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Copper-catalyzed substitution reactions of acylal with organomanganese reagents

Madhukar B Deshmukh, Sunil D Jadhav* & Shashikant V Kadam

Department of Chemistry, Shivaji University, Kolhapur, Vidyanagar, Kolhapur 416 004, India.

E-mail: jadhav.sd@rediffmail.com

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A mild method for the copper-catalyzed substitution of aldehyde acylals with organomanganese reagents is reported. This operationally simple C-C bond-forming protocol uses different Cu(I) catalysts. Acylal from *trans*-cinnamaldehyde furnishes conjugated addition product when reacted with alkyl and aryl organomanganese reagents in presence of 10 mol % of $Cu(NCMe)_2(PPh_3)_2[BF_4]$ and 2 equivalent of Me_3Si-Cl as an accelerator. This reagent can be efficiently used in the substitution of one acetate group of aromatic acylal to form esters in high yield.

Keywords: Substitution, acylals, organomanganese reagents

Vicinal and remote (1, 3 and 1, 4) allylic diacetates[1] or acylal have been applied in the synthesis of many physiologically active and natural products. Allylic diacetates have been used in the synthesis of a 1,4-benzodioxane-ring system, which is present in a vast array of therapeutic agents[2]. These compounds have been of synthetic, mechanistic and biological importance for over 50 years. The catalytic allylic substitutions therefore provide potentially useful methods for the preparation of a wide range of chiral molecules. The copper(I) catalyzed allylic substitution reaction has generated a great deal of interest in recent years and several methods have been developed for substitution reactions. A broad range of organo-metallic compounds *viz.* organolithium, Grignard and organozinc reagents have been used in the allylic substitutions[3-8].

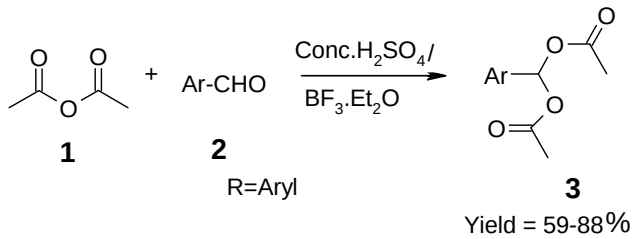
Efforts of this group have so far focused on the substitution reaction of geminal diacetates of aromatic aldehydes using organomanganese reagents in presence of $Cu(NCMe)_4[BF_4]$ and $Cu(NCMe)_2(PPh_3)_2[BF_4]$ as a catalyst.

Results and Discussion

In the present study, the acylal used were synthesized by either of the two methods. In the first method, aromatic aldehydes were treated with carboxylic anhydride in presence of sulphuric acid while in the second method, the acylals were obtained by treating carboxylic anhydride in the presence of boron trifluoride[9] (**Scheme I** and **Table I**). The use of different reagents[10-12] in acylal synthesis has also been reported.

The acylal were reacted with organomanganese reagents in presence of $Cu(NCMe)_4[BF_4]$ and $Cu(NCMe)_2(PPh_3)_2[BF_4]$ catalyst in dry THF or Et_2O solvent. The experiments, carried out with several 1,1-diacetates (**Table II**) indicated that the most significant product from these reactions was the ester resulting from displacement of one of the acetate groups with an alkyl or a phenyl group. The outcome of these ester formation reactions depended on the organomanganese reagent employed, the acylal, and the solvent used in the substitution reaction.

In present work the catalytic activity of both these catalysts in substitution reaction of acylal with alkyl and aryl organomanganese reagents has been explored (**Table II**). The comparative catalytic activity of $Cu(NCMe)_4[BF_4]$ in conjugate addition of *n*-butyl and phenyl manganese bromide to *trans*-cinnamaldehyde and it's allylic bisacetate has been reported. Conjugated yield[13a] of 61-84% was observed. The catalytic activity of $Cu(NCMe)_2(PPh_3)_2[BF_4]$ in conjugate addition of organomanganese reagents to α,β-unsaturated ester, enone and allylic chloride has been reported earlier[13b]. The simplicity of these reactions with $Cu(NCMe)_2(PPh_3)_2[BF_4]$ catalyst prompted the use of this catalyst in the substitution of one of the acetate groups of aromatic acylal with organomanganese reagents. Reaction of **3a** with butyl and phenyl manganese bromide afforded the corresponding conjugated product in high yields



