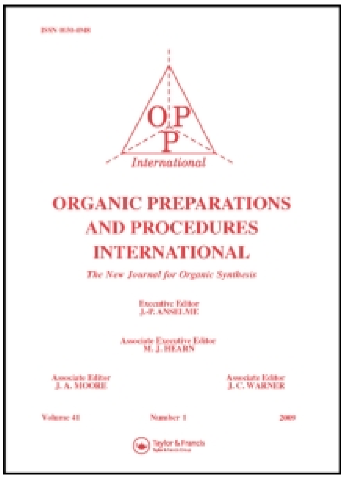

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EFFICIENCY OF THE URUSHIBARA NICKEL CATALYZED ATMOSPHERIC HYDROGENATION IN THE SYNTHESIS OF ANILINE DERIVATIVES

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11. B. Morgan and D. Dolphin, *J. Org. Chem.*, **52**, 5364 (1987).

12. J. A. Ballantine, A. H. Jackson, G. W. Kenner and G. McGillivary, *Tetrahedron, Suppl. No.7*, **22,** 241 (1966).

13. T. B. Wijesekera, J. B. ?. Paine and D. Dolphin, *J. Org. Chem.*, **63**, 1345 (1998).

14. H. W. Whitlock and R. Hanauer, *ibid.*, **33**, 2169 (1968).

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EFFICIENCY OF THE URUSHIBARA NICKEL CATALYZED ATMOSPHERIC HYDROGENATION IN THE SYNTHESIS OF ANILINE DERIVATIVES

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(05/10/00)

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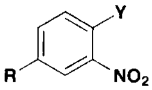
Although Urushibara catalysts can be used for the same catalytic reactions as Raney nickel catalysts,[1] their application have not been illustrated in the literature over the past twenty-five years except for two papers about their characterization.[2] Since Urushibara catalysts are prepared by a simple method and are not pyrophoric like Raney nickel catalysts, the exploitation of their practical uses would be significant for organic synthesis. We now report that some 4-substituted-2-nitroanilines (**1a**-**d**), 4-substituted-2-nitrophenols (**1e**) and nitrophenols (**1f**, **2**) are reduced to corresponding aniline derivatives in 80-90% yields by the atmospheric pressure catalytic hydrogenation using Urushibara nickel catalyst (U-Ni-A).



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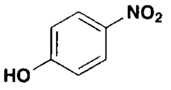

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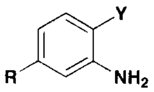

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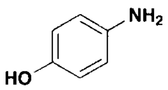

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a) R = CH_3, Y = NH_2 b) R = F, Y = NH_2 c) Cl, Y = NH_2
d) R = Br, Y = NH_2 e) R = CF_3, Y = OH f) R = H, Y = OH

These aniline derivatives (**3a-f**, **4**) which are important fine chemicals, have been synthesized from the corresponding nitro compounds by reduction with Fe, Sn, $SnCl_2$, alkali sulfides and catalytic hydrogenation. In comparison with those methods, U-Ni-A catalyzed hydrogenations possess some advantages. Firstly, the catalytic reactions may be carried out at atmospheric pressure in the liquid phase under mild warming (25-45°). In contrast, the reduction of the corresponding nitro compounds to **3a-c**, **3f** and **4** in the presence of Raney-nickel require pressure and heating.[9]

Table 1. Hydrogenation Conditions and Yields

Product	Solvent	Temp (°C)	Time (h)	Yield (%)	mp (°C)	*lit.* mp (°C)
3a	EtOH	40-45	1.5	85	90-91	88-89.5[3]
3b	EtOAc	35-45	4.0	80	90-92	89-91[4]
3c	EtOH	35-45	2.5	81	69-71	73-74[5]
3d	EtOH	35-45	4.0	82	65-66	63-64[6]
3e	EtOH	27-35	1.0	85	175-179	174-177[7]
3f	EtOH	25-30	4.0	88	123	121-122[8]
4	EtOH	30-45	4.0	91	184-186	186-187[7]

Second, the experimental results showed that the U-Ni-A may be used repeatedly and regenerated. If the catalyst was kept under nitrogen at room temperature for about a week, it may be reused directly. If the catalyst is deactivated, it may be regenerated by suspending in 20% acetic acid on a water bath (40-50°) for 2 hours.[10] Table **2** shows a ten run absorption rate of hydrogen in the preparation of 4-methyl-1,2-benzenediamine (**3a**) from 4-methyl-2-nitroaniline (**1a**) in the presence of a repeatedly used U-Ni-A catalyst.

Table 2. Absorption Rate of Hydrogen[a)]

Entry	1	2	3	4	5	6	7	8	9	10
Absorption rate (mL/min)	18	20	26	26	24	23	24	23	20	20

a) Refers to the rate of absorption of hydrogen, which is slow at the beginning, when it becomes stable.

Third, in contrast with the reduction in the other chemical agents, the products obtained by catalytic hydrogenation using U-Ni-A catalysts are easily isolated, required less organic solvent and are obtained in good purity. Only compounds **3e** and **4** required recrystallization from ethanol, due to the formation of a salt because of the slightly acidic reaction conditions. Compound **3f** was recrystallized from benzene. Since the title aniline derivatives have a measurable solubility in water, their isolation and purification is cumbersome and requires more solvent with the use of other chemical reducing agents.

