

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SAN FRANCISCO]

Reductions with Hydrazine Hydrate Catalyzed by Raney Nickel. III. Effect of the Catalyst on the Reduction of 2,2'-Dinitrophenyl

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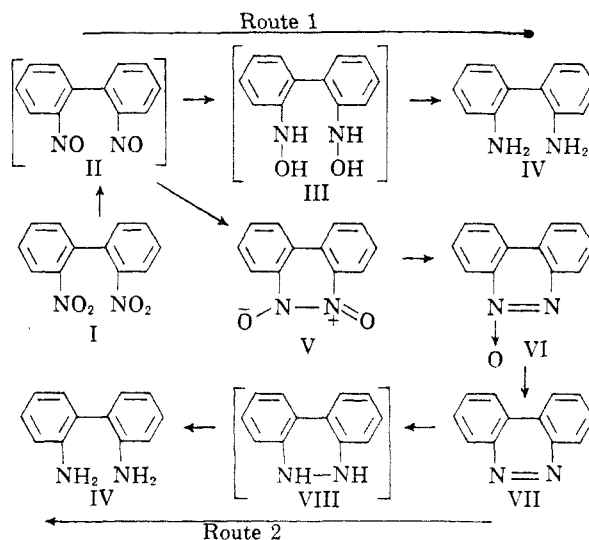
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The reduction of 2,2'-dinitrophenyl to 2,2'-diaminobiphenyl proceeds by two mechanisms. A quantitative yield of 2,2'-diaminobiphenyl is obtained using active Raney nickel which contains negligible amounts of aluminum. Using old catalysts with high contents of aluminum, benzo[c]cinnoline-5,6-dioxide, benzo[c]cinnoline-5-oxide and benzo[c]cinnoline can be isolated in good yield. Benzo[c]cinnoline can be reduced to 2,2'-diaminobiphenyl. 2,2'-Diaminobiphenyl can be separated from benzo[c]cinnoline.

Aromatic nitro compounds are reduced to the corresponding amines with hydrazine hydrate in ethanol using Raney nickel as a catalyst.³ Blood and Noller⁴ found that the reduction of 2,2'-dinitrophenyl by this method gave erratic results. Bavin⁵ used palladized charcoal, as well as Raney nickel, and also obtained erratic results. It is known that large solvent volumes favor amine formation and small volumes give intermediate reduction products.⁶ We now find that the activity and type of Raney nickel catalyst can be critical.

In a large volume of ethanol, 2,2'-dinitrophenyl (I) is easily and quantitatively reduced to 2,2'-diaminobiphenyl (IV) with approximately eight to ten moles of 100% hydrazine hydrate, if reduction is conducted rapidly with active W-2 Raney nickel. This catalyst contains a negligible amount of aluminum. Catalysts high in aluminum, such as W-7, W-6, or W-5, need more hydrazine to cause complete reduction; for example, with fresh W-7 about eighteen moles are required. With older catalyst more reducing agent is needed; for example, with two-year-old W-5 about forty moles is required. Reduction carried out slowly also requires more hydrazine.

The initial reaction after introduction of catalyst is exothermic and nitrogen is rapidly evolved. The reaction soon slows down considerably and ammonia begins to be evolved also. At this point the 2,2'-dinitrophenyl has been reduced to either diamine or benzo[c]cinnoline-5,6-dioxide (V). The proposed mechanism can be represented⁷ by Route 1 and Route 2. The nitro compound is probably first



reduced to 2,2'-dinitrosobiphenyl (II), which can either be reduced to 2,2'-dihydroxylaminobiphenyl (III) and then to the diamine (Route 1) or cyclized to the dioxide (Route 2). With a pure nickel catalyst the nitroso groups are probably reduced so rapidly to the diamine that there is not much cyclization to the dioxide (almost colorless solution), while with a catalyst high in aluminum, cyclization predominates (reddish-brown solution). Catalyst age does not appreciably affect this step.

As the Route 2 mechanism proceeds, a yellow color appears. The dioxide is first reduced to benzo[c]cinnoline-5-oxide (VI) and then to benzo[c]cinnoline (VII) which is yellow. The yellow color is slowly discharged and an almost colorless to dark reddish-brown solution is again formed. Benzo[c]cinnoline is presumably reduced to 5,6-dihydrobenzo[c]cinnoline (VIII) and finally to the diamine.

The reduction of benzo[c]cinnoline to the diamine is difficult. The amount of hydrazine hydrate needed to completely reduce benzo[c]cinnoline becomes enormous as catalyst age increases. W-2 Raney nickel does not deteriorate as rapidly on aging as high-aluminum catalysts (e.g., W-7). For this reason fresh W-2 requires about 16 moles of hydrazine hydrate and three-month-old W-2 about 26

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(3) D. Balcom and A. Furst, *J. Am. Chem. Soc.*, **75**, 4334 (1953).

