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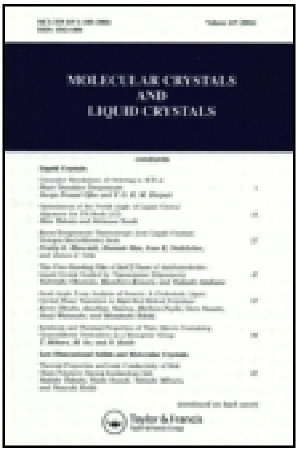

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Novel Photochromic Naphthopyran Derivatives V/A New General Synthetic Methodology

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NOVEL PHOTOCHROMIC NAPHTHOPYRAN DERIVATIVES *VIA* NEW GENERAL SYNTHETIC METHODOLOGY

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Abstract A new method for the synthesis of 2*H*-naphtho[1,2-b]pyrans in good yield has been developed. The pyrans were synthesised by double lithiation of 2-bromo-1-naphthol, reaction with an α,β-unsaturated aldehyde or ketone to give substituted hydroxymethylnaphthol intermediates, followed by cyclodehydration. Reaction of lithium 2-lithio-1-naphthoxide with heteroaryl aryl ketones has given 2*H*-naphtho[1,2-b]pyrans fused to a benzannelated heterocyclic ring system. The photochromic and tribochromic properties of these new compounds are intrinsically linked to the nature of the heteroatom, and to its position in the molecule with respect to the pyran oxygen. Reaction of lithium 2-lithio-1-naphthoxide with heteroaryl methyl ketones did not yield fused benzannelated heterocyclic naphthopyrans, but gave heteroaryl vinylnaphthol derivatives by an alternative dehydration mechanism. They are photochromic, presumably by keto-enol tautomerism. The colourless photochromic compounds show colour changes to yellow, orange or red.

INTRODUCTION

Photochromic naphthopyran derivatives colour upon exposure to ultraviolet light and undergo thermal bleaching and are of interest for use in the sunglass industry.[1] 2*H*-Naphtho[1,2-b]pyrans have a much greater quantum efficiency for colouring in unfiltered sunlight, but generally possess longer half-lives of the coloured forms at ambient temperatures compared to 3*H*-naphtho[2,1-b]pyrans.[1] The many available methods for the synthesis of 2*H*-naphtho[1,2-b]pyrans work less well than for

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3*H*-naphtho[2,1-b]pyrans, which has meant that a considerably larger number of 3*H*-naphtho[1,2-b]pyran derivatives have been synthesised and investigated. It was our intention to synthesise photochromic 2H-naphtho[1,2-b]pyran derivatives, with a variety of substituents in the pyran ring, in order to assess their potential for the sunglass application. During the course of our investigation, it became apparent that there was a lack of general methodology for accessing all but the simplest 2*H*-naphtho[1,2-b]pyrans in good yields.[2]

In 1984, Talley[3] used lithium 2-lithiophenoxide to synthesise a variety of 2*H*-benzopyran derivatives *via* its reaction with α,β-unsaturated aldehydes and ketones. Their method was extended to the synthesis of a simple 3H-naphtho[2,1-b]pyran derivative, and could be applied to the synthesis of a whole series of 2*H*-naphthopyran derivatives where the nature of the substituent in positions 2, 3 and 4 is controlled by reaction with the relevant α,β-unsaturated carbonyl precursor.

