

## LETTERS TO THE EDITOR

SYNTHESIS OF BENZO(f) CHROMONE BY PHOTOOXIDATIVE CYCLISATION OF 2-STYRYL- $\gamma$ -PYRONE

B. VEERA MALLAIAH AND G. SRIMANNARAYANA  
Department of Chemistry, Osmania University,  
Hyderabad 500 007, India.

PHOTOOXIDATIVE cyclization of stilbene derivatives is found to be a facile method to synthesize phenanthrenes although the yields are low<sup>1</sup>. In this communication, we report, a facile photooxidative cyclization of 2-styryl- $\gamma$ -pyrone (II) to benzo(f)chromone (IV) in 25% yield.

2-Methyl-5-methoxy $\gamma$ -pyrone (I)<sup>2</sup> on condensation with benzaldehyde in the presence of aq. sodium hydroxide furnished *trans* 5-methoxy-2-styryl-4H-1-pyran-4-one (II). (I) Was synthesized starting from Kojic acid by a three-step sequence<sup>2</sup>.

The irradiation of a dilute methanolic solution of (II) in presence of iodine (using a medium pressure mercury arc lamp of OMEGA long wavelength model, 300 W) yielded 2-methoxy-1H-naphtho[2,1-b]pyran-1-one (IV) in 25% yield via oxidative photocyclization of unisolable *cis* isomer (III). The starting  $\gamma$ -pyrone (II) was recovered in 72% yield.

The structure of the photoproduct IV was confirmed by analytical and physical data and also by an unambiguous synthesis which involves the following steps: Benzo(f)chromanone (V)<sup>3</sup> on treatment with amyl nitrite and hydrochloric acid gave 3-hydroxybenzo(f)chromone (VII) via an unisolable 3-oximinoderivative (VI). Methylation of VII furnished 3-methoxybenzo(f)chromone (2-methoxy-1H-naphtho[2,1-b]pyran-1-one) (IV). The photoproduct IV was found to be identical in all respects (mp, mmp and superimposable i.r.) with the authentic 3-methoxybenzo(f)chromone synthesized by the above route.

## 5-Methoxy-2-styryl-4H-1-pyran-4-one (II)

To a solution of aq. sodium hydroxide (50 ml, 50% w/v) allomaltol monomethyl ether (I)<sup>2</sup> (1.5 g) and benzaldehyde (1 ml) were added. The reaction mixture was kept at room temperature for 15 hr and poured into ice (100 g) where upon 5-methoxy-2-styryl-4H-1-pyran-4-one (II) separated as a pale yellow solid. It crystallised from methanol as pale yellow prisms (1 g; 40%), mp 152–54°. (Found: C, 73.50; H, 5.37; calculated for C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>, 73.69; H, 5.26%). M<sup>+</sup> m/e 228.

I.R. (KBr):  $\nu_{\max}$  = 1620 ( $\gamma$ -pyrone carbonyl); 1310 and 960 (*trans* ethylenic absorptions); 750 and 690

(out-of-plane C—H bending vibrations of mono substituted benzene ring); 1600, 1550 and 1500 cm<sup>-1</sup> (aromatic,  $-\dot{C}=\dot{C}-$  stretching vibrations).

U.V. (MeOH):  $\lambda_{\max}$  = 240 (log  $\epsilon$  = 4.26); 328 nm (4.50). P.M.R. was not recorded due to its poor solubility in common organic solvents.

## 3-Methoxybenzo(f)chromone (2-Methoxy-1H-naphtho[2,1-b]pyran-1-one) (IV):

To a solution of 5-methoxy-2-styryl-4H-1-pyran-4-one (II) (114 mg, 0.5 mmol) in methanol (250 ml) taken in quartz flask, iodine (63 mg) was added and the solution irradiated by a medium pressure mercury arc lamp (OMEGA long wave length model, 300 W) for 55 hr. The solution was concentrated under reduced pressure when most of the iodine was removed along with the solvent. The crude semi-solid product was chromatographed over silica gel (20 g) and eluted with petr. ether (b.p. 60–80°) (fractions 1 to 4, each 10 ml), benzene (fractions 5 to 10, each 10 ml) and chloroform (fractions 11 to 15, each 10 ml and 16 to 20, each 50 ml). The petr. ether and first two fractions of benzene (fractions 1 to 6) yielded iodine. The latter fractions of benzene and earlier chloroform fractions (fractions 7 to 15) yielded 2-methoxy-1H-naphtho[2,1-b]pyran-1-one (IV) as brown solid. It crystallised from methanol as brown needles (28 mg; 25%), m.p. 40°. (Found C, 74.26; H, 4.50; Calculated for C<sub>14</sub>H<sub>10</sub>O<sub>3</sub>; C, 74.33; H, 4.4%). M<sup>+</sup> m/e 226.

