Photochemical Synthesis of Some Mono-Substituted Chrysenes

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The formation of chrysene derivatives by irradiation of styrylnaphthalenes, in the presence of an oxidising agent, has been extensively studied[1-9], but the scope of the reaction has so far been very limited.

We now report the synthesis, from appropriate styrylnaphthalenes (Table 1), of chrysenes substituted by chloro,cyano, acetyl, and carboxy groups, embracing all the six substituent positions of the hydrocarbon. Earlier[2, 10] it had been reported that stilbenes do not undergo photocyclisation if substituted by an acetyl group.

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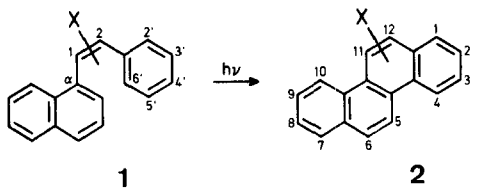
Table 1. 1-(α-Naphthyl)-2-phenylethenes (**1**)

Product No.	Substituents X	Method	Yield [%]	m.p. or b.p./torr	Molecular formula[a]	I.R. (KBr) ν [cm⁻¹]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
1a	1-CN	A	73	184–187°/0.7	$C_{19}H_{13}N$ (255.3)	2203 (CN)	6.83 (s, H-2); 8.05 (m, *peri*-H); 7.0–8.2 (m, H_{arom})
1b	1-COOH	B	32[b]	164–165°	$C_{19}H_{14}O_2$ (274.3)	1680 (CO)	6.7–8.0 (m, H_{arom}); 8.08 (s, H-2); 10.8 (br, COOH)
1c	1-COOH, 2′,6′-di-Cl	B	19[b]	221–222°	$C_{19}H_{12}Cl_2O_2$ (343.2)	1690 (CO)	6.8–8.0 (m, H_{arom}); 8.07 (s, H-2); 8.9 (br, COOH exchangeable with D_2O)
1d	2-CN	A	74[c]	112°	$C_{19}H_{13}N$ (255.3)	2218 (CN)	7.3–8.1 (m, H_{arom}); 8.18 (H-1)
1e	2′-CO—CH_3	C	55[c]	79–80°	$C_{20}H_{16}O$ (272.3)	1670 (CO)	2.48 (s, CH_3); 7.0–8.0 (m, H_{arom} + H_{olefin})
1f	2′-CN	D	92[d]	124–125°	$C_{19}H_{13}N$ (255.3)	2220 (CN)	6.8–8.2 (m, H_{arom} + H_{olefin})
1g	3′-CO—CH_3	C	70[e]	83–84°	$C_{20}H_{16}O$ (272.3)	1680 (CO)	2.53 (s, CH_3); 6.7–8.3 (m, H_{arom} + H_{olefin})
1h	4′-CO—CH_3	C	72[f]	91°	$C_{20}H_{16}O$ (272.3)	1670 (CO)	2.67 (s, CH_3); 7.21 (d, H-1); 7.3–8.45 (m, H_{arom} + H-2; $J_{H\text{-}1/H\text{-}2}$ = 16.0 Hz)
1j	4′-CN	D	81[g]	132–133°[h]	$C_{19}H_{13}N$ (255.3)	2217 (CN)	6.95 (d, H-2); 7.85 (d, H-1); 7.1–8.25 (m, H_{arom}); $J_{H\text{-}1/H\text{-}2}$ = 16.5 Hz)

[a] All products gave satisfactory microanalyses (C ±0.4, H ±0.2, N ±0.5, Cl ±0.2).
[b] From glacial acetic acid.
[c] From ethanol.
[d] From methanol.
[e] From cyclohexane.
[f] From benzene/ethanol.
[g] From benzene.
[h] Lit.[4] m.p. 131–132°.

No rearrangements were observed during the cyclizations of **1** to **2** (Table 2). *ortho*-Acetylstyrylnaphthalene gave rise to a 2:1 ratio of the expected 1-acetylchrysene and of chrysene itself (i.e. with elimination of an acetyl group). Photocyclization of 1-(α-naphthyl)-2-(2′,6′-dichlorophenyl)-1-carboxyethene (**1**; X = 2′,6′-di-Cl and 1-COOH) gave an 82% yield of 1-chlorochrysene-11-carboxylic acid (**2**; X = 1-Cl, 11-COOH) involving loss of one *ortho*-chlorine group. Cyclization of *o*-cyanostyrylnaphthalene, however, proceeded normally. 1-(3′-Acetylphenyl)-2-(α-naphthyl)-ethene gave mixtures of 2- and 4-acetylchrysenes, with the former predominating.

