihydro-4-(3H)-phenanthrenone (**10**) with polyphosphoric acid under thermodynamically controlled conditions in 25% yield. Since ketone **10** was prepared by a three-step synthesis[5c,8] in 14% yield, this route to ketone **9** is inadequate because it is too long and low yielding (overall yield 3.5%). We, therefore, turned our attention to a shorter and facile synthesis of ketone **9**. We have explored, successfully, a one-pot procedure based on the Diels-Alder cycloaddition[11] of the commercially available compounds, α,α,α',α'-tetrabromo-o-xylene (**11**) and 2-cyclohexen-1-one (**12**) (Scheme 2). Whereas no reaction occurred under thermal conditions because of the low reactivity of 2-cyclohexen-1-one[12] (**12**), under high pressure[13] (9 kbar) in DMF and in presence of NaI, anthracenone **9** was obtained directly in 32% overall yield. This one-pot procedure is clearly superior in yield and convenience to the four-step synthesis previously discussed.



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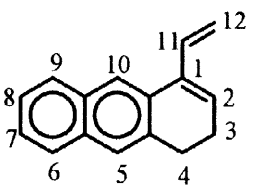

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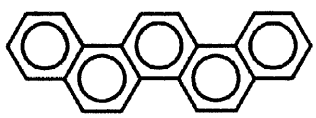

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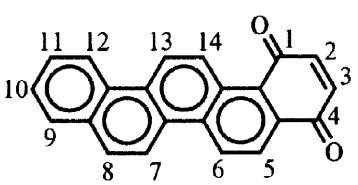

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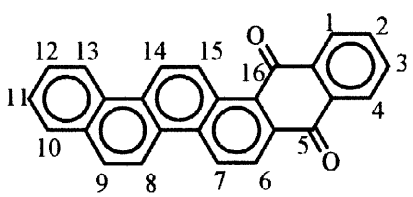

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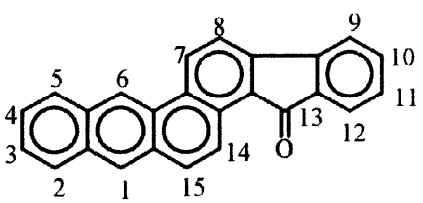

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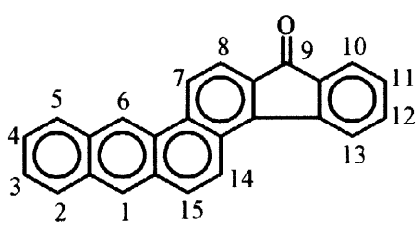

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Scheme 1

The synthesis of the [5]phenacenes **3-5** was based on the cycloaddition of the 3,4-dihydro-1-vinylphenanthrene (**1**) with benzyne (**13**), 1,4-benzoquinone (**14**) and 1,4-naphthoquinone (**15**).

