

SYNTHESES IN THE BIPHENYL SERIES

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Biphenyl has been known to the organic chemist since the work of Fittig² in 1862, and several of its derivatives have been prepared and described in the literature. The previous high cost of biphenyl and its derivatives has greatly limited the amount of research on these materials. Recent industrial developments in this country have made available for the first time large quantities of biphenyl at a relatively low cost. Consequently its derivatives not only become of scientific interest, but are today in part within the range of commercial development.

As a preliminary to the possible synthesis of azo dyes of the biphenyl benzidine type a search of the literature was made for the necessary intermediates and their sources. This search revealed the incomplete condition of the literature in regard to the reduction products of mono nitrobiphenyls and that electrolytic reduction had not been reported.

Zimmerman³ has prepared small amounts of the p-azoxybiphenyl or 4,4'-diphenylazoxybenzene, p-axobiphenyl or 4,4'-diphenylazobenzene, and p-hydrazobiphenyl or 4,4'-diphenylhydrazobenzene by chemical reduction of 4-nitrobiphenyl. Friebel and Rossow⁴ have similarly prepared in small amounts the intermediate reduction products of 2-nitrobiphenyl.

Our first work deals with the application of electrolytic methods to the reduction of the isomeric nitrodiphenyls.

Experimental

Material and Apparatus. The o- and p-nitrobiphenyl were prepared according to the method of Jenkins, McCollough, and Booth.⁵ The o-nitrobiphenyl used was purified by distillation under vacuum and had a m.p. of 35-36°. The p-nitrobiphenyl recrystallized from alcohol melted at 113°.

An electrolytic cell of the divided type was used, consisting of a 50 x 125 mm. Coors porous cup suspended in a tall form, one liter pyrex beaker. A coil of 3 mm. iron wire served as the anode. The cathodes were cut from a good commercial grade of the sheet metal, 5 x 24 x 0.2 cm., with a 2 cm. lead of the same material, which served as a support. These sheets were bent to such cylindrical shape as to fit snugly against the inner surface of the glass cell and had an effective reducing surface of about 125 sq. cm. A small mechanical stirrer of 1,000 r.p.m. operated between the anode cup and the cathode. The assembled cell was placed in a water bath for temperature control.

¹ Condensed form of a thesis submitted in partial fulfillment for the Ph.D. degree.

² Fittig: Ann. 121, 363. 1862.

³ J. Zimmerman: Ber. 13. 1960. 1880.

⁴ G. Friebel and B. Rossow: J. prakt. Chem. 63, 458. 1901.

⁵ R. L. Jenkins, R. McCollough, and C. F. Booth: Ind. and Eng. Chem. 22, 31. 1930.

Reduction of o-Nitrobiphenyl at a Nickel Cathode. Using a 10% sodium hydroxide solution as anolyte and a solution of 10 g. of o-nitrobiphenyl in 250 ml. of 95% ethyl alcohol as catholyte, a current of 2.3 amperes was passed through the cell for four hours. The temperature was maintained at 75°. Reduction proceeded nicely with little evolution of hydrogen during the first two hours. Then hydrogen appeared and continued to be copiously evolved. The solution changed color from yellow through orange to a light red. The alcoholic catholyte was cooled and filtered and yielded 7.14 g. of light brown crystals of impure azoxybiphenyl. After recrystallization from acetone 5.61 g. or 63.8% of white o-azoxybiphenyl, or 2,2'-diphenyl-azoxybenzene, was obtained melting at 155°. The total quantity of electricity used was 9.52 ampere hours or 236% theoretical quantity to reduce to azoxybiphenyl, but only a slight amount of azobiphenyl was produced.

Reduction of o-Nitrobiphenyl at a Lead Cathode. Using a 10% sodium hydroxide solution as anolyte and 10 g. of o-nitrobiphenyl in 250 ml. of 95% alcohol as catholyte, a current of 2.1 amperes was passed through the cell for four and one-half hours while maintaining the temperature at about 75°. The solution changed color from yellow through orange to a dull red, and a dense gray deposit formed on the lead cathode. This deposit and the precipitate in the catholyte was carefully collected and transferred to Soxhlet's apparatus and extracted with acetone to remove the product from any insoluble debris from the cell. The yield of white crystals from acetone was 6.87 g. or 81.0% of the theoretical yield of o-hydrazobiphenyl or 2,2'-diphenylhydrazobenzene, m.p. 183°.

Reduction of p-Nitrophenyl at a Nickel Cathode. Using a 10% sodium hydroxide solution as anolyte and 10 g. of p-nitrobiphenyl in 250 ml. of 95% alcohol as catholyte, a current of 2.2 amperes was passed through the cell for two and one-half hours while the temperature was maintained at 70°. A finely divided, bright yellow precipitate formed which was readily separated from the catholyte by filtration. The yield was 7.98 g. or 90.6%. The p-azoxybiphenyl, or 4,4'-diphenyl-azoxybenzene, recrystallized from benzol melted at 212°; after recrystallization from alcohol the m.p. was 213°.

