

## A Convenient Synthesis of 6,12-Disubstituted Chrysenes.

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**Summary:** 6,12-Dimethylchrysene has been synthesised, by photo-oxidative cyclization of 2-methyl-1-[ $\alpha$ -(4-methylnaphthyl)]-2-phenylethene. Similarly, irradiations of 2-methyl-1-[ $\alpha$ -(4-methoxynaphthyl)]-2-phenylethene, 2-cyano-1-[ $\alpha$ -(4-methylnaphthyl)]-2-phenylethane and 2-cyano-1-[ $\alpha$ -(4-methoxynaphthyl)]-2-phenylethene yielded 6-methoxy-12-methyl, 6-cyano-12-methyl and 6-cyano-12-methoxychrysenes respectively. No migration of substituents was observed.

### Introduction

Although monosubstituted [1-4] 1,3-disubstituted [2], 1,7-disubstituted [5], and 3,9-disubstituted chrysenes [3] have been available by photochemical cyclization reactions in moderate yield, yet the independent synthesis of chrysenes have been obtained only by tedious synthetic pathways [6,7] in very poor yields. It has been reported that some 6,12-disubstituted chrysenes are readily obtained by electrophilic substitution reactions [8-10], but their structures were not conclusively demonstrated. Chrysenes are interesting polycyclic aromatic compounds in that they are known to be carcinogenic [11] and carcinostatic [12].

We now report a convenient synthesis of 6,12-dimethylchrysene(8) and three more 6,12-disubstituted chrysenes (9-11) in improved yield, involving four steps.

The starting materials 4-methyl-1-naphthaldehyde(1), and 4-methoxy-1-naphthaldehyde(2) were prepared in 75% and 68% yields respectively, by formylation of 1-methylnaphthalene and 1-methoxynaphthalene with  $\alpha, \alpha$ -dichloromethyl methyl ether, using titanium(IV) chloride [13]. 1-(Phenyl-

ethyl)-triphenylphosphonium bromide(3) was prepared by the reaction of 1-bromo-ethylbenzene with triphenylphosphine as described in the literature [4].

The disubstituted styrylnaphthalenes(4) and (5) were prepared in fairly good yields (table 1) by reacting the phosphonium salt(3) with the 4-methyl- and 4-methoxy-1-naphthaldehyde(1) and (2) respectively in a Wittig reaction [4]. Other disubstituted styrylnaphthalenes (6) and (7) were also prepared in good yields (table 1) by the reaction of benzyl cyanide with (1) and (2) respectively [14].

Irradiation of the styrylnaphthalenes(4-7) in dry hexane, containing a small amount of iodine gave after 24h at room temperature 6,12-disubstituted chrysenes (8-11) in moderate yield. Chrysenes (8-11) were very insoluble in hexane and precipitated from solution as they were formed, and this fact may account for the relatively moderate yield of chrysene compounds (table 2).

The H-8 (peri-H) chemical shifts 9.22 and 9.26 ppm of compounds (1)

Table-1: Styrylnaphthalene (4-7):

Compound	Method	Yield (%)	m.p. (°C)	Molecular formula <sup>a</sup>	<sup>1</sup> H-NMR(CDCl <sub>3</sub> ) [δPPM]
4	A	31	91-92	C <sub>20</sub> H <sub>18</sub>	2.58(s,3H,CH <sub>3</sub> );2.70(s,3H,CH <sub>3</sub> );7.0-8.37 (m,12H,H <sub>arom</sub> +H <sub>olefin</sub> ).
5	A	42	106-107	C <sub>20</sub> H <sub>18</sub> O	2.61(s,3H,CH <sub>3</sub> );3.74(s,3H,OCH <sub>3</sub> );6.8-8.07 (m,11H,H <sub>arom</sub> +H <sub>olefin</sub> );8.14 (m,1H,peri-H)
6 <sup>b</sup>	B	58	120-121 <sup>c</sup>	C <sub>20</sub> H <sub>15</sub> N	2.63(s,3H,CH <sub>3</sub> );7.1-8.0(m,11H <sub>arom</sub> );8.16(s,1H <sub>olefin</sub> )
7 <sup>d</sup>	B	50	138-139 <sup>e</sup>	C <sub>20</sub> H <sub>15</sub> NO	3.78(s,3H,OCH <sub>3</sub> );6.9-8.1(m,11H <sub>arom</sub> );8.2(s,1H <sub>olefin</sub> )

a) All new compounds gave satisfactory microanalysis (C±0.4,H±0.2,N±0.3); b) ir (KBr) 2217 cm<sup>-1</sup>(CN); c) From ethanol; d) ir (KBr) 2221 cm<sup>-1</sup>(CN), e) From ethanol.

