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Reduction of Olefinic bond of Chalcones and related enones by BER-Ni_2B System in Solid Phase

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Abstract
The selective reduction of olefinic bond in α,β-unsaturated carbonyl compounds gives a very simple route to the synthesis of carbonyl compounds. Borohydride Exchange Resin (BER)-Ni_2B system has been successfully utilized to reduce olefinic bond of chalcogens and related enones under biphasic condition to the corresponding carbonyl compounds in high yield, the work-up procedure being a simple one.

Keywords: *Chalcones, enones, BER-Ni_2B, solid phase reduction.*

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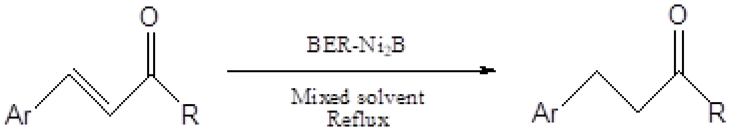
I. INTRODUCTION

α,β-unsaturated carbonyl compounds have two reducible groups: carbon-carbon double bond and carbon-oxygen double bond. The carbonyl group is reduced to alcohol by a number of reducing agents, of which lithium aluminiumhydride and other metallic hydrides are the most commonly used [1]. The conjugated double bond may or may not be reduced, depending on the substrates, reagents and reaction conditions. For example, the C=O bond of α,β-unsaturated ketones is selectively reduced with AlH_3 and with diisobutyllithium hydride. Also, both $LiAlH_4$ [2] and $NaBH_4$ [3] predominantly reduce only C=O bond of C=C-C=O system in most cases. In certain cases [4], these reagents may also reduce double bond in conjugation with C=O bond, as well as reducing the C=O bond. Double reduction of α,β-unsaturated carbonyl compounds is avoided by the use of AlH_3 or $NaBH_4$ in the presence of lanthanide chloride (e.g. $LaCl_3$, $CeCl_3$, $SmCl_3$ etc) [5] which selectively reduces C=O bonds in the presence of conjugated C=C bonds. Other reagents that can reduce selectively the C=O of α,β-unsaturated carbonyl compounds include [6, 7, 8, 9] 9BBN, Et_3SiH, lithium-n-butylborohydride or diisobutylaluminiumhydride. On the other hand, C=C bond can be selectively reduced in the presence of conjugated C=O bonds by hydrogenation with $RhCl(PPh_3)_3$, the Wilkinson catalyst [10, 11], as catalyst. Hydrogenation in presence of pentacyanocobaltate(II), $[Co(CN)_5]^{3-}$; and $(PPh_3)_3RuClH$ is also effective in selective reduction of C=C bond of α,β-unsaturated carbonyl compounds. Apart from these homogeneous hydrogenation of α,β-unsaturated carbonyl compounds, heterogeneous catalyst (Adam's platinum oxide) is also used in the selective hydrogenation of chalcones [12] to produce β-phenylpropiophenone in high yield. This selective reduction of C=C bond of α,β-unsaturated carbonyl ketones (particularly chalcones and related enones), which are very easy to prepare, gives a very simple route to the synthesis of carbonyl compounds which are said to be the "Backbone of Organic Synthesis". Thus the development of new reducing agents and methodologies, which are relatively simpler than the existing ones, is necessary so as to give a new direction in this field.

II. RESULTS AND DISCUSSION

The synthetic utility of Borohydride Exchange Resin (BER)-Ni_2B system as reducing agent is well documented in our earlier work [13] and therein, we utilized the system for successful reduction of C-4 exocyclic double bond of oxazolones. In this study, we too utilized the same system for selective reduction of olefinic bond in α,β-unsaturated ketones (particularly chalcones and related enones), prepared by standard method, to give saturated ketones.

In a typical run, the chalcones and the related enones were dissolved in a methanol based mixed solvent and refluxed with BER-Ni_2B till a colourless solution is obtained. The colour is due to presence of conjugated system ArCH=CHCOAr. This characteristic makes it easy to follow the reduction of these compounds as in the case of oxazolone. The progress of the reduction was also monitored by TLC. Reduction of the olefinic bond here destroys conjugation and results in the decolourization and formation of saturated ketones. The yield of the ketones was about 80% and recovery involved simple filtration and reduced pressure removal of the solvents. The reaction is illustrated in scheme-I.



