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Facile Synthesis of Azo Compounds from Aromatic Nitro Compounds using Magnesium and Triethylammonium Formate

G. R. Srinivasa,[A] *K. Abiraj*,[A] *and D. Channe Gowda*[A,B]

[A] Department of Studies in Chemistry, University of Mysore, Mysore, Karnataka 570006, India.
[B] Author to whom correspondence should be addressed (e-mail: dcgowda@yahoo.com).

Magnesium/triethylammonium formate is a convenient reagent for the reduction of aromatic nitro compounds to corresponding symmetrically substituted azo compounds. Various azo compounds containing additional reducible substituents, including halogen, nitrile, acid, phenol, ester, and methoxy 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.

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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 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 in strongly acid and alkaline media. Nowadays, heterogeneous catalytic transfer hydrogenation has proved to be a potent choice for reduction of organic compounds.[6–11] In comparison with catalytic hydrogenation or other reduction methods, catalytic transfer hydrogenation has real and potential advantages such as low cost, rapidity, mild conditions that usually avoid strong acids or bases, selectivity, simple operation and work-up, and broad applicability.

The application of triethylammonium formate as a hydrogen donor in the catalytic transfer hydrogenation of a variety of organic compounds has been reported.[12–14] In our previous study, we have successfully employed magnesium for the transfer hydrogenolysis of some commonly used protecting groups in peptide synthesis.[15] Here we report the synthesis of symmetrical functionalized azo compounds by the reductive coupling of nitro arenes using magnesium and triethylammonium formate in methanol at room temperature (Scheme 1).

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 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 are tolerated. The reduction of nitro compounds to azo compounds was completed within two to three hours at room temperature. The course of the reaction was monitored by thin layer chromatography and IR spectroscopy. The disappearance of asymmetric and symmetric stretching bands near 1520 and 1345 cm^{-1} due to the N⟶O bond of NO_2 and appearance of strong band between 1630 and 1575 cm^{-1} due to N=N stretching clearly indicates the conversion. The work-up and isolation of the products were simple. Thus all the compounds reduced to azo compounds were characterized by comparison of their TLC, IR and ^1H NMR spectra, and melting points with authentic samples. Two control experiments, carried out using nitro compounds with either triethylammonium formate or magnesium powder, did not yield the desired products.

$$2\ X\text{–}Ar\text{–}NO_2 \xrightarrow[MeOH,\ r.t.]{HCO_2HNEt_3/Mg} X\text{–}Ar\text{–}N{=}N\text{–}Ar\text{–}X$$

Scheme 1. Reductive coupling of nitro arenes. X = Cl, Br, CN, CH_3, OCH_3, COOH, $COCH_3$, OH.

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, a mixture of products is yielded, probably due to the coupling of reduction intermediates with the free amino group. Nitro sulphonic acids gave a precipitate insoluble in the solvents employed and, thus, this system is not helpful in obtaining azo compounds. This procedure will therefore be of general use for the preparation of functionalized azo compounds, specifically in cases where mild reaction conditions are required, and it is less expensive compared to existing methods.

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Table 1. Synthesis of Azo Compounds from Nitro Arenes using HCO_2HNEt_3/Mg

^{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

Nitro compound	Time [h]	Product	Yield of isolated product [%]	Melting point [°C]	
				Found	Lit.[16]
Nitrobenzene	2.0	azobenzene	93	67–68	68
p-nitrobiphenyl	2.5	azobiphenyl	84	248–252	250
p-Nitrophenol	2.2	2,2′-dihydroxyazobenzene	92	174–175	173–175
o-Nitrotoluene	2.4	2,2′-dimethylazobenzene	90	54–56	55
m-Nitrotoluene	2.0	3,3′-dimethylazobenzene	93	55–57	55
m-Nitroanisole	2.5	3,3′-diethoxyazobenzene	88	90–92	91
m-Chloronitrobenzene	2.5	3,3′-dichloroazobenzene	84	100–102	101
o-Nitroanisole	2.0	2,2′-diethoxyazobenzene	92	130–132	131
o-Chloronitrobenzene	2.8	2,2′-dichloroazobenzene	90	135–137	137
p-Nitrotoluene	2.6	4,4′-dimethylazobenzene	88	144–145	144
p-Ethoxynitrobenzene	3.0	4,4′-diethoxyazobenzene	86	159–162	160
p-Chloronitrobenzene	2.0	4,4′-dichloroazobenzene	92	186–187	188
1-Nitronaphthalene	3.0	1,1′-azonaphthalene	91	188–191	190
2-Nitronaphthalene	2.5	2,2′-azonaphthalene	87	207–209	208

Experimental

A suspension of an appropriate nitro compound (1 g) and magnesium powder (2 g) in methanol (10 mL) was stirred with triethylammonium formate (4 mL) under N_2 at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered through celite and washed with solvent. The combined filtrate and washings were evaporated under vacuum. The residue was taken into 15 mL chloroform or ether, washed twice with 15 mL saturated brine, 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 to yield the desired product.

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