Scheme I

Table I — Acylal prepared from aromatic aldehydes

Entry	Synthetic method	Ar	Product	Isolated Yield %
1	I	(a) Ph-CH=CH-	**3a**	62
2	I	(b) 4-Me-Ph-	**3b**	87
3	I	(c) 4-MeO-Ph-	**3c**	61
4	II	(d) 4-Cl-Ph-	**3d**	88
5	II	(e) 3-NO_2-Ph-	**3e**	92

Method I: Reaction of aldehyde with acetic anhydride in presence of conc. H_2SO_4
Method II: Reaction of aldehyde with acetic anhydride in presence $BF_3.OEt_2$.

(entries 1 and 2). It was found that **3a-c** reacted with alkyl and aryl organomanganese reagents in the absence of catalyst with corresponding formation of ester in lower yields (entries 2, 4, 10 and 14) as compared to catalytic reactions. But the catalytic substitution reactions resulted in improved yields in the presence of 1-2 equivalent of Me_3SiCl as an accelerator. Thus, **3a** on reaction with phenyl manganese bromide afforded the product in 84% yield in presence of 10 mol % of $Cu(NCMe)_2(PPh_3)_2[BF_4]$ and 1 equivalent of Me_3SiCl (entry 3). **3b** gave the substituted product in highest yield with butyl and phenyl manganese bromide (entries 5 and 9). However, when isopropyl manganese bromide was used, the desired product could not be obtained in significant yield (entry 8). This might be due to the steric effect of the isopropyl group present in the organomanganese reagents. **3c** afforded excellent substitution with phenyl and butyl manganese bromide reagents (entries 11 and 13). It was thought that substitution with isopropyl manganese bromide in **3c** would be higher, but once again significant yield could not be obtained even in presence of 2 equivalent of Me_3SiCl (entry 12). Acylal derived from *p*-chlorobenzaldehyde, **3d** afforded good substitution yields with phenyl manganese bromide in presence of 1 equivalent of Me_3SiCl (entry 15). In case of acylal derived from 3-nitrobenzaldehyde **3e**, it was thought that there would be less substitution yields with butyl manganese bromide reagent due to electron withdrawing effect of nitro group. But surprisingly, higher substituted yields were obtained (entry 17).

Highly sterically hindered isopropyl manganese bromide, resulted in poor substitution of one acetate group in acylal. Therefore, dialkyl and trialkyl organomanganate have been used with **3b**, in order to test the scope of the reaction (**Table III**)

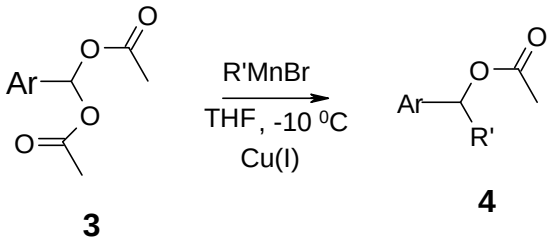
Moderate to good substituted product yields were found with these reagents. When isopropyl manganese bromide was used, it resulted in the formation of 42% product in presence of 10 mol % CuI catalyst. However, in presence of *i*-$Pr_3MnMgBr$, higher yields of substitution resulted when the same catalyst was used (entry 3). In comparison with Cu (I) catalyst, improved substitution were observed with $Cu(NCMe)_2(PPh_3)_2[BF_4]$ catalyst (entries 2 and 4). These results showed that manganates having secondary and tertiary alkyl ligands such as *i*-Pr_2MnBr and *i*-$Pr_3MnMgBr$ gave substitution of one acetate group in 51-61% alongwith an unidentified complex mixture.

The yields of ester formation with substitution of one acetate group tended to vary in a somewhat regular fashion. When phenyl manganese bromide was used, the yields of ester were higher (entries 3, 9, 13, and 15). The formation of ester was high when THF was used as solvent as compared to Et_2O. Organomanganese reagents with high steric hindrance resulted in poor substitution of one acetate group in acylal.

