

A one-step efficient general method for the synthesis of naphthopyrones: A first synthesis of spiro[naphthalene-2, 4'-phenanthrene] carbocycles

JAYSUKHLAL R MERCHANT* and NEVILLE V FERNANDES

Organic Chemistry Research Department, D G Ruparel College, Senapati Bapat Marg, Bombay 400 016, India

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Abstract. A new synthesis of naphthopyrones and hexahydrospiro[naphthalene-2,4'-phenanthrene]-1,1'-diones has been accomplished by the Friedel–Crafts reaction of various 1-tetralones with α, β -unsaturated acids in the presence of polyphosphoric acid (PPA).

Keywords. Tetralones; α, β -unsaturated acids; 4H-naphtho(1,2-*b*)pyrone; spiro[naphthalene-2,4'-phenanthrene]-1,1'-dione.

1. Introduction

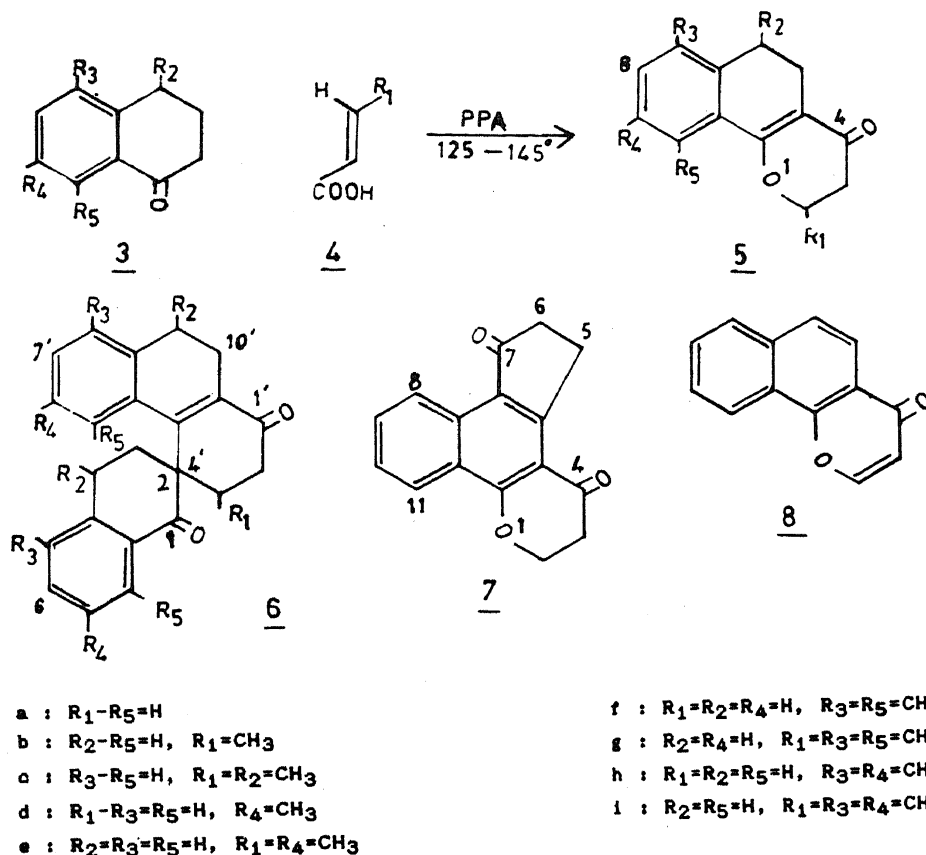
Naphthopyrones and related *o*-heterocycles form an interesting class of compounds. This is mainly due to their widespread occurrence in nature (Dean 1963; Kulkarni *et al* 1972) and the number of biological activities they exhibit. For example, β -lapachone (1) and a number of its synthetic derivatives (Schaffner-Sabba *et al* 1984) have been shown to be active against the retrovirus reverse transcriptase. Further, a new series of antiallergic compounds (Nohara *et al* 1975, 1977) (2) possessing naphthopyrone moiety has been reported. Apart from these, other biological effects such as anticonvulsant (Ambrogini and Passerini 1976) and antitubercular (Annigeri *et al* 1966) activities have been reported (Ronald 1975).

It can thus be seen that naphthopyrones are important intermediates in the synthesis of many naturally occurring and pharmacologically important compounds. A survey of literature reveals that this ring system could be synthesised by methods which either involve a number of steps (von Strandtmann *et al* 1972) or give a mixture of products (Schaffner-Sabba *et al* 1984). Therefore a simple and practical method for their synthesis is highly desirable. With this in mind we sought to develop a new method for the synthesis of this class of compounds from readily available starting materials. The envisioned route, as evident from the retrosynthetic perspective, basically involves condensation of enolisable aromatic ketones, such as 1-tetralone, with α, β -unsaturated acids in the presence of an acid, e.g. polyphosphoric acid (PPA).

2. Results and discussion

To begin with we reacted 1-tetralone (1 eq.) with acrylic acid (2 eq.) in the presence of freshly prepared PPA at 125°C. The reaction afforded three products (scheme 1) after

*For correspondence



Scheme 1.

careful chromatography. Elution with pet. ether (60°–80°): benzene (1:1) yielded a yellow solid (60%). This major product was assigned the structure 5a on the basis of spectroscopic and analytical data.

The IR spectrum of 5a, the expected product, revealed the presence of an α , β -unsaturated carbonyl group at 1650 cm^{-1} . The ^1H NMR spectrum of 5a showed a triplet at δ 2.7 for the methylene protons next to the carbonyl group and a corresponding triplet at δ 4.63 for the methylene next to the heterocyclic oxygen, indicating the presence of a pyran-4-one structure. Additional proof for this structure was obtained by dehydrogenating 5a with Pd/C in refluxing diphenyl ether to 4H-naphtho(1,2-*b*)pyran-4-one (8). In a separate experiment, 8 was also prepared by a known method reported in the literature (von Strandtmann *et al* 1972) (mixed melting points and superimposable IR spectra). The mass spectrum ($m/z = 328$) and elemental analysis ($\text{C}_{23}\text{H}_{20}\text{O}_2$) of the second component (yield 10%) suggested that two moles of 3a had reacted with one mole of acrylic acid. The ^1H NMR spectrum was of little help in evaluating the structure because of its complex nature and the close proximity of a number of proton resonances. Its ^{13}C NMR spectrum (proton coupled and decoupled) showed signals corresponding to twenty-three carbon atoms including two carbonyls at δ 197.4 and δ 196.7 and one singlet at δ 49.2 for the spiro carbon. In order to complete the structure elucidation of this compound we relied on the information provided by homonuclear 2D as well as decoupling experiments (figures 1 and 2).

