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Acetic Acid-Assisted Copper Methanesulfonate Catalyst for Chemoselective Conversion of Aldehydes to Acylals

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Abstract: A new catalytic system has been discovered by combining copper methanesulfonate with acetic acid for chemoselective conversion of aldehydes to acylals in high yields at ambient temperature under solvent-free conditions. The efficiency of this system might result from the "double activation" of Brønsted–Lewis acid catalysis on aldehydes.

Keywords: Acylals, Brønsted acidity, copper methanesulfonate, Lewis acidity

INTRODUCTION

Superacidic systems that may be formed by mixing appropriate Lewis and Brønsted acids have been the subject of much academic and industrial research. Such complexation (ideally between an inactive Lewis acid and an

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inactive organic acid toward a specific reaction) has been used efficiently in many types of electrophilic substitutions.[1,2] In this article, the mixture of copper methanesulfonate (CMS) with acetic acid as a new catalytic system is applied in synthesizing acylals.

Acylals (geminal diacetates) have been used as suitable protecting groups for aldehydes because of their stability in mildly acidic and basic media. The preparation of acylals has been achieved by the reaction of aldehydes with Ac_2O under the catalysis of strong protic acids such as H_2SO_4, H_3PO_4, CH_3SO_3H,[3] and H_2NSO_3H[4]; Lewis acids such as $InCl_3$,[5] $Fe_2(SO_4)_3 \cdot xH_2O$,[6] $Cu(OTf)_2$,[7] $Bi(OTf)_3 \cdot xH_2O$,[8] $Bi(NO_3)_3 \cdot 5H_2O$,[9] $Sc(OTf)_3$,[10] $LiBF_4$,[11] PCl_3,[12] and I_2[13]; and other types of catalysts such as ZrO_2/SO_4^{2-},[14] Amberlyst-15,[15] and HY-zeolite.[16] Although some improvements have been observed in these methods, there are still some limitations, such as the long reaction time, the highly corrosive and expensive catalysts, strictly reactive condition (N_2 atmosphere), and the large excess of Ac_2O (5–10 equiv.). Therefore, the development of an efficient, inexpensive, and green protocol is of interest. For the CMS-HOAc catalytic system, methanesulfonates that act as water-tolerant Lewis acid catalysts have been well documented.[17,18] Properties such as low toxicity and cost, air tolerance, and their recyclability make them superior to common Lewis acids. Moreover, HOAc is a cheap protonic acid, environmentally benign, commercially available, and easy to handle. The system overcomes the problems encountered with classical catalysts.

RESULTS AND DISCUSSION

The catalytic activities of CMS, HOAc, and CMS-HOAc in synthesizing acylal from benzaldehyde are compared in Table 1. In a model reaction of

Table 1. Comparison of CMS, HOAc, and CMS-HOAc catalysts in synthesizing acylal from benzaldehyde

$$\mathrm{PhCHO} + \mathrm{Ac_2O} \xrightarrow[\text{solvent-free, rt}]{\text{catalyst}} \mathrm{PhCH(OAc)_2}$$

Catalyst			
CMS (0.6 mmol)	HOAc (24 mmol)	Time (h)	Yield (%)[a]
Without	Without	72	0
With	Without	1.3	9
With	Without	3	42
With	Without	7	89
With	With	1.3	94
Without	With	51	0

[a] Isolated yields.

benzaldehyde (30 mmol) and Ac_2O (60 mmol), a controlled experiment was carried out first and the results show no reaction occurred even after 3 days. After 0.6 mmol of CMS was added, the reaction proceeded slowly, and the conversion of benzaldehyde reached 89% after 7 h. Under the same condition, the conversion of benzaldehyde increased to 94% only after 1.3 h, when CMS was mixed with HOAc. However, acetic acid does not induce the reaction in the absence of CMS.

