11. G. H. Lee, J. P. Shields, and E. H. Piepmeier, *Spectrochim. Acta*, **43B**, 1485 (1988).
12. J. P. Shields, Gae H. Lee, and E. H. Piepmeier, *Appl. Spectrosc.*, **42**, 684 (1988).
13. S. L. Morgan and S. N. Deming, *Anal. Chem.*, **46**, 1170 (1974).
14. L. Ebdon, M. R. Cave, and D. J. Mowthorpe, *Anal. Chem. Acta*, **115**, 179 (1980).
15. S. Greenfield and D. T. Burns, *Anal. Chim. Acta*, **113**, 205 (1980).
16. J. A. Nelder and R. Mead, *Computer J.*, 7, 308 (1965).
17. S. N. Deming and S. L. Morgan, *Anal. Chem.*, **45**, 278A (1973).
18. L. A. Yarbro and S. N. Deming, *Anal. Chim. Acta*, **73**, 391 (1974).
19. A. E. Brookes, J. J. Leary, and D. W. Golightly, *Anal. Chem.*, **53**, 720 (1981).
20. P. W. J. M. Boumans, Theory of Spectrochemical Excitation, Plenum, New York, U.S.A. (1966).

Catalytic Hydrogenation of Aromatic Nitro Compounds over Borohydride Exchange Resin Supported Pd (BER-Pd) Catalyst

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Received November 4, 1992

Aromatic nitro compounds are selectively hydrogenated to the corresponding amines in high yields at room temperature and atmospheric pressure using BER-Pd catalyst without affecting ketone, ether, ester, nitrile or chloro groups also present. Especially the nitro group in 4-nitrobenzyl alcohol, methyl 4-nitrobenzyl ether and N-N-dimethyl 4-nitrobenzylamine is selectively hydrogenated with this catalyst to give the corresponding amines without hydrogenolysis of benzylic groups. And aromatic nitro compound can be reduced selectively in the presence of aliphatic nitro compound.

Introduction

Selective catalytic hydrogenation of aromatic nitro groups is important in organic synthesis, particularly when a molecule has several other reducible moieties. Although platinum, palladium or nickel catalysts may be used, nickel catalyst usually requires high pressure and platinum catalyst is regarded more selective than palladium[1] especially when the nitroaromatics also contain benzylic groups[2] or halogen[3]. Sometime ago carbon supported platinum catalyst was produced *in situ* by borohydride reduction, and nitroaromatics could be rapidly reduced to the corresponding amino derivatives at room temperature and atmospheric pressure[4].

On the other hand, Borohydride Exchange Resin (BER), readily prepared from anion exchange resion (chloride form) and aqueous sodium borohydride solution[5], is an quarternary ammonium borohydride, borohydride ion being attached on the resin. It exhibits unique reducing characteristics[6a,b] in alcoholic solvents besides the simple work up procedures[6a]. In this paper we wish to report the preparation of palladium catalyst on BER (BER-Pd) and selectivity of the catalyst in the reduction of nitroaromatics.

Results and Discussion

Preparation of Borohydride Exchange Resin Supported Palladium (BER-Pd). BER (0.5 mmol in BH_4^-) was placed in the reactor flask of Brown automatic hydrogenator[7], and flushed with nitrogen. Solution of $PdCl_2$ (0.05 mmol) in 20 m*l* ethanol (95%) was added with stirring at room temperature. Hydrogen evolution ceased in 10 min. and the preparation of BER-Pd is completed. Hydrolysis of BER-Pd thus prepared revealed the existence of approximately 0.45 mmol of BH_4^-.

Characteristics of BER-Pd Catalyst. We studied briefly the effect of temperature and catalyst/substrates ratio on the reduction of nitrobenzene. When 10 mmol of nitrobenzene is hydrogenated over 0.05 mmol Pd on BER-Pd, the hydrogenation was completed in 220 min at 0℃, 90 min at 25℃ and 80 min at 40℃. Therefore we carried out hydrogenation at room temperature. When we changed the amount of nitrobenzene hydrogenated on the fixed amount of BER-Pd (0.05 mmol) from 5 to 10, 25, 50 mmol, the time for complete reduction were 60 to 90, 180, and 390 min (Figure 1). We chose the ratio 1/200, that is 10 mmol of nitro compound was reduced over 0.05 mmol of BER-Pd.