With the help of the ^1H COSY plot of 6a it was relatively easy to decipher the region between δ 6.9 and 8.2 into two sets (4 protons each) of aromatic protons. The protons of the naphthalene system are deshielded to a larger extent due to the carbonyl function contiguous to the aromatic ring. In the region δ 1.5–3.5 unambiguous correlation was observed between four protons (magnetically nonequivalent). The molecular model of 6a clearly showed such a system ($\text{CH}_2\text{--CH}_2$) as the one present in the ring B. Fortunately, the multiplet pattern at δ 3.3 is readily recognised as a doublet–triplet–doublet because of its symmetry and apparent simplicity. This multiplet can be considered as a pattern of four distorted doublets in which the two inner peaks overlap to give a seven-peak multiplet ($J_{\text{avg}} = 6.1, 13.8, 18.02$ Hz). Irradiation at δ 3.3 ppm resulted in the collapse of the multiplet at δ 2.0 into a double triplet ($J = 10.2, 3.2$ Hz). Irradiation at 2.0 ppm resulted in the collapse of the multiplet at δ 3.3 into a double doublet ($\text{C}_4\text{--H}_a, J = 18.2, 15.2$ Hz) corresponding to one geminal and one axial-axial interaction. Also, irradiation at 2.0 ppm resolved the complex multiplet (2H) at δ 2.9–3.05 into two sets of double doublets. The *dd* at δ 2.93–3.01 showed $J = 18.2; 5.0$ Hz ($\text{C}_4\text{--H}_e$) and the *dd* at δ 2.98–3.05 showed $J = 15.1; 4.8$ Hz ($\text{C}_3\text{--H}_a$). Irradiation at 2.98 ppm resulted in the collapse of the multiplet at δ 3.3 into a double doublet ($J = 15.3; 6.7$ Hz). Hence the peak at δ 2.0 is due to the equatorial proton at C_3 . The complex multiplet at δ 2.2–2.7 integrating for eight protons belongs to the phenanthrene nucleus. The regiochemistry of 6a was thus established.

Mechanistically the formation of 6a could be explained as follows (Rowlands 1985):

- (i) 1-tetralone (3a) reacts with its enol form to give intermediate I (Evans and Smith 1954; Metz 1972);
- (ii) acylation of intermediate I with acrylic acid to give intermediate II;
- (iii) cyclisation of II to give 6a (scheme 2).

The third compound isolated in 2% yield showed a strong absorption for the carbonyl group at 1680 cm^{-1} whereas its mass spectrum gave M^+ at $m/z = 252$ with molecular formula $\text{C}_{16}\text{H}_{12}\text{O}_3$ which was well supported by its elemental analysis. A comparison with the molecular formula of 5a indicates the addition of three carbon atoms which could come from acrylic acid moiety. In our earlier work it was observed that the cyclopentanone ring attached to the naphthalene nucleus exhibits IR frequency in the region of 1680 cm^{-1} . Therefore structure 7a was assigned to this product. Further confirmation was obtained from its ^1H NMR spectrum wherein, out of four aromatic protons, the one in the proximity of the carbonyl group was seen at δ 9.2. Unambiguous proof for this structure was obtained when the same compound 7a was isolated from the reaction of α -naphthol with acrylic acid in the presence of PPA (mixed melting points and superimposable IR). In order to obtain an insight into the mechanism involved in the formation of this product, compound 5a was reacted with acrylic acid in the presence of PPA under similar conditions when 7a was isolated (mixed melting points and superimposable IR spectra). This clearly indicates that in the reaction 5a, which is formed first, gets dehydrogenated and further reacts with another molecule of acrylic acid to give 7a. We have also observed that the reaction of 3a with acrylic acid is highly dependent on the stoichiometry of the reactants. This effect is shown in table 1.

We next turned our attention to the reaction of 3a with crotonic acid in the presence of PPA as described previously in the ratio 1:2 respectively. In this case only one

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 First pulse width 90.0 degrees
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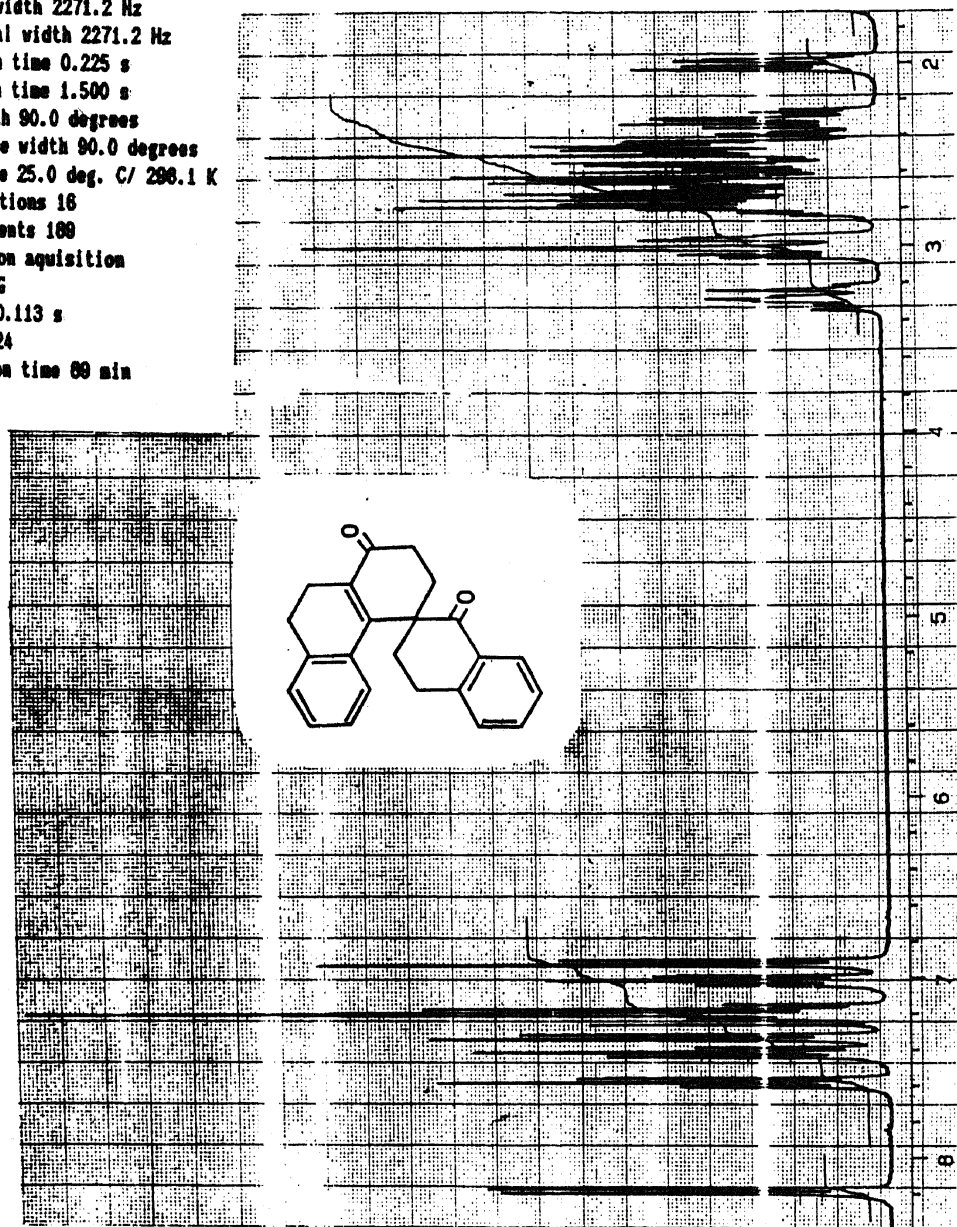


Figure 1a. (Continued facing page.)

compound **5b** was isolated in 83% yield. However, when the ratio of the reactants was changed to 2:1, compound **6b** (yield 36%), was isolated along with **5b** (yield 40%) after column chromatography.