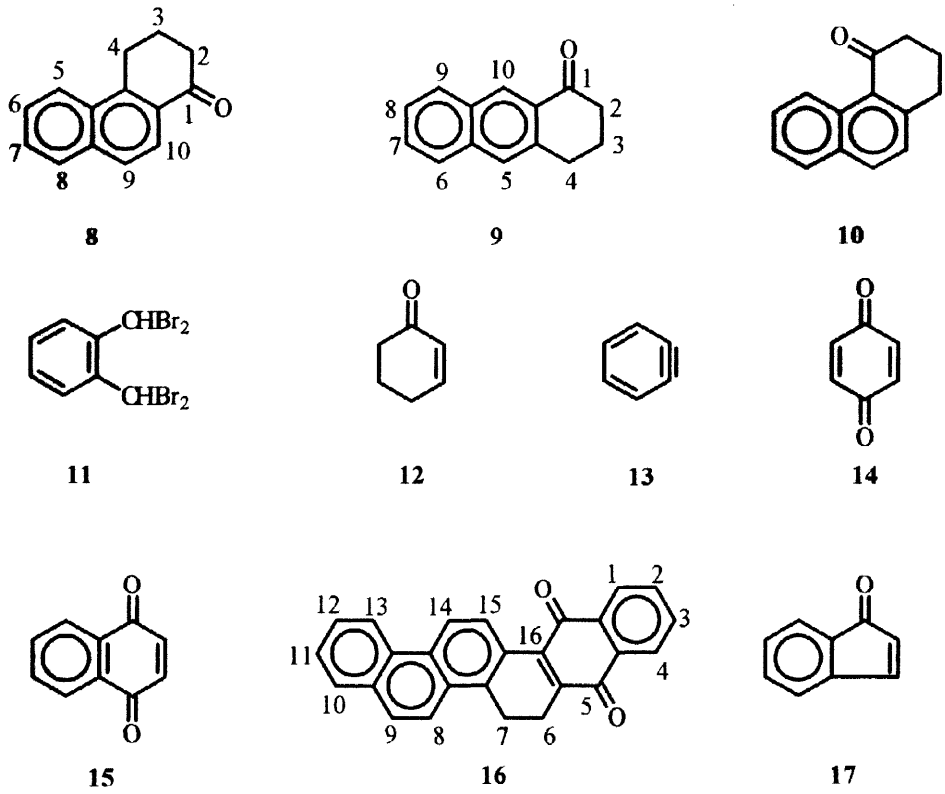
Diels-Alder reaction of diene **1** with benzyne (**13**) led to a 1:1:3 mixture of three products which was then converted to [5]phenacene (**3**) by DDQ oxidation-aromatization in 30% overall yield[14]. When a toluene solution of **1** and **14** was heated under reflux for 20 h, a mixture of the [5]phenacenequinone (**4**) and two of its hydroderivatives, as shown by GC-MS analysis, was obtained. Treatment of the mixture with DDQ afforded the desired quinone **4**, in 37% overall yield; the structure was assigned by ^{1}H-NMR spectroscopy. The NOE effect observed between H(6) and H(7), and H(12) and H(13), in addition to the characteristic shift values of protons H(6), H(7), H(13) and H(14) (see experimental), allowed an unambiguous structural assignment.

The ethylaluminumdichloride-catalyzed Diels-Alder reaction of the diene **1** with 1,4-naphthoquinone (**15**) in dichloromethane solution at 35°C led to a tetrahydroderivative of quinone **5** (GC-MS) (71%) which was then oxidized by DDQ in refluxing benzene by the usual procedure to give a product (90%) which was isolated and purified. Surprisingly, structural analysis based on ^{1}H- and ^{13}C-NMR spectroscopy showed this product to be the 6,7 dihydro-phenacenequinone (**16**) instead of the expected quinone **5**. Structural assignment of compound **16** follows mainly from ^{1}H-{H} NOE experiments: mutual dipolar contacts between H-7 and H-8 protons were observed. The aromatization by DDQ, in this case, was more difficult and therefore required more drastic conditions. Benzo[5]phenacenequinone **5** was prepared by DDQ oxidation in refluxing xylene either of the dihydroderivative **16** or directly of the tetrahydroderivative obtained in the Diels-Alder reaction (20-35%). The assignments of proton and carbon chemical shifts of this compound were performed by COSY and HETCOR experiments and by comparison with the assignments given for quinone **4**.

This new approach to the synthesis of [5]phenacenes is short, and an alternative to the photocyclodehydrogenation of 1,2-diarylethenes and can also be extended to the synthesis of phenacenes of different length by using appropriate dienes and dienophiles.

Fluorenoanthracenes represent another class of polycyclic aromatic compounds potentially of interest as new materials. The synthetic route to fluorenoanthracenes that has been explored here involves the Diels-Alder reaction of diene **2** and the subsequent aromatization of the cycloadducts.

