Available online at www.sciencedirect.com

Dyes and Pigments 71 (2006) 68–72

www.elsevier.com/locate/dyepig

Microwave-assisted rapid synthesis of 1,4-diketo-pyrrolo[3,4-*c*]-pyrroles' derivatives under solvent-free conditions

Ahmad Shaabani [a,*], Minoo Dabiri [a], Ayoob Bazgir [a], Kamaladin Gharanjig [b]

[a] *Department of Chemistry, Shahid Beheshti University, P.O. Box 19396-4716, Tehran, Iran*
[b] *Iran Color Research Center (ICRC), P.O. Box 16765-654, Tehran, Iran*

Received 8 December 2004; received in revised form 7 June 2005; accepted 15 June 2005
Available online 24 August 2005

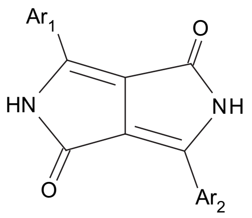
Abstract

The 1,4-diketo-pyrrolo[3,4-*c*]-pyrroles' derivatives are easily synthesized in good yields upon exposure to microwave irradiation under solvent-free conditions and reaction times are considerably reduced.

Keywords: 1,4-Diketo-pyrrolo[3,4-*c*]-pyrrole; Solvent-free; Microwave irradiation; Organic pigment; Nitrile

1. Introduction

3,6-Diaryl-1,4-diketopyrrolopyrrol (DPP) compounds are well-known as important organic pigments. Generally, these pigments are described by the formula wherein Ar_1 and Ar_2 are aryl groups [1].



DPP derivatives are useful as polymer soluble dyes or as pigments with high coloring strength and good fastness properties, especially fastness to heat [1]. DPP was first isolated as one of the several unexpected by-products from reaction of benzonitrile and ethyl bromoacetate in the presence of activated zinc–copper complex [2], however, the yield obtained was rather low.

The initial poor yield of this reaction was improved by using succinic acid diester and aromatic nitrile in an organic solvent and in the presence of a strong base at an elevated temperature, the DPP pigments are obtained in relatively good yields [3–6]. Another synthetic modification of the succinic acid principle was found by Closs and Gompper in the reaction of succindiamide with *N*,*N*-dimethylbenzamide diethyl acetal [7].

Even though a number of modified methods under improved conditions have been reported, most of them suffer from drawbacks such as unsatisfactory yields, high temperature and very long reaction times. Thus, the development of an efficient and versatile method for the preparation of DPP is an active ongoing research area and there is scope for further improvement toward reduced reaction times and improved yields. Microwave activation stands among alternative routes during the past decade due to the drastic reduction in reaction times.

In continuation of our previous work on microwave-assisted organic transformation and phthalocyanines based pigment synthesis [8,9], we herein wish to describe

---

* Corresponding author. Fax: +98 21 2403041.
E-mail address: a-shaabani@cc.sbu.ac.ir (A. Shaabani).

0143-7208/$ - see front matter © 2005 Published by Elsevier Ltd.
doi:10.1016/j.dyepig.2005.06.002

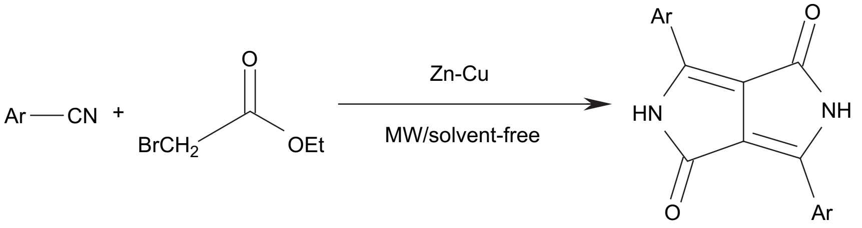
a facile preparation of 1,4-diketo-pyrrolo[3,4-*c*]-pyrroles' derivatives in the absence of any solvent, which reduced considerably the reaction times in a process that is accelerated by microwave irradiation.

