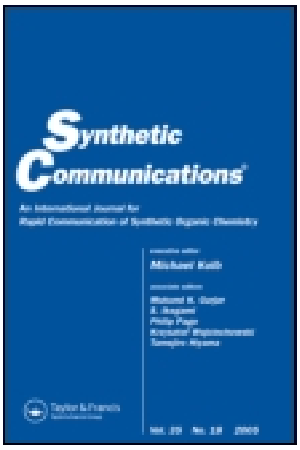
This article was downloaded by: [University of Chicago Library]
On: 27 July 2013, At: 01:58
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

$Mo(CO)_6$ Mediated Selective Reduction of Azides and Nitro Compounds to Amines Under Neutral Conditions

Dr. Suresh Iyer [a] & Girish M. Kulkarni [a]
[a] Organic Chemistry Synthesis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, 411 008, India

Published online: 16 Aug 2006.

To cite this article: Dr. Suresh Iyer & Girish M. Kulkarni (2004) $Mo(CO)_6$ Mediated Selective Reduction of Azides and Nitro Compounds to Amines Under Neutral Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 34:4, 721-725, DOI: 10.1081/SCC-120027720

To link to this article: http://dx.doi.org/10.1081/SCC-120027720

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

SYNTHETIC COMMUNICATIONS®
Vol. 34, No. 4, pp. 721–725, 2004

$Mo(CO)_6$ Mediated Selective Reduction of Azides and Nitro Compounds to Amines Under Neutral Conditions[#]

Suresh Iyer* **and Girish M. Kulkarni**

Organic Chemistry Synthesis Division, National Chemical Laboratory,
Pune, India

ABSTRACT

$Mo(CO)_6$ selectively reduces various azides and nitro compounds to the corresponding amines in refluxing ethanol.

Key Words: $Mo(CO)_6$; Azides; Nitro compounds; Selective reduction; Neutral.

There are several reports on the selective reduction of azides and nitro compounds. Pd/C-$HCOONH_4$, triphenylphosphine in water, boranes, Zn/NH_4Cl, Sm-$AlCl_3 \cdot 6H_2O$, $FeCl_3$/NaI, $FeCl_3$/Zn, LiCl/$NaBH_4$, Sm/TMSCl/

[#] NCL communication no. 6651.

*Correspondence: Dr. Suresh Iyer, Organic Chemistry Synthesis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-411 008, India; Fax: + 91-20-589-3153; E-mail: siyer@dalton.ncl.res.in.

DOI: 10.1081/SCC-120027720
0039-7911 (Print); 1532-2432 (Online)

www.dekker.com

H_2O, Fe/NH_4Cl, $Zn/HCOONH_4$, catalytic transfer hydrogenation, catalytic hydrogenation, Fe porphyrin/$NaBH_4$, Fe Phthalocyanine/$NaBH_4$, In/HCl, transfer hydrogenation catalyzed by metal oxides in i-C_3H_7OH, FeS-NH_4Cl in methanol–water mixture are some of the recent and traditional methods of selective reductions of azides and nitro compounds.[1] Aryl nitro compounds undergo deoxygenation and reduction in the presence of metal carbonyls. Phenyl azide reacts with $Fe_2(CO)_9$ to form aniline and diphenyl urea in acetonitrile/water mixture.[2] The reaction of azides with transition metal complexes in protic solvents has been shown to form various products apart from reduction of the azide.[3] Aryl nitro compounds undergo deoxygenation and formation of nitrene complexes with cyclopentadienyl molybdenum dicarbonyl dimer.[4a,b] We report in this communication the $Mo(CO)_6$ mediated reduction of azides and nitro compounds to amines in ethanol.

Refluxing solutions of the azides and nitro compounds in the presence of stoichiometric quantity of $Mo(CO)_6$ (1 eq.) in ethanol, produces the amines in high yields (80–95%). The results of our experiment is shown in Tables 1 and 2.

Table 1. $Mo(CO)_6$ mediated reduction of azides.[a]

S. No.	Azides	Time, h	Yield %
1	$C_6H_5 \cdot N_3$	2.5	59
2	$4\text{-}CH_3O \cdot C_6H_4 \cdot N_3$	3	84
3	$4\text{-}Cl \cdot C_6H_4 \cdot N_3$	2	88
4	$4\text{-}NO_2 \cdot C_6H_4 \cdot N_3$	6.5	74
5	$2\text{-}COOH \cdot C_6H_4 \cdot N_3$	6.5	96
6	$1\text{-}C_{10}H_7 \cdot N_3$	24	90
7	$C_6H_5 \cdot CH_2 \cdot N_3$	1.5	56
8	$C_6H_5 \cdot CON_3$	6	43
9	$4\text{-}CH_3 \cdot C_6H_4 \cdot SO_2N_3$	24	80
10	$C_6H_5 \cdot CH{=}CH \cdot CH_2 \cdot N_3$	24	nr
11	$C_6H_{11} \cdot N_3$	24	86
12	$2\text{-}NO_2 \cdot C_6H_4 \cdot N_3$	6	45
13	$4\text{-}CH_3O \cdot C_6H_4 \cdot N_3$	4	12[b]
14	$4\text{-}CH_3O \cdot C_6H_4 \cdot N_3$	24	11[c]
15	$4\text{-}CH_3O \cdot C_6H_4 \cdot N_3$	24	14[d]

