Bull. Chem. Soc. Ethiop. **2025**, 39(1), 131-139.
DOI: https://dx.doi.org/10.4314/bcse.v39i1.11

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

CHEMOSELECTIVE METAL FREE DEALLYLATION OF α-ALLYL-PHENYL-CARBOXYLIC ESTERS UNDER REDUCTION CONDITION

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(Received April 5, 2024; Revised September 27, 2024; Accepted October 3, 2024)

ABSTRACT. A simple and efficient method for chemoselective deallylation of –COO-allyl group in presence of C-allyl group has been developed. C-allyl cleavage of α-methylene compounds was successfully completed by refluxing with excess sodium borohydride in methanol. The reagent's stability, ready availability and ease of handling encourage its usage for deallylation.

KEY WORDS: C-allyl cleavage, Sodium borohydride, Chemoselectivity, Reduction

INTRODUCTION

The allyl groups for protecting carboxylic acid are now generally used for the synthesis of peptides [1-3] and the liquid–solid phase synthesis [4-8]. Although several methods have been developed for the deprotection of allyl groups, Pd° complex in presence of nucleophiles were highly effective [9, 10]. Palladium-catalyzed hydrosilylation leads to allylsilanes effectively but further investigation for deallylation not been reported [11]. The variety of nucleophiles have been reported to use as allyl scavenger that includes $NaBH_4$ [10], $LiBH_4$ [12], $NaBH_3CN$ [13, 14], Bu_3SnH, DIBAH [15-17], HCOOH, $LiBHEt_3$ [13-14], dimidinebarbutaric acid [18], phthallimide, $LiAlH_4$ [19], potassium hexanoate, $HCOO^-$ etc. The major drawback of these methods is availability and side reactions limit its usage in organic synthesis. The use of excess nucleophile however decreases the atom efficiently and sometimes causes problems during purification of the products. Berkefeld and co-workers reported cleavage of allyl ethers by Ni-H precatalyst and excess Brønsted acid [20]. Although O-allyl and N-allyl functional groups are deallylated by this method, the synthesis of complex nickel hydride required two steps is need to think of its use. Recently, O-deallylation was promoted by cobalt hydride catalyst, oxone, silane (TMDSO) and CoSalen complex [21]. We aspire to use less number of catalysts and reduce number of steps in deallylation of allyl esters. So, cleavage of allyl esters by using sodium borohydride in dimethylsulphoxide was explored [22]. The reaction was performed at room temperature and progress well in all weather conditions. Most importantly the activation by transition metal complexes was not required. Reaction of α-allyl carboxylic esters was also carried out in dimethylsulphoxide and iodine catalyst. It resulted in the cyclization of α-allyl esters to γ-butyrolactones [23].

Chemoselectivity allows chemists to bring out targeted product by allowing reaction at specific position and keeping other reactive sites in the molecule intact [24]. It also simplifies reactions of complex molecules by attacking specific functional groups while leaving others unchanged [25]. So, we wanted to examine sodium borohydride for chemoselective deallylation of α-allyl-esters and accomplished it successfully. In present work, we report the application of

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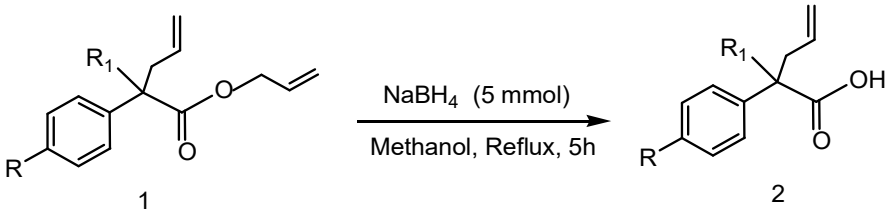
sodium borohydride in selective cleavage of allyl group in various α-allyl allyl phenyl acetates and α-allyl-esters in methanol.

RESULTS AND DISCUSSION

The use of sodium borohydride as a reducing agent in organic chemistry has been known over 60 years [26, 27]. Mild reducing properties of it allow for considerable selectivity in the reduction of organic compounds. Aldehydes and ketones are in general readily converted into their corresponding alcohol in the presence of variety of functional groups. The mild reaction condition, ease of work up and high yields contribute to the widespread use of sodium borohydride as hydride transfer reagent for reduction of aldehydes and ketones. A hydroxylic solvent is required for reduction. We previously used dimethylsulphoxide as a solvent in the deallylation process with sodium borohydride. Now, O-deallylation process is investigated by using hydroxylic solvent.

