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Contributed paper

Synthesis of diethyl 2H-naphtho[2,1,b]pyran-2,3-dicarboxylate and some related compounds as UV absorbers

A.M. Asiri and I.M.I. Ismail
Department of Chemistry, Faculty of Science, King Abdul-Aziz University, Jeddah, Saudi Arabia

Abstract
Purpose – Synthesis and evaluation of new naphthopyran and related compounds as ultraviolet absorbers.
Design/methodology/approach – The new naphthopyran and related compounds were prepared using new synthesis methodology which gave new derivatives via positions not accessible by traditional methods.
Findings – A new method for the preparations of naphthopyran was developed. The naphthopyran compounds prepared had promising UV absorption/protection capabilities.
Practical implications – The new compounds synthesised had unique character enabling them to be used in applications such as UV absorber and sunscreen.
Originality/value – New method of synthesis and the possibility of using the naphthopyran derivatives as UV absorber in many applications.

Keywords Organic compounds, Ultraviolet radiation

Paper type Research paper

Introduction

Naphthopyrans are important heterocycles and are found in many natural products (Cameron *et al.*, 1992). There have been a number of comprehensive reviews describing the synthesis of the naphthopyrane ring systems (Strandtmann *et al.*, 1968; Matloubi-Moghaddam *et al.*, 1966; Saidi and Fibrous-Zare, 1994). 2*H*-Naphthopyrans are a well known class of organic photochromic compounds, which find many applications in the industry of sunglasses and photochromic screens (Hirshberg and Fisher, 1954; McArdle, 1992). For example, the yellow 2*H*-naphthopyran 1 undergoes photo-coloration to give the red opened form 2, upon irradiation with UV light (e.g. 366 nm) (Scheme 1, Figure 1).

Recently (Yavari and Ramazani, 1996), it had been reported that diethyl 2*H*-benzopyran-2,3-dicarboxylate was efficiently prepared in high yield via protonation of the highly reactive intermediate produced in the reaction of diethyl acetylenedicarboxylate and triphenylphosphine by 2-hydroxybenzaldehyde. The intermediate underwent an intramolecular Wittig reaction to produce the derivative 3. Later, this reaction was found to be general and it was used to synthesize diethyl 2*H*-naphtho-[2,1,*b*]pyran-2,3-dicarboxylates 4 from 2-hydroxy-1-naphthaldehyde (Yavari and Ramazani, 1997). In this report we wish to record our reinvestigation on compound 4 and some of its related compounds as ultraviolet absorbers.

Experimental

Melting points were recorded on a Thomas-Hoover capillary melting apparatus without correction. Microanalyzes were carried out using a Perkin-Elmer 240B Analyzer. IR spectra were taken as KBr disk on a Nicolet Magna 520 FTIR spectrometer. H^1-NMR spectra were recorded in $CDCl_3$ on a Brucker DPX 400 MHz spectrometer using TMS as an internal standard. C^{13}-NMR spectra were recorded in $CDCl_3$ on a Brucker DPX 100 MHz. UV-visible spectra were taken on a Perkin-Elmer Lambda 25 UV-vis spectrophotometer.

Materials

Diethyl acetylenedicarboxylate, triphenyl phosphine, hydrazine hydrate and 2-hydroxy-1-naphthaldehyde, used in the investigation reported here, were all supplied by Aldrich chemicals Co.

Diethyl 2H-naphtho[2,1,-b]pyran-2,3-dicarboxylate 4

Triphenylphosphine (13.1 g, 0.05 mol) and 2-hydroxy-1-naphthaldehyde (8.6 g, 0.05 mol) were dissolved in dichloromethane (100 ml) and stirred at room temperature for 30 min and then cooled to −10 °C. Diethyl acetylenedicarboxylate (8.5 g, 0.05 mol) dissolved in

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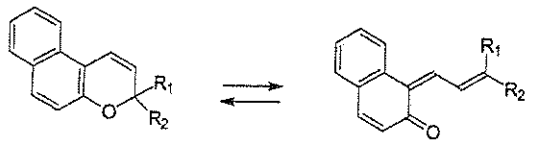
Figure 1 Scheme 1



