SHORT PAPER

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Facile transfer hydrogenation of chromones†

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Refluxing a solution of chromones in methanol containing ammonium formate and Pd–C leads to facile hydrogenation to chromanones.

Keywords: chromones, transfer hydrogenation, chromanones

Catalytic transfer hydrogenation process provides an efficient and viable alternative to the conventional hydrogenation procedure involving the use of hazardous hydrogen gas.[1] The facile reduction of a variety of olefinic substrates and functional groups attests to the versatility of this procedure. Ammonium formate has often been the hydrogen source of choice due to its efficiency and convenience.[2] In connection with certain investigations we needed a simple and efficient method for the reduction of chromones to chromanones. Attempted reduction of chromones using hydride donors such as $NaBH_4$[3] or hydrogenation using noble metal catalysts[4] has been reported to lead to complex mixtures from over-reduction. In a report involving the use of DIBAL-H for the reduction of isoflavones, a single example of reduction of a chromone to chromanone in moderate yield has been cited.[5] In view of such discouraging reports, we decided to try the transfer hydrogenation protocol employing ammonium formate and Pd–C and report here the successful reduction of a variety of chromones to chromanones in excellent yield as shown in Table 1.

The results with a variety of chromones as shown in Table 1 reveals the high efficiency of this methodology. The other points to be noted are the stability of acid-sensitive functionalities, the elimination of halogen attached to the aromatic ring[6] (entry 9) and the cleavage of benzylic C-O bond[7] (entry 7). Although aryl ketones have been reported to be reduced to the alcohols by a combination of ammonium formate and Raney nickel in methanol,[8] under the present conditions the carbonyl group remained intact.

In summary, the transfer hydrogenation protocol involving ammonium formate and Pd–C in methanol is an excellent method for the reduction of chromones to chromanones in high yield and supplements the growing list of applications to the reduction of various olefins and functional groups. The inexpensive nature of the reagents complements the operational convenience.

Experimental

General: Melting points were taken on a Kofler hot stage apparatus and are uncorrected. Solid samples were crystallised and liquids were subjected to preparative layer chromatography to obtain analytical samples. IR spectra are for chloroform solutions and NMR spectra for CCl_4 solutions at 60 MHz unless otherwise stated.

Representative procedure for hydrogenation: A solution of the chromone (**1**, 160 mg, I mmol) and ammonium formate (190 mg, 3 mmol) in methanol (5 ml) containing Pd–C (10%, 50 mg) was refluxed for 3 h. The catalyst was filtered and the residue after removal of methanol was extracted with ether. The ether extract was washed with water and dried over anydrous sodium sulfate. Removal of ether afforded the chromanone (**1a**) in 93% yield, pure for all practical purposes and with spectral properties identical to an authentic sample.

Chromones (**1**[9], **2**[10], **3**[9], **4**[11], **5**[12], **6**[13], **7**[14]) and chromanones (**1a**[9]) and (**3a**[9]) are known compounds.

Preparation of chromone (**8**): To an ice-cooled, stirred slurry of sodium hydride (2.2 g, 50% dispersion in oil) in anhydrous ether (15 ml) under nitrogen, a mixture of 2-hydroxy-4-methyl acetophenone (2.9 g, 19 mmol) and diethyl oxalate (5.6 g, 38 mmol) was added slowly and the reaction mixture was left overnight. It was then poured into ice water and acidified with cold dilute hydrochloric acid (5N) and extracted with ether. The ether extract was washed with water and concentrated. The residue was mixed with dilute hydrochloric acid (5N, 20 ml) and stirred for 10–12 h. It was the extracted with ether, dried over sodium sulfate and concentrated to afford the chromone (**8**) as a colourless solid, 2.9g (64%), crystallised from ether – petroleum ether, m.p. 55–57°C; IR 1749, 1651 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.46 (t, *J* 6Hz, 3H), 2.61 (s, 3H), 4.52 (q, *J* 6 Hz, 2H), 7.1 (s, 1H), 7.3 (d, *J* 8.2 Hz, 1H), 7.45 (s, 1H), 8.1 (d, *J* 8.1 Hz, 1 H). Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.24; H, 5.17. Found: C, 66.94; H, 4.93.