2. Results and discussion

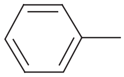
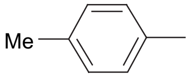
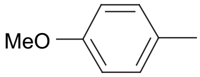
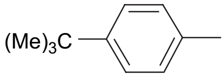
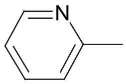
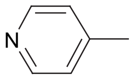
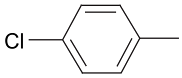
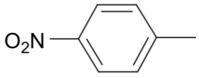
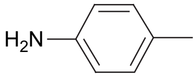
The experimental procedure involves a simple mixing and grinding of ethyl bromoacetate, benzonitrile and zinc–copper couple and irradiating the reaction mixture in a microwave oven for about 10 min in the absence of any solvent. The microwave oven was a domestic National model NN-6653 (maximum 900 W) with five select power levels (one of which was used for this experiment; high 100% wattage). This extremely rapid, manipulatively simple, and inexpensive protocol avoids the use of excess and toxic solvents. The results for various DPP derivatives are summarized in Table 1.

To explore the scope and limitations of this reaction, we extended the procedure to various *para*-substituted benzonitriles. We found that the reaction proceeds efficiently with benzonitrile and electron-releasing *para*-substituted benzonitriles (X = CH_3, $(CH_3)_3C$, CH_3O), but it did not proceed when electron-withdrawing

Table 1
Comparison of synthesis of DPP derivatives using ethyl-2-bromoacetate (**I**) and diethyl succinate (**II**) as raw materials



1 2 3a-i

Entry **3**	Ar	Yields (%)			
		I[a]	**I**[b]	**II**[a]	**II**[b]
a		71	22[c]	31	28[d]
b		59	–	23	23[d]
c		43	–	21	24[d]
d		53	–	27	25[d]
e		64	–	35	63[d]
f		67	–	37	68[d]
g		No reaction	15[c]	29	31[d]
h		No reaction	–	No reaction	No reaction[d]
i		No reaction	–	No reaction	No reaction[d]

[a] Under microwave irradiation.

[b] Classical heating conditions.

[c] From ref. [3].

[d] From ref. [12].

para-substituted benzonitrile (X = NO_2 and Cl) and strongly electron donating groups (X = NH_2) were used.

In addition, we have studied the synthesis of 1,4-diketo-pyrrolo[3,4-*c*]-pyrroles' derivatives by using diethyl succinate under microwave irradiation. As indicated in Table 1, the reaction yields are considerably decreased relative to using ethyl-2-bromoacetate.

In conclusion, we have developed a convenient and rapid procedure for the synthesis of DPPs using domestic microwave oven for a few minutes under solvent-free conditions including "dry" media.

3. Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 Mass Spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 Spectrometer. ^1H NMR spectrums were recorded on a BRUKER DRX-500 AVANCE Spectrometer at 500.13 MHz. NMR spectra were obtained from solutions in DMSO-d_6 using TMS as internal standard. UV/visible spectra were recorded with a Shimadzu 2100 Spectrophotometer. XRD and SEM measurements were carried out on X′Pert model and SEM model XL30 supplied by Philips Company, respectively. The chemicals used in this work were purchased from Fluka Chemical Company (Buchs Switzerland). *para*-*tert*-Butyl benzonitrile and Zn–Cu couple were prepared according to published procedures [10,11].

