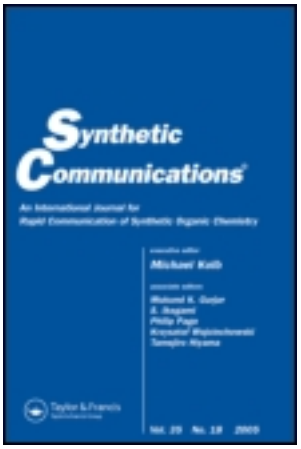

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Novel and Efficient Hydrogenative Cleavage of Azo Compounds to Amine(s) Using Chitosan-Supported Formate and Magnesium

X. H. Yu [a b], X. J. Ma [a], S. P. Jin [a b] & Y. Z. Zhen [a]

[a] College of Chemistry and Chemical Engineering, Hexi University, Zhangye, China

[b] Key Laboratory of Hexi Corridor Resource Utilization of Gansu Universities, Zhangye, China

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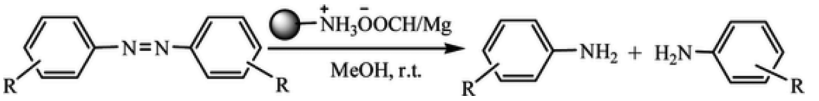
NOVEL AND EFFICIENT HYDROGENATIVE CLEAVAGE OF AZO COMPOUNDS TO AMINE(S) USING CHITOSAN-SUPPORTED FORMATE AND MAGNESIUM

X. H. Yu,[1,2] X. J. Ma,[1] S. P. Jin,[1,2] and Y. Z. Zhen[1]

[1]*College of Chemistry and Chemical Engineering, Hexi University, Zhangye, China*

[2]*Key Laboratory of Hexi Corridor Resource Utilization of Gansu Universities, Zhangye, China*

GRAPHICAL ABSTRACT



Abstract *A convenient and efficient method for the hydrogenative cleavage of azo compounds to corresponding amine (s) using chitosan-supported formate as hydrogen donor in conjunction with low-cost magnesium powder is reported. This method was found to be highly facile with selectivity over several other functional groups, such as halogen, alkene, nitrile, carbonyl, ether, amide, methoxy, and hydroxyl groups. Furthermore, this mild, exceedingly efficient, and highly chemoselective method simplifies the handling and separation procedures.*

Keywords Azo compounds; catalytic transfer hydrogenation; chitosan-supported formate; magnesium

INTRODUCTION

The reduction of azo compounds to the corresponding amine(s) is a useful transformation both in the laboratory and in industry because of the fact that aromatic amines were essential intermediates for the synthesis of dyes, pharmaceuticals, and agricultural chemicals.[1,2] Catalytic transfer hydrogenation (CTH) using hydrogen donors is considered to be more safe, cost-effective, selective, rapid, and environmentally friendly than other methods available for the reduction of azo compounds.[3–5] Ammonium formate was found to be more convenient and efficient compared to other hydrogen donors.[6,7] However, ammonium formate itself did have some limitations. This reagent could sublime and block the reaction apparatus, and it released the gaseous by-products (ammonia and carbon dioxide) through the

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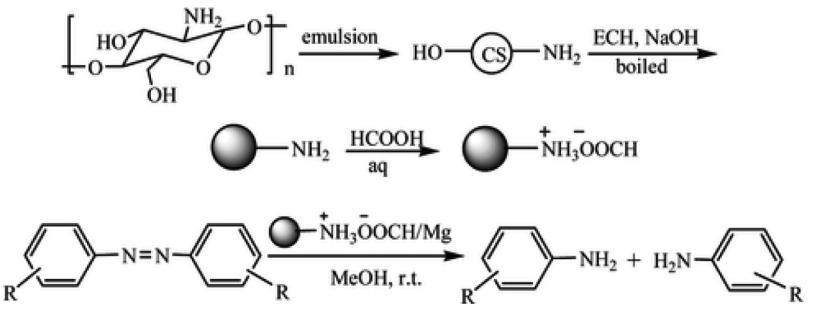
Address correspondence to X. H. Yu, College of Chemistry and Chemical Engineering, Hexi University, Zhangye 734000, China. E-mail: yuxinghai455@163.com



Scheme 1. Hydrogenative cleavage of azo compounds using CSF and magnesium in methanol.

