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Microwave Assisted Synthesis of Heterocyclic Fused Quinones in Dry Media.

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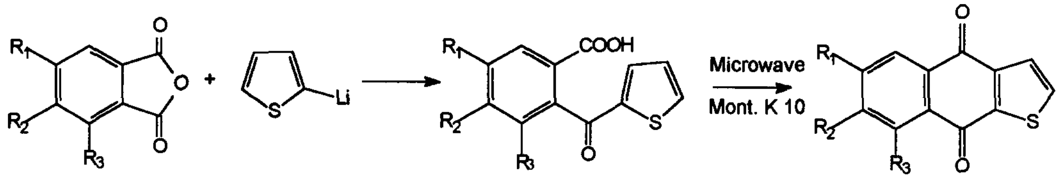
Abstract: *Microwave assisted cyclization of several 2-thenoylbenzoic acids 2 catalysed with clays in dry media is studied. Some clays were tested and Montmorillonite K-10, free of quarz and feldspar, was shown to be an effective catalyst for their easy conversion into the corresponding heterocyclic fused quinone in good yields. A specific effect of microwave irradiation accelerating the reaction with respect to conventional heating in the same conditions is observed.*

Since the discovery of metallic behaviour in charge-transfer (CT)[1] complexes of the donor tetrathiafulvalene (TTF) and the acceptor tetracyano-*p*-quinodimethane (TCNQ), the chemistry of molecular conducting materials has been widely developed[2]. With regard to the acceptor component, TCNQ[3] and *N,N'*-dicyanoquinone diimine (DCNQI)[4] derivatives have been usually prepared from the corresponding quinone. The importance of the introduction of heteroatoms into the component molecules of CT is recognised as one of the requisites to attain high electric conductivity[5] and some of us described the synthesis of π-extended TCNQ and DCNQI derivatives containing a sulphur atom[6]. There, the synthesis of thieno[2,3-b]-1,4-naphtoquinone (**3a**) and the corresponding dichloro derivative (**3b**) were carried out by cyclization of 2-(2-thenoyl)benzoic acids (**2a**) and (**2b**) respectively by heating at 140° for several hours with phosphorus pentachloride and aluminum trichloride as the catalyst in dry nitrobenzene as solvent. The removal of nitrobenzene by distillation prior to the isolation of the product is needed.

It has been previously shown that clay surfaces are efficient acid catalysts and supports for Friedel-Crafts reactions[7], and, particularly, in the synthesis of anthraquinone from *o*-benzoylbenzoic acid.[8] Furthermore, the combination of dry medium conditions and microwave activation[9] was shown to be the best situation.[10]

In order to improve the synthesis of this kind of sulphur containing quinones, we wish to report now a simple and general procedure, in solvent-free conditions, for the synthesis of heterocyclic quinones (**3**), starting from the respective 2-thenoylbenzoic acid with Montmorillonite K10 as support and using microwave irradiation as energy source. Under these milder conditions, the sulphur containing quinones (**3**) were obtained in good yields and notably shorter reaction times.

Synthesis of 2-thenoylbenzoic acids (**2a-e**) was carried out by reaction of the corresponding phthalic anhydride (**1**) with 2-thienyllithium, improving the yields previously obtained[6] for **2a** and **2b** by using the analogous magnesium derivative; 2-(2-thenoyl)benzoic acids **2c-e**[11] were not previously described in the literature.



1 **2** **3**

As acidic minerals for the cyclization reaction of acid **2a** we applied clays, such as bentonite, Montmorillonites K10 and KSF, and Tonsil. The results of exploratory experiments are given in table 1. The best yield was afforded with Montmorillonite K10 after removing quarz and feldspar ("purified" Montmorillonite). The amount of solid support employed have a significant influence on the yield; the optimum result was obtained by using a *w/w* 1:5 ratio substrate/solid support.

Table 1

Entry	**Clay**[a]	**Ratio 2a/Clay** (w/w)	**time** (min.)	**Yield of 3a**
1	Bentonite	1/2	3,5	0
2	Tonsil	1/5	3	20
3	Tonsil	1/7	3	17
4	Montmorillonite K10	1/1	3	13
5	Montmorillonite K10	1/4	3	30
6	Montmorillonite K10	1/5	3	54
7	Montmorillonite K10	1/7	2,5	21
8	Montorillonite K10 "Purified"	1/5	3,5	60
9	Montmorillonite KSF	1/1	4	0
10	Montmorillonite KSF	1/5	4	25
11	Montmorillonite KSF "Purified"	1/5	4	30

[a] Montmorillonite KSF, Montmorillonite K10 and Bentonite supplied from Fluka; Tonsil supplied from Süd Chemie A.G.

Mineral composition of Montmorillonites K10, KSF and bentonite were determinated by X-Ray difraction (Philips PW1710). Samples analyses (table 2) show a high proportion of laminar philosilicates for Montmorillonites K10 and KSF and practically 100% for bentonite; nevertheless, pH determination of an aqueous solution of this clay displays a basic value and justify the lack of catalytic activity of this support. In the case of Mont. K10 and KSF, quarz and feldspar were removed.[12] This "purification" of clay leads to an improved catalitic activity.