SCHEME -I

Ar = substituted phenyl
R = phenyl or methyl
(cyclic enones are also reduced)

EXPERIMENTAL

The starting chalcones and other enones were prepared and purified according to standard procedure before use. All solvents were dried and purified by standard methods. Amberlite IRA-400 macroporous type according to Rohm & Haas specifications with type analysis strong base quarternary-NMe_3, 20-30 mesh, Cl^- form, styrene DVB (8%) was chosen as the anion exchanger. The resin beads were washed several times with deionised water before use. Melting points were determined in open capilliaries and uncorrected. Elemental analyses were performed on a Hitachi 026 CHN-analyzer. IR were recorded in KBr pallets on a Perkin Elmer 1600 FT-IR spectrometer. Chromatography was done on prepared silica gel G plates.

Preparation of BER

40 g of wet anion exchange resin, Amberlile IRA-400-(Cl^-) form was slurry packed in 100 mL sintered glass funnel mounted on a filtering flask. Then 400 mL of aqueous $NaBH_4$ (0.5M) was slowly passed through the resin over a period of 60 min. Resulting resin was washed with distilled water thoroughly until free from excess $NaBH_4$. The borohydride exchange resin (BER) was then dried in vacuum at 65^0C for 2 hours.

Estimation of Borohydride content in BER

The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 0.8 N HCl according to the following equation :

$$\underset{\text{BER}}{\text{Polymer--}BH_4^-} + HCl + H_2O = \text{Polymer--}Cl^- + 4H_2 + B(OH)_3$$

The results are summerized in the table-I.

Table-I
Estimation of Borohydride content in BER

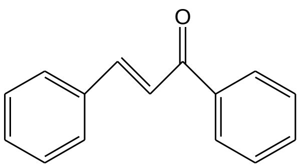
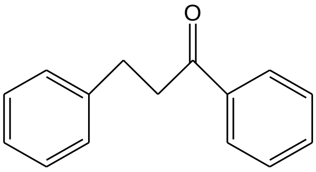
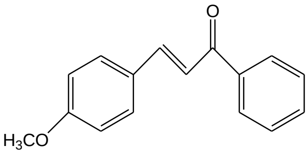
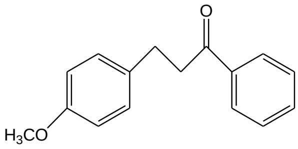
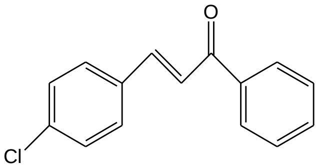
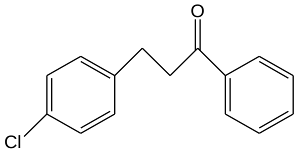
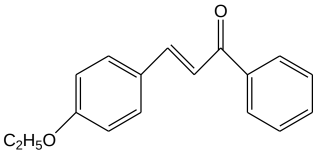
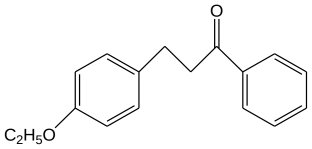
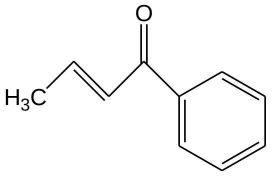
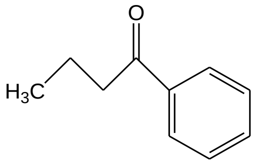
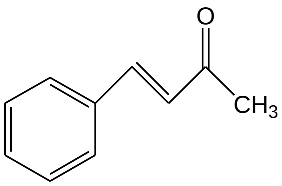
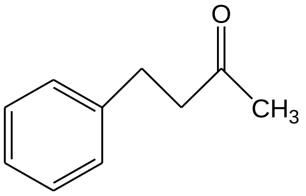
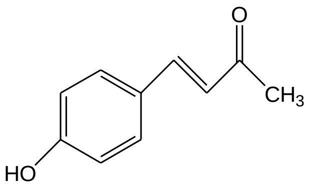
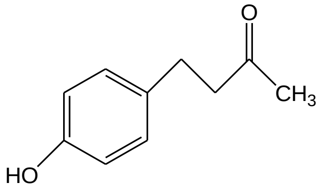
Sl. No.	Amount of BER taken (g)	Estimated Borohydride contents (m mol)	Estimated Borohydride contents (m mol/g resin)	Mean m mol/g resin
1.	1.0	2.5	2.5	2.6
2.	2.0	5.2	2.6	
3.	3.0	7.8	2.6	
4.	5.0	13.0	2.6	