Note: All products were characterized by IR and ^1H NMR.

[a] Reaction conditions: ArN_3 (1 mmol) : $Mo(CO)_6$ (1 mmol), ethanol (10 mL), reflux.

[b] $Fe(CO)_5$;

[c] $W(CO)_6$;

[d] $Cr(CO)_6$.

Table 2. $Mo(CO)_6$ mediated reduction of aryl nitro compounds.[a]

S. No.	$ArNO_2$	Time, h	Yield, %
1	$4\text{-}CH_3 \cdot C_6H_5 \cdot NO_2$	24	54
2	$4\text{-}Cl \cdot C_6H_5 \cdot NO_2$	24	83
3	$4\text{-}NO_2 \cdot C_6H_4 \cdot CH{=}CH \cdot C_6H_4$	24	84
4	$4\text{-}NO_2 \cdot C_6H_4 \cdot CH{=}CH \cdot COOC_2H_5$	24	17.5
5	$2\text{-}I \cdot C_6H_5 \cdot NO_2$	24	96

Note: All products were characterized by IR and ^1H NMR.

[a] Reaction conditions: $ArNO_2$ (1 mmol) : $Mo(CO)_6$ (1 mmol), ethanol (10 mL), reflux (24 h).

The azides could be selectively reduced in the presence of Cl, COOH, NO_2. Cinnamyl azide could not be reduced under these reaction conditions. Benzoyl azide and 4-toluenesulphonyl azide gave good yields of the reduced amide. The reductions were complete in 1.5–24 h, with longer reaction times for the TsN_3, cyclohexyl and 1-naphthyl azide. Reductions of 4-methoxyphenyl azide in the presence of $Fe(CO)_5$, $W(CO)_6$ and $Cr(CO)_6$ gave low yields of 4-anisidine.

Aryl nitro compounds could be reduced in the presence of stoichiometric $Mo(CO)_6$, in refluxing ethanol. 4-Chloro nitro benzene gave 83% yield of the 4-chloro aniline, while the reduction of 4-nitro toluene was incomplete, giving only 54% yield of 4-toluidine, along with recovered starting material (31%). The reduction of the nitro group was selective in the presence of Cl, COOEt and olefin. 4-Nitro stilbene gave selectively 84% yield of the 4-amino stilbene, while 4-nitro ethyl cinnamate gave very low yields (17.5%) of 4-amino ethyl cinnamate, without reduction of the olefin. 2-Iodo nitro benzene could similarly be selectively reduced to 2-iodo aniline.

The $Mo(CO)_6$ reduction of the aryl azides and nitro compounds probably proceeds by formation of metal nitrenes.[3] Evidence for this is available in the reaction of cyclopentadienyl Mo dicarbonyl dimer with aryl nitro compounds to form Mo nitrene complexes, iron carbonyl reaction with azides and nitro compounds to form iron nitrenes and $W(CO)_5 \cdot THF$ reaction with bulky azides.[4a,b] In the case of the nitro compounds, deoxygenation of the nitro group occurs by carbonylation with metal carbonyl.[5] The oxygen of the NO_2 combines with the metal carbonyl to form CO_2 with formation of metal nitrene, which gets protonolyzed to form the amine. Azides, similarly form metal nitrenes by loss of nitrogen followed by protonolysis. Photochemical reduction by irradiating with a Hg coated lamp gave low yields of the reduction product from both tosylazide and 4-nitrotoluene.

This is a facile, neutral, cleaner reaction condition and catalyst for the selective reduction of azides and nitro compounds to amines and amides compared to the other available reagents and reactions.[1] The yields and selectivity are comparable to the reported methods and the cost of $Mo(CO)_6$ (Aldrich: $52.50 for 10 g, Strem: $40.00 for 25 g) is reasonable for the laboratory use of the reagent.

