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AMMONIUM SULPHATE - MAGNESIUM PROMOTED SELECTIVE REDUCTION OF AROMATIC NITRO COMPOUNDS

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Various nitroarenes and 2,1,3-benzooxadiazole-1-oxides were selectively and rapidly reduced to their corresponding amino and diamino compounds respectively in high yields using $(NH_4)_2SO_4-Mg/Al/Bi$, a new reduction system.

There has been growing interest in the use of metallic elements in synthetic chemistry and various metals have been successfully used for this purpose. Selective reduction of nitro compounds is an area of considerable synthetic potential, particularly when a molecule has several other reducible functionalities. Therefore, numerous new reagents have been developed for the reduction of nitro compounds, some of which are incompatible with other substituents on the aromatic ring. In continuation of our studies on metal catalysts, we would

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like to report here the first example of $(NH_4)_2SO_4$ -Mg, promoted selective reduction of nitroarenes and 2,1,3-benzooxadiazole-1-oxides to the corresponding amines and diamines respectively. This new system reduced with ease a wide variety of nitroarenes (1) directly to the corresponding aromatic amines and many functional groups can

be tolerated. When magnesium metal is replaced by aluminium or bismuth the reduction proceeds effectively and the products were obtained in almost comparable yields.

In a typical experiment , a solution of 4-chloro nitrobenzene (1.6 g, 0.01 mol) was added to a mixture of magnesium (1.4 g, 0.06 mol) and ammonium sulphate (0.10 mol, dissolved in 3 ml of water) in methanol (20 ml). The resulting mixture was stirred at 50° C for 0.5 hr., and after usual work-up the product 4-chloroaniline was obtained in 90% yield. Similarly benzofuroxan oxides (3) were reacted and the corresponding diamines were obtained in (80-85)% yields. The results are summerised in the table. In the case of carbonyl substituted nitroarenes, the corresponding aniline was obtained in high yield without any further reduction of carbonyl group. Furthermore, aromatic halides showed remarkable

Table: Reduction of aromatic nitro compounds by $(NH_4)_2SO_4-Mg/Al/Bi$ system⁶.

Entr	y R	Time min.	Yield (%) ⊍ith Mg	Yield (%) .with A	Yield (%) 1 with 8:	M.p. (°C)	Reported m.p.
1a	p - C1	30	90	85	76	68 -6 9	69-71
1ь	p-1	25	83	80	60	62-63	62-63
1c	p-Me	20	80	75	7 5	45-46	45-46
1d	p-NH20C	10	83	7 9	70	180-81	181-82
1 e	p-H0 ₂ C	20	75	7 0	72	188-89	188-89
1 F	p-MeC	35	75	80	75	57 - 58	5 7- 60
1 g	p-Et 0 ₂ C	15	80	80	75	88-90	88-90
1h	p-CH3CO	15	75	75	70	104-06	106-07
1 i	p-CN	32	78	80	75	82-83	83 - 85
3a	н	15	80	75	70	101-02	102-03
3ь	5(6)-01	20	85	-	-	72-73	76
3 c	5(6)-Me	20	80		-	87 - 88	89-90

selectivity to give the amino product without giving any dehalogenation. As iodo groups are often cleaved by catalytic hydrogenation and metal-acid reductions⁴. nitrosobenzene and 2,1,3-benzoexadiazole-1-oxides were reduced to form the corresponding azobenzene and dieximes respectively⁵. During our studies we found that 2,1,3-benzoexadiazole-1-oxides were reduced with $(NH_4)_2SO_4$ -Mg system at ambient temperature to produce the corresponding amines respectively as the sole product.

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In conclusion, these results demonstrated a rapid versatile and selective reducing system for a wide variety of nitro compounds in the presence of other functional groups for e.g. -C=N, -C=O, -COOEt, -COOH, Cl,I etc. The method is chemoselective and the reagents employed are readily available, inexpensive, stable, easy to handle and non toxic.

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- 6. The products were identified by comparision of M.p. and spectral data with standard samples.

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