EXPERIMENTAL SECTION

All melting points were determined with a X-4MP apparatus and are not corrected. NMR spectra were recorded on a Bruker AC-P200 spectrometer in $CDCl_3$, Hexamethyldisilane (HMDS) as an internal standard. The 4-substituted- 2-nitroanilines and 4-trifluoromethyl-2-nitrophenol were prepared according to literature procedures.[3-6,8] *o*- and *p*-Nitrophenol, $NiCl_2 \bullet 6H_2O$, Zn powder and electrolytic H_2 are commercial products in C.P or A.R purity and were used without further purification.

Preparation of U-Ni-A.- To a suspension of Zn dust (6.3 g, 10 mmol) in water (1.5 mL) was added rapidly a solution of $NiCl_2.6H_2O$ (5 g, 21 mmol) in water (5 mL) with vigorous magnetic stirring. Stirring was continued until the evolution of hydrogen had abated. The resulted mixture was decanted and the precipitated nickel was washed three times with water (3 x 25 mL). To the precipitate was added 20% acetic acid (94 mL) and the mixture was heated (40-50°) on a water bath with magnetic stirring for 30 min and allow to stand at room temperature for 30 min. The solution was decanted and the precipitate was washed with water until neutral, and then washed three times with ethanol (25 mL). The catalyst may be then stored under absolute alcohol (20 mL).

General Procedure for Catalytic Hydrogenation.- The hydrogenation procedure (*Fig. 1*) is similar to that commonly used for atmospheric pressure technique.[11] The above-prepared U-Ni-A catalyst, 20 mL of solvent and a solution of 15-20 mmol of the nitro compound in 80 mL solvent were placed in the reaction bottle. The system was evacuated and refilled with hydrogen three times (3 x 200 mL). The hydrogenation bottle was warmed to the temperature indicated in Table 1, with stirring and hydrogen was led into the reaction bottle. When the theoretical amount of hydrogen had been consumed, the reaction was stopped and the mixture was allowed to stand for 0.5 hr, the solution was decanted and the catalyst was washed twice with the solvent. The combined solution was evaporated under diminished pressure to give the desired products

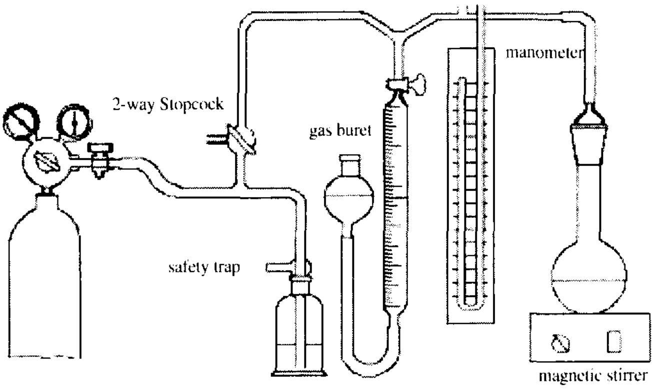

Fig. 1. Schematic of low pressure hydrogenation apparatus

REFERENCES

1. K. Hata, I. Motoyama and K. Sakai, *Org. Prep. Proced. Int.*, **4**, 180(1972).

2. a) J. C. Klein and D. M. Hercules, J. Catal., **82**, 424 (1983); b) J. Isaac and M. Fisher, *ibid.*, **101**, 28 (1986).

3. J. C. Cavagnol and F. Y. Wisetogle, *J. Am. Chem. Soc.*, **69**, 795 (1947).

4. M. Bil, *Chem. Ind.* (London), 198 (**1969**).

5. D. M. Hall and E. E. Turner, *J. Chem. Soc.*, 702 (**1945**).

6. J. G. Wilson and F. C. Hunt, *Australian J. Chem.*, **36**, 2317 (1983).

7. US Patent 3,079, 435 (26 Feb.1963); *Chem. Abstr.*, **59**, 6314h (1963).

8. M. R. Pettit and J. C. Tatlow, *J. Chem. Soc.*, 3853 (**1954**).

9. M. Freifelder, *Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary*, John Wiley & Sons, New York, NY, 1978

10. J. F. Chen, F. Q. Qu and X. L. Huang, J. Wuhan. Univ. (Natural Sci Ed), **44**, 679 (1998); *Chem. Abstr.*, **131**, 215832g (1999).

11. L. M. Harwood and C. J. Moody, Experimental Organic Chemistry: Principles and Practice, Oxford, *Blackwell Scientific Pub.* 52, **1989**.

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AN IMPROVED SYNTHESIS OF α-METHOXY-α-(TRIFLUOROMETHYL)-PHENYLACETIC ACID (MOSHER'S ACID)

Submitted by
(06/02/00)

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Mosher's acid, α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA), is a valuable and useful reagent used for the determination of the enantiomeric purity and the absolute configuration of alcohols and amines, among other things.[1,2] During the course of an investigation into the use of chiral solvents for enantioselective organic and inorganic transformations, we required substantial quantities