hydride caused exothermic decarboxylation with elimination of the theoretical amount of carbon dioxide. The reaction mixture was worked up by hydrolizing the boron trifluoride complex that was formed. No more anhydride could be detected, the decarboxylation yielding ethyl benzoate exclusively, in excellent yield.

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SUMMIT, N. J.

[CONTRIBUTION FROM THE CARWIN CO.]

Ketones as Catalysts in the Reduction of Aromatic Nitrogen Compounds

ADNAN A. SAYIGH

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The use of aromatic ketones in catalytic amounts in the methanolic sodium hydroxide reduction of *o*-nitrotoluene has considerably improved the yields of the desired azoxytoluene; further reduction of the latter and of azoxybenzene to their hydrazo derivatives has been effected by the use of a catalytic amount of 9-fluorenone.

Aromatic hydrazo compounds are available *via* the reduction of azoxy or azo compounds,[1-10] which are intermediates in the properly controlled reduction of nitro compounds. The direct reduction of nitro compounds to the corresponding hydrazo derivatives can be accomplished with zinc dust and sodium hydroxide or electrolytically; both procedures have been used to give the simplest member, hydrazobenzene.[7,11]

The chemical reduction of *o*-nitrobromobenzene to dibromohydrazobenzene is accomplished with the halo groups remaining intact[12]; many electrolytic reduction procedures have been reported with yields varying from 50 to 95%.[10,13]

A magnesium-magnesium iodide system has also been employed as a reducing agent for the azobenzenes.[14]

The earliest method of reducing aromatic nitro compounds[4] to their azoxyderivatives by the use of methanolic sodium methoxide is limited in its application, mainly because the reduction of the nitro compounds does not proceed beyond the azoxy stage, and it is confined to substituted nitrobenzenes in which the substituents are not affected by the reagent. Thus, in the case of *o*-chloronitrobenzene, considerable displacement of the chloride with methoxide ion occurs, and in the case of nitrotoluenes, extensive intramolecular oxidation-reduction takes place.[15]

In order to extend the scope of this method to the reduction of azoxy and azo compounds to their hydrazo derivatives and to improve the yields of the former, a number of catalysts were investigated. In the reduction of *o*-nitrotoluene (Table I), the addition of 3–5% of a ketone as a catalyst to the reducing medium has considerably increased both the yield and the purity of azoxytoluene; also, 9-fluorenone is an effective catalyst in the reduction of azo and azoxy benzene and toluene (Table I) to their corresponding hydrazo derivatives.

Bamberger, *et al.*[16] proposed that the formation of azoxybenzene in the reduction of nitrobenzene results from condensation between the intermediates phenyl hydroxylamine and nitrosobenzene; this has been further confirmed by Ogata, *et al.*,[17] who also found that a rapid equilibrium takes place between phenyl hydroxylamines and nitrosobenzene. The poor yield of azoxytoluene encountered in the methanolic sodium hydroxide reduction of *o*-nitrotoluene could be attributed in

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(1) H. E. Bigelow and D. B. Robinson, *Org. Syntheses*, **Coll. Vol. III**, 103 (1955).

(2) R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **70**, 3738 (1948).

(3) M. Busch and K. Schulz, *Ber.*, **62**, 1458 (1929).

(4) H. S. Fry and J. L. Cameron, *J. Am. Chem. Soc.*, **49**, 864 (1927); C. M. Suter and F. B. Dains, *J. Am. Chem. Soc.*, **50**, 2733 (1928).

(5) H. E. Bigelow and A. Palmer, *Org. Syntheses*, **Coll. Vol. II**, 57 (1943).

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(7) P. Ruggli and M. Kinovker, *Helv. Chim. Acta*, **17**, 396 (1934).

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(9) C. Weygand, *Organic Preparations*, Interscience Publishers, New York, 1945, p. 249.

(10) S. Swann, Jr., *Technique of Organic Chemistry*, A. Weissberger, Ed., Vol. II, Interscience Publishers, New York, 1956, p. 486.

(11) L. Gattermann and H. Wieland, *Laboratory Methods of Organic Chemistry*, The Macmillan Company, New York, 1938, p. 184.

(12) H. R. Snyder, C. Weaver, and C. D. Marshall, *J. Am. Chem. Soc.*, **71**, 289 (1949).

(13) S. Swann, Jr., *Trans. Electrochem. Soc.*, **69**, 307 (1936); **77**, 479 (1940).