*3.1. Typical procedure: synthesis of 1,4-diketo-pyrrolo[3,4-c]-pyrroles by ethyl bromoacetate using microwave irradiation under solvent-free conditions (**3a**).*

Benzonitrile (0.21 g, 2 mmol), ethyl bromoacetate (0.50 g, 3 mmol) and Zn–Cu couple (0.4 g) were mixed and placed in a 25-ml beaker and was inserted into a screw-capped Teflon beaker and irradiated in a microwave oven at high power for 10 min. Upon completion of the reaction, the residue was washed with hot DMF (4 ml) and DMF filtrated was diluted with water (15 ml) and stirred for 5–10 min. The separated red solid was filtered under suction and washed with methanol (10 ml) to afford the pure product **3a** (0.41 g, 71%). Mp > 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3115 (NH), 1640 (C=O), 1610, 1597, 1493, 1449; λ_{max}/nm (DMSO) 506, 472, 320, 304; ^1H NMR (DMSO-d_6): δ_H 7.57 (6H, bs, arom), 8.47 (4H, bs, arom), 11.32 (2H, bs, 2NH); MS (*m*/*z*, %) 288 (M^+, 98), 157 (16), 129 (19), 104 (45), 77 (71), 44 (100).

Selected data for **3b**: Mp > 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3415 (NH), 1633 (C=O), 1599, 1555, 1504, 1433; λ_{max}/nm (DMSO) 516, 482, 445, 321; ^1H NMR (DMSO-d_6): δ_H 2.39 (6H, s, $2CH_3$), 7.37 (4H, d, ^3J 7.4 Hz, arom), 8.36 (4H, d, ^3J 7.4 Hz, arom), 11.20 (2H, bs, 2NH); MS (*m*/*z*, %) 316 (M^+, 65), 143 (14), 118 (28), 91 (36), 44 (100).

Selected data for **3c**: Mp > 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3120 (NH), 1631 (C=O), 1594, 1504, 1436, 1403; λ_{max}/nm (DMSO) 517, 480, 445, 335; ^1H NMR (DMSO-d_6): δ_H 3.31 (6H, s, $2OCH_3$), 7.10 (4H, d, ^3J 9.0 Hz, arom), 8.43 (4H, d, ^3J 8.9 Hz, arom), 11.14 (2H, bs,

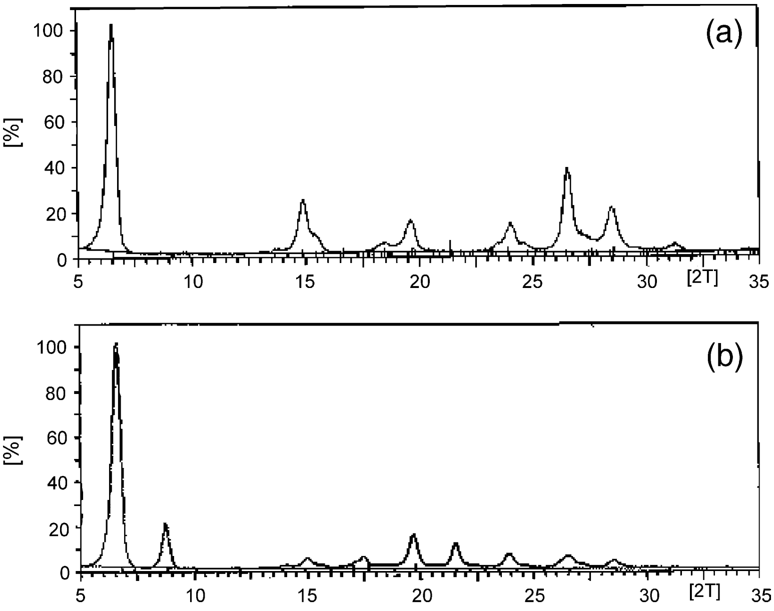


Fig. 1. Powder XRD pattern of 3,6-diphenyl-1,4-diketopyrrolopyrrol under classical heating conditions (a) and using microwave irradiation (b).

