REDUCTION OF HALOGENATED NITROBENZENES[1]

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ABSTRACT

2-Chloronitrobenzene and 2,5-dichloronitrobenzene were reduced with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol. The effects of sodium hydroxide, temperature, time, Tergitol, and Lignosol were studied for the arsenite and dextrose reductions. 2-Bromonitrobenzene was also reduced with sodium arsenite and dextrose in alkaline medium. These reductions gave rise to four new phenazine derivatives. 2,4-Dinitrochlorobenzene, when reduced with sodium arsenite, in alkaline medium, yielded only 2,2′-dichloro-5,5′-dinitroazoxybenzene.

INTRODUCTION

In 1841, Zinin (14) prepared azoxybenzene for the first time by reducing nitrobenzene and showed that the compound was an intermediate product in the formation of aniline. Since that time many other interesting and useful substances have been obtained from nitrobenzene, for instance, nitrosobenzene, phenylhydroxylamine, azobenzene, and hydrazobenzene.

A great variety of reagents have been used effectively to reduce nitrobenzenes. With an alkaline medium the formation of azoxy compounds was favored. Reduction with sodium and potassium methoxides and ethoxides proved to be efficient. Klinger and Pitschke (9) reduced *m*-dinitrobenzene to *m*-dinitroazoxybenzene with sodium methoxide and similarly Lachmann prepared azoxybenzene from nitrobenzene. Other reagents such as sodium amalgam and alcohol, stannous chloride, ferrous sulphate, and zinc dust in alkaline media have been extensively used. Elbs (5) electrolyzed nitrobenzene in a strong sodium hydroxide solution and obtained hydrazobenzene as the main product.

Flürscheim and Simon (6) reduced 3,5-dichloro-4-bromonitrobenzene to the azoxy compound in quantitative yield with stannous chloride in acid medium, but in general an alkaline medium is best to prepare azoxy compounds.

In 1928, Zechmeister and Rom (13) reduced 3-bromonitrobenzene with zinc dust in alcoholic saturated ammonium chloride solution and obtained 3,3′-dibromoazoxybenzene.

Sodium arsenite has been used to a limited extent so far for nitro compounds, for instance, Loesner (11) prepared azoxybenzene from nitrobenzene with this reagent in strong alkaline solution. Bigelow and Steeves (2) have successfully obtained azoxy derivatives by using sodium arsenite. In 1949, Gaudry and Keirstead (7) reduced seven chloronitrobenzenes to azoxybenzenes with alkaline solutions of dextrose and sodium arsenite.

The object of the present work was to investigate the reduction of halogenated nitrobenzenes with sodium arsenite, dextrose, lactose, maltose, sodium hydroxide and alcohols, and potassium hydroxide and ethanol.

THEORETICAL PART

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

In order to identify all the products formed, the reduction of 2-chloronitrobenzene with

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TABLE I

REDUCTION OF HALOGENATED NITROBENZENES WITH SODIUM ARSENITE

								Yield, %			
Compound	Amount, moles	As_2O_3, moles	NaOH, moles	H_2O, ml.	CH_3OH, ml.	Time, hr.	Temp., ° C.	Starting material	Azoxy	Amine	Phenazines
2-Chloronitrobenzene	0.32	0.25	2.00	300	130	3	80	15	39	2.2	$C_{12}H_9O_3N_2Cl$, 1.8
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	85	14	36	1.7	$C_{12}H_9O_3N_2Cl$, 2.1
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	12	80	11	39	4.2	$C_{12}H_9O_3N_2Cl$, 1.8
2-Chloronitrobenzene	0.32	0.25	1.75	300	130	3	80	18	22	Traces	$C_{12}H_9O_3N_2Cl$, 3.8
2-Chloronitrobenzene	1.91	1.52	10.50	1800	780	1	88	29	26	3.1	$C_{12}H_9O_3N_2Cl$, 5.0
2,5-Dichloronitrobenzene	0.33	0.28	1.62	300	130	2	81	19	37	0.6	$C_{12}H_7O_3N_2Cl_3$, 2.7 $C_{12}H_7O_2N_2Cl_3$, 0.1
2,5-Dichloronitrobenzene	0.78	0.76	5.25	900	390	2	85	1	78	Traces	$C_{12}H_7O_3N_2Cl_3$, 3.2 $C_{12}H_7O_2N_2Cl_3$, 1.0
2-Bromonitrobenzene	0.27	0.25	1.75	300	130	3	82	28	13	Traces	$C_{12}H_9O_3N_2Br$, 0.06
2,4-Dinitrochlorobenzene	0.33	0.25	1.75	250	130	2	82	1	3	Nil	Nil

