

Chemoselective Synthesis of 1,1-Diacetates from Aldehydes in the Presence of $\text{Al}(\text{HSO}_4)_3$ under Mild Solvent-Free Conditions*

B. F. Mirjalili^a, M. A. Zolfigol^b, A. Bamoniri^c, M. A. Amrollahi^a, and N. Sheikhan^a

^a Department of Chemistry, College of Science, Yazd University, P.O. Box 89195-741, Yazd, Iran
e-mail: fmirjalili@yazduni.ac.ir

^b Department of Chemistry, College of Science, Bu-Ali Sina University, Hamadan, Iran

^c Department of Chemistry, College of Science, Kashan University, Kashan, Iran

Abstract—A novel efficient procedure has been developed for the preparation of acylals in high yields by reaction of the corresponding aldehydes with acetic anhydride in the presence of $\text{Al}(\text{HSO}_4)_3$ as catalyst under mild (room temperature) solvent-free conditions.

DOI: 10.1134/S1070428007060085

Acylals attract interest as an alternative to acetals for the protection of aldehyde group due to their stability in basic and neutral media. From the synthetic viewpoint, 1,1-diacetates are important as precursors of 1-acetoxy dienes for Diels–Alder reactions [1] and intermediate products in various transformations, including nucleophilic substitution reactions [2–6].

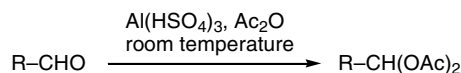
Known syntheses of acylals from aldehydes and acetic anhydride involve strong protic acids, such as sulfuric, methanesulfonic, and phosphoric, and Lewis acids, e.g., WCl_6 [7] or ZrCl_4 [8]. In the recent years, several reagents and catalysts have been proposed, in particular $\text{P}_2\text{O}_5/\text{SiO}_2$ [9], NBS [10], $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ [11], $\text{In}(\text{OTf})_3$ [12], $\text{Bi}(\text{OTf})_3 \cdot x\text{H}_2\text{O}$ [13], zirconium sulfophenyl phosphonate [14], $\text{H}_2\text{NSO}_3\text{H}$ [15], LiBF_4 [16], zinc montmorillonite [17], and heteropolycompounds such as Wells–Dawson acid [18] or aluminum dodecatungstophosphate [19].

According to recently reported data, many reactions proceed more effectively in the solid state than in solution. Solvent-free techniques offer such advantages as reduced pollution, low cost, simplicity of handling, and easy workup. These factors are especially important for large-scale processes. Analogous advantages (specifically, reduced reactor and plant corrosion and environmentally safe disposal) are inherent to the use of solid acids instead of, e.g., sulfuric acid. Inorganic acidic salts such as $\text{Al}(\text{HSO}_4)_3$ [20, 21] may be recommended as reagents and catalysts in the above reac-

tions. Although publications on the use of these salts in synthetic practice are few in number, in the recent years more attention has been given to their synthetic potential in organic chemistry. To the best of our knowledge, there are no published data on the synthesis of acylals with the aid of $\text{Al}(\text{HSO}_4)_3$. Aluminum(III) hydrogen sulfate is a stable nonhygroscopic crystalline substance that is insoluble in most organic solvents.

In continuation of our studies on the application of metal hydrogen sulfates in organic synthesis, the present communication describes a convenient method for the preparation of acylals from the corresponding aldehydes and acetic anhydride in the presence of $\text{Al}(\text{HSO}_4)_3$. The reactions were carried out at room temperature without a solvent using 4–9 mol % of the catalyst (Scheme 1, see table).

Scheme 1.



R = Ar, Alk (see table).

The catalytic effect of $\text{Al}(\text{HSO}_4)_3$ may be rationalized in terms of the presence of a hydrogen sulfate ion as a source of proton and of an Al^{3+} cation acting as a Lewis acid. The proposed procedure combines chemical and environmental advantages of solvent-free reactions. Our results show that $\text{Al}(\text{HSO}_4)_3$ effectively catalyzes transformations of aromatic aldehydes, in-

* The text was submitted by the authors in English.