The cycloaddition of diene **2** with 3-bromo-indan-1-one in the presence of triethylamine to generate[5b] 2-inden-1-one (**17**) *in situ*, afforded a mixture of four cycloadducts (58%) that was treated with DDQ in benzene[5] to give a 3:1 mixture of the regioisomer fluorenoanthracenes **6** and **7** (87%) which were separated and purified by column chromatography. Their structure was assigned by NMR spectroscopy. The pertinent data are reported in the Experimental Section. Proton and carbon shift assignments were based on COSY, ^{1}H-{^{1}H} NOE and HETCOR experiments. The regiochemistry of the carbonyl function of ketones **6** and **7** is based on ^{1}H-{^{1}H} NOE experiments; mutual dipolar contacts between H(8) and H(9) were observed for **6** and between H(13) and H(14) for **7**.



Scheme 2

In conclusion a synthetic approach to [5]phenacenes and fluorenoanthracenes has been described. This methodology may be used to synthesize polycyclic compounds of various length as well as their heterocyclic analogs.

Experimental section[15]

M.ps. were determined on a Buchi 510 melting point apparatus and are uncorrected. I.R. spectra were recorded on a Perkin Elmer 983 spectrophotometer. Mass spectra were observed on a Hewlett Packard 5970 GC-MS instrument (70 eV). NMR spectra were run at room temperature on a Varian Associates VXR-400 multinuclear instrument.

3,4-Dihydro-1-vinylphenanthrene (1). The reaction of vinylmagnesium bromide with phenanthrenone **8** (2g, 10.2 mmol) was accomplished according to a previous procedure[9] to afford a crude alcohol (2.02 g) which was used for the next reaction without purification.

A solution of phosphorus tribromide (0.9 ml, 9.5 mmol) in dichloromethane (10 ml) was added at -10°C dropwise and under nitrogen, to a solution of the crude alcohol (2.02 g) in dry DMF (31.4 ml). The reaction mixture was stirred at 0°C for 3 h and then allowed to reach room temperature. Lithium bromide (2.6 g) and lithium carbonate (3.3 g) were added and the resulting mixture was heated at 100°C, under stirring, for 3 h. After cooling at 0°C, the mixture was acidified with 2N hydrochloric acid and then extracted with ether. The combined extracts were

dried (Na_2SO_4) and then the solvent removed under reduced pressure. The residual oil was purified by column chromatography on silica gel eluting with hexane to give pure diene **1** (1.05 g) in 50% overall yield; m.p. 140-141°C (methanol) [Lit[9]: oil]; ^{1}H-NMR ($CDCl_3$) δ 2.41 (bt, 2H, Hs-3), 3.16 (bt, 2H, Hs-4), 5.23 (dd, 1H, J= 10.1, 2.3 Hz, H-12), 5.56 (dd, 1H, J= 17.4, 2.3 Hz, H-12), 6.28 (bs, 1H, H-2), 6.70 (dd, 1H, J= 17.4, 10.1 Hz, H-11), 7.41-7.47 (m, 2H, H-6, H-7), 7.54 (d, 1H, J= 8.0 Hz, H-10), 7.69-7.79 (m, 2H, H-8, H-9), 8.06 (d, 1H, J= 8.0 Hz, H-5); ^{13}C-NMR ($CDCl_3$) δ 22.9 (C-3), 23.1 (C-4), 115.3 (C-12), 122.9 (C-10), 123.7 (C-5), 125.1 (C-6), 125.9 (C-7, C-2), 126.0 (C-9), 128.5 (C-8), 135.9 (C-11); MS, m/e (rel. intens) 206 (M+, base), 178 (69), 165 (53), 139 (6), 115 (6), 89 (36), 76 (26), 51 (11). Anal.Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.22; H, 6.83.

