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High Pressure Diels-Alder Reactions of 2-Vinyl-3,4-Dihydronaphthalene. Synthesis of Cyclopenta[c]- and Indeno[c]Phenanthrenones.

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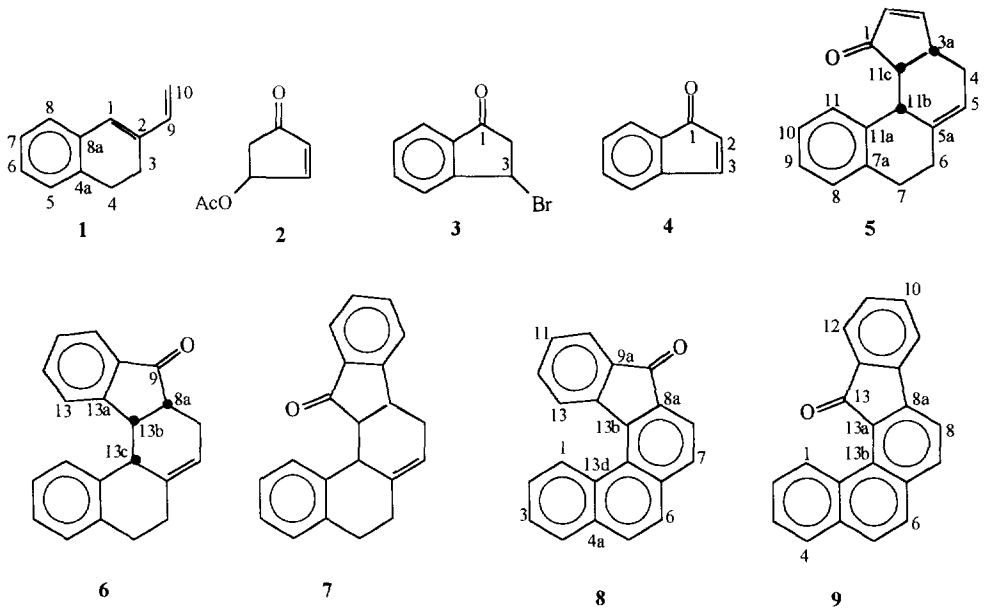
Abstract. A new shorter synthesis of 2-vinyl-3,4-dihydro-naphthalene has been described. The Diels-Alder reactions of this diene with 4-acetoxy-2-cyclopenten-1-one, 3-bromoindan-1-one and inden-1-one under high pressure conditions are reported. A two step synthesis of cyclopenta[c]-and indeno[c]phenanthrenones is discussed. Structure analysis by ^{1}H and ^{13}C NMR spectroscopy is presented.

Polycyclic aromatic hydrocarbons (PAH) are widely distributed environmental contaminants formed by incomplete combustion of fossil fuels and other organic matter. In recent years increasing attention has been devoted to cyclo- and polycyclopentafused PAH because of their chemical and biological properties[1,2]. Whereas cyclopenta[a]phenanthrenes and their derivatives have been extensively investigated[3] much less has been done for the isomer cyclopenta[b]- and cyclopenta[c]phenanthrenes because of their relative synthetic inaccessibility. Recently we reported[4] a new two-step route for the synthesis of cyclopenta[c]phenanthrenes by Diels-Alder reaction of 2-vinylnaphthalene, a diene commercially available but low reactive. Since we are interested in developing efficient and flexible syntheses of cyclopentafused PAH based on the cycloaddition of vinylarenes to rapidly construct the basic skeleta and in consideration of the higher reactivity of the dihydrovinylarenes[4,6], we studied a new synthesis of 2-vinyl-3,4-dihydronaphthalene[7] (**1**). Herein we report a more convenient two-step synthesis of diene **1** and show its synthetic utility for the efficient assembly of cyclopenta[c]- and indeno[c]-phenanthrenones by Diels-Alder reaction with 4-acetoxy-2-cyclopenten-1-one (**2**), 3-bromoindan-1-one (**3**) and inden-1-one (**4**).

