

The Reductive Potential of Dodecacarbonyltri-iron on Basic Alumina

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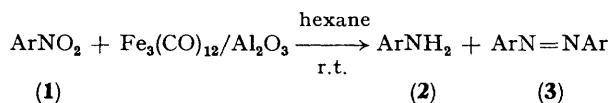
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Summary Dodecacarbonyltri-iron on basic alumina constitutes a simple, mild, and convenient method for reducing nitroarenes to aromatic amines.

By-products of these reactions were the azo compounds (3, 4—7% yield). The inertness of the carbonyl-group in the reaction of *p*-nitrobenzophenone is noteworthy.

The recent publications by Basset, Chauvin, and co-workers^{1,2} concerning the formation of the hydrido(undecacarbonyl)triferrate anion, $\text{HFe}_3(\text{CO})_{11}^-$, by interaction of dodecacarbonyltri-iron with alumina prompts us to report our results in this area. One of us has described the use of hexacarbonylmolybdenum, supported on alumina or silica, for effecting desulphurization³ and dehalogenation⁴ reactions under gentle conditions.

The reduction of nitrobenzenes to anilines was examined as a basis for determining the utility of $\text{Fe}_3(\text{CO})_{12}$ on alumina as a reagent system in synthesis. The trinuclear iron hydride, $\text{HFe}_3(\text{CO})_{11}^-$, generated by stirring a hexane solution of $\text{Fe}_3(\text{CO})_{12}$ with basic alumina (Woelm; dried *in vacuo* at 150—200 °C) until the adsorbant turned red (*ca.* 2 h), was treated with an equimolar amount of a nitro-



pound (1) overnight at room temperature. Work-up (trituration of the solid with ether or methylene chloride, followed by silica gel chromatography with hexane-ether) gave the aromatic-amines (2) in 40—79% yields (Table).

TABLE. Yields of aromatic amines (2).

(1)	(2) ^a	Yield ^b /%
<i>p</i> -Nitrotoluene	<i>p</i> -Toluidine	64
<i>m</i> -Nitrotoluene	<i>m</i> -Toluidine	40
<i>o</i> -Nitroanisole	<i>o</i> -Anisidine	51
<i>p</i> -Nitroanisole	<i>p</i> -Anisidine	73
<i>p</i> -Chloronitrobenzene	<i>p</i> -Chloroaniline	70
<i>p</i> -Nitrobenzophenone	<i>p</i> -Aminobenzophenone	68
2-Nitrofluorene	2-Aminofluorene	79

^a Products were identified by comparison with authentic materials. ^b The quoted yields are of the pure, isolated products and are not gas chromatography yields.

This heterogeneous reaction occurs under significantly milder conditions than the homogeneous one (refluxing benzene, 10—17 h)⁵ and the isolation of pure products is also much simpler.

In conclusion, dodecacarbonyltri-iron on alumina is a reducing reagent system of considerable potential.

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⁴ H. Alper and L. Pattee, *J. Org. Chem.*, 1979, **44**, 2568.

⁵ J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, 1972, **37**, 930.