3,4-Dihydro-1-(2H)-anthracenone (9). The cycloaddition between α,α,α',α'-tetrabromo-*o*-xylene (**11**) (0.935 g, 2.22 mmol) and 2-cyclohexen-1-one (**12**) (0.216 g, 2.25 mmol) in presence of NaI (2.14 g) was accomplished[11] in DMF (15 ml), at 60°C, 9 kbar for 17 h. The mixture was then diluted with dichloromethane (60 ml) and washed with an aqueous sodium bisulfite solution, saturated brine and dried (Na_2SO_4). Concentration of the solvent under reduced pressure afforded a residue which was purified by chromatography, using a Merk Lichoprep Si 60 pre-packed column; elution with hexane gave 0.14 g (32%) of the pure ketone **9**; m.p. 95-96°C (hexane) [lit[10] 95°C, petroleum ether].

3,4-Dihydro-1-vinylanthracene (2). A solution of tricyclic ketone **9** (1 g, 5.10 mmol) in dry THF (3ml) was added at room temperature, dropwise to a 1M THF solution of vinylmagnesiumbromide (16 ml). Then the mixture was allowed to stand at ambient temperature for 7 h. After that the mixture was worked up as usual to give a crude alcohol that was directly used in the next reaction.

The dehydration of the alcohol was performed according to the procedure above described for diene **1**. The diene was purified by column chromatography on neutral alumina. Elution with hexane gave diene **2** (0.4 g, 40%); m.p. 46-47°C (hexane); ^{1}H-NMR ($CDCl_3$) δ 2.38 (m, 2H, J= 7.6, 4.8 Hz, H-3), 2.92 (t, 2H, J=7.6 Hz, H-4), 5.27 (d, 1H, J=10.9 Hz, H-12), 5.62 (d, 1H, J= 17.4, 10.9 Hz, H-11), 7.57-7.74 (m, 6H, aromatic Hs); ^{13}C-NMR δ 23.6 (C-3), 28.8 (C-4), 115.5 (C-12), 122.4 (C-10), 125.2 (C-7), 125.4 (C-5), 125.7 (C-8), 126.9 (C-6 or C-9), 127.6 (C-2), 127.9 (C-6 or C-9), 132.8 (C-10a), 135.3 (C-1 or C-4a), 135.7 (C-10), 136.7 (C-4a or C-1); MS, m/e (rel. intensity) 206 (M+, 100), 191 (92), 178 (90). Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.11; H, 6.86.

[5]Phenacene (3). A solution of anthranilic acid[16] (0.6 g, 4.38 mmol) in DME (2.6 ml) was added dropwise over 5 min, to a stirred mixture of isoamylnitrite (0.4 g, 3.33 mmol) and diene **1** (0.35 g, 1.70 mmol) in DME (4.6 ml) heated at reflux temperature. The reaction mixture was then cooled at 40°C and a DME solution (0.9 ml) of isoamylnitrite (0.4g, 3.33 mmol) was again added. The mixture, heated at reflux temperature, was again added with a DME (1.7 ml) solution of anthranilic acid (0.6 g, 4.38 mmol), dropwise over 5 min. The mixture was heated at reflux temperature for 15 min; then 95% ethanol (2 ml) was added and the mixture poured into an ice-cooled 0.7 M aqueous NaOH solution (18 ml). The precipitate was collected on a Buchner funnel, washed with a cooled 80% aqueous solution of methanol and dried, to give a 1:1:3

mixture (0.16 g) of three products having different degrees of aromatization as shown by GC-MS analysis.

A benzene solution of these compounds (7 ml, 0.16 g) and DDQ (0.52 g) was heated at reflux temperature for 16 h, under nitrogen. After cooling, the reaction mixture was diluted with benzene (10 ml), washed with 10% KOH aqueous solution and saturated brine, then dried (Na_2SO_4) and concentrated in vacuo. Column chromatography of the residue on silica eluting with hexane gave pure [5]phenacene (**3**) (0.14 g, 30% yield); m.p. 363-364°C [lit[2] 364°C]; I.R., ^{1}H-NMR and MS data are in agreement with those reported in the literature[17].

