

## Reactions of dialkoxynaphthalenes with cyclic $\alpha,\beta$ -unsaturated acids

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**Abstract.** Synthetically useful substituted hexahydrobenzofluoren-11-ones and tetrahydropentalenonaphthalen-10(H)-ones are prepared in one step by the reaction of cyclic  $\alpha,\beta$ -unsaturated acids, namely, 1-cyclohexene-1-carboxylic acid and 1-cyclopentene-1-carboxylic acid, with substituted dialkoxynaphthalenes in the presence of polyphosphoric acid. The stereochemistry at the C/D ring junction is determined from the  $^1\text{H}$  NMR and by decoupling experiments.

**Keywords.** 1-Cyclohexene-1-carboxylic acid; 1-cyclopentene-1-carboxylic acid; hexahydrobenzofluorenone; tetrahydropentalenonaphthalenone.

### 1. Introduction

In a project for the synthesis of polycyclic compounds, we investigated the reaction of dialkoxynaphthalenes with cyclic  $\alpha,\beta$ -unsaturated acids, such as 1-cyclohexene-1-carboxylic acid (A) and 1-cyclopentene-1-carboxylic acid (B) (Wheeler and Lerner 1956) in the presence of polyphosphoric acid (PPA) at 90–95°C. The products isolated after column chromatography were identified as hexahydrobenzofluoren-11-one and tetrahydropentalenonaphthalen-10(H)-one derivatives. Similar types of compounds have been reported as intermediates for the synthesis of C-nor- and C-nor-D-homosteroids (Eglinton *et al* 1956). The methods hitherto available for the synthesis of the above are elaborate and inconvenient. We describe here a simple one-step synthesis giving about 40 to 50% yields of the above compounds.

### 2. Results and discussion

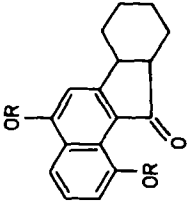
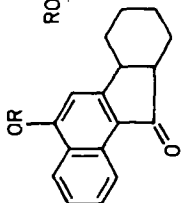
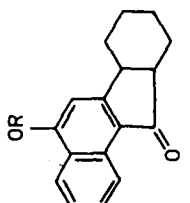
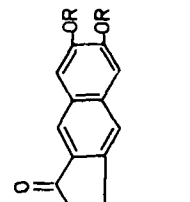
1,5-Dimethoxynaphthalene with acid (A) afforded 1,5-dimethoxy-6b,7,8,9,10,10a-hexahydro-11H-benzo(a) fluoren-11-one (Ia) in the presence of PPA. The spectral data are given in table 1.

Theoretically, a number of structures are possible for the product, depending on whether a Friedel-Crafts acylation has occurred first followed by cyclisation or a Michael type addition has taken place followed by ring closure (Chart 1).

Out of these possible structures the linear structure (I'a) is ruled out on the basis of the UV spectrum of Ia (table 1) which supports the angular structure as the data are similar to those of the known angular structures (Moffatt 1966). The structure I'a is ruled out on the basis of  $^1\text{H}$  NMR data (table 1), since the C<sub>6</sub> proton in Ia appears at  $\delta$  6.72 and in the alternate structure I'a it would have appeared

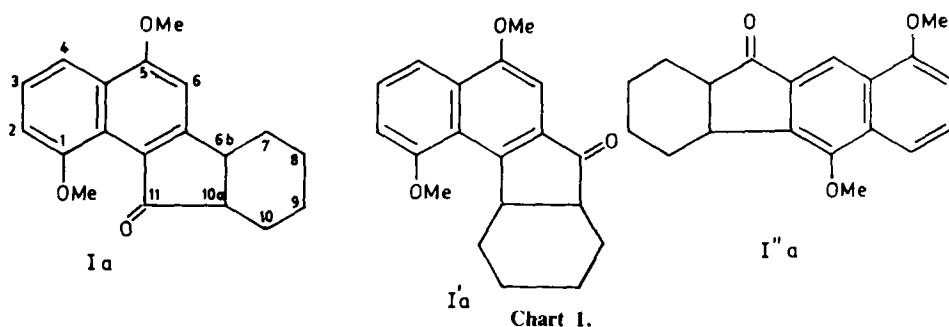
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Table 1.

