Selective reduction of carbon–carbon double bonds of aryl substituted chalcones with $Zn/CH_3COONH_4/C_2H_5OH/H_2O$

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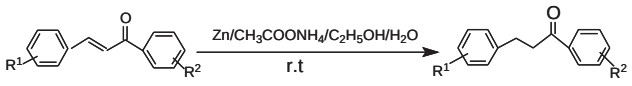
In this paper, 12 aryl substituted chalcones are easily reduced to the corresponding saturated carbonyl compounds using $Zn/CH_3COONH_4/C_2H_5OH/H_2O$ under mild condition with excellent yields for the first time.

Keywords: selective reduction, carbon-carbon double bonds, zinc powder, ammonium acetate, aryl substituted chalcone

Selective reduction of carbon–carbon double bonds of α,β-unsaturated carbonyl compounds has always been a challenging problem in organic synthesis. It has been thoroughly exploited and continues to attract attention. Of the reductive systems described in the literature, transition metal such as Pd, Rh, Pt, Ni, Cu, Ir, Co and their complexes are usually utilised as catalysts,[1-3] Yeast species have also been developed to catalyse selective reduction of α,β-unsaturated carbonyl compounds.[4-6] Hydrides of Sn, Se, Te, B[7-11] and sodium dithionite[12-15] have good effect as reductants. Although these systems have their own merits, they often have some drawbacks: the use of a catalyst to enhance the selectivity and efficacy of most of these systems is indispensable, the preparation of catalysts is not easy, catalysts and reductants are not inexpensive, reaction conditions are not mild, operation is not convenient, reaction time is not short.

Aryl substituted chalcones are typical α,β-unsaturated carbonyl compound. Systems reported on the selective reduction of carbon–carbon double bonds of them are available.[16-20] They have the shortcomings as well as the systems reviewed above. In this paper, $Zn/CH_3COONH_4/C_2H_5OH/H_2O$ is reported as a new, simple selective reduction system. 12 aryl substituted chalcones are easily reduced selectively to the corresponding saturated carbonyl compounds with this system at room temperature (Scheme 1, Table 1). Compared with all the above systems, the merits of the system lie in accessible reagents, 100% selectivity (proved by GLC), mild reaction conditions, easy work- up, short reaction time, excellent yields and environmental acceptability.

In conclusion, we have developed a simple, novel, highly efficient and economical method for selective reduction of carbon–carbon double bonds of aryl substituted chalcones. We believe that the present method is an important addition to existing methods of selective reduction of α,β-unsaturated carbonyl compounds. Further investigation is now in progress.



1 2

a: R^1=H, R^2=H **b:** R^1=H, R^2=p-OCH_3
c: R^1=o-Br, R^2=p-OCH_3 **d:** R^1=p-OCH_3, R^2=H
e: R^1=p-F, R^2=H **f:** R^1=H, R^2=p-Cl
g: R^1=p-CH_3, R^2=H **h:** R^1=p-Cl, R^2=p-OCH_3
i: R^1=p-Cl , R^2=H **j:** R^1=p-OCH_3, R^2=p-Cl
k: R^1=p-CH_3, R^2=p-OCH_3 **l:** R^1=Cl, R^2=Cl

Scheme 1

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Table 1 Selective reduction of carbon–carbon double bonds of aryl substituted chalcones with $Zn/CH_3COONH_4/C_2H_5OH/H_2O$

Product	Reaction time	Yield/%	M.p/°C
2a	90min	90%	68–69.5
2b	90min	92%	95–97
2c	75min	94%	60–61
2d	105min	88%	64–65
2e	75min	92%	59–60
2f	75min	96%	75–76
2g	105min	88%	37.5–38
2h	75min	93%	68–70
2i	75min	95%	53–54
2j	75min	94%	59.5–61.5
2k	90min	91%	63–65
2l	75min	92%	82–83

Experimental

Melting points were determined on a Kolfler micro melting point apparatus without correction. IR spectra were recorded on a FTS-40 spectrophotometer in KBr. ^{1}H NMR spectra were measured with a Bruker DPX-400 instrument for $CDCl_3$ solution using TMS as internal standard. MS spectra were done using an Agilent spectrometer. Elemental analyses were performed on an Elementar VarioEL instrument.