(4) Private communication.

(5) P. M. G. Bavin, *Can. J. Chem.*, **36**, 238 (1958).

(6) A. Furst and R. E. Moore, *J. Am. Chem. Soc.*, **79**, 5492 (1957).

(7) The bracketed intermediates are probable, but not yet demonstrated experimentally.

while fresh W-7 needs about 22 moles and four-month-old W-7 about 72. Very old catalysts still did catalyze the benzo[c]cinnoline reduction, but only with huge amounts of reducing agent; for example, 1 $\frac{1}{2}$ -year-old W-2 required about 200 moles. The aluminum content in the catalyst seems to have much less effect than the age.

The diamine solution from reduction of benzo[c]cinnoline or benzo[c]cinnoline-5-oxide is always colorless, but that from reduction of the dioxide is always reddish-brown. The color is probably caused by a side reaction of the dioxide with hydrazine or one of its decomposition products. The colored by-product is present only in traces and was not identified. The persistent color of the diamine from the dinitro reduction *via* Route 2 presumably has the same explanation.

The presumed intermediate 5,6-dihydrobenzo[c]cinnoline has not been isolated. Evidence for an intermediate has been found by spectral analysis of a partially reduced solution of benzo[c]cinnoline.⁸ Chemical analysis showed only the presence of the diamine. Täuber⁹ isolated this cyclic hydrazo compound as the hydrochloride after reduction of benzo[c]cinnoline with zinc and hydrochloric acid, and reports that the free base is immediately oxidized to benzo[c]cinnoline on exposure to air. In our present work no precautions against oxidation were taken.

From polarographic reduction studies of the dioxide, monoxide and benzo[c]cinnoline, Roos, Kahan, and Leach¹⁰ postulate that the hydrazo compound is the end product. Radell, Spialter, and Hollander¹¹ hydrogenated benzo[c]cinnoline successfully to the diamine using Raney nickel catalyst while Blood and Noller¹² found that benzo[c]cinnoline-5,6-dioxide was hydrogenated to benzo[c]cinnoline, using either Raney nickel or Adams catalyst, but no further. With the hydrazine and Raney nickel method, the diamine is definitely the end product of Route 2.

Use of a small solvent volume and an old catalyst with high aluminum content causes the insoluble dioxide to precipitate. The yields are highly erratic and optimum conditions seem to depend on the catalyst. Two-year-old W-5 was effective if the reaction was carried out rapidly at a temperature between 55–60°. Three-month-old W-7 worked with a longer time and slightly higher temperature. Fresh catalysts with high aluminum contents gave reactions which could not be properly controlled, but did produce dioxide occasionally. Old W-2 yielded no dioxide.

(8) R. E. Moore, W. Silva, and W. Maroney, unpublished work.

(9) E. Täuber, *Ber.*, **24**, 3081 (1891).

(10) S. Roos, G. Kahan, and W. Leach, *J. Am. Chem. Soc.*, **74**, 4122 (1952).

(11) J. Radell, L. Spialter, and J. Hollander, *J. Org. Chem.*, **21**, 1051 (1956).

(12) A. E. Blood and C. R. Noller, *J. Org. Chem.*, **22**, 711 (1957).

Reduction to benzo[c]cinnoline-5-oxide was best achieved by continuing the reaction until most of the dioxide had redissolved. Further delay resulted in a mixture of the monoxide and benzo[c]cinnoline which was extremely difficult to separate. Separation of small amounts of dioxide from the monoxide was easier because of the enormous difference in solubility in cold ethanol.

Reduction to benzo[c]cinnoline was easy. Hydrazine hydrate had to be decreased if active catalysts containing aluminum were used, since these catalysts were able to reduce benzo[c]cinnoline to the diamine. Old W-2 gave a low yield of benzo[c]cinnoline and, as already mentioned, required a large amount of hydrazine hydrate to reduce benzo[c]cinnoline; this supports the assumption that the aluminum is mainly responsible for cyclization, and that the diamine is produced mainly *via* Route 1.

Some catalysts (*e.g.*, W-7) contain absorbed sodium hydroxide; however, this did not seem to promote cyclization, since a well-washed W-7 catalyst still produced the same results, as did W-2 containing absorbed alkali.