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TABLE I

Compound	Catalyst, g.	Product	Yield, %
o-Nitrotoluene[a]	None	Azoxytoluene	62
o-Nitrotoluene[a]	9-Fluorenone, 5	Azoxytoluene	93
o-Nitrotoluene[a]	Benzanthrone, 5	Azoxytoluene	90
o-Nitrotoluene[a]	Anthrone, 5	Azoxytoluene	84
o-Nitrotoluene[a]	Benzophenone, 5	Azoxytoluene	78
o-Nitrotoluene[a]	Xanthone, 5	Azoxytoluene	76
Azoxybenzene[b]	None	Azoxybenzene	—
Azobenzene[b]	9-Fluorenone, 5	Hydrazobenzene	98
Azoxybenzene[b]	9-Fluorenone, 5	Hydrazobenzene	98
Azoxytoluene[b]	9-Fluorenone, 5	Hydrazotoluene	83

[a] In this experiment, 137 g. (1 mole) of *o*-nitrotoluene was reduced with 80 g. of sodium hydroxide and 80 g. of methanol.
[b] In this experiment, 140 g. of azo or azoxy compound was reduced with 108 g. of sodium hydroxide and 192 g. of methanol.

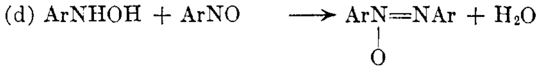
large part to an extensive oxidation of the methyl group in *o*-nitrotoluene.[15] The addition of a catalytic amount of a ketone, therefore, appears to decrease the extent of this side reaction by increasing both the rate of the formation of nitrosotoluene and its subsequent reduction to *o*-tolylhydroxylamine; the latter, in turn, condenses with the nitroso compound to give azoxytoluene. Similarly 9-fluorenone acts as a catalyst in the reduction of azo and azoxy compounds to their hydrazo derivatives with methanolic sodium hydroxide, a reagent quite ineffective for this reduction without the catalyst. In both of these cases, 9-fluorenone has presumably acted as an intermediary in the reaction; its role as a catalyst, therefore, must involve its initial reduction to fluorenol by the reducing medium, resulting in the formation of the rapid oxidation-reduction system[18,19] fluorenone-fluorenol, equation (a), which is essential in effecting further reduction of the azo and azoxy compounds to their hydrazo derivatives. In fact, fluorenol was an equally effective catalyst in these reductions, and when fluorenone was refluxed in methanolic sodium hydroxide, it was converted quantitatively to fluorenol. The various steps in the reductions could be formulated by the following reaction sequence:

(a) $\mathrm{Fluorenone + CH_3ONa \longrightarrow Fluorenol + HCOONa}$

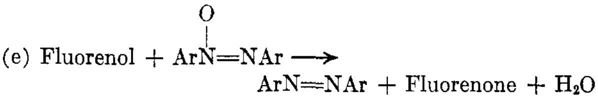
$\mathrm{Fluorenone \rightleftharpoons Fluorenol}$

(b) $\mathrm{Fluorenol + ArNO_2 \longrightarrow Fluorenone + ArNO + H_2O}$

(c) $\mathrm{Fluorenol + ArNO \rightleftharpoons Fluorenone + ArNHOH}$



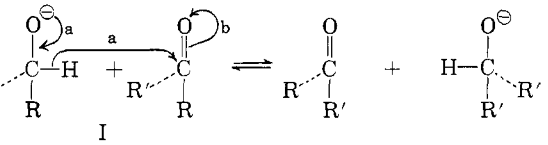
(d) $\mathrm{ArNHOH + ArNO \longrightarrow Ar\underset{\displaystyle O}{\underset{|}{N}}{=}NAr + H_2O}$



(e) $\mathrm{Fluorenol + Ar\overset{\displaystyle O}{\overset{|}{N}}{=}NAr \longrightarrow ArN{=}NAr + Fluorenone + H_2O}$

(f) $\mathrm{ArN{=}NAr + Fluorenol \rightleftharpoons ArNHNHAr + Fluorenone}$

The mechanism for the base-catalyzed carbinol-carbonyl equilibrium was formulated by Woodward, *et al.*,[20] in close analogy to Hammett's mechanism for the Cannizzaro reaction,[21] involving the direct transfer of hydrogen with its two bonded electrons from the carbinol carbon to the carbonyl carbon. Further, Doering and Aschner[22] have demonstrated that the mechanism of the equilibrium proceeds through a carbon to carbon transfer of hydrogen with its electrons, and was unaffected by substances which often inhibit free-radical chain reactions. The role of the alkoxide is probably to facilitate hydride transfer (I, Process a)



I

and to increase the acceptor capacity of the carbonyl carbon (I, Process b). In fact, in the absence of alkoxide ion, such an equilibrium is too slow to be detectable.

