Application of Lead and Ammonium Formate as a New System for the Synthesis of Azo Compounds

Shankare Gowda, D. Channe Gowda*

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, Karnataka, 570 006 India
Fax +91(82)1421263 ; E-mail: dcgowda@yahoo.com

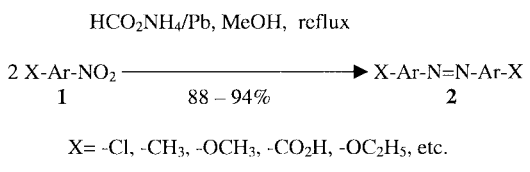
Received 15 October 2001; revised 29 January 2002

Abstract: Aromatic nitro compounds containing additional reducible substituents such as acid, phenol, halogen, ester functions are reduced to the corresponding symmetrically substituted azo compounds by employing lead and ammonium formate in methanol or tetrahydrofuran or dioxane medium at reflux temperature. The conversion occurs without hydrogenolysis or hydrogenation of −Cl, $-OCH_3$, $-OC_2H_5$, $-CO_2H$, moieties, which are prone to undergo reduction. The conversion is reasonably fast, clean and high yielding.

Key words: catalytic transfer hydrogenation, nitro compounds, azo compounds, lead ammonium formate, reduction

Reduction is an important tool in the hands of organic chemists. There are many methods available for the reduction of organic compounds.[1-5] However, these methods have one or more limitations. Heterogeneous catalytic transfer hydrogenation[5] and metal mediated reactions[6-8] are gaining more potential due to their simple work up and selectivity. Lead and its compounds[3,5,9-17] are widely used in organic synthesis, but lead powder has not been used in the field of heterogeneous catalytic transfer hydrogenation. There are few methods reported in the literature for the synthesis of intermediates like aryl hydroxyl amines,[18] azoxy compounds,[16,19] hydrazo compounds[20] and azo compounds.[21-26] Most of the methods documented in the literature are associated with cyclization, rearrangement and isomerization in the presence of strong acid or alkaline medium.

Here, we wish to report the synthesis of azo compounds **2** by catalytic transfer hydrogenation of nitro arenes **1** by using lead powder with ammonium formate in methanol or tetrahydrofuran or in dioxane medium at reflux temperature. Among the solvents used, methanol is the best one (Scheme 1).



Scheme 1

By using this method, we can synthesize a number of symmetrically substituted azo compounds **2** directly from nitro compounds **1** in a single step. Synthesis of unsymmetrically substituted azo compounds leads to the formation of a mixture, which needs extensive purification and yields are low (less than 30%). Moreover, ammonium formate in the presence of Raney Ni,[27] 5% Pt/C[28] or 10% Pd/C[29] directly converts nitro compounds to amines. This new system reduced with ease a wide variety of nitro compounds to corresponding azo compounds and many functional groups are tolerated. The reduction of nitro compounds to azo compounds was completed within one to three hours. The course of reaction was monitored by thin layer chromatography and IR spectra. The disappearance of asymmetric and symmetric stretching bands near 1520 cm^{-1} and 1345 cm^{-1} due to N····O of NO_2 and appearance of strong band between 1630−1575 cm^{-1} due to N=N stretching in the IR spectrum clearly indicates the conversion. There is no absorption between 3500−3300 cm^{-1} indicating the absence of NH_2 group. The work-up and isolation of the products were easy. Thus, all the compounds reduced to azo compounds (few examples are listed in Table) and were characterized by comparison with the thin layer chromatography, IR spectra and melting points of the authentic samples. A control experiment using nitro compounds with ammonium formate but without lead powder, does not yield the desired product. Another control experiment using nitro compound with lead powder in the absence of ammonium formate also did not yield the desired product. In order to test the selectivity, reduction was attempted with *p*-dichloro benzene, *p*-chloro-*m*-cresol, β-naphthol, cinnamic acid, acetanilide, benzoic acid, anisole, phenyl acetate, under similar conditions. However, the reaction failed to give any reduced product. The yields are virtually quantitative and analytically pure.