In order to show the generality of this new method we reacted several methyl and dimethyl 1-tetralones with acrylic as well as crotonic acids in the presence of PPA. In all these cases only the corresponding naphtho(1,2-*b*)pyrones were isolated in 65–85% yield. In the case of 4-methyl-1-tetralone (**3c**) and crotonic acid the product **5c** was

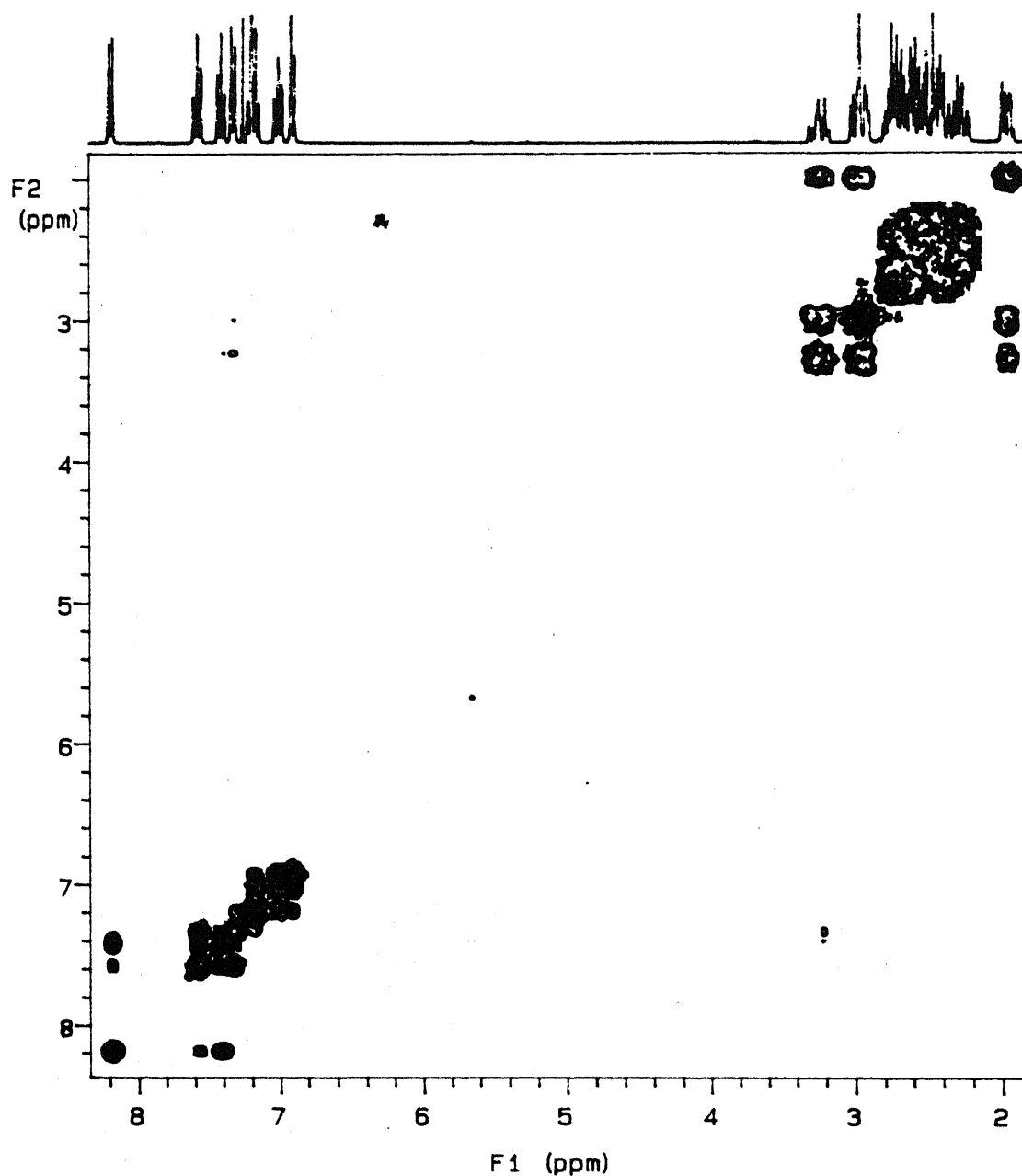


Figure 1a. (Caption on p. 115.)

obtained which can exist as two diastereoisomers in the ratio 54:46 as evident from its ^1H NMR (300 MHz) spectrum.

3. Experimental section

All melting points are recorded in open capillaries and are uncorrected. Silica gel (60–120 mesh) was used for chromatography throughout. The homogeneity of compounds was ascertained by tlc on silica gel-G plates using different solvent systems and spots were developed in an iodine chamber. IR spectra were recorded on a Perkin–Elmer 781 spectrophotometer. UV spectra were recorded on a Shimadzu UV 240 spectrophotometer.

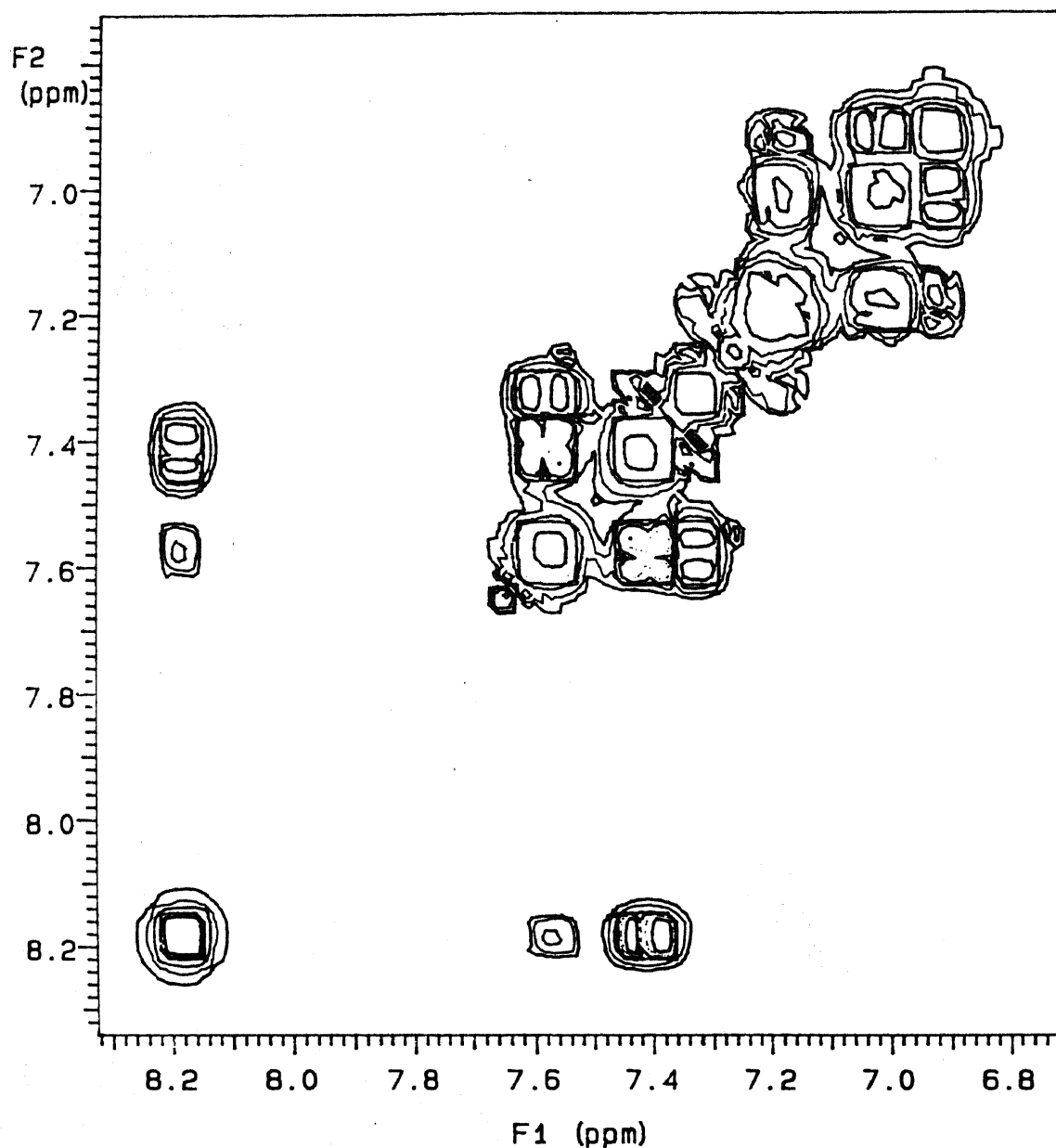


Figure 1b. (Caption on facing page.)

