THE PREPARATION OF AMINES AND HYDRAZO COMPOUNDS USING HYDRAZINE AND PALLADIZED CHARCOAL[1]

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ABSTRACT

The reduction of nitro compounds to amines by ethanolic hydrazine and palladized charcoal probably proceeds through the nitroso and hydroxylamine derivatives. This reagent is shown to be useful for the reduction of azo to hydrazo compounds.

The reduction of nitro compounds to amines using ethanolic hydrazine and Raney nickel (2, 3) or palladized charcoal (10, 24) as catalyst offers many advantages over classical reducing agents. In particular, the catalyzed hydrazine reductions are very rapid and give high yields of easily isolable amines without the use of special apparatus.

The earlier work showed that hydrazine–palladium was useful for the preparation of aniline, the toluidines, phenylenediamines, *p*-aminobenzoic acid, and aminofluorescein (24), and the amino derivatives of polynuclear hydrocarbons (10). The present work, most of which is summarized in Table I in the Experimental section, extends the usefulness of the method and points out some limitations.

The reduction of 2,2′-dinitrodiphenyl proceeded erratically, the products obtained depending on the activity of the catalyst. A highly active palladium-on-charcoal catalyst gave 2,2′-diaminodiphenyl in good yield, but a less active one gave a mixture of the diamine with benz-[*c*]-cinnoline. The latter compound could be obtained pure in 92% yield using Raney nickel of low activity[3] as catalyst.

Ortho- and *p*-chloronitrobenzene and *p*-nitrophenylacetonitrile did not give pure amines. 2,5-Dichloronitrobenzene gave, very rapidly, an excellent yield of β-(2,5-dichlorophenyl)-hydroxylamine and, more slowly, 2,5-dichloroaniline. 2-Chloro-5-nitroterephthalic acid (11) and 2-fluoro-5-nitrotoluene gave good yields of the amines.

The reduction of nitrobenzene, which has been reviewed by Sidgwick (25), is known to proceed through nitrosobenzene and β-phenylhydroxylamine to aniline, much of our knowledge being due to Haber (17) and Brand (4, 5, 6). Goldschmidt showed (13, 14, 15, 16) that the relative rates of reduction were in the order nitrosobenzene > β-phenylhydroxylamine > nitrobenzene, explaining the difficulty encountered in isolating nitrosobenzene as a reduction product except under rigorously controlled conditions. In alkaline media nitrosobenzene and β-phenylhydroxylamine condense to form azoxybenzene, giving rise to another series of reduction products.

The hydrazine–palladium reagent reduces nitro- and nitroso-benzene and β-phenylhydroxylamine to aniline, but azo- and azoxy-benzene are reduced to hydrazobenzene.[4] These facts suggest that the reduction of nitro compounds to amines by this reagent proceeds through monomeric compounds, as shown below in route I. The isolation of

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[3] *The Raney nickel catalyst was W1 (1, 8), which had been stored for several months at 0° under absolute methanol.*

[4] *It is interesting to note that fermenting yeast will reduce nitro- and nitroso-benzene and β-phenylhydroxylamine but not azo- or azoxy-benzene, to aniline (23).*

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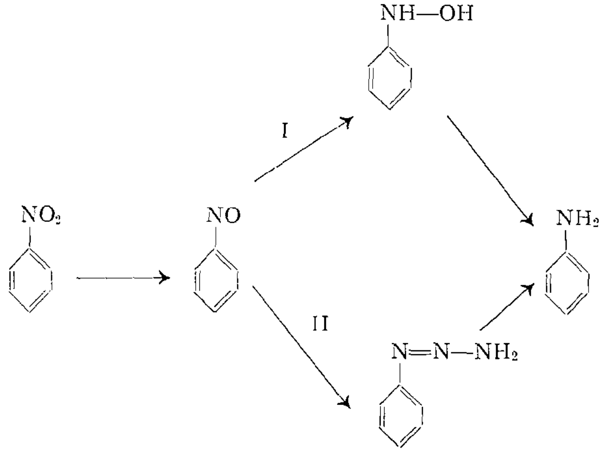
β-(2,5-dichlorophenyl)-hydroxylamine as a reduction product of 2,5-dichloronitrobenzene lends strong support to this mechanism.



An alternative mechanism is shown, route II, based on the known easy condensation of nitrosobenzene with many amines and phenylhydrazine. Hydrazine was found to react rapidly with nitrosobenzene but the red oil obtained appeared to be stable to hydrazine–palladium, making route II improbable.

The reduction of azobenzene to hydrazobenzene by hydrazine–palladium is a considerable improvement on the usual zinc – alcoholic potash method. An excess of hydrazine is advantageous since it appears to protect the hydrazobenzene during crystallization. Hydrazo-*o*-diphenyl was also prepared in good yield, and the method may prove to be generally useful for the preparation of hydrazo compounds.

EXPERIMENTAL

Melting points are uncorrected. The active palladium-on-charcoal catalyst was 10%, supplied by Baker and Co., Newark, New Jersey; the less active catalyst was an old sample.

The reductions were carried out essentially as described by Pietra (24). Most of the results are presented in Table I. Wherever possible the identity of a product was confirmed by taking the melting point of a mixture with an authentic sample, and by taking the infrared spectrum. Many of the amines were acetylated to aid isolation.

o-Chloronitrobenzene did not give a pure product. *p*-Chloronitrobenzene gave, after several crystallizations from benzene, impure *p*-chloroacetanilide (27%), m.p. 171–175° (lit. m.p. 178° (19)).

