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Lithium Trifluoromethanesulfonate (LiOTf) as a Recyclable Catalyst for Highly Efficient Acetylation of Alcohols and Diacetylation of Aldehydes under Mild and Neutral Reaction Conditions

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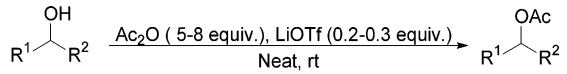
Abstract: A variety of alcohols and aldehydes were reacted with acetic anhydride at room temperature in the presence of a catalytic amount of lithium triflate (LiOTf) to produce the corresponding esters and 1,1-diacetates, respectively, in good to excellent yields under essentially neutral reaction conditions. Sensitive functional groups such as $PhCO_2-$, OMe, and OTBDMS ethers survived intact under the described reaction conditions.

The acetylation of alcohols is one of the most frequently employed reactions in organic synthesis that is normally carried out using acetic anhydride or acetyl chloride in the presence of tertiary amine bases such as either pyridine or triethylamine,[1] protonic or Lewis acids,[2] or sometimes solid acid catalyst.[3] The rate of acetylation in the basic conditions is known to be raised multifold if 4-(dimethylamino)pyridine (DMAP) is used as a cocatalyst.[4] In 1993, Vedejs et al. introduced Bu_3P as a less basic catalyst than amines for acetylation of alcohols.[5] Very recently, it has been shown that metal triflates such as $Sc(OTf)_3$[6] and $Bi(OTf)_3$[7] as well as Me_3SiOTf[8] are excellent catalysts for efficient acetylation of various types of structurally diverse alcohols with acetic anhydride. Although these methods ensure good results in many instances, there is still a great demand for mild and especially neutral catalysts to generate esters. In our development of new methods for functional group transformation, we have been especially interested in exploring the potential uses of various types of neutral catalysts.[9] In this regard, we have found that LiOTf is a mild and *neutral* Lewis acid catalyst for highly chemoselective dithioacetalization of aldehydes,[10] transdithioacetalization of acetals and acylals,[11] and chemoselective tetrahydropyranylation of alcohols under neutral reaction conditions.[12] LiOTf has also been shown to be a good catalyst for the chemoselective aminolysis of oxiranes and glycosylation of nucleophiles under mild and neutral reaction conditions.[13] In this paper, we wish to disclose a new mild and efficient protocol for acetylation of a variety of alcohols using Ac_2O (5−8 equiv) in the presence of catalytic amounts of LiOTf (0.2 equiv) under neutral conditions (Scheme 1).

SCHEME 1



Compounds that we acetylated in this protocol are primary, allylic, benzylic, hindered and unhindered secondary, and sterically hindered tertiary alcohols, the results of which are summarized in Table 1. We first examined the acetylation of benzyl alcohol using Ac_2O (5.0 equiv) in the absence of LiOTf. The reaction was very sluggish so that the corresponding acetate was formed in low yield even after 24 h (Table 1, entry 1). However, in the case of simple primary and secondary alcohols, the reactions progressed smoothly at room temperature in the presence of LiOTf to afford excellent yields of the corresponding acetate esters (Table 1, entries 2−13). Moreover, primary and secondary allylic alcohols underwent smooth acetylation under the same reaction conditions (Table 1, entries 14−16). In general, it is known that diaryl carbinols can also easily dimerize in the presence of acidic catalyst.[14]

However, benzhydrol as a model substrate was acetylated in 91% yield using Ac_2O (6.0 equiv) in the presence

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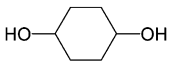
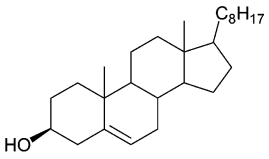
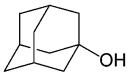
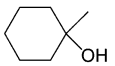
TABLE 1. Acetylation of Alcohols Using Ac_2O in the Presence of LiOTf at Room Temperature