decomposition. It gave deposits on the cold surfaces of the reactor lines, which could create significant problems when performed on a large scale. In addition, the use of ammonium formate as hydrogen donor often posed complications during isolation and purification of water-soluble products. For this reason, immobilized formate on polymeric supports has been developed to solve the problems and offer advantages over the conventional solution-phase reactions in terms of clean and green processes. In the past few years, several strategies have been reported to employ the polymer-supported formate as hydrogen donors in CTH.[8–10] However, most of these cases have been performed using synthetic polymers, which are unfriendly to the environment and rather complicated to prepare. Consequently, the development of biodegradable, nontoxic, and readily and cheaply available catalyst is highly desired.

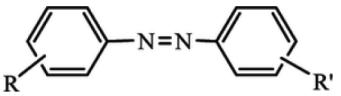
Chitosan, an abundant and renewable natural polymer, has unique properties such as biocompatibility, biodegradability, and nontoxicity.[11,12] Recently chitosan and its derivatives have attracted much attention as polymeric supports in various fields, especially the supported catalysis that deals with oxidation and reductive hydrogenation reactions.[13–16] In view of the rapid development of chitosan-supported chemistry over the past few years, papers have very rarely reported employing the chitosan-supported formate as hydrogen donor in CTH. In this work, we prepared highly porous chitosan resins used epichlorohydrin (ECH) as cross-linking agent by reaction with the hydroxyl groups while retaining the amine groups of chitosan. This prevents the dissolution of CTS in acid and chemicals. When the cross-linked chitosan resins were treated with a formic acid solution, the chitosan-supported formate (CSF) were obtained. Our investigations revealed that the utilization of the CSF as hydrogen donor in conjunction with magnesium to cleave the azo derivatives into the corresponding amine(s) was cost-effective, rapid, and simple (Scheme 1).

RESULTS AND DISCUSSION

A series of structurally varied azo compounds underwent reduction by this methodology and the results are summarized in Table 1.

The reactions were rapid (8–20 min) and high yielding (86–95%) and selectively reduced azo compounds to the corresponding amine(s). The sensitive functional groups, such as halogen (Table 1, entries 8 and 9), alkene (Table 1, entry 10), nitrile

Table 1. Reduction of azo compounds by CSF and magnesium

Entry		Temp (°C)/ time (min)	Yields[a] (%)	Melting point (°C) Found	Melting point (°C) Literature
1	R=H, R′=H	25/10	94	112[b]	114[18]
2	R=3-CH_3, R′=3′-CH_3	25/10	95	124–125[c]	125[18]
3	R=2-CH_3, R′=2′-CH_3	25/12	91	142–143[c]	144[18]
4	R=2-$C(CH_3)_3$, R′=2′-$C(CH_3)_3$	65/20	89	231–232[d]	233[19]
5	R=4-OCH_3, R′=4′-OCH_3	25/18	90	58–59	57[18]
6	R=4-OH, R′=4′-OH	25/12	95	189–191	189[17]
7	R=4-$CONH_2$, R′=4′-$CONH_2$	25/13	92	181	183[18]
8	R=2-Br, R′=2′-Br	25/20	86	28–30	30[18]
9	R=4-Cl, R′=4′-Cl	25/15	87	71	72[17]
10	R=4-vinyl, R′=4′-vinyl	25/12	92	242[d]	249[18]
11	R=4-CHO, R′=4′-CHO	25/14	90	70–71	71[18]
12	R=4-CN, R′=4′-CN	25/17	88	84–85	86[19]
13	R=3-$COCH_3$, R′=3′-$COCH_3$	25/18	90	98–99	99[18]

[a]Yields refer to pure isolated products.
[b]Isolated as acetyl derivative.
[c]Isolated as benzoyl derivative.
[d]Boiling point.

(Table 1, entry 12), and carbonyl (Table 1, entries 11 and 13), remained unaffected under this transfer hydrogenation condition. In addition, many other functional groups such as amide, methoxy, acid, ether, and hydroxyl are also compatible with the present system. It is worth noting that we discovered the reactions were sensitive to the steric and electronic effects of the substituents. The little-substituted azo compounds were easily reductive to the corresponding amine(s). While the more sterically azo compounds have been inefficient, good conversion has been obtained at reflux temperature with longer reaction times (Table 1, entry 4). The results also revealed that electron-donating groups facilitate the reactions and electron-withdrawing groups enhance the extent of reaction period.