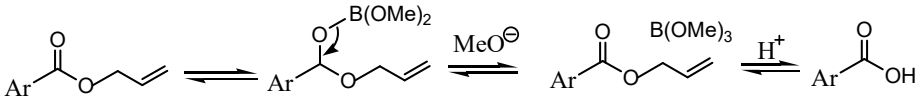
The deallylation simply proceed by the treatment of allyl carboxylic ester with sodium borohydride (5 mmol) in methanol at room temperature for 48 hours. The cleavage was remarkably accelerated under reflux condition furnishing α-allyl carboxylic acid in a very high yield in 5 hours. There is margined difference in the yield when methanol was used as solvent. While on increase in molecular weight of alcohol, yield decreases. In butanol yield of the product was lowest. Encouraged by double benefit of increased yield and substantial reduction on reaction time we proceeded to conduct deprotection of several α-allylallyl phenyl acetate derivatives. The results are summarized in Table 1. It is noteworthy that nitro, methoxy, ester, chloro group remain unaffected. In all substrates (**1a-p**) that have C-allyl or O-allyl group, only O-allyl group of ester was selectively cleaved to give corresponding α-allyl phenyl acetic acid under reflux in methanol. We found that $NaBH_4$/MeOH might interact with the C-allyl group if excess of sodium borohydride (8-10 mmol) was used for 12 hours. The product mixture was analyzed by NMR. The phenyl acetic acid (30%) was one of the product identified showing that α-allyl group also undergo reductive deallylation.

The rate of deallylation of substrate **1a**, **1b**, **1c** were studied and observed that rate of reaction for these substrates are **1a** > **1b** > **1c**. Fields of deprotection for O-allyl ester bearing electron donating methoxy group was higher as compared to electron withdrawing group like nitro. Some α-allylallyl carboxylic esters of aliphatic acids also undergo deallylation but at longer time under reflux.



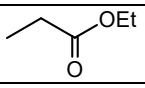
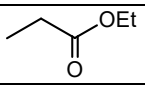
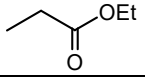
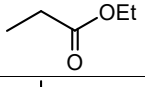
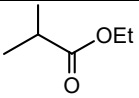
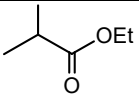
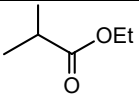
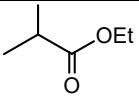
Scheme 1. Deallylation of α-allyl allyl phenyl acetate.

While no detailed mechanistic study has yet undertaken, we propose that the reaction proceeded via the formation of trimethoxyborane which form a π-complex with alkene which on hydrolysis afforded deallylated product acids as in Scheme 2.

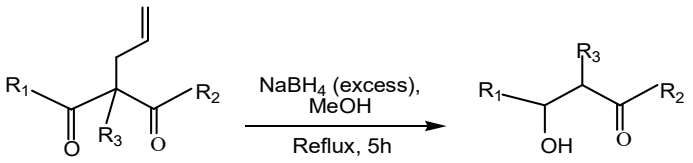


Scheme 2. A proposed mechanism for deallylation of α-allyl allyl carboxylic esters.

Table 1. Result of deallylation of α-allyl allyl phenyl acetate.

Entry	R	R_1	Time (h)	Yield % (**a-p**)
1a	H	H	6	79
1b	OMe	H	6	84
1c	NO_2	H	4	70
1d	Cl	H	5	82
1e	H	$PHCH_2$	4	75
1f	OMe	$PHCH_2$	7	82
1g	NO_2	$PHCH_2$	3.5	72
1h	Cl	$PHCH_2$	4	81
1i	H		5	80
1j	OMe		5	85
1k	NO_2		5.5	73
1l	Cl		5	82
1m	H		4	70
1n	OMe		6	80
1o	NO_2		4.5	78
1p	Cl		5	80