Hydrogenation of Representative Aromatic Nitro Compounds over BER-Pd. Hydrogenation was carried out, using Brown automatic hydrogenator[4] at room temperature, 10 mmol of nitro compounds being hydrogenated over 0.05 mmol of Pd in BER-Pd. The results are summarized in Table 1.

As shown in Table 1, aromatic nitro compounds can be reduced to the corresponding amines in 1-6 h at room temperature in high yields without affecting ketone, ester, ether, hydroxy or nitrile groups also present. However, in the case of 4-chloronitrobenzene, we could obtain only 64% yield of chloroaniline together with 30% aniline, the dechlorinated

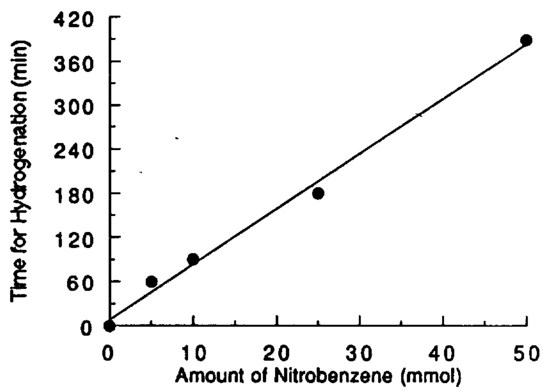
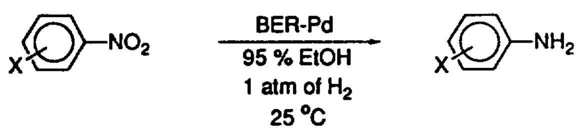


Figure 1. Relation of Reaction Time *vs.* Amount of Nitrobenzene in Fixed Amount of Palladium Catalyst (0.05 mmol).



X = H, ketone, ester, ether, carboxylic acid, hydroxy, nitrile, chloro, CH_2OH, CH_2OR, or CH_2NR_2

Scheme 1.

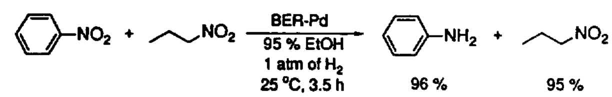
Table 1. Hydrogenation of Aromatic Nitro Compounds over BER-Pd[a]

Nitro compound	Reaction time (h)	Product	Yield (%)[b]
nitrobenzene	1.5	aniline	99
4-nitrophenol	1.5	4-aminophenol	95
4-nitroacetophenone	2.5	4-nitroacetophenone	91
2-nitroanisole	1.5	2-nitroanisole	96
2-nitrobenzoic acid	2.5	2-nitrobenzoic acid	99
ethyl 4-nitrobenzoate	3.0	ethyl 4-nitrobenzoate	96
4-nitrobenzonitrile	4.5	4-nitrobenzonitrile	96
1-nitronaphthalene	10.0	1-nitronaphthalene	99
4-chloronitrobenzene[c]	9.0	4-chloroaniline	87(90)[d]
4-nitrobenzyl alcohol	5.5	4-nitrobenzyl alcohol	99
methyl-4-nitrobenzyl ether	1.0	methyl-4-aminobenzyl ether	94
N,N-dimethyl-4-nitrobenzylamine	2.0	N,N-dimethyl-4-aminobenzylamine	98
4-nitrobenzyl acetate	3.5	4-toluidine	96

[a] Hydrogenation of 10 mmol of aromatic nitro compounds at 25℃, 1 atm over 0.05 mmol of Pd in BER-Pd in 20 m*l* 95% ethanol. [b] Isolated yields. [c] 20 mmol of HCl was added. [d] Yield was determined by GC.

product. Since the free amino group could accelerate the dehalogenation[8], we repeated the reaction by adding 2 mol equiv. of HCl, and we could isolate 4-chloroaniline in 87% yield. On the other hand, the nitro group in 4-nitrobenzyl alcohol, methyl 4-nitrobenzyl ether and N,N-dimethyl 4-nitrobenzylamine was selectively reduced with BER-Pd to give the corresponding aminobenzyl derivatives. But in case of 4-nitrobenzyl acetate it was reduced to 4-toluidine by consuming 4.0 equiv. of H_2. We also tested the selectivity of 2- and 4-nitro groups in 2,4-dinitrophenol and 2,4-dinitrobenzoic acid, however, no selectivity was observed in these cases.