Preparation of chromone (**9**): A mixture of 6-chloro chromone – 3-carboxaldehyde[15] (380 mg), ethylene glycol (10 ml) and toluene-*p*-sulfonic acid (15 mg) in toluene (20 ml) was refluxed for 7h using a Dean–Stark water separator. It was the cooled, washed with saturated sodium bicarbonate solution, water and solvent removed. The residue was subjected to column chromatography over silica gel. Elution with ethyl acetate – petroleum ether furnished the acetal (**9**) as a colourless solid, 400 mg (88%), m.p. 130–132°C, IR 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.98 (s, 4H), 6.0 (s, 1H), 7.5 (s, 1H), 7.58 (d, *J* 7.9 Hz, 1H), 8.10 (s,1H), 8.16 (d, *J* 8.0 Hz, 1H). Anal. Calcd. for $C_{12}H_9O_4Cl$: C, 57.02; H, 3.56. Found: C, 57.13; H, 3.44.

Chromanone (**2a**): IR 1689 cm^{-1}; ^1H NMR δ 1.68 (d, *J* 6.1 Hz, 3H), 2.48 (s, 3H), 2.67 (d, *J* 4.9 Hz, 2H), 4.23–4.92 (m, 1H), 6.8 (s,1H), 6.86 (d, *J* 7.8 Hz, 1H), 7.78 (d, *J* 7.8 Hz, 1H). Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.0;H, 6.81. Found: C, 75.18; H, 6.42.

Chromanone (**4a**): IR 1684 cm^{-1}; ^1H NMR δ 1.07, 1.17 (2d, *J* 6.0 Hz, 3H), 1.25, 1.48 (2d, *J* 6.0 Hz, 3H), 2.34 (s, 3H), 2.39–2.45 (m, 1H), 3.86–4.60 (m, 1H), 6.63, 6.69 (2s, 1H), 6.98, 7.03 (2d, *J* 8.0 Hz, 1H), 7.64,7.91 (2d, *J* 8.0 Hz, 1H). Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.78; H, 7.36. Found: C, 75.34; H, 7.0.

Chromanone (**5a**): IR 1686 cm^{-1}; ^1H NMR δ 2.46 (s, 3H), 3.49 (s, 3H), 3.68 (t, *J* 6.8 Hz, 1H), 4.31 (d, *J* 6.8 Hz, 2H), 6.60 (s, 1H), 6.74 (d, *J* 8.1 Hz, 1H), 7.70 (d, *J* 8.0 Hz, 1H). Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.24; H, 5.85.

Chromanone (**6a**): IR 1685 cm^{-1}; ^1H NMR δ 1.46, 1.62 (2d, *J* 6.0 Hz, 3H), 3.49, 3.82 (2s, 3H), 3.51–3.73 (m, 1H), 4.2–4.83 (m, 1H), 6.8–7.9 (m, 4H). Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found: C, 68.54; H, 5.92.

The phenol (**7a**): ^1H NMR δ 2.43 (s, 3H), 2.87–3.29 (m, 4H), 6.75 (d, *J* 8.2 Hz, 1H), 6.82 (s, 1H,), 7.61 (d, *J* 8.1 Hz, 1H), 7.36 (br s, 5H). Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.67. Found; C, 80.34; H, 6.23.

Chromanone (**8a**): m.p. 95–97°C; IR 1753, 1689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.46 (s, 3H), 3.04 (q, *J* 8.4 Hz, 2H), 3.92 (s, 3H), 5.11 (t, *J* 8.4Hz, 1H), 6.88 (d, *J* 8.0 Hz, 1H), 6.93 (s, 1H), 7.80 (d, J 8.0 Hz, 1H). Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.45. Found: C, 65.85; H, 5.03.

Chromanone (**9a**): IR 1683 cm^{-1}; ^1H NMR δ 3.74 (s, 4H), 3.96 (d, J 7.2Hz, 1H), 4.43–4.94 (m, 2H), 6.90–7.88 (m, 4H). Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H,5.45. Found; C, 65.25; H, 5.32.

