Selective Hydrogenation of 2,6-Dinitroanilines

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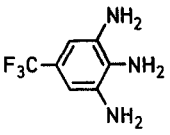
The selective reduction of *m*-dinitrobenzenes to *m*-nitroanilines has provided the basis for the synthesis of otherwise unattainable compounds. These reductions have most commonly involved the sulfide ion in a basic medium. Such conditions become a problem when substituted *m*-dinitrobenzenes are used and this was the problem faced in this laboratory when a number of nitroorthophenylene diamines were required as intermediates. The reductions of 2,6-dinitroanilines to 3-nitro-*o*-phenylene diamines have been reported using ammonium sulfide[1] or sodium hydrosulfide[2]; however, these reagents gave only moderate yields and product mixtures difficult to purify. Two of the intermediates contained functional group which gave a reaction with the basic conditions causing the yield to be reduced. Thus, reaction of methyl 4-amino-3,5-dinitrobenzoate[3] (**1e**, X= $COOCH_3$) gave a 21% yield of the corresponding diamine using sodium hydrosulfide, and the corresponding acid, **1b**, precipitated from the reaction medium.

To avoid these problems a catalytic hydrogenation technique was investigated. Reduction of 4-amino-3,5-dinitrobenzotrifluoride (**1c**)[4] over 10% palladium on carbon in ethanol/chloroform at room temperature and 3 atm[5] gave complete reduction to the triamine **3** which was isolated as the hydrochloride and gave a base with m.p. 91–91.5°, the spectroscopic properties of which were consistent with the structure **3**.



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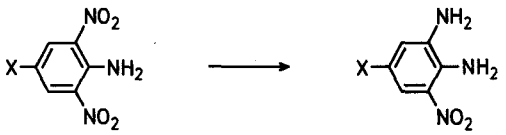
Moderation of hydrogenation occurred by using 1,2-dimethoxyethane instead of ethanol as solvent and selectivity of the reduction to the nitro-*o*-phenylene diamines was achieved in good to excellent yields which were superior in every case to those reported using the basic sulfides (Table).

General Procedure:
A solution of the dinitroaniline (600 mmol) in 1,2-dimethoxyethane (150 ml) and chloroform (15 ml) was hydrogenated over 10% palladium on charcoal (600 mg) at low pressure (3 atm) and ambient temperature. The mixture was allowed to absorb the theoretical amount of hydrogen required to reduce one nitro group

Table. Selective Hydrogenation of 2,6-Dinitroanilines



1 2

	X	Reaction time	M.p.	Lit. m.p.	Recryst. solvent	Yield (%)	Reference
a	$COOC_2H_5$	15 h	199–200°	—	C_6H_6/C_6H_{14}	63[a]	—
b	COOH	3 h	275°	275°		89	5
c	CF_3	1 h	123.5–125°	121–123°	CCl_4	58	6
d	CH_3	1.5 h	152–154°	152–154°	H_2O	81	1
e	$COOCH_3$	—[b]	214–215.5°	—	—	21[c]	—

[a] Analysis: $C_9H_{11}N_3O_4$ (225.2) calc. C 48.00 H 4.92 N 18.66 found 48.22 4.90 18.30

[b] Using sodium hydrosulfide.

[c] Bright red platelets; analysis: $C_8H_9N_3O_4$ (211.2) calc. C 45.50 H 4.29 N 19.90 found 45.93 4.35 20.05

to an amino function (3 mol-eq.). The reaction was stopped, and the catalyst was removed by filtration through a Celite pad. The filtrate was poured into an evaporating dish and the solvent was allowed to evaporate in a hood. [Compound **2** is isolated simply by pouring the filtrate into a large excess of chloroform and collecting the resulting precipitate by filtration.] Recrystallization from the appropriate solvent afforded the desired phenylenediamines as bright red solids.

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