EXPERIMENTAL

2,2'-Diaminobiphenyl from 2,2'-dinitrobiphenyl. Two milliliters of 100% hydrazine hydrate (0.04 mole) was added to a solution of 1.22 g. of 2,2'-dinitrobiphenyl (0.005 mole) in 40 ml. of hot 95% ethanol. Freshly prepared W-2 Raney nickel catalyst¹³ was added at intervals sufficient to maintain a vigorous reaction without causing excessive frothing. The initial reaction was exothermic and nitrogen was rapidly evolved. After a short time (2–3 minutes) the solution became almost colorless, ammonia began to be evolved also, and the reaction subsided. External heat was applied and the reaction continued until all the hydrazine had decomposed, during which time the solution turned yellow and finally almost colorless (light pink or brown).¹⁴ The catalyst was filtered off and the filtrate immediately evaporated to dryness (darkens on standing). The yield of crude diamine,¹⁵ slightly brown in color, was 0.91 g. (99%), m.p. 76–79°. After several recrystallizations from ethanol the diamine was obtained as colorless plates, m.p. 78–79° (reported, m.p. 77.5–78.5°¹¹ and 79–80°¹²).

The procedure above was found inconvenient for larger preparations since reduction could not be conducted rapidly, resulting in a mixture of diamine and benzo[c]cinnoline. The following method was more satisfactory: One tablespoon of fresh W-2 catalyst was added to a hot solution (*ca.* 65°) of 24.4 g. of 2,2'-dinitrobiphenyl (0.1 mole) in one liter of 95% ethanol. Fifty milliliters of 100% hydrazine hydrate (1.0 mole) was added dropwise to maintain a vigorous reaction. (Important.) After the initial reaction had subsided (appearance of yellow color and odor of ammonia), more catalyst was added and the mixture heated on the

(13) Six-week-old W-2 Raney nickel was found to be satisfactory.

(14) With older W-2 catalysts and those with high contents of aluminum it was found necessary to add more hydrazine hydrate in small portions at a time to completely discharge the yellow color. Catalyst had to be added regularly, since it became deactivated as the reaction proceeded.

(15) If the diamine contains benzo[c]cinnoline, a brilliant yellow color appears when a sample is treated with concentrated hydrochloric acid.

steam bath to complete reduction. Reduction was complete in about 15 min. The catalyst was filtered off and the filtrate immediately evaporated to dryness under reduced pressure. The yield of crude diamine was 18.2 g. (99%), m.p. 76–79°.

2,2'-Diaminobiphenyl from benzo[c]cinnoline. To 0.225 g. of benzo[c]cinnoline (0.00125 mole) in 15 ml. of ethanol was added 1 ml. of 100% hydrazine hydrate (0.02 mole). The solution was heated with some freshly prepared W-2 Raney nickel.¹⁶ Ammonia and nitrogen were evolved. Reduction was complete when the solution had become completely colorless (about 10 minutes). The yield of crude diamine was 99%, m.p. 76–79°.

*Purification of 2,2'-diaminobiphenyl containing benzo[c]cinnoline.*¹⁵ The crude diamine was dissolved in a small amount of dilute hydrochloric acid and the yellow solution was neutralized with ammonium hydroxide until a faint milky appearance persisted. During this time benzo[c]cinnoline precipitated and the intense yellow which it shows in acidic solution disappeared. If the crude diamine contained a large amount of benzo[c]cinnoline, the latter was removed periodically so that it would not interfere with the detection of the end point. After filtering off the last precipitate of benzo[c]cinnoline, the filtrate of diamine monohydrochloride was treated with decolorizing carbon at room temperature until the filtrate was completely colorless. The decolorizing carbon was washed thoroughly with several small portions of water and the combined filtrates were basified with ammonium hydroxide. The diamine first appeared as a colorless oil which solidified on standing. In this manner the crude diamine was usually obtained as a pale tan powder, m.p. 76–79°. After recrystallization from ethanol (about 2 ml./gram), colorless plates, m.p. 78–79°, were obtained.

Using this procedure for the separation of the diamine from benzo[c]cinnoline, 2,2'-diaminobiphenyl could be prepared in good yield using an old W-2 Raney nickel or even a catalyst with a high aluminum content. For example, a 72% yield of the diamine and a 20% yield of benzo[c]cinnoline was obtained using the procedure described for benzo[c]cinnoline and 1½-year-old W-2 catalyst.

