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Photochromic 2,2-Disubstituted Naphthopyrans

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Novel 2,2-disubstituted naphthepyrans which contain a dimethyl, diphenyl, spiro adamantyl, spirofluorenyl at position 2, show photochromic compounds which undergo a colourless to colour change in unfiltered sunlight and exhibit a rapid thermal fade at ambient temperaures.

INTRODUCTION

In his review of the photochromic properties of benzopyrans[1], Bertelson reported that Becker and Michle found that 2H-1-benzopyrans are photochromic and that the colour change was caused by heterolytic cleavage of a C—O bond in the benzopyran to give a coloured o^--quinonoid form which can exist in two isomeric forms[2]. A list of a variety of photochromic benzo and naphthopyran derivatives were taken from Becker's studies[2]. Some photochromic benzopyrans occur naturally and it has been suggested that their photochromism may play a role in the photoperiodic responses of plant system. While the substituents vary in the aromatic ring of the benzopyran, many naturally occurring benzopyrans have the two methyl substituents in the 2-position and no substituents in the 3- and 4-positions such as eupatoriochromene, evoidonol, alloevodionol and ageratochromene[3].

Photochromic properties of benzopyran derivatives have been studied at very low temperature (−196°C) by Becker and Kolc[4]. Margerum and Miller[5] noted that some photoisomerizations are readily apparent at room temperatures, colour changes include those to yellow and orange, substituents have a pronounced effect on the stability of the coloured forms and that unidentified irreversible side reactions occur particularly in the presence of oxygen.

2,2-Dimethylbenzopyran has been studied by Padwa *et al.*[6] who observed that it gave, on irradiation in methanol, two photoproducts, arising from 1,2- and 1,4-addition of methanol to the o^--quinonoid coloured form. Both products reverted to the original benzopyran and methanol on standing in the dark when the reaction was carried out in acetone. An irreversible 1,7-hydrogen shift took place to give the phenol. These and other related studies have led to the general assumption that 2,2-dimethyl substituted benzopyrans fatigue on photo irradiation, others by addition of a hydroxylic solvent or, in the absence of a hydroxylic solvent, by an irreversible 1,7-hydrogen shift process.

Naphthopyrans with their additional benzannelation show an absorption band

in the near ultraviolet characteristic of naphthalene derivatives. The absorption bands also show additional bathochromic shift due to the 1- or 2-vinyl substituent on the naphthalene nucleus in the naphthopyran photodegradation products due to photooxidation of the impurity or photooxidation of dimethyl naphthopyran[7,8]. The isomeric photochromic 2,2-disubstituted-2H-naphtho-[1,2-b]-pyran has been patented[9].

2,2-Diphenyl-2H-(1,2b)-naphthopyran has been reported to undergo a colour change to orange[10]. Synthesis of some 2-substituted chromenes which change to yellow or orange on exposure to sunlight, reverse thermally at ambient temperature in the dark and which are largely free from fatigue will be discussed in this paper.

EXPERIMENTAL

Melting points were determined on a Rechert hot stage microscope with thermometer which has been calibrated against a known standard. Nuclear magnetic resonance spectra were recorded for solution in $CDCl_3$ on Perkin-Elmer R32 nmr spectrophotometer (90 MHz). Chemical shifts are reported as δ values in parts per million downfield from the international standard tetra-methyl silane.

Preparation of 4 (p-Methoxyphenyl)-7-methoxy-1-hydroxy naphthalene

(a) *4,4-Bis-(p-methoxyphenyl)-3-butenoic acid:* Aluminium trichloride (42 g, 0.31 mole) was suspended in 1,2-dichloroethane (200 cm^3) at 0°C. Succinoyl chloride (35 g, 25 cm^3, 0.23 mole) and anisol (46.6, 48 cm^3, 0.44 mole) were mixed and added over 45 min with stirring. A deep red solution was obtained, it was maintained at 0°C for 5 h and then stirred overnight at ambient temperature. The viscous mixture was diluted with an equal volume of chloroform and poured carefully onto water. The colours were discharged. The yellow organic layer was separated and extracted with chloroform, dried and evaporated, leaving the acid as a yellow oil (33.7 g, 0.11 mole), nmr 7.39–6.79 (8H, m aromatic); 6.12 (1H, t, J 7.5 Hz, vinyl); 3.81 and 3.85 (6H, two singlets, methoxy); 3.23 (2H, d, J 7.5 Hz, methylene).