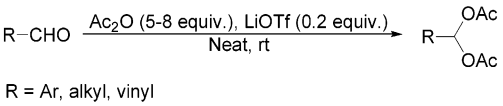
Entry	R^1	R^2	Subst./Ac_2O/LiOTf	Time (h)	Yield[a] (%)
1	Ph	H	1:5:0.0	24	44[b]
2	Ph	H	1:5:0.2	11	97[3a]
3	4-(Cl)C_6H_4	H	1:5:0.2	12	95[28a]
4	4-(*i*-Pr)C_6H_4	H	1:5:0.2	13	96
5	4-(MeO)C_6H_4	H	1:5:0.2	13	96[28b]
6	3-(Cl)C_6H_4	H	1:5:0.2	12	93[28a]
7	$PhCH_2CH_2CH_2$	H	1:5:0.2	15	93[2a, 28a]
8	*c*-$C_6H_{11}CH_2CH_2$	H	1:5:0.2	15	95
9	Ph	CH_3	1:6:0.2	17	96[6b]
10	Ph	Et	1:6:0.2	16	96[28c]
11	4-(Me)C_6H_4	Et	1:6:0.2	16	95[28h]
12			1:8:0.3	16	90[28d]
13			1:8:0.2	31	82[8a]
14	*n*-C_5H_{11}	vinyl	1:6:0.2	16	91[28e]
15	$(CH_3)_2C{=}CHCH_2$	H	1:5:0.2	15	96[28f, h]
16	$PhCH{=}CHCH_2$	H	1:5:0.2	15	93[2h]
17	Ph	Ph	1:6:0.3	34	91[c, 28a]
18			1:6:0.3	30	93[28g, h]
19			1:6:0.3	30	92[d, 6b]

[a] Isolated yields. [b] GC yield. [c] No etherification product was observed. [d] No elimination product was detected.

of LiOTf (0.3 equiv) without any dimerization (Table 1, entry 17). Interestingly, hindered tertiary alcohols such as 1-methylcyclohexanol and adamantanol were also converted to the corresponding acetates in excellent yields (entries 18, 19), without the formation of any detectable elimination products (entry 19). The last two observations are undoubtedly due to the neutral feature of LiOTf in our described protocol (Table 1, entries 17, 19).

1,1-Diacetates, on the other hand, are ambident substrates containing two types of reactive carbon centers, the carbon atom of the protected aldehyde function and the carbonyl group in the ester moieties.[15] The relative acid stability of 1,1-diacetates is another interesting feature of such 1,1-diacetates in the field of *protection*−*deprotection* chemistry.[16] 1,1-Diacetates are also synthetically important precursors for the preparation of 1-acetoxydienes, valuable synthetic intermediates for Diels−Alder cycloaddition reactions. In general, the preparation of 1,1-diacetates was achieved under the catalysis of strong protonic acids such as H_2SO_4,[17] H_3PO_4, and CH_3SO_3H.[18] However, in recent years, Lewis acids such as $ZnCl_2$,[19] $FeCl_3$,[16] PCl_3,[20] I_2,[21] $Sc(OTf)_3$,[22] NBS,[23] and also inorganic solid catalysts like Nafion-H,[24] Zeolites,[25] and clay[26] have received attention for this purpose. Very recently, it has been shown that $LiBF_4$ is a mild and efficient Lewis acid catalyst for the conversion of aldehydes into 1,1-dicarboxylates.[27] Once again, we observed that no considerable amount of the corresponding 1,1-diacetate was formed upon the reaction of benzaldehyde with Ac_2O in the absence of LiOTf (Table 2, entry 1). On the other hand, with the use of acetic anhydride (5−8 equiv), various types of aromatic aldehydes can effectively be converted into 1,1-diacetates in the presence of a catalytic amount of LiOTf (0.2 equiv) under neutral conditions (Scheme 2, Table 2). Moreover, the protocol could also equally work with aliphatic as well as α,*β*-unsaturated aldehydes (Table 2, entries 21, 22).

SCHEME 2



Highly deactivated aldehydes as well as hindered aldehydes were also diacetylated in excellent yields under similar reaction conditions (Table 2, entries 3, 8−11). Moreover, sensitive groups such as −OMe, −OCOPh, thiophene ring, and TBDMS ethers are stable under the described reaction conditions (Table 2, entries 9−13, 18−20). It is also worth mentioning that ketones such as acetophenone did not give any acylals with the above catalyst even after 48 h (Table 2, entry 23). Therefore, we also investigated the possible chemoselective protection of aldehydes in the presence of ketones. As shown in Scheme 3, when a 1:1 mixture of benzaldehyde and

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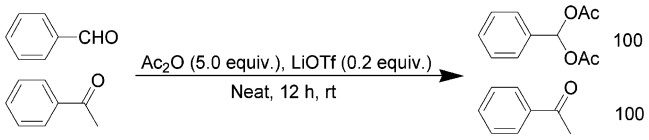
TABLE 2. Acetylation of Aldehydes Using Ac_2O in the Presence of LiOTf at Room Temperature