Experimental Section

^1H NMR spectra were recorded in $CDCl_3$ solution on JEOL JNM-GX 270 and Brucker WH-400 MHz and ^{13}C NMR on Avance-200 MHz instruments. For ^{13}C NMR spectra, the chemical shifts are reported with $CDCl_3$ (77.0 ppm) as internal reference while tetramethylsilane (TMS, 0.00 ppm) was used as reference for ^1H NMR spectra. The IR spectra were recorded on Perkin-Elmer Spectrum One FTIR Spectrometer. The mass spectra were obtained on a Finnigan-MAT 1020 (electron impact ionization, EI) machine and a VG-ZAB (fast atom bombardment ionization, FAB) machine (EPSRC Service, Swansea). Merck silica gel (230-400 mesh) was used for column chromatography, and thin-layer chromatography (TLC) was run on Merck precoated silica gel 60-F_{254} plates. Concentrations of the Grignard reagent were determined by titration[14]. All

Table II — Copper catalyzed substitution of acylal with R′MnBr

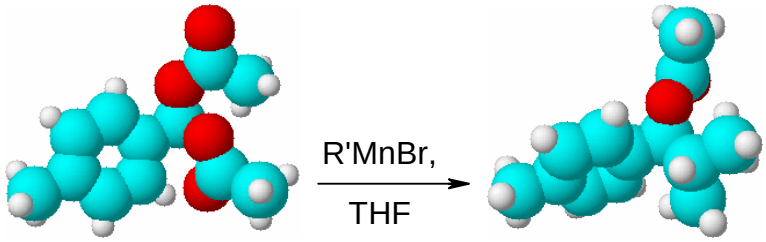


3 **4**

Entry	Substrate	Cu (I) 10 mol %	R′	Solvent	Additive (equiv.)	Product %Yield of **4**
1	**3a**	C	*n*-Bu	THF	Me_3SiCl(1)	76 **4a**
2	**3a**	-	*n*-Bu	Et_2O	-	61 **4a**
3	**3a**	D	Ph	THF	Me_3SiCl(1)	84 **4b**
4	**3a**	-	Ph	THF	-	72 **4b**
5	**3b**	D	*n*-Bu	THF	-	81 **4c**
6	**3b**	C	*n*-Bu	THF	Me_3SiCl(2)	82 **4c**
7	**3b**	C	*n*-Bu	Et_2O	-	78 **4c**
8	**3b**	C	*i*-C_3H_7	Et_2O	Me_3SiCl(2)	42 **4d**
9	**3b**	D	Ph	THF	Me_3SiCl(1)	97 **4e**
10	**3b**	-	Ph	THF	-	83 **4e**
11	**3c**	D	*n*-Bu	THF	Me_3SiCl(1)	68 **4f**
12	**3c**	D	*i*-C_3H_7	THF	Me_3SiCl(2)	38 **4g**
13	**3c**	D	Ph	THF	-	92 **4h**
14	**3c**	-	Ph	THF	-	81 **4h**
17	**3d**	D	Ph	THF	Me_3SiCl(1)	71 **4i**
16	**3d**	C	*n*-Bu	THF	-	79 **4j**
15	**3e**	C	*n*-Bu	THF	-	84 **4k**

All reactions were carried out on 1 mmol scale, at-10°C
The yields are determined by analytical method. The mass balance is starting material.
C: $Cu(NCMe)_4[BF_4]$, D: $Cu(NCMe)_2(PPh_3)_2[BF_4]$.

Table III — Copper catalyzed substitution of acylal with organomanganese reagent



Entry	R′	Cu(I) 10 mol %	Solvent	% Yield
1	*i*-Pr	CuI	THF	42
2	*i*-Pr_2	$Cu(NCMe)_2(PPh_3)_2[BF_4]$	THF	51
3	*i*-Pr_3	CuI	THF	48
4	*i*-Pr_3	$Cu(NCMe)_2(PPh_3)_2[BF_4]$	Et_2O/THF	61

All reactions were carried out on 1 mmol scale, at-10°C and 1 equiv. of Me_3SiCl
The yields are determined by analytical method. The mass balance is starting material

reactions were carried out in flame-dried glassware under N_2 atmosphere, unless stated otherwise. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl solution. $Cu(NCMe)_4[BF_4]$[15] and $Cu(NCMe)_2(PPh_3)_2[BF_4]$[16] were prepared according to literature procedures. Me_3Si-Cl was used without further purification.