TABLE II

REDUCTION OF HALOGENATED NITROBENZENES WITH DEXTROSE

								Yield, %			
Compound	Amount, moles	Dextrose, moles	NaOH, moles	H_2O, ml.	CH_3OH, ml.	Time, hr.	Temp., ° C.	Starting material	Azoxy	Amine	Phenazines
2-Chloronitrobenzene	0.17	0.13	0.76	270	—	$\frac{1}{2}$	80	7	78	Nil	$C_{12}H_9O_3N_2Cl$, 2.0
2-Chloronitrobenzene	0.17	0.13	0.75	230	80	3 1	80 60	32	45	1.0	$C_{12}H_9O_3N_2Cl$, 0.5
2-Chloronitrobenzene	0.17	0.13	0.75	70	—	2	100	Nil	96	Nil	Nil
2-Chloronitrobenzene	1.00	0.75	10.50	1500	480	$\frac{3}{4}$	88	55	21	3.0	$C_{12}H_9O_3N_2Cl$, 1.8
2,5-Dichloronitrobenzene	0.17	0.13	0.75	400	—	$\frac{3}{4}$	80	4	78	Traces	$C_{12}H_7O_2N_2Cl_3$, 1.6 $C_{12}H_7O_2N_2Cl_3$, 1.3
2,5-Dichloronitrobenzene	0.17	0.13	0.75	225	—	$\frac{3}{4}$	70	18	88	0.8	$C_{12}H_7O_3N_2Cl_3$, 1.3 $C_{12}H_7O_2N_2Cl_3$, 1.9
2-Bromonitrobenzene	0.06	0.05	0.27	90	30	2	86	5	19	0.3	$C_{12}H_9O_3N_2Br$, 1.7

sodium arsenite in alkaline medium was carried out by means of an efficient procedure described in the experimental part. The purple substance obtained, chlorotrihydroxydihydrophenazine, was shown to be a phenazine derivative by degradation and its structure will be discussed in a forthcoming publication.

Many experiments were carried out to increase the yields, a few of which are mentioned in Table I. The effects of the concentration of sodium hydroxide, temperature, and time were thoroughly investigated.

The formation of 2,2′-dichloroazoxybenzene and of chlorotrihydroxydihydrophenazine was shown to be dependent upon the concentration of sodium hydroxide. The yield of 2-chloroaniline was not greatly influenced. Variation of the temperature had a profound effect on the reaction. The optimum temperature for the formation of the azoxy compound was found to be 85° C. and for the highest yield of chlorotrihydroxydihydrophenazine, 80° C. Lower temperature favored the formation of the amine. The refluxing time was an important factor, but the reduction was not influenced by the rate of stirring.

It was thought of interest to determine the effect of dispersing agents. Tergitol-08 (4) was used in an attempt to facilitate the reaction taking place. The yield of the azoxy compound was increased but that of chlorotrihydroxydihydrophenazine was decreased. It appears that better mixing of the reactants due to Tergitol-08 favors the formation of the azoxy compound rather than that of the phenazine. Lignosol (1) was also used but this was not simply a dispersing agent for it is known to contain the reducing sugar glucose. The effect of Lignosol was similar to that of Tergitol-08.

In order to prepare chlorotrihydroxydihydrophenazine in sufficient quantities, several large scale reductions were carried out. With large quantities the yield of chlorotrihydroxydihydrophenazine was raised to 5.0% as indicated in Table I.

The yield of chlorotrihydroxydihydrophenazine from the sodium arsenite reduction of 2-chloronitrobenzene was originally so small that it was possible that the compound was formed only from impurities present in the practical starting material. To verify that this was not the case, 2-chloronitrobenzene which had been purified by steam distillation was used. Chlorotrihydroxydihydrophenazine was still isolated but in lower yield. This showed that impurities, like 4-chloronitrobenzene for instance, influenced the formation of the phenazine.

Accordingly, various substances, for instance 2-nitrophenol, 4-nitrophenol, and 2-chloroaniline, were added in a series of reductions. Both 2-nitrophenol and 2-chloroaniline increased the yield of chlorotrihydroxydihydrophenazine but 4-nitrophenol did not.

The effect of the solvent on the reduction was investigated. When no alcohol was present there was no formation of the phenazine or amine and the yield of the azoxy compound was low. Methanol and ethanol increased the yield of chlorotrihydroxydihydrophenazine. With isopropanol, the yields of all the products were very low. The solvent is very important and determines the course of the reduction, as shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

Dextrose in alkaline medium has had limited use as a reducing agent for nitrobenzenes. Noetling (12) prepared azoxybenzene and Lacy and Brouillard (10) obtained 2,2′-dichloroazoxybenzene. In 1951, Galbraith, Degering, and Hitch (8) used dextrose and sodium hydroxide to reduce a few aromatic nitro compounds.

TABLE III

EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2-CHLORONITROBENZENE

Water, ml.	Alcohol, ml.	Temp., ° C.	Yield, %			
			$C_6H_4O_2NCl$	Azoxy	Amine	$C_{12}H_9O_3N_2Cl$
300	No alcohol	107	50	5	Nil	Nil
300	Methanol, 130	80	5	23	0.5	8.1
130	Methanol, 250	80	10	35	Traces	8.9
300	Ethanol, 130	85	16	28	1.0	13.9
180	Ethanol, 250	82	28	7	Nil	5.1
180	Isopropanol, 250	87	48	5	0.2	0.1

In the present work, the reduction of 2-chloronitrobenzene with dextrose in alkaline medium was further studied. A few of the results obtained are given in Table II. The effects of the concentration of sodium hydroxide and time were investigated separately. The concentration of sodium hydroxide was found to be of importance. The refluxing time greatly influenced the reduction; the yield of the azoxy compound was increased when the period of refluxing was lengthened but that of chlorotrihydroxydihydrophenazine was decreased.