Approximate Solubility in Grams Per 100 cc. of Solution

Solute	Solvent	Temperature			
		75°	55°	45°	20°
o-Azoxybiphenyl	Acetone	...	8.30	6.04	2.58
o-Azoxybiphenyl	Alcohol 95%	1.20	0.52	...	0.11
o-Azoxybiphenyl	Ether	0.59
o-Hydrazobiphenyl	Benzene	14.60	7.90	...	3.08
o-Hydrazobiphenyl	Acetone	...	2.38	1.74	0.74
o-Hydrazobiphenyl	Alcohol 95%	0.95	0.11	...	0.03
p-Azoxybiphenyl	Benzene	4.57	2.35	...	0.64
p-Azoxybiphenyl	Acetone	...	0.49	...	0.15
p-Azoxybiphenyl	Alcohol 95%	0.08	0.04	...	0.01

Reduction of p-Nitrophenyl at a Lead Cathode. Under similar conditions to the above, but using 300% theoretical quantity of current, an orange precipitate was formed, melting at 220°. After four successive crystallizations from benzol the product melted at 239°. Since Zimmerman⁶ gives the m.p. of p-azobiphenyl, or 4,4'-diphenyl-azobenzene, as 247° we conclude that our product from benzol was probably contaminated with a small amount of p-azoxybiphenyl.

Discussion

A series of preliminary experiments showed that o-azoxybiphenyl and o-hydrazobiphenyl may be produced by the electrolytic reduction of o-nitrobiphenyl in alkaline alcoholic solution, the former preferably at a nickel cathode and the latter at a lead cathode. The o-azobiphenyl is formed in only small amounts, probably by oxidation of the hydrazobiphenyl. Reduction to the hydrazo state does not occur readily at the nickel, copper, or zinc cathodes, and the latter two do not give as pure a product of o-azoxybiphenyl as does nickel.

From a series of some thirty reductions of o-nitrobiphenyl to o-hydrazobiphenyl at a lead cathode, in which the different conditions were systematically varied, the following was concluded. Sodium hydroxide solution is preferable to sodium carbonate as anolyte. Used without the addition of sodium acetate, sodium carbonate has the disadvantage of greater cell resistance and less current efficiency. The addition of sodium acetate improves the conductivity and efficiency of a carbonate solution as anolyte, but does not improve a sodium hydroxide solution. An optimum concentration of hydroxide solution was found to be from 5 to 10% by weight. Lower concentrations gave a smaller yield and a large increase in cell resistance, while higher concentrations did not decrease the resistance appreciably but did cause more rapid corrosion of the anode cup and a slight decrease in the yield. The yield was found to be greater as the temperature of the alcoholic catholyte was increased, and 140% of the theoretical quantity of electricity was found necessary for a fair (80%) yield. A further excess produced only a slight improvement in the yield.

Reduction of p-nitrobiphenyl at a nickel cathode proceeded satisfactorily to the azoxy state with very little evolution of hydrogen. Further reduction at the nickel cathode was not affected. The pure p-azoxybiphenyl, thus prepared and crystallized from alcohol, had a m.p. of 213°, which is 8° higher than that given by Zimmerman⁷ for p-azoxybiphenyl solution.

prepared by heating 4-nitrobiphenyl in alcoholic potassium hydroxide solution.

Reduction at a lead cathode gave an impure product, largely p-azoxybiphenyl with some higher melting product, most likely the corresponding hydrazo compound which Zimmerman found to melt at 247°.

A New Series of Diphenyl-benzidine Dyes

One of the purposes of preparing o-hydrazobiphenyl was to determine whether or not it might be rearranged to the corresponding di-

⁶ J. Zimmerman: Ber. 13, 1960. 1880.

⁷ J. Zimmerman: Ber. 13, 1960. 1880.

phenylbenzidine which would serve as the nucleus for a new series of azo dyes. Schultz⁸ and others have shown *o*-hydrazotoluene to undergo rearrangement to *o*-tolidine in the presence of hydrochloric acid, and Schultz, Rhode, and Vicari⁹ have proved the product to be 3,3'-dimethyl-4,4'-diamino-biphenyl. Friebel and Rossow¹⁰ state that after treating *o*-hydrazobiphenyl with hydrochloric acid in a sealed tube at room temperature for 48 hours, 80% of the material was recovered unchanged. When, on the other hand, fuming hydrochloric acid was used in a sealed tube at 100°, or even as low as 60 or 70°, they obtained complete rearrangement in two hours. Assuming that the rearrangement was identical with that of *o*-hydrazotoluene to *o*-tolidine the resulting diamine was 3,3'-diphenyl-4,4'-diamino-biphenyl or *o*-diphenyl-benzidine.¹¹

Our investigation has shown that it is necessary to use fuming hydrochloric acid in a sealed tube. Since the solubility of *o*-hydrazobiphenyl in aqueous solutions is quite low, its state of division is an important factor in the speed of rearrangement. By using a finely divided product it was found that 90% or more of the hydrazobiphenyl would undergo rearrangement to the diamine in 1.18 gravity hydrochloric acid when maintained at 55° for 24 hours. It was further found that a temperature above 55° for 24 hours was of no advantage and that rearrangement would take place readily at 40°, and slowly at a temperature as low as 25°.

o-Diphenyl-benzidine is readily purified by recrystallization from hot dilute hydrochloric acid solution and is amenable to diazotization in the presence of nitrous acid between the temperatures -5 and +15°. Diazotization is slow at the lower temperature due to the slight solubility of the diamine, but temperatures above 15° are not desirable because its diazonium salt is less stable than that of the *o*-tolidine.