Dialkoxy-naphthalene used	Compound number	Eluting solvent a:b*	m.p. (°C)	Molecular formula	Analysis (%)		Spectral data	
					Calcd C	Found H		
 Ia - R = Me Ib - R = Et	Ia	40:60	119-20	C <sub>19</sub> H <sub>20</sub> O <sub>3</sub>	77.0 (76.8)	6.8 (6.8)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log $\epsilon$ ): 233 (4.37); 253 (4.33); 316 (3.88); 338 (3.89) nm. IR (Nujol) $\nu_{\text{max}}$ : 1700 (>C=O); 1590, 1510, 840 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.15-2.5 (8H, m, CH <sub>2</sub> -7,8,9,10); 2.7-3.0 (1H, q, C <sub>10a</sub> H); 3.15-3.5 (1H, q, C <sub>6a</sub> H); 4.0 (6H, s, two-OCH <sub>3</sub> ); 6.72 (1H, s, C <sub>6</sub> H); 7.0 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.3 (1H, t, C <sub>3</sub> H); 7.88 (1H, d, J = 8 Hz, C <sub>4</sub> H).	
	 IIa - R = Me IIb - R = Et	IIa	40:60	128-29	C <sub>19</sub> H <sub>20</sub> O <sub>3</sub>	77.0 (77.3)	6.8 (6.6)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log $\epsilon$ ): 239 (4.41); 325 (4.00) nm. IR (Nujol) $\nu_{\text{max}}$ : 1700 (>C=O); 1640, 1600, 1530 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.15-2.4 (8H, m, CH <sub>2</sub> -7,8,9,10); 2.7-3.0 (1H, q, C <sub>10a</sub> H); 3.3-3.5 (1H, q, C <sub>6a</sub> H); 4.0 (6H, d, two -OCH <sub>3</sub> ); 6.7 (1H, s, C <sub>6</sub> H); 7.0 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>3</sub> H); 8.1 (1H, d, J = 8 Hz, C <sub>4</sub> H); 8.56 (1H, d, J = 2 Hz, C <sub>1</sub> H).
		IIb	60:40	110-11	C <sub>21</sub> H <sub>24</sub> O <sub>3</sub>	77.8 (77.6)	7.4 (7.3)	IR (Nujol) $\nu_{\text{max}}$ : 1700 (>C=O); 1580, 1520, 1480 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.25-2.5 (14H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -7,8,9,10); 2.8-3.0 (1H, q, C <sub>10a</sub> H); 3.1-3.4 (1H, q, C <sub>6a</sub> H); 4.2 (4H, q, two -OCH <sub>3</sub> ); 6.7 (1H, s, C <sub>6</sub> H); 7.0 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.3 (1H, t, C <sub>3</sub> H); 7.88 (1H, d, J = 8 Hz, C <sub>4</sub> H).
	 IIIa - R = Me	IIIa	40:60	128-29	C <sub>19</sub> H <sub>20</sub> O <sub>3</sub>	77.0 (76.8)	6.8 (6.8)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log $\epsilon$ ): 233 (4.37); 253 (4.33); 316 (3.88); 338 (3.89) nm. IR (Nujol) $\nu_{\text{max}}$ : 1700 (>C=O); 1590, 1510, 840 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.15-2.5 (8H, m, CH <sub>2</sub> -7,8,9,10); 2.7-3.0 (1H, q, C <sub>10a</sub> H); 3.15-3.5 (1H, q, C <sub>6a</sub> H); 4.0 (6H, s, two-OCH <sub>3</sub> ); 6.72 (1H, s, C <sub>6</sub> H); 7.0 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.3 (1H, t, C <sub>3</sub> H); 7.88 (1H, d, J = 8 Hz, C <sub>4</sub> H).
 IVa - R = Me IVb - R = Et		IVa	40:60	119-20	C <sub>19</sub> H <sub>20</sub> O <sub>3</sub>	77.0 (76.8)	6.8 (6.8)	UV $\lambda_{\text{max}}^{\text{MeOH}}$ (log $\epsilon$ ): 233 (4.37); 253 (4.33); 316 (3.88); 338 (3.89) nm. IR (Nujol) $\nu_{\text{max}}$ : 1700 (>C=O); 1590, 1510, 840 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.15-2.5 (8H, m, CH <sub>2</sub> -7,8,9,10); 2.7-3.0 (1H, q, C <sub>10a</sub> H); 3.15-3.5 (1H, q, C <sub>6a</sub> H); 4.0 (6H, s, two-OCH <sub>3</sub> ); 6.72 (1H, s, C <sub>6</sub> H); 7.0 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.3 (1H, t, C <sub>3</sub> H); 7.88 (1H, d, J = 8 Hz, C <sub>4</sub> H).