Table-2: 6,12-Disubstituted-chrysenes (8-11):

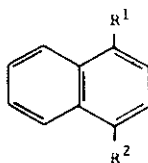
Compound	Yield (%)	m.p. (°C)	Molecular formula <sup>a</sup>	<sup>1</sup> H-NMR (CDCl <sub>3</sub> ) [δPPM]
8	46 <sup>b</sup>	238-239	C <sub>20</sub> H <sub>16</sub>	2.95(s,3H,CH <sub>3</sub> );7.75-7.93(m,4H <sub>arom</sub> );8.13-8.47 (m,2H,H-1 and H-7);8.63(s,2H,H-5 and H-11); 8.83(m,2H,H-4 and H-10).
9	42 <sup>b</sup>	219-220	C <sub>20</sub> H <sub>16</sub> O	2.81(s,3H,CH <sub>3</sub> );3.96(s,3H,OCH <sub>3</sub> );7.82-8.05(m,4H <sub>arom</sub> ); 8.18-8.49 (m,2H,H-1 and H-7);8.60(s,H-11);8.72 (s,H-5);8.96(m,2H,H-4 and H-10).
10 <sup>d</sup>	58	241-242	C <sub>20</sub> H <sub>13</sub> N	2.76(s,3H,CH <sub>3</sub> );7.51-8.0(m,4H <sub>arom</sub> ) 8.15-8.34(m,2H, H-1 and H-7); 8.46-8.74(m,2H,H-4 and H-10); 8.83 (s,H-11);8.97 (s,H-5).
11 <sup>f</sup>	65 <sup>e</sup>	230-231	C <sub>20</sub> H <sub>13</sub> NO	3.92(s,3H,OCH <sub>3</sub> );7.72-8.20(m,5H <sub>arom</sub> );8.43(m,H-1); 8.56-8.81(m,2H,H-4 and H-10);8.95 (s,2H,H-5 and H-11).

a) All new compounds gave satisfactory microanalysis (C±0.4,H±0.21,N±0.15); b) From benzene; c) Lit.[9] m.p.238°; d) ir (KBr) 2231 cm<sup>-1</sup>(CN); e) From benzene/ethanol, f) ir (KBr) 2238 cm<sup>-1</sup>(CN).

and (2) respectively confirm the hydrogen bonding of the carbonyl oxygen to the peri hydrogen [15]. The olefinic protons in compounds (6) and (7) experience a greater deshielding effect than in compounds (4) and (5). This can be ascribed to the electron withdrawing effect of the cyano group on the vicinal carbon atom. The spectra of compounds (8-11) were similar in pattern but differ from that of chrysene. Memory et al. [16] found that protons at H-4, -5, -10, and -11 in chrysene itself were abnormally deshielded and occurred downfield by approximately 0.65 ppm. The substituents at positions 6 and 12 in compounds (8-11) will exert a deshielding effect upon H-1 and H-7, i.e. a peri-effect. The singlet which is equivalent to two protons can be assigned to H-5 and H-11 which would be expected to resonate at a lower field because of the steric effect, the effect being similar to that observed for the H-5 in 6-substituted chrysenes [1] and for the H-5 in 4-bromophenanthrene [17].

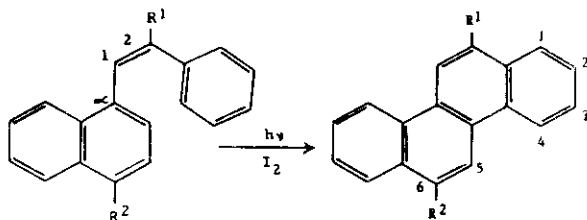
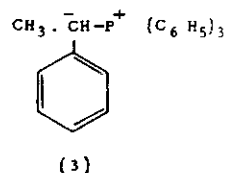
## Experimental

All melting points are uncorrected. The i.r. spectra were recorded on a Pye Unicam SP 3-100 spectrometer using KBr discs. The  $^1\text{H-NMR}$  were measured on a Varian FT-80A spectrometer using tetramethylsilane as an internal standard ( $\delta=0$  ppm) and deuteriochloroform solvent; chemical shifts are given in , (ppm). Compounds (8) and (9) were previously reported by Buu Hoi et al. [9] and Jacquignon et al. [10] respectively. Compounds (4-7), (10) and (11) being new, their structures have been securely established by  $^1\text{H-NMR}$ , IR, microanalysis, and the method of synthesis. Two methods were used for the preparation of the styrylnaphthalenes (4-7); a typical example is given for each method.