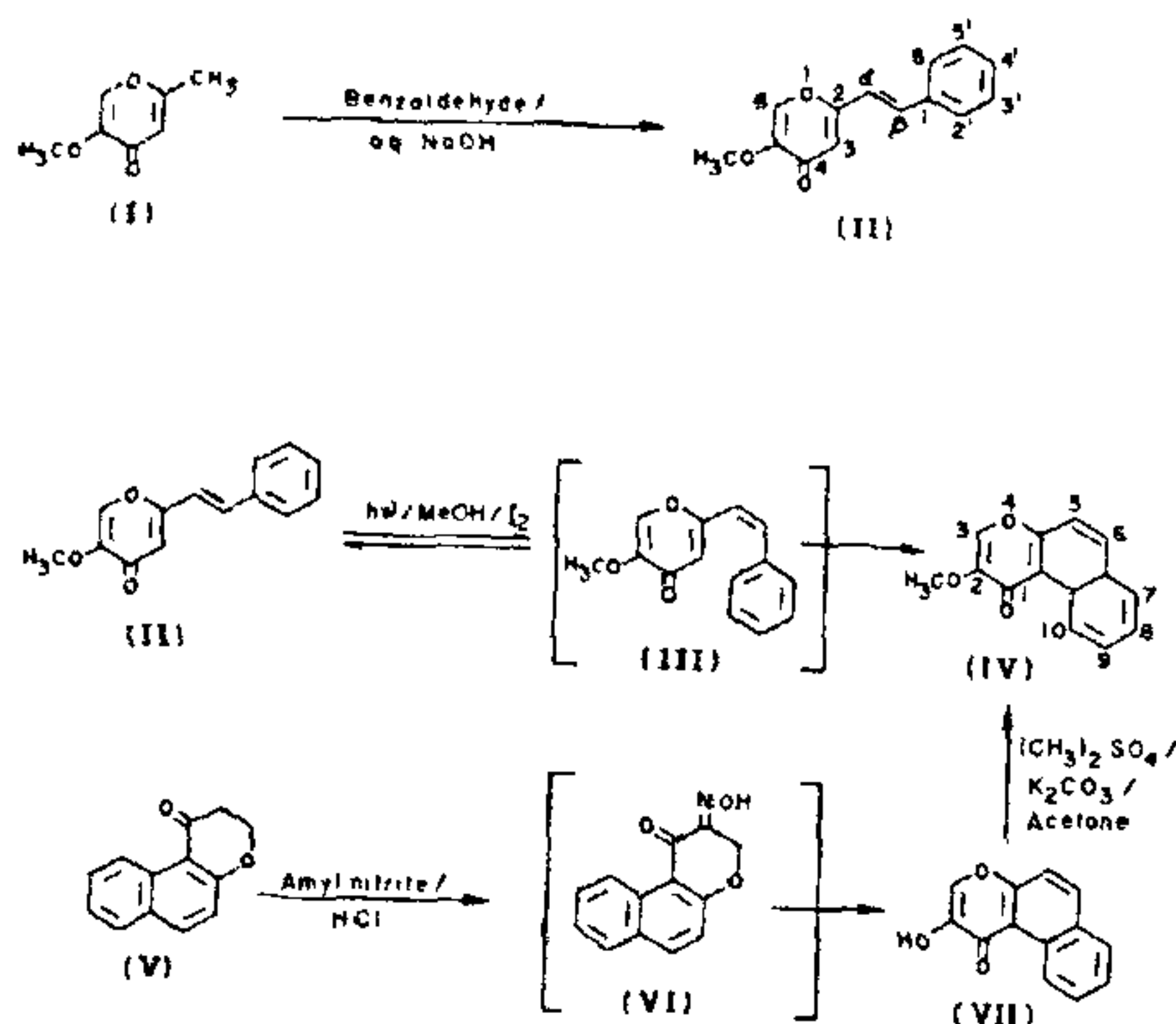
M.S: m/e (relative intensity) = 226 (M<sup>+</sup>, 30%); 183 (M—CH<sub>3</sub>—CO, 100%); 225 (M—H, 25%); 198 (M—CO, 20%); 167 (M—CO—OCH<sub>3</sub>, 30%); 155 (M—CH<sub>3</sub>—CO—CO, 15%); 170 (RDA, 44%); 56 (RDA, 46%); 171 (RDA with H transfer, 15%).

I.R. (KBr):  $\nu_{\max}$  = 1640 ( $\gamma$ -pyrone carbonyl) 1610, 1545, 1505 cm<sup>-1</sup> (Aromatic,  $-\dot{C}=\dot{C}-$  stretching vibrations).

U.V. (MeOH):  $\lambda_{\max}$  = 228 (log  $\epsilon$  = 4.55); 260 (4.50); 324 nm (4.28).

