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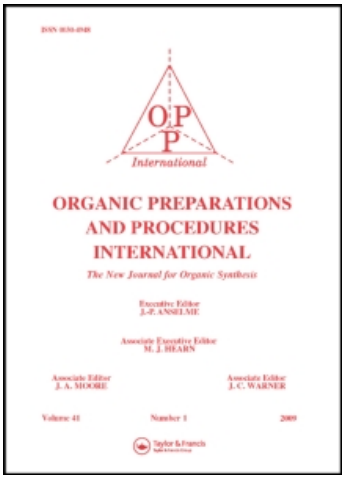


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# ULTRASONICALLY ACCELERATED SYNTHESES OF FURAN-24-DICARBALDEHYDE FROM 5-HYDROXYMETHYL-2-FURFURAL

Louis Cottier[a]; Gérard Descotes[a]; Jaroslaw Lewkowski[b]; Romuald Skowroñski[b]
[a] Université Lyon 1, ESCIL Laboratoire de Chimie Organique II, URA-CNRS, Villeurbanne Cedex, FRANCE [b] Department of Organic Chemistry, University of Lódz, Łódz, POLAND

**To cite this Article** Cottier, Louis , Descotes, Gérard , Lewkowski, Jaroslaw and Skowroñski, Romuald(1995) 'ULTRASONICALLY ACCELERATED SYNTHESES OF FURAN-24-DICARBALDEHYDE FROM 5-HYDROXYMETHYL-2-FURFURAL', Organic Preparations and Procedures International, 27: 5, 564 — 566
**To link to this Article: DOI:** 10.1080/00304949509458502
**URL:** http://dx.doi.org/10.1080/00304949509458502

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## ULTRASONICALLY ACCELERATED SYNTHESES OF FURAN-2,5-DICARBALDEHYDE FROM 5-HYDROXYMETHYL-2-FURFURAL

*Submitted by* (12/12/94)

Louis Cottier*†, Gérard Descotes†, Jaroslaw Lewkowski‡ and Romuald Skowroñski‡

† *Université Lyon 1, ESCIL*
*Laboratoire de Chimie Organique II, URA-CNRS N°463*
*43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, FRANCE*

‡ *University of Lódz, Department of Organic Chemistry*
*Narutowicza 68, 90-136 £ódz, POLAND*

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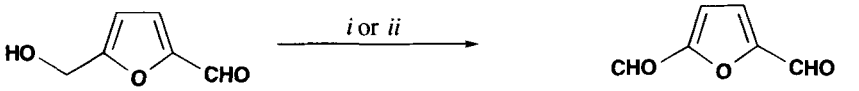
Furan-2,5-dicarbaldehyde (**2**) is an important starting compound for syntheses of annulene oxides,[1] mixed porfines[2] and various macrocycles.[3] Compound **2** has been synthesized from 2-diethoxymethylfuran,[4] 2,5-*bis*-hydroxymethylfuran[5] or furan-2,5-dicarbonitrile.[6] It may also be obtained by the regioselective oxidation of 5-hydroxymethyl-2-furfural **1** (HMF), which would be a good starting material, since it is easily accessible by the acid-catalyzed dehydration of carbohydrates.[7,8] van Reizendam *et al.*[9] oxidized **1** with lead tetracetate to yield dialdehyde **2** in poor yield. Chromium trioxide in pyridine[10] or nitrogen dioxide in DMSO[11] gave **2** in 70 and 76% yield respectively while oxidization of HMF with barium manganate leading to afforded **2** in 92% yield.[12]




*i*) DMSO-$K_2Cr_2O_7$, 100° or ))) *ii*) $Me_3N{\bullet}NCl$-$CrO_3/Al_2O_3/CH_2Cl_2$, reflux or )))

We recently reported the synthesis of **2** from **1** using pyridinium chlorochromate with aluminium oxide[13] and from 5-(trialkylsilyl)oxymethyl-2-furfural using azobisisobutyronitrile-*NBS* pair.[14] We now describe two methods for the conversion of HMF to **2** accelerated by ultrasound, in satisfactory yields.

