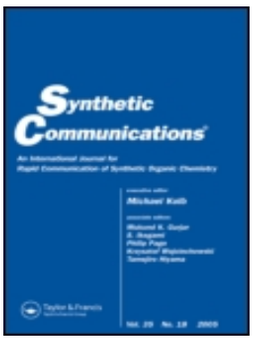

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Lead-Catalyzed Synthesis of Azo Compounds by Ammonium Acetate Reduction of Aromatic Nitro Compounds

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ABSTRACT

Lead/ammonium acetate is a convenient reagent for the reduction of aromatic nitro compounds to the corresponding symmetrically substituted azo compounds. Various azo compounds containing additional reducible substituents such as halogen, nitrile, acid, phenol, ester, methoxy, etc., functions 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.

Key Words: Catalytic transfer hydrogenation; Nitro compounds; Azo compounds; Lead; Ammonium acetate.

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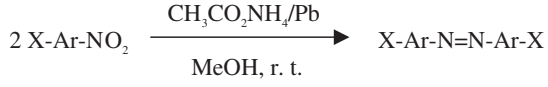
Azo compounds have been widely utilized as dyes and analytical reagents. They can also be used as indicators in chemical laboratories and as stains in biological field. There are many methods available for the synthesis of azo compounds.[1–5] Most of the methods documented in the literature are associated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

Although there are a good number of methods available for the reduction of organic compounds,[6] there still remain the important problems of reaction, i.e., many of them need drastic conditions and/or costly reagents. Catalytic hydrogenation is also commonly used,[7] although the success of reaction is sensitive towards catalyst, solvent, and substrate. Further, catalytic hydrogenation employs highly diffusible, low molecular weight, flammable hydrogen gas, and requires pressure equipment. Nowadays, heterogeneous catalytic transfer hydrogenation method has proved to be a potent choice for 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 such as: (i) low cost, (ii) rapidity, (iii) mild conditions, usually avoiding strong acid or base, (iv) selectivity, (v) simple operation and work up, and (vi) broad applicability.

The earlier works showed that ammonium acetate was useful reagent in the synthesis of many organic compounds[14,15] including β-amino acids.[16] Lead and its compounds[17–20] are widely used in organic synthesis. Lead powder is used to deactivate 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 nitro arenes by using lead powder with ammonium acetate in methanol at room temperature (Sch. 1). Various azo compounds containing additional reducible substituents such as halogen, nitrile, acid, phenol, ester, methoxy, etc., functions have been synthesized in a single step.

Inspection of the data in Table 1 clearly shows that the method can be conveniently applied for the synthesis of several structurally different symmetrically substituted azo compounds. Synthesis of unsymmetrically



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

Scheme 1.

Table 1. Reduction of nitro compounds to azo compounds using $CH_3CO_2NH_4$/Pb.

Nitro compound	Time (in h)	Product	Yield (%)[a]	Melting point (°C)	
				Found	Lit.[21]
Nitrobenzene	2.0	Azobenzene	91	66–67	68
p-Nitrobiphenyl	2.4	Azobiphenyl	87	248–250	250
p-Nitrophenol	2.5	2,2′-Dihydroxyazobenzene	90	174–175	173–175
o-Nitrotoluene	2.8	2,2′-Dimethylazobenzene	91	54–55	55
m-Nitrotoluene	2.4	3,3′-Dimethylazobenzene	93	55–56	55
m-Nitroanisole	2.0	3,3′-Diethoxyazobenzene	89	90–92	91
m-Chloronitrobenzene	2.0	3,3′-Dichloroazobenzene	87	101–102	101
o-Nitroanisole	2.2	2,2′-Diethoxyazobenzene	80	130–132	131
o-Chloronitrobenzene	3.0	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	82	159–162	160
p-Chloronitrobenzene	2.0	4,4′-Dichloroazobenzene	82	185–187	188
1-Nitronaphthalene	3.0	1,1′-Azonaphthalene	90	188–191	190
2-Nitronaphthalene	2.8	2,2′-Azonaphthalene	91	207–209	208

[a]Yields of isolated pure products.
^{1}H 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.

substituted azo compounds leads to the formation of a mixture, which needs extensive purification and yields are low (less than 30%). This new system reduced with ease a wide variety of nitro compounds to the corresponding azo compounds and many other reducible functional groups being tolerated. The reduction of nitro compounds to azo compounds was completed within 2–3 h. The course of reaction was monitored by TLC and IR spectra. The disappearance of asymmetric and symmetric stretching bands near 1520 and 1345 cm^{-1} due to N⋯⋯O of NO_2 and appearance of a strong band between 1630 and1575 cm^{-1} due to N=N stretching in IR spectra clearly indicates the conversion. The work-up and isolation of the products were easy. Thus all the compounds reduced to azo compounds were characterized by comparison of their TLC, IR spectra, ^{1}H NMR spectra, and melting points with authentic samples. A control experiment was carried out using nitro compounds with ammonium acetate but without lead powder, did not yield the desired product. Further, another control experiment was also carried out using nitro compound with lead powder in the absence of ammonium acetate was also not yielded the desired product.

The mechanism for the formation of azo compound probably involves initial reduction of nitro compound to nitroso and hydroxylamine products, which then condense to form azo compounds. This is evidenced by the isolation and characterization of the intermediate hydroxylamine compounds. Ammonium acetate in the presence of palladium on carbon or zinc directly converts nitro compounds into amines (Gowda et al., personal communication). However, lead being a weak catalyst cannot efficiently reduce the intermediate azo compounds to amines. However, 4–6% of amino product was obtained along with major azo product. The percentage of amino compounds increased up to 20% if the reaction mixture was stirred for very long time.

The scope of this new general 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. 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., halogens, $-CN$, $-CH_3$, $-OCH_3$, $-CO_2H$, $-COCH_3$, $-OH$ etc. The reduction was also carried out with the nitro compounds bearing bromomethyl sulphonic acid, oximino, amino, and dialkyl amino groups. In these cases, the bromo methyl, dialkyl amino, and oximino groups are compatible under the experimental conditions. But, in the case of amino substituted nitro compounds, mixtures of products are yielded, probably due to the coupling of reduction intermediates with the free amino group. Nitro sulphonic acids gave precipitate, which are insoluble in the solvents employed and thus, this procedure is not helpful to such type of compounds for obtaining azo compounds. This procedure will therefore be of general use for the preparation of azo compounds, specifically in cases where mild reaction condition is required and it is less expensive compared to existing methods.

EXPERIMENTAL

Materials

All the nitro compounds and ammonium acetate were purchased from Aldrich Chemical Company (USA). Lead powder (325 mesh size, 99.5% pure, packed under argon) 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 used obtained from SISCO Research Laboratories.

Typical Procedure

A suspension of an appropriate nitro compound (10 mmol) and lead powder (30 mmol) in methanol (15 mL) was stirred with ammonium acetate (20 mmol) under nitrogen atmosphere at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered through celite pad, washed with solvent. The combined filtrate and washings are evaporated under vacuum. The residue was taken in to 30 mL chloroform or ether, washed twice with 30 mL saturated brine solution and finally with water. The organic layer was dried over anhydrous magnesium sulphate and evaporation of the organic layer followed by purification either by preparative TLC or by column chromatography to yield the desired product.

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