The scope of this new general procedure is shown in Table. In most cases, the reactions were completed within 1−3 hours. Lead powder can be reused after thorough washing. These results demonstrate a rapid versatile and selective reducing system for wide variety of nitro compounds in the presence of other functional groups for e. g. $-CO_2H$, −Cl, $-OC_2H_5$, $-CH_3$. The reduction was also carried out with the nitro compounds bearing bromomethyl sulphonic acid, oximino, amino and dialkyl amino groups. In these cases, the bromomethyl, dialkyl amino and oximino groups are compatible under the experimental conditions. However, in the case of amino substituted nitro

Synthesis 2002, No. 4, 15 03 2002. Article Identifier:
1437-210X,E;2002,0,04,0460,0462,ftx,en;E07001SS.pdf.

ISSN 0039-7881

Table Reduction of Nitro Compounds to Azo Compounds using Ammonium Formate/Lead Powder

Nitro Compound. **1**	Reaction Time (h)	Product **2**	Yield (%)	Melting Point (ºC)	
				Found	Lit.[30]
Nitrobenzene	1.0	azobenzene	92	66−68	68
o-Nitrotoluene	1.75	2,2′-dimethylazobenzene	92	54−56	55
m-Nitrotoluene	1.25	3,3′-dimethylazobenzene	94	55−56	55
m-Nitroanisole	1.5	3,3′-diethoxyazobenzene	93	90−93	91
m-Chloronitrobenzene	1.5	3,3′-dichloroazobenzene	92	101−102	101
o-Nitroanisole	2.0	2,2′-diethoxyazobenzene	90	130−133	131
o-Chloronitrobenzene	1.75	2,2′-dichloroazobenzene	90	135−138	137
p-Nitrotoluene	1.5	4,4′-dimethylazobenzene	94	144−146	144
p-Ethoxynitrobenzene	1.5	4,4′-diethoxyazobenzene	93	159−161	160
p-Chloronitrobenzene	1.0	4,4′-dichloroazobenzene	94	185−187	188
1-Nitronaphthalene	3.0	1,1′-azonaphthalene	90	188−191	190
2-Nitronaphthalene	2.5	2,2′-azonaphthalene	88	207−209	208

compounds, a mixture of products are obtained, probably due to the coupling of reduction intermediates with the free amino group. Nitro sulphonic acids gave insoluble precipitates and thus, this procedure is not helpful to those type of compounds. Furthermore, this system does not require a pressure apparatus, strong acid or alkaline medium. Ammonium formate also has the advantage of being readily available, inexpensive, stable, and nontoxic. It may be added to the reaction in a single portion and products can be easily separated from the reaction mixture. This procedure will therefore be of general use for the preparation of azo compounds, specifically in cases where mild reduction is required and it is less expensive compared to existing methods.

All the nitro compounds and ammonium formate were purchased from Aldrich Chemical Company (USA). Lead powder was purchased from SISCO Research Laboratories Pvt. Ltd., Bombay (India). All the solvents used were of analytical grade or were purified according to standard procedures. TLC was carried out on silica gel plates obtained from Whatman Inc. The melting points were determined by using Thomas-Hoover melting point apparatus and are uncorrected. IR spectra were recorded on SHIMADZU FTIR- 8300 spectrometer. For preparative tlc, the plates were prepared from Kieselgel 60 GF_{254}, Merck, Darmstadt and for column chromatography 60−120 mesh silica gel was obtained from SISCO Research Laboratories.

General procedure

A suspension of an appropriate nitro compound (1 g) lead powder (2 g, 325 mesh size, 99.5% pure, packed under Ar) in MeOH or in any other suitable solvent (10 mL) was stirred and refluxed with ammonium formate (3 g) under N_2 atm. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through celite pad, washed with solvent. The combined filtrate and washings were evaporated under vacuum. The residue was taken in $CHCl_3$ or Et_2O (15 mL), washed with sat. brine soln (2×15 mL) and finally with H_2O. The organic layer was dried over anhyd $MgSO_4$ and the solvent was removed using rotary evaporator. For further purification, the residue was purified either by preparative TLC or by column chromatography.