Amine 2-borane complex has been used for the deallylation process and formation of trimethoxyborane is a very well-known reaction. We demonstrated the metal free deallylation of diallyl carboxylic esters by using sodium borohydride in methanol. The reaction could be conducted simply by refluxing allyl ester with the inexpensive, handy reducing reagent in alcohol. Sodium borohydride also completed C-deallylation in presence of methanol. The α-allyl carboxylic ester (**3c**) was subjected to deallylation by treating it with $NaBH_4$/MeOH. The product was characterised by their signals in ^{1}H NMR. In ^{1}H NMR spectrum of product, the signals at 1.19 (d, 3H, CH_3), 1.27 (t, 3H, CH_3), 2.28 (q, 1H, CH) was observed. Allyl protons were observed at 2.45 (m, 4H, CH_2), 5.07 (dd, 4H, CH_2) and 5.68 (m, 2H). These results have confirmed that under the given condition, instead of deallylation there was a reduction of compound. Finally, refluxing the compound **(3c)** with excess quantity of sodium borohydride resulted in deallylation reaction (Scheme 3).



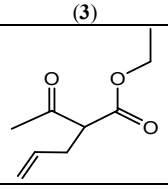
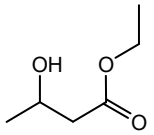
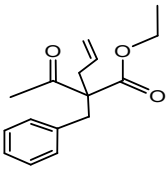
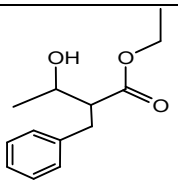
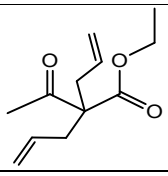
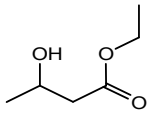
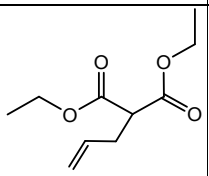
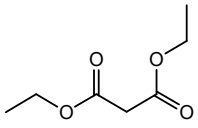
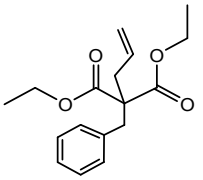
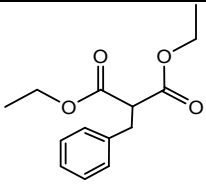
3a-m

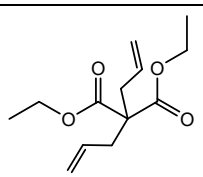
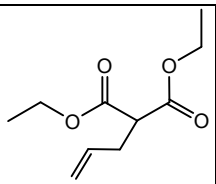
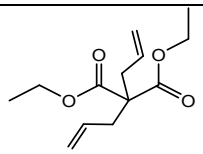
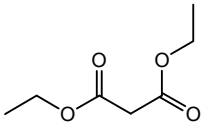
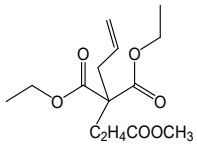
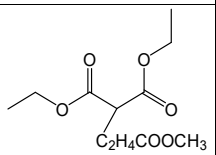
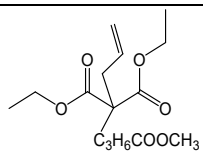
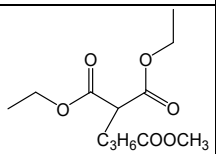
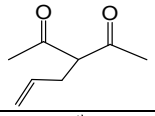
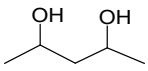
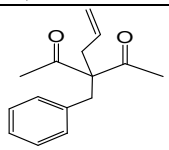
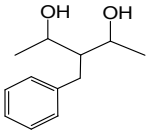
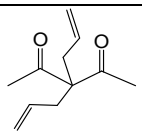
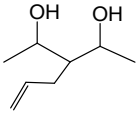
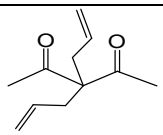
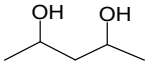
4a-m

R_1=CH_3, OC_2H_5
R_2=CH_3, OC_2H_5
R_3=H, $PhCH_2$, $CH_2CH{=}CH_2$, $C_2H_4COOCH_3$, $C_3H_6COOCH_3$

Scheme 3. C-deallylation in active methylene compounds by using $NaBH_4$/MeOH.

Table 2. C-deallylation in active methylene compounds by using $NaBH_4$/MeOH.