entry	R^1	R^2	substrate/ Ac_2O/LiOTf	time (h)	yield[a] (%)
1	Ph	H	1:5:0.0	24	11[b]
2	Ph	H	1:5:0.2	12	96[21]
3	3-(Br)C_6H_4	H	1:6:0.2	14	96
4	2,6-$(Cl)_2C_6H_3$	H	1:8:0.2	19	95
5	4-(Me)C_6H_4	H	1:5:0.2	12	95[20]
6	3-(Me)C_6H_4	H	1:5:0.2	12	93
7	4-(*i*-Pr)C_6H_4	H	1:5:0.2	12	95
8	2,4,6-$(Me)_3C_6H_2$	H	1:8:0.2	20	89
9	4-(MeO)C_6H_4	H	1:8:0.2	29	91[21]
10	3-(MeO)C_6H_4	H	1:8:0.2	22	95
11	2,5-$(MeO)_2C_6H_3$	H	1:8:0.2	36	90
12	4-($PhCO_2$)C_6H_4	H	1:8:0.2	16	89
13	4-(MeS)C_6H_4	H	1:8:0.2	21	93
14	3-(NO_2)C_6H_4	H	1:6:0.2	12	93[26a]
15	4-(NO_2)C_6H_4	H	1:6:0.2	15	94[21]
16	2-(NO_2)C_6H_4	H	1:6:0.2	16	90[26b]
17	2-naphthyl	H	1:8:0.2	17	86[25a]
18	2-thenyl	H	1:8:0.2	31	87[25a]
19	4-(TBDMSO)C_6H_4	H	1:8:0.2	26	91
20	3-(TBDMSO)C_6H_4	H	1:8:0.2	21	96
21	*n*-propyl	H	1:5:0.2	23	90[21]
22	$CH_3CH{=}CH$	H	1:5:0.2	25	92[21]
23	Ph	CH_3	1:8:0.2	48	nr

[a] Isolated yields. [b] GC yield.

SCHEME 3



acetophenone was allowed to react with acetic anhydride (5.0 equiv) in the presence of LiOTf (0.2 equiv) and the reaction mixture was worked up after 12 h, NMR analysis of the crude products consisted of a 1:1 mixture of benzaldehyde diacetyl acetal and acetophenone. However, unfortunately both aliphatic and aromatic aldehydes showed similar reactivity and, in our system, no chemoselectivity was observed.

In continuation of our studies, we interestingly found, for the first time, that LiOTf can be effectively recovered from the reaction mixture during the workup procedure by a simple evaporation of the aqueous phase and subsequent recrystallization of the solid residues. The percent of recovery in most cases was more than 90% without any changes in the Lewis acid properties. This undoubtedly renders the above protocol relatively environmentally acceptable and makes LiOTf a strictly *neutral* and *recoverable* Lewis acid in organic synthesis. Further application of LiOTf and the other neutral catalysts are currently ongoing in our laboratories.

Experimental Section

General Procedure for Acetylation of Alcohols. To a solution of alcohol (2 mmol) and acetic anhydride (5−8 mmol) was added LiOTf (0.4−0.6 mmol) at room temperature, and the mixture was stirred until complete disappearance of the starting material (as monitored by TLC or GC). After completion, the reaction was quenched with water (25 mL), and the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was separated, washed with saturated $NaHCO_3$ (2 × 25 mL) and water (15 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the almost pure acetates. Further purification of products was achieved by column chromatography to afford pure acetate(s) (Table 1).

General Procedure for the Preparation of 1,1-Diacetates. To a magnetically stirred solution of aldehyde (2 mmol) and freshly distilled acetic anhydride (5−8 mmol) was added LiOTf (0.4 mmol) at room temperature, and the mixture was stirred until complete disappearance of starting material (as monitored by TLC). After completion, the reaction was quenched with water (25 mL), and the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The aqueous layer was separated and could be evaporated under reduced pressure to afford the crude recycled catalyst. The organic layer was separated, washed with saturated $NaHCO_3$ (2 × 25 mL) and water (15 mL), and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave the almost pure 1,1-diacetate. Further purification using column chromatography gave the corresponding pure product (Table 2).

Recovery of the Catalyst LiOTf from These Reactions. The aqueous layer was separated in the first stage of the above workup procedure and could be evaporated under reduced pressure to afford the crude recycled catalyst. After evaporation of water, the resulting solid residue was recrystalized in CH_3CN to give the corresponding pure LiOTf in 90−91% recovery after drying at 110 °C for 12 h.

2-Cyclohexylethyl Acetate. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 3.95−3.98 (t, J = 6.9 Hz, 2H), 1.90 (s, 3H), 1.51−1.60 (m, [4 + 1]H), 1.37−1.42 (m, 2H), 1.24 (m, 1H), 1.04−1.13 (m, 3H), 0.79−0.84 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 170.73, 62.52, 35.95, 34.50, 33.10, 26.41, 26.12, 20.77.

4-*i*-Propylbenzyl Acetate. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.45−7.47 (d, J = 7.4 Hz, 2H), 7.35−7.37 (d, J = 7.4 Hz, 2H), 4.83 (s, 2H), 2.85−2.90 (septet, J = 7.1 Hz, 1H), 2.01 (s, 3H), 1.27−1.29 (d, J = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 171.02, 151.24, 136.10, 127.32, 126.59, 72.47, 34.55, 24.85, 20.11.

