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SELECTIVE AND SEQUENTIAL HYDROGENATION OF NITROAROMATICS CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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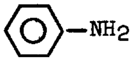
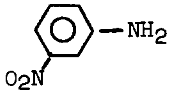
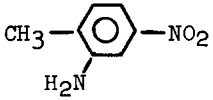
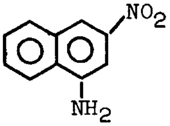
The intrinsic high degree of selectivity characteristic of many homogeneous catalytic systems is now well recognized, but this aspect of $C-NO_2$ hydrogenation has for the most part been overlooked. We have described in a previous paper the application of dichlorotris(triphenylphosphine)ruthenium(II), and related ruthenium and iron complexes, to the hydrogenation of nitroparaffins to secondary alkyl primary amines[1]. Here we report on the unusual selectivity properties exhibited by solutions of $RuCl_2(PPh_3)_3$ when applied to the catalytic hydrogenation of nitroaromatics. The reduction of $PhNO_2$ proceeds rapidly at initial $PhNO_2/Ru$ mole

$$PhNO_2 + 3H_2 \longrightarrow PhNH_2 + 2H_2O \qquad (1)$$

ratios of 200 or more to give aniline in near quantitative yields (eq 1). Other substituent groups, including halogen, alkoxide, alkyl, aryl, ester and nitrile, may also be present without suffering degradation during the $C-NO_2$ reduction[2]. Generally the introduction of a second nitro group into the aromatic ring increases the rate of reduction, and for p-dinitrobenzene, hydrogenation proceeds smoothly to give p-nitroaniline in good yields (see Table I). Other dinitroaromatics, including m-dinitrobenzene, may also be reduced to the corresponding nitroaniline derivatives by this technique, or reduction may be allowed to proceed to the fully reduced diamines.

The ability of the homogeneous $RuCl_2(PPh_3)_3$ solutions to selectively hydrogenate dinitroaromatic substrates to their partially reduced derivatives may be put

TABLE 1

		Reaction	--------Major Products---------	
Nitroaromatic	Conversion(%)[a]	Time,Min	Identity[b]	Selectivity(Mole %)
Nitrobenzene	100	45		96[c]
p-Nitrotoluene	100	180		92[d]
p-Dinitrobenzene	95	75		91
m-Dinitrobenzene	77	210		73
2,4-Dinitrotoluene	42	180		91
1,3-Dinitronaphthalene	95	120		71

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[a] Hydrogenation Conditions: 2.5-4.0 mM $RuCl_2(PPh_3)_3$ in 1:1 (V/V) benzene, ethanol; 0.1-0.72 M $PhNO_2$; 120-135°; 80 atm H_2.

[b] Identified by nmr, ir, glpc and, in some cases, by elemental analyses.

[c] Run in presence of 0.14 M KOH, selectivity to aniline in absence of alkali, 89%.

[d] Selectivity to amine for other p-substituted nitrobenzenes; p-Cl, 89 mole %; p-Br, 67 mole %; p-OH, 96 mole %; p-CH_3O, 81 mole %; p-CN, 78 mole %.

to further advantage where one wishes to sequentially hydrogenate dinitroaromatic, nitroaromatic mixtures. This is illustrated in Figure 1 for an equimolar mixture of nitrobenzene and p-dinitrobenzene. The following reaction sequence is observed: 1) Initial selective reduction of the p-dinitrobenzene component to p-nitroaniline. 2) Concurrent reduction of the nitrobenzene and newly formed p-nitroaniline components. Here it is considered significant that almost all (>90%) of the p-dinitrobenzene is converted to p-nitroaniline prior to any significant reduction of the nitrobenzene, or reduction of the intermediate p-nitroaniline to p-phenylenediamine. Similar cases of sequential hydrogenation are now being investigated for other mononitro-dinitroaromatic mixtures.

The high degree of selectivity achieved here in hydrogenating polynitroaromatics to nitroamines is unusual, particularly for non-hindered dinitroaromatics such as m- and p-dinitrobenzene[3,4]. The hydrogenation of m-dinitrobenzene over platinum black is reported by Vesely and Rein[5] to yield m-nitroaniline, but for most heterogeneous catalysts, reduction proceeds without breaks in the kinetic curves[3]. We are not aware of any previous illustration of sequential hydrogenation as depicted in Figure 1.

For $RuCl_2(PPh_3)_3$ catalysis, rates of hydrogenation of para substituted nitroaromatics (vide supra) vary by a factor of about ten, but these moderate differences in rate cannot, by themselves, account for the observed selectivity. A second factor is likely to be preferential complexation of the dinitroaromatic components with the catalytically active ruthenium hydrido species[1] as a result of the greater degree of N-O bond polarization[6]. Certainly this explanation is consistent with the improved selectivity observed in hydrogenating para versus meta dinitrobenzenes (Table 1), and with the order of sequential hydrogenation exemplified in Figure 1.

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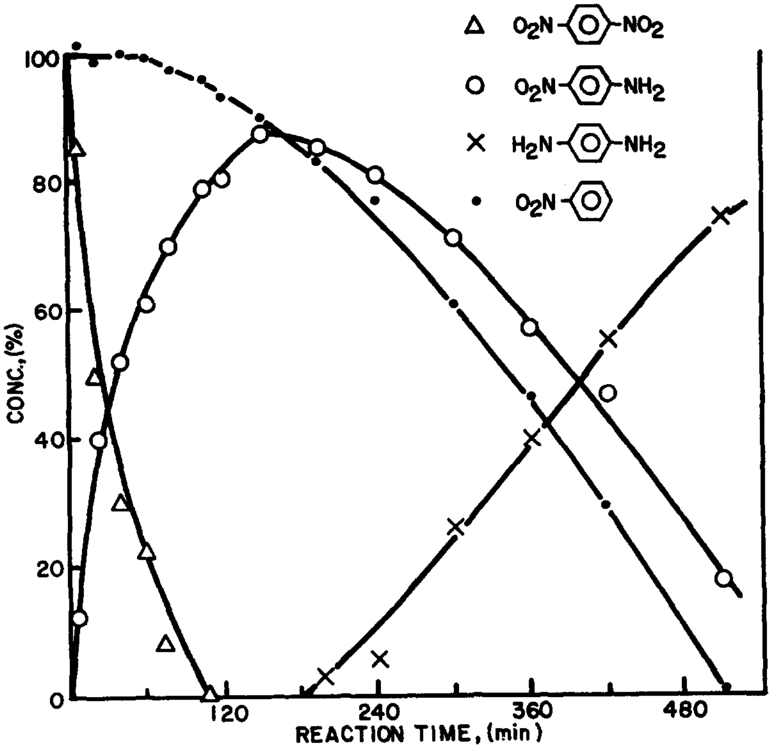

FIGURE 1[a,b]. The sequential hydrogenation of an equimolar p-dinitrobenzene-nitrobenzene mixture.

[a] Run conditions: 2.5 mM $RuCl_2(PPh_3)_3$; 0.13 M $C_6H_4(NO_2)_2$; 135°; 80 atm H_2.

[b] A small quantity of aniline is formed during p-dinitrobenzene reduction, aniline formation from nitrobenzene is not included in this Figure, but is estimated to be produced in > 85 mole % yield.

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