Finally, we examined the selectivity of the hydrogenation between aromatic nitro compound and aliphatic nitro compound. Since aliphatic nitro compounds are hydrogenated considerably slower than aromatic nitro compounds, we thought that selective hydrogenation of aromatic nitro compound could be possible in the presence of aliphatic nitro compound. Indeed, we could reduce nitrobenzene to aniline with an excellent selectivity in the presence of nitropropane (Eq. (1)).



(1)

Experimental Section

Materials. $NaBH_4$ (98%, Nisso Ventron) was used without further purification. Anion exchange resion (Amberlite IRA-400 [20-50 mesh]) was used for supporting polymer of BER. Commercial grade, 95% ethanol was used as solvent. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. Methyl 4-nitrobenyl ether, 4-nitrobenzyl acetate, N,N-dimethyl 4-nitrobenzylamine were prepared using standard synthetic methods[9,10]. In all cases, physical constants and ^1H-NMR agreed satisfactorily with those reported in literature.

Brown Automatic Hydrogenator. For the hydrogenation of nitro compounds, Brown Automatic Hydrogenator was constructed as shown Reference 7.

Preparation of Borohydride Exchange Resin (BER). 10 g of wet chloride-form anion exchange resion (Amberlite IRA-400 [20-50 mesh]) was slurry-packed with water into a 100 m*l* fritted glass column which connected to a water aspirator. Then 200 m*l* of aqueous sodium borohydride solution (0.1 M) was slowly passed through the resin over a period of 30 minutes. The resulting resin was washed thoroughly with distilled water until free of excess $NaBH_4$. The borohydride form anion exchange resin was then dride *in vacuo* at 60℃ for 5 h. The dride resin was analyzed for borohydride content by hydrogen evolution on acidification with 2 N HCl and the average capacity of BER was found to be 3.3 mmol of BH_4^- per gram. The dried resin was stored under nitrogen at 4℃. The hydride content was constant over 6 weeks.

Preparation of Borohydride Exchange Resin Supported Palladium (BER-Pd). BER (150 mg, 0.5 mmol in BH_4^-) was placed in the reactor flask of the automatic hydrogenator, and flushed with nitrogen. With stirring, solution of palladium chloride (9 mg, 0.05 mmol) in 95% ethanol (20 m*l*) was injected into the reactor through the injection port rapidly at room temperature. The stirring was continued until hydrogen evolution ceased (5-10 min). The hydrolysis of BER-Pd thus prepared evolved 1.8 mmol of hydrogen, therefore BER-Pd contains 0.45 mmol BH_4^- together with 0.05

mmol Pd on the resin.

General Procedure of Hydrogenation. The hydrogenation was carried out in Brown Automatic Hydrogenator. The reaction flask, containing BER-Pd *in situ* prepared from BER (0.5 mmol in BH_4^-) and $PdCl_2$ (0.05 mmol) in 95% ethanol, was immersed in a water bath and maintained at 25℃ and then flushed with 1 *l* of hydrogen generated by injection of *ca.* 11 m*l* of sodium borohydride solution (1 M) into the hydrogen generator flask with stirring. The burette containing sodium borohydride solution (1 M) in 95% ethanol (stabilized with NaOH) was attached to hydrogen generator flask and then the height of the burette was adjusted to the position at which solution begins to flow just below or above the atmospheric pressure. To the reaction flask was added 10 mmol of substrate by syringe and then the reaction was initiated with stirring. The progress of hydrogenation was followed by measuring the volume of $NaBH_4$ solution used.