EXPERIMENTAL PROCEDURE

4-Chlorophenyl azide (0.153 g, 1 mmol) and $Mo(CO)_6$ (0.264 g, 1 mmol) was refluxed in ethanol (15 ml) for 2–24 h and monitored by TLC. After completion, the reaction mixture was concentrated on a rotary evaporator, extracted with ethyl acetate, filtered over celite, concentrated and purified by column chromatography over silica gel (100–200 mesh) to give 4-chloro aniline (0.112 g, 88 %).

ACKNOWLEDGMENTS

We thank the DST for a research grant and GMK thanks CSIR for a SRF.

REFERENCES

1. (a) Amantini, D.; Fringuelli, F.; Pizzo, F.; Vaccaro, L. Org. Prep. Proc. Int. **2002**, *109* (34(2)), 111; (b) Schriven, E.F.V.; Turnbull, K. Chem. Rev. **1988**, *88* (2), 297; (c) Firouzabadi, H.; Tamami, B.; Kiasat, A.R. Synth. Commun. **2000**, *30* (4), 587; (d) Wu, H.; Chen, R.; Zhang, Y. Synth. Commun. **2002**, *32* (2), 189; (e) Ram, S.; Ehrenkaufer, R.E. Synthesis **1988**, 91; (f) Knouzi, N.; Vaultier, M.; Carrie, R. Bull. Chem. Soc. Fr. **1985**, *5*, 815; (g) Salunkhe, A.M.; Veeraghavan, R.P.; Brown, H.C. Tetrahedron **2002**, *58* (50), 10059; (h) Lin, W.; Zhang, X.; He, Z.; Jin, Y.; Gong, L.; Mi, A. Synth. Commun. **2002**, *32* (21), 3279; (i) Zhang, J.-M.; Zhang, Y.-M; Hecheng, H. **2002**, *10* (6), 498; (j) Kamal, A.; Ramana, K.V.; Ankati, H.; Ramana, A.V. Tetrahedron Lett. **2002**, *43* (38), 6861; (k) Pathak, D.; Laskar, D.D.; Prajapati, D.; Sandhu, J.S. Chem. Lett. **2000** (7), 816; (l) Ding, J.C.; Wu, H.Y. Chin. Chem. Lett. **2001**, *12* (8), 659; (m) Chandrasekhar, S.; Narasihmulu, Ch. Tetrahedron Lett. **2000**, *41* (41), 7969; (n) Gowda, D.; Channe, M.B.; Gowda, S. Ind. J. Chem. Sec. B. **2001**, *40B* (1), 75; (o) Pratap, T.V.; Baskaran, S. Tetrahedron Lett. **2001**, *42* (10), 1983; (p) Massenova, A.T.;

Sassykova, L.R. Eura. Chim-Tech. J. **2000**, *2* (1), 101; (q) Gowda, D.C.; Mahesh, B. Synth. Commun. **2000**, *30* (20), 3639; (r) Wilkinson, H.S.; Tanoury, G.J.; Wald, S.A.; Senanayaka, C.H. Tetrahedron Lett. **2001**, *42* (2), 167; (s) Lee, J.G.; Choi, K.; Koh, H.Y.; Kim, Y.; Kang, Y.; Cho, Y.S. Synthesis **2001** (1), 81; (t) Jyothi, T.M.; Rao, B.S.; Sugunan, S. Ind. J. Chem. Sec. A. **2000**, *39A* (10), 1041; (u) Desai, D.G.; Swami, S.S.; Dabhade, S.K.; Ghagare, M.G. Synth. Commun. **2001**, *31* (8), 1249.

2. (a) Alper, H. Inorg. Chem. **1972**, *11* (5), 1972; (b) Alper, H.; Edward, J.T. Can. J. Chem. **1970**, *48*, 1543; (c) Nitta, M.; Kobayashi, T. Bull. Chem. Soc. Jpn. **1984**, *57* (4), 1035; (d) Iqbal, A.F.M. Tetrahedron Lett. **1971**, *37*, 3385; (e) Iqbal, A.F.M. Chemtech. **1974**, 566.
3. Cenini, S.; La Monica, G. Inorg. Chimica. Acta **1976**, *18*, 279.
4. (a) Alper, H.; Petrignani, J.-F.; Einstein, F.W.B.; Willis, A.C. J. Amer. Chem. Soc. **1983**, *105*, 1701; (b) Massey, S.T.; Mansour, B.; McElwee-White, L. J. Organomet. Chem. **1995**, *485* (1–2), 123.

Received in India May 21, 2003

Downloaded by [University of Chicago Library] at 01:58 27 July 2013

Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/ Order Reprints" link below and follow the instructions. Visit the U.S. Copyright Office for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on Fair Use in the Classroom.

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our Website User Agreement for more details.

Request Permission/Order Reprints

Reprints of this article can also be ordered at

http://www.dekker.com/servlet/product/DOI/101081SCC120027720