RESULTS AND DISCUSSION

2-Acetyl-1-tetralone was chosen as starting material to synthesize diene **1** in view of both its commercial availability and the incorporation of functionalities which could be easily converted to a diene moiety. We found that diene **1** could be made conveniently in a two-stage reaction sequence: reduction of carbonyl groups with sodium borohydride in ethanol followed by dehydration with phosphorus oxychloride in pyridine[8,9] of the crude mixture of the diols, in 67% overall yield. When the dehydration was accomplished with TsOH in benzene the yield fell because of diene polymerization. We also attempted the route based on the conversion of the diols to the corresponding dichloroderivatives and subsequent dehydrochlorination. The last reaction under a variety of conditions failed, however, to yield useful quantities of diene **1**.



The Diels-Alder reactions of 4-acetoxy-2-cyclopenten-1-one (**2**)[10] require Lewis acid catalysis[11] and/or high pressure[12,13] because of the low reactivity of this dienophile. When diene **1** and ketone **2** interacted at atmospheric pressure in dichloromethane solution in presence of $EtAlCl_2$, tetracyclic ketone **5** was formed regioselectively and endo-diastereoselectively in 15% yield. The primary cycloadduct underwent β-elimination of acetic acid under reaction conditions to afford α,β-unsaturated ketone **5**[11d] . A much better yield (70%) was obtained when the **1-2** cycloaddition was accomplished at 10 Kbar without catalyst (see Table). Treatment of tetracyclic ketone **5** over Pd/charcoal catalyst according to a previously reported procedure allowed the conversion to the known cyclopenta[c]phenanthren-1-one,[4] in 60% overall yield (previous total yield was 32%). The all cis-arrangement of H(3a), H(11b) and H(11c) of ketone **5** is supported by the analysis of the interproton coupling values, i.e. $J_{11b,11c}=J_{11c,3a}= 6.5$Hz and the ^1H-^1H NOE experiments. Selective pre-irradiation of the resonance due to H(11c) resulted in signal enhancement of the resonances attributed to H(3a), H(11b) and H(11). The conversion of **5** to the previously prepared cyclopenta[c]phenanthren-1-one confirmed the regiochemistry of the carbonyl function depicted in the formula[4].

Table. Diels-Alder reactions of 2-vinyl-3,4-dihydronaphthalene (**1**) with ketones **2-4**

ketone	diene/ ketone[a]	reaction temperature (°C)	reaction time (h)	pressure (Kbar)	product(s)	yield (%)[b]
2	1.5	20	2		**5**	15
	1.5	35	66	10	**5**[c]	70
3	1.3	d	3		**6,7**[e]	75
	1.3	50	3	7	**6,7**	75
4	1.3	50	3	7	**6,7**	70

[a] Ratio of equivalents; [b] The reaction yields refer to the isolated compounds;[c] Two products of unknown constitution account for 8% of the product mixture.[d] The reaction mixture was heated at reflux temperature. [e] Not isolated in pure form (see ref.15).

In order to synthesize the indeno[c]phenanthrenones the cycloaddition reaction of diene **1** with 3-bromoindan-1-one (**3**), which is a precursor of inden-1-one (**4**), was investigated. Bromoketone **3** was prepared by treating indanone with NBS[14] according to a described procedure. The use of AIBN instead of benzoyl peroxide allowed the yield to be increased from 55% to 94%.

When a carbon tetrachloride solution of the crude bromoketone **3** and diene **1** (see Table) was heated under reflux and added of triethylamine dropwise, the inden-1-one (**4**) was generated "in situ" and trapped by the diene to afford a 5:1 mixture of the cycloadducts **6** and **7**[15], respectively, in 75% yield. The major component of the mixture was isolated by column chromatography and then converted to the fully aromatized ketone **8** by treatment over a Pd/charcoal catalyst[4,16,20]. A lower regioselectivity (**6**/**7**=3) was observed when the reaction was accomplished under high pressure conditions. The cis-relationship of H(8a), H(13b), and H(13c) of ketone **6** followed from both the vicinal coupling values, i.e. $J_{13b,13c}=J_{13b,8a}=7$Hz and the results of the NOE experiments. This stereochemistry causes a spatial arrangement in which, as shown by an examination of the Dreiding models, H(13) proton is above the plane of the other aromatic ring end. The close proximity of the aromatic ring is responsible for the remarkable upfield shift of H(13) proton. The identification of H-13 proton was based on its mutual dipolar contacts with H(12) and H(13b) protons and on the long range connectivities with C(9a), C(11) and C(13a) carbons. The above discussed results justify the regiochemical assignment of the carbonyl group of the five-membered ring. Support to the structure of **6** was given also by the conversion to the known ketone **8**[20] by treatment over Pd/C catalyst. The NOE effect (proximity effect) between H(1) and H(13) protons of fully aromatized ketone **8**, as well as their downfield shifts (8.91 and 8.13 ppm respectively) indicated an helicene type structure.

