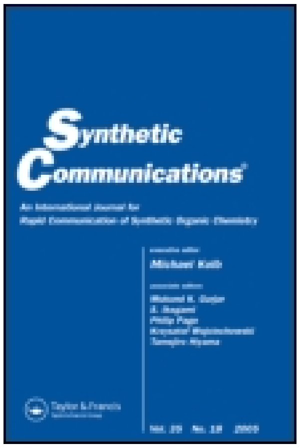

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A Simple and Efficient Method for the Reduction of Azo Compounds

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ABSTRACT

Reduction of azo compounds using hydrazine hydrate as reducant without catalyst is described, which proceeded smoothly in mild condition and did not pollute the environment.

There are many methods of reduction of azo compounds reported in the literature. Of many reductive systems, traditional metals such as Li,[1,2] Cu,[3] Na,[4] and their complexes are usually used as reductants. Organic compounds such as sulfonyl hydrazide,[5] anilines,[6]

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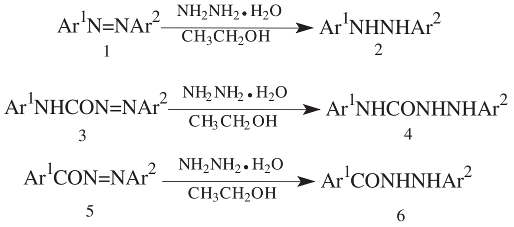
substituted aliphatic amines,[6] saturated acyclic hydrocarbon[7] have good effect as reductants. It was reported that azobenzene had also been successfully reduced by catalytic hydrogenation,[8] sodium amalgam,[9] aluminum amalgam,[10] zinc in alcoholic ammonia,[11] and stannous chloride[12] in ethanolic sodium hydroxide. Although these systems have their own merits, they also have drawbacks, for example: reaction conditions are not mild, catalysts and reductants are expensive, operation are tedious, the functionality such as the nitro and carbonyl groups contained azo compounds are also reduced, and in some cases, azo compounds are easily over reduced to arylamines, not the desired product.

Hydrazine hydrate is well known as reductant. It has been used in a variety of reactions. In previous study, it was reported that with hydra-



$$\underset{1}{Ar^1N{=}NAr^2} \xrightarrow[CH_3CH_2OH]{NH_2NH_2 \cdot H_2O} \underset{2}{Ar^1NHNHAr^2}$$

$$\underset{3}{Ar^1NHCON{=}NAr^2} \xrightarrow[CH_3CH_2OH]{NH_2NH_2 \cdot H_2O} \underset{4}{Ar^1NHCONHNHAr^2}$$

$$\underset{5}{Ar^1CON{=}NAr^2} \xrightarrow[CH_3CH_2OH]{NH_2NH_2 \cdot H_2O} \underset{6}{Ar^1CONHNHAr^2}$$

Scheme 1.

Table 1. Results of reduction of azo compounds.

Entry	Ar^1	Ar^2	Reaction time (min)	M.p. (°C)	Lit. m.p. (°C)	Yield (%)
2a	C_6H_5	C_6H_5	30	121–123	125–127[15]	92
2b	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	20	131–132	133–134[15]	88
2c	p-ClC_6H_4	p-ClC_6H_4	30	121–122	122[15]	91
2d	p-$CH_3OC_6H_4$	C_6H_5	40	69–71	71–72[15]	88
2e	p-BrC_6H_4	p-BrC_6H_4	35	128–130	130[15]	94
2f	3,4-$Me_2C_6H_3$	3,4-$Me_2C_6H_3$	20	104–106	106–107[15]	91
4a	p-FC_6H_4	C_6H_5	20	144–146	147–148[16]	69
4b	p-ClC_6H_4	C_6H_5	30	182–184	184–186[16]	90
4c	p-BrC_6H_4	C_6H_5	30	200–202	204–205[16]	79
4d	p-$CH_3C_6H_4$	C_6H_5	180	204–205	207–209[16]	86
4e	m-ClC_6H_4	C_6H_5	20	156–158	159–160[16]	70
6a	p-$O_2NC_6H_4$	C_6H_5	45	193	193–195[17]	77

zine hydrate with catalyst (such as Cu^{++}),[13] reduction of symmetrical multiple bonds proceeded readily, whereas reactions of more polar functions were more difficult. Cinnamic acid has been selectively reduced with hydrazine hydrate catalyzed by Raney Ni to produce 3-phenylpropanoic acid.[14] We tried to reduce azo compounds with hydrazine hydrate without catalyst. It was demonstrated that this is an effective reagent to reduce azo compounds. All actions proceeded smoothly with good yields. The results are summarized in Table 1. Compared to the above systems, merits of this system lie in convenient operation, mild reaction condition, easily accessible reagents, high selectivity, and without pollution.

EXPERIMENTAL

Typical Procedure

Hydrazine hydrate (1 mL) was added to a solution of azo compounds (0.2 mmol) in ethanol (5 mL). The reaction mixture was heated at 60°C. After being stirred for 20 min–3 h (the reaction was detected by the color, which changed from deep red to colorless). The solution was poured into ice. Then, the crystals obtained were filtrated and dried. The crude product was recrystallized from 95% ethanol.

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