Communications

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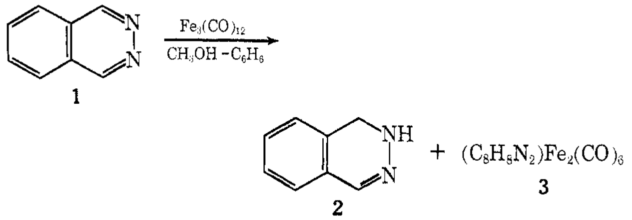
A Convenient Reduction of the Carbon–Nitrogen Double Bond

Summary: The carbon–nitrogen double bond can be conveniently reduced by reaction of the appropriate organic (or organometallic) compound with a mixture of triiron dodecacarbonyl [$Fe_3(CO)_{12}$] and methanol in benzene.

Sir: Recent interest in the use of hydridoiron carbonyl complexes as reagents for hydrogenating α,β-unsaturated carbonyl compounds[1] and for preparing aromatic amines from nitro compounds[2] prompts the author to communicate a new, simple method for reducing a carbon–nitrogen double bond.

Treatment of phthalazine (**1**) with $Fe_3(CO)_{12}$ in refluxing methanol–benzene for 12–16 hr {conditions which generate the hydridoundecacarbonyltriferrate anion [$HFe_3(CO)_{11}^-$]}, followed by chromatography on Florisil, gave 1,2-dihydrophthalazine (**2**, mp 83.5–85.0°) in 54% yield and a small amount of complex **3**. Controlled potential electrolysis is the only other reported way for effecting direct conversion of **1** to **2**.[3]



1 **2** **3**

The generality of this hydridoiron carbonyl reduction was demonstrated by similar reaction of $Fe_3(CO)_{12}$–CH_3OH with a number of Schiff bases bearing various substituents. The results listed in Table I indicate that this transformation occurs in reasonable–very good yields and hence shows promise as a synthetically useful organic reaction.

TABLE I

Reactant	Product[a]	Yield, %
1	**2**	54
N-(*p*-Methoxybenzylidene)aniline	*p*-Methoxy-*N*-phenylbenzylamine	52
p-*n*-Butyl-*N*-(*p*-methoxybenzylidene)aniline	*p*-Methoxy-*N*-(*p*-*n*-butylphenyl)benzylamine	62
N-Benzylideneaniline	*N*-Benzylaniline	88
p-Hexyloxy-*N*-(ferrocenylidene)aniline	*p*-Hexyloxy-*N*-phenylferrocenylmethylamine	83
N-(*p*-carbomethoxybenzylidene)aniline	*p*-Carbomethoxy-*N*-phenylbenzylamine	71
N-Isopropylidene-*n*-butylamine	Isopropyl-*n*-butylamine	47

[a] Known products were identified by comparison of melting points and spectral data with those reported in the literature. Satisfactory analytical data was obtained for new compounds.

The following procedure is typical. A mixture of $Fe_3(CO)_{12}$ (2.67 g), dry methanol (2.7 ml), and dry benzene (35 ml) was refluxed with stirring under nitrogen for 2.25 hr. *p*-Hexyloxy-*N*-(ferrocenylidene)aniline (1.56 g, 4.0 mmol), dissolved in benzene (10 ml), was added to the hydridoiron carbonyl solution and the resulting mixture was refluxed for 15 hr. The solution was cooled and filtered, and the filtrate was evaporated *in vacuo*. The residue from evaporation was chromatographed on Florisil to give *p*-hexyloxy-*N*-phenylferrocenylmethylamine on elution with petroleum ether (bp 38–50°).

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DEPARTMENT OF CHEMISTRY
STATE UNIVERSITY OF NEW YORK
AT BINGHAMTON
BINGHAMTON, NEW YORK 13901
HOWARD ALPER

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(1) R. Noyori, I. Umeda, and T. Ishigami, *J. Org. Chem.*, **37**, 1542 (1972).

(2) J. M. Landesberg, L. Katz, and C. Olsen, *ibid.*, **37**, 930 (1972).

(3) H. Lund and E. T. Jensen, *Acta Chem. Scand.*, **24**, 1867 (1970).

Formylation of Aromatic Compounds with Hexamethylenetetramine and Trifluoroacetic Acid

Summary: A variety of aromatic compounds have been converted to aldehydes *via* a facile formylation process employing hexamethylenetetramine and trifluoroacetic acid.

Sir: In the Duff reaction,[1-3] hexamethylenetetramine is employed, usually with glyceroboric acid, to convert highly activated aromatic compounds to their formyl derivatives. The process is quite limited in scope, having been most widely used in the conversion of phenols to *o*-hydroxybenzaldehyde derivatives. The required conditions are rigorous, and the yields are generally low.

When the hexamethylenetetramine is used in conjunction with trifluoroacetic acid, a variety of aromatic compounds, including simple hydrocarbons, can be converted to imine products which are transformed to the aryl aldehydes on hydrolysis (eq 1). The required

$$\mathrm{ArH} + \mathrm{C_6H_{12}N_4} \xrightarrow[2.\ \mathrm{H_2O}]{1.\ \mathrm{CF_3COOH}} \mathrm{ArCHO} \qquad (1)$$

conditions are mild, and good yields of pure products can be easily isolated. A high order of para regioselectivity is exhibited.

Thus, a mixture of 12.2 g of 2,6-xylenol (100 mmol),

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(1) J. C. Duff, *J. Chem. Soc.*, 547 (1941).

(2) C. F. H. Allen and G. W. Leubner, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 866.

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