Under the condition of aldehyde (30 mmol) and Ac_2O (60 mmol), a series of aldehydes were subjected to a diacetoxylation reaction under catalysts of CMS or CMS-HOAc. The results are summarized in Table 2. As can be seen from Table 2, the reactions catalyzed by CMS proceeded with difficulty. In most cases, CMS alone failed to catalyze the reactions. It is noteworthy that the combination of CMS with HOAc is very efficient for the diacetoxylation reaction of aldehydes. The aromatic aldehydes, α,β-unsaturated and aliphatic aldehydes, afforded the corresponding 1,1-diacetates in high yields and purity. Aromatic aldehydes with electron-withdrawing group such as nitro required comparatively longer reaction time (12 h, entry 9). Phenol groups were also protected for the acetylation of the hydroxyl groups in vanillin, 4-hydroxybenzaldehyde, and salicylal, which afforded the corresponding triacetates (entries 10, 11, and 12). Additionally, *p*-dimethylaminobenzaldehyde failed to give the corresponding 1,1-diacetate because of the strong electron-donating ability of dimethylin and a degree of tautomerization between a quinoid structure and the aldehyde. Another reason may be the coordination of nitrogen in dimethylin with the Cu^{2+} in CMS (entry 13). The chemoselectivity of this method was demonstrated using equimolar benzaldehyde and acetophenone in the presence of a catalytic amount CMS-HOAc for 9 h; exclusively diacetate of benzaldehyde was obtained, and the quantitative acetophenone remained because of the electron-donating ability and the steric effect of the methyl group (entry 15).

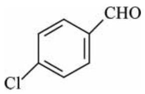
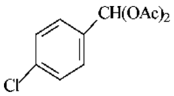
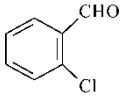
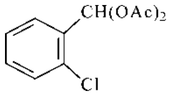
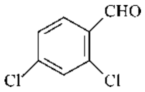
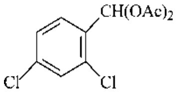
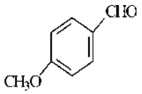
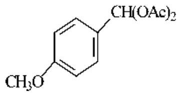
A series of experiments confirmed that both CMS and HOAc are indispensable for the conversion of aldehydes to acylals. The observed investigations demonstrated a Brønsted acid–assisted Lewis acid catalysis. The efficiency of this system might result from the “double activation” of Brønsted–Lewis acid catalysis on aldehydes.

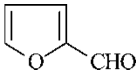
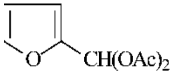
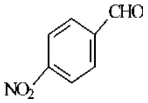
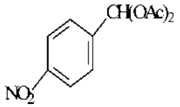
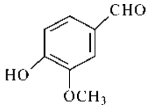
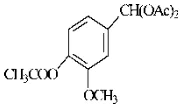
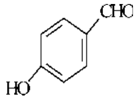
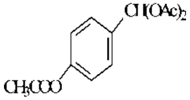
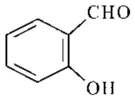
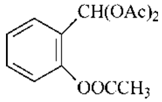
CONCLUSION

In conclusion, this is the first example of using a cooperative catalysis system, combining a Lewis acid and a Brønsted acid, for synthesizing acylals. Although the exact mechanism is uncertain, the use of an inexpensive catalyst, the solvent-free condition, and excellent yields of the products make this procedure more economic and environmentally friendly. Further investigation of the mechanism and applications of the new catalytic system is ongoing in our laboratory.