1,7-	IIIa	184-85	$C_{19}H_{20}O_3$	77-0 (77-3)	6.8 (6-6)	IR (Nujol) $\nu_{\max}$ : 1685 (>C=O); 1590, 1520, 1480 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-12-2-35 (8H, m, CH <sub>2</sub> -7,8,9,10); 2-68-2-98 (1H, q, C <sub>10a</sub> H); 3-35-3-56 (1H, q, C <sub>6b</sub> H); 4-0 (6H, d, two -OCH <sub>3</sub> ); 6-72 (1H, s, C <sub>6</sub> H); 7-3 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>2</sub> H); 7-57 (1H, d, J = 2 Hz, C <sub>4</sub> H); 9-03 (1H, d, J = 8 Hz, C <sub>1</sub> H).	7.4 (7-5)	UV $\lambda_{\max}^{MeOH}$ (log $\epsilon$ ): 239 (3-85), 257 (3-80); 328 (3-38) nm. IR (Nujol) $\nu_{\max}$ : 1680 (>C=O); 1640, 1600, 1520 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-3-2-4 (14H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -7,8,9,10); 2-6-3-0 (1H, q, C <sub>10a</sub> H); 3-2-3-55 (1H, q, C <sub>6b</sub> H); 4-25 (4H, q, two -OCH <sub>3</sub> ); 6-7 (1H, s, C <sub>6</sub> H); 7-15 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>3</sub> H); 8-2 (1H, d, J = 8 Hz, C <sub>4</sub> H); 8-55 (1H, d, J = 2 Hz, C <sub>1</sub> H).	77-8 (77-7)	70:30	124-25	$C_{21}H_{24}O_3$	IVb	70:30	124-25	$C_{21}H_{24}O_3$	77-8 (77-7)	7.4 (7-5)	UV $\lambda_{\max}^{MeOH}$ (log $\epsilon$ ): 239 (3-85), 257 (3-80); 328 (3-38) nm. IR (Nujol) $\nu_{\max}$ : 1680 (>C=O); 1640, 1600, 1520 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-3-2-4 (14H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -7,8,9,10); 2-6-3-0 (1H, q, C <sub>10a</sub> H); 3-2-3-55 (1H, q, C <sub>6b</sub> H); 4-25 (4H, q, two -OCH <sub>3</sub> ); 6-7 (1H, s, C <sub>6</sub> H); 7-15 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>3</sub> H); 8-2 (1H, d, J = 8 Hz, C <sub>4</sub> H); 8-55 (1H, d, J = 2 Hz, C <sub>1</sub> H).
2,3-	IVa	158-59	$C_{19}H_{20}O_3$	77-0 (76-9)	6.8 (6-7)	UV $\lambda_{\max}^{MeOH}$ (log $\epsilon$ ): 264-5 (4-33); 307 (3-81) nm. IR (Nujol) $\nu_{\max}$ : 1680 (>C=O); 1620, 1500, 1480 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-1-2-5 (8H, m, CH <sub>2</sub> -1,2,3,4); 2-7-3-0 (1H, m, C <sub>10a</sub> H); 3-6-3-85 (1H, m, C <sub>4a</sub> H); 4-0 (6H, d, two -OCH <sub>3</sub> ); 7-12 (1H, s, C <sub>5</sub> H); 7-2 (1H, s, C <sub>10</sub> H); 7-5 (2H, s, C <sub>6</sub> and C <sub>9</sub> H).	7.4 (7-3)	IR (Nujol) $\nu_{\max}$ : 1680 (>C=O); 1620, 1520, 1480 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-0-2-35 (14H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -1,2,3,4); 2-65-3-0 (1H, m, C <sub>10a</sub> H); 3-65-3-95 (1H, m, C <sub>4a</sub> H); 4-2 (4H, q, two -OCH <sub>3</sub> ); 7-2 (1H, s, C <sub>5</sub> H); 7-3 (1H, s, C <sub>10</sub> H); 7-6 (2H, s, C <sub>6</sub> and C <sub>9</sub> H).	77-8 (77-9)	10:90	158-59	$C_{19}H_{20}O_3$	IVb	10:90	164-65	$C_{21}H_{24}O_3$	77-8 (77-9)	7.4 (7-3)	IR (Nujol) $\nu_{\max}$ : 1680 (>C=O); 1620, 1520, 1480 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1-0-2-35 (14H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -1,2,3,4); 2-65-3-0 (1H, m, C <sub>10a</sub> H); 3-65-3-95 (1H, m, C <sub>4a</sub> H); 4-2 (4H, q, two -OCH <sub>3</sub> ); 7-2 (1H, s, C <sub>5</sub> H); 7-3 (1H, s, C <sub>10</sub> H); 7-6 (2H, s, C <sub>6</sub> and C <sub>9</sub> H).