P.M.R. (CDCl<sub>3</sub>):  $\delta$  10.00 (d, 1H, J<sub>10H, 9H</sub> = 8.0 Hz, C<sub>10H</sub>); 7.6 (s, 1H, C<sub>3H</sub>); 7.7 to 8.0 (m, 5H Aromatic); 3.8 (s, 3H, —OCH<sub>3</sub>); The latter chloroform fractions (fractions 16 to 20) on concentration under reduced pressure gave the starting material 5-methoxy-2-styryl-4H-1-pyran-4-one (II). 82 mg (72%).

Authentic synthesis of 2-methoxy-1H-naphtho[2,1-b]pyran-1-one



(i) *Synthesis of 2-hydroxy-1H-naphtho[2,1-b]pyran-1-one (VII)*. A solution of benzo(f) chromanone (V)<sup>3</sup> (6 g) in methanol (40 ml) was kept in an ice chest and small quantities of amyl nitrite (18 g) and conc. hydrochloric acid (36 ml) were alternately added with shaking. The resulting solution gradually turned up red and after complete addition the reaction mixture was gently heated on a flame for 2 hr. The reaction mixture was poured into ice (100 g) whereupon a brown yellow solid was precipitated. It was filtered and crystallised from methanol as yellow flakes (3 g, 48%); m.p. 130–32° (Found: C, 73.60; H, 3.74 calculated for C<sub>13</sub>H<sub>8</sub>O<sub>3</sub> C, 73.58; H, 3.77%). M<sup>+</sup> m/e 212.

(ii) *2-Methoxy-1H-naphtho[2,1-b]pyran-1-one (IV)*

A mixture of 2-hydroxy-1H-naphtho[2,1-b]pyran-1-one (VII) (1 g), dimethyl sulphate (0.7 ml), potassium carbonate (10 g) and acetone (150 ml) was refluxed for 10 hr. The solution was distilled to remove acetone and crushed ice added to the residue. The brown semi-solid, that separated, crystallized from methanol as brown needles of 2-methoxy-1H-naphtho[2,1-b]pyran-1-one (IV) (0.97 g, 90%), m.p. 40°. The photoproduct (IV) was found to be identical in all respects (mp, mmp and superimposable i.r.) with the authentic sample of 2-methoxy-1H-naphtho[2,1-b]pyran-1-one.

8 February 1982

## X-RAY SPECTROSCOPIC DETERMINATION OF THE VALENCE STRUCTURE OF THE SPINEL NiMnCrO<sub>4</sub>

P. D. BHALERAO

Institute of Science, Nagpur 440 001, India.

ALTHOUGH some information about the spinel NiMnCrO<sub>4</sub> is available<sup>1</sup>, it was thought worthwhile to study the spinel x-ray spectroscopically, to determine its valence structure uniquely. The compound NiMnCrO<sub>4</sub> was prepared by the oxide method<sup>2</sup> and the formation was confirmed by the x-ray powder method. The observed  $1/d^2$  values for various reflections along with the calculated  $1/d^2$  values and observed and calculated intensities of the various diffraction lines are given in table 1. The x-ray spectroscopic results for manganese and chromium ions are given in table 2 and 3 respectively. The detailed procedure for calculation of intensities and x-ray spectroscopic determination of oxidation states of cations have already been reported<sup>3</sup>.

TABLE 1

*X-ray diffraction data of the spinel NiMnCrO<sub>4</sub>*

hkl	$1/d^2$		Intensity	
	Obs.	Cal.	Obs.	Cal.
111	0.0447	0.0438	10	5.3
220	0.1178	0.1169	25	24.7
311	0.1604	0.1604	100	100
222	0.1788	0.1754	10	8.8
400	0.2372	0.2339	25	22.4
422	0.3530	0.3510	10	9.5
511	0.3940	0.3949	30	24.5
440	0.4666	0.4678	50	52.3
533	0.6329	0.6434	10	10.5
731	0.8510	0.8528	15	14.3
751	1.0796	1.0950	<5	5.8
555				1.9
844	1.3859	1.4016	30	31.6
951	1.5453	1.5622	20	18.5

$$a = 8.28 \pm 0.02 \text{ \AA}$$

The possible valence structures for this spinel are

- (i) Ni<sup>+2</sup>Mn<sup>+3</sup>Cr<sup>+3</sup>O<sub>4</sub><sup>-2</sup> (ii) Ni<sup>+2</sup>Mn<sup>+4</sup>Cr<sup>+2</sup>O<sub>4</sub><sup>-2</sup>  
 (iii) Ni<sup>+3</sup>Mn<sup>+2</sup>Cr<sup>+3</sup>O<sub>4</sub><sup>-2</sup> (iv) Ni<sup>+3</sup>Mn<sup>+3</sup>Cr<sup>+2</sup>O<sub>4</sub><sup>-2</sup>

1. Sang, C. S. and Suk Kyu Lee, *Synthesis*, 1980, 116 and references cited therein.
2. Yabuta, J., *J. Chem. Soc.*, 1924, 125, 575.
3. Chakravarthi, D. and Dutta, J., *J. Indian Chem. Soc.*, 1939, 16, 639.