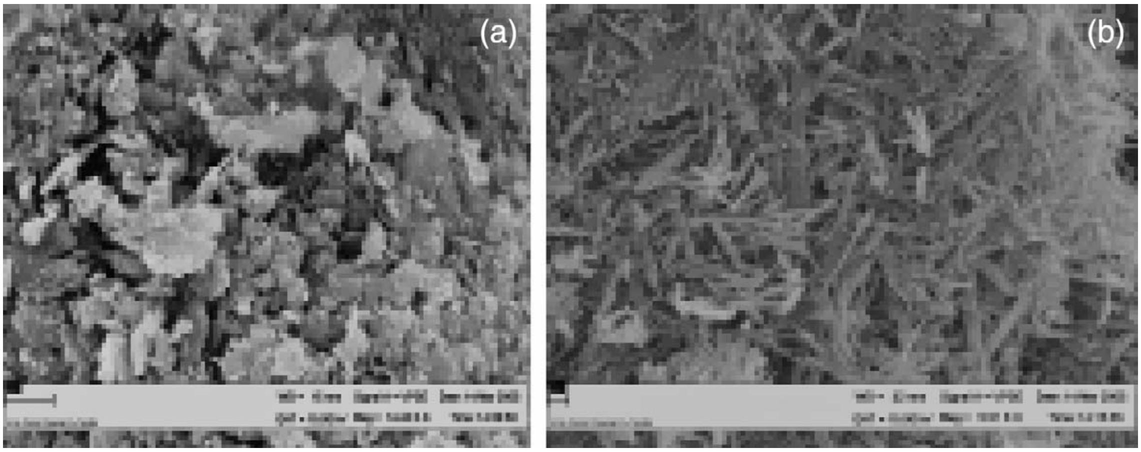


Fig. 2. SEM micrograph of 3,6-diphenyl-1,4-diketopyrrolopyrrol under classical heating conditions (a) and using microwave irradiation (b).

2NH); MS (*m*/*z*, %) 348 (M^+, 81), 174 (16), 134 (57), 77 (12), 44 (100).

Selected data for **3d**: Mp $>$ 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3138 (NH), 1638 (C=O), 1606, 1563, 1450; λ_{max}/nm (DMSO) 506, 472, 406, 303; MS (*m*/*z*, %) 400 (M^+, 41), 343 (26), 158 (37), 77 (72), 43 (100).

Selected data for **3e**: Mp $>$ 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3220 (NH), 1683 (C=O), 1600, 1566, 1472; λ_{max}/nm (DMSO) 515, 480, 407, 392; MS (*m*/*z*, %) 290 (M^+, 100), 248 (26), 158 (37), 78 (72), 52 (45).

Selected data for **3f**: Mp $>$ 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3120 (NH), 1659 (C=O), 1584, 1536, 1496; λ_{max}/nm (DMSO) 514, 480, 373, 350; MS (*m*/*z*, %) 290 (M^+, 100), 262 (26), 158 (37), 78 (42), 51 (59).

Selected data for **3g**: Mp $>$ 300 °C; IR (KBr) (ν_{max}, cm^{-1}): 3125 (NH), 1639 (C=O), 1604, 1492; λ_{max}/nm (DMSO) 516, 480, 409, 327; MS (*m*/*z*, %) 358 ($M^+ + 1$, 11), 281 (23), 239 (37), 183 (42), 43 (100).

3.2. Powder XRD

In common with most pigments, the pigments synthesized with classical heating conditions and microwave irradiation have been studied by X-ray diffraction. The comparison of XRD of the pigments synthesized under classical heating conditions and microwave irradiation method showed that they are not isostructural (Fig. 1). There are three peaks at 8.785, 17.470 and 21.515(2θ) for the pigment synthesized using microwave irradiation, whereas these peaks are not seen in the pigment synthesized under classical heating conditions. The differences in the crystalline structure of the pigments can affect hiding power and tinctorial strength.

3.3. SEM micrograph

Morphological differences between the pigments synthesized under classical heating conditions and using microwave irradiation have been studied by SEM micrograph. The pigment synthesized using microwave irradiation has rod morphology, whereas the pigment synthesized with classical heating conditions exists as flake shape. (Fig. 2).