Typical procedure: A 0.01M solution of 3-phenyl-1-(4-chlorphenyl)-1-propenone(1f) in 95% ethanol (50ml) was added to water (8ml) containing 3.9g ammonium acetate (50mmol) at room temperature and stirred vigorously with 0.273g zinc powder (3.75mmol, 'AnalaR') added in five equal portions at intervals of 15min. Stirring was continued for further 15min. (monitored by TLC). The suspended material was removed by filtration and washed with ethanol and the filtrate was evaporated under reduced pressure nearly to dryness then ice-cold water was added to the residual material. After filtration, the crude product was recrystallised from 95%ethanol, yield: 96%.

Compound **2a:** White tabular. MS (*m/z*): 210(M^+), 105(100), 91, 77, 51. IR (KBr) ν_{max}: 3062, 3026, 2923, 2865, 1682, 1596, 1581, 1495(cm^{-1}). ^{1}H NMR ($CDCl_3$) δ(ppm): 3.05–3.09 (t, 2H, CH_2), 3.29–3.33 (t, 2H, CH_2), 7.18–7.98 (m, 10H, Ar-H). Anal. calcd. for $C_{15}H_{14}O$: C, 85.57; H, 6.72. Found: C, 85.32; H, 6.75.

Compound **2b:** White tabular. MS (*m/z*): 240(M^+), 135(100), 107, 92, 77. IR (KBr) ν_{max}: 3063, 3027, 2975, 2935, 2843, 1671, 1603, 1577, 1508(cm^{-1}). ^{1}H NMR ($CDCl_3$) δ(ppm): 3.04–3.08 (t, 2H, CH_2), 3.23–3.27 (t, 2H, CH_2), 3.86 (s, 3H, CH_3), 6.91–7.97 (m, 9H, Ar-H). Anal. calcd. for $C_{16}H_{16}O_2$: C, 79.96; H, 6.72. Found: C, 79.85; H, 6.78.

Compound **2c:** White stick. MS (*m/z*): 239, 135(100), 107, 92, 77. IR (KBr) ν_{max}: 3080, 3057, 2972, 2938, 2841, 1674, 1597, 1507, 1466(cm^{-1}). ^{1}H NMR ($CDCl_3$) δ(ppm): 3.15–3.19 (t, 2H, CH_2), 3.24–3.28 (t, 2H, CH_2), 3.86 (s, 3H, CH_3), 6.91–7.98 (m, 8H, Ar-H). Anal. calcd. for $C_{16}H_{15}BrO$: C, 60.19; H, 4.74. Found: C, 60.24; H, 4.62.

Compound **2d:** White tabular. Ms (*m/z*): 240(M^+), 121(100), 135, 105, 91, 77. IR (KBr) ν_{max}:3000, 2960, 2934, 2837, 1681, 1609, 1597, 1581(cm^{-1}). ^{1}H NMR ($CDCl_3$) δ(ppm): 3.00–3.03 (t, 2H, CH_2), 3.25–3.29 (t, 2H, CH_2). 3.79 (s, 3H, CH_3), 6.82–7.97 (m, 9H, Ar-H). Anal. calcd. for $C_{16}H_{16}O_2$: 79.96; H, 6.72. Found: C, 80.12; H, 6.70.

Compound **2e:** White tabular. MS (*m/z*): 228(M^+), 105(100), 77, 51. IR(KBr) ν_{max}: 3054, 3040, 2936, 2870, 1683, 1596, 1579, 1510 (cm^{-1}). ^{1}H NMR ($CDCl_3$) δ(ppm): 3.03–3.07 (t, 2H, CH_2), 3.26–3.30

(t, 2H, CH_2), 6.95–7.96 (m, 9H, Ar-H). Anal. calcd. for $C_{15}H_{13}FO$: C, 78.91; H, 5.74. Found: C, 79.10; H, 5.70.