\* a = Petroleum ether (b.p. 60-80°); b = benzene.



downfield due to the anisotropic effect of the carbonyl group (Merchant and Upasani 1981). 1,5-Diethoxynaphthalene reacted similarly to give Ib (table 1 for spectral data).

The reaction of 1,5-dimethoxynaphthalene with acid (B) in presence of PPA yielded 1,5-dimethoxy-7,8,9,9a-tetrahydro-pentaleno[2,1-a]naphthalen-10(6bH)-one (Ic) (spectral data in table 2).

The structure Ic is in full agreement with the spectral data. 1,5-Diethoxynaphthalene reacted similarly with acid (B) to yield Id.

Similarly, 1,6-dimethoxy-(diethoxy)-naphthalene reacted with acid (A) to afford 2,5-dimethoxy-(diethoxy)-6b,7,8,9,10,10a-hexahydro-11H-benzo(a)-fluoren-11-one (IIa-b).

In the above structures, the ring D is fused *cis* to ring C as the *cis* fusion is most favoured thermodynamically (March 1977). This fact is supported by the  $^1\text{H}$  NMR spectra and the decoupling experiments.

The  $^1\text{H}$  NMR data of IIa is given in table 1. The  $J$  values are found to be 6.6, 6.1 and 8.5 Hz for the 6b proton and 6.6, 6.9 and 6.5 Hz for the 10a proton. The  $J$  value 6.6 which is the same in both the cases corresponds to that for the methine protons, and is less than 8 Hz. Hence, the two rings are *cis* fused. The rings are constantly flipping, thus changing the environments of the methine protons from axial to equatorial and vice-versa (more than  $10^3$  times per second). Hence the net result will be the average.

The possibility for the *trans* fusion can be ruled out as in this case the methine protons would have to be *trans* (March 1977) (axial-axial only) with each other and the  $J_{10a-6b}$  would have been above 8 Hz. Decoupling experiments confirm *cis* fusion. Irradiation at 1.3 ppm resulted in the collapse of the multiplet for H-6b into a doublet with  $J$  around 6.6 Hz. The  $^{13}\text{C}$  NMR spectrum values are given below as a matter of interest.

$^{13}\text{C}$  NMR of IIa – 21.8 (*t*, C-9), 22.14 (*t*, C-8), 23.2 (*t*, C-7), 30.38 (*t*, C-10), 39.17 (*d*, C-10a), 48.31 (*d*, C-6b), 55.44 (*s*,  $\text{OCH}_3$ ), 55.86 (*s*,  $\text{OCH}_3$ ), 98.72 (*d*, C-3), 102.98 (*d*, C-6), 117.87 (*d*, C-4), 119.93 (*s*, C-4a), 121.99 (*s*, C-11b), 124.12 (*d*, C-1), 132.7 (*s*, C-6a), 160.8 (*s*, C-5), 161.8 (*s*, C-11a), 164.5 (*s*, C-2), 207.03 (*s*, C-11).

Heating 1,6-dimethoxy-(diethoxy)-naphthalene with acid (B) in the presence of PPA yielded 2,5-dimethoxy-(diethoxy)-7,8,9,9a-tetrahydro-pentaleno[2,1-a]naphthalen-10(6bH)-one (IIc-d).

