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An Efficient Microwave-Assisted Method to Obtain 5-nitrofurfural Without Solvents on Mineral Solid Supports

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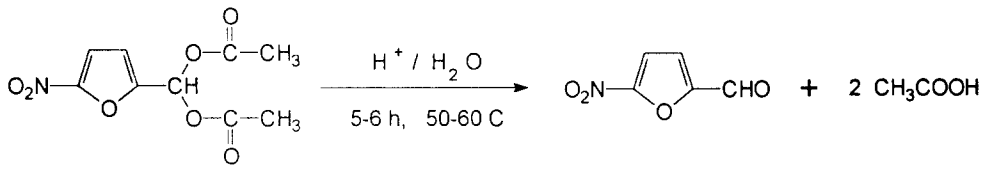
Abstract: 5-nitrofurfural (5-NF) was quantitatively prepared by deacetylation of its geminal diacetate on K10 Montmorillonite under microwave irradiation without solvent.

Due to their advantages in cleanliness, economy, selectivity and efficacy with respect to traditional methods, domestic microwave ovens have recently been used in organic synthesis, to carry out reactions catalyzed by mineral solid supports.[1,2]

One of the conventional methods widely used for the deacetylation of 5-nitro-2-furfural diacetyl acetal (5-NFDA) is the hydrolysis with concentrated sulfuric acid[3] according to the reaction:



5-NFDA 5-NF

Furan compounds are very unstable in an aqueous acidic medium in which resins are formed[4] and the yield of this reaction is about 83 % of crude product. This should be purified by recrystallization or distillation under reduced pressure.

Selective deacetylation by microwave irradiation on solid supports without solvent has been reported in which the disadvantages presented by conventional methods (oxidation, resinification, etc.) are avoided.[5,6] With these methods higher yields are attained in shorter times and the crude products present a high purity.

Recently, Varma[6] reported the preparation of aryl aldehydes from their geminal diacetates by impregnation of neutral alumina for column chromatography and irradiation in a domestic microwave oven. The present paper deals with the microwave-assisted deacetylation of 5-NFDA to obtain 5-NF. This furan compound is an important intermediate for the preparation of a great variety of compounds with therapeutic application.[7]

The initial experiments were performed according to the description of Varma.[6] The results were not satisfactory because of resinification and the low yields obtained with alumina as support, so we decided to explore some other acidic solid materials in different reaction conditions.

Experimental results are shown in Table 1. The best results were obtained when 1 g of 5-NFDA was dispersed into 4 g of K10 Montmorillonite, and this mixture was exposed to microwave irradiation during 2 min at a power of 355 Watts in a domestic oven.

Table 1
Deacetylation of 5-NFDA dispersed into different mineral solid supports at a power of 355 Watts.

Reaction conditions	Supports			
	Alumina 90 T	Silicagel 60 G	TOBA(*)	K10
5-NFDA/support ratio	1/4	1/4	1/4	1/4
reaction time (min)	2	2	2	2
final temperature (C)(**)	80-90	90-95	90-100	95-100
purity[a]	low	low	medium	very high
yield[b] (% 5-NF)	5	6	50	>99

(*) Cuban volcanic glass.[8]

(**) These temperatures were measured immediately after the reaction using a glass thermometer.

[a] Determined by thin layer chromatography (TLC)

[b] Determined by gaseous chromatography (GC).

It should be noted that 5-NF was obtained in almost quantitative yields and of a high purity without any further purification.

Additionally, some other experiments were performed by impregnating K10 Montmorillonite with 5-NFDA, in order to compare these results with those obtained with the dispersion method. An experiment

carried out with conventional heating (oil bath) was also included for the sake of comparison. The results are presented in Table 2.

Table 2
Comparison of different methods to support 5-NFDA and different modes of heating (oil bath or microwave irradiation).

Run	Support method	Mode of heating	yield (%)
1	D	Microwave	>99
2	D	Oil bath (110 C)	negligible
3	I	Microwave	80

5-NFDA/support ratio: 1/4, reaction time: 2 min.
D- Dispersion.
I - Impregnation.

It could be seen that the dispersion method is more effective, and that the effect of the microwave irradiation is not solely thermal, since conventional heating at the same temperature was not effective for a same reaction time.

Further investigations are needed to explain the facts described. Nevertheless, our results show already that the synthesis of 5-NF on mineral supports can be successfully induced by microwave irradiation. This gives rise to easier, cleaner, more efficient and more selective processes than traditional methods.

EXPERIMENTAL

5-NFDA was synthesized in our laboratory according to conventional methods reported in the literature (mp 88-90 C, from ethanol).[3]

The mineral supports used were: 90 T neutral alumina and 60 G silicagel from Merck, K10 Montmorillonite from Fluka and TOBA (Cuban volcanic glass characterized by Vega).[8]

Impregnation of the different supports with 5-NFDA was performed by dissolving 1 g of 5-NFDA in a minimum amount of dichloromethane (1-2 ml), adding 4 g of mineral support and rotoevaporating the mixture under reduced pressure at room temperature.

Dispersion of 5-NFDA into the different supports was done by gently mixing both solids using a Teflon rod to avoid any damage to the support particles. The quantities of 5-NFDA and mineral support used were the same as in the impregnation method.

All the solvents employed were HPLC grade from BDH.

The reactions were carried out in a domestic microwave oven from Sanyo which allows the selection of output power up to 900 Watts.

The final temperature attained in the reaction was determined by introducing a glass thermometer into the reaction mixture and homogenizing it, in order to obtain a temperature value representative of the whole mass.

TLC analyses were run on 60 F_{254} silicagel chromatoplates from Merck with a mixture of toluene:ethanol 20:3 as eluent.

GC analyses were performed in an apparatus from Shimadzu with flame ionization detector and OV-101 column (1 m x 3 mm) on Chromosorb W-HP. The temperature was programmed from 80 to 250 C at 8 C/min (injector temperature 300 C). The retention times were 4.25 min and 12.00 min for 5-NF and 5-NFDA respectively.

REFERENCES

1- Loupy A., Bram G., Sansoulet J.: New J. Chem., **1992**, 16, 233.

2- Bram G., Loupy A. Villemin D.: "Solid Supports and Catalysts in Organic Synthesis", Ed. Smith K., Ellis Horwood Ltd., Chichester, England, **1992**, pp. 302-326.

3- Jurasek, J.: "Zaklady Organickej Chemie", Bratislava, Czechoslovakia, **1980**, pp. 188-275.

4- Dunlop A.P., Peters F.N.: "The Furans", American Chemical Society Monograph Series R.P.C., N.Y. 36, USA, **1953**, pp. 362-363.

5- Varma R.S., Varma M., Chatterjee A.K.: J. Chem. Soc. Perkin Trans. I, **1993**, 999.

6- Varma R.S., Chatterjee A.K., Varma M.: Tetrahedron Letters, **1993**, 34, 3207.

7- U.S. Patent 3, 262, 930 (**1964** and **1966**) to Bayer AG.

8- Vega N., Reyes L., Rodríguez D.: Revista CENIC, Ciencias Químicas, **1990**, 21, 106.

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