Several factors were varied simultaneously: refluxing time, temperature, and methanol and water contents. The yield of 2,2′-dichloroazoxybenzene was increased to 96%. A low temperature for the first hour followed by higher temperature for the remainder of the refluxing period was particularly favorable for azoxy formation. When ethanol instead of methanol was used as a solvent, the yields of the amine and azoxy compounds were decreased, but that of chlorotrihydroxydihydrophenazine was increased.

In general, the yield of 2,2′-dichloroazoxybenzene was much higher when dextrose was used instead of sodium arsenite. It was the opposite for chlorotrihydroxydihydrophenazine, the yield being lower. Both methods gave low yields of amine as expected with mild reducing agents.

Reduction of 2-Chloronitrobenzene with Lactose

In view of the successful use of dextrose as a reducing agent for nitrobenzenes, it was of interest to try other reducing sugars for this purpose. 2-Chloronitrobenzene was reduced for the first time with lactose in alkaline medium; 2,2′-dichloroazoxybenzene and 2-chloroaniline were isolated together with chlorotrihydroxydihydrophenazine. An important feature of the reduction with lactose was that tar formation was negligible, greatly facilitating the extraction of the azoxy compound.

Reduction of 2-Chloronitrobenzene with Maltose

Maltose was also used to reduce 2-chloronitrobenzene and the results were similar to those obtained with lactose.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

It was thought that the alcohol present in the reaction mixture was not merely acting as a solvent and this idea was supported by the fact that replacing methanol by ethanol led to increased yields of chlorotrihydroxydihydrophenazine. In order to see if there was any reaction, 2-chloronitrobenzene was heated with sodium hydroxide and alcohols. With ethanol, 2,2′-dichloroazoxybenzene and chlorotrihydroxydihydrophenazine were formed but no amine. With methanol, the only product isolated was 2-chloroaniline.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

When 2-chloronitrobenzene was treated with potassium hydroxide and ethanol, there was no formation of a phenazine. The main product of the reduction was 2,2′-dichloroazobenzene. 2,2′-Dichloroazoxybenzene and 2-chloroaniline were also formed.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene was reduced with sodium arsenite in alkaline medium. Two new compounds were obtained and shown to be phenazine derivatives by degradation to phenazine. An efficient procedure was developed to isolate them completely together with the other products: 2,5-dichloroaniline, 2,2′,5,5′-tetrachloroazoxybenzene, sodium arsenate, and sodium carbonate.

In order to prepare the new phenazines in sufficient quantities, many reductions were carried out and two are mentioned in Table I. The effect of alcohols was studied. Experiments were performed in the absence of alcohol and in the presence of methanol, ethanol, and isopropanol. With no alcohol present, 2,5-dichloroaniline was formed in good yield. With methanol, the yield of the azoxy compound was raised. With ethanol, the yields of trichlorotrihydroxydihydrophenazine and trichlorodihydroxydihydrophenazine were increased. As expected, with isopropanol the yield of trichlorotrihydroxydihydrophenazine was low and no trichlorodihydroxydihydrophenazine was isolated, but 2,5-dichloroaniline was obtained in high yield. The results are given in Table IV.

TABLE IV

EFFECT OF ALCOHOLS ON THE SODIUM ARSENITE REDUCTION OF 2,5-DICHLORONITROBENZENE

Alcohol, ml.	Temp., ° C.	Yield, %				
		$C_6H_3O_2NCl_2$	Azoxy	Amine	$C_{12}H_7O_3N_2Cl_3$	$C_{12}H_7O_2N_2Cl_3$
No alcohol	91	23	41.6	14.0	2.3	0.4
Methanol, 130	82	Nil	73.0	0.6	6.2	1.0
Methanol, 250	79	Nil	64.0	1.0	6.6	1.1
Ethanol, 130	86	6	64.0	7.0	14.0	1.9
Ethanol, 250	83	6	42.3	11.0	3.5	0.8
Isopropanol, 130	86	25	43.9	12.0	2.3	Nil

Reduction of 2,5-Dichloronitrobenzene with Dextrose

The reduction of 2,5-dichloronitrobenzene with dextrose in alkaline medium was studied. Two experiments are mentioned in Table II.

The reaction was found to be dependent upon the concentration of sodium hydroxide and the temperature. Tergitol-08 was added in a series of reductions and the yield of the azoxy compound was increased to 85%. Reduction with dextrose in the presence of ethanol gave higher yields of 2,5-dichloroaniline and trichlorotrihydroxydihydrophenazine, but no trichlorodihydroxydihydrophenazine was isolated.

Reduction of 2,5-Dichloronitrobenzene with Lactose

Lactose in alkaline medium was employed to reduce 2,5-dichloronitrobenzene and the main product was 2,2′,5,5′-tetrachloroazoxybenzene. 2,5-Dichloroaniline was also isolated together with the trichlorohydroxydihydrophenazines. Tar formation was negligible. The details are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was also treated with maltose in alkaline medium. The results were similar to those obtained with lactose and are shown in Table V.