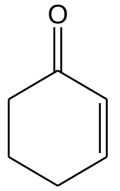
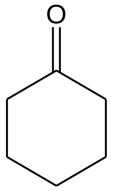
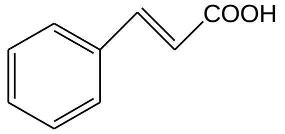
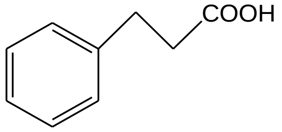
The average capacity of BER was found to be 2.6 m mol of BH_4^- per gram of the resin. The dry resin was stored under nitrogen atmosphere at room temperature and the hydride content was found to be constant over 6 weeks.

Reduction of chalcones and related enones
(General procedure)

To 3.33g (10 mmoles) of BER was added Ni(OAc)$_2$.4H$_2$O (0.25g, 1 mmole) and the mixture was stirred gently at room temparature. A black coating of Ni$_2$B was formed. After one minute, 25mL of a solution containing 10 mmoles of the substrate in an appropriate mixed solvent was added, and the mixture stirred under reflux for an appropriate time when the yellow colour of the solution turned colourless. The resin was removed by filtration, volume of the filtrate was reduced and the contents poured into ice-cold water whence product precipitated. The product was washed several times with water, dried and recrystallized from CHCl$_3$ (yield 85-90%). The reduction can be followed conveniently by observing the colour change of the solution and periodical TLC. The authenticity of the products was established by their melting points, elemental analyses and spectral data. The physical characteristics of products are given in table-II.

Table-II
Physical characteristics of reduced chalcogens and related enones

Sl. No.	Substrate	Product	Reaction time (hr)	*Yield (%)	M.P. (°C) Obs (lit)	R$_f$**
1.			4	85	73 (73)	0.75
2.			6	80	120 (128)	0.63
3.			6	75	139 (136)	0.75
4.			8	78	92 (98)	0.70
5.			4	72	Liquids***	0.70
6.			8	82	62 (65)	0.62
7.			8	80	83 (82)	0.82

8.			5	89	Liquids***	0.65
9.			6	88	46 (48)	0.78

Preparation & Purification of chalcones and related enones

1. 1,3-diphenylprop-2-en-1-one :

A solution of 11g of sodium hydroxide in 100 mL of water and 61 mL of rectified spirit was placed in a 250 mL bolt-head flask provided with a mechanical stirrer. The flask was immersed in a bath of crushed ice and 26g (0.21 mol) of freshly distilled acetophenone was added to it and stirred, and then to it 23g (22mL, 0.21 mol) of pure benzaldehyde was added. The temperature was kept at about 25^0C and vigorous stirring was continued until the mixture was so thick that stirring was no longer effective (2.5 hrs). The reaction mixture was kept in refrigerator overnight. The product so formed was filtered with suction on a Buchner funnel and washed with cold water untill the washing was neutral to litmus, and then with ice cold rectified spirit. The crude product (chalcone) was dried in air and recrystallized from rectified spirit. The melting point was found to be 55^0C (lit. $56\text{-}57^0$C).

2. 1-phenyl-3-($4^{/}$-methoxy)phenylprop-2-en-1-one :

It was prepared according to the procedure mentioned in the preparation of compound 1 by taking 4-methoxybenzaldehyde (anisaldehyde) instead of benzaldehyde. The melting point was found to be 98^0C (lit. 102^0C).

3. 1-phenyl-3-($4^{/}$-chloro)phenylprop-2-en-1-one :

It was prepared according to the procedure mentioned in the preparation of compound 1 by taking 4-chlorobenzaldehyde instead of benzaldehyde. The melting point was found to be 112^0C (lit. $114\text{-}116^0$C).

4. 1-phenyl-3-($4^{/}$-ethoxy)phenylprop-2-en-1-one :

It was prepared according to the procedure mentioned in the preparation of compound 1 by taking 4-ethoxybenzaldehyde instead of benzaldehyde. The melting point was found to be 77^0C (lit. 75^0C).

5. 1-phenylbut-2-en-1-one :

It was prepared according to the procedure mentioned in the preparation of compound 1 by taking acetaldehyde instead of benzaldehyde. The melting point was found to be 98^0C (lit. 102^0C).