To obtain optimum reduction conditions, a wide range of solvents were carried out. Methanol is found to be the best one as far as the solubility of substrate and rate of reaction is concerned. Furthermore, we observed 3–4 equivalents of CSF and 1–2 equivalents of magnesium were ideal for reduction at room temperature. A control experiment was carried out using azo compounds with CSF but without magnesium powder. Remarkably, we found the substrate was unconverted throughout the experiment, and nothing of reductive products was obtained. This clearly indicates that magnesium is essential to carry out the reduction.

The separation of products from the reaction mixture is simple and involves, in most of the reactions, direct removal of the catalyst and resin by filtration and evaporation of the solvent under vacuum. The crude product, so isolated, was of excellent purity for most purposes. Hence, this procedure is highly advantageous to obtain water-soluble aromatic amines in good yields.

In conclusion, we developed a novel, convenient, and efficient method for the hydrogenative cleavage of azo compounds using CSF and low-cost magnesium

powder. This CTH method combines the advantages of polymer-supported chemistry with the flexibility of CTH technique, such as cost-effectiveness way, safe reaction medium, rapidity, and ease of operation. In addition, the use of CSF as hydrogen source is chemoselectivity to sensitive functional groups and highly helpful to obtain aromatic amine in pure form with no workup. Further investigations on other useful applications of this chitosan-supported formate to many other reductive functional group transformations are in progress and will be the subject of future reports.

EXPERIMENTAL

Chitosan with a deacetylation percentage of approximately 99% was a product of Shanghai Fuqiang Biochemical Co. Ltd. (China) and was purified before use by dissolving and precipitating it several times, extracting in Soxhlet apparatus in acetone for 24 h, and drying at 40 °C under vacuum. Epichlorohydrin and formic acid were obtained from Shanghai Chemical Ltd. (China). Magnesium powder was purchased from Beijing Chemical Ltd. (China). The other substances were either commercial products used as purchased or were prepared according to literature procedures. All of the solvents used were analytical grade and purified according to standard procedures. Thin-layer chromatography (TLC) was carried out on silica-gel plates obtained from Shanghai Chemical Ltd. (China). The melting points were determined by using a TX-4 melting-point apparatus and are uncorrected. Infrared (IR) spectra were taken with KBr pellets on a Perkin-Elmer FTIR 1725 spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Mercury-Plus 400 MHz spectrometer using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as internal standard.

Preparation of Chitosan-Supported Formate

The highly porous chitosan resins were made by an emulsion method using chitosan powder dissolved in 2.0% acetic acid aqueous and paraffin oil with Span 80.[17] A volume of 10 mL of 12.5 mol L^{-1} ECH was added to the chitosan solution and maintained at 60 °C for 2 h. Subsequently, 50 mL of 0.1 mol L^{-1} NaOH was added dropwise and the system was boiled for 3 h under constant stirring. The products obtained were filtered, washed several times with distilled water and ethanol, and then dried in a vacuum. Finally, the resins were packed in a column and exchanged with an excess of 50% solution of formic acid repeatedly to get the CSF. The resulting resins were washed with water several times, dried under vacuum, and used directly for catalytic reduction.

General Procedure for the Reduction of Azo Compounds

The experimental procedure for our reduction of azo compounds using CSF and magnesium is very simple. To a flame-dried flask equipped with a magnetic stirrer and condenser, the suspension of appropriate azo compound (5 mmol) in methanol (15 mL), CSF (1 g), and magnesium (5 mmol) were added and stirred under a nitrogen atmosphere at room temperature. Progress of the reaction was monitored by TLC until the starting material was consumed completely. Then the catalyst

and resin were removed by filtration, and the solvent was evaporated under vacuum. All of the products were purified by silica-gel chromatography eluted with PE–EtOAc = 5:1 and characterized by comparison of their TLC, melting points, IR spectra, ^{1}H NMR, and ^{13}C NMR spectra.