Entry	**3**	Starting (**3**)	**4**	Product (**4**)	Time (h)	Yield (**4**) %
1	**3a**		**4a**		5	58
2	**3b**		**4b**		5	61
3	**3c**		**4c**		8	69
4	**3d**		**4d**		5	57
5	**3e**		**4e**		5	65

6	**3f**		**4f**		5	63
7	**3g**		**4g**		9	59
8	**3h**		**4h**		5	61
9	**3i**		**4i**		5	60
10	**3j**		**4j**		5	56
11	**3k**		**4k**		5	62
12	**3l**		**4l**		5	68
13	**3m**		**4m**		9	62

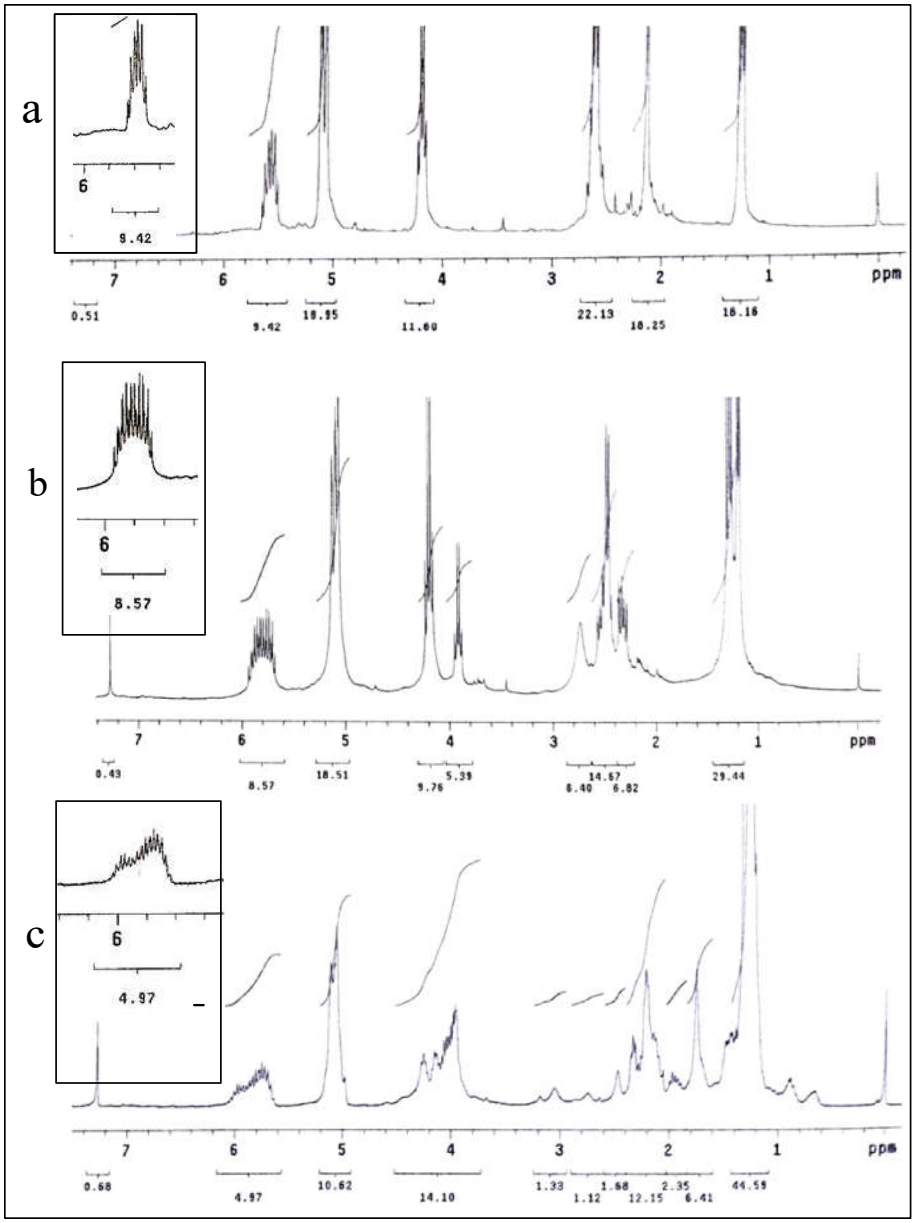


Figure 1. Transallylation shift of C-allyl group to O-allyl. A) ^{1}H NMR spectra of compound **3c**, b) ^{1}H NMR spectra of compound **5** obtained by stirring **3c** with $NaBH_4$ (3 equ) at r.t. c) ^{1}H NMR spectra of compound **6** obtained by refluxing **3c** with $NaBH_4$ (excess).