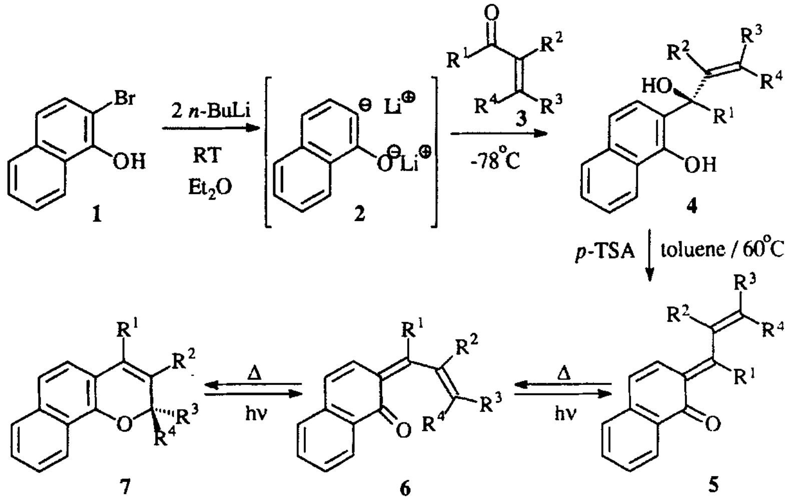
Irie and Uchida[4] have shown that a metallated heterocycle can undergo nucleophilic addition to 2-hydroxy-1-naphthaldehyde derivatives which, after cyclodehydration, gives 3*H*-naphthopyran derivatives with a heterocycle fused across the 2 and 3 positions of the pyran ring. This approach could be reversed by reacting lithium 1-lithio-2-naphthoxide with a heterocyclic aldehyde or ketone prior to cyclodehydration.

Talley's method[3] was developed for the synthesis of simple 2*H*-naphthopyran derivatives as well as to more complex fused systems, similar to those of Irie and Uchida.[4]

RESULTS AND DISCUSSION

2-Bromo-1-naphthol (**1**) was synthesised by the method of Pearson *et al*,[5] by the use of *N*-bromodimethylamine as an *ortho*-specific brominating agent. Double lithiation of naphthol **1** with 2 equivalents of *n*-butyllithium at room temperature, and subsequent reaction with α,β-unsaturated aldehyde or ketone **3** at -78°C gives hydroxynaphthol **4**, which undergoes acid-catalysed dehydration to give naphthopyran **8** (Scheme 1).

SCHEME 1



The reactions of lithium 2-lithio-1-naphthoxide (2) with some α,β-unsaturated aldehydes and ketones[6] are summarised in Table 1. The steric effect of a substituent into position 4 caused loss of room temperature photochromism. However, photochromism could still be observed at low temperatures (<-20°C). The introduction of a saturated ring across positions 3 and 4 (where ketone 3 is (R)-(+)-pulegone) caused total loss of photochromic properties at ambient and low temperatures. Rapid degradation occurred upon exposure to 366nm radiation.

TABLE 1

	R^1	R^2	R^3	R^4	Yield [a]	m.p.
7a	H	H	Me	Me	29%	oil [7]
7b	H	H	Ph	Ph	45%	130°C [8]
7c	H	H	Ph	3-MeBT [b]	30%	165-7°C
7d	Me	H	Me	Me	20%	oil [7]
7e	Ph	H	Ph	Ph	18%	155°C
7f	-CH$_2$-CH(Me)-CH$_2$-CH$_2$-		Me	Me	23%	oil

[a]-based on recrystallised or kugelrohr distilled products;
[b]-3-MeBT = 3-methylbenzo[b]thiophen-2-yl

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The reactions of lithium 2-lithio-1-naphthoxide (**2**) with aroyl heterocycles[9] (Scheme 2) are summarised in Table 2. The physical properties of the naphthopyran derivatives (**10** and **11**) are intrinsically linked to the nature and position of the heteroatom, and the steric nature of the substituents (Ar and R). Fused derivatives of benzothiophene, in which the two heteroatoms are *anti* not *syn* to each other (compounds **10a-c**), exhibit room temperature photochromism, colouring to orange or red upon exposure to UV light (λ=366nm), and bleaching thermally.