Benzenamine (Entry 1, C_6H_7N). Colorless oil. IR (KBr), ν (cm^{-1}): 3457 cm^{-1}, 3345 cm^{-1}, 3066 cm^{-1}, 3005 cm^{-1}, 1618 cm^{-1}, 1498 cm^{-1}, 1320 cm^{-1}, 1274 cm^{-1}, 1150 cm^{-1}, 1025 cm^{-1}, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.54 (s, br, 2H), 6.58–6.63 (m, 2H), 6.72–6.77 (m, 1H), 7.11–7.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 114.9, 116.2, 130.1, 138.2.

m-Toluidine (Entry 2, C_7H_9N). Colorless oil. IR (KBr), ν (cm^{-1}): 3223 cm^{-1}, 3040 cm^{-1}, 3002 cm^{-1}, 1623 cm^{-1}, 1498 cm^{-1}, 1463 cm^{-1}, 1306 cm^{-1}, 1288 cm^{-1}, 1166 cm^{-1}, 776 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.25 (s, 3H), 3.52 (s, br, 2H), 6.27 (m, 2H), 6.91 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 22.8, 114.5, 120.9, 132.1, 146.8;

o-Toluidine (Entry 3, C_7H_9N). Colorless oil. IR (KBr), ν (cm^{-1}): 3378 cm^{-1}, 3022 cm^{-1}, 1621 cm^{-1}, 1586 cm^{-1}, 1495 cm^{-1}, 1469 cm^{-1}, 1302 cm^{-1}, 1268 cm^{-1}, 1033 cm^{-1}, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 2.19 (s, 3H), 3.56 (s, br, 2H), 6.62 (d, J = 7.6 Hz, 1H), 6.69 (t, J = 7.6 Hz, 1H), 6.98–7.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 17.6, 115.6, 119.1, 123.2, 127.6, 130.8, 144.7.

4-*tert*-Butylbenzenamine (Entry 4, $C_{10}H_{15}N$). Colorless oil. IR (KBr), ν (cm^{-1}): 3353 cm^{-1}, 2963 cm^{-1}, 1627 cm^{-1}, 1463 cm^{-1}, 1363 cm^{-1}, 1266 cm^{-1}, 1190 cm^{-1}, 827 cm^{-1}, 645 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 1.29 (d, J = 6.8 Hz, 12H), 3.58 (s, br, 2H), 6.96–6.72 (m, 2H), 7.14–7.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 33.4, 39.7, 116.1, 125.6, 139.1, 143.4.

p-Anisidine (Entry 5, C_7H_9NO). Purple solid. IR (KBr), ν (cm^{-1}): 3419 cm^{-1}, 3348 cm^{-1}, 3001 cm^{-1}, 1627 cm^{-1}, 1509 cm^{-1}, 1466 cm^{-1}, 1297 cm^{-1}, 1239 cm^{-1}, 1181 cm^{-1}, 825 cm^{-1}, 726 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.44 (s, br, 2H), 3.89 (s, 3H), 6.64 (dd, J = 6.8, 2.0 Hz, 2H), 6.78 (dd, J = 6.8, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 57.2, 114.4, 116.8, 140.6, 153.0.

4-Aminophenol (Entry 6, C_6H_7NO). White solid. IR (KBr), ν (cm^{-1}): 3331 cm^{-1}, 3274 cm^{-1}, 3014 cm^{-1}, 2901 cm^{-1}, 1612 cm^{-1}, 1507 cm^{-1}, 1473 cm^{-1}, 1254 cm^{-1}, 1237 cm^{-1}, 1092 cm^{-1}, 965 cm^{-1}, 823 cm^{-1}, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.44 (s, br, 2H), 5.15 (s, 1H), 6.52 (dd, J = 6.0, 2.0 Hz, 2H), 7.42 (dd, J = 6.0, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 57.2, 116.4, 117.8, 142.6, 149.3.

4-Aminobenzamide (Entry 7, $C_7H_5N_2O$). White solid. IR (KBr), ν (cm^{-1}): 3331 cm^{-1}, 3274 cm^{-1}, 3014 cm^{-1}, 2901 cm^{-1}, 1612 cm^{-1}, 1507 cm^{-1}, 1473 cm^{-1}, 1254 cm^{-1}, 1237 cm^{-1}, 1092 cm^{-1}, 965 cm^{-1}, 823 cm^{-1}, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 4.44 (s, br, 2H), 5.45 (s, br, 1H), 6.52 (dd, J = 6.0, 2.0 Hz, 2H), 7.02 (dd, J = 6.0, 2.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 116.8, 124.6, 129.2, 152.3, 169.3.

