

# An easy synthesis of thermochromic ethylenes under microwave irradiation<sup>†</sup>

Didier Villemin<sup>a\*</sup>, Messaoud Hachemi<sup>b</sup> and Mohamed Hammadi<sup>b</sup>

<sup>a</sup>Ecole Nationale Supérieure d'Ingénieurs de Caen, ISMRA, CNRS UMR 6507, Université de Caen, F-14050, Caen, France

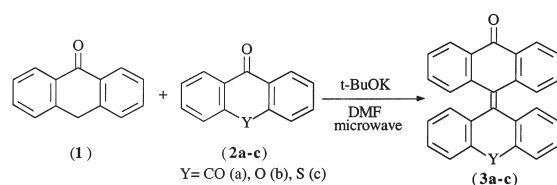
<sup>b</sup>Université de Boumerdès Faculté des Sciences, 35000 Boumerdes, Algeria

Thermochromic ethylenes were obtained by the reaction of anthrone with tricyclic ketones or terephthalaldehyde in DMF in the presence of potassium *tert*-butoxide under reflux (8h) or under microwave irradiation (10 min.).

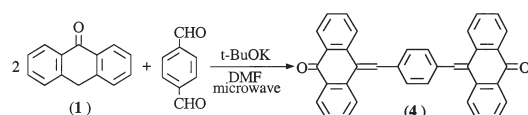
**Keywords:** thermochromic compound, microwave, condensation

Overcrowded bistricyclic aromatic ethylenes show thermochromic and photochromic properties.<sup>1</sup> Reversible thermochromic compounds are useful in display devices. These thermochromic and photochromic properties are due to the easy formation of radicals by thermolysis or photolysis of the ethylenic double bond.<sup>2</sup> This behaviour can be predicted by semi-empirical or *ab-initio* calculation.<sup>3</sup>

We have already described<sup>4</sup> the condensation of anthrone with piperonal on potassium fluoride on alumina under microwave irradiation. More recently the condensation of anthrone with seven aromatic aldehydes in ethanol under microwave irradiation was also described.<sup>5</sup>



**Scheme 1** Synthesis of overcrowded bistricyclic aromatic ethylenes (**3a-c**).



**Scheme 2** Synthesis of the diene (**4**).

Herein we wish to report for the first time the preparation of thermochromic overcrowded bistricyclic aromatic ethylenes under microwave irradiation.<sup>6</sup> The reaction was performed with a small quantity of DMF and with potassium *tert*-butoxide as a basic catalyst. Although the reaction can be catalysed by potassium fluoride on alumina, the use of potassium *tert*-butoxide allows more easy recovery of the solid product and the basic catalyst is easily eliminated by washing with

water. A small quantity of solvent (DMF) was used. The large molecular mass of the starting material and its high melting point do not allow for good mixing of the reactants when the reaction is conducted without a solvent. Also without a solvent, the reaction was observed to be incomplete. Anthrone (**1**) with anthraquinone (**2a**) or xanthone (**2b**) or thioxanthone (**2c**) gave products (**3a-c**) according to the Scheme 1. With terephthalaldehyde and anthrone, the diene (**4**) was obtained as shown in Scheme 2. Although the yield under microwave irradiation and under reflux were quite similar, the reaction time (10 min) in comparison to that effected by classical heating (8h) was much shorter. The reaction was conducted with the new commercially available mono-mode resonance cavity Discover® (2450 MHz).

All products have melting point greater than 300°C and were identified by their spectra (<sup>1</sup>H and <sup>13</sup>C NMR, IR and mass spectra). All products had correct quantitative elemental analysis and gave only one spot on a TLC plate. The chemical shift of CO in carbon resonance spectroscopy (<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ(CO)) are characteristic of the compounds prepared and are reported in Table 1.

Many thanks to CEM Corporation<sup>7</sup> for generous lending of their Discover® apparatus.