SCHEME 2

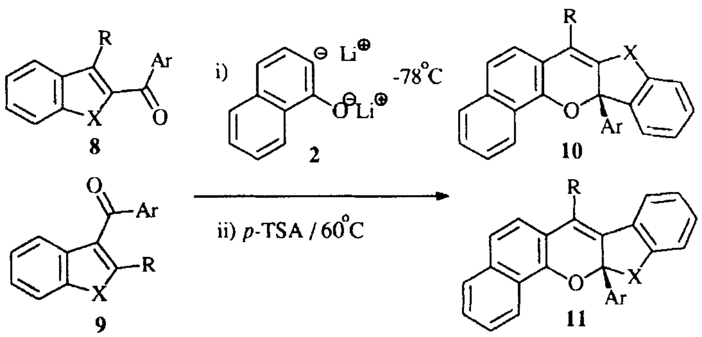

TABLE 2

	X	Ar	R	Yield[a]	m.p.	induced λ_{max} (ε)[b]	$t_{½}$[c]
10a	S	Ph	Me	29%	171°C	436nm(6730)	<3 secs
10b	S	Ph	Ph	49%	197°C	438nm(7940)	90 secs
10c	S	p-anisyl	Ph	21%	169°C	458nm(6960)	73 secs
10d	O	Ph	Ph	20%	205°C	d	d
10e	N-Me	Ph	Ph	36%	177°C	d,e	d,e
11a	O	Ph	Ph	29%	189°C	d	d
11b	N-Me	Ph	Ph	32%	148°C	588nm(11590)	d,f

[a]-based on recrystallised or kugelrohr distilled products; [b]-10^{-4}M solutions in toluene; [c]-Half-life of the coloured form at 25 °C; [d]-not photochromic; [e]-isolated as the coloured form; [f]-tribochromic

12b*H*-7,12b-Diphenylbenzothieno[3,2-b]naphtho[2,1-e]pyran (**10b**) photorearranged upon prolonged irradiation, giving 6b,12-Diphenyl-6b*H*-[1]benzothiopyrano[3,2-b]-naphtho[1,2-b]furan (**14**) in quantitative yield. Its structure was established by X-ray crystallography[10] (Figure 1). The photorearrangement (Scheme 3) is thought to proceed

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via an intramolecular, photochemical cycloaddition of the coloured *o*-quinonoidal ring open form of the naphthopyran(**12**), to give the unstable intermediate (**13**) which thermally undergoes sulphur bond migration to give product (**14**).

SCHEME 3

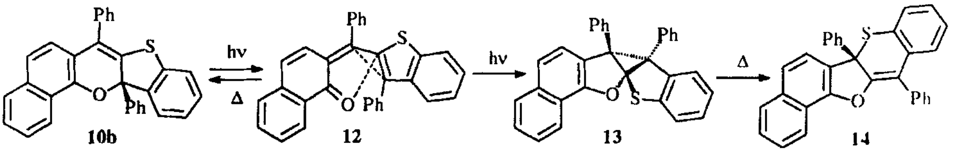
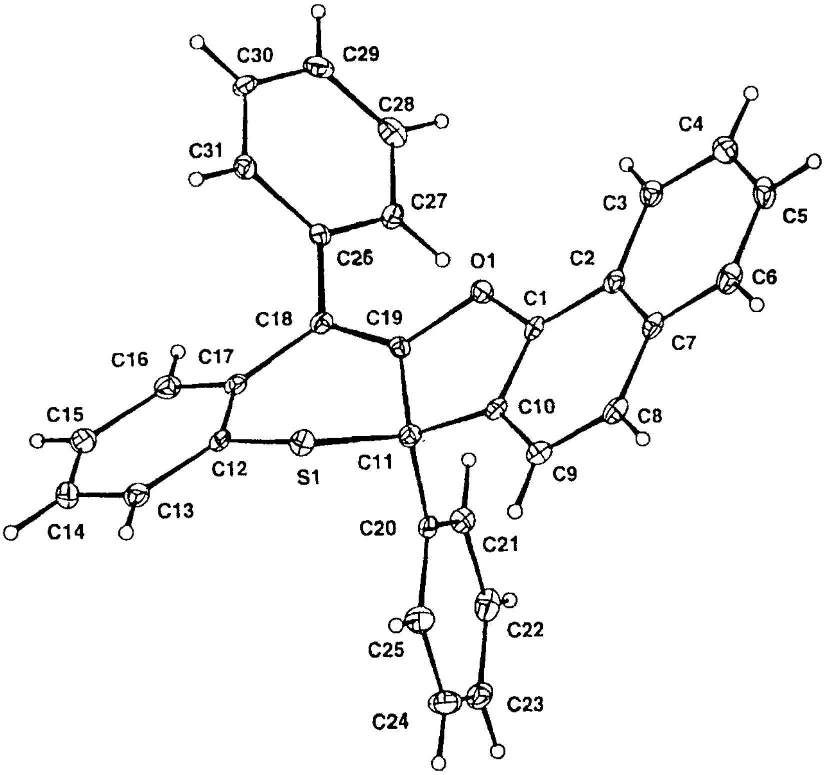