We have tried C-allyl cleavage in various active methylene compounds by $NaBH_4$/MeOH reagent. During these reactions it was observed that first allylic compound shows reduction of C=O group to C-OH. Then some of the C-allylic groups get converted to O-allyl group. In ^{1}H NMR spectrum of diallylic ethyl acetoacetate (**3c**), allylic CH proton appears at δ 5.51 as a multiplet. But after reduction of compound two multiplets are observed at δ 5.66 and 5.95. These results enable us to think about transallylation shift of C-allyl group to O-allyl in the same compound.

EXPERIMENTAL

*General procedure for deallylation of α-allyl allyl phenyl acetate (**1a-p**)*

To a solution of α-allyl allyl phenyl acetate (1 mmol), 5 equivalent of sodium borohydride was added in presence of methanol. The reaction mixture was refluxed for 5 hours. After cooling, the reaction mixture was acidified by 2N HCl and the residue was extracted with ethyl acetate (10 mL) and dried over Na_2SO_4. The product was purified by column chromatography (hexane/ethyl acetate, 9:1). C-deallylation (3a-m) was also completed by following the same procedure.

*Ethyl 2-acetylpent-4-enoate (**3a**)*. IR: 1643, 1735 cm^{-1}; ^{1}H NMR: δ 1.26 (t, 3H), 2.25 (s, 3H), 2.58 (dd, J = 6.8, 6.8 Hz, 2H), 3.50 (t, 3H), 4.17 (q, 2H), 5.04 (m, 2H), 5.68 (m, 1H).

*Ethyl 2-acetyl-2-benzylpent-4-enoate (**3b**)*. IR: 1644, 1735 cm^{-1}; ^{1}H NMR: δ 1.26 (t, 3H), 1.94 (t, 3H), 2.54 (dd, J = 7.1, 7.4 Hz, 2H), 3.19 (s, 2H), 4.05 (q, 2H), 5.10 (dd, J = 3.3, 3.8 Hz, 2H), 5.63 (m, 1H), 7.01 (Ar, 5H).

*Ethyl 2-acetyl-2-allylpent-4-enoate (**3c**)*. IR: 1643, 1734 cm^{-1}; ^{1}H NMR: δ 1.23 (t, 3H), 2.13 (s, 3H), 2.53 (m, 4H), 4.15 (q, 2H), 5.06 (dd, J = 4.8, 4.9 Hz, 4H), 5.51 (m, 2H).

*Diethyl 2-allylmalonate (**3d**)*. IR: 1643, 1732 cm^{-1}; ^{1}H NMR: δ 1.22 (t, 6H), 2.57 (dd, J = 7.4, 7.1 Hz, 2H), 3.38 (t, 1H), 4.13 (q, 4H), 5.03 (dd, J = 11, 6.3 Hz, 2H), 5.57 (m, 1H).

*Diethyl 2-allyl-2-benzylmalonate (**3e**)*. IR: 1644, 1734 cm^{-1}; ^{1}H NMR: δ 1.20 (t, 6H), 2.54 (dd, J = 6.3, 5.5 Hz, 2H), 3.21 (s, 2H), 4.14 (q, 4H), 5.11 (dd, J = 10.4, 3.3 Hz, 2H), 5.71 (m, 1H), 7.07 (Ar, 5H).

*Diethyl 2,2-diallylmalonate (**3f**)*. IR: 1643, 1732 cm^{-1}; ^{1}H NMR: δ 1.22 (t, 6H), 2.62 (dd, J = 6.8, 7.1 Hz, 4H), 4.17 (q, 4H), 5.03 (dd, J = 11.2, 4.1 Hz, 4H), 5.63 (dm, 2H).

*Diethyl 2-allyl-2-methyl acrylic malonate (**3h**)*. IR: 1643, 1734 cm-1; ^{1}H NMR: δ 1.23 (t, 6H), 2.16 (dd, J = 7.4, 7.1 Hz, 2H), 2.29 (dd, J=7.1, 7.4 Hz, 2H), 2.61 (d, J=7.4 Hz, 2H), 3.65 (s, 3H), 4.16 (q, 4H), 5.07 (dd, J = 9.9, 7.1 Hz, 2H), 5.57 (m, 1H).