[5]Phenacenebenzoquinone (4). A solution of 1,4-benzoquinone (**14**) (0.34 g, 3.05 mmol) and diene **1** (0.21 g, 1.02 mmol) in toluene (5 ml) was heated at reflux temperature for 20 h. The solution was then cooled, diluted with toluene (10 ml), washed with saturated brine and dried (Na_2SO_4). Evaporation of the solvent gave a residue which was chromatographed on column (SiO_2). Elution with toluene allowed the unreacted diene and two products, which were shown (GC-MS) to be hydroderivatives of **4**, to be recovered. The mixture of these two products was treated with DDQ (0.8 g) in benzene (5 ml) at reflux temperature for 5 h and then worked up as usual. Column chromatography of the residue on SiO_2 eluting with toluene gave pure **4** (0.12 g) in 37% overall yield; m.p. 263-264°C (dec.); I.R. (nujol): 1647 (s, C=O) cm^{-1}; ^{1}H-NMR (DMSO-$CDCl_3$) δ 7.11 (d, 1H, J= 10.2 Hz, H-2), 7.17 (d, 1H, J= 10.2 Hz, H-3), 7.78 (dd, 1H, J=7.8, 7.0 Hz, H-10), 7.84 (dd, 1H, J= 8.0, 7.0 Hz, H-11), 8.14 (d, 1H, J= 7.8 Hz, H-9), 8.20 (d, 1H, J= 9.1 Hz, H-8), 8.38 (d, 1H, J=8.8 Hz, H-5), 8.92 (d, 1H, J= 9.1 Hz, H-7), 8.97 (d, 1H, J= 8.0 Hz, H-12), 9.11 (d, 1H, J=9.6 Hz, H-13), 9.41 (d, 1H, J= 8.8 Hz, H-6), 9.70 (d, 1H, J=9.6 Hz, H-14); ^{13}C-NMR[4] [due to the low solubility only the CH carbons were observed] δ 119.6, 120.9, 121.8, 123.1, 123.9, 125.5, 125.7, 126.5, 126.6, 128.1, 134.1, 139.2. Anal. Calcd for $C_{22}H_{12}O_2$: C, 85.70; H, 3.92. Found: C, 85.68; H, 3.94.

Benzo[5]phenacenequinone (5). A 1M hexane solution of $EtAlCl_2$ (1 ml, 10 mmol) was added to a dichloromethane (10 ml) solution of 1,4-naphthoquinone (**15**) (0.33g, 2.03 mmol) and the resulting mixture was stirred at ambient temperature[18] for 30 min. Then a dichloromethane solution (10 ml) of the diene **1** (0.5 g, 2.43 mmol) was added and the mixture was stirred at room temperature, under nitrogen, for 2h. The reaction mixture was then poured into ice-water and extracted with chloroform. The combined extracts were washed with an aqueous $NaHCO_3$ solution, dried (Na_2SO_4) and evaporated in vacuo to give a residue which was chromatographed on silica gel. Elution with 9:1 hexane-ethyl acetate afforded a pure compound (0.52 g, 71%) which was shown (GC-MS, elemental analysis) to be a tetrahydroderivative of **5**; I.R. (nujol) 1676 (s, C=O) cm^{-1}; MS, m/e (rel. intensity) 362 (M^+, 4), 360 (base), 331 (18), 302 (21), 150 (15). Anal. Calcd for $C_{26}H_{18}O_2$: C, 86.17; H, 5.01. Found: C, 86.13; H, 5.00.

Two different approaches were used for aromatizing this compound.