Elemental analysis was done on the Carlo Erba M00-1106 instrument. ^1H and ^{13}C NMR spectra (300 MHz) were recorded at the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay on a Varian XL 300. Mass Spectra were obtained using the Finnigan Mat 1020 C automated GC/MS quadrupole mass spectrometer at the National Chemical Laboratories, Pune.

3.1 Preparation of 1-tetralones

1-Tetralone (**3a**) and 4-methyl-1-tetralone (**3c**) were prepared according to the method described in Organic Synthesis (Olson and Bader 1963). Other substituted 1-tetralones (De Barry and Sanders 1933) were prepared by an improved method already described in literature (Eisenbraun *et al* 1971).

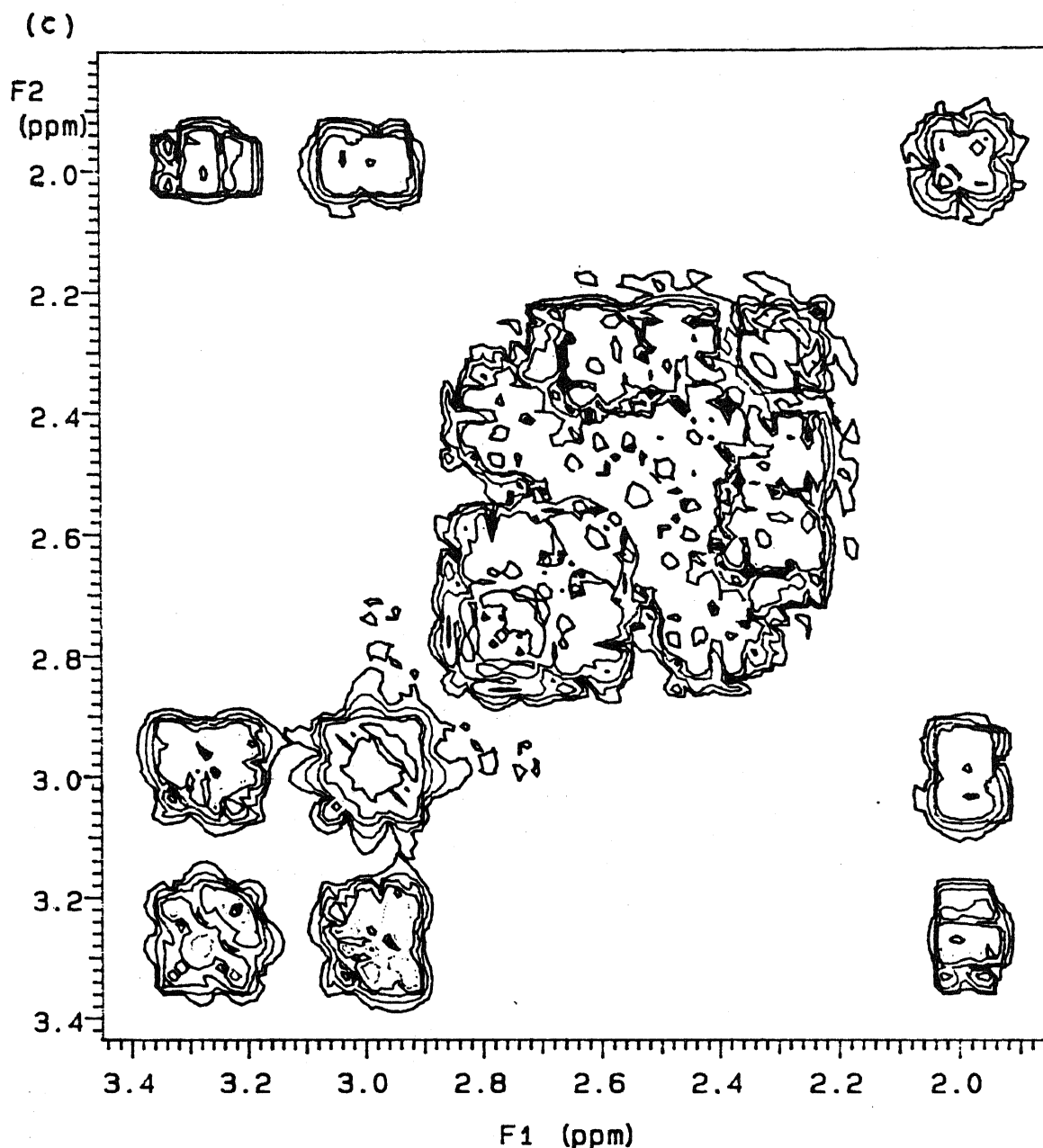


Figure 1. (a) A 300 MHz ^1H homonuclear COSY NMR spectrum of **3b**. (b) Expansion of the region δ 6.8–8.4 ppm. (c) Expansion of region δ 1.9–3.4 ppm.

3.2 General procedure for the synthesis of 2,3,5,6-tetrahydro-4H-naphtho(1,2-b)pyran-4-ones

To freshly prepared polyphosphoric acid (PPA) [40 g, prepared from phosphorus pentoxide (20 g) and phosphoric acid (> 98%, 10 ml) heated to 100°C for 0.5 h] preheated to 125°C, were added the respective 1-tetralone (\approx 2 g, 0.015 mol) and acrylic acid (2.2 g, 0.03 mol). The reaction mixture was maintained at this temperature for 4.5 to 5.0 h with mechanical stirring. It was then cooled, quenched with ice water and left overnight. The solid obtained was separated by filtration. The residue as well as the

filtrate were extracted separately with chloroform. The combined chloroform extracts were washed thoroughly with sodium hydroxide (10%), water and dried (MgSO_4). Evaporation of the solvent left an oily residue which was chromatographed on silica gel. Elution with appropriate solvents yielded the respective products.