Reduction of 2,2'-dinitrobiphenyl to intermediates. To 1.22 g. of 2,2'-dinitrobiphenyl (0.005 mole) in 15 ml. of ethanol was added 1.5 ml. of 100% hydrazine hydrate (0.030 mole). The mixture was heated until a clear solution was obtained and then some old W-5, W-6 or W-7 Raney nickel catalyst added.¹⁷

(a) *Benzo[c]cinnoline-5,6-dioxide.* The temperature was maintained at 55–65° while the reaction was kept at a moderate rate by adding more catalyst, if necessary. The mixture turned green on addition of the catalyst, and after a short time (3–15 min.), it became slightly reddish-brown. Colorless crystals of the dioxide appeared. At this point the mixture was cooled at the tap and filtered when effervescence had almost ceased. The solid was washed thoroughly with ethanol and then with acetone. The dioxide was then extracted with cold chloroform, and the solution filtered and evaporated to dryness. The total yield of white to very pale yellow crystals amounted to 0.14–0.51 g. (13–48%), m.p. 234–236° (dec.) [reported, m.p. 240°⁹ and 233–236°¹⁰ (dec.)]. A sample was purified by recrystallization from ethanol. Its ultraviolet spectrum was identical with that in the literature.¹⁸

(b) *Benzo[c]cinnoline-5-oxide.* The procedure for the monoxide was the same as that for the dioxide except that

(16) Six-week-old W-2 Raney nickel and freshly prepared W-7 and W-5 were also effective, but needed about 1.5 ml. of 100% hydrazine hydrate using the above procedure. Older catalysts, especially those high in aluminum, required more reducing agent.

(17) Two and three-month-old W-7 gave good results.

(18) S. Roos and I. Kuntz, *J. Am. Chem. Soc.*, **74**, 1297 (1952).

the reaction was allowed to proceed until most of the dioxide had redissolved. The mixture was then filtered and the filtrate evaporated to dryness. The reddish-brown residue was recrystallized from dilute ethanol, using decolorizing carbon and filter aid, and the filtrate cooled to 5–10° for several hours. The precipitate of crude monoxide was dissolved in ethanol at room temperature and the solution cooled to 0° for several hours to precipitate most of the dioxide along with a considerable amount of the monoxide. After filtering off the precipitate, the solution was then concentrated to a small volume and deposited 0.37 g. of light tan needles, m.p. 139–141° (reported, m.p. 139°¹⁹ and 139–140°¹⁰), on strong cooling. An additional yield of 0.21 g., m.p. 141–145°, was obtained from the precipitate of dioxide and monoxide by repeating the procedure above. The total yield was 59%. Both samples gave the same ultraviolet spectrum as that reported in the literature.¹⁸

The melting point was compared with that of a sample prepared by the oxidation of benzo[c]cinnoline with hydrogen peroxide. A solution of 225 mg. of benzo[c]cinnoline (0.00125 mole) in 5 ml. of glacial acetic acid and 0.5 ml. of 30% hydrogen peroxide was heated on the steam bath for 3 hr. An additional 0.5 ml. of peroxide was then added and the solution heated for an additional 9 hr. The solution was immediately²⁰ diluted with water to 20 ml. and allowed to stand at 5–10° for an hour. The yield of pale yellow needles was 215 mg. (88%), m.p. 136–139°.

(c) *Benzo[c]cinnoline.* The original mixture was heated (cautiously at first) until all the hydrazine had decomposed or until the color had changed from green through reddish-brown to a distinct yellow-brown.²¹ The catalyst was filtered off and the filtrate evaporated to dryness. The reddish mass was recrystallized from ethanol to give 0.56–0.72 g. of yellow needles (62–80%), m.p. 155–156° (reported, m.p. 156°⁹ and 156–158°¹¹). The ultraviolet spectrum agreed with that reported in the literature.²²

The dioxide and monoxide were also reduced to benzo[c]cinnoline by a similar procedure in yields of 88 and 97% respectively. The reduction of the dioxide behaved like the reduction of 2,2'-dinitrobiphenyl and gave an impure benzo[c]cinnoline, possibly due to a side reaction of the dioxide with hydrazine or one of its decomposition products. The crude benzo[c]cinnoline obtained by the reduction of the monoxide was fairly pure, m.p. 153–156°.

Reaction of benzo[c]cinnoline-5,6-dioxide with hydrazine. A small amount of the dioxide was stirred with a concentrated solution of hydrazine hydrate in ethanol. When all the solid had dissolved (1–3 days), a dark red solution resulted. The solvent and excess hydrazine hydrate were evaporated off and the reddish solid residue thoroughly dried. The infrared spectrum was identical with that of benzo[c]cinnoline-5-oxide. Despite the red color the spectrum gave no indication for any large amount of impurity.

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(19) F. Ullmann and P. Dieterle, *Ber.*, **37**, 23 (1904).

(20) If the solution was allowed to stand at room temperature for a short time before dilution with water, the product acquired a green color.

(21) If active W-5, W-6 or W-7 Raney nickel is used, the reaction should be stopped shortly after the yellow color appears, since the excess hydrazine hydrate can reduce some of the benzo[c]cinnoline to the diamine in the presence of active catalyst.

(22) G. M. Badger, R. S. Pearce, and R. Pettit, *J. Chem. Soc.*, 3199 (1951).