1,1-Diacetoxy-1-(4-benxoyloxyphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 8.19−8.21 (d, J = 8.4 Hz, 2H), 7.73 (s, 1H), 7.64−7.67 (tt, J = 7.50, 1 Hz, 1H), 7.59−7.61 (d, J = 8.4 Hz, 2H), 7.50−7.53 (t, J = 7.50 Hz, 2H), 7.27−7.28 (d, J = 8.4 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.75, 164.96,152.01, 134.07, 133.27, 131.30, 130.26, 128.68, 128.18, 122.03, 89.09, 20.88.

1,1-Diacetoxy-1-(2,5-dimethoxyphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.98 (s, 1H), 7.04−7.05 (d, J = 3.0 Hz, 1H), 6.87−6.89 (dd, J = 9.0 Hz, 3.0 Hz, 1H), 6.82−6.84 (d, J = 9.0 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.10 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.51, 153.68, 151.34, 124.96, 115.49, 113.15, 112.51, 85.61, 56.41, 55.84, 20.83.

1,1-Diacetoxy-1-(4-thiomethylphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.61 (s, 1H), 7.39−7.41 (d, J = 8.3 Hz, 2H), 7.21−7.22 (d, J = 8.3 Hz, 2H), 2.42 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.70, 140.94,132.16,127.19, 126.17, 89.55, 20.80, 15.36.

1,1-Diacetoxy-1-(2,6-dichlorophenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 8.13 (s, 1H), 7.20−7.22 (d, J = 8.5 Hz), 7.12−7.16 (*pseudo* t, J = 8.5 Hz), 1.98 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 166.24, 135.44, 131.14, 130.34, 129.35, 87.41, 20.38.

1,1-Diacetoxy-1-(3-*tert*-butyldimethylsilyloxyphenyl)-methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.59 (s, 1H), 7.17−7.20 (t, J = 8.0 Hz, 1H), 7.05−7.07 (d, J = 8.0 Hz, 1H), 6.95−6.96 (t, J = 2.0 Hz, 1H), 6.80−6.83 (dd, J = 8.0 Hz, 2.4 Hz), 2.04 (s, 6H), 0.96 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.34, 155.78, 137.13, 129.65, 121.23, 119.56, 118.36, 89.40, 25.70, 20.63, 18.19, −4.43.

1,1-Diacetoxy-1-(4-*tert*-butyldimethylsilyloxyphenyl)-methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.59 (s, 1H), 7.01−7.05 (d, J = 8.4 Hz, 2H), 6.68−6.73 (d, J = 8.4 Hz, 2H), 1.95 (s, 6H), 0.92 (s, 9H), 0.18 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.55, 154.22, 132.68, 127.85, 124.38, 89.68, 23.59, 21.03, 18.21, −4.65.

1,1-Diacetoxy-1-(3-bromophenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.58 (s, 1H), 7.55 (s, 1H), 7.33−

7.38 (dd, J = 15.1 Hz, J = 7.9 Hz, 2H), 7.11−7.14 (t, J = 7.9 Hz), 1.98 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.43, 137.89, 132.69, 130.43, 129.68, 125.50, 122.46, 88.66, 20.56.

1,1-Diacetoxy-1-(3-methoxyphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.64 (s, 1H), 7.27−7.30 (t, J = 7.9 Hz, 1H), 7.07−7.09 (d, J = 7.9 Hz, 1H), 7.04 (s, 1H), 6.89−6.92 (dd, J = 7.9 Hz, J = 2.3 Hz, 1H), 3.78 (s, 3H), 2.09 (s, 6H). ^{13}C NMR(125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.72, 159.81, 137.01, 129.79, 118.93, 115.36, 112.22, 89.55, 55.30, 20.80.

1,1-Diacetoxy-1-(4-*i*-propylphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.67 (s, 1H), 7.44−7.46 (d, J = 8.0 Hz, 2H), 7.25−7.26 (d, J = 8.0 Hz, 2H), 2.89−2.93 (septet, J = 6.9 Hz, 1H), 2.08 (s, 6H), 1.21−1.22 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.44, 150.54, 133.18, 126.81, 126.68, 89.83, 34.04, 23.92, 20.76.

1,1-Diacetoxy-1-(2,4,6-trimethylphenyl)methane. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 8.19 (s, 1H), 6.89 (s, 2H), 2.62 (s, 9H), 2.11 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C, TMS): δ 168.63, 139.34, 137.76, 129.74, 128.88, 88.76, 20.92, 20.58, 19.87.

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Supporting Information Available: NMR spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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