1 2

dichloromethane (20 ml) was added dropwise over period of 20 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 2 days. The solvent was removed under reduced pressure and the residue was purified by column chromatography over silica gel using ether-toluene as an eluent. The solvent was removed under reduced pressure and the product was obtained as bright yellow cubes from toluene (14.7 g, 90 per cent), m.p. 58-60°C (lit., 53-55°C from ethanol). The infrared absorption was found to be at 1,725 and 1701 cm^{-1} (C=O), 1,630 cm^{-1} (C=C), 1,275 and 1,117 cm^{-1} (C—O). Relevant results of ^1H NMR are as follows, δ_C 13.7 (CH_3), 14.1 (CH_3), 60.1 (CH_2O), 61.1 (CH_2O), 70.9 (CHO), 112.5, 117.3, 119.4, 119.3, 121.4, 124.5, 127.8, 128.6, 129.0, 129.9, 133.1, 152.7, 163.6 (C=O) and 168.4 (C=O).

2H-naphtho[2,1,-b]pyran-2,3-dicarboxylic acid 6
A solution of diethyl 2*H*-naphtho[2,1,-*b*]pyran-2,3-dicarboxylate 4 (1.2 g, 3.67 mmol) and alcoholic KOH (10 ml, 10 per cent) was refluxed for 6 h. The solution was left to cool to room temperature, then poured onto water and acidified using concentrated hydrochloric acid (pH=5). The solid that isolated was filtered and washed with water and then with ethanol (2 × 20 ml) to give the crude product 6, which was crystallized from chloroform-toluene mixture to give the pure diacid as yellow-green crystals (0.85 g, 85 per cent), m.p. 200-202°C; (found: C, 66.53; H, 3.51. $C_{15}H_{10}O_5$ requires C, 66.69; H, 3.70 per cent); max/cm^{-1} 1,710 and 1,685 (C=O), 1,622 (C=C).

2H-naphtho[2,1,-b]pyran-2,3-dicarboxylic anhydride 7
2*H*-Naphtho[2,1,-*b*] pyran-2,3-dicarboxylic acid 6 (0.5 g, 1.85 mmol) was dissolved in dichloromethane (10 ml) and cooled to 0°C before adding a solution of acetyl chloride (5 ml) in dichloromethane (10 ml), dropwise over a period of 30 min. Then, the reaction mixture was refluxed for 4 h, and excess acetyl chloride was removed under reduced pressure to give the crude anhydride. The pure anhydride 8 was obtained after crystallization from ethanol as yellow crystals (0.40 g, 86 per cent), m.p. 230-232°C; (found: C, 71.24; H, 2.98. $C_{15}H_8O_4$ requires C, 71.45; H, 3.17 per cent); max/cm^{-1} 1,810 and 1,760 (C=O), 1610 (C=C).

2H-naphtho[2,1,-b]pyran-2,3-hydraziде 8
A solution of diethyl 2*H*-naphtho[2,1,-b]pyran-2,3-dicarboxylate 4 (1.0 g, 3.06 mmol) and hydrazine hydrate (5 ml) in ethanol (15 ml) was refluxed for 6 h, then cooled to room temperature. The precipitated solid was filtered, washed with ethanol (2 × 10 ml) and dried. Recrystallisation from chloroform-toluene mixture gave the hydrazide 8 as light yellow crystals (0.72 g, 88 per cent), m.p. 180-182 °C (found: C, 67.56; H, 3.61; N, 10.38. $C_{15}H_{10}N_2O_3$ requires C, 71.45; H, 3.17 per cent). Maximum IR absorption was found at 3,299 cm^{-1} (NH), 1,655 cm^{-1} (C=O) and 1,612 cm^{-1} (C=C).

Results and discussion

Compound 4 was prepared as previously reported (Yavari and Ramazani, 1997) and its structure was further investigated by H-H-COSY, H,C-COSY, NOE and DEPT techniques. In the NOE experiment, irradiation at 5.90 ppm caused enhancement of the signals at 8.23 ppm. The H-NMR spectrum is shown in Figure 2. The diester 4 was obtained as yellow crystals and when irradiated with UV lamp emitting at 366 nm, no photo-coloration was observed even at very low temperature (e.g. −78°C). This may be due to the steric interaction of the two diethylcarboxylate groups in the ring opened form 5 (Scheme 2, Figure 3) causing the photo-coloration reaction less favoured and cannot be detected.