## Experimental

<sup>1</sup>H and <sup>13</sup>C NMR (reference from internal Me<sub>4</sub>Si) were recorded on a Bruker AC 250 instrument from solution in CDCl<sub>3</sub>. FT IR spectra were recorded on a Perkin-Elmer 16 PC spectrometer.

*General procedure: example synthesis of bianthrone:* (i) *Classical heating:* Anthrone (597 mg, 3 mmol), anthraquinone (624 mg, 3 mmol), potassium *tert*-butoxide (55 mg, 0.3 mmol) and dimethylformamide (5 ml) were stirred and refluxed for 8h. Water (50 ml) was added and the mixture was cooled with ice. The solid was obtained by filtration was washed with water (10 ml) and dried at 110°C.

(ii) *Under microwave irradiation:* A mixture of anthrone (597 mg, 3 mmol), anthraquinone (624 mg, 3 mmol), potassium *tert*-butoxide (55 mg, 0.3 mmol) and dimethylformamide (1 ml) was irradiated in a Discover® mono-mode microwave irradiator for 10 min (150 W).

**Table 1** Synthesis of thermochromic ethylenes under classical conditions or under microwave irradiation

Carbonyl compound	N°	microwave yield (%)	heating yield (%)	<sup>13</sup> C δ(CO) ppm	formula	Calculated (%)	Found (%)
Anthrone	3a	94	96	184.67	C <sub>28</sub> H <sub>16</sub> O <sub>2</sub>	H 4.20 C 87.48	H 4.16 C 87.45
Xanthone	3b	95	94	171.62	C <sub>27</sub> H <sub>16</sub> O <sub>2</sub>	H 4.33 C 87.08	H 4.29 C 86.98
Thioxanthone	3c	96	95	180.35	C <sub>27</sub> H <sub>16</sub> OS	H 4.15 C 83.48	H 4.12 C 83.42
Terephthalaldehyde	4	84	87	163.12	C <sub>36</sub> H <sub>22</sub> O <sub>2</sub>	H 4.56 C 88.87	H 4.52 C 88.82

\* To receive any correspondence.

<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Ice cooled water (50 ml) was added and the product was obtained by filtration. The product was dried at 110° C and crystallised from ethanol.

Received 22 October 2002; accepted 11 November 2002  
Paper 02/1612

### References

- 1 U.P. Biedermann; I. Agranat, J.J. Stezowski, *J. Chem. Soc. Chem. Commun.*, 2001, 954.
- 2 (a) H.H. Richtol, R.L. Strong, L. Dombrowski, *J. Isr. J. Chem.* 1974, **12**, 791; (b) G. Kortuem, W. Zoller, *Chem. Ber.* 1970, **103**, 2062; (c) I. Agranat, M. Rabinovitz, H.R. Falle, G.R., Luckhurst, J.N. Ockwell, *J. Chem. Soc. B* 1970, 294; (d) S. Kazama, M. Kamiya, Y. Akahori, *Chem. Pharm. Bull.* 1991, **39**, 3103; (e) S. Kazama, M. Kamiya, Y. Akahori, *Chem. Pharm. Bull.* 1984, **32**, 5018; (f) S. Kazama, E. Sato, M. Kamiya, Y. Akahori, *Chem. Pharm. Bull.* 1980, **28**, 2216.
- 3 S. Nakatsuji, T. Yahiro, K. Nakashima, S. Akiyama, H. Nakazumi, *Bull. Chem. Soc. Jpn.* 1991, **64**, 1641.
- 4 A. Ben Alloum, B. Labiad, D. Villemin, *J. Chem. Soc. Chem. Commun.*, 1989, 386.
- 5 Jian-Feng Zhou, Shu-Jiang Tu, Jun-Cai Feng, *J. Chem. Res. (S)* 2001, 414.
- 6 B.L. Hayes, *Microwave Synthesis-Chemistry at the Speed of Light*, CEM publishing, Matthews, 2002.
- 7 CEM Corporation PO Box 200, Matthews NC28106-0200, USA.