3.4. Color characteristics of the synthesized pigments

The color characteristics of the pigments synthesized were measured and the positive values of a^* and b^* for both the pigments showed that they are red-yellow; but they are not identical in chroma and lightness. The pigments synthesized with microwave irradiation have less chroma and more lightness compared to microwave irradiation. (Table 2)

Table 2
Color characteristics of the synthesized pigments (120 μ)

Method type	Conditions	L^*	a^*	b^*	c^*	h^*
Conventional heating	Based on alkyd resin without other pigment	50.822	55.168	55.111	77.979	44.970
Microwave irradiation	Based on alkyd resin without other pigment	77.363	14.92	13.156	19.892	41.404
Conventional heating	Based on alkyd resin containing TiO_2	69.794	28.391	15.506	32.35	28.642
Microwave irradiation	Based on alkyd resin containing TiO_2	85.104	8.322	4.693	9.554	29.422
Substrate	–	90.601	0.764	4.081	4.152	100.606

Table 3
Contrast ratio values of paints

Method type	Conditions	Contrast ratio
Conventional heating	Based on alkyd resin without other pigment	4.529[a]
Microwave irradiation	Based on alkyd resin without other pigment	6.132[a]
Conventional heating	Based on alkyd resin containing TiO_2	99.617[b]
Microwave irradiation	Based on alkyd resin containing TiO_2	86.584[b]

[a] Pigment concentrate in paint is 0.2%.
[b] Pigment concentrate in paint is 1.2%.

The contrast ratio values on white to black for paint film containing the synthesized pigments showed that the hiding power of the both pigments are relatively weak [12]; however, the pigment synthesized with classical heating conditions method has more hiding power compared to microwave irradiation method. This can be attributed to morphology and crystalline structure of the pigments. (Table 3).

The light fastness and bleeding resistance of synthesized pigments have been studied. To test the light fastness, each of the pigment was dispersed into a mixture of nitrocellulose and alkyd (short oil) resins and exposed to a xenon arc lamp for 60 h (according to Peugeot, D271389). The light fastness for each pigment was obtained according to the blue-scale. The degree of light fastness for both the pigments was 6, which is very good.

The measurements of bleeding resistance of pigments synthesized in water and toluene (according to ASTM D279-87) showed that both the pigments have excellent bleed resistance.

Acknowledgement

Financial support from the Research Council of Shahid Beheshti University is acknowledged.

References

[1] Zollinger H. Color chemistry: synthesis, properties and applications of organic dyes and pigments. VCH; 1991. p. 241–4.

[2] Farnum DG, Mehta G, Moore GGI, Siegal FP. Tetrahedron Lett 1974;2549.

[3] Iqbal A, Cassar L, Ciba-Geigy. Europ Pat 61426; 1983 [chem abst. 98: 73838n].

[4] Iqbal A, Cassar L, Rochat AC, Pfenninger J, Wallquist O. J Coat Technol 1988;60:1.

[5] Iqbal A, Jost M, Kirchmary R, Pfenninger J, Rochat AC, Wallquist O. Bull Soc Chim Belg 1988;97:615.

[6] Rochat AC, Cassar L, Iqbal A, Ciba-Geigy. Europ Pat 94911; 1983 [chem abst. 100: 87260q].

[7] Closs F, Gompper R. Angew Chem Int Ed Engl 1987;26:552.

[8] Shaabani A. J Chem Res Synop 1998;672.

[9] Shaabani A, Safari N, Bazgir A, Bahadoran F, Sharifi N, Jamaat PR. Synth Commun 2003;33:1717.

[10] Organicum, practical handbook of organic chemistry. Addison-Wesley Publishing Company, INC; 1973. p. 564–5.

[11] Erdik E. Tetrahedron 1987;43:2203.

[12] Herbest W, Hunger K. Industrial organic pigments. VCH; 1997. p. 55.