A few of the more simple dis-azo compounds were prepared to determine if coupling did take place to produce a dyestuff, and to compare the dyeing properties of the diphenyl-benzidine product with the corresponding one prepared from *o*-tolidine under identical conditions. No attempt was made to compare the great number of dyes possible, nor to determine either the best conditions for coupling or the best methods of application to the fabrics.

The following compounds were prepared by diazotizing *o*-diphenylbenzidine and coupling the resulting tetra-azonium salt with some common intermediates in the usual manner:

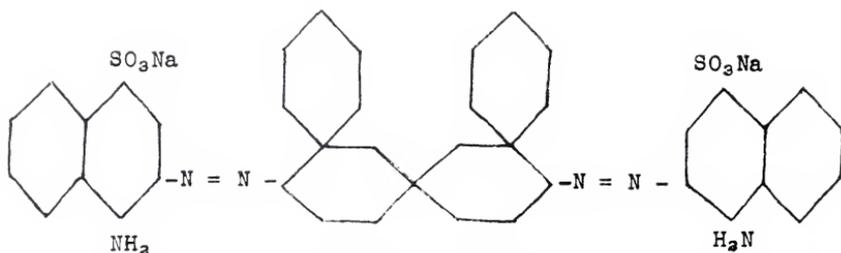
1. From *o*-diphenyl-benzidine and naphthionic acid: the sodium salt of 3,3'-diphenyl-4,4'-diazo-biphenyl-bis-*a*-naphthylamine-4-sulfonic acid.

⁸ G. Schultz: Ber. 17, 467. 1884.

⁹ G. Schultz, C. Rohde, and F. Vicari: Ber. 37, 1401. 1904. Ibid., Ann. 352, 111. 1907.

¹⁰ G. Friebel and B. Rossow: J. prakt. Chem. 63, 460. 1901.

¹¹ Friebel and Rossow gave the above formula for the diamine but named it *m*-diphenylbenzidine. In accordance with the accepted nomenclature of *o*-tolidine or 3,3'-dimethyl-4,4'-diphenylbenzidine, as *o*-dimethylbenzidine, we have preferred to use the term *o*-diphenylbenzidine for 3,3'-diphenyl-4,4'-diamino-biphenyl.



2. From *o*-diphenyl-benzidine and H acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-8-amino-1-naphthol-3,6-disulfonic acid.

3. From *o*-diphenyl-benzidine and Broenner's acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-B-naphthylamine-6-sulfonic acid.

4. From *o*-diphenyl-benzidine and chromotropic acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-1,8-dihydroxy-naphthalene-3,5-disulfonic acid.

5. From *o*-diphenyl-benzidine and J acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-2-amino-5-naphthol-7-sulfonic acid.

6. From *o*-diphenyl-benzidine and R acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-2-naphthol-3,6-disulfonic acid.

7. From *o*-diphenyl-benzidine and Gamma acid: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-2-amino-8-naphthol-6-sulfonic acid.

8. From *o*-diphenyl-benzidine and beta-naphthol: the sodium salt of 3,3'-diphenyl-4,4'-disazo-biphenyl-bis-beta-naphthol. Insoluble.)

The corresponding *o*-tolidine dyes were made parallel with the above and the following general observations noted. The diphenyl-benzidine dyes are less soluble than the tolidine dyes, have a slightly greater color intensity in equal molar concentrations, and give similar though not identical colors. They dye silk, cotton, and rayon directly, but due to their limited solubilities give better results when made in the fabric. On silk they are equal or superior to the tolidine dyes in general appearance; on rayon, they are equal or only slightly inferior to them; while on cotton they are in some instances equal, but usually inferior to them. They compare well in fastness to washing with the tolidine dyes.

Summary

o-Nitrobiphenyl has been electrolytically reduced to *o*-azoxybiphenyl at a nickel cathode, and to *o*-hydrazobiphenyl at a lead cathode.

p-Nitrobiphenyl has been electrolytically reduced to *p*-azoxybiphenyl at a nickel cathode.

The approximate solubilities of *o*-azoxy-, *o*-hydrazo-, and *p*-azoxybiphenyl in some common solvents have been determined.

Conditions favorable to the rearrangement of *o*-hydrazobiphenyl to *o*-diphenyl benzidine have been determined.

A few examples of a new series of diphenyl-benzidine dyes have been prepared and compared with the corresponding *o*-tolidine dyes made under identical conditions.