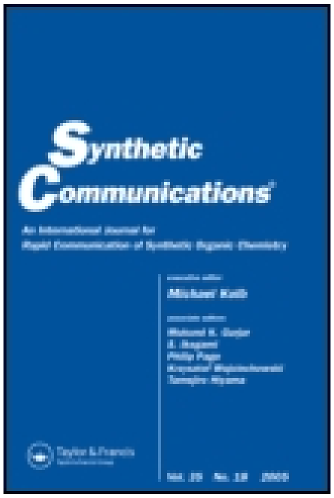
This article was downloaded by: [University of Sussex Library]
On: 19 August 2015, At: 04:43
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: 5 Howick Place, London, SW1P 1WG



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Application of Amberlite IRA-400 (Basic) as a Base in Heck Reaction

S. B. Solabannavar [a] , V. B. Helavi [a] , U. V. Desai [a] & R. B. Mane [a]

[a] Department of Chemistry , Shivaji University , Kolhapur, India

Published online: 17 Aug 2006.

To cite this article: S. B. Solabannavar , V. B. Helavi , U. V. Desai & R. B. Mane (2003) Application of Amberlite IRA-400 (Basic) as a Base in Heck Reaction, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:3, 361-365, DOI: 10.1081/SCC-120015763

To link to this article: http://dx.doi.org/10.1081/SCC-120015763

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 3, pp. 361–365, 2003

Application of Amberlite IRA-400 (Basic) as a Base in Heck Reaction[†]

S. B. Solabannavar, V. B. Helavi, U. V. Desai, and R. B. Mane*

Department of Chemistry, Shivaji University,
Kolhapur, India

ABSTRACT

Amberlite IRA-400 (basic) has been used as a base in the Heck reaction and the generated quarternary ammonium salt might also be assisting in the reaction. The reaction is clean, simple and yields are high. The resin can be regenerated, recycled and the work-up procedure becomes simple compared to other bases used.

Palladium catalyzed olefin arylation/alkenylation developed primarily by Heck,[1] is a well established method for the coupling of activated olefins with aromatic/vinylic halides.[2] A base is generally added to the Heck reaction[3] to regenerate Pd(o) from 'HPdx' by neutralization of Hx.

[†] Dedicated to the memory of Late Dr. Nitiraj R. Mane.

*Correspondence: R. B. Mane, Department of Chemistry, Shivaji University, Kolhapur-416 004, India; E-mail: rbmane@yahoo.co.in.

DOI: 10.1081/SCC-120015763
0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

In the Heck reaction cycle, after the migratory insertion comes the step in which Pd(o) is released by PdH elimination to give alkene.

The termination occurs by nucleophilic attack at Pd, which either by nucleophilic substitution or by reductive elimination of co-ordinated nucleophile leads to the release of Pd(o). If PdH is not scavenged fast by base, the readdition to the double bond may occur.

Trialkyl amines, carbonates, bicarbonates, acetates, potassium phosphate, alkoxides, hydroxides have been used as bases in Heck reaction.[4] We report here the application of amberlite IRA-400 (basic) as a base in the Heck reaction.

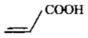
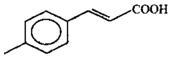
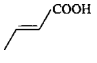
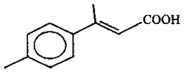
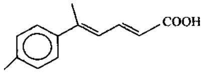
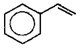
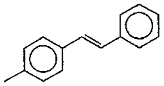
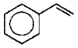
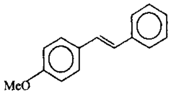
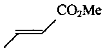
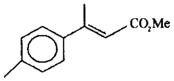
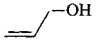
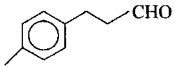
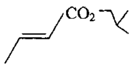
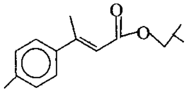
The reactions of aryl halides with olefins using palladium acetate, amberlite IRA-400 (basic) resin in DMF have been carried out in high yields and purity (Table 1). The products at 2, 3 and 6 are important intermediates for the synthesis of natural products prepared earlier by multistep sequences. The Heck reaction with sorbic acid is interesting and yields δ-substitution product. The amberlite resin acts as a base and is converted into the quaternary ammonium iodide which might also be assisting the Heck reaction. There are reports in the literature[4,5] that quaternary ammonium salts can effect the reduction of Pd(II) to Pd(o) and thus stabilize palladium catalyst, leading to acceleration of the Heck reaction. Thus the use of amberlite IRA-400 (basic) serves dual purpose in assisting the Heck reaction.

The reaction is clean, simple and the resin can be regenerated and recycled. The work-up procedure becomes simple compared to other bases used.

GENERAL PROCEDURE

A mixture of palladium acetate (45 mg, 0.2 m mol), aryl halide (*p*-iodotoluene/*p*-iodo anisole, 20 m mol), olefinic compound (25 m mole) and amberlite IRA-400 (basic) 2 g in dry DMF (6 mL) was stirred at 80°C for 2 to 8 h. It was cooled and filtered to remove resin which was washed with ether. The organic layer was diluted with water and extracted with ether. The ether layer was washed with water and dried over anhydrous sodium sulphate. Removal of ether furnished the solid products which were purified by recrystallization using suitable solvent and liquids were purified by passing through chromatography column (silica gel, pet. ether).

Table 1. Heck reaction of *p*-iodo toluene/*p*-iodoanisole.