2-Bromobenzenamine (Entry 8, C_6H_6BrN). Red solid. IR (KBr), ν (cm^{-1}): 3443 cm^{-1}, 3326 cm^{-1}, 1605 cm^{-1}, 1475 cm^{-1}, 1441 cm^{-1}, 1298 cm^{-1}, 1067 cm^{-1},

1017 cm^{-1}, 746 cm^{-1}, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.79 (s, br, 2H), 6.35–6.41 (m, 1H), 6.63 (dd, $J = 8.8$, 2.0 Hz, 1H), 6.90–6.94 (m, 1H), 7.14 (dd, $J = 8.8$, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 116.9, 118.0, 120.7, 129.4, 133.3, 148.1.

4-Chloroaniline (Entry 9, C_6H_6ClN). Yellow solid. IR (KBr), ν (cm^{-1}): 3407 cm^{-1}, 3309 cm^{-1}, 2901 cm^{-1}, 1613 cm^{-1}, 1494 cm^{-1}, 1285 cm^{-1}, 1175 cm^{-1}, 1085 cm^{-1}, 1002 cm^{-1}, 825 cm^{-1}, 640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.66 (s, br, 2H), 6.48 (d, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 118.4, 121.8, 130.4, 147.8.

4-Vinylbenzenamine (Entry 10, C_8H_9N). White solid. IR (KBr), ν (cm^{-1}): 3445 cm^{-1}, 3362 cm^{-1}, 1623 cm^{-1}, 1516 cm^{-1}, 1414 cm^{-1}, 1284 cm^{-1}, 1239 cm^{-1}, 1180 cm^{-1}, 1085 cm^{-1}, 834 cm^{-1}, 691 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.71 (s, 2H), 5.05 (d, $J = 10.8$, 1H), 5.56 (d, $J = 17.4$, 2H), 6.62 (m, 1H), 6.64 (d, $J = 8.4$, 2H), 7.24 (d, $J = 8.4$ Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 110.02, 115.03, 127.39, 128.37, 136.58, 146.25.

4-Aminobenzaldehyde (Entry 11, C_7H_7NO). Yellow solid. IR (KBr), ν (cm^{-1}): 3050 cm^{-1}, 2850 cm^{-1}, 2730 cm^{-1}, 1705 cm^{-1}, 1649 cm^{-1}, 1453 cm^{-1}, 823 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.78 (s, br, 2H), 6.65 (d, $J = 8.4$ Hz, Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H), 9.68 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ113.4, 125.5, 132.2, 154.7, 189.6.

4-Aminobenzonitrile (Entry 12, $C_7H_6N_2$). White solid. IR (KBr), ν (cm^{-1}): 3465 cm^{-1}, 3361 cm^{-1}, 3199 cm^{-1}, 2914 cm^{-1}, 2206 cm^{-1}, 1618 cm^{-1}, 1593 cm^{-1}, 1507 cm^{-1}, 1307 cm^{-1}, 1164 cm^{-1}, 830 cm^{-1}, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 4.32 (s, br, 2H), 6.72 (dd, $J = 6.8$, 2.0 Hz, 2H), 7.33 (dd, $J = 6.8$, 2.0 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 99.8, 117.2, 127.4, 133.7, 149.8.

3-Aminoacetophenone (Entry 13, C_8H_9NO). Yellow solid. IR (KBr), ν (cm^{-1}): 3545 cm^{-1}, 3455 cm^{-1}, 2957 cm^{-1}, 1670 cm^{-1}, 1634 cm^{-1}, 1610 cm^{-1}, 1593 cm^{-1}, 1501 cm^{-1}, 1466 cm^{-1}, 1364 cm^{-1}, 1334 cm^{-1}, 1301 cm^{-1}, 1246 cm^{-1}, 889 cm^{-1}, 781 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.52 (s, 3H), 4.00 (s, br, 2H), 6.86 (dd, $J = 8.0$, 1.6 Hz, 1H), 7.20–7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 27.3, 113.9, 118.5, 119.7, 129.4, 138.1, 147.1, 198.7.

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