(b) *1-Acetyl-4-(p-methoxyphenyl)-7-methoxy-1-hydroxy naphthalene:* 4,4-Bis-(*p*-methoxy phenyl)-3-butenoic acid (33.79 g, 0.11 mole) was dissolved in acetic anhydride (100 cm^3) with anhydrous sodium acetate (8.59 g, 0.1 mol). The solution was boiled for 5 h during which a crimson oil was developed. The acetic anhydride was removed by distillation under reduced pressure and the residue was extracted with chloroform, washed with water (2×150 cm^3) and dried. removal of solvent left 1-acetyl-4-(*p*-methoxy phenyl)-7-methoxy-1-hydroxy-naphthalene as a crimson oil (23 g, 0.08 mole), nmr 7.90–6.95 (9H, m, aromatic); 3.87 and 2.92 (6H, two singlets, methoxy); 2.50 (3H, S, methyl).

(c) *4-(p-phenyl)-7-methoxy-1-hydroxynaphthalene:* Hydrolysis of 1-acetyl-4-(*p*-methoxyphenyl)-7-methoxy-1-hydroxy naphthalene by boiling with 8% w/s methanolic sodium hydroxide for 2 h left a brown solid after evaporation of solvent. The solid was dissolved in water, acidified, extracted into ether and dried. Removal of solvent left a dark oil (19 g, 0.07 mole) which gave a green poweder

on trituration with ethanol; m.p. 165–166°C; NMR 7.90–6.75 (9H, m, aromatic); 3.95 and 3.90 (6H, two singlets, methoxy).

The general methods for the preparation of 2-H naphthopyrans

The substituted propargyl acetate (0.1 mole) was added gently to 1-naphthol (0.1 mole) in dichlorobenzene (90 mL). The reaction mixture was refluxed for 24 h, cooled and washed with sodium hydroxide solution and then with water; removed the solvent *in vacuo* and the residue gum was purified by chromatography on silica gel using petroleum (60–80°C) as eluent. Removal of the solvent left the naphthopyrans.

The following compounds were prepared by a similar process:

6-(*p*-methoxyphenyl)-9-methoxy 2,2-dimethyl naphtho-[1,2-b]-pyran (1), as an oil, nmr 7.80–6.90 (8H, complex aromatic); 6.39 (1H, d, J 10 Hz, vinyl); 5.60 (1H, d, J 10 Hz, vinyl); 3.90 (3H, S, methoxy) 3.80 (3H, S, methoxy); 1.50 (6H, S, methyl).

6-(*p*-methoxyphenyl)-9 methoxy-2,2-diphenyl-naphtho-[1,2-b]-pyran (2), as a mauve oil; nmr 7.70–6.80 (17 H, complex, aromatic), 6.63 (1H, d, J10.5 Hz, vinyl) 6.08 (1H, d, J 10.s, vinyl), 5.83 (3H, s, methoxy), 5.75 (3H, s, methoxy).

6-(*p*-methoxyphenyl)-9-methoxy-(2,2-spiro-2-adamantyl)naphtho-(1,2-b)-pyran (3), m.pt. 206°C; nmr 7.86–7.66 (2H, m, aromatic), 7.46–7.26 (2H, m, aromatic); 7.14–6.96 (4H, complex aromatic); 6.55 (1H, d, J 10 Hz, C-4, vinyl); 6.21 (1H, d, J10 Hz, C-3, vinyl), 3.96 and 3.95 (6H, two singlets, methoxy); 2.72–1.40 (14H, adamantyl).

6-(*p*-methoxyphenyl)-9-methoxy(2,2-spiro-9-fluorenyl)-naphtho-[1,2-b]-pyran (4), 7.74–7.66 (4H, complex aromatic); 7.40–7.22 (6H, complex aromatic); 7.15 (1H, d, J 7 Hz, vinyl); 7.10–7.08 (1H, m, aromatic); 7.05 (2H, d, AA′, BB′ coupled, J 9 Hz, aromatic); 6.81 (2H, d, AA′, BB′ coupled, J 9 Hz, aromatic), 6.02 (1H, s, aromatic); 4.79 (1H, d, J 7 Hz, vinyl shielded by fluorenyl); 4.02 (3H, s, methoxy), 3.78 (3H, s, methoxy).