References

(1) *Comprehensive Organic Synthesis*, Vol. 8 (Reduction); Trost, B. M.; Fleming, I., Eds.; Pergamon press: Oxford, **1991**.
(2) Rylander, P. N. In *Hydrogenation Methods*; Academic press: New York, **1985**, 365.
(3) Popp, F. D.; Schultz, H. P. *Chem. Rev.* **1962**, *62*, 19.
(4) Harmon, R. E.; Gupta, S. K.; Brown, D. J. *Chem. Rev.* **1973**, *73*, 21.
(5) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129.
(6) Gowda, D. C.; Mahesha, B.; Gowda, S. *Indian J. Chem.* **2001**, *40B*, 75.
(7) Pitts, R. M.; Harison, J. R.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 955.
(8) Banik, B. K.; Suhendra, M.; Banik, I.; Becker, F. F. *Synth. Commun.* **2000**, *30*, 3745.
(9) *Comprehensive Organic Synthesis*, Vol. 7 (Oxidation); Trost, B. M.; Fleming, I.; Ley, S. V., Eds.; Pergamon press: Oxford, **1991**.
(10) (a) March, J. In *Advanced Organic Chemistry*; Wiley Eastern Ltd.: New Delhi, **1986**, 3rd ed., 331. (b) March, J. In *Advanced Organic Chemistry*; Wiley Eastern Ltd.: New Delhi, **1986**, 3rd ed., 1091.
(11) Lindlar, H. *Helv. Chim. Acta* **1952**, *35*, 446.
(12) Lindlar, H.; Dubuis, R. *Org. Synth.* **1966**, *46*, 89.
(13) Leonard, N. J.; Swann, S. Jr.; Fuller, G. *J. Am. Chem. Soc.* **1954**, *76*, 3193.
(14) Bergman, I.; James, J. C. *Trans. Faraday Soc.* **1954**, *50*, 60.
(15) Gakenheimer, W. C.; Hartung, W. H. *J. Org. Chem.* **1944**, *9*, 85.
(16) Azoo, J. A.; Grimshaw, J. *J. Chem. Soc. C* **1968**, 2403.
(17) March, J. In *Advanced Organic Chemistry*; Wiley Eastern Ltd.: New Delhi, **1986**, 3rd ed, 345–399.
(18) Rondestvedt, C. S.; Johnson, T. A. *Synthesis* **1977**, 850.
(19) Tadros, W.; Ishak, M. S.; Bassilli, E. *J. Org. Chem.* **1959**, 627.
(20) Bavin, P. M. G. *Can. J. Chem.* **1958**, *36*, 238.
(21) Vogel, A. I.; Watling, A.; Watling, J. *J. Chem. Educ.* **1958**, *35*, 40.
(22) Moore, R. E.; Furst, A. *J. Org. Chem.* **1958**, *23*, 1504.
(23) Hutchins, R. O.; Lamson, D. W.; Rua, L.; Cynthia, M.; Bruce, M. *J. Org. Chem.* **1971**, *36*, 803.

(24) (a) Kirk-Othmer, In *Encyclopedia of Chemical Technology*, 4th ed, Vol. 3; Grant, M. H., John Wiley & Sons: New York, **1992**, 821–875. (b) March, J. In *Advanced Organic Chemistry*; Wiley Eastern Ltd.: New Delhi, **1986**, 3rd ed., 177. (c) March, J. In *Advanced Organic Chemistry*; Wiley Eastern Ltd.: New Delhi, **1986**, 3rd ed., 1156.
(25) Dubonosov, A. D.; Galichev, S. V.; Chernoivanov, V. A.; Bren', V. A.; Minkin, V. I. *Russ. J. Org. Chem.* **2001**, *37*, 67.
(26) Blokhina, N. I.; Shakhkel, 'Dyan I. V.; Atroshchenko, Y. M.; Alifanova, E. N.; Gitis, S. S.; Kaminskii, A. Y.; Moiseev, D. V. *Russ. J. Org. Chem.* **2001**, *37*, 67.
(27) Gowda, D. C.; Gowda, A. S. P.; Baba, A. R.; Gowda, S. *Synth. Commun.* **2000**, *30*, 2889.
(28) Gowda, D. C.; Mahesha, B. *Synth. Commun.* **2000**, *30*, 3639.
(29) Ram, S.; Ehrenkaufer, R. E. *Tetrahedron Lett.* **1984**, *25*, 3415.
(30) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed; Revised by Furniss, B. S.; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R., Eds.; ELBS with Longman: Singapore, **1997**, 1393.