Doering and Aschner[23] have used the rapid oxidation-reduction system fluorenol—fluorenone in the stereochemical equilibration of optically active secondary alcohols and the epimerization of fenchol.

To illustrate the mechanism of the fluorenol-catalyzed reduction of an aromatic nitro compound, nitrobenzene to azoxybenzene, two schemes could be written: (A) where the nitrogen, the least electronegative atom, is shown to be the

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(18) R. H. Baker and H. Adkins, *J. Am. Chem. Soc.*, **62**, 3305 (1940); H. Adkins, *J. Chem. Ed.*, **19**, 218 (1942).

(19) We have found that this system could be used also as catalyst in effecting the reduction of 2-dimethylaminomethyl-4-methylphenol with methanolic sodium hydroxide to 2,4-dimethylphenol at 90°, while in the absence of such catalyst temperatures as high as 220° are required; thus, R. B. Woodward and W. E. Doering, *J. Am. Chem. Soc.*, **67**, 860 (1945), reduced 7-hydroxy-8-piperidinomethylisoquinoline to 7-hydroxy-8-methylisoquinoline with methanolic sodium methoxide at 220° for ten hours, and similar conditions were used by Conforth, Conforth, and Robinson, *J. Chem. Soc.*, 682 (1942), in the reduction of piperidinomethylphenols.

(20) R. B. Woodward, N. Wendler, and F. Butschy, *J. Am. Chem. Soc.*, **67**, 1426 (1945).

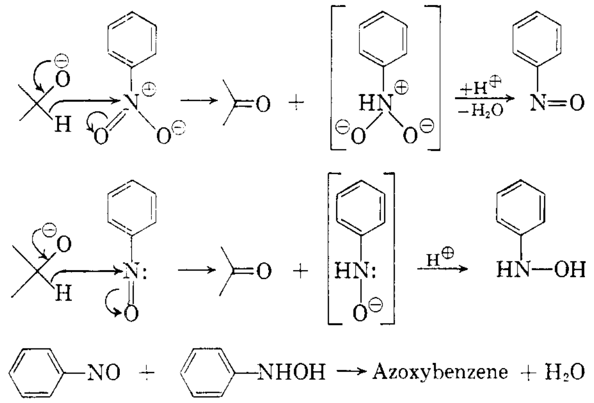
(21) L. P. Hammett, *Physical Organic Chemistry*, McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 350–353.

(22) W. von E. Doering and T. C. Aschner, *J. Am. Chem. Soc.*, **75**, 393 (1953).

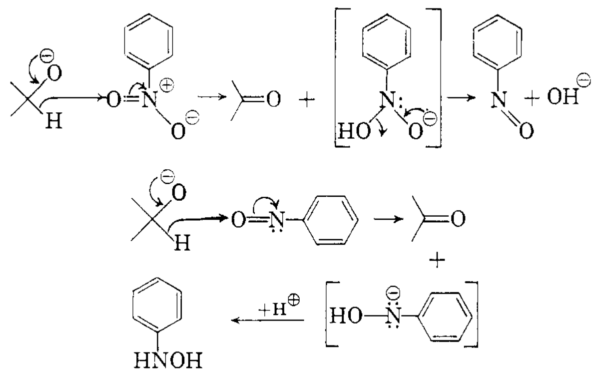
(23) W. von E. Doering and T. C. Aschner, *J. Am. Chem. Soc.*, **71**, 838 (1949).

hydride acceptor, in analogy to the alkoxide reduction of ketones, where the electropositive carbonyl carbon atom is the hydride acceptor; and (B) where the oxygen atom is the acceptor. There is, however, no evidence at this time in favor of either mechanism.

Scheme A:



Scheme B:



A mechanism essentially similar to the above could be written for the further reduction of azoxy and azo compounds to the corresponding hydrazoderivatives.