It appears that these reducing sugars are ideal for the reduction of nitrobenzenes to

TABLE V

REDUCTIONS OF 2,5-DICHLORONITROBENZENE WITH OTHER REDUCING AGENTS

								Yield, %				
Compound	Amount, moles	Reducing agent, moles	NaOH, moles	H_2O, ml.	Alcohol, ml.	Time, hr.	Temp., ° C.	Starting material	Azoxy	Amine	Phenazines	
2,5-Dichloronitrobenzene	0.17	Lactose, 0.17	0.75	300	Methanol, 100	2	88	5	36	1.1	$C_{12}H_7O_3N_2Cl_3$, $C_{12}H_7O_2N_2Cl_3$, $C_{12}H_7O_3N_2Cl_3$,	0.9 0.3 1.0
2,5-Dichloronitrobenzene	0.17	Maltose, 0.17	0.75	270	Methanol, 100	2½	88	14	34	0.5	$C_{12}H_7O_2N_2Cl_3$,	0.4
2,5-Dichloronitrobenzene	0.32	—	1.75	300	Methanol, 130	2	85	79	2	0.8	Nil	
2,5-Dichloronitrobenzene	0.32	—	1.75	160	Methanol, 250	2	83	82	2	0.5	Nil	
2,5-Dichloronitrobenzene	0.32	—	1.75	300	Ethanol, 130	2	84	7	12	13.0	$C_{12}H_7O_3N_2Cl_3$,	2.8
2,5-Dichloronitrobenzene	0.32	—	1.75	180	Ethanol, 250	2	82	10	37	11.5	$C_{12}H_7O_3N_2Cl_3$,	3.0
2,5-Dichloronitrobenzene	0.06	KOH, 0.38	—	—	Ethanol, 100	2	85	1	Nil*	23.4	Nil	

*2,2′,5,5′-*Tetrachloroazobenzene was obtained. Yield, 9%.*

TABLE VI

PHENAZINES FROM REDUCTIONS OF HALOGENATED NITROBENZENES

				Analysis							
				Calculated, %				Found, %			
Compound	M.p., ° C.	Formula	Color	C	H	N	Halogen	C	H	N	Halogen
Chlorotrihydroxydihydrophenazine	156	$C_{12}H_9O_3N_2Cl$	Purple	54.45	2.43	10.59	13.40	54.25	3.47	10.40	13.65
Trichlorotrihydroxydihydrophenazine	127–128	$C_{12}H_7O_3N_2Cl_3$	Red	43.20	2.12	8.39	31.89	43.10	2.30	8.50	32.17
Trichlorodihydroxydihydrophenazine	154	$C_{12}H_7O_2N_2Cl_3$	Yellow	45.38	2.23	8.82	33.49	45.20	2.39	8.98	33.81
Bromotrihydroxydihydrophenazine	167–168	$C_{12}H_9O_3N_2Br$	Red	46.62	2.93	9.06	25.85	46.84	3.04	9.33	25.71

azoxy compounds. The use of other agents like alcoholic potassium hydroxide and sodium alcoholate in alcoholic solution was limited by such factors as low yields, impure products, or violent reactions.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

In view of the increased yields of the phenazines when the reduction was performed in the presence of ethanol, it was thought of value to determine if this effect was due to some reducing action of ethanol in alkaline medium. Thus 2,5-dichloronitrobenzene was heated with sodium hydroxide and alcohols. With methanol, small amounts of the amine and azoxy compound were formed, but no phenazines were isolated, as shown in Table V. With ethanol, 2,2′,5,5′-tetrachloroazoxybenzene and 2,5-dichloroaniline were obtained in higher yields. Trichlorotrihydroxydihydrophenazine was isolated but no trichlorodihydroxydihydrophenazine. This result showed that the alcohol did not merely act as a solvent.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol in an attempt to prepare the new chlorohydroxydihydrophenazines. The main product of the reaction was 2,5-dichloroaniline, as mentioned in Table V. Interesting features were that no azoxy compound or phenazines were isolated, but 2,2′,5,5′-tetrachloroazobenzene was formed.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—Zechmeister and Rom (13) reduced 2-bromonitrobenzene with magnesium and methanol and obtained 2,2′-dibromoazoxybenzene. In the present work, 2-bromonitrobenzene was reduced with sodium arsenite in alkaline medium. The main product was 2,2′-dibromoazoxybenzene, and the others were 2-bromoaniline and a bromotrihydroxydihydrophenazine, as shown in Table I.

Reduction with dextrose.—Reduction of 2-bromonitrobenzene with dextrose in alkaline medium gave similar results, indicated in Table II, but the yields of the products were higher.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

In 1914, Brand and Eisenmenger (3) reported the formation of a dichlorodinitroazoxybenzene by the electroreduction of 2,4-dinitrochlorobenzene. In the present work, 2,4-dinitrochlorobenzene was reduced with sodium arsenite in alkaline medium and 2,2′-dichloro-5,5′-dinitroazoxybenzene was isolated, as mentioned in Table I. This compound had the same melting point, 163–164° C., as that given by Brand and Eisenmenger for their product. However, no amine or phenazine compounds were detected in the preparation.