Finally the reaction of inden-1-one (**4**) was also examined. This compound was prepared by dehydrobromination of 3-bromoindan-1-one (**3**) with *sym*-collidine[17]. Inden-1-one (**4**) is a light yellow oil which polymerizes very easily and is difficult to handle because it is vesicant and lachrimator. When inden-1-one (**4**) interacted with diene **1** at 50°C under high pressure conditions (7Kbar) for 3h, a 1:1 mixture of ketones **6** and **7** was obtained in 70% yield. Aromatization of a mixture of cycloadducts allowed the tetracyclic aromatized regioisomer **9** to be obtained. These two alternative procedures provide synthetically useful routes to the indeno[c]phenanthrenones. The structure of the aromatic pentacyclic ketone **9** was based on the analysis of the ^{1}H and ^{13}C NMR spectra which evidenced four condensed aromatic rings. The regiochemistry of the carbonyl function was supported by the large downfield shift of H(1) proton (9.90 ppm) associated with the steric proximity of the carbonyl function.

In conclusion, a facile synthesis of 2-vinyl-3,4-dihydronapthalene (**1**) starting from a commercially available product has been described. The easy availability of this reactive diene opens short and convenient synthetic routes toward cyclopenta[c]- and indeno[c]phenanthrenones. The latter compounds are useful intermediates for the sinthesis of benzo[e]pyrenes and indenopyrenes.

EXPERIMENTAL SECTION

IR spectra were recorded in chloroform solution on a Perkin Elmer 983 spectrometer. Absorption chromatography was carried out on a Merck Lichoprep Si 60 pre-packed column. Methylene chloride was distilled from CaH_2. Melting points were determined on a Buchi 510 melting point apparatus. All compounds gave correct elemental analyses. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Associates VXR-400 multinuclear instrument in $CDCl_3$. The assignment of proton and carbon chemical shifts, ^{13}C multiplicities, and interproton coupling constants were performed by standard one- and two-dimensional FT NMR techniques. Assignment of carbon-carbon connectivities involving quaternary carbon atoms was made by means of selective 2D INEPT experiments. Homonuclear ^{1}H {^{1}H} NOE data were obtained by the difference method using the frequency cycling techniques for selective preirradiation. The starred signals for compounds **5** and **9** may be interchanged.

2-Vinyl-3,4-dihydronaphthalene (1): A solution of 2-acetyl-1-tetralone (2g, 10.6 mmol) in ethanol (105 mL) was heated at reflux temperature. Sodium borohydride (2.5g, 66.1mmol) dissolved in water (42 mL) was added dropwise to the refluxing solution. The resulting mixture was refluxed for an additional 2.5h. Then half of the solvent was removed by vacuum distillation and the resulting mixture extracted with chloroform. The combined extracts were washed with saturated brine, dried (Na_2SO_4) and evaporated under vacuum to afford a mixture of diols (2g) which was used without purification for the next step.