Table 2. Comparison of CMS and CMS-HOAc systems catalyzed conversion of aldehydes to acylals

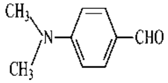
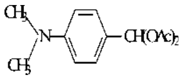
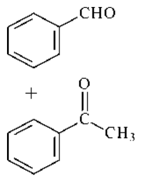
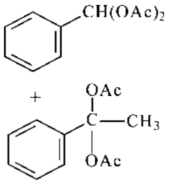
$$\mathrm{RCHO} + \mathrm{Ac_2O} \xrightarrow[\text{solvent-free, rt}]{\text{CMS–HOAc}} \mathrm{RCH(OAc)_2}$$

				Yield (%)[a]		MP (°C) or bp (Torr)	
Entry	R	Time (h)	Product	Cat: CMS	Cat: CMS + HOAc[b]	Observed	Reported
1	PhCHO	1.3	$PhCH(OAc)_2$	9	94	44–45	44–46[4]
2		4		0	85	79–80	79–80[13]
3		8		0	85	55–56	56–57[3]
4		9		0	88	97–99	101–102[4]
5		2.5		7	78	60–62	64–65[3]

6		4		8	79	50–52	52–53[13]
7		2		6	67	80–82	84–86[5]
8	$CH_3CH{=}CHCHO$	4	$CH_3CH{=}CHCH(OA)_2$	0	92	88–90/15	89–90/15[16]
9		12		0	84	118–120	123–125[5]
10[c]		10		14	86	91–92	91–92[19]
11[c]		11		0	66	91–93	89–90[19]
12[c]		11		0	73	102–103	102–103[6]

(*continued*)

Table 2. Continued

Entry	R	Time (h)	Product	Yield (%)[a]		MP (°C) or bp (Torr)	
				Cat: CMS	Cat: CMS + HOAc[b]	Observed	Reported
13		25		0	0	—	—
14	CH_3CH_2CHO	7	$CH_3CH_2CH(OAc)_2$	0	73	70–73/18	72–74/20[16]
15[d]		9		0 0	95 0	—	—

[a] Isolated yields and the purity of the products were determined by ^1H NMR and GC.

[b] CMS 0.6 mmol and HOAc 24 mmol.

[c] Four equiv. of Ac_2O were used.

[d] Equimolar mixture of benzaldehyde and acetophenone; the percentage of the products in the reaction mixtures was deterimined by GC analysis.

EXPERIMENTAL

Melting points were determined using RY-1 micromelting-point apparatus and are uncorrected. Gas chromatographic analysis was carried out on a Perkin-Elmer Auto System XL gas chromatograph. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX series Fourier Transform instrument. ^{1}H NMR spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ using TMS as an internal standard. Elemental analyses were carried out on an EA 2400II elemental analyzer (Perkin-Elmer).

General Procedure for the Preparation of Acylals

A mixture of aldehyde (30 mmol), Ac_2O (60 mmol), CMS (0.6 mmol), and HOAc (24 mmol) were magnetically stirred at ambient temperature for an appropriate time (monitored by GC). After the reaction, most of the mixture solidified gradually, and 20 mL of CH_2Cl_2 was added to dissolve the solid product. The organic layer was washed twice with saturated Na_2CO_3 solution (20 mL), dried (Na_2SO_4), and evaporated to yield the almost pure product. The product was purified further by crystallization from cyclohexane or by column chromatography on silica gel (ethyl acetate/hexane, 1:9 as the eluent). All the acylals were characterized by IR, ^{1}H NMR, and elemental analysis.

Analytical Data for Selected Compounds

1,1-Diacetoxy-1-propenyl methane (entry 8): colorless liquid, IR (KBr): 3020, 1761, 1392, 1250, 1214 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 6.70$ (d, $J = 7$ Hz, 1H), 6.04–5.11 (m, 2H). 2.13–1.90 (m, 9H). Anal. calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.67; H, 7.17.

1,1-Diacetoxy-1-ethyl methane (entry 14): colorless liquid, IR (KBr): 3000, 1760, 1460, 1432, 1246, 1204, 1115, 1061, 1014, 966 cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 6.72$ (t, $J = 6$ Hz, 1H), 2.10 (s, 6H). 1.40–2.13 (m, 2H), 1.02 (t, 3H). Anal. calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.81; H, 7.25.

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