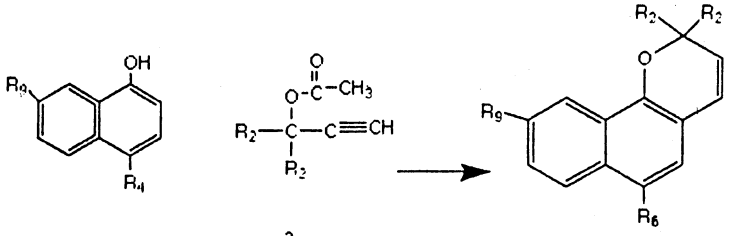
6-phenyl-(2,2-spiro-2′-adamantyl)-naphtho-[1,2-b] pyran (5), nmr 8.33 (1H, d, broad, C-10); 7.90–7.27 (8H, complex aromatic); 7.14 (1H, S, C-5); 6.56 (1H, d, J 10 Hz, C-4, vinyl); 6.17 (1H, d, J 10 Hz, C-3, vinyl); 2.75–1.50 (14H adamantyl).

6-Chloro-(2,2-spiro-2′-adamantyl)-naphtho-[1,2-b] pyran (6), nmr 2.41–813 (2H, m, aromatic); 7.62–7.50 (2H, m, aromatic); 7.31 (1H, S, C-5); 6.51 (1H, d, 10Hz, C-4, vinyl); 6.23 (1H, d, J 10 Hz, C-3, vinyl); 2, 74–142 (14H adamantyl).

2,2-Di-(*p*-chlorophenyl)-2H-naphtho-(1,2-b) pyran (7), m.p. 129°C, nmr 8.25 (1H, d, J 8 Hz, 10-H); 7.72 (1H, d, J 8 Hz, 7-H); 7.5–7.15 (12H, m, aromatic); 6.65 (1H, d, J 9 Hz, 4-H); 6.05 (1H, d, J 9 Hz, 3-H).

RESULTS AND DISCUSSION

As expected the reaction of 1-naphthol derivatives with the substituted propargyl acetate gave the crude naphthopyran. The reaction involves a Claisen rearrangement followed by a 1,5-hydrogen shift, with electrocyclic ring closure to complete the process (Fig. 1).



1 2 3

	R_2, R_2	R_6	R_9
3a	CH_3, CH_3	(*p*-Methoxy)phenyl	Methoxy
3b	Ph, Ph	(*p*-Methoxy)phenyl	Methoxy
3c	Admantyl	(*p*-Methoxy)phenyl	Methoxy
3d	Flourenyl	(*p*-Methoxy)phenyl	Methoxy
3e	Admantyl	Phenyl	Hydrogen
3f	Admantyl	Chloride	Hydrogen
3g	*p*-chlorophenyl,	Hydrogen	Hydrogen

Fig. 1

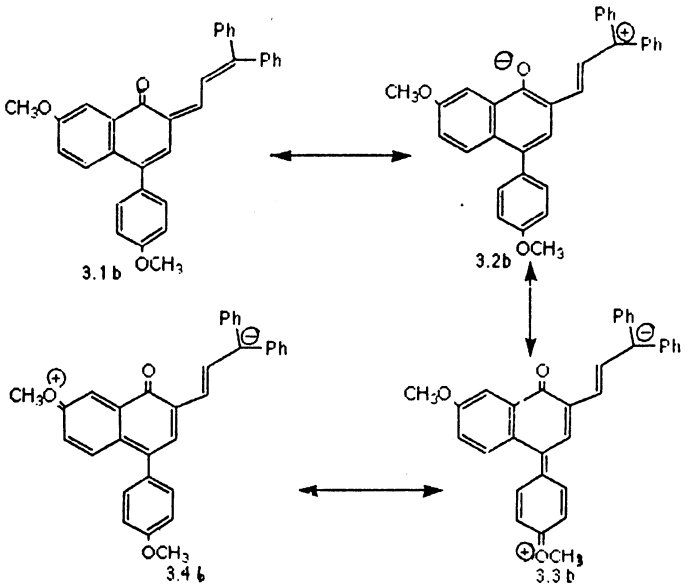


Fig. 2

The ultra-violet visible spectrum of the naphthopyran (1) in toluene shows a broad absorption into near ultra-violet which tails off at 400 nm. Irradiation with a flash-gun generated on orange-red colour (λ_{max} 482 nm) which persisted at ambient temperature for many hours. Irradiation of the naphthopyran (1) results

in a rapid degradation of the photochromic compound, each flash generating less colour than the previous one on continued irradiation.

