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A New Selective Catalytic Acetalization Method Promoted by Microwave Irradiation

Dipok J. Kalita, Ruli Borah and Jadab C. Sarma*

Organic Chemistry Division, Regional Research Laboratory
Jorhat 785006, Assam, India

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Abstract : *A new selective method of acetalization of aldehydes and cyclic ketones with 1,2-diols or alcohols catalyzed by Iodine under microwave irradiation is reported.* © 1998 Published by Elsevier Science Ltd. All rights reserved.

Reactions promoted by microwave irradiation are advantageous in many ways because of short reaction time, cleaner reaction products and solvent free reaction conditions[1]. Several reactions of synthetic importance such as alkylation[2], condensation[3], halogenation[4], oxidation[5] etc. have been satisfactorily done under microwave irradiation. Recently Moghaddam *et al*[6] and Perio *et al*[7] had mentioned the use of microwave radiation in catalytic protection of carbonyl group as 1,3-dioxolane using TsOH or $FeCl_3$ as catalyst. Herein we also wish to report a catalytic acetalization method promoted by microwave irradiation using a new catalyst.

1,3 dioxolanes and 1,3 dioxanes are the most commonly used cyclic acetals and are generally prepared by reaction of the carbonyl group with ethane-1,2-diol or propane-1,3-diol in the presence of an acid catalyst[8]. Chan *et al*[9] had reported the use of TMSCl as an effective catalyst for acetalization while Daniele *et al*[10] had used $BuSnCl_3$ as a catalyst for the same. In a recent report Cramarossa *et al*[11] had reported the use of AlFe-Pillared montmorillonite catalyst for this purpose.

In addition to carbonyl group protection during a reaction sequence, acetals have many practical applications also[12].

While exploring our interest on iodine as an effective catalyst for reactions like acetylation[13] and 1,1-diacetate formation from aldehydes[14] we have examined its efficacy as a catalyst for acetalyzation of aldehydes and ketones. But conventional method of refluxing the reaction mixture of the substrate, ethane-1,2-diol and iodine in THF did not yield any product even after 4 hr of heating. When the same reaction was carried out under microwave irradiation for just 5 minutes, it yielded a clean product. A blank reaction of an aldehyde and ethane 1,2-diol under microwave irradiation for 10 minutes did not yield any product and the reactants were recovered. The catalyst is effective even in solvent free condition with the compound in glycol. The following table shows few examples of aldehydes and ketones that formed 1,3-dioxolane under this condition.

It has been observed that cyclic ketones react very fast and efficiently while the acyclic ones remain unchanged under this reaction condition. This gives an added selectivity to differentially protect the cyclic keto group leaving the acyclic one free for further manipulation. Further selectivity was observed between saturated and α,β-unsaturated aldehyde and ketone also. Carvone under similar reaction condition yielded carvacrol where as 16-dehydropregnenolone acetate remained unchanged. In an isolated example cyclohexanone was mixed with ethyl methyl ketone (1:1) and subjected to the same reaction conditions only to get carbonyl protection in case of cyclohexanone and substrate recovery in the case of ethyl methyl ketone. Even in the case of 25% water solution of glutaraldehyde both the carbonyl groups are protected giving a moderate yield of the product. When ethane 1,2-diol was replaced with other alcohols like methanol or ethanol the aldehyde and the ketone yielded the corresponding acetals in good yield.

In a typical reaction p-nitrobenzaldehyde (1 mmol) was dissolved in 2 ml of THF and to it 6 mmol of ethane-1,2-diol was added followed by 0.1 mmol of iodine. The mixture was irradiated in a conventional microwave

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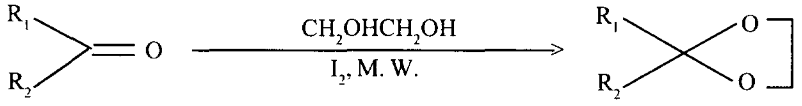
oven giving power setting at 4 of a 7 point scale and time setting at 5 minutes. On completion, the mixture was diluted with chloroform, washed with a dilute solution of sodium thiosulfate followed by water. The organic layer was dried over anhydrous sodium sulfate and distilled under reduced pressure to get 83% yield of the isolated product.

The present procedure of acetalization is a better alternative to the existing ones due to its selectivity, comparable yield in a short reaction time, easy to handle and cheap catalyst, simple reaction procedure and nonrequirement of dry solvent and water removal technique.



Table[a]

Sl No.	Substrate	Power level	Time (min)	Yield (%)
1.	Benzaldehyde	4	7	85
2.	p-Nitrobenzaldehyde	4	5	83
3.	p-Chlorobenzaldehyde	4	7	90
4.	Anisaldehyde	4	7	87
5.	Glutaraldehyde	5	8	55
6.	Cyclohexanone	1	4	92
7.	Methyl cyclohexanone	2	4	83
8.	Cholestanone	2	4	98
9.	Tetrahydrocarvone	2	4	98
10.	Ethyl methyl ketone	1	4	No reaction
11.	Diacetone alcohol	2	4	Decomposition
12.	Pregnenolone acetate	2	4	No reaction
		4	5	No reaction

[a] All the products are characterised by comparison with authentic samples in TLC and by spectroscopic analyses.

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