(1) :  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{CH}_3$

(2) :  $\text{R}^1 = \text{CHO}$ ,  $\text{R}^2 = \text{OCH}_3$



(4) :  $\text{R}^1 = \text{R}^2 = \text{CH}_3$

(5) :  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{OCH}_3$

(6) :  $\text{R}^1 = \text{CN}$ ,  $\text{R}^2 = \text{CH}_3$

(7) :  $\text{R}^1 = \text{CN}$ ,  $\text{R}^2 = \text{OCH}_3$

(8) :  $\text{R}^1 = \text{R}^2 = \text{CH}_3$

(9) :  $\text{R}^1 = \text{CH}_3$ ,  $\text{R}^2 = \text{OCH}_3$

(10) :  $\text{R}^1 = \text{CN}$ ,  $\text{R}^2 = \text{CH}_3$

(11) :  $\text{R}^1 = \text{CN}$ ,  $\text{R}^2 = \text{OCH}_3$

### 4-Methyl-1-naphthaldehyde, (1):

This was prepared by the reaction of 1-methylnaphthalene (22.5g),  $\alpha, \alpha$ -dichloromethyl methyl ether (18.0g), and titanium (IV) chloride (51.0g) according to the procedure of Aslam et al. [13] m.p.  $34^\circ$  (lit. [18] m.p.  $34^\circ$ ). ir (film) at  $1692\text{ cm}^{-1}$  ( $\text{C=O}$ );  $^1\text{H-NMR}$  signals at  $\delta 2.28$  (s, 3H,  $\text{CH}_3$ ),  $\delta 7.07$ - $7.87$  (m,  $5\text{H}_{\text{arom}}$ ),  $\delta 9.22$  (m, peri-H),  $\delta 10.15$  (s, CHO).

### 4-Methoxy-1-naphthaldehyde, (2):

This compound was obtained from 1-methoxynaphthalene by a method analogous to the preparation of aldehyde (1). m.p.  $35^\circ$  (lit [15]. m.p.  $34^\circ$ ). ir (film) at  $1698\text{ cm}^{-1}$  ( $\text{C=O}$ );  $^1\text{H-NMR}$  signals at  $\delta 3.62$  (s, 3H,  $\text{CH}_3$ ),  $\delta 6.71$ - $7.56$  (m,  $4\text{H}_{\text{arom}}$ ),  $\delta 8.10$  (m, 1H, H-5),  $\delta 9.26$  (m, peri-H),  $\delta 10.18$  (s, CHO).

*Styrylnaphthalenes (4-7) : Typical procedures:*

**Method A :** To a solution of (15.7g) phosphonium bromide (3) in dry ethanol (36 ml) was added freshly prepared 0.2M sodium ethoxide in ethanol solution (190 ml) at r.t. with stirring. A solution of 4-methyl-1-naphthaldehyde (5.59g) in dry ethanol (12 ml) was then added with stirring over 5 min. The mixture was boiled under reflux for 16 h, cooled, and extracted with chloroform. The extract was washed with water, and dried. Evaporation of the solvent gives a brown residue, which is then dissolved in benzene (50 ml) and chromatographed on a column of silica gel, eluting with benzene. Evaporation of the solvent gives a pale yellow solid. Crystallization gave needles of 2-methyl-1-[ $\alpha$ -(4-methylnaphthyl)] -2-phenylethene, yield: 2.8g (31%); m.p. 91-92° (methanol).

**Method B:** Benzyl cyanide (7.6 g) in absolute ethanol (5 ml) was added to a solution of sodium ethoxide, prepared from sodium (0.5 g) and absolute ethanol (10 ml). 4-Methyl-1-naphthaldehyde (11.10 g) is then added over 10 min with stirring, the mixture being then warmed over a steam bath for 30 min. The product was obtained by extraction with chloroform, washing the extract with water, drying and removal of the solvent. Distillation then gives compound (6) as a creamy solid, yield : 11.20 g (64%); m.p. 120-121° (methanol).

*Photochemical Cyclisations; General Procedure:*

A mixture of the styrylnaphthalene (0.35 g) and iodine (0.15g) was dissolved in redistilled hexane (1l) in a pyrex photochemical flask fitted with a magnetic stirrer. The solution is irradiated using a Hanovia 90 watt medium pressure mercury lamp, sur-

rounded by a water-cooled quartz jacket, for 24h at r.t. with constant stirring. The solvent etc were removed using a rotatory evaporator under reduced pressure. The solid residue is then dissolved in benzene (50 ml) and the solution passed through a short column of chromatographic alumina eluting with benzene. The eluate was evaporated to dryness and the residue obtained was purified by crystallization.

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