Following the published procedure,[15] we performed the oxidation of 5-hydroxy-methyl-2-furfural (**1**) with DMSO-potassium dichromate oxidative complex. However, only a 48% yield of the

desired dialdehyde **2** was obtained. When the time of the reaction was extended, compound **2** was obtained in 58%; however, the application of ultrasonic irradiation to the reaction mixture afforded **2** in 75% yield. Acharaya *et al.*[16] have already reported the oxidation of primary alcohols to aldehydes with trimethylammonium chlorochromate (TMACC). We utilized this reagent for the oxidation of **1** by the described method and obtained the dialdehyde **2** in 48% yield; the yield increased to 57% by heating the solid mixture obtained by grinding together HMF adsorbed on aluminium oxide, TMACC and molecular sieves, with ultrasonic irradiation, dialdehyde **2** was obtained in 72% yield.

## EXPERIMENTAL SECTION

All solvents were routinely distilled and dried prior to use. DMSO-potassium dichromate oxidizing complex[15] and TMACC[16] were prepared following published procedures. Aluminium oxide (Merck) 1st degree of activity, neutral was used as received; HMF (Sudzucker Gmbh) was crystallized prior to use. All spectra were recorded on a Varian 200 Gemini ($^1$H NMR, 200 MHz) and a SPECORD 75 (IR) apparatus. Ultrasonic reactions were performed in Prolabo Transsonic 275 ultrasonic cleaning bath (35 kHz, 85 W of output power).

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**Oxidation of 5-Hydroxymethyl-2-furfural with $K_2Cr_2O_7$-DMSO Oxidative Complex**.- HMF (1.26 g, 10 mmol) was added to the solution of $K_2Cr_2O_7$ (10 g) in 100 mL of DMSO. The solution was then heated at 100° for 5 hrs. Then, the mixture was cooled, diluted with 100 mL of water and extracted with methylene chloride (3×100 mL). Organic layers were washed with water.The solutions were extracted with methylene chloride and the collected organic layers were dried over $MgSO_4$ and evaporated. The solid residue was recrystallized from $CCl_4$ to give 0.72 g (58%) of the product **2** as white crystals, mp 108-109°, lit.[4] 109-110°.

When the mixture was irradiated with ultrasounds for 30 min at room temperature, work-up as above gave 0.93 g (75%) of the product **2** as white crystals, mp 108-109° identical to the sample above.

**Oxidation of 5-Hydroxymethyl-2-furfural (1) with TMACC-$Al_2O_3$ Oxidative System**.- HMF (1.26 g, 10 mmol) was adsorbed on $Al_2O_3$ (30 g), dried and the resulting solid was ground together with molecular sieves 4Å (400 mg) and TMACC (5.85 g, 30 mmol). Molecular sieves were previously dried at 350° for 48 hrs. The whole solid mixture was suspended in 20 mL of methylene chloride and refluxed for 3 hrs. Then, the suspension was filtered off, washed with methylene chloride and the joined organic layers were washed with water. The washing solution was extracted with methylene chloride; the collected organic layers were dried over $MgSO_4$ and evaporated. The solid residue was recrystallized from $CCl_4$ to achieve 0.7 g (75%) of the product **2** as white crystals, mp 108-109° identical to the sample above.

When the whole solid mixture was suspended in 20 mL of methylene chloride and irradiated with ultrasounds for 1 hr, at room temperature, work-up the dialdehyde **2** as given above gave 0.89 g (72%) of **2** as white crystals, mp 108-109° identical to the sample above.

IR (KBr): 2920(-CHO), 1690(C=O), 1580, 1520, 1410($C_{furan}$) $cm^{-1}$.

$^1$H NMR ($CDCl_3$): δ 7.35 (s, =CH-CH=), 9.85 (s, CHO).

**Acknowledgement**.- Authors are grateful to Südzucker Gmbh (Germany) for providing HMF.

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