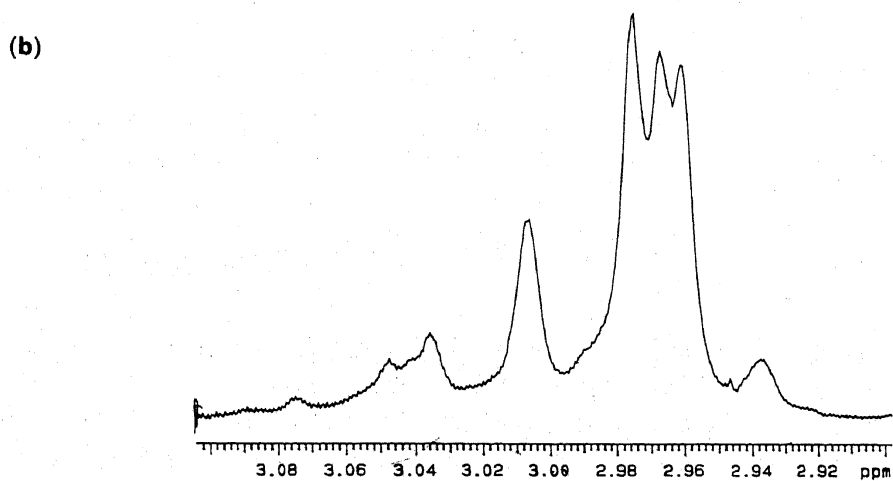
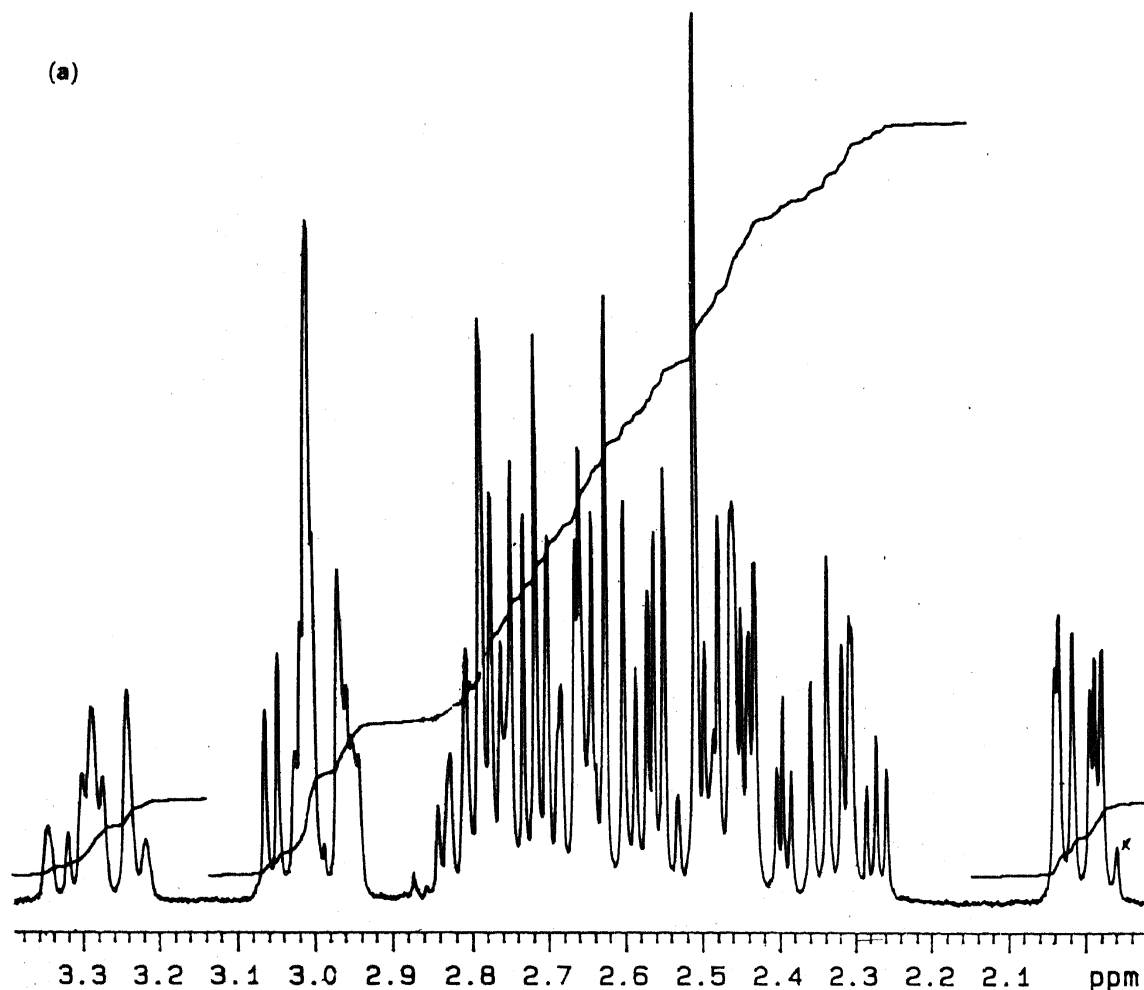


Figure 2. (a and b) (Caption on facing page.)

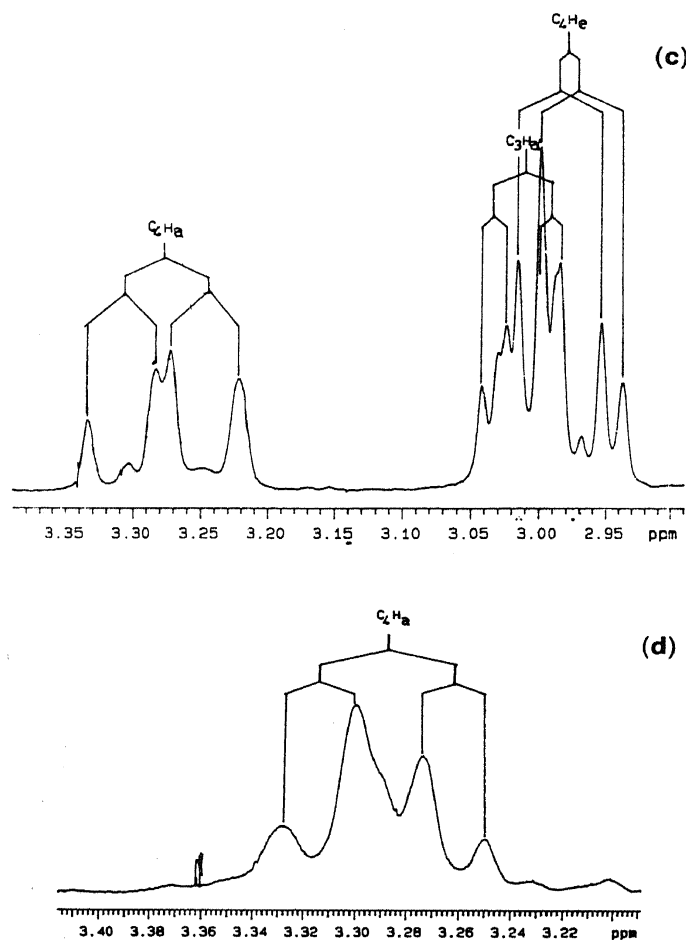


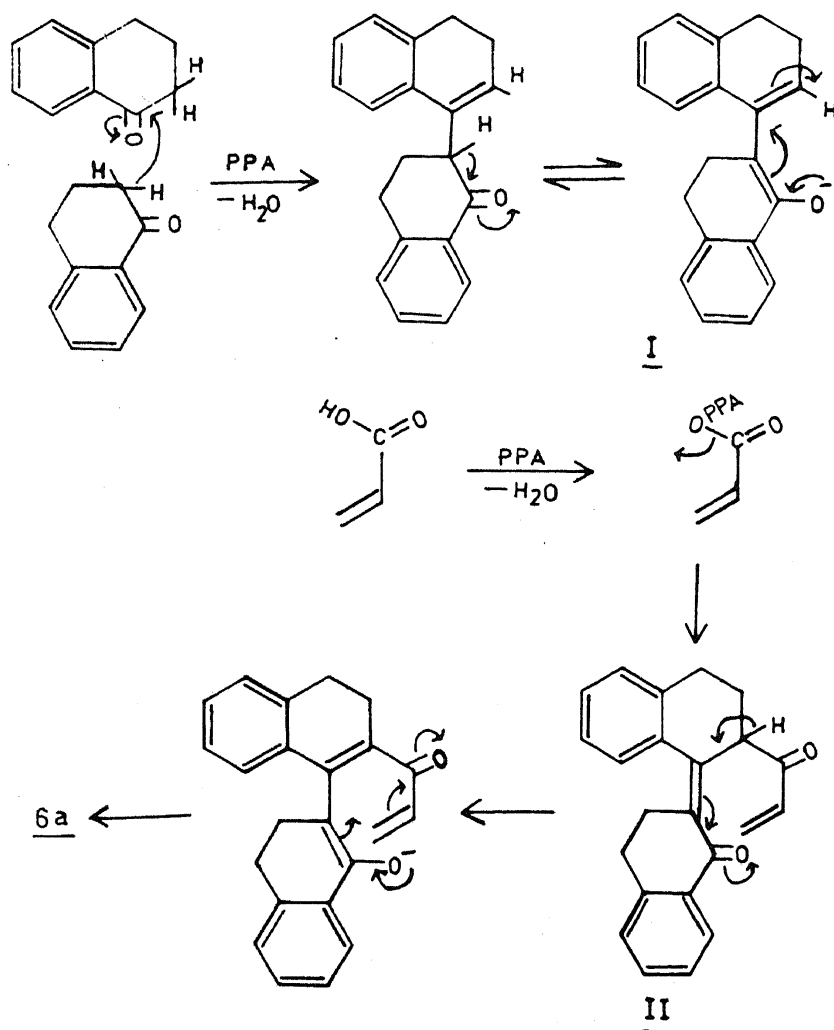
Figure 2. 300 MHz ^1H NMR spectrum of **3b**, region δ 1.9–3.4 (a), decoupled at δ 3.3 ppm (b), δ 2.0 ppm (c), and δ 2.98 ppm (d).

