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MICROWAVE PROMOTED ACETALIZATION OF ALDEHYDES AND KETONES

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ABSTRACT: *Aldehydes and ketones are readily acetalized under microwave irradiation with ethylene glycol in the presence of p–toluenesulfonic acid(PTSA), ferric(III) chloride or acidic alumina.*

Acetalization is now frequently used as an important synthetic means for protecting aldehydes or ketones in the course of preparation of a variety of multifunctional complex organic molecules. So far, several methods have been developed for this purpose[1]. Acetalization reactions are generally catalyzed by acids and proceed with azeotropic removal of water, using

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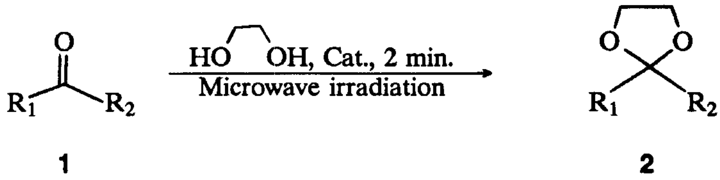
Dean−Stark apparatus. The main disadvantages of these methods are; the use of toxic solvents such as benzene for the azeotropic removal of water, use of uncommon reagents[2−3], long reaction times and difficult work−up.

Recently, several publications have described the use of commercially available microware ovens for accelerating the rate of organic reactions[4−12]. The reported reactions times for these transformations are remarkably shorter, and the work−up conditions are easier than similar reaction in the absence of microwave irradiation. We thought that acetalization of carbonyl compounds can be accelerated by microwave irradiation in the absence of any solvent, using an open flask in order that the water from the reaction products can be evaporated, due to microwave absorption.

Now, we would like to report a new, fast and convenient procedure for convertion of carbonyl compounds(**1**) to the corresponding 1,3−dioxolanes(**2**), under two minutes microwave irradiation and in the presence of an acidic catalyst.



Different acids, including p−toluenesulfonic acid(PTSA), a Lewis acid($FeCl_3$) and an acidic absorbent(acidic aluminia) were tested. The results are summarized in table I. The best result was obtained when an excess of ethylene glycol(10−15 mol equivalent) was used in the presence of catalytic amount of acid(0.015−0.05 mol equivalent), under two minutes irradiotion in a nonmodified domestic microwave oven. PTSA and $FeCl_3$ were found to be less efficient catalyst for furfural and aromatic ketones(entries 9,13, Table I).

Table I

Entry	Substrate	PTSA[a,b] Yield(%)[c]	$FeCl_3$[a,b] Yield(%)[c]	Al_2O_3[a,b] Yield(%)[c]
1	Heptanal	96	97	75
2	$PhCH_2CH_2CHO$	88	91	95
3	Cinnamaldehyde	–[d]	75	66
4	PhCHO	81	77	90
5	$o-MeOC_6H_4CHO$	90	95	92
6	$p-ClC_6H_4CHO$	96	97	91
7	$p-O_2NC_6H_4CHO$	97	83	96
8	$p-MeC_6H_4CHO$	82	95	93
9	Furfural	–[e]	43	88
10	Cycloheptanone	88	85	63
11	Menthone	83	68	59
12	$PhCH_2CH_2COCH_3$	86	70	81
13	$PhCOCH_3$	71	52	46
14	$p-O_2NC_6H_4COCH_3$	86	70	81
15	$m-O_2NC_6H_4COCH_2Cl$	98	88	90

a) Reaction time for all of the reactions is two minutes.

b) The mole ratio of catalyst to substrate is 0.015 for PTSA, 0.05 for $FeCl_3$, and 10–15 for Acidic Alumina.

c) Isolated yields are reported. The products were compared with spectra of the authentic samples (ir, nmr, m.p. & b.p.).

d) Many products.

e) Polymerized.

Table II

Entry	Substrate	$TiCl_4$[a,b] Yield(%)[c]	$AlCl_3$[a,b] Yield(%)[c]	$ZnCl_2$[a,b] Yield(%)[c]
1	Heptanal	74	95	91
2	$PhCH_2CH_2CHO$	86	85	90
3	o-$MeOC_6H_4CHO$	92	92	90
4	p-ClC_6H_4CHO	94	94	95
5	p-$O_2NC_6H_4CHO$	98	80	75
6	p-MeC_6H_4CHO	80	91	92
7	$PhCH_2CH_2COCH_3$	69	75	78
8	p-$O_2NC_6H_4COCH_3$	95	92	81
9	m-$O_2NC_6H_4COCH_2Cl$	92	93	83

a) Reaction time for all of the reactions is two minutes.

b) The mole ratio of catalyst to substrate is 0.02 for $TiCl_4$, 0.02 for $AlCl_3$, and 0.06 for $ZnCl_2$.

c) Isolated yields are reported. The products were compared with spectra of the authentic samples (ir, nmr, m.p. & b.p.).

Other Lewis acids($TiCl_4$, $AlCl_3$, $ZnCl_2$) were also tested and the results are presented in table II. The yields are also high and comparable to those reported for PTSA and $FeCl_3$(Table I).

This method is rapid and very convenient. It constitutes a considerable improvment of acetalization reactions when compared to classical ones.

Experimental Section

Microwave irradiation were carried out with a commercial microwave oven AEG MICROMAT 625, 650 W at 2450 MHZ. Acidic Aluminium oxide of 70–230 mesh was Merck origin.

General procedure for acetalization

A mixture of a carbonyl compound(2.5 mmol), ethylene glycol(20−40 mmole) and acidic catalyst(0.04−15 mmol), was placed in 25 ml beaker and were irradiated for two minutes. The mixture was cooled to ambient temprature and the product(s) was extrated(petrol ether/EtOAc, 80/20; 3×15 ml) and purified with a short silica gel column(eluent, prtrol ether/EtOAc, 20/1). The products were identified by their IR, ^{1}H−NMR spectra, comparison with their authentic samples and hydrolysis of them provided original aldehydes and ketones.

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