The styrylnaphthalenes **1** were synthesised using one of four standard procedures for olefin synthesis (Methods A–D). They had predominantly the *trans*-configuration.



1 **2**

All melting points are uncorrected. ^{1}H-N.M.R. spectra were recorded at 60 MHz on a Varian T 60 spectrometer. Four methods were used for the preparation of the styrylnaphthalenes **1**; a typical example is given for each method. They were shown by gas chromatography (column of 3% OV17 at 200°) to have the predominant (80–95%) *trans*-configuration.

Styrylnaphthalenes 1; Typical Procedures:

Method A[12]: 1-Naphthylacetonitrile (10.8 g) in absolute ethanol (4 ml) is added to a solution of sodium ethoxide, prepared from sodium (0.5 g) and absolute ethanol (10 ml). Benzaldehyde (6.9 g) is then added over 10 min with stirring, the mixture then being warmed over a steam bath for 15 min. The product is obtained by extraction with chloroform, washing the extract with water, drying with sodium sulphate, and removal of the solvent. Distillation then gives compound **1a** as a pale yellow oil; yield: 12.6 g (73%).

Method B[13]: Potassium naphthylacetate (12.2 g), benzaldehyde (5.8 g), and acetic anhydride (80 ml) are heated at 135–140° for 3 h. The mixture is cooled and poured into 1 normal hydrochloric acid (800 ml). After 24 h the clear supernatant solution is poured off and the yellow residue is extracted with boiling potassium carbonate solution. The combined alkaline extracts are decolourised (charcoal) and then acidified with 10 normal hydrochloric acid. The white precipitate is filtered off and dried; crude yield: 4.8 g; m.p. 162–164°. Pure compound **1b** is obtained after two crystallisations as silvery plates; yield: 4.2 g (32%).

Method C: To methylmagnesium iodide, prepared from methyl iodide (1.42 g) and magnesium (0.24 g) in dry ether (25 ml), is added 1-(α-naphthyl)-2-(2′-cyanophenyl)-ethene (**1f**; 0.618 g) in anhydrous toluene (25 ml) over 15 min. The ether is carefully distilled off, the mixture is then boiled gently for 6 h, and cooled. Excess aqueous ammonium chloride is then added with stirring. The organic layer is evaporated, and the residue boiled with 30% hydrochloric acid (30 ml) for 6 h. The mixture is cooled, and extracted with chloroform, the extract washed with water, and then dried. Evaporation of the solvent gives a dark brown residue. The pure 1-(α-naphthyl)-2-(2′-acetylphenyl)-ethene (**1e**) is obtained as a creamy solid, after chromatography on alumina (from benzene) and crystallisation; yield: 0.36 g.

Method D[14]: To a solution of potassium *t*-butoxide, prepared under nitrogen from potassium (1.05 g) and dry *t*-butanol (40 ml), dry ether (40 ml) is added. 1-Naphthylmethylphosphonium chloride[15] (11.8 g) is then added with stirring, and the mixture stirred for a further 20 min. A solution of *o*-bromobenzaldehyde (5.0 g) in dry ether (15 ml) is then added over 15 min, and the mixture is set aside overnight. The solvent is then removed, the residue taken up in benzene, the extract washed with water, dried, reduced to low bulk, and chromatographed on a column of silica gel eluting with benzene. Evaporation of the solvent gives a yellow

Table 2. Chrysenes (**2**)

