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CATALYTIC TRANSFER HYDROGENATION OF AROMATIC NITRO COMPOUNDS BY EMPLOYING AMMONIUM FORMATE AND 5% PLATINUM ON CARBON

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Aromatic nitro compounds were reduced to respective amines in high yields by using 5% platinum on carbon with ammonium formate or formic acid as hydrogen donor. It was observed that the former was more efficient donor than the later. Further we have found that reduction of nitro groups occurs without hydrogenolysis of halogens and the reducible substituents which remains unchanged under the reaction conditions.

The synthetically and industrially important reduction of nitro compounds to amines has been effected in many ways¹⁻¹¹. In the past 30 years catalytic transfer hydrogenation has demonstrated great potential value in organic and biological chemistry¹²⁻¹⁵. Recently reported¹⁶ catalytic transfer hydrogenation with ammonium formate and palladium catalyst constitute a mild, simple and rapid reduction of nitro groups¹⁷. Further this system has also been successfully employed for reduction of several other functional groups¹⁸⁻²⁰. Removal of halogen from aromatic nuclei is frequently observed and yet not desirable with palladium catalyst^{21,22}. In search for selective reduction of nitro compounds in the presence of other functional groups, particularly in the presence of halogens, we

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Table : Reduction of aromatic nitro compounds to corresponding amines^a.

No.	Nitro compound	Reaction time in min		Product	Yield ^b (%)	Melting Point(°C)	
		HCOONH ₄	HCOOH			Found	Lit
1.	Nitrobenzene	60	180	Aniline ^c	90	162-164	160-163
2.	p-Nitrophenol	45	60	p-aminophenol	91	185-186	184-187
3.	o-Nitrophenol	60	100	o-aminophenol	89	173-175	173-174
4.	p-Nitroaniline	50	120	p-phenylenediamine	90	143-144	140-143
5.	o-Nitroaniline	60	125	o-phenylenediamine	91	103-104	102-105
6.	m-Nitroaniline	45	45	m-phenylenediamine	92	63-66	63-65 ^d
7.	p-Nitrotoluene	30	45	p-toluidine	93	44-45	44-46
8.	m-Nitrotoluene	25	45	m-toluidene	91	65-66	65-66 ^d
9.	o-Nitrotoluene	30	45	o-toluidene	92	199-200	199-200
10.	2,4-Dinitrotoluene	60	75	2,4-diaminotoluene	90	98-99	98-99
11.	α-Nitronaphthalene	15	30	α-naphthylamine	89	49-50	48-50
12.	β-Nitronaphthalene	15	30	β-naphthylamine	90	112-113	113-114
13.	p-Nitrobenzoic acid	20	75	p-aminobenzoic acid	86	188-189	186-189
14.	o-Nitrobenzoic acid	30	45	o-aminobenzoic acid	88	146-147	145-146
15.	m-Dinitrobenzene	30	30	m-phenylenediamine	91	65-66	63-65
16.	2,4-Dinitrophenol	45	90	2,4-diaminophenol	92	79-80	77-79

17.	3,5-Dinitrobenzoic acid	10	30	3,5-diaminobenzoic acid	93	238-239	236-239 ^d
18.	2,2'-Dinitrodibenzyl	60	85	2,2'-diaminodibenzyl	85	222-223	221-224
19.	p-Nitrophenyl acetate	45	120	p-aminophenyl acetate ^d	91	150-151	147-150
20.	p-Nitrobenzaldehyde	60	120	p-aminobenzaldehyde	80	72-73	72-73
21.	p-Nitrobenzamide	30	60	p-aminobenzamide	82	182-183	182-183
22.	p-Nitroanisole	30	60	p-anisidine	83	57-58	57-58
23.	N-(4-Nitrophenyl)acetamide	30	60	N-(4-aminophenyl)acetamide	90	304-306	305-306
24.	N-(3-Nitrophenyl)benzamide	30	60	N-(3-aminophenyl)benzamide	91	239-240	239-240
25.	1-Chloro-2-nitrobenzene	45	60	o-chloroaniline	90	98-99	98-99 ^c
26.	1-Chloro-3-nitrobenzene	45	60	m-chloroaniline	89	71-72	71-72 ^d
27.	1-Chloro-4-nitrobenzene	45	60	p-chloroaniline	89	70-71	70-71
28.	1-Bromo-2-nitrobenzene	45	60	o-bromoaniline	90	98-99	98-99 ^c
29.	1-Bromo-3-nitrobenzene	45	60	m-bromoaniline	92	86-87	86-87 ^d
30.	1-Bromo-4-nitrobenzene	45	60	p-bromoaniline	90	65-66	66-67
31.	2,6-dichloro-1-nitrobenzene	45	60	2,6-dichloroaniline	91	39-40	40-41

(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) Melting points of benzoyl derivatives;

(d) Melting points of acetyl derivative.

wish to report a mild, simple, rapid and selective reduction of aromatic nitro compounds to the corresponding amino derivatives using ammonium formate or formic acid in presence of 5% platinum on carbon as catalyst.

The reducible substituents which remains unchanged under the reaction condition as well as at reflux temperature are ethenes, ethynes, nitriles, carbonyl compounds and their derivatives, acids and their derivatives, alcohols, ethers, phenols, lactones and halogens. The selectivity of our method is demonstrated by several examples listed in table. In most of the cases, the reduction was completed within 60 min (with HCOONH_4 donor) and the reduction time can be reduced to less than 10 min by performing the reduction at reflux temperature. Further it has been found that formic acid was less effective donor than ammonium formate with 5% Pt catalyst. The yields were virtually quantitative and analytically pure. All products were characterised by comparison of their t.l.c., IR and melting point with authentic samples. The catalyst recovered was washed with water and ethanol and could be reused without apparent loss of activity. This method effect the reduction of NO_2 to NH_2 even in the presence of halogens which is not possible with palladium catalyst.

We believe that the present procedure offers an attractive alternative for other methods available for the reduction of aromatic nitro compounds. Its principal advantages are : the avoidance of strong acid medium and harsh reagents, the ease of manipulation, very mild conditions of the reaction, selectivity, and excellent yields for a wide variety of nitro compounds.

EXPERIMENTAL

A suspension of an appropriate nitro compound (5 mmol) and 5% Pt-C (0.2-0.3g) in methanol or in any suitable solvent (5ml) was stirred with

ammonium formate (0.5g) at room temperature. After completion of the reduction (monitored by t.l.c), the catalyst was filtered off and washed with methanol. The combined washings and filtrate was evaporated *in vacuo*. The residue was taken up in organic solvent (ether or CHCl_3), washed with saturated NaCl to remove ammonium formate. The organic layer on evaporation gave the desired amino derivative.

The experiment was carried out with 90% HCOOH in place of HCOONH_4 and following the same procedure as described above. The experiment was also performed at reflux temperature to check the feasibility of reduction of other functional groups.

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