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Regio- and Stereoselective Hydrogenation of Conjugated Carbonyl Compounds via Palladium Assisted Hydrogen Transfer by Ammonium Formate

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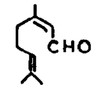
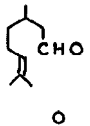
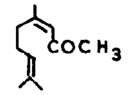
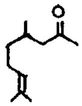
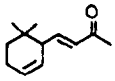
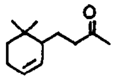
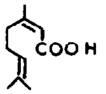
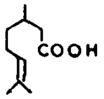
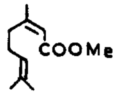
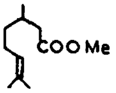
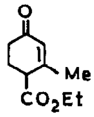
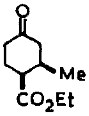
Abstract: Excellent regio- and stereoselectivity has been achieved in the hydrogenation of C=C bond conjugated to carbonyl group in presence of olefin by ammonium formate/Pd-C system.

Selective hydrogenation of C=C bond of conjugated carbonyl compounds in presence of other isolated double bonds is an important as well as a difficult reaction.[1] As hydrogen from gas cylinder is potentially explosive and requires to be used with caution in a special apparatus, search for alternative methods to conventional hydrogenation procedures such as heterogeneous and homogeneous catalytic transfer hydrogenation is still going on.[2] Ammonium formate/Pd-C system is a versatile catalytic hydrogen transfer agent and has been used for the reduction of various functionalities.[3] Surprisingly, this reagent has not been employed for the reduction of carbon-carbon double bond until recently.[4] But no significant effort has yet been made to utilise this potential reagent for the regio- and stereoselective hydrogenation of double bonds excepting Rao's recent report of stereoselective reduction of a few cyclic α,β-unsaturated ketones.[4b] In this letter we wish to disclose that ammonium formate/Pd-C is a very efficient reagent in the selective hydrogenation of C=C bond conjugated to carbonyl group without affecting other isolated double bonds present in the molecule.

The experimental procedure is very simple and straightforward. The conjugated carbonyl compound (1 mmol) was stirred with ammonium formate (6 mmol) and 10% Pd-C (30 mg) in methanol (10 ml) for a certain period of time as required to complete the reaction. The catalyst was filtered through a short plug of silica gel and the product was isolated by usual work up. Representative examples of conjugated aldehyde, ketone, carboxylic acid and ester are found to undergo exclusive hydrogenation at the α,β-unsaturated position leaving the other double bond unaffected (Table 1). Hagemann's ester (entry 6) under such treatment produced exclusively the cis product, the identity of which was established by gc comparison with authentic sample obtained by catalytic hydrogenation.

The reductions are quite fast and the yields are almost quantitative. Cortese and Heck[5] reported similar regioselective hydrogenation of citral and β-ionone using formic acid and trialkyl amine; but these required unusually long reaction time

Table 1: Hydrogenation of Conjugated Carbonyl Compounds with Ammonium Formate/Pd-C.

entry	substrate	temp. (°C)	time(h)	product	yield(%)[a]
1		25	4[b]		92
2		25	2		94
3		25	0.5		94
4		70	3		92
5		25	1		95
6		70	0.5		96

[a] All yields refer to pure isolated products. [b] The reaction is run in petrol (60-80°C).

(citral - 44 h, β-ionone - 20 h). Our present method eliminates this drawback. Moreover, the mild condition, excellent selectivity, quantitative yield, operational simplicity, easy availability and low cost of the reagent make this methodology more useful and practical alternative to usual hydrogenation procedure and other alternative methods.

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References and Notes.

1. Hudlicky, M. 'Reductions in Organic Chemistry', Ellis Horwood Limited : Chichester, England, 1984.
2. (a) Johnstone, R.A.W.; Wilby, A.H.; Entwistle, I.D. Chem. Rev. **1985**, 85, 129. (b) Hudlicky, T.; Zingde, G.S.; Natchus, M.G. Tetrahedron Lett. **1987**, 28, 5287. (c) Cabrera, A.; Alper, H. Tetrahedron Lett. **1992**, 33, 5007. (d) Holleben, M.L. A.v.; Zucolotto, M.; Zini, A.C.; Oliveira, E.R. Tetrahedron **1994**, 50, 973.
3. Ram, S.; Ehrenkaufer, R.E. Synthesis **1988**, 91.
4. (a) Ram, S.; Spicer, L.D. Synth. Commun. **1992**, 22, 2683. (b) Rao, H.S.P.; Reddy, K.S. Tetrahedron Lett. **1994**, 35, 171.
5. Cortese, N.A.; Heck, R.F. J. Org. Chem. **1978**, 43, 3985.

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