A mixture of the diols (2g), dry pyridine (250 mL) and phosphorus oxychloride (1.4 mL) was refluxed for 3h under nitrogen. Then most of the pyridine was evaporated under vacuum, and the residue poured into ice-cold 10% H_2SO_4 solution and extracted with ether. The combined extracts were washed with sodium bicarbonate solution, dried (Na_2SO_4) and evaporated under reduced pressure to give a residue which was chromatographed on column. Elution with n-hexane gave 1.1g (67%) of the diene **1**[7]: ^{1}H NMR δ 2.48 (dd, 2H, J= 7.5, 1.3Hz, Hs-3), 2.89 (t, 2H, J=7.5Hz, Hs-4), 5.14 (dd, 1H, J=10.5, 1.2 Hz, H-10), 5.34 (dd, 1H, J=17.5, 1.2 Hz, H-10), 6.43 (dd, 1H, J=1.3, 1.0 Hz, H-1), 6.55 (ddd, 1H, J=17.5, 10.5, 1.0 Hz, H-9), 7.05 (ddd, 1H, J=6.8, 1.5, 1.0 Hz, H-8), 7.10-7.16 (ms, 3H, H-5, H-6, H-7); ^{13}C NMR δ 22.35 (C-3), 27.74 (C-4), 112.79 (C-10), 126.54 (C-5, C-8), 127.05*, 127.29* (C-6, C-7), 128.20 (C-1), 134.57*, 135.7* (C-2, C-8a), 137.80 (C-4a), 138.55 (C-9); MS, m/e (rel.intens.) 156 (M^+, base), 141 (82), 128 (97), 115 (64), 76 (20).

Diels-Alder reaction of 4-acetoxy-2-cyclopenten-1-one (2) with diene 1. The cycloaddition performed at atmospheric pressure in dichloromethane solution was catalyzed by $EtAlCl_2$ (0.5 equiv.) All operations for preparing the mixture were executed in a dry-box. Complexation time (40 min) and complexation temperature (20°C) were used[18]. The reaction under high pressure conditions was performed according to a previously described method [4,19] in presence of a small amount of hydroquinone. At the end the reaction mixtures were worked up as usual. The ratio of the reagents, as well as the reaction conditions, are reported in the Table. Tetracyclic ketone **5** was purified by column chromatography; gradient elution (95:5 to 90:10 hexane-ethyl acetate mixtures) led to the pure product.

3a,4,6,7,11b,11c, Hexahydrocyclopenta[c]phenanthren-1-one (5): colorless oil; IR 1700 (s, C=O), 1653 (w, C=C) cm^{-1}; ^{1}H NMR δ 2.32 (m, 2H, Hs-4), 2.33 (m, 1H, H-6), 2.43 (ddd, 1H, J=14.0, 4.0, 3.8 Hz, H-6), 2.49 (ddd, 1H, J=14.6, 12.0, 3.8 Hz, H-7), 2.63 (ddd, 1H, J=14.6, 4.5, 4.0 Hz, H-7), 2.94 (dd, 1H, J=6.5, 6.5 Hz, H-11c), 3.45 (m, 1H, J=6.5, 6.0, 3.0, 2.2 Hz, H-3a), 3.63 (dd, 1H, J=6.5, 2.2 Hz, H-11b), 5.50 (ddd, 1H, J=7.0, 3.0, 2.2 Hz, H-5), 6.09 (dd, 1H, J=5.5, 1.9 Hz, H-2), 7.11 (dd, 1H, J=7.1, 2.2 Hz, H-8), 7.17 (ddd, 1H, J=7.1, 7.0, 1.6 Hz, H-9), 7.25 (ddd, 1H, J=7.1, 7.0, 1.2 Hz, H-10), 7.31 (dd, 1H, J=7.1, 1.6 Hz, H-11), 7.37 (dd, 1H, J=5.5, 2.2 Hz, H-3); ^{13}C NMR δ 26.43 (C-4), 29.46 (C-7), 30.76 (C-6), 40.42 (C-11b), 42.00 (C-3a), 50.00 (C-11c), 117.71 (C-5), 125.91 (C-9), 126.34 (C-10), 128.00 (C-8, C-11), 136.03 (C-11a), 136.16 (C-2), 139.73*,140.27* (C-5a, C-7a), 165.89 (C-3), 209.22 (C-1); MS, m/e (rel. intens.) 236 (M^+, 29), 165 (35), 156 (36), 155 (base), 141 (38), 128 (53), 115 (49), 82 (49).

Treatment of ketone **5** over a Pd/charcoal catalyst according to a previously reported procedure[4] led to the known cyclopenta[c]phenanthren-1-one in 85% yield.