6. 4-phenylbut-3-en-1-one :

20.2 mL (0.4 mol) of pure benzaldehyde and 40 mL (1.1 mol) of pure acetone were placed in 250 mL flask equipped with a mechanical stirrer. The reaction vessel was then immersed in a bath of cold water and to it 5 mL of 10% sodium hydroxide solution was added slowly (during 30 minutes) keeping the temperature between $25\text{-}30^0$C. The mixture aws stirred at room temperature for further two hours. The mixture was then rendered just acidic to litmus by addition of dilute hydrochloric acid. The content was transferred to a separatory funnel and the yellow organic layer was removed. The remaining aqueous layer was extracted with 10 mL of toluene and the extract was then added to the organic layer. The mixed extract was then washed with 10 mL of water and dried with a little magnesium sulphate. The toluene was removed by distillation at atmospheric pressure and the residue was distilled under reduced pressure. On cooling, the product (4-phenylbut-3-en-1-one) solidifies. Pure product was obtained by recrystallization from light petroleum (40-60^0C) and the melting point was found to be 43^0C(lit. 42^0C).

7. 4-($4^{/}$-hydroxy)phenylbut-3-en-2-one :

It was prepared according to the procedure mentioned in the preparation of compound 6 by taking 4-hydroxybenzaldehyde instead of benzaldehyde. The melting point was found to be 88^0C (lit. 90^0C).

8. Cyclohex-2-en-1-one :

It was obtained from E-merk (India) Ltd. and was used as obtained.

9. Cinnamic acid :

It was obtained from E-merk (India) Ltd. and was used as obtained.

SPECTRAL STUDIES OF REDUCED PRODUCTS

1) 1,3-diphenylpropan-1-one :

Found : C, 85.75; H, 6.71; Calc. C, 85.71; H, 6.66
IR: 1700 (ketonic C=O),

2) 1-phenyl-3-($4^{/}$-methoxy)phenylpropan-1-one :

Found : C, 80.05; H, 6.69; Calc. C, 80.00; H, 6.66,
IR: 1695 (ketonic C=O), 1260 (C-O-C str.)

3) 1-phenyl-3-($4^{/}$-chloro)phenylpropan-1-one :

Found : C, 73.60; H, 5.29; Calc. C, 73.61; H, 5.31,
IR: 1692 (ketonic C=O)

4) 1-phenyl-3-($4^{/}$-ethoxy)phenylpropan-1-one :

Found : C, 81.45; H, 5.62; Calc. C, 81.60; H, 5.60,
IR: 1698 (ketonic C=O), 1262 (C-O-C str.)

5) 1-phenylbutan-1-one :

This compound was converted to its 2,4-dinitrophenylhydrazone derivative and melting point of the derivative was found to be 192^0C (lit. 190^0C). The spectral data were found to be as follows :
Found : C, 58.59; H, 4.91; N,16.98; Calc. C, 58.53; H, 4.87,
N, 17.07
IR: 1620 (-NO_2 str.), 1655 (C=N str.)

6) 4-phenylbutan-2-one :

Found : C, 81.55; H, 5.63; Calc. C, 81.60; H, 5.60,
IR: 1715 (ketonic C=O)

7) 4-($4^{/}$-hydroxy)phenylbutan-2-one :

Found : C, 80.00; H, 5.43; Calc. C, 79.68; H, 5.46,
IR: 1717 (ketonic C=O), 3620 (O-H str.)

8) Cyclohexanone :

This compound was converted to its 2,4-dinitrophenylhydrazone derivative and melting point of the derivative was found to be 160^0C (lit. 162^0C). The spectral data were found to be as follows :
Found : C, 52.01; H, 4.97; N,20.86; Calc. C, 51.79; H, 5.03, N, 20.14
IR: 1627 (-NO_2 str.), 1642 (C=N str.)

7) 3-phenylpropanoic acid (Dihydrocinnamic acid) :

Found : C, 69.60; H, 7.22; Calc. C, 69.56; H, 7.24,
IR: 1710 (carboxylic acid C=O), 2920 (O-H str., broad)

III. CONCLUSION

BER-Ni$_2$B system is successfully used in carrying out "Solid Phase" reduction of olefinic bond of chalcones and related enones. Although several attempts were earlier made to reduce the double bond cleanly, none of the methods tried so far has been found satisfactory in terms of simplicity of the procedure and ease of recovery of products. But this study establishes the simple method for reduction of olefinic bond of chalcones and related enones in high yield with ease of recovery of product.

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