For this compound, two sets of  $J$  values were obtained, namely 2.6, 8.5, 6.2 Hz for the 6b proton and 1.8, 9.2, 6.2 Hz for the 9a proton. The  $J$  value 6.2 which is the

Table 2.

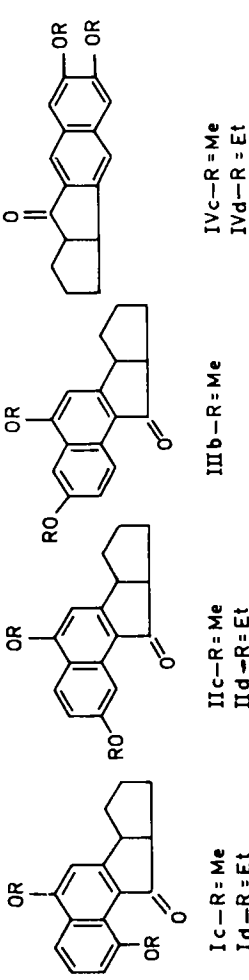
Dialkoxy-naphthalene used	Compound number	Eluting solvent a:b*	m.p. (°C)	Molecular formula	Analysis (%)		Spectral data
					Calcd C	Found H	
	Ic	90:10	140-41	C <sub>18</sub> H <sub>18</sub> O <sub>3</sub>	76.6 (76.4)	6.4 (6.5)	UV λ <sub>max</sub> <sup>MeOH</sup> (log ε): 235 (4.38); 255 (4.34); 320 (3.9) nm. IR (Nujol) ν <sub>max</sub> : 1700 (>C=O); 1600, 1520 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) δ: 1.15-2.25 (6H, m, CH <sub>2</sub> -7,8,9); 2.8-3.25 (1H, q, C <sub>9a</sub> H); 3.4-3.75 (1H, q, C <sub>6a</sub> H); 4.1 (6H, d, two -OCH <sub>3</sub> ); 6.72 (1H, s, C <sub>6</sub> H); 7.0 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.4 (1H, t, C <sub>3</sub> H); 7.8 (1H, d, J = 8 Hz, C <sub>4</sub> H).
	Id	90:10	114-15	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	77.4 (77.5)	7.1 (6.9)	IR: 1700 (>C=O); 1640, 1520, 1460 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) δ: 1.15-2.4 (12H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -7,8,9); 2.8-3.2 (1H, q, C <sub>9a</sub> H); 3.35-3.8 (1H, q, C <sub>6a</sub> H); 4.2 (4H, q, t, -OCH <sub>2</sub> ); 6.7 (1H, s, C <sub>6</sub> H); 6.95 (1H, d, J = 8 Hz, C <sub>2</sub> H); 7.3 (1H, t, C <sub>3</sub> H); 7.8 (1H, d, J = 8 Hz, C <sub>4</sub> H).
	Iic	20:80	135-36	C <sub>18</sub> H <sub>18</sub> O <sub>3</sub>	76.6 (76.6)	6.4 (6.4)	UV λ <sub>max</sub> <sup>MeOH</sup> (log ε): 240 (4.41); 328 (4.61) nm. IR (Nujol) ν <sub>max</sub> : 1680 (>C=O); 1640, 1600 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) δ: 1.25-2.5 (6H, m, CH <sub>2</sub> -7,8,9); 3.0-3.4 (1H, q, C <sub>9a</sub> H); 3.56-3.93 (1H, q, C <sub>6a</sub> H); 4.1 (6H, d, two -OCH <sub>3</sub> ); 6.7 (1H, s, C <sub>6</sub> H); 7.1 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>3</sub> H); 8.13 (1H, d, J = 8 Hz, C <sub>4</sub> H); 8.56 (1H, d, J = 2 Hz, C <sub>1</sub> H).
	Iid	30:70	131-32	C <sub>20</sub> H <sub>22</sub> O <sub>3</sub>	77.4 (77.5)	7.1 (7.3)	IR (Nujol) ν <sub>max</sub> : 1680 (>C=O); 1640, 1590 (ar) cm <sup>-1</sup> . NMR (CDCl <sub>3</sub> ) δ: 1.3-2.4 (12H, m, two -CH <sub>3</sub> , CH <sub>2</sub> -7,8,9); 3.0-3.4 (1H, q, C <sub>9a</sub> H); 3.5-3.9 (1H, q, C <sub>6a</sub> H); 4.25 (4H, q, two -OCH <sub>2</sub> ); 6.7 (1H, s, C <sub>6</sub> H); 7.1 (1H, dd, J = 2 Hz, J = 8 Hz, C <sub>3</sub> H); 8.2 (1H, d, J = 8 Hz, C <sub>4</sub> H); 8.55 (1H, d, J = 2 Hz, C <sub>1</sub> H).

