# MICROWAVE-ASSISTED ACRIDONES PREPARATION USING AN INORGANIC ACIDIC SOLID SUPPORT

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**ABSTRACT:** A novel preparation in 'dry media' of acridone derivatives using microwave-activation is described.

## INTRODUCTION

Microwave-assisted organic synthesis has become a method of great interest (1-4). Application of this technique to inorganic and solid state synthesis has been shown to have significant advantages (5).

Recently, bentonite clay was used for performing acid-catalysed cyclodehydratation of o-benzoylbenzoic acid (ref. 64-66 quoted in 1) and for the Beckmann rearrangement of ketoximes (6).

It is well known (7) that the most useful general method for preparing acridones is by the ring closure of the corresponding diphenylamine-2-carboxylic acids using sulphuric acid, polyphosphoric acid or phosphorus oxychloride as cyclizing agents. This method is very tedious and it is accompanied by the formation of much waste sulphuric acid, quite undesirable from the environmental point of view. So, we tried to change this method by using an inorganic acidic support, namely, bentonite instead of the above mentioned ring closure agents. The substrates (diphenylamine-2-carboxylic acids) were absorbed on bentonite and irradiated with microwaves.

## EXPERIMENTAL

Our treatment precinct is an original one and consists of a parallelipipedic microwave-cavity, H101 resonance mode. The condition of maximum field distribution on the material was fulfilled by using at the end of the cavity a mobile short circuit. Bentonite was used also for concentrating the electromagnetic field in the substrate.

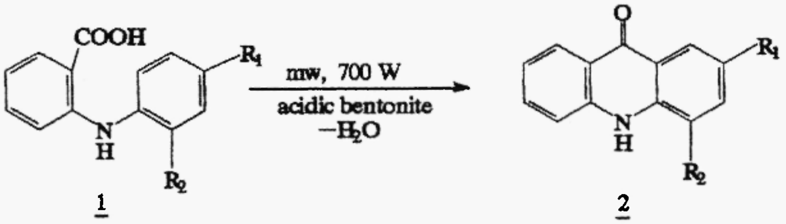
The reactions were performed in a quartz open vessel. M.p. are uncorrected. The reactions were monitored by TLC on "MERCK" silicagel 60 F 254 plates eluting with 8:2 benzene:ethanol, the visualisation was done using a 254 nm UV lamp. The bentonite is original from Gurasada (Roumania) and has the following composition: $SiO_2$ (73.4%), $Al_2O_3$(14.35%), $Fe_2O_3$(1.72%), CaO(0.52%), MgO(2.32%), $K_2O$(0.44%), $Na_2O$(0.29%), $TiO_2$(0.24%). In order to obtain an acidic bentonite, it was treated at boiled with concentrated hydrochloric acid. The resulting pH of the solid material was 3÷4. The best ratio of diphenylamino-2-carboxylic acids to solid support was proved to be 2 mmol/5g. The identity of compounds 2a-e was checked-up by microanalyses and confirmed by comparison of TLC of these compounds with those of authentic samples.

**General procedure for acridones preparation**

Diphenylamino-2-carboxylic acid 1 (2mmol) was dissolved into a minimum volume of acetone and absorbed on Gurasada acidic bentonite (5 g). The solvent was then evaporated and the dry mixture was irradiated with microwave (see Table). The resulting acridone 2 was extracted with the proper boiling solvent and work-up was carried out as is indicated in the literature (see Table).

## RESULTS AND DISCUSSION

The preparation of microwave-assisted acridones was achieved according to the following scheme:



a) $R_1=R_2=$ H
b) $R_1=$ H; $R_2=$ Cl
c) $R_1=NO_2$; $R_2=$ H
d) $R_1=OCH_3$; $R_2=$ H
e) $R_1=$ H; $R_2=CH_3$

The results of our experiments are shown in the table. Our data show that solid-state preparation of acridones using microwaves is extremely convenient from the practical viewpoint. In general, the reagents and the solid support are efficiently mixed in an appropriate solvent, which is then evaporated.

procedure for acridones preparation very attractive.

**Table.** Acridones prepared by microwave irradiation at 700 W (2.45 GHz).

| Compounds | Microwave | | | Conventional | | |
|---|---|---|---|---|---|---|
| | Time (sec) | Yield (%) | m.p.(° C) [lit.m.p.] (lit.quotation) | Time (hours) | Yield (%) | Cycliza-tion agent (lit.) |
| Acridone 2a | 25 | 85 | 353-355 [350] (7) | 4 | 90 | $H_2SO_4$ (7) |
| 4-Chloroacridone 2b | 60 | 70 | >360 [>360] (8) | _ | _ | $H_2SO_4$ (8) |
| 2-Nitroacridone 2c | 30 | 82 | > 360 [>360] (9) | 1.5 | 83 | $POCl_3$ (9) |
| | | | | _ | 77.5 | $H_2SO_4$(10) |
| | | | | _ | _ | $POCl_3$ (11) |
| 2-Methoxyacridone 2d | 45 | 78 | 279 [278] (12) | 2 | 70 | $H_2SO_4$(12) |
| 4-Methylacridone 2e | 60 | 71 | 345-347 [345-346] (13) | 5 | _ | $H_2SO_4$ (13) |

## CONCLUSION

Although microwave-assisted organic synthesis in 'dry media' is in its infancy, the above acridones preparation demonstrate once more that a great simplification of procedure can be achieved and ,generally, the organic reactions take place more this way rapidly, safely and with higher yields.

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