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The synthesis of azo compounds from nitro compounds using lead and triethylammonium formate

G. R. Srinivasa, K. Abiraj and D. Channe Gowda*

Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, Karnataka 570 006, India

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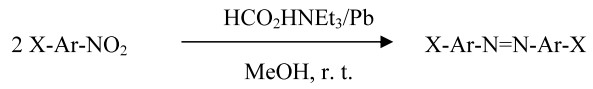
Abstract—Aromatic nitro compounds were reduced to the corresponding symmetrically substituted azo compounds using lead as catalyst and triethylammonium formate as hydrogen donor. Various azo compounds containing additional reducible substituents including halogens, nitrile, acid, phenol, ester, methoxy functions, etc, have been synthesized in a single step by the use of this reagent. The conversion is reasonably fast, clean, high yielding and occurs at room temperature in methanol.

Azo compounds are widely utilized as dyes and analytical reagents. They can also be used as indicators in chemical laboratories and as stains in the biological field. There are many methods available for the synthesis of azo compounds.[1–5] Most of the methods documented in the literature are associated with cyclization, rearrangement and isomerization side reactions in strong acid and alkaline medium.

Although there are a good number of methods available for the reduction of organic compounds,[6] limitations include the use of harsh conditions and/or costly reagents. Catalytic hydrogenation is also commonly used,[7] although the success of reaction is sensitive towards catalyst, solvent and substrate. Furthermore, catalytic hydrogenation employs highly diffusible, low molecular weight, flammable hydrogen gas and requires pressure equipment. Recently, heterogeneous catalytic transfer hydrogenation has proved to be a potent procedure for the reduction of organic compounds.[8–13] In comparison with catalytic hydrogenation or with other methods of reduction, catalytic transfer hydrogenation has many real and potential advantages.

The application of triethylammonium formate as a hydrogen donor in the field of catalytic transfer hydrogenation of organic compounds has been reported.[14–16] Lead and its compounds[2,17–20] have been used in organic synthesis, e.g. lead powder deactivates the catalytic activity of palladium. These modified palladium catalysts are used to reduce alkynes to alkenes.[9] Here we wish to report the synthesis of azo compounds by catalytic transfer hydrogenation of nitroarenes by using lead powder with triethylammonium formate in methanol at room temperature (Scheme 1). Various azo compounds containing additional reducible substituents including halogens, nitrile, acid, phenol, ester, methoxy functions, etc, have been synthesized in a single step.

Inspection of the data in Table 1 clearly shows that the method can be conveniently applied to the synthesis of symmetrically substituted azo compounds. This new system reduced with ease a wide variety of nitro compounds to the corresponding azo compounds with many other reducible functional groups being tolerated. The reduction of the nitro compounds to the azo compounds was completed within two to three hours. The course of reaction was monitored by TLC and IR. The disappearance of asymmetric and symmetric stretching bands near 1520 cm^{-1} and 1345 cm^{-1} due to the N⋯O of NO_2 and the appearance of a strong band between 1630–1575 cm^{-1} due to N=N stretching in the IR spectra clearly indicated the conversion. All the azo compounds prepared were characterized by comparison



X= -Cl, -Br, -CN, -CH_3, -OCH_3, -CO_2H, -$COCH_3$, -OH.

Scheme 1.

Keywords: catalytic transfer hydrogenation; nitro compounds; azo compounds; lead; triethylammonium formate.
* Corresponding author. Tel.: res: 0821-344348, office: 0821-515525, ext: 48; fax: 091-0821-421263/518835; e-mail: dcgowda@yahoo.com

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Table 1. Reduction of nitro compounds to azo compounds using HCO_2HNEt_3/Pb[a]