$R_1 - R_5 = \text{H}$: 2,3,5,6-Tetrahydro-4H-naphtho(1,2-b)pyran-4-one (**5a**): Pale yellow crystals from benzene: pet. ether (60–80), m.p., 60°C. UV λ^{MeOH} nm(log ϵ): 210(4.0), 232(4.3), 325(4.4). IR(KBr)(ν , cm^{-1}): 1650(C=O), 1620, 1595(Ar). ^1H NMR(300 MHz, CDCl_3) δ : 2.62(t, $J = 8.23$ Hz, 2H, $\text{CH}_2 - 5$), 2.7(t, $J = 6.8$ Hz, 2H, $\text{CH}_2 - 3$), 2.82(t, $J = 8.23$ Hz, 2H, $\text{CH}_2 - 6$), 4.63(t, $J = 6.8$ Hz, 2H, $\text{CH}_2 - 2$), 7.22(dd, $J = 7.3$ Hz, 1H, CH – 7), 7.28(dt, $J = 7.5, 1.46$ Hz, 1H, CH – 8), 7.36(dt, $J = 7.3, 1.46$ Hz, 1H, CH – 9), 7.69(dd, $J = 7.5, 1.3$ Hz, 1H, CH – 10). Analysis – Calculated for $\text{C}_{13}\text{H}_{12}\text{O}_2$: C, 78.0; H, 6.0%. Found: C, 77.9; H, 6.2%. MS: (m/z , 70 eV): 200(M^+), 172, 156, 144, 118, 115, 90.

2,4-Dinitrophenylhydrazone derivative: Orange red crystals from benzene, m.p. 243–44°C. Analysis – Calculated for $\text{C}_{19}\text{H}_{15}\text{N}_4\text{O}_5$: N, 14.8%. Found: N, 15.0%.

Semicarbazone derivative: Pale yellow needles from benzene: pet. ether (60 – 80), m.p. 231–32°C. Analysis – Calculated for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}_2$: N, 16.3%. Found: N, 16.15%.

$R_1 - R_5 = \text{H}$: 2',3,3',4',9',10'-Hexahydrospiro[naphthalene-2,4'-phenanthrene]-1,1'-dione (**6a**): Crystallised from chloroform:ethanol as colourless prisms, m.p. 180–81°C. UV λ^{MeOH} nm(log ϵ): 212(4.2), 237(4.1), 252(4.2), 298(4.2). IR(KBr)(ν , cm^{-1}): 1695, 1680 (C=O); 1620, 1580(Ar). ^1H NMR (300 MHz, CDCl_3) δ : 2.0(m, $J = 10.2, 6.4$, 3.2



Scheme 2.

Hz, 1H, $\text{CH}_a - 3$), 2.24–2.9(m, 8H, $\text{CH}_2 - 2', 3', 9', 10'$), 2.9–3.01(br m, $J = 18.2, 4.9, 3.2$ Hz, 1H, $\text{CH}_e - 4$), 2.98–3.05(br m, $J = 15.1, 10.1, 4.9$ Hz, 1H, $\text{CH}_a - 3$), 3.29(ddd, $J = 18.2, 15.2, 6.4$ Hz, 1H, $\text{CH}_a - 4$), 6.92(d, $J = 7.7$ Hz, CH – 8), 7.02(dt, $J = 7.9, 2.0$ Hz, 1H, CH – 6), 7.14–7.25(m, 2H, CH – 5', 7'), 7.33(d, 1H, CH – 5), 7.43(t, $J = 7.7$ Hz, 1H, CH – 7), 7.58(dt, $J = 7.8, 1.5$ Hz, 1H, CH – 6), 8.2(dd, $J = 7.9, 1.3$ Hz, 1H, CH – 8). ^{13}C NMR (300 MHz, CDCl_3): 197.42(s), 196.75(s), 151.9(s), 142.1(s), 139.42(s), 136.48(s), 133.74(d), 131.32(s), 130.68(s), 128.77(d), 128.42(d), 128.15(d), 127.89(d), 127.04(d), 126.92(d), 125.44(d), 49.19(s, C 2–4'), 33.31(t), 31.84(t), 29.28(t), 27.73(t), 24.85(t), 20.54(t). Analysis – Calculated for $\text{C}_{23}\text{H}_{20}\text{O}_2$: C, 84.14; H, 6.09%. Found: C, 84.0; H, 5.98%. MS (m/z , 70 ev): 328(M^+), 224, 196, 181, 168, 139.

2,4-Dinitrophenylhydrazone derivative: Orange crystals from chloroform:benzene, m.p. 254–55°C. Analysis – Calculated for $\text{C}_{29}\text{H}_{24}\text{N}_4\text{O}_5$: N, 11.02%. Found: N, 11.2%.

$R_1 - R_5 = \text{H}$: 2,3,5,6-Tetrahydrocyclopenta[3',2'–3,4]naphtho(1,2-b)-pyran-4,7-dione (7a): Crystallised from chloroform:pet. ether (60–80) as colourless needles, m.p.

Table 1. Reaction of 1-tetralone (3) with acrylic acid.

1-Tetralone (moles)	Acrylic acid (moles)	Temperature (°C)	Eluting solvent X:Y:Z	Products (% yield)
1	2	125	1:1:—	5a (60)
			—:1:—	6a (10)
			—:8:2	7a (02)
2	1	135–140	1:1:—	5a (08)
			—:1:—	6a (65)
			—:8:2	7a (nil)
1	2	140–145	1:1:—	5a (50)
			—:1:—	6a (20)
			—:8:2	7a (10)

X = pet. ether (60°–80°), Y = benzene, Z = chloroform.

276–77°C. UV λ^{MeOH} nm(log ϵ): 277(4.9), 278(4.9), 290(4.7), 305(4.8), 314(4.8), 354(4.6), 369(4.6). IR(KBr) (ν , cm^{-1}): 1680(s, C=O), 1620, 1548(Ar). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 2.75(m, 2H, $\text{CH}_2 - 6$), 2.96(t, $J = 6.6$ Hz, 2H, $\text{CH}_2 - 3$), 3.53(m, 2H, $\text{CH}_2 - 5$), 4.85(t, $J = 6.6$ Hz, 2H, $\text{CH}_2 - 2$), 7.59(ddd, $J = 7.02, 8.39, 1.37$ Hz, 1H, CH – 10), 7.79(ddd, $J = 8.24, 7.02, 1.37$ Hz, 1H, CH – 9), 8.32(ddd, $J = 8.39, 1.37, 0.765$ Hz, 1H, CH – 8), 9.2(d, $J = 8.24$ Hz, 1H, CH – 11). Analysis – Calculated for $\text{C}_{16}\text{H}_{12}\text{O}_3$: C, 76.19; H, 4.76%. Found: C, 76.32; H, 4.5%. MS: (m/z , 70 ev): 252(M^+), 224, 196, 181, 168, 139.

