

Summary

Azobenzene is reduced by the system $\text{Mg} + \text{MgI}_2$ to iodomagnesium-hydrazobenzene according to the reaction $\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5 + \text{Mg} + \text{MgI}_2 \longrightarrow \text{C}_6\text{H}_5(\text{MgI})\text{N}-\text{N}(\text{MgI})\text{C}_6\text{H}_5$.

Azoxybenzene is reduced by the binary system to azobenzene or to the hydrazobenzene derivative according to the amount of reducing agent employed.

Substituted azobenzenes and azoxybenzenes react in the manner of the unsubstituted compounds except that in certain instances reduction proceeds to a considerable extent beyond the hydrazobenzene stage.

Nitrosobenzene is reduced principally to iodomagnesium-hydrazobenzene according to the following formulation: $2\text{C}_6\text{H}_5\text{N}=\text{O} + 3\text{Mg} + 3\text{MgI}_2 \longrightarrow \text{C}_6\text{H}_5(\text{MgI})\text{N}-\text{N}(\text{MgI})\text{C}_6\text{H}_5 + 2(\text{MgI})_2\text{O}$. Azobenzene is formed as an intermediate product in this reaction.

The results obtained, in agreement with those of previous studies, lend support to the hypothesis that the active reducing agent is MgX , generated by interaction of magnesium and magnesium halide.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OHIO STATE UNIVERSITY]

CONDENSATIONS OF SECONDARY AMINES WITH NAPHTHOLS AND ALDEHYDES. II

BY WALLACE R. BRODE AND JOSEPH B. LITTMAN

RECEIVED JANUARY 10, 1931

PUBLISHED APRIL 6, 1931

In earlier papers by the authors a description has been given, of the preparation¹ of a few condensation products of the type which might be associated with the intermediates formed in the Claisen or Knoevenagel reactions, and the resolution of one of these condensation products (1-(α -1-piperidylbenzyl)-2-naphthol),² into its optical antipodes. The present paper describes the preparation of several more condensation products involving other aromatic and aliphatic aldehydes. A preparation is also described in which α -naphthol is used in place of β -naphthol in these condensations.

The mechanism of the α -naphthol condensation was shown to be the same as that of the β -naphthol condensation by the preparation of the α -naphthol derivative through the interaction of benzylidene-dipiperidine and α -naphthol.

The structure of the naphthol derivative (2-(α -1-piperidylbenzyl)-1-

¹ Littman and Brode, *THIS JOURNAL*, **52**, 1655 (1930).

² Brode and Littman, *ibid.*, **52**, 5056 (1930).

naphthol) was assigned by analogy from similar condensation products which have been previously prepared and analyzed.^{3,4,5}

Experimental

The tertiary amines described in this paper were prepared by the following general method: 0.1 mole of naphthol (α - or β -) and 0.1 mole of aldehyde were dissolved in 10 cc. of absolute alcohol and to this solution 0.1 to 0.15 mole of secondary amines was added. The solution generally darkened in color and a rise in temperature was noted. On standing from two days to five months the crystalline amine separated out, which was then easily recrystallized from ligroin-alcohol or benzene-alcohol mixtures. The yields varied from 20 to 70% of the theoretical. The hydrochlorides were prepared by passing dry hydrogen chloride gas into a benzene solution of the amine.

TABLE I
PREPARATION, CONSTANTS AND ANALYSES OF AMINES

Amine (β -Naphthol)	Naphthol	Aldehyde	Amine	M. p., °C.	Analyses, %	
					Calcd.	Found
1-(α -Di- <i>n</i> -propylaminobenzyl)-2-	β -	Benz-	Di- <i>n</i> -Pr	95	N, 4.2	4.06
1-(α -Dimethylaminoanisyl)-2-	β -	Anis-	Dimethyl ^a	132	N, 4.56	4.37
1-(α -1-Piperidylanisyl)-2-	β -	Anis-	Piperidine	134.5	Cl, 9.2	9.07
1-(α -Dimethylaminopiperonyl)-2-	β -	Piperonal	Dimethyl ^a	120	N, 4.36	4.34
2-(α -1-Piperidylbenzyl)-1-	α -	Benz-	Piperidine	110	Cl, 10.0	9.9

^a An excess of dimethylamine was introduced as a gas.

The tertiary amine, 2-(α -1-piperidylbenzyl)-1-naphthol is very soluble in ether and only slightly soluble in alcohol. The alcohol solution is colored light yellow and on heating the color becomes very intense. On cooling the alcohol solution in a freezing mixture, the color disappears and on warming it reappears. This process may be repeated many times with no apparent effect on the resulting crystalline product or its melting point.

Summary

Several new condensation products formed by the interaction of secondary amines, aromatic aldehydes and β -naphthol have been prepared and described. A description is also given of the application of this type of condensation to secondary amines, aromatic aldehydes and α -naphthol.

COLUMBUS, OHIO

³ Betti, *Gazz. chim. ital.*, **31**, II, 209 (1901).

⁴ Borche and Berkhout, *Ann.*, **330**, 104 (1904).

⁵ Auwers and Dombrowski, *ibid.*, **344**, 289 (1906) [indicates condensation in 4 position].