EXPERIMENTAL PART*

Reduction of 2-Chloronitrobenzene with Sodium Arsenite

A sodium arsenite solution was prepared by treating arsenic trioxide (50.0 g., 0.25 mole) with water (50 ml.). The mixture was stirred until a thick white paste was formed. Sodium hydroxide (70.0 g., 1.75 moles) was cautiously added together with water (250 ml.) in small portions. Heat was evolved and gradually the solution became colorless.

Several attempts were made to reduce 2-chloronitrobenzene by sodium arsenite which had not been freshly prepared from arsenic trioxide and sodium hydroxide. No reaction

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All melting points are uncorrected.

occurred. Therefore, to reduce 2-chloronitrobenzene, it is absolutely necessary to use freshly prepared sodium arsenite.

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in methanol (130 ml.) and the solution was placed in a 1-liter three-necked flask. The flask was fitted with a powerful stirrer, thermometer, and a small reflux condenser. The freshly prepared solution (300 ml.) of sodium arsenite was added through the side neck of the flask and the temperature was raised to 80° C. by means of a heating jacket. This temperature was maintained for 3 hours, the contents of the flask being refluxed vigorously all the time. In the first stage of the reduction the color was yellow and it gradually changed to orange, then red, and finally purple.

After being refluxed, the contents of the flask were separated, as indicated in Fig. 1, by steam distillation into two parts: mixture I, which remained in the reaction flask, and a distillate, II. The distillate, II, was acidified with hydrochloric acid and filtered to separate the pale yellow plates of 2-chloronitrobenzene, m.p. 32.5° C. Yield, 5%. The filtrate was made alkaline with sodium hydroxide and extracted with ether. The ethereal extract was evaporated to dryness and the residue was converted into the acetyl derivative of 2-chloroaniline. The yield of 2-chloroaniline was 0.5%.

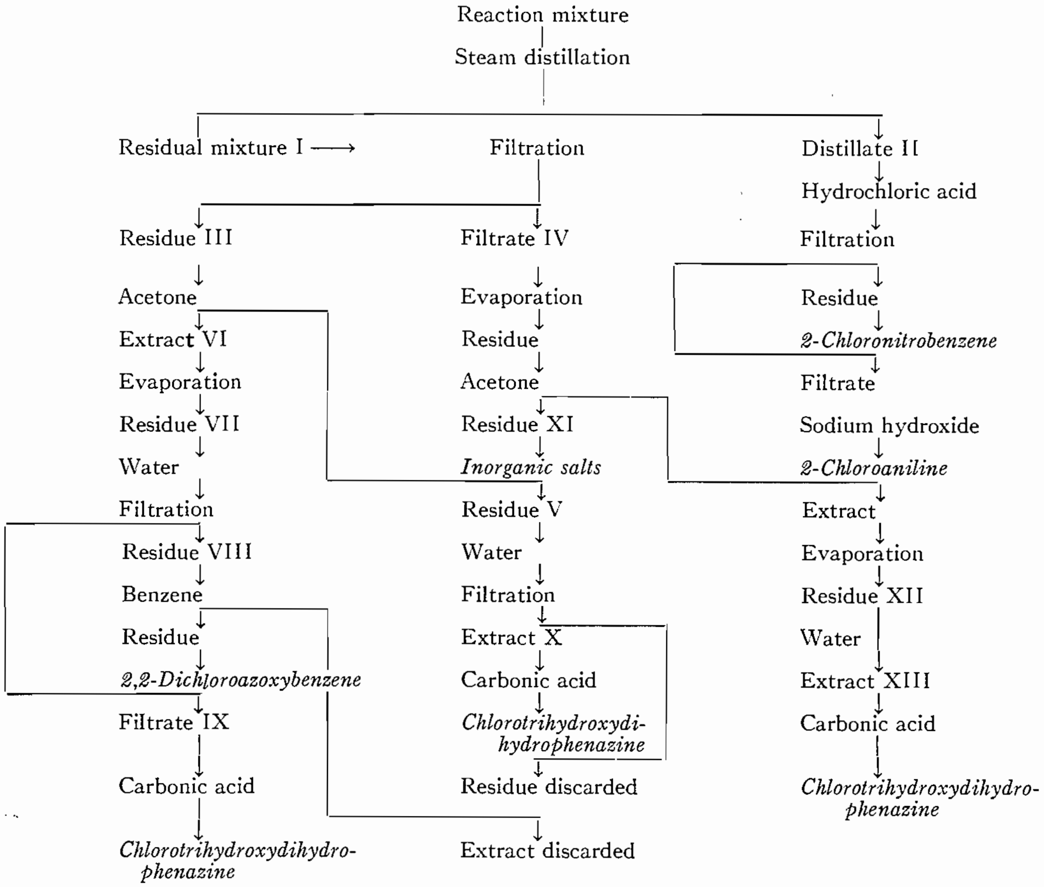

FIG. 1. Reduction of 2-chloronitrobenzene with sodium arsenite.

