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SELECTIVE REDUCTION OF AROMATIC NITRO COMPOUNDS CONTAINING O- AND N-BENZYL GROUPS WITH HYDRAZINE AND RANEY NICKEL

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Abstract: *The selectivity in the catalytic reduction of aromatic nitro compounds containing O-benzyl, N-benzyl or chlorine with hydrazine and Raney nickel was studied.*

The reduction of aromatic nitro compounds can be realized by means of hydrazine in the presence of several catalysts as., for example, Pd-C, Pt-C or Raney Ni[1]. However, the selectivity of these reductions is known only in haloaromatic nitro compounds[2]. To date, no systematic study has been made of the reduction of aromatic nitro compounds containing hydrogenolyzable groups such as benzyl, although this type of reduction has been accomplished using $SnCl_2$-HCl[3], Fe-HCl[4], Zn/HCl[5] or, more recently, by direct catalytic hydrogenation in the presence of PtO_2- K_2CO_3[6] or Pt-C[7]. It has been found that the selective reduction of aromatic nitro compounds containing O-benzyl, N-benzyl or chlorine is easily obtained by refluxing for 5-10 minutes a methanolic solution of the nitro compound with hydrazine hydrate (5 equivalents) and Raney Ni(∿ 150 mg). The advantages of this procedure are the avoidance of strong acidic media and that no pressure apparatus is needed.

The reduction of m-nitrophenyl benzyl ether provides an example of the method: To a refluxing mixture of 1.25 g (25 mm) of hydrazine hydrate, 20 ml of methanol and 150 mg of Raney Ni, a solution of 1.145 g (5 mm) of m-nitrophenyl benzyl ether in 20 ml of methanol was added dropwise. After addition was completed reflux was maintained for 10 minutes. The Raney Ni was separated by filtration over Celite and the solvent evaporated. Dry hydrogen chloride was bubbled into the residue dissolved in benzene. The yield of m-aminophenyl benzyl ether hydrochloride was 96%.

Similar results were obtained with other nitro compounds (Table I), no other products were isolated from the reaction mixtures. When the reaction was applied to the reduction of o-chloro or p-chloro-m-nitrophenyl benzyl ether, the corresponding halogenated anilines were obtained without traces of dehalogenated products. The products were identified by elemental analysis, IR, NMR and mass spectra evidence.

T A B L E I

Reduction of aromatic nitro compounds with hydrazine and Raney Ni.

Compound	Product	% Yield	Melting Point or Boiling Point (Literature)
o-nitrophenyl benzyl ether	o-aminophenyl benzyl ether	73	112°-113°/0.1 mm (125-131°/0.2 mm)[3]
m-nitrophenyl benzyl ether	m-aminophenyl benzyl ether	96[a]	143°-144° (d)
p-nitrophenyl benzyl ether	p-aminophenyl benzyl ether	40	141°-142°/0.1 mm (201-202°/11 mm)[8]
2,4-dinitrophenyl benzyl ether	2,4-diaminophenyl benzyl ether	69[b]	135° (d)
2-chloro-3-nitro phenyl benzyl ether	2-chloro-3-amino phenyl benzyl ether	92	oil[c]
4-chloro-3-nitro phenyl benzyl ether	4-chloro-3-amino phenyl benzyl ether	79	77°-78°
o-nitrophenyl benzyl amine	N-benzyl-o-phenylen-diamine	70[a]	138° (d)
4-benzylamino-3-nitro toluene	N^4-benzyl-3,4-diamino toluene	62[a]	120° (122°)[5]

[a]Isolated as hydrochloride. [b]Isolated as dihydrochloride. [c]Homogeneous by TLC.

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