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LETTERS

Indium-mediated allylation of *gem*-diacetates to homoallylic acetates in aqueous media[†]

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Abstract

Indium-mediated allylation of *gem*-diacetates gave excellent yields of the corresponding homoallylic acetates in aqueous media. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: gem-diacetates; allyl bromide; indium; homoallylic acetates.

Geminal-diacetates are ambident substrates containing two types of reactive carbon centres, the carbon atom of a protected aldehyde function and the carbonyl group in the ester moieties. In general, carbon nucleophiles will predominantly attack the former centre and displace one of the acyloxy groups affording substitution products in good yields.[1] Although, *gem*-diacetates are readily available from the corresponding aldehydes, these compounds have received little attention as substrates for nucleophilic substitution reactions.[2] Many methods, including palladium*(0) catalyzed substitution reactions[3] are associated with limitations regarding selectivity and compatibility. The recent report[4] on $Sc(OTf)_3$ catalyzed addition of allyltrimethylsilane to aldehydes in the presence of acetic anhydride gave a mixture of products containing the homoallylic alcohol, diacetate and di-allylated product along with the desired homoallylic acetates. Thus, an efficient and selective procedure for the substitution reactions of diacetates is needed.

In recent years, there has been increasing interest in indium-mediated transformations[5] because of certain unique properties inherent to indium. Furthermore, indium metal is stable to boiling water or alkali and doesn't form oxides readily in air. Such special properties of indium indicate that it is perhaps a promising metal for aqueous Barbier–Grignard type reactions.[6] Even though indium has been used extensively in carbonyl addition reactions,[7] it has not been used for the substitution reactions of *gem*-diacetates and acetals. Herein, we wish to report a mild and selective method for the synthesis of homoallylic acetates through the allylation of *gem*-diacetates using indium metal and allyl bromide in aqueous media. The mildness of the reaction conditions make it possible to use the indium metal for mono substitution of diacetates without formation of any side products including aldehydes, pinacols and

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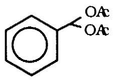
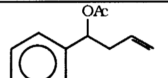
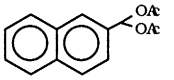
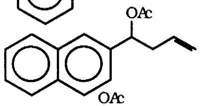
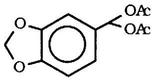
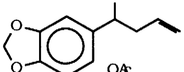
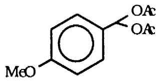
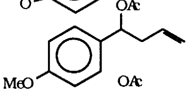
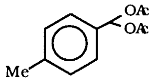
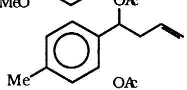
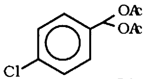
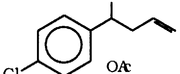
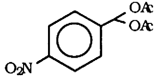
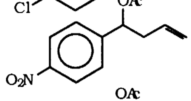
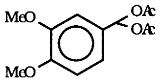
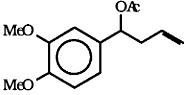
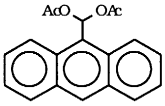
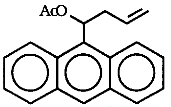
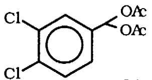
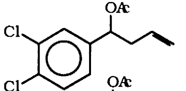
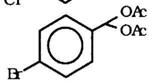
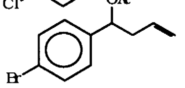
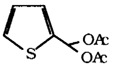
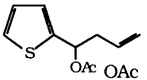
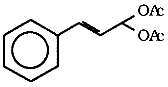
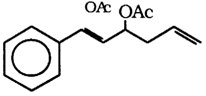
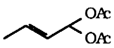
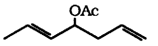
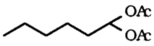
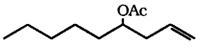
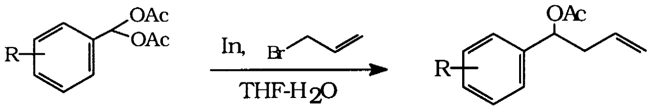
Table 1
Mono-allylation of *gem*-diacetates with allyl indium bromide in aqueous media

Entry	Substrate (1)	Product^a (2)	Reaction (h.)	Yield^b (%)
a			3.5	82
b.			4.0	78
c			3.5	85
d			3.0	87
e			3.0	84
f.			3.0	80
g.			5.0	70
h			3.0	79
i.			4.5	72
j.			4.0	78
k			3.5	80
l.			2.5	88
m			4	68
n			3.5	51
o.			2.5	53

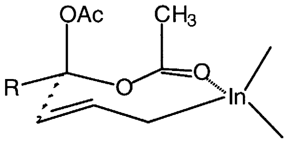
a : All products were characterised by ^{1}H NMR, and Mass spectra.
b : Isolated yields after column chromatography on silica gel are reported.

homoallylic alcohols. The reaction of aromatic diacetates with an equimolar ratio of allyl bromide and indium metal in THF:H_2O (4:1), resulted in the formation of the mono-allylated products in good yields[8] while aliphatic and allylic diacetates gave homoallylic acetates in moderate yields. Furthermore, it is of interest to observe that homoallylic alcohols were formed in good yields when diacetates were reacted with allylic magnesium bromide in THF at room temperature. The formation of homoallylic alcohols



Scheme 1.

may be attributed to the hydrolysis of homo allylic acetates with magnesium in THF whereas no such hydrolysis was observed by indium salts. Allylic magnesium bromides are known to react with esters resulting in the regeneration of parent aldehydes which give addition products whereas allylic indium bromide doesn't react with esters forming substitution products. Although, we could not establish the reaction mechanism by experiments, it may proceed as follows.



The reactions are clean and afford high yields of mono-substitution products at room temperature in a short reaction time. The results summarized in Table 1 clearly indicate the generality of the reaction for a variety of diacetates (Scheme 1).

In conclusion, we have described a new and efficient method for the synthesis of homoallylic acetates in good yields in aqueous media. Indium is found to be effective and highly selective metal for this transformation.

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8. Typical procedure: A mixture of indium powder (10 mmol), allyl bromide (12 mmol) and substrate **1c** (10 mmol) in THF (16 ml) and H_2O (4 ml) was stirred at room temperature for 3.5 h, until completion of the reaction was observed by TLC. Then the reaction was quenched with saturated ammonium chloride (20 ml) and extracted twice with ether (2×30 ml). The organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo to yield the crude product which was further purified by column chromatography on silica gel (100–200 mesh), and eluted with ethyl acetate:hexane gradient mixture (2:8) to afford the pure product **2c** as a colourless liquid. Representative data for compound **2c**: ^{1}H NMR ($CDCl_3$): δ 2.0 (s, 3H), 2.45–2.55 (m, 2H), 5.0–5.15 (m, 2H), 5.55–5.65 (m, 1H), 5.7 (m, 1H), 6.0 (s, 2H), 6.75–6.85 (m, 3H).