Li_2MnCl_4: Manganous (II) chloride (1 M) and lithium chloride (2 M) were vacuum dried in oven at 120°C for 3 hr and then Na dried THF was added to form the "ate" complex of Li_2MnCl_4. Organomanganese reagents were prepared by adding Grignard reagent to the "ate" complex prior to use.

RMnCl: 1 mmole of Li_2MnCl_4 and 1.2 mmole of RMgBr were stirred in 5 mL dry THF between-10 to 0°C for 1 hr. A brown suspension was formed.

R_2MnCl: 1 mmole of Li_2MnCl_4 and 2 mmole of RMgBr were mixed at 0°C for 30 min in 5 mL of THF to form a brown-black suspension and used directly.

$R_3MnMgBr$: A suspension of 1 mmol anhydrous Li_2MnCl_4 in 10 mL THF was added to 3 mmole of RMgBr in THF at 0°C under stirring for 30 min and then stirred at RT to form brown suspension of the reagent.

Syntheses of 1,1-diacetates

3a-c was synthesized on a 40 mmole scale by method I, which is based on the work of Gregory[17] and **3d-e** were prepared by method II.

Method I: Acetic anhydride (60 mmole) and aromatic aldehyde (60 mmole) were cooled in an ice bath and mixed with each other and two drops of conc. H_2SO_4 was added, and the mixture stirred till there was confirmation of the formation of the product (monitored on TLC). The reaction mixture was quenched with sat. Na_2CO_3 solution. Then the reaction mixture was extracted with Et_2O (2 × 30 mL). It was then washed with water (300 mL), and dried over $MgSO_4$. After evaporation of Et_2O, the crude product was subsequently purified by recrystallization from ethanol.

Method II: Acetic anhydride (0.28 mole) and $BF_3.OEt_2$ (10 drops) were introduced in a round-bottomed flask, equipped with a dropping funnel, a stirring magnet, and a thermometer, and immersed in salt-ice slush. Aldehyde (0.14 mole) was added slowly with stirring, and the mixture was stirred at RT for 2-3 hr. The product mixture was poured into a 10% aq. solution of NaOAc (200 mL) and stirred rapidly for 20 min. An oily layer was formed. The product was extracted with ether (3 × 50 mL), the extracts were combined, and washed with aq. $NaHCO_3$ followed by water. After drying (anhyd. $MgSO_4$) the crude product was concentrated under vacuum and purified by recrystallization from ethanol.

General procedure for copper-catalyzed organomanganese reagents with acylal

To a freshly prepared solution of Li_2MnCl_4 (1 mL, 1.0 M, 1 mmole) was added dropwise a solution of *n*-BuMgBr (1.0 mL, 1.1 M, 1.2 mmole) in THF over a period of 15 min, at 0°C using a gas-tight syringe. After completion of addition, the reaction mixture was stirred for another 30 min and then cooled to-10°C. Then 10 mol % of $Cu(NCMe)_2(PPh_3)_2[BF_4]$ and 1.5 equiv. of Me_3Si-Cl in 5 mL dry THF was added and the contents again stirred for 20 min. The acylal (1.0 mmole) dissolved in THF (2 mL) was added dropwise to the organomanganese reagent during 15-30 min. After complete addition, the reaction mixture was stirred for 1-2 hr and then quenched with saturated aq. NH_4Cl (6 mL) and 2 M aq. NH_4OH (4 mL). After the mixture was stirred for 30 min the organic phase was collected and the aqueous layer was extracted with Et_2O (4 × 5 mL). The combined organic layers were washed with brine, dried over anhyd. $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography gave the pure products.

Characterization of products

Specified spectral data are recorded for pure isomers using ^1H NMR, IR and ^{13}C NMR techniques. In a few cases it was not possible to obtain a pure isomer (entry 3, 5 and 12) and in these cases the ^1H NMR spectra were recorded from a mixture of isomers.