Table 2 (Contd.)

1,7-	IIIb	158-59	$C_{18}H_{18}O_3$	76.6 (76.5)	6.4 (6.3)	IR (Nujol) $\nu_{max}$ : 1680 (>C=O); 1580, 1510 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.12-2.3 (6H, <i>m</i> , CH <sub>2</sub> -7,8,9); 3.0-3.25 (1H, <i>q</i> , C <sub>9a</sub> H); 3.6-3.85 (1H, <i>q</i> , C <sub>6b</sub> H); 4.0 (6H, <i>d</i> , two -OCH <sub>3</sub> ); 6.8 (1H, <i>s</i> , C <sub>6</sub> H); 7.35 (1H, <i>dd</i> , <i>J</i> = 2 Hz, <i>J</i> = 8 Hz, C <sub>2</sub> H); 7.55 (1H, <i>d</i> , <i>J</i> = 2 Hz, C <sub>4</sub> H); 9.05 (1H, <i>d</i> , <i>J</i> = 8 Hz, C <sub>1</sub> H).
2,3-	IVc	20.80	$C_{18}H_{18}O_3$	76.6 (76.8)	6.4 (6.1)	UV $\lambda_{max}^{MeOH}$ (log $\epsilon$ ): 224 (4.34); 254 (4.38); 263 (4.35); 309 (3.92) nm. IR (Nujol) $\nu_{max}$ : 1680 (>C=O); 1620, 1520 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.1-2.3 (6H, <i>m</i> , CH <sub>2</sub> -1,2,3); 3.0-3.4 (1H, <i>m</i> , C <sub>10a</sub> H); 3.75-4.0 (1H, <i>m</i> , C <sub>3a</sub> H); 4.1 (6H, <i>d</i> , two -OCH <sub>3</sub> ); 7.2 (1H, <i>s</i> , C <sub>4</sub> H); 7.35 (1H, <i>s</i> , C <sub>9</sub> H); 7.6 (2H, <i>s</i> , C <sub>5</sub> and C <sub>8</sub> H).
	IVd	10.90	$C_{20}H_{22}O_3$	77.4 (77.6)	7.1 (7.2)	IR (Nujol) $\nu_{max}$ : 1700 (>C=O); 1620, 1520 (ar) $cm^{-1}$ . NMR (CDCl <sub>3</sub> ) $\delta$ : 1.0-2.3 (12H, <i>m</i> , two -CH <sub>3</sub> , CH <sub>2</sub> -1,2,3); 3.0-3.4 (1H, <i>m</i> , C <sub>10a</sub> H); 3.75-4.0 (1H, <i>m</i> , C <sub>3a</sub> H); 4.32 (4H, <i>q</i> , two -OCH <sub>3</sub> ); 7.25 (1H, <i>s</i> , C <sub>4</sub> H); 7.35 (1H, <i>s</i> , C <sub>9</sub> H); 7.6 (2H, <i>s</i> , C <sub>5</sub> and C <sub>8</sub> H).

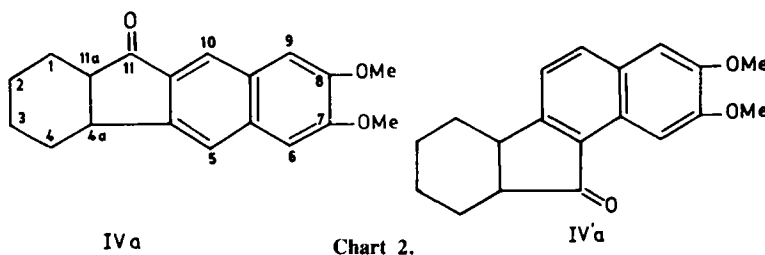
\* a = Petroleum ether (b.p. 60-80°); b = benzene.