3-Bromoindan-1-one (3). This compound was prepared as follows[14]: indanone (5g, 37.8 mmol), NBS (6.7g, 37.8 mmol) and AIBN (50 mg) were refluxed in carbon tetrachloride (60 mL) for 2.5h under nitrogen. The solution was cooled, succinimide removed by filtration, and the filtrate evaporated under reduced pressure to yield 7.5 g (94%) (previous yield: 55%[14])of bromoketone **3** which was practically pure as shown by ^{1}H NMR analysis; ^{1}H NMR: δ 2.7-3.5 (m, 2H, Hs-2), 5.5 (m,1H, H-3), 7.2-7.8 (m, 4H, aromatic Hs).

Diels-Alder reactions of 3-bromo-indan-1-one (3). The cycloadditions were accomplished at atmospheric pressure (A) and under high pressure conditions (B) (see Table).

A) A solution of 3-bromoindanone (**3**) (1g, 4.7 mmol) and diene **1** (1g, 6.4 mmol) in carbon tetrachloride (12 mL) was heated at reflux temperature and added dropwise (30 min) of a carbon tetrachloride (20 mL) solution of triethylamine (0.6g, 5.9 mmol). The mixture was then refluxed for 3h. The mixture was cooled and worked up as usual to afford a 5:1 mixture of cycloadducts **6** and **7** in 75% yield.

B) The cycloaddition was accomplished[4,19] in carbon tetrachloride in presence of a small amount of hydroquinone (see Table for the ratios of the reagents) using a ratio bromoketone/triethylamine =1. The reaction was then worked up as usual to lead to a 3:1 mixture of compounds **6** and **7** in 75% yield.

Column chromatography of the crude reaction mixture eluting with 46:1 hexane/ethyl acetate gave pure pentacyclic ketone **6**.

5,6,8,8a,13b,13c,Hexahydro-9H-indeno[2,1-c]phenanthren-9-one (6). m.p. 117-118°C (ethyl ether); IR 1700 (s, C=O), 1653 (w, C=C) cm^{-1}; ^1H NMR δ 1.38 (ddd, 1H, J=14.6, 9.0, 8.5 Hz, H-5), 2.16 (m, 2H, Hs-6), 2.27 (m, 1H, H-8), 2.35 (dd, 1H, J=14.6, 3.5 Hz, H-5), 2.89 (ddd, 1H, J=14.2, 7.5, 2.0 Hz, H-8), 3.05 (ddd, 1H, J=7.0, 7.0, 2.0 Hz, H-8a), 3.89 (dd, 1H, J=7.0, 2.0 Hz, H-13c), 4.03 (dd, 1H, J=7.0, 7.0 Hz, H-13b), 5.65 (m, 1H, H-7), 5.77 (d, 1H, J=7.6 Hz, H-13), 7.04 (d, 1H, J=7.5 Hz, H-4), 7.12 (dd, 1H, J=7.6, 7.2 Hz, H-12), 7.23 (dd, 1H, J=7.5, 7.2 Hz, H-11), 7.25 (dd, 1H, J=7.5, 7.3 Hz, H-3), 7.36 (dd, 1H, J=7.3, 7.2 Hz, H-2), 7.51 (d, 1H, J=7.2 Hz, H-1), 7.63 (d, 1H, J=7.5 Hz, H-10); ^{13}C NMR δ 25.06 (C-8), 29.12 (C-5), 30.31 (C-6), 41.93 (C-13c), 46.20 (C-13b), 48.06 (C-8a), 120.40 (C-7), 122.55 (C-10), 126.47 (C-3), 126.80 (C-2), 126.86 (C-13), 127.43 (C-11), 128.29 (C-4), 128.82 (C-1), 133.70 (C-12), 136.80 (C-13d), 138.74 (C-13a), 139.30 (C-6a), 140.69 (C-4a), 154.68 (C-9a), 209.40 (C-9); MS, m/e (rel. intens) 286 (M^+, 2), 156 (base), 141 (22), 128 (26), 115 (21).