The mixture, I, remaining in the reaction flask after steam distillation was filtered; a residue, III, and a deep red filtrate, IV, were obtained. Residue III was extracted with acetone, giving a residue, V, and a deep red colored extract, VI.

The acetone extract, VI, was evaporated to dryness. The black residue, VII, thus obtained was first extracted with a large volume of boiling water to give a residue, VIII, and a deep red filtrate, IX, which was treated with carbon dioxide to produce a red precipitate of chlorotrihydroxydihydrophenazine, recrystallized from ethanol as purple needles, m.p. 156° C. Yield, 0.5%. This product was shown to be a phenazine derivative by degradation. A small quantity was ground with zinc dust and the mixture poured into a pyrex test tube and covered with an equal volume of zinc dust. The zinc dust was heated gently first and the mixture of zinc dust and the compound was heated later to a dull red heat. A pale yellow product was obtained as a sublimate on the cooler part of the test tube. It was recrystallized from petroleum ether as yellow needles, m.p. 171° C. alone or with an authentic sample of phenazine.

The residue VIII was treated several times with cold ethanol to remove tars. Further treatments with benzene and charcoal yielded almost pure 2,2′-dichloroazoxybenzene which was recrystallized from a mixture of benzene and ethanol, as light yellow needles, m.p. 56° C. alone or with an authentic sample. Yield, 23%. An alternative procedure for obtaining crude 2,2′-dichloroazoxybenzene from the acetone extract VI was to precipitate the crude material with water and recrystallize from aqueous ethanol.

The residue V from steam distillation, which was insoluble in acetone, was extracted with copious volumes of boiling water. The portion insoluble in water (0.1 g.) was discarded and the red aqueous solution, X, upon treatment with carbon dioxide, yielded a red precipitate. Several recrystallizations from ethanol or glacial acetic acid gave purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. Yield, 3.8%.

The deep red liquid, IV, from the reaction flask, after steam distillation, was evaporated to dryness. A purple-gray mass was obtained. Extraction with acetone gave a grayish-white residue, XI, and a red colored solution. A purple residue, XII, was obtained upon removal of the solvent and was extracted with large volumes of boiling water. Treatment of the extract, XIII, with carbon dioxide gave a red product which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 155–156° C. Yield, 1.3%. The grayish-white residue, XI (132 g.), insoluble in acetone, was treated with the following solvents: benzene, ether, methanol, ethanol, and petroleum ether. It was insoluble in all these solvents, but soluble in water; a portion of the residue dissolved in water was tested for arsenate using copper sulphate solution. A blue precipitate was obtained, indicating the presence of arsenate. A small amount, when heated on a platinum wire, gave a positive test for sodium.

The chlorotrihydroxydihydrophenazine prepared was very soluble in glacial acetic acid, soluble in benzene, ether, carbon tetrachloride, pyridine, and aniline, fairly soluble in acetone and ethanol, slightly soluble in methanol and petroleum ether, and insoluble in water. The total yield of chlorotrihydroxydihydrophenazine was 5.5%. The analysis is given in Table VI, and the structure will be discussed in a forthcoming publication.

Reduction on a larger scale.—Several reductions were carried out on a larger scale. The details of the experiment which gave the best yield of chlorotrihydroxydihydrophenazine, 5.0%, are given in Table I.

Effect of sodium hydroxide.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with sodium arsenite solutions containing arsenic trioxide

(50.0 g., 0.25 mole), water (300 ml.), and various quantities of sodium hydroxide (1.25–2.00 moles). The reaction mixture was refluxed for 3 hours at 80° C.

The optimum amount of sodium hydroxide for the best yield of the phenazine derivative (3.8%) was 1.75 moles and for that of the azoxy compound (39%) was 2.00 moles, as indicated in Table I.

Effect of temperature.—2-Chloronitrobenzene (50.0 g., 0.32 mole) dissolved in methanol (130 ml.) was reduced with a sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole), water (300 ml.), and sodium hydroxide (70.0 g., 1.75 mole). The mixture was refluxed for 3 hours in all the experiments and the temperature was varied from 70° to 85° C.

The temperature could not be varied over a wide range, because the highest temperature possible was that of the boiling point of the solution and the lowest was 70° C., the temperature needed to prevent solidification of the reaction mixture.

The optimum temperature for the best yield of the azoxy compound (36%) was 85° C. and for that of the phenazine derivative (3.8%) was 80° C., as shown in Table I.

Effect of time.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced in the same way as described above using a temperature of 80° C., but the reaction time was varied from 1 to 48 hours.

The optimum refluxing time for the best yield of the azoxy compound (39%) was 12 hours, and for that of the phenazine derivative (3.8%) was 3 hours, as shown in Table I.

Effect of Tergitol-08.—2-Chloronitrobenzene (50.0 g., 0.32 mole) was reduced again under the same conditions as previously mentioned, in the presence of different quantities (0.25 to 1.00 ml.) of Tergitol-08. Tergitol-08 (0.5 ml.) increased the yield of the azoxy compound by 10%.

Effect of Lignosol.—In another series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) varying amounts (0.25 to 5.00 g.) of Lignosol were added. The use of Lignosol (5.00 g.) increased the yield of the azoxy compound by 8%.