Compound **2f:** White tabular. MS (*m/z*): 244(M^+), 139(100), 111, 91. IR (KBr) ν_{max}: 3060, 3027, 2951, 2863, 1683, 1604, 1587, 1571(cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 3.05–3.08 (t, 2H, CH_2), 3.25–3.29 (t, 2H, CH_2), 7.19–7.91 (m, 9H, Ar-H). Anal. calcd. for $C_{15}H_{13}ClO$: C, 73.60; H, 5.36. Found: C, 73.10; H, 5.40.

Compound **2g:** White tabular. MS (*m/z*): 224(M^+), 209, 119, 105(100), 91, 77. IR(KBr) ν_{max}: 3051, 2945, 2920, 2862, 1684, 1645, 1595, 1579(cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 2.32 (s, 3H, CH_3), 3.01–3.05 (t, 2H, CH_2), 3.25–3.29 (t, 2H, CH_2), 7.09–7.97 (m, 9H,Ar-H). Anal. calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.20. Found: C, 85.60; H, 7.15.

Compound **2h:** White tabular. MS (*m/z*): 274(M^+), 135(100), 107, 92, 77. IR (KBr) ν_{max}: 3019, 2970, 2928, 2843, 1680, 1604, 1576, 1512 (cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 2.99–3.03 (t, 2H, CH_2), 3.19–3.22 (t, 2H, CH_2), 3.85 (s, 3H, CH_3), 6.90–7.92 (m, 8H, Ar-H). Anal. calcd. for $C_{16}H_{15}ClO_2$: C, 69.93; H, 5.51. Found: C, 69.60; H, 5.45.

Compound **2i:** White stick. MS (*m/z*): 244(M^+), 125, 105(100), 77, 51. IR (KBr) ν_{max}: 3034, 2918, 2882, 1670, 1596, 1580, 1493 (cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 3.01–3.05 (t , 2H, CH_2), 3.25–3.28 (t, 2H, CH_2), 7.15–7.95 (m, 9H, Ar-H). Anal. calcd. for $C_{15}H_{13}ClO$: C, 73.60; H 5.36. Found: C, 73.71; H, 5.44.

Compound **2j:** White stick. MS (*m/z*): 274(M^+), 139, 121(100), 108, 91, 77. IR (KBr) ν_{max}: 3003, 2964, 2938, 2838, 1677, 1611, 1588, 1571(cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 2.98–3.02 (t, 2H, CH_2), 3.21–3.25 (t, 2H, CH_2), 3.79 (s, 3H, CH_3), 6.83–7.89 (m, 8H Ar-H). Anal. calcd. for $C_{16}H_{15}ClO_2$: C, 69.93; H, 5.51. Found: C, 69.71; H, 5.48.

Compound **2k:** White needles. MS (*m/z*): 254(M^+), 135(100), 118, 105, 92, 77. IR (KBr) ν_{max}: 3053, 2966, 2916, 2843, 1671, 1606, 1579, 1510(cm^{-1}). H NMR ($CDCl_3$) δ(ppm): 2.32 (s, 3H, CH_3), 2.99–3.03 (t, 2H, CH_2), 3.20–3.24 (t, 2H, CH_2), 3.86(s, 3H, CH_3), 6.91–7.95 (m, 8H, Ar-H). Anal. calcd. for $C_{17}H_{18}O_2$: C, 80.27; H, 7.14. Found: C, 80.35; H, 7.22.

Compound **2l:** White stick. MS (*m/z*): 278(M^+), 243, 139(100), 125, 111, 75. IR (KBr) ν_{max}: 3026, 2949, 2873, 1683, 1589, 1573, 1491(cm^{-1}). ^1H NMR ($CDCl_3$) δ(ppm): 3.01–3.05 (t, 2H, CH_2), 3.22–3.26 (t, 2H, CH_2), 7.16–7.89 (m, 8H, Ar-H). Anal. calcd. for $C_{15}H_{12}Cl_2O$: C, 64.52; H, 4.34. Found: C, 64.47; H, 4.40.

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