It has been suggested that the conversion of the two-diethyl ester groups to the less steric groups would increase the chance of the photo-coloration to proceed.

Thus, hydrolysis of diethyl 2*H*-naphtho-[2,1,*b*]pyran-2,3-dicarboxylates 4 using alcoholic KOH resulted in the

Figure 2 H-NMR spectrum of naphthopyran 4

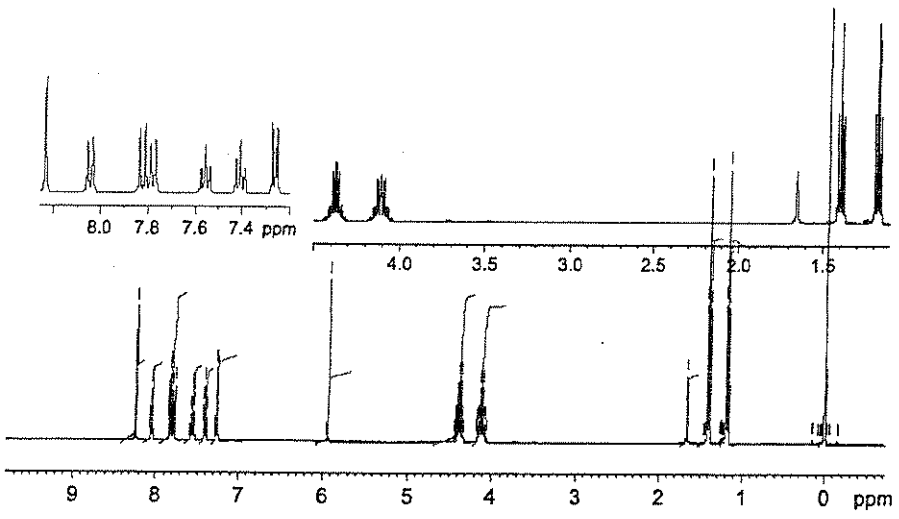
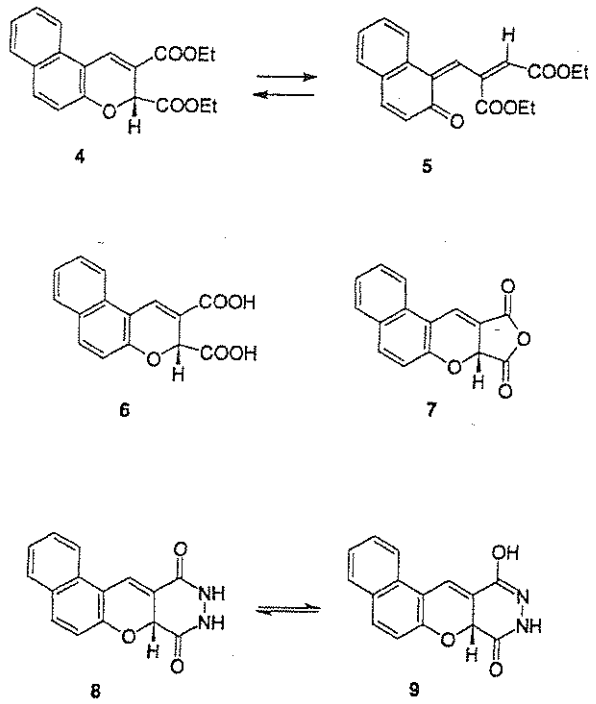


Figure 3 Scheme 2



complete hydrolysis of the two ester groups and the formation of the dicarboxylic acid derivative **6**. H^1-NMR spectrum of compound **6** revealed the absence of the protons of the two-ethoxy signals. Moreover, when the diacid **6** was subjected to dehydration using acetyl chloride as dehydrating agents, the dicarboxylic acid anhydride **7** was obtained in a good yield.

Unfortunately, when both diacid **6** and its anhydride **7** were subjected to irradiation with UV light, both in solid and solution, no coloration was observed either at room temperature or at −78°C, as was the case for the diethyl ester derivative **4**.