Effect of purity of starting material.—In order to show that the chlorotrihydroxydihydrophenazine formed during the reduction of 2-chloronitrobenzene was not due to impurities in the starting material, reductions were carried out using purified material. The phenazine was still isolated.

Effect of addition of substances.—2-Nitrophenol, 4-nitrophenol, and 2-chloroaniline were added in a series of reductions of 2-chloronitrobenzene. Only 2-nitrophenol and 2-chloroaniline increased the yield of the phenazine.

Effect of alcohols.—A series of reductions of 2-chloronitrobenzene (50.0 g., 0.32 mole) was carried out using arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70.0 g., 1.75 mole) in the presence of alcohols. The reaction mixtures were refluxed for 3 hours. The results are shown in Table III.

Reduction of 2-Chloronitrobenzene with Dextrose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.) and the solution placed in a 1-liter three-necked flask fitted with an efficient stirrer, thermometer, and reflux condenser. Sodium hydroxide (30.0 g., 0.75 mole) and water (250 ml.) were added and the reaction mixture heated to 60° C. At that temperature a thick sirup of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was slowly added. The mixture was refluxed at 88–89° C. for 40 minutes. The reaction mixture was steam distilled until no more viscous droplets appeared in the steam distillate, which was later treated with hydrochloric acid and filtered. The residue was recovered 2-chloronitrobenzene, m.p. 33° C. Yield, 38%.

The acid distillate was made alkaline with sodium hydroxide and extracted with ether. Removal of the ether from the extract gave a residue, which was converted to the acetyl derivative of 2-chloroaniline, m.p. 87–88° C. The yield of 2-chloroaniline was 1.9%. The solution from steam distillation was filtered, and the filtrate discarded. A black residue was obtained, which was extracted with acetone, the acetone extract evaporated to dryness, and the residue, 2,2′-dichloroazoxybenzene, recrystallized from ethanol, m.p. 56° C. alone or with an authentic sample. Yield, 35%. The portion of the residue not soluble in acetone was extracted with large volumes of hot water, and the extract treated with carbon dioxide. A red flocculent precipitate was obtained, which was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. Yield, 1.4%. Calculated for $C_{12}H_9O_3N_2Cl$: C, 54.45%; H, 3.43%; N, 10.59%; Cl, 13.40%. Found: C, 54.30%; H, 3.55%; N, 10.53%; Cl, 13.67%.

Reduction on a larger scale.—2-Chloronitrobenzene was reduced on a larger scale and the experimental details are given in Table II.

Effect of sodium hydroxide.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was carried out, using a paste of dextrose (23.0 g., 0.13 mole) in water (15 ml.), added in portions. The concentration of sodium hydroxide present was varied by using different amounts of water (70 to 370 ml.) in the reaction mixtures. The reaction mixtures were refluxed at 80° C. for 30 minutes. The same extraction procedure as previously described was used. A 10% solution was the optimum for the best yield of the azoxy compound (78%) and also for the phenazine derivative (2.0%).

Effect of time.—A series of reductions of 2-chloronitrobenzene (26.2 g., 0.17 mole) was performed, using a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole), water (230 ml.), and methanol (80 ml.). The reaction mixtures were refluxed at 80° C. for varying times (10 to 180 minutes). With a refluxing time of 3 hours the yield of the azoxy compound was raised to 45% from 23% obtained after 10 minutes refluxing.

Effect of time, temperature, methanol, and water.—The same procedure as in the previous series was used but time, temperature, methanol, and water contents were varied. The dextrose paste was added in portions. The yield of the azoxy compound was raised to 96%; the reaction conditions are shown in Table III.

Effect of ethanol.—2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in ethanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (230 ml.) were added. The reaction mixture was heated to 60° C. and a paste of dextrose (23.0 g., 0.13 mole) in water (20 ml.) was added slowly. The mixture was refluxed at 86–87° C. for 2 hours. Steam distillation was followed by the usual extraction treatment and the products were isolated. Unreacted 2-chloronitrobenzene (yield, 9%) was recovered. A trace of 2-chloroaniline was formed. 2,2′-Dichloroazoxybenzene (yield, 20%) and chlorotrihydroxydihydrophenazine (yield, 4.4%) were obtained.

Reduction of 2-Chloronitrobenzene with Lactose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (80 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 50° C. and a thick paste of lactose (46.1 g., 0.17 mole) in water (30 ml.) was added.

The reaction mixture was refluxed at 87–88° C. for 2 hours, the color of the mixture changing from orange to a final deep red. Steam distillation gave a distillate containing recovered 2-chloronitrobenzene, m.p. 32.5° C. Yield, 8%. The remainder of the acid distillate was made alkaline and extracted with ether, the ethereal extract evaporated, and the residue converted to the acetyl derivative, m.p. 87–88° C. Only a trace of the amine 2-chloroaniline was formed.

The residue in the reaction flask was extracted with acetone, the solvent removed from the extract, and the residue recrystallized from ethanol. Further recrystallizations from aqueous ethanol gave pale yellow needles of 2,2′-dichloroazoxybenzene, m.p. 56–57° C. alone or with an authentic sample. Yield, 43%.

