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Note

Formic acid with 10% palladium on carbon : A reagent for selective reduction of aromatic nitro compounds

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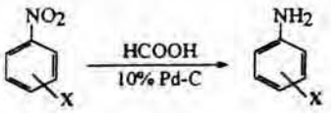
The nitro group in aromatic nitro compounds also containing reducible substituents such as carbonyl, ethene, ethyne, nitrile, acid, phenol etc, is selectively and rapidly reduced at room temperature to corresponding amino derivatives in good yield employing formic acid in the presence of 10% palladium on carbon. The catalyst could be recovered and reused after washing with water and ethanol, and the results obtained indicate further, there is no apparent loss of catalytic activity.

The development of selective, mild, rapid and effective reduction of nitro compounds is still an area of considerable synthetic interest, particularly when a molecule has several other reducible moieties. Numerous new reagents have been developed for reduction of aromatic nitro compounds[1-11]. In the past 30 years catalytic transfer hydrogenation has demonstrated great potential value in organic and biological chemistry[12-15]. Recently reported[16] catalytic transfer hydrogenation with ammonium formate and palladium catalyst constitutes a mild, simple and rapid reduction of nitro groups [17, 18]. Further, this system has also been successfully employed for reduction of several other functional groups [19, 20]. In view of these observations and in continuation of our studies on catalytic transfer hydrogenation, we report herein a mild, simple, rapid, and selective reduction of aromatic nitro compounds to the corresponding amino derivatives by employing formic acid as a catalytic hydrogen transfer agent in the presence of 10% palladium on carbon.

The functional groups which did not interfere with the reductions are ethenes, ethynes, nitriles, carbonyl and their derivatives (oximes, hydrazones, phenyl hydrazones and semicarbazones), acids and their derivatives (amides, esters, anhydrides), alcohols, ethers, phenols and lactones. Typical examples of the



X = Any reducible substituents other than halogens

application of this new procedure are listed in the **Table I**. All the products were characterised by comparison of their TLC, IR and melting points with authentic samples. In most of the cases, the reduction is over within 3-30 min , however, for 2,2′-dinitrodibenzyl, the reaction completion period was 60 min. The yields were virtually quantitative and analytically pure. However, the method fails to reduce NO_2 to NH_2 in case of halogen substituted aromatic nitro compounds. Further, we have observed that the reaction could be stopped virtually at any desired time by the mere addition of a small amount of chloride, bromide or iodide to the reaction mixture. These observations suggest that halide ion may deactivate the Pd-C catalyst. Moreover, the catalyst could be recoverd and reused after washing with water followed by ethanol, without any apparent loss of activity.

These results demonstrate that formic acid in the presence of 10 % Pd-C is a rapid, versatile and selective reducing system for a wide range of nitro compounds in the presence of other functional groups such as carbonyl, nitrile, ethene, etc. This system being readily available and easy to operate, produces products in good yields, and in high purities without necessitating for further purification. The obvious advantages of the proposed method over the previous methods are: (*i*) selective reduction of aromatic nitro compounds in the presence of other reducible groups, (*ii*) rapid reaction, (*iii*) high yields of substituted anilines, (*iv*) avoidance of strong acidic media, and (*v*) no pressure apparatus is needed. Therefore, the present method because of its simplicity and high selectivity, constitutes a useful alternative to the commonly accepted procedure for the synthesis of various aromatic amino derivatives.

Experimental Section

General procedure for the reduction of

Table I – Reduction of aromatic nitro compounds to corresponding amines[a]

Sl.No.	Nitro compound	Reaction period (in min)	Product	Yield[b] (%)
1	Nitrobenzene	2	Aniline[c]	90
2	*p*-nitrophenol	10	*p*-Aminophenol	91
3	*o*-Nitrophenol	30	*o*-Aminophenol	89
4	*m*-Nitrophenol	10	*m*- Aminophenol	92
5	*p*-Nitroaniline	3	*p*-Phenylenediamine	90
6	*o*-Nitroaniline	10	*o*-Phenylenediamine	91
7	*m*- Nitroaniline	5	*m*-Phenylenediamine	92
8	*p*-Nitrotoluene	3	*p*-Toluidine	93
9	*m*-Nitrotoluene	5	*m*- Toluidine[c]	91
10	*o*-Nitrotoluene	10	*o*-Toluidine[c]	92
11	2,4-Dinitrotoluene	15	2,4-Diaminotoluene	90
12	α-Nitronaphthalene	5	α-Naphthylamine	89
13	β- Nitronaphthalene	5	β-Naphthylamine	90
14	*p*-Nitrobenzoic acid	5	*p*-Aminobenzoic acid	86
15	*o*-Nitrobenzoic acid	30	*o*-Aminobenzoic acid	88
16	*m*-Nitrobenzoic acid	5	*m*-Aminobenzoic acid	87
17	*m*-Dinitrobenzene	10	*m*-Phenylenediamine	91
18	2,4-Dinitrophenol	30	2,4-Diaminophenol	92
19	3,5-Dinitrobenzoic acid	15	3,5-Diaminobenzoic acid	93
20	2,2′-Dinitrodibenzyl	60	2,2′-Diaminodibenzyl	85
21	*p*-Nitrophenyl acetate	15	*p*-Aminophenyl acetate[d]	91
22	*p*-Nitrobenzaldehyde	10	*p*-Aminobenzaldehyde	80
23	*p*-Nitroacetophenone	10	*p*-Aminoacetophenone	85
24	*p*-Nitrobenzamide	10	*p*-Aminobenzamide	82
25.	*p*-Nitroanisole	15	*p*-Anisidine	83
26	*p*-Nitrocinnamic acid	10	*p*-Aminocinnamic acid	84
27	*p*-Nitrobenzonitrile	15	*p*-Aminobenzonitrile	85
28	*p*-Nitrophenylacetonitrile	20	*p*-Aminophenylacetonitrile	82
29	3-[(*p*-Nitrobenzoyl)oxy]propyne	10	3-[(*p*-Aminobenzoyl)oxy]propyne	80
30	*N*-(4-Nitrophenyl)acetamide	10	*N*-(4-Aminophenyl)acetamide	90
31	*N*-(2-Nitrophenyl)acetamide	30	*N*-(2-Aminophenyl)acetamide	90
32	*N*-(3-Nitrophenyl)benzamide	20	*N*-(3-Aminophenyl)benzamide	91
33	*N*-(4-Nitrophenyl)benzamide	30	*N*-(4-Aminophenyl)benzamide	90

[a] The experiment was performed with more than 50 different compounds with other reducible moieties
[b] Isolated yields are based on the single experiment and yields were not optimized
[c] Isolated as its benzoyl derivative
[d] Isolated as its acetyl derivative

aromatic nitro compounds. To a stirred suspension of an appropriate nitro compound (5 mmoles) and 10% Pd-C (0.2-0.3g) in methanol (2.5 mL), 90% formic acid (2.5 mL) was added. The resulting reaction mixture (exothermic and effervescent) was stirred at room temperature. After completion of the hydrogenation (monitored by TLC), the mixture was filtered through celite and washed with methanol. The combined washings and filtrate were evaporated under reduced pressure, suspended in water and neutralised with ammonia. The resulting solid was filtered directly or extracted with an organic solvent (ether or $CHCl_3$) and dried over anhyd. Na_2SO_4. The organic layer on evaporation gave the desired amino derivative.

The experiment was also performed at reflux temperature and following the same procedure as described above to check the feasibility of reduction of other functional groups.

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