Product No.	Substituents X	Yield [%]	m.p. (Lit. m.p.)	Molecular formula[a]	I.R. (KBr) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]
2a	5-CN	76[b]	165.5°	$C_{19}H_{11}N$ (253.3)	2218 (CN)	7.4–8.1 (m, H_{arom}); 8.3 (s, H-6); 8.45–8.7 (m, H-10 and H-11); 9.7 (m, H-4)
2b	5-COOH	60[c]	223–224° (225–226°)[13]	—	1688 (CO)	7.4–8.3 (m, H_{arom}); 8.3 (s, H-6); 8.73 (d, H-11); 8.5–9.0 (m, H-4 and H-10); 11.6 (br, COOH, exchangeable with D_2O); $J_{H\text{-}10/H\text{-}11}$ = 9.0 Hz
2c	1-Cl, 11-COOH	82[c]	260–261° (dec.)	$C_{19}H_{11}ClO_2$ (306.7)	1683 (CO)	7.4–8.3 (m, H_{arom}); 8.57 (s, H-12); 8.79 (d, H-5); 8.45–8.95 (m, H-4 and H-10)
2d	6-CN	94[d]	196–197°	$C_{19}H_{11}N$ (253.3)	2240 (CN)	7.2–8.0 (m, H_{arom}); 8.15 (m, H-7); 8.75–8.4 (m, H-4, H-10, H-11); 8.95 (s, H-5)
2e	1-CO—CH_3[e]	52[f]	201.5°	$C_{20}H_{14}O$ (280.4)	1678 (CO)	2.80 (s, CH_3); 7.2–8.0 (m, H_{arom}); 7.95 (d, H-12); 8.45–9.05 (m, H-4, H-5, H-10, H-11); $J_{H\text{-}11/H\text{-}12}$ = 9.2 Hz
2f	1-CN	95[d]	228–229°	$C_{19}H_{11}N$ (253.3)	2220 (CN)	7.6–8.3 (m, H_{arom}); 8.44 (d, H-12); 8.55–9.1 (m H-4, H-5, H-10, H-11); $J_{H\text{-}11/H\text{-}12}$ = 9.2 Hz
2g	2-CO—CH_3	50[f]	255° (252–253°)[11]	—	1668 (CO)	2.74 (s, CH_3); 8.0–8.35 (m, H_{arom}); 8.5–9.0 (m, H-4 H-5, H-10, H-11)
2g′	4-CO—CH_3	24[g]	120.5°	$C_{20}H_{14}O$ (280.4)	1693 (CO)	2.38 (s, CH_3); 7.4–8.0 (m, H_{arom}); 8.08 (d, H-11) 8.59 (d, H-5); 8.61 (m, H-3); $J_{H\text{-}5/H\text{-}6}$ = 9.1 Hz $J_{H\text{-}11/H\text{-}12}$ = 8.9 Hz
2h	3-CO—CH_3	78[h]	158° (159°)[11]	—	1678 (CO)	2.72 (s, CH_3); 7.3–8.2 (m, H_{arom}); 8.25–8.85 (m H-5, H-10, H-11); 9.17 (d, H-4)
2j	3-CN	94[h]	200–201° (200–201°)[4]	—	2218 (CN)	7.6–8.3 (m, H_{arom}); 8.4–8.9 (m, H-5, H-10, H-11) 9.03 (d, H-4)

[a] All new compounds gave satisfactory microanalyses (C ±0.5, H ±0.23, N ±0.16, Cl ±0.4).
[b] From methanol.
[c] From acetic acid.
[d] From benzene/ethanol.
[e] By-product is chrysene; yield: 26%; m.p. 254–255°.
[f] From benzene.
[g] From benzene/light petroleum.
[h] From ethanol.

viscous oil, which solidifies on cooling to give *1-(α-naphthyl)-2-(2′-bromophenyl)-ethene* as pale yellow crystals; yield: 6.5 g (77%); m.p. 74–74.5° (from ethanol).

$C_{18}H_{13}Br$	calc.	C 69.91	H 4.24	Br 25.84
(309.2)	found	69.42	4.61	25.88

A stirred mixture of the above styrylnaphthalene (3.09 g), copper(I) cyanide (2.24 g), and dimethyl sulphoxide (25 ml) is boiled gently for 2 h[16]. The resultant mixture is poured into a solution of iron(III) chloride (8.0 g) in 2 normal hydrochloric acid (100 ml). The product is taken up in chloroform, the extract washed with water, and dried. Evaporation of the solvent affords a brown oil, which solidified. Pure *1-(α-naphthyl)-2-(2′-cyanophenyl)-ethene* (**1f**) is obtained after chromatography over a short column of alumina (elution with 1 : 1 benzene/ether) and a final crystallisation; yield: 2.33 g (92%).

Photocyclisations; General Procedure:
A mixture of the styrylnaphthalene (0.35 g) and iodine (0.15 g) is dissolved in redistilled cyclohexane (1 l) in a pyrex photochemical flask fitted with a magnetic stirrer. The solution is irradiated using a Hanovia 90 watt medium pressure mercury lamp, surrounded by a water-cooled quartz jacket, for 24 h at room temperature with constant stirring. The solvent, etc. are 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. The eluate is evaporated to dryness and the residue obtained is purified by crystallisation. Where mixtures are obtained the components are separated by preparative T.L.C. (alumina, thickness 1.0 mm, benzene solvent).

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