EXPERIMENTAL[24]

Azoxytoluene. In a 1-l. four-necked round bottom flask, equipped with a thermometer, condenser, addition funnel, and Trubore mechanical stirrer, were placed 80 g. of sodium hydroxide flakes and 80 g. of methanol. The reaction flask was heated to reflux; 5 g. of 9-fluorenone was added; the temperature was 85°. *o*-Nitrotoluene (137 g., 1 mole) was then added dropwise, over a period of 1 hr. 35 min.; during the addition the temperature rose to 102°. Heating and stirring were continued for 5 hr., at the end of which it was steam distilled to remove 9-fluorenone, *o*-toluidine, and any unreacted *o*-nitrotoluene. The temperature of the reaction mixture was not allowed to rise above 110°; this was accomplished by occasional addition of water.

The reaction mixture was cooled to 80° and extracted with 300 ml. of benzene, which was filtered in case insoluble tar was present. The benzene was evaporated on a steam bath by blowing with inert gas or it was distilled with vacuum. An oil was obtained which crystallized immediately on cooling to room temperature. The solid weighed 105.7 g. (93% yield); after one crystallization from benzene-hexane mixture, it melted at 58–60° (reported[25] m.p. 58.5°). Its infrared spectrum was identical with that of azoxytoluene.

Catalysts other than 9-fluorenone used under the above conditions were: benzanthrone (3.5 g.), yield of azoxytoluene, 90%; anthrone (5 g.), yield, 84%; benzophenone (5 g.), yield, 78%; xanthone (5 g.), yield, 76%.

Hydrazotoluene. In a 1-l. three-necked round bottom flask equipped with condenser, thermometer, and Trubore stirrer, were placed azoxytoluene (140 g., 0.62 mole), sodium hydroxide (108 g.), methanol (192 g.), and 9-fluorenone (5 g.); the mixture was heated to reflux while agitating for 46 hr.; the temperature was 96–98°. At the end of the reaction time, the reaction mixture became tan in color, and after addition of 400 ml. of methanol, it was cooled to room temperature and filtered. The solid was washed thoroughly with water to free the solid hydrazotoluene from sodium formate and alkali. After drying the solid hydrazotoluene, it was crystallized from ethanol; it then weighed 110 g. (84% yield), m.p. 163–165° (reported m.p. 165°,[26] 150°[27]); its infrared spectrum showed it to be identical with hydrazotoluene. In addition to hydrazotoluene, a mixture of azoxy- and azotoluene was also isolated.

Hydrazobenzene. In a 1-l. three-necked, round bottom flask, equipped with condenser, thermometer, and Trubore mechanical stirrer, were placed azoxybenzene (140 g., 0.7 mole), sodium hydroxide (108 g.), methanol (192 g.), and 9-fluorenone or 9-fluorenol (5 g.); the mixture was heated to reflux while agitating for 46 hr; the temperature was 96–98°. At the end of the reaction time the reaction mixture became tan in color and 500 ml. of water were added dropwise to dissolve sodium formate and to precipitate the hydrazobenzene which was filtered with suction, washed thoroughly with about 1.5 l. of water, and dried thoroughly. The solid, after crystallization from ethanol, weighed 130 g., amounting to a quantitative yield, m.p. 126–128° (reported m.p. 131,°[28] 127°,[29] 124°[30]). Its infrared spectrum showed it to be identical with an authentic sample of hydrazobenzene.

9-Fluorenol. In a 500-ml. flask equipped with a thermometer, stirrer, and condenser were placed 54 g. of sodium hydroxide (A.R.), 96 g. of commercial methanol, and 5 g. of 9-fluorenone. The reaction mixture was heated to reflux with stirring for 5 hr; it was cooled and filtered. The solid containing sodium formate was washed thoroughly with water, dried, and found to weigh 5 g. (quantitative yield), m.p. 148–150° (reported m.p. 158°,[31] 153°[32]). Its infrared spectrum was identical with that of an authentic sample prepared according to Hochstein.[33]

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NORTH HAVEN, CONN.

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(24) All melting points are corrected.

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(27) B. Rassow, *J. Prakt. Chem.*, **84**, 335 (1911).

(28) E. H. Rodd, *Chemistry of Carbon Compounds*, Elsevier Publishing Co., New York, 1954, p. 357.

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(30) L. Gattermann and H. Wieland, *Laboratory Methods of Organic Chemistry*, The Macmillan Co., New York, 1938, p. 183; R. H. McKee and B. G. Gerapostolou, *Trans. Electrochem. Soc.*, **68**, 329 (1935).

(31) J. Loevenich, W. Becker, and T. Schröder, *J. Prakt. Chem.*, **127**, 248 (1930).

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(33) F. A. Hochstein, *J. Am. Chem. Soc.*, **71**, 305 (1949).