Chemoselective transformation of aldehydes into the corresponding acylals in the presence of $\text{Al}(\text{HSO}_4)_3$

Run no.	Aldehyde	Ratio RCHO– $\text{Al}(\text{HSO}_4)_3$ – Ac_2O , mmol	Reaction conditions ^a	Time, min	Yield, ^b %
1	4-Nitrobenzaldehyde	3:0.138:3	A	5	85
2	3-Nitrobenzaldehyde	3:0.138:3	A	5	80
3	2-Chlorobenzaldehyde	3:0.276:3	A	5	83
4	4-Chlorobenzaldehyde	3:0.276:3	A	5	86
5	Benzaldehyde	3:0.276:3	A	5	75
6	2-Ethoxybenzaldehyde	3:0.276:3	^c	60	68
7	2-Nitrocinnamaldehyde	3:0.138:3	^c	20	72
8	3-Methoxybenzaldehyde	3:0.276:3	A	5	60
9	2,4-Dichlorobenzaldehyde	3:0.138:3	A	5	88
10	2,6-Dichlorobenzaldehyde	3:0.138:3	A	5	80
11	2-Cyanobenzaldehyde	3:0.276:3	A	5	75
12	4-Cyanobenzaldehyde	3:0.276:3	A	5	82
13	Vanillin	3:0.138:3	B	30	68 ^d (22) ^e
14	2-Furaldehyde	3:0.138:3	A	15	40 ^f
15	Hydrocinnamaldehyde ^g	3:0.138:3	A	5	20
16	Isobutyraldehyde ^g	3:0.138:3	A	5	30
17	4-Dimethylaminobenzaldehyde	3:0.138:3	A B	5 30	0 3–5 ^h

^a A: grinding in a mortar at room temperature; B: heating at the boiling point.

^b Yield of isolated product.

^c The reaction was carried out in hexane at room temperature.

^d Triacetate.

^e 4-Acethoxy-3-methoxybenzaldehyde.

^f Unidentified polymeric product.

^g The reaction was accompanied by aldol condensation.

^h Calculated on the reacted aldehyde.

cluding those having electron-withdrawing substituents in the benzene ring, into the corresponding acylals (see table, run nos. 1–4, 9–12). It should be noted that the yields of acylals with electron-withdrawing substituents in analogous reactions catalyzed by $\text{AlPW}_{12}\text{O}_{40}$ [19] were much poorer.

Some aliphatic and aromatic ketones were also tried in this reaction. However, cyclohexanone, 5-methylhexan-2-one, acetophenone, and 4-nitroacetophenone failed to react with acetic anhydride on grinding in a mortar over a period of 5 min at room temperature or on heating at the boiling point over a period of 60 min. Probably, the proposed procedure ensures chemoselective protection of an aldehyde group in the presence of a ketone group. No expected acylal was obtained from 4-dimethylaminobenzaldehyde and acetic anhydride in the presence of $\text{Al}(\text{HSO}_4)_3$ on grinding in a mortar at

room temperature. Presumably, the reactivity of that aldehyde is strongly reduced due to strong donor effect of the dimethylamino group. It should also be noted that the reaction with vanillin gave the corresponding triacetoxo derivative (run no. 13), i.e., the phenolic hydroxy group underwent acetylation as well.

Thus we have developed a convenient and effective catalytic procedure for the chemoselective transformation of various aldehydes into the corresponding acylals at room temperature without a solvent using a relatively nontoxic and inexpensive catalysts.

EXPERIMENTAL

All reagents were purchased from Fluka, Merck, or Aldrich. Aluminum(III) hydrogen sulfate was prepared by the procedure described in [20]. The products were

identified by their physical constants and spectral data (IR, ^1H NMR).

3-Nitrobenzylidene diacetate. A mixture of 0.453 g (3 mmol) of 3-nitrobenzaldehyde, 0.3 ml (3 mmol) of acetic anhydride, and 0.043 g (0.138 mmol) of $\text{Al}(\text{HSO}_4)_3$ was ground in a mortar over a period of 5 min at room temperature. The progress of the reaction was monitored by TLC using methylene chloride–petroleum ether (3:2) as eluent. After 5 min, the conversion was more than 99%. When the reaction was complete, the mixture was treated with diethyl ether, the precipitate was filtered off, the filtrate was washed with a saturated aqueous solution of NaHCO_3 (2×25 ml) and water (30 ml), and the organic phase was dried over anhydrous Na_2SO_4 , filtered, and evaporated. Yield 0.58 g (86%), colorless crystalline substance, mp 65–66°C; published data [12]: mp 64–66°C. The other acylals were synthesized in a similar way.

The authors thank the Research Affairs at the Yazd University, Bu-Ali Sina University, and Kashan University for the financial support to this work.

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