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# Silica gel Catalyzed Synthesis of Quinophthalone Pigments Under Solvent-Free Conditions Using Microwave Irradiation

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**Abstract**: Condensations of anhydrides and quinaldine derivatives are accelerated by microwave irradiation under solvent free conditions in the presence of silica gel as catalyst.

Keywords: Quinophthalone; Pigments; Silica gel; Solvent-Free Conditions; Microwaves.

#### Introduction

Quinophthalones have achieved great significance in organic synthesis [1-4]. Many studies have shown these compounds to be rich sources of innovative chemistry as a number of pharmaceutical products and dyestuffs contain this ring system [5-11]. Their ability to act as ligands that form stable complexes with different cations is also well known [12]. Several methods for the preparation of quinophthalones have been reported such as treatment of phthalic anhydrides and a mixture of quinaldine with nitrobenzene [13],  $ZnCl_2$  [14-17] or sodium hydride [18] and reactions of quinoline N-oxides/ $\beta$ -diketones [19]. Some of the methods mentioned above suffer from various drawbacks including long reaction times, low yield of products, difficult operating conditions and tedious work-up. Recently the application of microware irradiation has gained popularity in organic synthesis [20-25], particularly in chemical reactions with reagents impregnated on solid mineral supports, especially those that are efficient in dry media, due to their selectivity, high reaction rates, cleaner formation of products and operational simplicity. In this connection, we now report a simple synthetic procedure for the preparation of quinophthalone pigments under microwave irradiation catalyzed by silica gel (Scheme 1).

#### Scheme 1



#### **Results and Discussion**

To choose the best among the various common solid supports such as silica gel, alumina and montmorillonite K-10 clay, etc., a comparative study was done using phthalic anhydride and 2-methylquinoline (1) as a representative starting material (Table 1). Samples were irradiated with microwave radiation (700 W) in the presence of a variety of solid supports. The results indicated that silica gel was clearly the best catalyst for our purposes and consequently this substance was selected as the support for subsequent experiments.

<b>Table 1.</b> Quinophinatone preparation in the presence of unreferit catarys	Table 1.	Quinophthalone	preparation in the	presence of different catal	ysts.
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Run	Quinophthalone yield (%)	Time (min.)	Catalyst	
1	15	8	None	
2	35	5	Alumina	
3	30	5	K-10 Clay	
4	97	2	Silica gel	

Next a variety of quinophthalones were prepared from a variety of phthalic anhydrides and 2-methylquinolines under microwave irradiation (700 W) in the presence of silica gel. All reactions were easily performed in a beaker and product formation was noted observed after 2 min. The results are summarized in Table 2.

In all the <sup>1</sup>H-NMR spectra of the quinophthalone products the NH group appeared in the  $\delta$  14-16 region as a broad singlet. The integral of this signal was proportional to one proton and no signal was observed in the aliphatic region corresponding to a C-H. From this data we conclude that the compounds are exclusively in the enaminone form. The <sup>13</sup>C-NMR data was also consistent with the proposed structures in all cases. In the IR spectra the C=O/C=C groups were observed around 1635-1670 cm<sup>-1</sup> [26-32].

Entry	R <sup>1</sup>	$\mathbf{R}^2$	Product <sup>a</sup>	Yield <sup>b</sup> (%)	m. p. (found) (°C)	m. p. (lit.) (°C)
1	Н	Н	<b>3</b> a	97	240-241	240 (13)
2	Н	Cl4	<b>3</b> b	95	>345	>310 (13)
3	Н	5,6 0	Зс	94	>370	>396 (33)
4	Н	5, 6-(COOMe) <sub>2</sub>	3d	91	362-363	363 (33)
5	4-Me	Н	3e	85	241-242	241 (13)
6	4-Ph	Н	3f	87	270-271	270 (31)
7	3-OH	Н	3g	86	266-267	267 (13)
8	3 <b>-</b> OH	Cl4	3h	85	>350	>310 (13)
9	6-Me	Н	3i	93	202-203	203 (16)
10	Н	1 or $4 - NO_2^c$	3j	82	360	361 (32)

**Table 2.** Preparation of quinophthalones from phthalic anhydrides and 2-methylquinolines under microwave irradiation.

<sup>a</sup> All products exhibited spectral data (IR, <sup>1</sup>H-and <sup>13</sup>C-NMR) consistent with their proposed structures. <sup>b</sup> Yields refer to isolated pure products.

<sup>c</sup> The exact location of the NO<sub>2</sub> group is not clear.

# Conclusions

We believe the reported method offers a mild, simple and efficient route for the preparation of quinophthalone pigments. Its ease of work up, high yields and short reaction times make it a useful addition to modern synthetic methodologies.

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# Experimental

# General

All products are known compounds and their physical data, IR and NMR spectra were essentially identical with those of authentic samples. IR spectra were recorded as KBr pellets on a Shimadzu IR-470 spectrometer. <sup>1</sup>H-NMR spectra were determined on a Bruker AC80 or JEOL EX-90 instruments.

#### A typical experimental procedure

The preparation of quinoline yellow (**3a**), is illustrative of the general procedure employed. To a mixture of 2-methylquinoline (1 mmol, 143 mg) and phthalic anhydride (1 mmol, 148 mg) placed in an open glass container, silica gel (silica gel 60, 230-240 mesh Merck, 300mg) was added and the reaction mixture was irradiated in a microwave oven at 700 W power for 2 minutes. Upon completion of the reaction, as followed by TLC, the product was extracted into ethanol (3 x 10 mL). The solvent was evaporated and the resulting crude material was purified on a silica gel plate to afford 2-(2-quinolinyl)-1H-indene-1,3-(2H)-dione (**3a**) in 97% yield (cf. Table 2). <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  7.41-8.61 (m, 11H, aromatic H), 14.18 (s, 1H, NH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>)  $\delta$  99.45-151.21 (aromatic C), 190.80, 194.87 (carbonyl C); IR (KBr) 1710, 1650, 1610, 1565 cm<sup>-1</sup>.

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Samples Availability: Compounds 1-10 are available from MDPI.

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