					Physical constants	
Entry	Olefin	Product	Reaction Time (h)	Yield (%)	Obs. (°C)	Lit. (°C)
1			5	86.4	196–198	198–199[6a]
2			5	79.5	128–130	—
3			8	52	168–170	172[6b]
4			2	92.8	118–120	120[6a]
5			2	90.4	134–136	135–136[6c]
6			5	84.3	275(l)^a	—
7			5	86.5	220–224(l)^a	220–230(1)^a [6a]
8			8	90.0	260(l)^a	—

(l)^{a}Liquid, yields refer to pure isolated products.

Spectral Data for the Unknown Compounds

3-(4-Methyl-phenyl) 2-butenoic acid (2): IR: 1674 cm^{-1}. PMR [$CDCl_3$]; δ 2.35 (3H, s, Ar-CH_3), 2.59 (3H, s, vinylic-CH_3), 6.17 (1H, s, vinylic-H), 7.20 (2H, d, $J = 8$ Hz, Ar-H), 7.41 (2H, d, $J = 8$ Hz, Ar-H). MS (70 eV) m/e 176 (M^+).

Methyl-3-(4-methyl-phenyl crotonate (6): IR: 1716 cm^{-1}. PMR ($CDCl_3$): δ 2.35 (3H, s, Ar-CH_3), 2.56 (3H, s, vinylic-CH_3), 3.74 (3H, s, OCH_3), 6.13 (1H, s, vinylic-H), 7.14 (2H, d, $J = 8$ Hz, Ar-H), 7.39 (2H, d, $J = 8$ Hz, Ar-H). MS (70 eV) m/e 190 (M^+).

Methyl-3-(4-methyl-phenyl) isobutyl crotonate (8): IR: 1713, 1628 cm^{-1}. PMR ($CDCl_3$): δ 0.99 (6H, d, $J = 7$ Hz, gem-dimethyl), 2.00 (1H, m, $J = 7$ Hz, methine-H), 2.38 (3H, s, Ar-CH_3), 2.58 (3H, s, vinylic-CH_3), 3.95 (2H, d, $J = 7$ Hz,–O–$C\underline{H}_2$–), 6.16 (1H, bs, vinylic-H), 7.20 (2H, d, $J = 8$ Hz, Ar-H, ortho to methyl), 7.41 (2H, d, $J = 8$ Hz, Ar-H, meta to methyl). MS (70 eV) m/e 232 (M^+).

REFERENCES

1. (a) Heck, R.F. J. Am. Chem. Soc. **1968**, *90*, 5518; (b) Heck, R.F.; Nolley, J.P. J. Org. Chem. **1972**, *14*, 2320.
2. (a) Heck, R.F. Acc. Chem. Res. **1979**, *12*, 146; (b) Org. React. **1982**, *27*, 345; (c) Daves, G.D.; Hallberg, A. Chem. Rev. **1989**, *89*, 1433; (d) Heck, R.F. In *Comprehensive Organic Synthesis*; Trost, B.M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4; (e) De Meijere, A.; Meyer, F.E. Angew Chem. Int. Ed. Engl. **1994**, *33*, 2379–2411; (f) De Meijere, A.; Braese, S. In *Transition Metal Catalyzed Reactions*; Davies, S.G., Murahashi, S.I., Eds.; Black Well Science: Oxford, 1999; (g) Reetz, M.T. In *Transition Metal Catalyzed Reactions*; Davies, S.G., Murahashi, S.I., Eds.; Black Well Science: Oxford, 1999; (h) Cabri, W.; Candiani, I. Acc. Chem. Res. **1995**, *28*, 2; (i) Jeffery, T. In *Advances in Metal—Organic Chemistry*; Liebeskind, L.S., Ed.; Jai Press Inc.: Green wich, CT, 1996; Vol. 5; (j) Crisp, G.T. Chem. Soc. Rev. **1998**, *27*, 427; (k) Brase, S.; de Meijere, A. In *Metal-Catalyzed Cross-Coupling Reactions*; Deiderich, F., Stang, P.J., Eds.; Wiley–VCH: New York, 1998; (l) Link, J.T.; Overman. In *Metal-Catalyzed Cross-Coupling Reactions*; Deiderich, F., Stang, P.J., Eds.; Wiley–VCH: New York, 1998; (m) Shibasaki, M.; Boden, C.O.J.; Kojima, A. Tetrahedron **1997**, *53*, 7371; (n) Overman, L.E. Pure Appl. Chem. **1994**, *66*,

1423; (o) Gibson, S.E.; Middleton, R.J. Contemp. Org. Synth. **1996**, *3*, 447.

3. Benhaddou, R.; Czernecki, S.; Ville, G.J. Chem. Soc. Commun. **1998**, 247.
4. Beletskaya, Irina P.; Cheprakov, Andrei V. Chem. Rev. **2000**, *100*, 3009–3066.
5. Deshmukh, R.R.; Rajagopal, R.; Srinivasan, K.V. Chem. Commun. **2001**, 1544.
6. (a) *Dictionary of Organic Compounds*, 5th Ed.; Buchingham, J., Macdonald, F., Eds.; Chapman and Hall: London, 1982; (b) Pedneker, P.K.; Chakravarti, K.K.; Paknikar. Ind. J. Chem. **1980**, *19B*, 607; (c) *Dictionary of Organic Compounds*, 4th Ed.; Pollack, J.R.A., Steyens, R., Eds.; Eyre and Spottiswoode (Publishers) Ltd.: London, 1965.

Received in the Netherlands January 14, 2002

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016