3,3-Diacetoxy-1*t*-phenyl-propene-(1), 3a: White crystalline solid. m.p. 86°C; ^1H NMR ($CDCl_3$): δ 7.1-7.6 (m, 6 H), 6.87 (d, *J* = 16 Hz, 1 H), 5.93 (dd, *J* = 16.7 Hz, 1 H), 2.1 (s, 6 H); IR (KBr): 1755, 1660, 1615, 1490, 1470, 1245, 1195, 1120, 1060, 1005, 940, 758 cm^{-1}; MS: *m/z* (%) 234.1 (P, 4), 190.4 (1), 175.1 (2), 133 (59), 131 (100), 115 (3), 104 (19), 77 (11), 63 (25), 43 (89).

(Acetyloxy)(4-methylphenyl) methyl acetate, 3b: White solid. m.p.78°C; ^1H NMR ($CDCl_3$): δ 7.63 (s, 1H) 7.3-7.4 (d, 2H, *J* = 8Hz), 7.1-7.2 (d, 2H, *J* = 8Hz), 2.35 (s, 3H), 2.10 (s, 6H); MS: *m/z* (%): 222, 179, 163, 121, 119, 91, and 43; ^{13}C NMR ($CDCl_3$):

δ 168.3, 139.6, 132.3, 130.1, 126.6, 89.8, 21.1 and 20.7; IR (KBr): 1765, 1750, 1230, 1205, 1070, 1005, 960, 930, 815 cm^{-1}.

(Acetyloxy)(4-methoxyphenyl) methyl acetate, 3c: Yellow white solid. m.p. 59°C. ^1H NMR ($CDCl_3$): δ 7.40 (s, 1H), 7.35 (d, *J* = 9 Hz, 2H), 6.75 (d, *J* = 9 Hz, 2H), 3.80 (s, 3H), 2.10 (s, 6H); IR (KBr): 1763, 1615, 1519, 1372, 1241, 1204 cm^{-1}; MS: *m/z* (%): 238, 195, 1179, 152, 135, 107, 93, 92.

(Acetyloxy)(4-chlorophenyl) methyl acetate, 3d: White solid. m.p. 78°C; ^1H NMR ($CDCl_3$): δ 7.68 (s, 1H), 7.34-7.50 (m, 4H), 2.13 (s, 6H); IR (Nujol): 1763, 1485, 1360, 1230, 1190 cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 168.3, 135.2, 134.2, 128.9, 128.1, 20.9, 89.1.

(Acetyloxy)(3-Nitrophenyl) methyl acetate, 3e: White solid.m.p.65°C; ^1H NMR ($CDCl_3$): δ 7.74 (s, 1H), 7.4-8.5 (m, 4H), 2.12(s, 6H); IR (Nujol):1758, 1536, 1458, 1233, 1200, 1094, 1055, 1014, 986, 915 and 818 cm^{-1}; ^{13}C NMR ($CDCl_3$): δ 168.4, 149.3, 136.9, 133.6, 130.5, 124.6, 121.9, 88.8, 20.8.

1-Phenyl hept-1-enyl-3-acetate, 4a (entry 1): ^1H NMR ($CDCl_3$): δ 7.4-7.1(m, 5H), 6.6(d, *J*= 7.2Hz, 1 H), 6.1(dd, *J*= 16, 7.1Hz, 1H), 5.4(q, *J*=7.1 Hz, 1H), 2.1(s and q, 5H), 1.7(m, 2H), 1.3-1.2(m, 2H), 0.9(t, *J*=7.1Hz, 3H); ^{13}C NMR($CDCl_3$): δ 171.3, 146.7, 134.1, 130.2, 127.7, 126.4, 117.3, 60.3, 29.3, 22.4, 20.8, 14.1 and 13.8; IR (KBr): 2930, 1744, 1634, 1494, 1452, 1375, 1239, 1047, 846, 758 and 698 cm^{-1}.