A. A benzene solution (18 ml) of the tetrahydroderivative (0.52 g) was treated with DDQ at reflux temperature for 5h to afford in high yield (90%) a compound which was purified by column chromatography eluting with toluene and shown to be (GC-MS; I.R.; ^{1}H- and ^{13}C- NMR) the 6,7-dihydroderivative-quinone **16**; m.p. 224-227°C (dec); I.R. (nujol) 1652 (s, C=O) cm^{-1}; ^{1}H-NMR (DMSO-$CDCl_3$) δ 2.96 (t, 2H, J= 8.5 Hz, Hs-6), 3.37 (t, 2H, J= 8.5 Hz, Hs-7), 7.64 (dd, 1H, J= 8.0, 6.9 Hz, H-11), 7.69 (dd, 1H, J= 8.2, 6.9 Hz, H-12), 7.77-7.83 (m, 2H, H-2, H-3), 7.83 (d, 1H, J= 9.2 Hz, H-9), 7.92 (d, 1H, J= 8.0 Hz, H-10), 8.09 (d, 1H, J= 9.2 Hz, H-8),

8.12-8.18 (m, 2H, H-1, H-4), 8.37 (d, 1H, J= 8.9 Hz, H-15), 8.67 (d, 1H, J= 8.9 Hz, H-14), 8.74 (d, 1H, J= 8.2 Hz, H-13); ^{13}C-NMR (DMSO-$CDCl_3$) δ 21.8 (C-6), 23.7 (C-7), 121.7 (C-14), 123.5 (C-8), 124.4 (C-13), 126.9 (C-1 or C-4), 127.7 (C-1 or C-4), 128.2 (C-11), 128.5 (C-9), 128.6 (C-12), 128.7 (C-15), 129.0 (C-9a), 129.6 (C-10), 130.2 (C-15a), 131.2 (C-7b), 132.4 (C-13a), 133.0 (C-4a or C-16a), 133.1 (C-13b), 133.9 (C-4a or C-16a), 134.7 (C-2 or C-3), 134.9 (C-2 or C-3), 137.6 (C-7a), 140.4 (C-15b), 144.3 (C-5a), 185.0 (C-5 or C-16), 185.3 (C-5 or C-16). Anal. Calcd for $C_{26}H_{16}O_2$: C, 86.65; H, 4.47. Found: C, 86.60; H, 4.48.

A xylene solution (5 ml) of the last compound (0.08 g) was again treated with DDQ (0.32 g). The reaction mixture was heated at reflux temperature for 20 h and then worked up as usual to give crude benzo[5]phenacenequinone (**5**) which was purified by HPLC on C-18 column. Elution with 4:1 CH_3CN-H_2O furnished 0.025 g (31%) of pure **5**: m.p. 212-213°C (3:1 hexane-ethyl acetate); IR ($CHCl_3$) 1663 (s, C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.65-7.84 (m, 4H, H-2, H-3, H-11, H-12), 7.85 (d, 1H, J= 8.52 Hz, H-8), 7.98 (d, 1H, J= 8.52 Hz, H-9), 8.04 (m, 1H, H-10), 8.05 (d, 1H, J= 9.15 Hz, H-14), 8.29 (m, 1H, H-1), 8.35 (m, 1H, H-4), 8.52 (d, 1H, J= 8.90 Hz, H-6), 8.86 (d, 1H, J= 8.29 Hz, H-13), 9.37 (d, 1H, J=8.90 Hz, H-7), 9.67 (d, 1H, J= 9.15 Hz, H-15); ^{13}C-NMR ($CDCl_3$) δ 122.6 (C-6), 126.1 (C-8, C-15), 126.4 (C-1), 126.5 (C-11 or C-12), 126.8 (C-11 or C-12), 127.4 (C-4), 128.0 (C-13), 128.8 (C-10), 129.4 (C-9), 130.6 (C-14), 133.5 (C-2 or C-3), 134.2 (C-2 or C-3), 134.5 (C-7), 127.2, 129.0, 129.1, 129.8, 131.5, 131.7, 132.4 133.0, 133.7, 135.4, 183.7, 186.1 (quaternary Cs); MS, m/e (rel. intens.) 358 (M+, base), 330 (11), 300 (26), 274 (3), 179 (5), 150 (20). Anal. Calcd for $C_{26}H_{14}O_2$: C, 87.13; H, 3.94. Found: C, 87.20; H, 3.93.