9H-Indeno[2,1-c]phenanthren-9-one (8) and 13H-Indeno[1,2-c]phenanthren-13-one (9): Indeno[c]phenanthrenones **8** and **9** were prepared by heating a pure sample of cycloadduct **6** (0.4g) or a mixture of **6** and **7** (0.4g)[15] in tryglime (12mL) over a 10% Pd/C catalyst (0.4g) at reflux temperature for 60h. After 24 and 48h, more catalyst (40mg + 40mg) was added. The reaction mixtures were worked up as usual and the crude reaction products were chromatographed on column.

(8): crystalline solid (eluted with hexane-ethylacetate 98:2); mp 148-149°C (ethylacetate)[20]; IR 1708 (s, C=O) cm^{-1} ; ^1H NMR δ 7.27 (dd, 1H, J=7.5, 7.5 Hz, H-11), 7.39 (dd, 1H, J=7.8, 7.5 Hz, H-12), 7.54 (dd, 1H, J=8.0, 7.5 Hz, H-2), 7.63 (d, 1H, J=8.9 Hz, H-6), 7.63 (dd, 1H, J=8.0, 7.5 Hz, H-3), 7.70 (d, 1H, J=7.5 Hz, H-10), 7.70 (d, 1H, J=7.9 Hz, H-7), 7.74 (d, 1H, J=8.9 Hz, H-5), 7.82 (d, 1H, J=7.9 Hz, H-8), 7.87 (d, !H, J=8.o Hz, H-4), 8.13 (d, 1H, J=7.8 Hz, H-13), 8.91 (d, 1H, J=8.0 Hz, H-1); ^{13}C NMR δ 121.07 (C-8), 123.92 (C-13), 124.15 (C-10), 124.93 (C-2), 127.11 (C-6), 127.87 (C-3), 128.05 (C-1, C-13c), 128.18 (C-4), 128.90 (C-11), 129.40 (C-7), 129.54 (C-13d), 129.58 (C-5), 133.36 (C-4a), 133.86 (C-12), 134.32 (C-6a), 134.69 (C-9a), 138.43 (C-8a), 142.71 (C-13b), 146.51 (C-13a), 193.90 (C-9); MS, m/e (rel. intens.) 280 (M^+, base), 252 (63), 250 (53), 125 (16), 112 (8).

(9): crystalline solid (gradient elution from 98:2 to 95:5 hexane-ethylacetate); mp 134-135°C; IR 1703 (s, C=O) cm^{-1}; ^1H NMR δ 7.29 (dd, 1H, J=7.6, 7.4 Hz, H-11), 7.46 (dd. 1H, J=7.5, 7.4 Hz, H-10), 7.53 (d, 1H, J=7.5 Hz, H-9), 7.60 (d, 1H, J=8.9 Hz, H-6), 7.65-7.66 (m, 3H, H-2, H-3, H-5), 7.67 (d, 1H, J=7.6 Hz, H-12), 7.71 (d, 1H, J=8.0 Hz, H-8), 7.82 (d, 1H, J=7.9 Hz, H-4), 7.97 (d, 1H, J=8.0 Hz, H-7), 9.90 (d, 1H, J=8.0 Hz, H-1); ^{13}C NMR δ 118.44 (C-8), 119.42 (C-9), 124.25 (C-12), 126.07 (C-2), 126.91 (C-6), 127.87 (C-4), 128.03*, 128.38* (C-3, C-5), 129.26 (C-11), 129.29*, 130.18*, 131.61* (C-6a, C-13b, C-13c), 130.11 (C-1), 133.88 (C-4a), 134.11 (C-12a), 134.38 (C-10), 134.69 (C-13c), 136.46 (C-7), 143.13 (C-8a), 147.21 (C-8b), 194.02 (C-13); MS, m/e (rel. intens.) 280 (M^+, 69), 279 (base), 250 (13), 140 (11), 125 (5), 124 (5), 44 (3).

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15. We were not able to obtain a pure crystalline sample of ketone 7 even after several crystallizations. It was shown to be a cycloadduct by GC-Mass measurements and by the conversion to the regioisomer aromatic ketone **9** by treatment of a reaction mixture, obtained by cycloaddition of inden-1-one (**4**) under high pressure conditions and enriched in ketone 7 by a rapid column chromatography, over a Pd/C catalyst.
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