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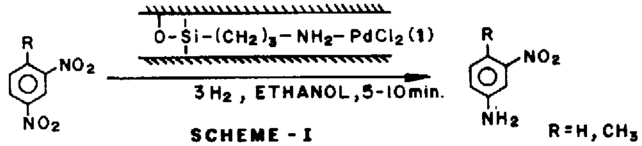
SELECTIVE AND SEQUENTIAL REDUCTION OF NITROAROMATICS BY MONTMORILLONITESILYLAMINEPALLADIUM(II) COMPLEX

K. Mukkanti, Y.V. Subba Rao and B.M. Choudary*

Homogeneous Catalysis Discipline
Regional Research Laboratory, Hyderabad 500 007, INDIA

Abstract : Nitroaromatics are sequentially and selectively hydrogenated in quantitative yields at room temperature and atmospheric pressure by interlamellarmontmorillonitepalladium(II) complex, a heterogenised homogeneous catalyst.

Selective and sequential reduction of nitroaromatics is of current interest[1]. Reagents[2], and heterogeneous catalyst[3] successfully induced the near quantitative selectivity in the reduction of nitroaromatics at moderate temperatures or pressures, and relatively long time. Although homogeneous catalytic systems are widely employed for selective hydrogenation of alkynes and alkenes, a few reports are available concerning C-NO_2 selective reductions. $RuCl_2$ $(PPh_3)_3$ could hydrogenate selectively polynitroaromatics with the aid of stringent experimental conditions (80 atm., 135°C)[4]. Herein we report a selective and sequential hydrogenation of nitroaromatics (Table 1) by a truely heterogenised homogeneous catalyst, interlamellar montmorillonitesilylaminepalladium(II) complex (1)[5] for the first time in quantitative yields. The hydrogenation of dinitroaromatics proceeds very rapidly to give mononitrocompounds selectively at room temperature and atmospheric pressure, initial nitroaromatics/Pd mole ratio is 200.



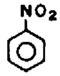
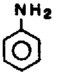
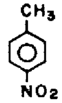
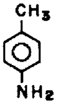
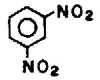
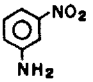
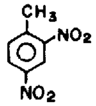
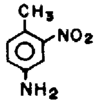
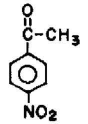
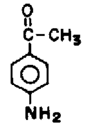
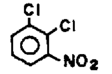
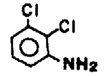
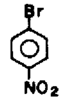
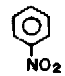
SCHEME - I

Thus m-dinitrobenzene, 2,4-dinitrotoluene (entry No. 3,4) are selectively and sequentially hydrogenated to nitroanilines and to diamines. The most impressive characteristic of the present catalytic system is that the aromatic systems are easily hydrogenated while aliphatic ones are inert. This advantage is put to practical use for selective hydrogenation of 2-(4-nitrophenyl)nitroethane (entry No.9) to 2-(4-aminophenyl)nitroethane. Nitro groups are preferentially subjected to sequential hydrogenation in presence of chloro, aldehyde and keto groups (entry No.5-7). However, the bromo group (entry No.8) is preferentially reduced in presence of nitro group.

Consistent activity and selectivity has been shown in hydrogenation of m-dinitrobenzene for four recycles. The elemental, XRD and IR data of the used catalyst are almost identical to the catalyst before hydrogenation. When the used catalyst was subjected to Bailer's method[6] 93% Pd was leached by ethanolic cyanide indicating the Pd in the used catalyst remains dominantly in the divalent state. The catalyst displayed negligible activity after treatment. All these results demonstrate that hydrogenation is effected via homogeneous route.

The simple, convenient and rapid method described here, compares well with other reducing agents/heterogeneous catalysts[2,3] and is superior to the use of homogeneous catalysts[4] with regard

TABLE-1 : SELECTIVE AND SEQUENTIAL HYDROGENATION OF NITROAROMATICS

ENTRY NO.	SUBSTRATE[a]	PRODUCT[b]	YIELD(%)[c]
1			98
2			97
3			99
4			98
5			95
6			97
7			95
8			98
9			98

a Hydrogenation conditions: 5.0 mmol of substrate, 100 mg (0.025 mmol of Pd) catalyst, 20 ml of ethanol; b Identified by IR, NMR, GLC and elemental analyses; c Isolated yields.

to selectivity. It also has the additional advantage of reusability, as demonstrated, when compared with the latter.

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4. J.F. Knifton, **Tetrahedron Lett.**, 2163 (1975); J.F. Knifton, **J.Org.Chem.,41**, 1200 (1976).
5. Catalyst synthesis is as follows: H-Montmorillonite(10.0g), which was prepared from natural montmorillonite K10(Fluka)by treating first with saturated NaCl followed by 0.1 N HCl, on reaction with 3-aminopropyltriethoxysilane (1.55g, 7.0 mmol) in dry toluene under reflux for 48 hrs to afford montmorillonite interlamellar 3-aminopropyltriethoxysilane. This on complexation with bis (benzonitrile)palladium(II)chloride (Aldrich) (2.0 mmol for 1.0 g ligand) in dry benzene gave the catalyst (1). For further details : Y.V. Subba Rao, K. Mukkanti and B.M. Choudary, **J.Mol.Cat.** (In press).
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