Hydrogenation of Aromatic Nitro Compounds over BER-Pd. Hydrogenation of 4-nitrophenol is representative. 1.391 g of nitrophenol (10 mmol) was added to the reaction flask containing 0.05 mmol of Pd on BER-Pd catalyst and hydrogenated at 25℃ and one atmospheric pressure. Hydrogenation ceased after three equiv. of hydrogen had been absorbed (90 min). Then the reaction mixture was filtered to remove the catalyst and solvent was removed on a rotary evaporator to give 1.04 g of 4-aminophenol (95% yield); mp. 186-188℃ (lit[11] 189.6-190.2℃).

Conclusions

1. Aromatic nitro compounds are selectively hydrogenated to the corresponding amines at room temperature and atmospheric pressure using BER-Pd catalyst without affecting other reducible groups also present, such as ketone, ether, ester, nitrile, chloro, benzyl alcohol, benzyl ether and benzylamino groups.

2. Aromatic nitro compound is selectively hydrogenated in the presence of aliphatic nitro compound.

Acknowledgement. This work was supported by the Lucky Company and the Organic Chemistry Research Center sponsored by the Korea Science and Engineering Foundation.

References

1. P. Rylander, *Catalytic Hydrogenation in Organic Synthesis*, Academic Press, New York, pp. 114-134 (1979).
2. M. A. Avery, M. S. Verlander, and M. Goodman, *J. Org. Chem.*, **45**, 2750 (1980).
3. F. S. Dovell and H. Greenfield *J. Am. Chem. Soc.*, **87**, 2767 (1965).
4. H. C. Brown and K. Swasankaran, *J. Am. Chem. Soc.*, **84**, 2828 (1962).
5. H. W. Gibson and F. C. Bailey, *J. Chem. Soc. Chem. Commun.*, 815 (1977).
6. (a) N. M. Yoon, K. B. Park, and Y. S. Gyoung, *Tetrahedron Lett.*, **24**, 5367 (1983); (b) G. W. Kabalka, P. P. Wadgaonkar, and N. Chatla, *Synth. Commum.*, **20**, 293 (1990) and references therein.
7. C. A. Brown and H. C. Brown, *J. Org. Chem.*, **21**, 3989 (1966).
8. R. Baltzly and A. P. Phillips, *J. Am. Chem. Soc.*, **68**, 261 (1946).
9. D. Horton, *Org. Syntheses, Coll.* Vol. **5**, John Wiley and Sons, New York, pp. 1-5 (1973).
10. (a) E. White, *Org. Syntheses, Coll.* Vol. **5**, John Wiley and Sons, New York, pp. 336-339 (1973); (b) H. C. Brown and D. Heim, *J. Am. Chem. Soc.*, **86**, 912 (1973); (c) H. C. Brown and D. Heim, *J. Org. Chem.*, **38**, 912 (1973).
11. *The Merck Index, 11th ed.*, Merck and Co. Inc., New Jersey, p. 475 (1989).

Synthesis and Radical Polymerization of *p*-(2,2,3,3-Tetracyanocyclopropyl)phenyl Acrylate and Methacrylate

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p-(2,2,3,3-Tetracyanocyclopropyl)phenyl acrylate (**3a**) and *p*-(2,2,3,3-tetracyanocyclopropyl)phenyl methacrylate (**3b**) were prepared by the reactions of bromomalononitrile with *p*-acryloyloxybenzylidenemalononitrile (**2a**) or *p*-methacryloyloxybenzylidenemalononitrile (**2b**), respectively. Compounds **3a** and **3b** were polymerized with free radical initiators to obtain the polymers with multicyano functionalities in the cyclopropane ring. The resulting polymer **4a** was soluble in acetone but the polymer **4b** was not soluble in common solvents. The inherent viscosities of polymers **4a** were in the range of 0.10-0.15 dL/g in acetone and those of **4b** were in the range of 0.20-0.30 dL/g in 98% sulfuric acid. Solution-cast films were cloudy and brittle, showing T_g values in the range of 106-125℃.

Introduction

Piezoelectric polymers have long been the subject of curiosity and have caused recent interest.[1] It is well-known that crystalline polymers having large dipole moment can exhibit piezoelectric effects if the main chains have all-planar zigzag