(2*E*)-1, 3-Diphenyl prop-2-enyl acetate, 4b (entry 3): ^1H NMR ($CDCl_3$): δ 7.2-7.6 (m, 11H, 2 × Ph + 1 CH), 6.84-6.9 (d, 1H, *J* = 17 Hz), 6.17 (dd, 1H, *J* = 10.5 and 17 Hz), 2.12 (s, 3H); IR (KBr): 1769, 1744, 1610, 1508, 1360, 1238, 1198, 1109, 1003, 954, 928 cm^{-1}.

1-(4-Methyl phenyl) pentyl acetate, 4c (entry 5): ^1H NMR ($CDCl_3$): δ 7.11-7.25 (m, 4H, *J* = 7.2 Hz), 5.69 (t, 1H, *J* = 7.2 Hz), 2.33 (s, 3H), 2.05 (s, 3H), 1.69-1.94 (m, 2H), 1.17-1.34(m, 4H), 0.87 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$): δ 170.2, 137.8, 137.4, 128.9, 126.6, 76, 35.8, 22.3, 21.2, 21.1, 13.9 IR (KBr): 3000, 2940, 1726, 1230, and 1009 cm^{-1}.

2-Methyl-1 NMR ($CDCl_3$): δ 7.12-7.26 (m, 4H), 5.43 (d, 1H, *J* = 7.8 Hz), 2.33 (s, 3H), 2.04-2.14 (s and m, 4H), 0.98 (d, 3H, *J* = 6.8 Hz), 0.79 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 170.3, 137.3, 136.8, 128.8, 127.2, 81.5, 33.5, 21.2, 21.2, 18.7, 18.5; IR (KBr): 2950, 1740, 1365, 1230, 1015 cm^{-1}.

(4-Methyl phenyl)(Phenyl) methyl acetate, 4e (entry 9): ^1H NMR ($CDCl_3$): δ 7.2-7.4 (m, 9H), 6.84 (s, 1H), 2.3 (s, 3H), 2.1 (s, 3H); IR (KBr): 1769, 1743, 1615, 1518, 1367, 1242, 1206, 1113, 1008, 959, 930 cm^{-1}.

1-(4-Methoxyphenyl) pentyl acetate, 4f (entry 11): ^1H NMR ($CDCl_3$): δ 6.8-7.8 (m, 4H), 5.66 (t, 1H, *J*=7.2Hz), 3.80(s, 3H), 2.02 (s, 3H), 1.87 (m, 2 H), 1.75 (m, 2H), 1.24-1.30 (m, 2H), 0.86 (t, 3H, *J*=7.2Hz); IR (KBr): 1736, 1602, 1514, 1372, 1245, 1175, 1033, 831 cm^{-1}.

1-(4-Methoxyphenyl)-2-methyl propyl acetate, 4g (entry 12): ^1H NMR ($CDCl_3$): δ 6.84-7.26 (m, 4H), 5.41 (d, 1H, *J* = 8 Hz), 3.79 (s, 3H), 1.91-2.14 (s and m, 4H), 0.78-.98 (d, 6H, *J* = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 70.3, 159.0, 131.8, 128.2, 113.5, 80.8, 55.1, 33.3, 20.8, 18.7; IR (KBr): 2921, 1716, 1492, 1353, 1220 cm^{-1}.

(4-Methoxyphenyl)(Phenyl) methyl acetate), 4h (entry 13): ^1H NMR ($CDCl_3$): δ 6.88-7.84 (m, 9H), 3.9 (s, 3H), 3.8 (s, 1H), 2.13 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 169.9, 159.2, 140.3, 131.8, 128.5, 128.3, 127.5, 126.6, 113.6, 76.5, 55.1, 21.1; IR (KBr): 1741, 1566, 1210, 1000, 672 cm^{-1}.

(4-Chlorophenyl)(Phenyl) methyl acetate, 4i (entry 15): ^1H NMR ($CDCl_3$): δ 7.23-7.34 (m, 9H), 6.84 (s, 1H), 2.15 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 169.8, 139.7, 138.8, 133.7, 130.8, 128.6, 128.4, 127.8, 126.9, 76.3, 21.1; IR (KBr): 1731, 1585, 1480, 1360, 1222 cm^{-1}.