*Diethyl 2-allyl-2-methylmethacrylic malonate (**3i**)*. IR: 1643, 1735 cm^{-1}; ^{1}H NMR: δ 1.20 (d, J = 3.5 Hz, 3H), 1.22 (t, 6H), 1.89 (dd, J = 1.6, 1.6 Hz, 2H), 2.36 (m, 1H), 2.55 (m, 2H), 3.61 (s, 3H), 4.07 (q, 4H), 5.04 (dd, J = 9.9, 7.1 Hz, 2H), 5.55 (m, 1H).

*3-Allylpentane-2,4-dione (**3j**)*. IR: 1639, 1697 cm^{-1}; ^{1}H NMR: δ 2.10 (s, 3H), 2.18 (s, 3H), 2.57 (m, 2H), 3.70 (t, 1H), 4.97 (m, 2H), 5.06 (dd, J=4.8, 4.9 Hz, 2H), 5.53 (m, 1H).

*3-Allyl-3-benzylpentane-2,4-dione (**3k**)*. IR: 1638, 1697 cm^{-1}; ^{1}H NMR: δ 2.10 (s, 3H), 2.12 (s, 3H), 2.6 (d, J = 7.1 Hz, 2H), 3.22 (d, J = 15.6 Hz, 1H), 5.13 (dd, J = 1.6, 4.9 Hz, 2H), 5.56 (m, 1H), 6.99 (m, 2H), 7.19 (m, 3H).

*3,3-Diallylpentane-2,4-dione (**3m**)*. IR: 1639, 1697 cm^{-1}; ^1H NMR: δ 2.10 (s, 6H), 2.63 (d, J = 7.4 Hz, 4H), 5.07 (dd, J = 6.3, 9.9 Hz, 4H), 5.44 (m, 2H).

*Ethyl 2-(1-hydroxyethy)pent-4-enoate (**4a**)*. ^1H NMR: δ 1.19 (d, J=6.4 Hz, 3H), 1.27 (t, 3H), 2.27 (m, 1H), 3.89 (m, 2H), 4.16 (q, 2H).

*Ethyl 2-acetyl-2- benzylpent-4-enoate (**4b**)*. ^1H NMR: δ 1.13 (d, J = 6.6 Hz, 3H), 1.25 (t, 3H), 2.13 (m, 1H), 3.19 (d, 2H), 3.88 (t, 2H), 4.06 (q, 2H), 7.06 (Ar, 5H).

*Diethyl malonate (**4d**)*. IR: 1186, 1371, 1732 cm^{-1}; ^1H NMR: δ 1.22 (s, 6H), 3.35 (s, 2H), 4.16 (q, 4H).

*Diethyl-2-benzylmalonate (**4e**)*. IR: 1644, 1734 cm^{-1}; ^1H NMR: δ 1.14 (t, 6H), 2.23 (d, J = 11.2 Hz, 2H), 3.19 (t, 1H), 4.07 (q, 4H), 7.09 (Ar, 5H).

*Diethyl-2-methyl acrylic malonate (**4h**)*. ^1H NMR: δ 1.26 (t, 6H), 2.18 (m, 2H), 2.29 (m, 2H), 3.41 (t, 1H), 3.67 (s, 3H), 4.11 (q, 4H).

*Pentane-2,4-diol (**4m**)*. ^1H NMR: δ 1.19 (d, J = 6.4 Hz, 3H), 1.24 (d, J = 6.3 Hz, 3H), 2.08 (m, 2H), 3.71 (m, 1H).

CONCLUSION

Under the reflux condition, sodium borohydride provides excellent chemoselectivity in the deallylation of –COO-allyl group in presence of C-allyl group. The selectivity observed is comparable to the previously reported methods. C-deallylation of α-methylene compounds was successfully completed by refluxing with excess $NaBH_4$ in methanol. It is observed that using this protocol, reduction reaction is preferred over deallylation. Also, intramolecular transallylation shift was detected from C-allyl group to O-allyl group in presence of $NaBH_4$/MeOH. The experimental simplicity, easy work-up procedure and low cost catalyst as compare to palladium mediated methods is noteworthy. Therefore, this new approach could be a beneficial addition to the current processes.

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