B: the tetrahydroderivative of **5** (0.2 g) in xylene (10 ml) was treated with a large excess of DDQ (1.2 g) and the reaction mixture heated at reflux temperature for 24 h. Usual work up provided the desired compound **5** in lower yield (20-23%).

Fluorenoanthracenes 6 and 7. The Diels-Alder cycloaddition between diene **2** and 2-inden-1-one (**17**) generated in situ by treatment of 3-bromoindan-1-one with triethylamine[5b] and the aromatization of cycloadducts by treatment with DDQ were carried out according to a previous procedure[5] in a 51% overall yield. Ketones **6** and **7** were separated by column chromatography (SiO_2) eluting with toluene:

6:m.p. 280-281°C (ligroin); IR (nujol) 1698 (s, C=O) cm^{-1}; ^{1}H-NMR (DMSO, 70°C) δ 7.37 (dd, 1H, J= 7.5, 6.8 Hz, H-11), 7.60-7.64 (m, 4H, H-3, H-4, H-10, H-11), 7.86 (d, 1H, J= 7.1 Hz, H-9), 8.05 (d, 1H, J= 9.2 Hz, H-15), 8.08 (d, 1H, J= 8.3 Hz, H-8), 8.11-8.75 (m, 4H, H-1, H-2, H-5, H-14), 9.19 (d, 1H, J= 8.3 Hz, H-7), 9.38 (bs, 1H, H-6); ^{13}C-NMR (DMSO, 70°C) δ 119.2 (C-8), 120.6 (C-14), 120.9 (C-9), 122.1 (C-6), 123.4 (C-12), 126.1 (C-4), 126.2 (C-3), 126.6 (C-13a), 127.0 (C-11), 127.5 (C-2), 127.7 (C-6a), 128.2 (C-5), 129.4 (C-13b, C-15a, C-11), 130.2 (C-7), 131.2 (C-6b), 131.3 (C-15), 131.7 (C-1a), 132.0 (C-5a), 133.9 (C-12a), 134.8 (C-10), 143.0 (C-8b), 144.6 (C-8a), 194.3 (C-13); Ms, m/e (rel. intens.) 330 (M+, base), 300 (17), 165 (12), 150 (14), 149 (7). Anal. Calcd for $C_{25}H_{14}O$: C, 90.89; H, 4.70. Found: C, 90.95; H, 4.69.

7: m.p. 248-250°C (ligroin); IR (nujol) 1699 (s, C=O) cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.31-7.53 (m, 2H, H-11, H-12); 7.56 (m, 2H, H-3, H-4), 7.71-7.90 (m, 3H, H-8, H-10, H-15), 8.01 (m, 1H, H-2), 8.03 (d, 1H, J=7.5 Hz, H-13), 8.08 (m, 1H, H-5), 8.22 (d, 1H, J=9.4 Hz, H-14), 8.32-8.71

(m, 2H, H-1, H-7), 9.08 (s, 1H, H-6); ^{13}C-NMR ($CDCl_3$) δ 121.4(C-8), 121.9 (C-14), 123.2 (C-6), 123.8 (C-13), 124.1 (C-7), 124.4 (C-10), 126.3 (C-4), 126.7 (C-3), 127.2 (C-1), 127.8 (C-2), 128.7 (C-5), 128.8 (C-11), 129.5 (C-15), 134.6 (C-12), 193.7 (C-9), 127.9, 128.8, 130.5, 132.4, 132.8, 133.1, 135.3, 136.6, 141.8, 145.3 (quaternary Cs); MS, m/e (rel. intens.) 330 (M+, base), 302 (20), 300 (29), 298 (9),150 (19). Anal. Calcd for $C_{25}H_{14}O$: C, 90.89; H, 4.70. Found: C, 90.83; H, 4.70.

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