1-(4-Chlorophenyl pentyl acetate), 4j (entry 16): ^1H NMR ($CDCl_3$):δ 7.13-7.26(m, 4H, *J*=7.2Hz), 5.7(t, 1H, *J*=7.2Hz), 2.34(s, 3H), 1.70-1.95(m, 2H), 1.17-1.36(m, 4H), 0.89(t, 3H, *J*=7.2 Hz); IR (KBr):3030, 2932, 1735, 1596, 1491, 1374, 1239 cm^{-1}.

1-(3-Nitrophenyl pentyl acetate), 4k (entry 17): ^1H NMR ($CDCl_3$):δ 7.13-7.28(m, 4H, ArH), 5.8(t, 1H, *J*=7.2Hz), 2.31(s, 3H), 1.71-1.95(m, 2H), 1.18-1.38(m, 4H), 0.9(t, 3H, *J*=7.2 Hz); IR (KBr): 3091, 2936, 1763, 1615, 1533, 1491, 1374, 1239 cm^{-1}.

Conclusion

In conclusion, the catalytic activity of $Cu(NCMe)_4[BF_4]$ and $Cu(NCMe)_2(PPh_3)_2[BF_4]$ complex have been compared in the substitution reaction of acylal achieving the higher yields of esters with an organomanganese reagents in THF. It is clear from these results that, for substitution reaction with organomanganese reagent, 10 mol % of $Cu(NCMe)_2(PPh_3)_2[BF_4]$ complex and 2 equivalent of

Me_3Si-Cl resulted in better substitution. It was found that in the highly sterically hindered organomanganese reagent substitution of only one acetate group resulted in acylal. The catalytic system has been extended to magnesium halide exchange in aromatic halides and trapping with electrophiles to form different fuctionalized derivatives. Further investigation into the scope and limitations of the reaction are currently in progress.

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References

1 Kanwarpal S, Kocchar B, Balkrishna B S, Deshpande R P, Rajadhyaksha S N & Pinnick H W, *J Org Chem,* 48, **1983**, 1765.
2 Goux C, Massacret M, Lhoste P & Sinou D, *Organometallics*, 14, **1995**, 4585.
3 Commercon A, Bourgain M, Delaumeny M, Normant J F & Villieras J, *Tetrahedron Lett*, 16, **1975**, 3837.
4 Barsantai P, Calo V, Lopez L, Marchese G, Naso F & Pesce G, *J Chem Soc Chem Commun*, **1978**, 1085.
5 Tseng C C, Paisley S D & Goering H L, *J Org Chem,* 51, **1986**, 2884.
6 Backvall J E, Sellen M & Grant B, *J Am Chem Soc*, 112, **1990**, 6615.
7 Backvall J E, Persson E S M & Bombrun A, *J Org Chem,* 59, **1994**, 4126.
8 Persson E S M, Van Klaveren M, Grove D M & Backvall J E, *Chem Eur J,* 1, **1995**, 351.
9 Man E H, Sanderson J J & Houser C R, *J Am Chem Soc*, 72, **1950**, 847.
10 Knoevenagel E, *Liebigs Ann Chem*, 402, **1914**, 111.
11 Kochhar K S, Bal B S, Deshpande R P, Rajadhyaksha S N & Pinnick H W, *J Org Chem*, 48, **1983**, 1765.
12 Smitha G & Reddy S C H, *Tetrahedron,* 59, **2003**, 9571.
13 a) Deshmukh M B, Jadhav S D, Mali A R, Suryawanshi A W, Anbhule P V, Jagtap S S & Deshmukh S A, *Synth Commn*, 35, **2005,** 2967.
b) Deshmukh M B, Jadhav S, Anbhule P V, Mali A R & Suryawanshi A W, *J Chem Res* (in press).
14 Taylor R J K, *Practical Approach in Chemistry*, (Oxford University Press, New York) **1994**, pp54-55.
15 Kubas G J, *Inorg Synth,* 28, **1990**, 68.
16 Green J, Sinn E, Woodward S & Butcher R, *Polyhedron*, 12, **1993**, 991.
17 Gregory M J, *Chem Soc (B),* **1970**, 1201.