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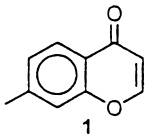
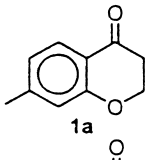
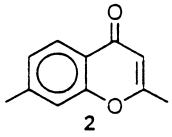
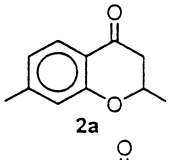
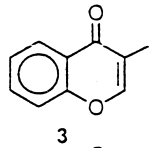
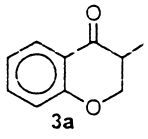
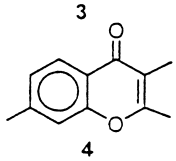
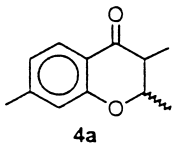
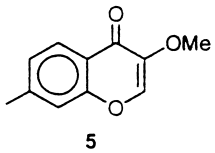
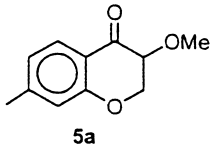
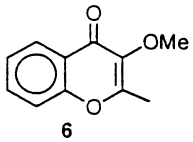
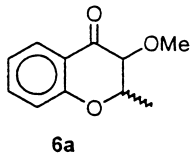
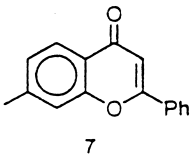
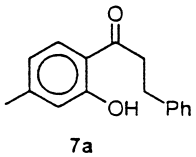
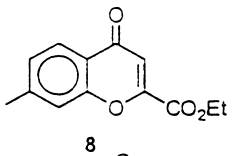
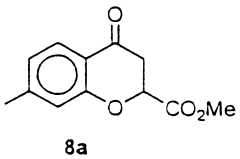
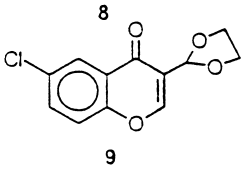
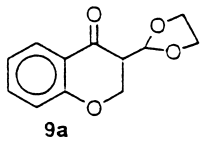
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1

Substrate	Time/h	Product	Yield/%
 1	3	 1a	93
 2	5	 2a	94
 3	5	 3a	93
 4	10	 4a	70[1,2]
 5	2	 5a	94
 6	7	 6a	94[1]
 7	2	 7a	95
 8	5	 8a	95[3]
 9	6	 9a	94

[1]Mixture of *cis* and *trans* isomers, [2]Ammonium formate (5 mmol) and Pd–C (150 mg) were used and some starting material was recovered (*ca* 15%). [3]*Trans* esterification took place.

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References

1 R.A.W. Johnstone and A.H. Wilby, *Chem.Rev*. 1985, **85**, 129.
2 (a) S. Ram and E.E. Ehrenkaufer, *Synthesis*, 1988, 91; (b) B.C. Ranu, A.K. Sarkar, S.K. Guchhhait and K. Ghosh, *J. Ind. Chem. Soc*. 1998, **75**, 690 and references cited therein.
3 K. Yamada, *Bull. Chem. Soc. Jpn*., 1962, 1329.
4 R.C. Elderfield (ed.), *Heterocyclic Compounds,* Vol. 2, John Wiley & Sons, N.Y. 1951, Chap. 8, pp. 257.
5 S. Antus, A. Gottsegen and M. Nogradi, *Synthesis*, 1981, 574.
6 N.A. Cortese and R.F. Heck, *J. Org. Chem*., 1977, **42**, 3491.
7 T. Bieg and W. Szeja, *Synthesis*, 1985, 76.
8 F.E. Chen, H. Zhang, W. Yuan, and W.W. Zhang, *Synth. Commun*. 1991, **21**, 107.
9 *Dictionary of Organic Compounds*, Vol. 4, Eyre & Spottiswoode Publishers Ltd. London 1965, p. 2157.
10 B.K. Ganguly and P. Bagchi, *J. Org. Chem*., 1956, **21**, 1415.
11 A. Nath, A. Ghosh and R.V. Venkateswaran, *J. Org. Chem.,* 1992, **57**, 1467.
12 J. Mal and R.V. Venkateswaran, *J. Org. Chem.,* 1998, **63**, 3855.
13 A. Nath, J. Mal and R.V. Venkateswaran, *J. Org. Chem.,* 1996, **61**, 4391.
14 *Dictionary of Organic Compounds*, Vol. 4, Eyre & Spottiswoode Publishers Ltd. London, 1965, p. 2196.
15 A. Nohara, T. Umetani and Y. Sanno, *Tetrahedron Lett.,* 1973, 1995.