FIGURE 1: X-Ray Structure of **14**



Naphthopyran derivatives **10d-e and 11a-c**, were not photochromic. However, crystals of 12,12a-Dihydro-7,12a-diphenyl-12-methylnaphtho[2',1':5,6]pyrano[2,3-b]-indole (**11c**) underwent a marked colour change from yellow to deep purple upon grinding. This property was first reported by Heller and Asiri in 1994[11]. 'Tribochromism'

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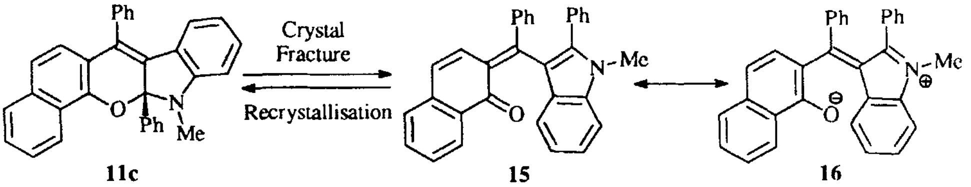
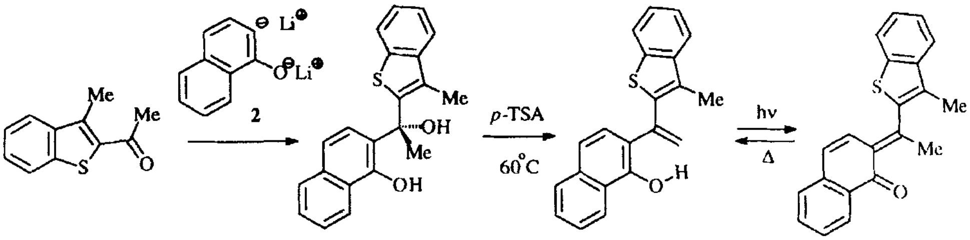
was defined by them as '*the phenomenon of crystals undergoing a major colour change upon mechanical grinding, where the induced colour does not revert back to the original colour when the fractured crystals are kept in the dark or exposed to the liquid or vapour of an organic solvent.*' It is believed that the yellow and purple forms of naphthopyran (**11c**) are the ring closed and ring open forms respectively (Scheme 4). In solution, the two forms are in equilibrium, the position of equilibrium being determined by the polarity of the solvent. In solvents of low polarity the yellow form predominates, whereas in solvents of high polarity the purple form predominates .The change in the position of equilibrium in different solvents can be determined by UV or NMR spectroscopy. It is suggested that the purple form has the character of the zwitterion (**16**) rather than the *o*-quinoid (**15**).

SCHEME 4



The reaction of lithium 2-lithio-1-naphthoxide with acetyl heterocycles[9] did not give the expected naphthopyran derivatives due to an alternative dehydration mechanism (For example, see Scheme 5). Products were photochromic not by electrocyclic reactions[12] but, presumably, by photoinduced keto-enol tautomerism (1,5-H-shift).[4]

SCHEME 5



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SUMMARY

A new method for the synthesis of photochromic 2*H*-naphthopyran derivatives which showed a colour change to yellow, orange or red, has been developed. This method should be applicable to the general synthesis of benzopyran and naphthopyran derivatives. Photochromic benzothieno[3,2-b]naphtho[2,1-e]pyran derivatives have been synthesised by this method also. A new series of tribochromic compounds, based on the naphtho[2',1':5,6]pyrano[2,3-b]indole nucleus, has been discovered.