In a typical experiment, the acid (50 mg) was intimately mixed with clay and the glass vessel (Pyrex) was placed into a bath of alumina-magnetite mixture of 1:1 *w/w* proportions (100 g.), which strongly adsorbs microwaves, and covered by a watch glass with dry ice[13] as cold wall. After irradiation and cooling, the quinone

Table 2

		Clay Minerals			Accesory minerals	
	pH	Smectite	Illite	Rectorite	Quarz	Feldspar
Commercial Mont. K-10	3,3	58	23	0	11	8
"Purified" Mont. K10	4,2	72	28	0	0	0
Commercial Mont. KSF	2,7	61	20	0	9	10
"Purified" Mont. KSF	4,0	75	25	0	0	0
Bentonite	8,1	0	0	97	0	<3

was removed by scraping. More product was isolated by extracting the support with CH_2Cl_2 in a continuous extraction apparatus. Yields are given in Table 3. No starting material could be recovered from the reaction mixture and yields were reduced after a prolongated irradiation time, probably due to decomposition of quinone particularly in the case of **3c** and **3d**.

Table 3

Conversion of 2-thenoylbenzoic acids 2 into quinones 3 on Montmorillonite K 10 in dry media.

Quinone	R_1	R_2	R_3	Microwave oven $^{a)}$; Yield (%)		Classical heating $^{b)}$
				Commercial K-10	Purified K-10	Yield (%) $^{c)}$
3a	H	H	H	54	60	17$^{d)}$
3b	Cl	Cl	H	68	92	41
3c	H	NO_2	H	16	21	32
3d	H	Me	Me	17	27	13
3e	H	H	OMe	15	43$^{e)}$	11

a) The irradiations were carried out in a domestic microwave oven (Miele M-310) at a power of 780 W for 3-5 minutes; the temperature of reaction mixture raised to aproximately 320°C.

b) Heated in a sand bath for 1h. at 320°C

c) Evaluated by weight of purified quinone.

d) 27% of phtalic anhydride was obtained as by-product.

e) **3e** is partly hydrolyzed to 7-hydroxithieno[2,3-b]-1,4-naphtoquinone.

In summary, this method provides an efficient synthesis of these kind of quinones, with better yields than those obtained by using Lewis acids as catalyst and nitrobenzene as solvent.[6] Here, the experimental procedure is much simpler, the resulting quinones are obtained in a very short period of time -<5 minutes- and the quinone sublimates, without need of further purification.[14]

In order to determine the possibility of existence of a specific microwave effect accelerating the reaction with respect to conventional heating,[15] a thermoregulated sand-bath at 320 °C was used as source of heat in comparative experiments (Table 3). The lower yields obtained with conventional heating, excepting **3c**, even after 1 hour of reaction, indicate that the effect of microwave is not purely thermal, as despicted in Table 3; the reaction is faster in the microwave environment than under conventional heating at the same temperature (classical heating for 4 minutes only affords starting material and traces of quinone).

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11. **2a:** yield: 80% (lit^6: 68%). m.p. 144-145°C; **2b:** yield: 96% (lit^6: 94%). m.p. 197-198°C; **2c:** yield: 46%, m.p.(H_2O): 184-186 °C. IR (KBr): 3000 (b), 1715, 1640, 1345 cm^{-1}. ^{1}H RMN (300 MHz, CD_3-SO-CD_3, δ ppm): 7.17 (q,1H), 7.31 (d, 1H), 7.80 (d, 1H), 8.15 (d, 1H), 8.56 (d, 1H), 8.65 (d,1H), 13.65 (bs, 1H). **2d:** yield: 10%, m.p. (H_2O): 167-169°C. IR (Nujol): 3000, 1670, 1600, 1560, 1500, 1360, 1300, 1270, 1200, 1160, 1030, 1000, 950 cm^{-1}. ^{1}H RMN (300 MHz, CD_3-SO-CD_3, ppm): 7.98 (d, 1H), 7.87 (s, 1H) 7.69 (dd, 1H), 7.36 (d, 1H), 7.25 (d, 1H), 7.05 (t, 1H), 6.20 (s,b, 1H), 2.45 (s, 3H). **2e:** yield: 25%, IR (Nujol): 3000, 1680, 1630, 1570, 1510, 1400, 1350, 1270, 1150, 1050, 850, 820 cm^{-1} .^{1}H RMN (300 MHz, CD_3-SO-CD_3, δ ppm): 7.70 (d, 1H), 7.64 (d, 1H), 7.49 (t, 1H), 7.26 (d, 1H), 7.21 (d, 1H), 7.03 (dd, 1H).
12. Quarz and feldspar were removed according to Barahona E. Ph. D. Thesis dissertation (Univ. Granada, 1974).
13. Non polar carbon dioxide absorbs slightly microwave energy.
14. **3c:** m.p. 182-84 °C. IR (Nujol): 1650, 1600, 1510, 1300, 1250 cm^{-1}. ^{1}H RMN (300 MHz, $CDCl_3$, δ ppm): 7.83 (dd, 2H), 8.45 (d, 1H), 8.59 (dd, 1H), 9.05 (d, 1H). **3d:** m.p. 179-181°C, IR (Nujol): 3000, 1670, 1600, 1520, 1390, 1315, 1290, 1250, 840, 740 cm^{-1}. ^{1}H RMN (300 MHz, $CDCl_3$, δ ppm): 8.14 (d,1H), 8.04 (s, 1H), 7.70 (m ,2H), 7.25 (d, 1H) **3e:** yellow oil, IR (Nujol): 1650, 1600, 1590, 1420, 1260, 1100, 1050 cm^{-1}. ^{1}H RMN (300 MHz, $CDCl_3$, δ ppm): 7.90-7.56 (m, 4H) ,7.34 (m, 1H), 4.08 (s, 3H).
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