same must be the coupling constant for the methine proton. This value is less than 8 Hz and hence the rings C/D are *cis* fused with each other. Decoupling experiments confirm *cis* fusion. Irradiation at 1.9 ppm resulted in the collapse of the multiplet at 3.75 into a doublet with  $J = 6.5$  Hz, which is the coupling constant for the methine protons. The  $^{13}\text{C}$  NMR values are given below as a matter of interest:

$^{13}\text{C}$  NMR of IIc – 24.36 (*t*, C-8), 30.5 (*t*, C-9), 32.5 (*t*, C-7), 44.33 (*d*, C-9a), 52.96 (*d*, C-6b), 55.48 (*s*,  $\text{OCH}_3$ ), 55.88 (*s*,  $\text{OCH}_3$ ), 99.15 (*d*, C-3), 103.04 (*d*, C-6), 117.96 (*d*, C-4), 120.04 (*s*, C-4a), 124.0 (*d*, C-1), 124.13 (*s*, C-10b), 132.04 (*s*, C-6a), 161.05 (*s*, C-5), 162.33 (*s*, C-10a), 164.62 (*s*, C-2), 208.54 (*s*, C-10).

When 1,7-dimethoxynaphthalene and 2,3-dialkoxynaphthalenes were reacted with acids (A) and (B) compounds IIIa to IVd were isolated in about 40% yields. The structures of the compounds were assigned on the basis of spectral and analytical data (tables 1 and 2).

2,3-Dimethoxynaphthalene reacted with acid (A) under the above mentioned conditions to give 7,8-dimethoxy-1,2,3,4,4a,11a-hexahydro-11H-benzo(b)fluoren-11-one (IVa) instead of the expected benzo(a)fluorenone. Its spectral data is given in table 1.



Of the possible structures, only structure IVa is in agreement with the NMR spectral evidence. In the NMR spectrum the aromatic protons at C-6 and C-9 appear as a two-proton singlet, whereas the C<sub>5</sub> and C<sub>10</sub> protons are observed as two different singlets. The singlet at  $\delta 7.2$  (attributed to C-10 proton) is shifted downfield due to the anisotropic effect of the carbonyl group, whereas in the alternate structure IV'a an AB pattern would have been observed for C<sub>5</sub>-C<sub>6</sub> protons along with two singlets and the proton at C-1 would have been shifted downfield due to the anisotropic effect of the carbonyl group. 2,3-Diethoxynaphthalene reacted similarly to give IVb.

2,3-Dialkoxynaphthalene reacts with acid (B) to yield 6,7-dialkoxy-2,3,3a,10a-tetrahydropentaleno[1,2-b]naphthalen-10(1H)-one (IVc-d).

All the above substituted hexahydrobenzofluorenones and pentalenonaphthalenones gave crystalline 2,4-dinitrophenylhydrazone derivatives.

### 3. Experimental

All melting points reported here are uncorrected values IR spectra were recorded on a Perkin-Elmer spectrophotometer. The UV spectra were recorded on a Shimadzu-240 spectrophotometer. The NMR spectra were recorded on a 60 MHz Varian instrument. Chemical shifts are quoted in  $\delta$  values relative to tetramethyl-

silane (TMS) as internal standard. The homogeneity of compounds was ascertained by TLC on silica gel G plates, and spots were developed in an iodine chamber. Neutral alumina<sup>1</sup> was used for column chromatography.

### 3.1 Reaction of dialkoxynaphthalene with cyclic $\alpha, \beta$ -unsaturated acids (A and B)

*General procedure:* Dialkoxynaphthalene (0.01 mole) and cyclic  $\alpha, \beta$ -unsaturated acid (0.02 mole) were heated in the presence of polyphosphoric acid [prepared from phosphorus pentoxide (10 g) and phosphoric acid (5 ml) preheated at 100°C for 0.5 hr]. The reaction mixture was kept at 90–95°C for a further 3 hr with occasional shaking. It was cooled and decomposed with ice water and left overnight. It was then extracted with chloroform. The chloroform layer was washed with saturated sodium hydrogen carbonate, water and dried over anhydrous sodium sulphate. The solvent was removed by distillation and the dark mass obtained was chromatographed over neutral alumina. Elution with appropriate solvent afforded the respective compounds (tables 1 and 2).

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