# 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 halogeno-nitroarenes 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.

*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 | 158 | 158 | 15 |
|  |  | 3,4,3′,4′-Tetrachloroazoxybenzene | 142 | 139 | 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-$Me_2N$ | 2·0 | 4,4′-Dis(dimethylamino)azoxybenzene‡ | 252 | 244·5 | 80 |
| 4-$Me_2N$ | 2·0† | 4,4′-Dis(dimethylamino)azobenzene | 278 | 266 | 85 |
| 3-$Me_2N$ | 1·5 | 3,3′-Dis(dimethylamino)azoxybenzene | 94 | 88—89 | 90 |
| 3-$Me_2N$ | 2·0† | 3,3′-Dis(dimethylamino)azobenzene | 116 | 118 | 95 |
| 3-$CO_2Et$ | 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.

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.

(*Received, July* 29*th*, **1968**; *Com.* 1045.)

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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.