As a final attempt to modify the structure of the naphthopyran nucleus, we reacted the diester **4** with hydrazine hydrate in ethanol, the hydrazide **8** was obtained in relatively good yield. The later showed IR absorption bands at 3,299 and 1,655 cm^{-1} for the NH and carbonyl groups,

Table I H-NMR data of compounds 4 and 6-8

Compound no.	H-2	H-4	H-5	H-6	H-7	H-8	H-9	H-10
4[a]	5.90	8.23	8.18	7.58	7.44	7.89	7.93	7.28
	J 1.1	*J* 1.1	*J* 8.35	*J* 7.96	*J* 7.20	*J* 8.4	*J* 8.8	*J* 8.82
				J 15	*J* 14.6			
6	5.92	8.22	8.03	7.55	7.67	7.77	7.80	7.27
	J 0.9	*J* 0.9	*J* 8.41	*J* 7.24	*J* 7.00	*J* 8.13	*J* 8.9	*J* 8.86
				J 14	*J* 13.3			
7	5.87	8.19	8.02	7.55	7.40	7.78	7.81	7.25
	J 1.0	*J* 1.0	*J* 8.34	*J* 7.7	*J* 7.5	*J* 8.3	*J* 8.95	*J* 8.83
				J 15.0	*J* 14.7			
8	5.83	8.06	8.15	7.57	7.41	7.82	7.25	7.11
	J 0.85	*J* .85	*J* 8.44	*J* 7.4	*J* 7.1	*J* 8.92	*J* 8.9	*J* 8.86
				J 14.5	*J* 14.5			

Note: [a]Other signals: 4.3, 4.05 (4H, q, 2 × CH_2O), 1.37, 1.12 (6H, t, 2 × CH_3)s; all *J* values are in Hz

respectively. This indicated that the compound existed completely in the lactam form **8** and hence no tautomerisation to the lactim form **9** was detected.

On the other hand, all prepared compounds **4-8** showed strong fluorescence in the solid state when exposed to UV light (366 nm) (Table I).

Ultraviolet absorption properties

The UV-visible spectra of the new pyrans are shown in Figures 4-7. In general, most of the derivatives show absorption bands in the region 300-400 nm and a valley near 350 nm. Finally, the pyran derivatives prepared are good

Figure 4 UV-visible spectrum of compound 4 in DMSO

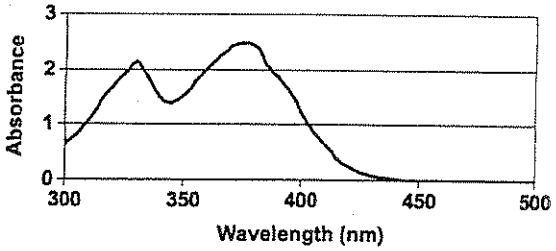


Figure 5 UV-visible spectrum of compound 6 in DMSO

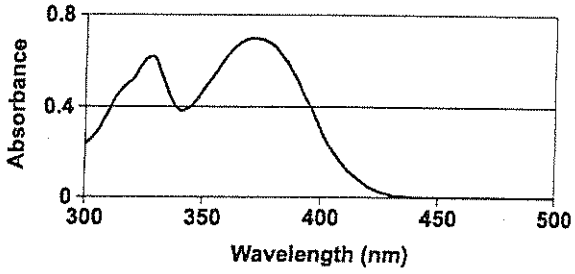


Figure 6 UV-visible spectrum of compound 7 in DMSO

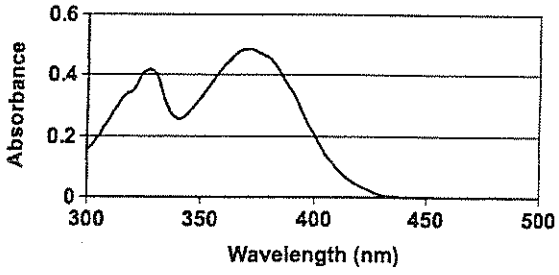
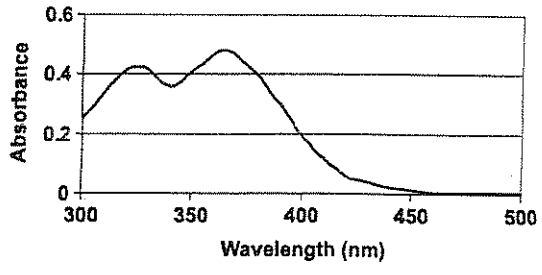


Figure 7 UV-visible spectrum of compound 8 in DMSO



candidates to be used as ultraviolet absorber for the UVB type in the range 300-400 nm.

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