REFERENCES

1. a) H. Dürr and H. Bouas-Laurent, Editors, Studies in Org. Chem. 40 - Photochromism Molecules and Systems (Elsevier Press, Amsterdam, 1990); b) R. Guglielmetti and A. Samat, Editors, Mol. Cryst. Liq. Cryst. (Proc. of the 1st Int. Symp. on Org. Photochromism, France, 1993), 246 (1994); c) J. M. Kelly, C. B. McArdle, M. J. de F. Maunder Editors, Photochemistry and Polymeric Systems (RSC, Oxford, 1993).
2. E. E. Schweizer and D. Meeder-Nycz in The Chemistry of Heterocyclic Compounds 31, Chromenes, Chromanones and Chromones, edited by G. P. Ellis (Wiley, London, 1977), chap. II, pp. 11-141.
3. a) J. J. Talley, Synthesis, 845 (1983); b) J. J. Talley, J. Org. Chem., 50, 1695 (1985).
4. a) M. Uchida and M. Irie, Chem. Letts., 2159 (1991); b) M. Uchida and M. Irie, Chem. Letts., 2257 (1992); c) M. Uchida and M. Irie, J. Amer. Chem. Soc., 115, 6442 (1993); d) M. Uchida, M. Kume and M. Irie, Bull. Chem. Soc. Jpn., 69, 1023 (1996).
5. D. E. Pearson, R. D. Wysong and C. V. Breder, J. Org. Chem., 32, 2358 (1967).
6. 3-Methyl-2-butenal, β-phenylcinnamaldehyde, mesityl oxide and (R)-(+)-pulegone were purchased from Aldrich Chemical Company; 1,3,3-triphenyl-2-propen-1-one was synthesised by the method of G. R. Clemo, J. Chem. Soc., 431 (1939).
7. R. Livingstone and R. B. Watson, J. Chem. Soc., 1509 (1957).
8. J. Cottam and R. Livingstone, J. Chem. Soc., 5228 (1964).

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9. 3-Methylbenzo[b]thiophene,[13a] 3-phenylbenzo[b]thiophene,[13b] 2- and 3-phenylbenzo[b]furan,[13c] and 1-methyl-2-phenyl(1*H*)indole[13d] were synthesised by literature procedures, as referenced, and acylated by Friedel-Crafts reactions using tin(IV) chloride as the Lewis-acid. 2-Benzoyl-1-methyl-2-phenyl(1*H*)indole was synthesised by the method of C. D. Jones and T. Suarez, J. Org. Chem., 37(23), 3622 (1972).

10. Crystal Data for compound **14**: $C_{31}H_{20}OS$, M_r=440.53, monoclinic, space group P2(1)/n, a=9.3240(4)Å, b=14.719(3)Å, c=16.3090(10)Å, β=99.020(5), V=2210.6(5)$Å^3$, Z=4, D_x=1.324 g cm^{-3}, R_1=0.0600, wR_2=0.0920 for all 3296 unique data and 298 parameters [R_1=0.0394 for data with $I>2\sigma(I)$]. Data were recorded using a FAST TV area detector defractometer and Mo-Kα radiation. The structure was solved by direct methods (SHELXS),[14a] and refined using full-matrix least squares methods in SHELX93.[14b] Hydrogen atoms were included in idealised positions with U_{iso} values linked to the U_{equs} of the parent atoms. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

11. a) A. M. A. Asiri, Ph.D. Thesis (University of Wales, 1994); b) H. G. Heller and A. M. Asiri, PCT Int. Appl. WO 94 26,729 (Cl. C07D307/02) 1994.

12. a) J. Kolc and R. S. Becker, J. Phys. Chem., 71, 4045 (1967); b) J. Kolc and R. S. Becker, Photochem. Photobiol., 12, 383 (1970).

13. a) R. P. Dickenson and B. Iddon, J. Chem. Soc. (C), 2733 (1968); b) J. E. Banfield, W. Davies and S. Middleton, J. Chem. Soc., 4791 (1956); c) W. Davies and S. Middleton, J. Chem. Soc., 822 (1958); d) H. M. Kissman, J. Amer. Chem. Soc., 74, 3948 (1952).

14. a) G. M. Sheldrick, SHELXS, University of Göttingen, 1986; b) G. M. Sheldrick, SHELX93, University of Göttingen, 1993.

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