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Palladium Assisted Transfer Hydrogenation of Cyclic α,ß-Unsaturated Ketones by Ammonium Formate

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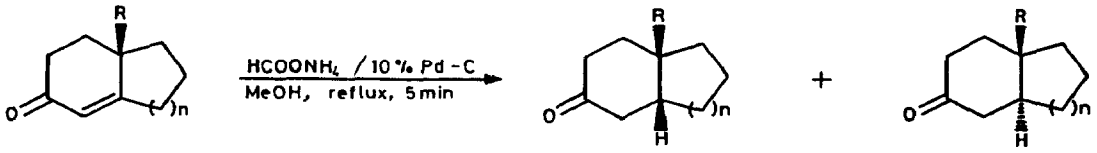
Abstract: α,ß-Unsaturated ketones can be hydrogenated conveniently under catalytic transfer hydrogenation conditions using ammonium formate / Pd-C (10%) in refluxing methanol.

Key Words: Transfer hydrogenation, ammonium formate, α,ß-unsaturated ketones

Alternative methods to conventional hydrogenation procedures such as heterogeneous and homogeneous catalytic transfer hydrogenation[1,2] have found widespread use in the reduction of a variety of functional groups[3]. These methods offer greater experimental convenience with most reactions complete within 1hr and use of elaborate apparatus can be avoided. Ammonium formate / Pd-C system is a versatile reagent for rapid and selective transfer hydrogenolysis[4]. Since the publication of a review article on the utility of ammonium formate in organic synthesis[4], this reagent has been used for reduction of the heterocyclic ring in quinolines[5], reduction of aryl ketones to alcohols[6], regioselective hydrogenolysis of benzyl glycosides[7,8], hydrogenolysis of dibenzyl uracils[9], reduction of diaryl oximes[10], reduction of α,ß-unsaturated nitroalkenes[11], reduction of hydroxy flavones[12] and isoflavones[13], reductive cyclisation of 2-nitro ß-styrenes to indoles[14], deoxygenation of heteroaromatic N-oxides[15], dechlorination of mono and polychlorinated aryl compounds[16] and reduction of nitro compounds to the corresponding amines[17]. However, to the best of our knowledge, hydrogenation of α,ß-unsaturated carbonyl compounds with this reagent and the stereoselectivity involved in such reductions are not known.

We wish to report that ammonium formate / Pd-C (10%) readily reduces cyclic α,ß-unsaturated ketones to the corresponding ketones under reflux in methanol in good yields within 5 min. We have chosen bicyclo[4.3.0]noneneones (**1a**, **1b**) and bicyclo[4.4.0]decaleneones (**1c** - **1e**) as substrates for the present study because of their inherent importance in steroid and terpenoid fields. Our results are summarised in the Table. It is noteworthy that, for some substrates, the observed stereoselectivity (entry 1, 3, 5) is different from that in conventional hydrogenation. For example, in the reduction of bicyclo[4.4.0]dec-1(2)-ene-3-one (**1c**) to cis-and trans-bicyclo[4.4.0]decan-3-ones (**2c**, **3c**) and 1-ethoxycarbonyl bicyclo[4.4.0]deca-5(6)-ene-4-one (**1e**) to 1-ethoxycarbonyl bicyclo[4.4.0]decan-4-ones (**2e**, **3e**), there is a cross-over in stereoselectivty (entry 3 and 5, Table). This is another indication of

Table: Transfer Hydrogenation of Cyclic α,β-Unsaturated Ketones



1 2 (cis) 3 (trans)

1a: n = 1, R = H; 2a: n = 1, R = H; 3a: n = 1, R = H
1b: n = 1, R = Me; 2b: n = 1, R = Me; 3b: n = 1, R = Me
1c: n = 2, R = H; 2c: n = 2, R = H; 3c: n = 2, R = H
1d: n = 2, R = Me; 2d: n = 2, R = Me; 3d: n = 2, R = Me
1e: n = 2, R = COOEt; 2e: n = 2, R = COOEt; 3e: n = 2, R = COOEt

Entry	Starting enone	Ratio[a,b] (cis:trans)		Yield (%)
1	1a	90:10	(100:00; 18)	85
2	1b	100:00	(100:00; 19)	80
3	1c	76:24	(43:57; 20)	92
4	1d	100:00	(100:00; 21)	86
5	1e	77:23	(05:>95; 22)[c]	76

a. Ratios in brackets refer to reported stereoselectivity under conventional hydrogenation conditions with solvent ethanol and a literature reference
b. Ratios were determined by integration of charcteristic peaks in ^1H NMR spectra (270MHz, $CDCl_3$) or from gas liquid chromotography results. Individual isomers were separated and characterised (ref. 23).
c. The observed stereoselectivity by conventional hydrogenation (H_2, 10% Pd-C, rt, 2-3 atm) using EtOAc as solvent was, cis : trans ratio = 12:88.

the different mechanisms in transfer and standard hydrogenation[2]. Reductions were very slow or did not take place if the reactions were attempted at room temperature or even at 50°C. Reduction of 1-ethoxycarbonyl bicyclo[4.3.0]non-5(6)-ene-4-one resulted in a complex mixture of products.

Experimental: A mixture of α,β-unsaturated ketone (1 mmol), $HCOONH_4$ (5 mmol) and 10% Pd-C (5% of the unsaturated ketone by weight) in redistilled methanol (20 ml) was refluxed for 5 minutes by which time reduction was complete (tlc). The catalyst was removed by filtration through a Celite pad and the product was isolated by standard work up.

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1955, 77, 48.
23. ^{1}H NMR and ^{13}C NMR values ($CDCl_3$, ppm) of characteristic resonance and lit. ref. no., if reporeted: **2a**: 39.10 (C1), 37.90 (C6) (ref. 24); **3a**: 47.44 (C1), 40.85 (C6) (ref. 24); **2b**: 1.12 (C1-Me) (ref. 19), 39.81 (C1), 46.41 (C6); **3b**: 0.95 (C1-Me) (ref. 19), 40.40 (C1), 48.33 (C6); **2c**: 38.94 (C1), 35.56 (C6) (ref. 24); **3c**: 43.67 (C1), 42.23 (C6) (ref. 24); **2d**: 1.19 (C1-Me) (ref. 25); 32.6 (C1), 39.1 (C6) (ref. 24); **3d**: 1.03 (C1-Me) (ref. 25), 37.6 (C1), 41.6 (C6) (ref. 24); **2e**: 4.22 (-OCH2-), 39.06 (C1), 47.24 (C6); **3e**: 4.19 (-OCH2-), 59.25 (C1), 40.40 (C6).
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