β-(2,5-Dichlorophenyl)-hydroxylamine

Hydrazine hydrate (4 ml.) was added to a suspension of 2,5-dichloronitrobenzene (5 g.) and active 10% palladium-on-charcoal (0.1 g.) in ethanol (100 ml.). The vigorous exothermic reaction was over in 2 minutes, as shown by a pronounced slackening in the rate of nitrogen evolution. After the catalyst was removed by filtration, the solution was poured into ice water (500 ml.). A white solid separated and was collected, washed, and dried by suction. The yield was almost quantitative.

Recrystallization was achieved by dissolving the product in hot benzene (100 ml.),

TABLE I[1]

Compound	Isolated as:	%	M.p.	Lit. m.p.
Nitrobenzene	Acetanilide	91	110–112	113–114 (19)
Nitrosobenzene	Acetanilide	93	109–111	113–114 (19)
β-Phenylhydroxylamine	Acetanilide	89	112–113	113–114 (19)
Azobenzene	Hydrazobenzene	84[2]	125–126	126–127 (19)
Azoxybenzene	Hydrazobenzene	79[2]	125–126	126–127 (19)
Azoxy-*o*-diphenyl	Hydrazo-*o*-diphenyl	70[2]	172–176[3]	182 (12)
4,6-Dinitro-*m*-xylene	N,N′-Diacetyl-4,6-diamino-*m*-xylene	87	290–292	295 (19)
1-Nitro-2-naphthylamine	1,2-Diaminonaphthalene[4]	85	96–98	98.5 (19)
5-Nitro-6-amino-2-methylpyridine	5,6-Diamino-2-methylpyridine	82	64–67	69–70 (20)
o-Nitrophenol	*o*-Aminophenol	88	171–173	174 (19)
2-Nitrofluorene[7]	2-Aminofluorene	97	127–128	129 (19)
2-Fluoro-5-nitrotoluene	6-Fluoroaceto-*m*-toluidide	88	76–77	74 (7)
2-Nitrodiphenyl	2-Aminodiphenyl	89	47–49	49–50 (19)
4-Nitrodiphenyl	4-Aminodiphenyl	92	51–53	50–52 (19)
2,2′-Dinitrodiphenyl[5]	N,N′-Diacetyl-2,2′-diaminodiphenyl	88	162–164	161 (19)
6,6′-Dimethyl-2,2′-dinitrodiphenyl	6,6′-Dimethyl-2,2′-diaminodiphenyl	63[6]	133–135	136 (19)

[1] *Yield and melting point refer to crude dried product unless otherwise indicated.*

[2] *Crystallized from ethanol containing hydrazine.*

[3] *Melting point with decomposition and dependent on the rate of heating.*

[4] *Characterized by condensation with phenanthraquinone to give 1,2;3,4;5,6-tribenzphenazine, yellow prisms from xylene, m.p. 272–273° (lit. m.p. 273° (21)).*

[5] *Using a catalyst of low activity, a mixture of the diamine with benz-[c]-cinnoline, m.p. 155–156°, was obtained.*

[6] *The low yield is probably due to the use of only 0.1 g. of nitro compound.*

[7] *Raney nickel has been used as the catalyst for this reduction, a yield of 100% being claimed (22).*

adding a little anhydrous magnesium sulphate to remove traces of water, and decanting off the supernatant solution. Addition of hot heptane gave, on cooling, long white needles, m.p. 95–96° with decomposition to a black tar. The melting point depended on both the rate of heating and the crystal size, powdered samples having m.p. 93–94° (lit. m.p. 93° (9)). The melting point was not depressed when the product was mixed with an authentic sample, prepared by Lapworth's general method (18). The identity was confirmed by oxidation to 2,5-dichloronitrosobenzene, m.p. 99–100° (lit. m.p. 101° (9)), and by comparison of infrared spectra. Sharp peaks at 3600 and 3340 cm.$^{-1}$ in the spectra of dilute chloroform solutions were probably O—H and N—H stretching bands since the spectrum of β-phenylhydroxylamine was identical in that region.

Recrystallized β-(2,5-dichlorophenyl)-hydroxylamine is stable at 0° but heating a benzene solution on the steam bath for a few minutes causes extensive decomposition to a brown tar.

When the reduction was carried out for 24 hours, 2,5-dichloroaniline was obtained, m.p. and mixed m.p. 49–50° (lit. m.p. 50° (9)).

Benz-[c]-cinnoline

2,2′-Dinitrodiphenyl was reduced using the general method described by Balcom and Furst (2). After the catalyst was removed by filtration, the filtrate was concentrated to give, on cooling, benz-[*c*]-cinnoline as yellow prisms, m.p. 155–156° (lit. m.p. 156° (19)). The yield was consistently greater than 90% when a weakly active Raney nickel catalyst was used.

Benz-[*c*]-cinnoline picrate crystallized from benzene as dark yellow prisms, m.p. 194–195° (lit. m.p. 194° (19)).

NOTE ADDED IN PROOF

Since this paper was accepted for publication, two more articles have become available (26, 27) which deal with some uses of hydrazine as a reducing agent in the presence of metal catalysts.

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