

[CONTRIBUTION NO. 258 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Catalytic Reduction of Azo Types of Compounds¹

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The purpose of this investigation was to study the reduction of azobenzene and *p*-aminoazobenzene, using hydrogen as the reducing agent, in contact with platinum and nickel catalysts.

The references² listed below pertain to the previous work done on the catalytic reduction of azobenzene. The products separated were hydrazobenzene, aniline, cyclohexylamine, dicyclohexylamine and ammonia. It was the purpose of the present work to study the conditions of time, temperature and kind of catalyst by which a maximum yield of hydrazobenzene could be produced. It was attempted to inhibit the further reduction to aniline by the addition of sulfuric acid and conversion to benzidine sulfate. Under the conditions here used, the reduction of aniline proceeds much more slowly than that of azobenzene or of hydrazobenzene and therefore does not seriously complicate the problem of separating reduction products.

Experimental

The hydrogenation of azobenzene and *p*-aminoazobenzene was carried out in a Burgess-Parr catalytic apparatus of the type using a maximum pressure of 50 lb. per sq. in. For those cases in which a temperature other than that of the room was desired, the reaction bottle was surrounded by a copper can. Through an opening at the top of the can, steam, vapor of boiling acetone, or ice water were introduced to give temperatures of 99, 55 and 5–8°, respectively. A second opening at the top was fitted with a thermometer. An opening at the bottom served as a drain.

Platinum and nickel were used as catalysts. The platinum catalyst was prepared according to the method of Adams, Voorhees and Shriner.³ The method used for the preparation of the nickel catalyst was that developed by Adkins and Cramer.⁴ It was freshly prepared each time and transferred to the reaction bottle in a stream of hydrogen.

(A) **Catalytic Reduction of Azobenzene.**—The accompanying table gives the experimental conditions and analytical results of several experiments using both platinum and nickel catalysts. In the course of analysis,

(1) Abstracted from part of a thesis presented by Leslie H. Andrews to the Graduate School in partial fulfillment of the requirements for the Ph.D. degree. Original manuscript received October 17, 1932.

(2) Sabatier and Senderens, *Bull. soc. chim.*, **35**, 259 (1906); Skita, *Ber.*, **45**, 3312 (1912); Brown and Henke, U. S. Patent 1,589,936 (1926).

(3) Adams, Voorhees and Shriner, "Organic Syntheses," Vol. VIII, p. 92.

(4) Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

hydrazobenzene is converted to benzidine and recorded as such. A description of a typical experiment (Expt. 2) follows.

A solution of 9.1 g. azobenzene in 150 cc. of 95% alcohol was shaken with hydrogen under 45 lb. pressure in the presence of 0.2 g. of platinum catalyst at room temperature (22–27°). Shaking was stopped after 0.05 mole of hydrogen had been absorbed (eight minutes). The catalyst was filtered off with suction, the filtrate treated with 10 cc. of concentrated sulfuric acid and warmed for forty-five minutes on a boiling water bath. The precipitate was filtered with suction, washed with alcohol and dried in a vacuum desiccator. The benzidine sulfate weighed 7.55 g., representing 4.92 g. of benzidine.

The filtrate from which the benzidine sulfate had been removed was evaporated to about 100 cc. and water added until the precipitation of azobenzene was complete. The azobenzene was filtered off with suction and washed with water. When dry it weighed 0.89 g.

The filtrate and washings were evaporated to 75 cc. to remove most of the alcohol. It was then made alkaline with 20% sodium hydroxide solution and extracted with 150 cc. of ether in three successive portions. The ether extract was dried with solid sodium hydroxide, after which the ether layer was separated. Dry hydrogen chloride was passed into the ether solution until precipitation was complete. The precipitate of aniline hydrochloride, when filtered, washed with dry ether and dried, weighed 3.29 g., representing 2.36 g. of aniline, m. p. 195–196°.

The following table shows the results of the reduction of azobenzene using platinum and nickel as catalysts.

Discussion of Table.—Azobenzene can be easily hydrogenated at room temperature without the presence of sulfuric acid, using platinum catalyst, to give mainly aniline. If azobenzene is hydrogenated in the absence of sulfuric acid until the hydrogen absorption corresponds to that required for reduction to hydrazobenzene, a mixture of hydrazobenzene, aniline and some unchanged azobenzene results. If the above type of reaction is carried out at low temperature (5–8°), the yield of hydrazobenzene is increased. If sulfuric acid is added to the reaction mixture with the idea of stopping the reduction at the hydrazo stage by converting it to the insoluble benzidine sulfate, the reduction takes place at a much slower rate at room or higher temperatures, and, in fact, the catalyst may become completely inactive. However, further additions of catalyst cause the reaction to proceed. The addition of sulfuric acid under these conditions results in very little, if any, increase in the yield of hydrazobenzene. When sulfuric acid is contained in the reduction mixture and the hydrogenation carried out at low temperature, the reduction goes rapidly and smoothly and results in a larger yield of hydrazobenzene.