2,4-Dinitrophenylhydrazone derivative: Bright red crystals from dioxane:chloroform, m.p. 332–33°C with decomposition. Analysis – Calculated for $\text{C}_{22}\text{H}_{15}\text{N}_4\text{O}_6$: N, 12.99%. Found: N, 12.85%.

$R_2 - R_5 = \text{H}$, $R_1 = \text{CH}_3$: *2-Methyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-b)-pyran-4-one (5b)*: Pale yellow crystals from benzene:pet. ether (60–80), m.p. 73–74°C. IR(KBr) (ν , cm^{-1}): 1650(C=O), 1610, 1595(Ar). $^1\text{H NMR}$ (80 MHz, CDCl_3) δ : 1.59(d, $J = 6.32$ Hz, 1H, CH – 2), 2.5–2.8(m, 6H, $\text{CH}_2 - 3, 5, 6$), 4.4–4.9(m, 1H, CH – 2), 7.23–7.34(m, 3H, CH – 7, 8, 9), 7.7(d, 1H, CH – 10). Analysis – Calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.5; H, 6.54%. Found: C, 78.3; H, 6.41%.

2,4-Dinitrophenylhydrazone derivative: Red crystals from benzene, m.p. 252°C.

$R_2 - R_5 = \text{H}$, $R_1 = \text{CH}_3$: *2',3,3',4,9',10'-Hexahydro-3'-methylspiro[naphthalene-2,4'-phenanthrene]-1,1'-dione (6b)*: Shining prisms from chloroform:ethanol, m.p. 228°C. IR(KBr) (ν , cm^{-1}): 1660(sbr, C=O), 1610, 1560(Ar). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.25(d, $J = 6.87$ Hz, 3H, $\text{CH}_3 - 3'$), 2.0(m, 1H, $\text{CH}_e - 3$), 2.1–2.9(m, 6H, $\text{CH}_2 - 2', 9', 10'$ & CH – 3'), 3.0(m, 2H, $\text{CH}_e - 4\text{CH}_a - 3$), 3.2(m, 1H, $\text{CH}_a - 4$), 6.9(d, $J = 7.8$ Hz, 1H, CH – 8'), 7.03(t, 1H, CH – 6'), 7.12–7.24(m, 2H, CH – 5', 7'), 7.32(d, 1H, CH – 5), 7.41(t, 1H, CH – 7), 7.57(dt, 1H, CH – 6), 8.22(d, 1H, CH – 8). Analysis – Calculated for $\text{C}_{24}\text{H}_{22}\text{O}_2$: C, 84.2; H, 6.43%. Found: C, 84.3; H, 6.3%.

$R_3 - R_5 = \text{H}$, $R_1 = R_2 = \text{CH}_3$: *2,6-Dimethyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-b)pyran-4-one (5c)*: 4-Methyl-1-tetralone (2 g, 0.013 mol) reacted with crotonic acid (1.9 g, 0.028 mol). Elution of the chromatogram with pet. ether (60–80): benzene (60:40) gave a pale yellow oil; yield 86%. On keeping the oil solidified and crystallised from

benzene:pet. ether (60–80) into colourless needles, m.p. 55–56°C. IR(KBr) (ν , cm^{-1}): 1660(C=O), 1610, 1595(Ar). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ : 1.23–1.26(*d*, $J = 9.46$ Hz, 3H, $\text{CH}_3 - 6$), 1.20–1.24(*d*, $J = 9.3$ Hz, 3H, $\text{CH}_3 - 6$), 1.549–1.569(*d*, $J = 6.26$ Hz, 3H, $\text{CH}_3 - 2$), 1.546–1.567(*d*, $J = 6.4$ Hz, 3H, $\text{C}_3 - 2$), 2.38–2.73(*m*, 4H, $2\text{CH}_2 - 3, 5$), 4.58–4.68(*m*, 1H, $2\text{CH} - 2$), 7.2–7.32(*m*, 2H, $2\text{CH} - 7, 9$), 7.34–7.42(*t*, 1H, $2\text{CH} - 8$), 7.72–7.76(*dd*, $J = 7.6, 1.4$ Hz, 1H, $2\text{CH} - 10$). Analysis – Calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.95; H, 7.02%. Found: C, 78.8; H, 6.9%.

$R_1 - R_3 = R_5 = \text{H}$, $R_4 = \text{CH}_3$: 9-Methyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-b)pyran-4-one (5d): 7-Methyl-1-tetralone (Eisenbraun *et al* 1971) (2.0 g, 0.013 mol) reacted with acrylic acid (1.9 g, 0.028 mol) in PPA (20 g). Elution of the chromatogram with pet. ether (60–80):benzene (50:50) afforded the naphthopyrone as an oil which was purified by bulb-to-bulb distillation (170°C/0.8 mm); yield 64%. IR(neat) (ν , cm^{-1}): 1660(C=O), 1610, 1565(Ar). $^1\text{H NMR}$ (80 MHz, CDCl_3) δ : 2.35(*s*, 3H, $\text{CH}_3 - 9$), 2.4–2.9(*m*, 6H, $\text{CH}_2 - 3, 5, 6$), 4.6(*t*, $J = 6.4$ Hz, 2H, $\text{CH}_2 - 2$), 7.1 (*d*, $J = 7.8$ Hz, 1H, $\text{CH} - 7$), 7.3(*d*, $J = 7.8$ Hz, 1H, $\text{CH} - 8$), 7.53(*s*, 1H, $\text{CH} - 10$). Analysis – Calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.5; H, 6.5%. Found: C, 78.63; H, 6.3%.

2,4-Dinitrophenylhydrazone derivative: Orange-red crystals from benzene, m.p. 218–19°C. Analysis – Calculated for $\text{C}_{20}\text{H}_{15}\text{N}_4\text{O}_5$: N, 14.5%. Found: N, 14.3%.

$R_2 = R_3 = R_5 = \text{H}$, $R_1 = R_4 = \text{CH}_3$: 2,9-Dimethyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-b)pyran-4-one (5e): 7-Methyl-1-tetralone (Eisenbraun *et al* 1971) 2 g, 0.013 mol) reacted with crotonic acid (2.4 g, 0.028 mol) in PPA (20 g). Elution of the chromatogram with pet. ether (60–80):benzene (60:40) afforded the naphthopyrone as a red oil which was purified by bulb-to-bulb distillation (188°C/2 mm); yield 63%. IR (neat) (ν , cm^{-1}): 1660(C=O); 1610, 1565(Ar). $^1\text{H NMR}$ (80 MHz, CDCl_3) δ : 1.5(*d*, $J = 6.2$ Hz, 3H, $\text{CH}_3 - 2$), 2.34(*s*, 3H, $\text{CH}_3 - 9$), 2.5–2.8(*m*, 6H, $\text{CH}_2 - 3, 5, 6$), 4.6 (*m*, 1H, $\text{CH} - 2$), 7.0(*d*, $J = 7.8$ Hz, 1H, $\text{CH} - 7$), 7.2(*d*, $J = 7.8$ Hz, 1H, $\text{CH} - 8$), 7.45 (*s*, 1H, $\text{CH} - 10$). Analysis – Calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.9; H, 7.0%. Found: C, 78.4; H, 7.4%.