The ultra-violet visible spectrum of the naphthopyran (2) in toluene shows a broad absorption into near ultra-violet, tailing off at 400 nm. Irradiation with a flash-gun results in an intense purple colouration with a maximum absorption in the near-visible region at 522 nm which represents a 40 nm bathochromic shift as compared with the naphthopyran (1).

On monitoring the thermal reversal at 522 nm, part of the intensely purple solution faded ($t_{1/2}$ 5 min) leaving a residual violet colour which persisted for many hours. The violet form also showed an inefficient optical bleach, requiring prolonged radiation at 546 nm before all the colour was lost.

Three chromophores can be considered to contribute to the ring opened species from the naphthopyran (2). The resonance structure (3.1b) represents the contribution from the most aromatic species, the two phenyl substituents acting as electron source to stabilize the positive charge. The structures (3.3b) and (3.4b) involve donation of electrons by the methoxy substituents and require the terminal phenyl rings to act as electron sinks, stabilizing the negative charge by delocalization (Fig. 2).

The chromophore which contributes the most to the colour is not obvious from studies on the naphthapyran.

The ultra-violet visible spectrum of the 9-methoxy-6-(*p*-methoxy phenyl) (2,2-spiro-2′-adamantyl)-naphtho-[1,2-b]-pyran (3) in toluene after irradiation gives a colourless to red heliochromic response (λ_{max} 484). Two fade rates are observed $t_{1/2}$ 150 sec and 12 h in toluene at 25°C. The absorbance maximum of the colour species was observed to be greater than that which would have been expected purely as a result of the 6-*p*-methoxy phenyl group.

The ultraviolet visible spectrum of the naphthopyran (4) in toluene shows a narrow absorption band in the near ultra-violet, tailing off at 350 nm. Irradiation with a flash gun results in very poor photocolouration to purple/mol 552 nm. Attempts to increase the intensity of the colour by further irradiation resulted in degradation and loss of the heliochromic properties. The poor photocolouration may be due to a high maternal filtering effect. The absorption maximum 552 represents a bathochromic shift of 40 nm as compared with the 2,2-diphenyl naphthopyran (2). From this observation, it appears that the major contribution to the colour of the ring opened the methoxy substituents.

6-phenyl-(2,2-spiro-2-adamantyl)-naphtho-[1,2-b]-pyran (5): The 6-phenyl substituent causes a small bathochromic shift of the absorption band of the uncoloured species. Irradiation with a flash-gun results in a change from colourless to orange (λ_{max} 452 nm). Two fade rates were observed, a fast initial fade ($t^{1/2}$ 90 sec) in toluene at 25°C and slower residual fade ($t^{1/2}$ 11 h).

Introduction of the 6-phenyl substituent did not show the expected large bathochromic shift of the long wavelength absorption band of the coloured species. It was expected that the 6-phenyl ring would contribtue considerably to the coloured species, but it appears that the benzannelation, which causes a hypsochromic shift of the absorption band in the visible region, is the dominant factor.

The absorption band of the uncoloured species in the near UV for the naphthopyran (6) shows a bathochromic shift of approximately 25 nm compared to the naphthopyran (1). Irradiation with a flash-gun results in a strong colourless to orange heliochromic response λ_{max} 449 nm. An initial fast fade ($t_{1/2}$ 56 min) and a slow fade ($t_{1/2}$ 11 h) in toluene at 25°C were observed. The bathochromic shift in the uncoloured species results in a greater sensitivity than (1); however, this is accompanied by a decrease in the fatigue resistance of the coloured species.

The ultra-violet visble spectrum of 2,2-di-(*p*-chloro-2H-naphtho-[1,2-b]-pyran (7) in toluene showed after irradiation of 1×10^{-4} M solution with light from a flashgun, resulted in an orange/red colouration (λ_{max} 472 nm) which fades rapidly at room temperature ($t_{1/2}$ = 18.5 min). The two *p*-chloro-phenyl groups caused a batchochromic shift of the long wavelength absorption band of the colour species in order of 36 nm compared with 2,2-dimethylnaphthopyran.

The results in all the examples show two coloured species were observed and are postulated to be *cis* and *trans o*-quinolides. Electron donating species of the 6-position in the naphtho-(1,2-b)-pyran results in a marked bathochromic shift in the long wavelength absorption band of the coloured species. The thermal fades of these compounds are also affected, with the residual fade being speed up due to steric interactions. Fatigue studies show that the substituent in the 6 and 9 positions increased the fatigue.

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