Azobenzene can be reduced to aniline in alcohol solution when shaken with hydrogen at 99° in the presence of nickel catalyst to give a good yield of aniline. When 1

TABLE I
REDUCTION OF 9.1 G. (0.05 MOLE) OF AZOBENZENE AT 45 LB. PRESSURE

Expt.	Purpose of experiment	Catalyst	Grams	95% alcohol, ^a cc.	Concd. H ₂ SO ₄ , cc.	Temp., °C.	H ₂ absorbed, mole	Time, min.	Yield, grams				
									Benzidine	Aniline	Azobenzene	Total	
1	To reduce to aniline	Pt	0.2	150	None	22-27	0.101	25	0.99 ^b	0.35 ^c	None	8.19	6.85
2	Attempt to stop at hydrazo stage by discontinuing when the H ₂ absorbed is one-half that above	Pt	.2	150	None	22-27	.060	8	4.92 ^b	2.36	0.89	8.17	
3	Effect of lower temperature	Pt	.2	200	None	5-8	.069	14	6.14 ^b	2.22	.25	8.61	
4	Attempt to stop at hydrazo stage by introducing H ₂ SO ₄ and converting to insol. benzidine sulfate	Pt	.3 ^d	200	10	22-27	.068	120 ^e	5.35	3.09	None	8.44	
5	Effect of lower temperature	Pt	.2	200	10	8	.072	20 ^e	7.45	1.05	None	8.50	
6	Effect of higher temperature	Pt	.3 ^d	100	10	99	.089	180 ^e	3.79	5.16	None	8.95	
7	Stopped before H ₂ absorption complete in attempt to increase yield of hydrazobenzene	Pt	.3 ^d	150	10	22-27	.050	57	2.82	2.29	2.73	7.84	
8	Lower temperature to increase yield of hydrazobenzene	Pt	.2	200	10	5-8	.056	10	7.33	0.97	None	8.30	
9	To reduce to aniline	Ni	1	100	None	99	.101	120	None	8.70	None	8.70	
10	Attempt to obtain hydrazobenzene by stopping when one-half reduced	Ni	1	150	None	99	.052	32	2.88	3.16	2.1	8.14	
11	Effect of lower temperature	Ni	1	150	None	55	.058	120	1.19	5.93	None	7.12	

^a The amount of solvent used was varied as the solubility of azobenzene decreased with decrease in temperature.

^b The hydrazobenzene was determined as benzidine. ^c This 0.35 g. of amine remained as residue after the aniline had distilled off. It could not be distilled without decomposition. ^d The reaction started with 0.2 g. of PtO₂·H₂O but the catalyst became inactive in a few minutes. Upon addition of 0.1 g. of catalyst reduction continued. ^e The velocity of the reaction was less at high temperatures than at 8°, requiring greater time to absorb an equivalent amount of hydrogen.

mole of hydrogen per mole of azobenzene is allowed to be absorbed, hydrazobenzene, aniline and unchanged azobenzene are found to be present. If the temperature is lowered to 55°, the hydrogen absorption takes place much more slowly with an increase in the amount of aniline and decrease in the amount of hydrazobenzene formed. Nickel does not appear to be as satisfactory as platinum catalyst for this type of reduction.

(B) **Catalytic Reduction of *p*-Aminoazobenzene.**—A solution of 9.85 g. (0.05 mole) of *p*-aminoazobenzene in 100 cc. of 95% alcohol was shaken with hydrogen under pressure of 45 lb. per sq. in. in the presence of 0.1 g. of platinum oxide for twenty minutes, at which point ab-

sorption of hydrogen ceased. Separation and analysis of reduction products gave 5.12 g. of *p*-phenylenediamine and 2.92 g. of aniline.

Summary

1. The catalytic reduction of azobenzene to hydrazobenzene and to aniline using platinum and nickel catalysts has been studied.

2. *p*-Aminoazobenzene has been hydrogenated to give *p*-phenylenediamine and aniline using platinum as catalyst.

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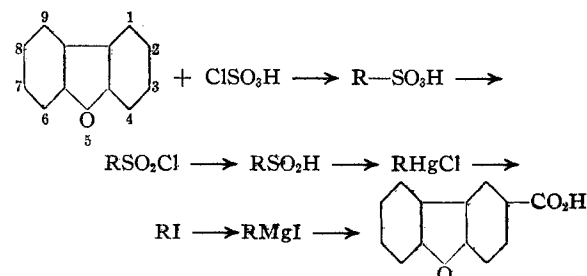
Dibenzofuran. I. Sulfonation

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Introduction

In connection with studies on the physiological properties of dibenzofuran derivatives it was necessary to determine the positions assumed by nuclear substituents. It has been found that sulfonation takes place with great ease and gives excellent yields. The following sequence of reactions was used to prove that the sulfonic grouping entered the 2-position.¹

(1) The system of numbering is the International Rules for Numbering of Organic Ring Systems. See Patterson, *THIS JOURNAL*, 47, 543 (1925). *Chemical Abstracts* uses these Rules in numbering all new ring systems, and beginning with Vol. 31 will number all systems according to the Rules.



Additional evidence for the 2-position was obtained by converting the dibenzofurylmercuric chloride to the known 2-bromodibenzofuran. However, there is a possibility that the 2-bromo-