The Reduction of Nitroarenes with Sodium Dihydrobis-(2-methoxyethoxy)aluminate

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SODIUM DIHYDROBIS-(2-METHOXYETHOXY)ALUMINATE[1] is a reducing agent of similar properties to lithium aluminium hydride and has recently been made available commercially.† The reagent is soluble in ethers and in aromatic hydrocarbons and is reported to be safer in use than lithium aluminium hydride. The latter reagent is known to reduce aromatic nitro-compounds to azo-derivatives.[2] During the reduction of halogenonitroarenes with lithium aluminium hydride,[3] iodine is usually eliminated, as is bromine, when *ortho* to the nitro-group or to a chlorine atom.

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† Chemapol, Prague, Czechoslovakia.

The reduction of aromatic nitro-compounds with this new reagent, in benzene, gives azo-compounds (Table) in yields comparable with those obtained using lithium aluminium hydride:

$$2ArNO_2 + 4NaH_2Al(OCH_2{\cdot}CH_2{\cdot}OMe)_2 \rightarrow ArN{:}NAr + 4NaAlO(OCH_2{\cdot}CH_2{\cdot}OMe)_2$$

With 1·5 mol. of the hydride the azoxy-compound is obtained.

In the reduction of halogeno-nitro-arenes, iodine and bromine are always eliminated but chlorine is retained. That elimination occurs prior to the formation of the azo-compound is indicated by the formation of azoxybenzene when bromonitrobenzenes are reduced with 2 mol. of the hydride. Furthermore, when only 1 mol. of hydride was used a small quantity of nitrobenzene was isolated.

The reaction is general (Table) and can be employed for the synthesis of symmetrically substituted chloro-, alkyl-, alkoxy-, dialkylamino-, and hydroxyalkyl-azo- and -azoxy-compounds, and of cyclic azo-compounds such as benzo[*c*]cinnoline. With chloro- and dimethylamino-nitrobenzenes, the reduction to the azoxy-compound is rapid but further reduction is slow and, for preparative purposes, a short period under reflux is advisable. Even under these conditions, 2,2′-dichloroazoxybenzenes are not reduced.

Reduction of nitroarenes with sodium ***dihydrobis***-(2-*methoxyethoxy*)*aluminate**

Nitrobenzene derivative	Hydride (mol.)	Product	M.p. Found	M.p. Lit.	Yield (%)
Nitrobenzene	2	Azobenzene	69	69	92
4-Me	2	4,4′-Dimethylazobenzene	144	144	95
4-MeO	2	4,4′-Dimethoxyazobenzene	164	165	83
2-Cl	2†	2,2′-Dichloroazoxybenzene	51—52	56	38
3-Cl	2†	3,3′-Dichloroazobenzene	101	101	85
4-Cl	1·5	4,4′-Dichloroazoxybenzene	158	158	78
4-Cl	2†	4,4′-Dichloroazobenzene	184	184	76
2,5-Cl$_2$	1·5	2,5,2′,5′-Tetrachloroazoxybenzene	141	145	35
3,4-Cl	2	3,4,3′,4′-Tetrachloroazobenzene 3,4,3′,4′-Tetrachloroazoxybenzene	158 142	158 139	15 40
2-Br	2	Azoxybenzene	35—36	36	62
3-Br	2·5	Azobenzene	69	69	84
4-Br	2	Azoxybenzene	34—36	36	75
2-I, 3-I, 4-I	2·5	Azobenzene	69	69	60—70
3-Br,4-Cl,5-Me	2·5†	4,4′-Dichloro-3,3′-dimethylazobenzene	166	166	65
4-Me$_2$N	2·0	4,4′-Dis(dimethylamino)azoxybenzene‡	252	244·5	80
4-Me$_2$N	2·0†	4,4′-Dis(dimethylamino)azobenzene	278	266	85
3-Me$_2$N	1·5	3,3′-Dis(dimethylamino)azoxybenzene	94	88—89	90
3-Me$_2$N	2·0†	3,3′-Dis(dimethylamino)azobenzene	116	118	95
3-CO$_2$Et	4·0†	3,3′-Dis(hydroxyethyl)azobenzene	106	106	68
(2-Nitronaphthalene)	2·0	2,2′-Azonaphthalene	205	208	78
(1-Nitronaphthalene)	2·0	No azo compound	—	—	—
(2,2′-Dinitrobiphenyl)	2·0	Benzo[*c*]cinnoline	156	156	76

* Reagent added to ice-cold solution of nitro-compound and the reaction allowed to proceed at room temperature for 20 min. unless stated otherwise; † Heated (reflux) for 30 min.; ‡ Product separated during reaction.

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[1] J. Vit, B. Casensky, and J. Machacek, Fr. Patent 1,515,582/ 1967.
[2] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, 1948, **70**, 3738.
[3] J. F. Corbett and P. F. Holt, *J. Chem. Soc.*, 1963, 2385.