2,4-Dinitrophenylhydrazone derivative: Orange red crystals from benzene, m.p. 210–11°C. Analysis – Calculated for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_5$: N, 13.7%. Found: N, 13.3%.

$R_1 = R_2 = R_4 = \text{H}$, $R_3 = R_5 = \text{CH}_3$: 7,10-Dimethyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-b)pyran-4-one (5f): 5,8-Dimethyl-1-tetralone (Eisenbraun *et al* 1971) (2 g, 0.012 mol) reacted with acrylic acid (1.8 g, 0.024 mol) in PPA (20 g). Elution of the chromatogram with pet. ether:benzene (50:50) afforded the naphthopyrone as a pale yellow oil which was purified by bulb-to-bulb distillation (192°C/1 mm); yield 78%. IR (neat) (ν , cm^{-1}): 1690(C=O), 1630, 1612(Ar). $^1\text{H NMR}$ (80 MHz, CDCl_3) δ : 2.16(*s*, 3H, $\text{CH}_3 - 7$), 2.33(*s*, 3H, $\text{CH}_3 - 10$), 2.5–2.8(*m*, 6H, $\text{C}_2 - 3, 5, 6$), 4.6(*t*, 1H, $\text{CH} - 2$), 6.95–7.5(*dd*, 2H, $\text{CH} - 8, 9$). Analysis – Calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.9; H, 7.0%. Found: C, 78.8; H, 7.15%.

2,4-Dinitrophenylhydrazone derivative: Orange-red crystals from benzene, m.p. 222–23°C. Analysis – Calculated for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_5$: N, 13.7%. Found: N, 14.05%.

$R_2 = R_4 = \text{H}$, $R_1 = R_3 = R_5 = \text{CH}_3$: 2,3,5,6-Tetrahydro-2,7,10-trimethyl-4H-naphtho(1,2-b)pyran-4-one (5g): 5,8-Dimethyl-1-tetralone (Eisenbraun *et al* 1971) (2 g, 0.012 mol) reacted with crotonic acid (2 g, 0.024 mol) in PPA (20 g). Elution in pet. ether(60–80):benzene (70:30) yielded the naphthopyrone as a red oil which was

purified by bulb-to-bulb distillation (198°C/1 mm); yield 71%. IR (neat) (ν , cm^{-1}): 1650 (C=O), 1610, 1595 (Ar). ^1H NMR (80 MHz, CDCl_3) δ : 1.57(*d*, $J = 6.22$ Hz, 3H, $\text{CH}_3 - 2$), 2.25(*s*, 3H, $\text{CH}_3 - 7$), 2.34(*s*, 3H, $\text{CH}_3 - 10$), 2.47–2.73(*m*, 6H, $\text{CH}_2 - 3, 5, 6$), 4.6(*m*, 1H, CH – 2), 6.9–7.4(*m*, 2H, CH – 8, 9). Analysis – Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.3; H, 7.4%. Found: C, 79.5; H, 7.7%.

2,4-Dinitrophenylhydrazone derivative: Red crystals from benzene, m.p. 219–20°C, Analysis – Calculated for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_5$: N, 13.3%. Found: N, 13.5%.

$R_1 = R_2 = R_5 = \text{H}$, $R_3 = R_4 = \text{CH}_3$: 7,9-Dimethyl-2,3,5,6-tetrahydro-4H-naphtho(1,2-*b*)pyran-4-one (5h): 5,7-Dimethyl-1-tetralone (Eisenbraun *et al* 1971) (2 g, 0.012 mol) reacted with acrylic acid (1.8 g, 0.024 mol) in PPA (20 g). Elution with pet. ether (60–80):benzene (60:40) afforded the naphthopyrone as a colourless oil which was purified by bulb-to-bulb distillation (170°C/1.5 mm), yield 68%. IR (neat) (ν , cm^{-1}): 1665 (C=O); 1595, 1550 (Ar). ^1H NMR (80 MHz CDCl_3) δ : 2.26, 2.34(*ss*, 6H, $2\text{CH}_3 - 5, 7$), 2.4–2.9(*m*, 6H, $\text{CH}_2 - 3, 5, 6$), 4.6(*t*, $J = 6.96$ Hz, 2H, $\text{CH}_2 - 2$), 6.85(*s*, 1H, CH – 8), 7.0(*s*, 1H, CH – 10). Analysis – Calculated for $\text{C}_{15}\text{H}_{16}\text{O}_2$: C, 78.9; H, 7.0%. Found: C, 79.0; H, 7.2%.

2,4-Dinitrophenylhydrazone derivative: Orange red crystals from benzene, m.p. 213–14°C. Analysis – Calculated for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_5$: N, 13.7%. Found: N, 13.4%

$R_2 = R_5 = \text{H}$, $R_1 = R_3 = R_4 = \text{CH}_3$: 2,3,5,6-Tetrahydro-2,7,9-trimethyl-4H-naphtho(1,2-*b*)pyran-4-one (5i): 5,7-Dimethyl-1-tetralone (Eisenbraun *et al* 1971) (2 g, 0.012 mol) reacted with crotonic acid (2 g, 0.024 mol) in PPA (20 g). Elution with pet. ether (60–80):benzene (50:50) afforded red oil which was purified by bulb distillation (187°C/1.5 mm); yield 84%. IR (neat) (ν , cm^{-1}): 1660 (C=O), 1610 (Ar). ^1H NMR (80 MHz, CDCl_3) δ : 1.5(*d*, $J = 6.2$ Hz, 3H, $\text{CH}_3 - 2$); 2.24, 2.23(*ss*, 6H, $\text{CH}_3 - 5, 7$), 2.4–2.9(*m*, 6H, $\text{CH}_2 - 3, 5, 6$), 4.6(*m*, 1H, CH – 2), 6.8(*s*, 1H, CH – 8), 7.01(*s*, 1H, CH – 10). Analysis – Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.3, H, 7.4%. Found: C, 79.6, H, 7.1%.

2,4-Dinitrophenylhydrazone derivative: Orange red crystals from benzene, m.p. 232–33°C. Analysis – Calculated for $\text{C}_{22}\text{H}_{22}\text{N}_4\text{O}_5$: N, 13.3%. Found: N, 12.9%.

*Dehydrogenation of 5a to 4H-naphtho(1,2-*b*)pyran-4-one (8)*: 5a (100 mg, 0.0005 mol) was taken in diphenyl ether (50 ml) to which was added Pd/C (10%, 10 mg). The mixture was refluxed for 36 h, cooled and filtered. The mixture was then subjected to steam distillation. The residue crystallised from pet. ether(60–80) as pale brown crystals, m.p. 120–21°C (95 mg, 96%). Further purification by sublimation (140°C) *in vacuo* (2 mm) gave colourless crystals, 123–24°C (lit. 121–23°C). IR (KBr) (ν , cm^{-1}): 1665(*s*, C=O), Analysis – Calculated for $\text{C}_{13}\text{H}_8\text{O}_2$: C, 79.6; H, 4.1%. Found: C, 79; H, 4.4%.

4. Conclusion

In summary, we have shown a simple and versatile method for the synthesis of naphtho(1,2-*b*)pyran-4-ones by condensation of various substituted 1-tetralones with α , β -unsaturated acids such as acrylic and crotonic acids. Further, the same reaction can be used to synthesise the hitherto unknown spiro[naphthalene-2,4'-phenanthrene]-1,1'-diones as the major product by proper control of stoichiometry and temperature of the reaction.

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