Nitro compound	Time (h)	Product	Yield (%)[b]	Melting point (°C)	
				Found	Lit.[21]
Nitrobenzene	2.0	Azobenzene	92	66–68	68
p-Nitrobiphenyl	2.5	Azobiphenyl	86	248–250	250
p-Nitrophenol	2.2	2,2′-Dihydroxyazobenzene	90	174–175	173–175
o-Nitrotoluene	2.4	2,2′-Dimethylazobenzene	91	54–56	55
m-Nitrotoluene	2.0	3,3′-Dimethylazobenzene	92	55–56	55
m-Nitroanisole	2.5	3,3′-Dimethoxyazobenzene	88	90–93	91
m-Chloronitrobenzene	2.5	3,3′-Dichloroazobenzene	86	101–102	101
o-Nitroanisole	2.0	2,2′-Dimethoxyazobenzene	90	130–133	131
o-Chloronitrobenzene	2.8	2,2′-Dichloroazobenzene	90	135–138	137
p-Nitrotoluene	2.6	4,4′-Dimethylazobenzene	89	144–146	144
p-Ethoxynitrobenzene	3.0	4,4′-Diethoxyazobenzene	88	159–161	160
p-Chloronitrobenzene	2.0	4,4′-Dichloroazobenzene	92	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

[a] ^1H NMR spectra were obtained on an AMX-400 MHz spectrometer in $CDCl_3$ as the solvent and TMS as internal standard. All of the products are known and the isolated products gave IR spectra in agreement with their structures.
[b] Yields of isolated pure products.

of their TLC, IR spectra, ^1H NMR spectra and melting points with authentic samples. A control experiment, using nitro compounds with triethylammonium formate but without lead powder, did not yield the desired product. Furthermore, an attempted reduction of a nitro compound using lead powder in the absence of triethylammonium formate did not yield the desired product. Synthesis of unsymmetrically substituted azo compounds leads to the formation of mixtures, which need extensive purification and the yields were low (less than 30%).

The initial reduction of the nitro compound to a hydroxylamine was evidenced by the isolation of phenylhydroxylamine (up to 30% yield) as a reaction intermediate during the course of reduction of nitrobenzene. Triethylammonium formate in the presence of palladium on carbon directly converts nitro compounds into amines.[15] However, lead being a weak catalyst, cannot reduce efficiently the intermediate azo compounds to amines. However, 4–6% of the amino products were obtained along with major azo products. The percentage of amino compounds increased up to 20% if the reaction mixture was stirred for more than 24 h.

The scope of this new procedure is shown in Table 1. In most cases the reactions were completed within 2–3 h. The lead powder can be reused after thorough washing. The reduction was also carried out with nitro compounds bearing bromomethyl, sulphonic acid, oximino, amino and dialkyl amino groups. In these cases, the bromomethyl, dialkylamino and oximino groups were compatible with the experimental conditions, but, in the case of amino substituted nitro compounds, a mixture of products were obtained, probably due to coupling of reduction intermediates with the free amino group. Nitroaryl sulphonic acids gave precipitates, which were insoluble in the solvents employed and thus this procedure is not applicable to such compounds for obtaining azo compounds.

General procedure

A suspension of the nitro compound (1 g) and lead powder (2 g) in methanol (10 mL) was stirred with triethylammonium formate (4 mL) under a nitrogen atmosphere at room temperature. After completion of the reaction (monitored by TLC), the reaction mixture was filtered through a Celite pad and washed with solvent. The combined filtrate and washings were concentrated under vacuum. The residue was taken up in 15 mL chloroform or ether, washed twice with 15 mL saturated brine solution and finally with water. The organic layer was dried over anhydrous magnesium sulfate and evaporation of the organic layer followed by purification either by preparative TLC or by column chromatography gave the desired product.

Note: Lead powder (325 mesh size, 99.5% pure, packed under argon) was purchased from SISCO Research Laboratories Pvt. Ltd., Bombay (India).

The triethylammonium formate was prepared by neutralizing slowly, equal moles of triethylamine and formic acid in an ice water bath, with constant stirring. The resulting triethylammonium formate solution was used as such in all reactions.

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