Drynap Reduction. III. The Preparation of Symmetrically-substituted Azo Compounds

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In a previous paper of this series,[1] one of the present authors showed that the reduction of nitrobenzene with a commercial sodium-lead alloy, "Drynap", in an ethanol solution is suitable for the preparation of azobenzene. The present experiment was undertaken to extend this reduction to the preparation of many kinds of symmetrically-substituted azo compounds.

Twenty-four kinds of aromatic nitro compounds were subjected to the Drynap reduction in an ethanol solvent at 40—50°C, and the reduced products were identified with the authentic compounds by mixed-melting-point determinations and by a study of their infrared spectra. The results are listed in Table 1.

As expected, *o*-, *m*-, and *p*-isomers of nitrotoluene, nitrochlorobenzene, and nitrobromobenzene were reduced with Drynap in an ethanol solution to the corresponding symmetrically-substituted azobenzenes in 70—90% yields.

Three isomers of nitroanisole were also subjected to the Drynap reduction under the same conditions, but the results were somewhat different. 3-Nitroanisole gave 3,3′-azoanisole in a 85% yield, but 2-nitroanisole gave 2,2′-azoxyanisole and 2,2′-azoanisole in comparable yields (35% and 40% respectively). On the other hand, 4-nitroanisole gave 4,4′-azoxyanisole exclusively (yield, 92%). 4-Nitrophenetole was also subjected to this reduction; 4,4′-azoxyphenetole was obtained in a 90% yield. In the reduction of nitroaniline, however, the materials were almost all recovered.

4-Nitroacetanilide, 4-nitrodiphenyl, and 2,5-dichloronitrobenzene were also treated with a sodium-lead alloy in an ethanol solvent; the corresponding azo compounds were obtained in tolerably good yields. 1-Nitronaphthalene was reduced with Drynap in the same way, but the products were 1,1-azonaphthalene and 1-naphthylamine (yields, 25% and 32% respectively). The yield of azonaphthalene was improved to 65% by keeping the reaction temperature at 0—5°C.

1,3-Dinitrobenzene, 2,4-dinitrotoluene, 2,4-dinitrochlorobenzene, and 2,4-dinitrobromobenzene were also subjected to the Drynap reduction, but the reaction mixture turned red-purple as soon as the sodium-lead alloy was added, and a resinous substance was obtained. Ethanol solutions of 5-nitroquinoline and 5-nitroisoquinoline turned purple and brown respectively with the alloy, and the objective azo products were not obtained. The above color development may be due to the formation of Meisenheimer-type complexes with

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[1] K. Tabei and K. Natou, This Bulletin, **39**, 2300 (1966).

TABLE 1. DRYNAP REDUCTION OF AROMATIC NITRO COMPOUNDS

Material	Product	Mp, °C	Yield, %
Nitrobenzene	Azobenzene		
2-Methyl-	2,2′-Dimethyl-	56	78
3-Methyl-	3,3′-Dimethyl-	54—55	75
4-Methyl-	4,4′-Dimethyl-	143	85
2-Chloro-	2,2′-Dichloro-	135	81
3-Chloro-	3,3′-Dichloro-	103—104	75
4-Chloro-	4,4′-Dichloro-	189	86
2-Bromo-	2,2′-Dibromo-	135	73
3-Bromo-	3,3′-Dibromo-	127	80
4-Bromo-	4,4′-Dibromo-	203—204	85
2-Methoxy-	2,2′-Dimethoxy-	141—142	40
	2,2′-Azoxyanisole	81	35
3-Methoxy-	3,3′-Dimethoxy-	77—78	85
4-Methoxy-	4,4′-Azoxyanisole	118 (134)*	92
4-Ethoxy-	4,4′-Azoxyphenetole	137 (165)*	90
4-Phenyl-	4,4′-Diphenyl-	248—250	35
4-Acetamino-	4,4′-Azoacetanilide	280—282	20
2,5-Dichloro-	2,2′,5,5′-Tetrachloro-	187—188	45
1-Nitronaphthalene	1,1′-Azonaphthalene-	197—198	25 (65)**
	1-Naphthylamine	50	32
Nitroanilines			failed
m-Dinitrobenzene and its CH_3-, Cl- and Br- deriv.			
5-Nitro-quinoline and isoquinoline			
4-Nitrobenzyl cyanide			

* Exhibits anisotropy; Turbid liquid turns clear at the parenthesized temperature.

** The reaction temperature was kept at 0—5°C.

an ethoxide anion.[2] Therefore, the present reduction seemed to be unsuitable for such dinitro and *N*-heterocyclic nitro compounds as those above.

A similar color development was encountered in the reduction of 4-nitrobenzyl cyanide; the reaction mixture turned wine-red as soon as the alloy was added. This color development may be due to the formation of sodium salt of 4-nitrobenzyl cyanide.[3]

From the above results, the Drynap reduction may be recommended as a convenient method for the preparation of symmetrically-substituted azo compounds from the corresponding nitro compounds except for a few particular cases. This reduction, however, seemed to be unsuitable for compounds sensitive to a nucleophilic attack such as di- and polynitro compounds or *N*-heterocyclic nitro compounds, since a complex formation or salt formation takes place prior to the reduction. On the other hand, an electron-donating group at the position para or ortho to the nitro group may depress the reactivity of the latter group.

Experimental

Materials. Commercial nitro compounds of a G. R. grade were purified by the usual methods and used. The authentic azo- and azoxy-compounds were derived from the corresponding nitro compounds by the usual methods.[4]

Reduction Procedure. To an ethanol solution (40—50 m*l*) of 1 g of a material (0.004—0.007 mol), 10 g of the commercial sodium-lead alloy "Drynap" (containing 0.04 mol of sodium metal) was added in small portions at 40—50°C. After the reaction mixture has been stirred for 1.5 hr, the ethanol solution was separated from the alloy and the residual spongy sludge was washed with ethanol. The ethanol solution and the washing solution were evaporated in one lot, and the residue was extracted with ether. The ether solution was washed with 5% hydrochloric acid and water, and dried over sodium sulfate.

The crude product obtained by the evaporation of ether was dissolved again in benzene and passed through an alumina column.

The product collected as a fraction was then separated from the solvent by evaporation and recrystallized from ethanol, ligroin, or a benzene-ligroin mixture.

Each product was identified with an authentic compound by mixed-melting-point determination and by a study of their infrared spectra.

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[2] J. Meisenheimer, *Ann.*, **323**, 205 (1902); D. L. Hammick and R. Foster, *J. Chem. Soc.*, **1954**, 2153; T. Abe, This Bulletin, **32**, 778 (1959); L. K. Dyall, *J. Chem. Soc.*, **1960**, 5160.

[3] V. v. Richter, *Ber.*, **21**, 2475 (1888); J. Lifschitz and F. W. Jenner, *ibid.*, **48**, 1730 (1915).

[4] E. C. Horning, "Organic Syntheses," Coll. Vol. III, p. 103 (1955); G. Schultz, *Ber.*, **17**, 465 (1884); L. Gattermann, "Die Praxis des Organischen Chemikers," Walter de Gruyter & Co., Berlin (1961), p. 162.