The residue remaining after acetone extraction was dissolved in hot water, the resulting solution cooled and treated with carbon dioxide to yield a red product. This was recrystallized from ethanol as purple needles of chlorotrihydroxydihydrophenazine, m.p. 156–157° C. alone or mixed with samples obtained with arsenite. Yield, 1.0%.

Reduction of 2-Chloronitrobenzene with Maltose

2-Chloronitrobenzene (26.2 g., 0.17 mole) was dissolved in methanol (75 ml.), and sodium hydroxide (30.0 g., 0.75 mole) and water (220 ml.) were added. The mixture was heated to 60° C. and a thick paste of maltose (46.1 g., 0.17 mole) in water (50 ml.) was added. The new mixture was refluxed at 89–90° C. for 1½ hours, the color deepening towards the end of the refluxing. It was steam distilled until no more solid material appeared in the distillate. The distillate was filtered, and yielded unreacted 2-chloronitrobenzene, m.p. 33° C. Yield, 11%. The acid filtrate was made alkaline and extracted with ether; removal of the solvent from the extract gave a small residue, which was converted into a small amount of the acetyl derivative of 2-chloroaniline, m.p. 88° C.

The residue in the flask was extracted with acetone, the solvent removed from the extract, and the residue taken up in ethanol. Recrystallization from aqueous ethanol yielded pale yellow needles of 2,2′-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 42%.

Extraction of the residue insoluble in acetone with hot water and treatment of the extract with carbon dioxide gave a red precipitate. Recrystallization from ethanol yielded purple needles of chlorotrihydroxydihydrophenazine, m.p. 156° C. alone or with samples obtained with arsenite. Yield, 1.2%.

Reduction of 2-Chloronitrobenzene with Sodium Hydroxide and Alcohols

2-Chloronitrobenzene (50.0 g., 0.32 mole) was dissolved in ethanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer and thermometer. Sodium hydroxide (70 g., 1.75 mole) and water (300 ml.) were added. The reaction mixture was refluxed at 85–86° C. for 3 hours and steam distilled. Unreacted 2-chloronitrobenzene was recovered in 73% yield. No 2-chloroaniline was isolated. Other products were identified as 2,2′-dichloroazoxybenzene (yield, 9%) and chlorotrihydroxydihydrophenazine (yield, 2.3%) by mixed melting point determinations.

An attempt was made to reduce 2-chloronitrobenzene with sodium hydroxide and methanol, the only products isolated being 2-chloroaniline (yield, 0.02%) and unreacted 2-chloronitrobenzene. Yield, 78%.

Reduction of 2-Chloronitrobenzene with Potassium Hydroxide and Ethanol

2-Chloronitrobenzene (52.5 g., 0.33 mole) was dissolved in ethanol (600 ml.). The mixture was heated to 50° C. and potassium hydroxide (60 g., 1.07 mole) was added slowly. A further portion (60.0 g., 1.07 mole) of potassium hydroxide was added when the temperature had been raised to 60° C. The reaction mixture was refluxed for 3 hours at 87° C. A very vigorous reaction took place.

Steam distillation gave only a trace of recovered 2-chloronitrobenzene; no 2-chloroaniline was precipitated when the steam distillate was made alkaline. The residue in the reaction flask was extracted with glacial acetic acid. Removal of the solvent from the extract gave a crude red product, which recrystallized from benzene as orange-red needles of 2,2′-dichloroazobenzene, m.p. 138° C. alone or with an authentic sample. Yield, 20%.

The portion of the residue insoluble in glacial acetic acid was treated with ethanol. Removal of the solvent gave crude yellow needles, which were recrystallized from ethanol as pale yellow needles, of 2,2′-dichloroazoxybenzene, m.p. 56° C. alone or with an authentic sample. Yield, 6%. No phenazine compounds could be detected in the remainder of the residue left after the above extraction.

Reduction of 2,5-Dichloronitrobenzene with Sodium Arsenite

2,5-Dichloronitrobenzene (63.4 g., 0.33 mole) was dissolved in hot methanol (130 ml.) and the solution placed in a 1-liter three-necked flask fitted with a stirrer, reflux condenser, and thermometer. A freshly prepared solution of sodium arsenite containing arsenic trioxide (56.2 g., 0.28 mole), sodium hydroxide (64.8 g., 1.62 mole), and water (300 ml.) was added. The reaction mixture was refluxed at 81° C. for 2 hours and treated according to the procedure described for 2-chloronitrobenzene, which is summarized in Fig. 1. Unreacted 2,5-dichloronitrobenzene, m.p. 56° C., was recovered in 19% yield, and 2,5-dichloroaniline, m.p. 49° C. alone or with an authentic sample, in 0.6% yield. In the reduction of 2-chloronitrobenzene, residue III was extracted with acetone, but in the reduction of 2,5-dichloronitrobenzene, residue III was extracted with large volumes of hot water, giving a residue, V, and a deep red colored extract, VI, which was treated with carbon dioxide to produce a red precipitate. This material was recrystallized from ethanol to give red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 2.7%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.1%. The residue V was washed with benzene and recrystallized from ethanol to give yellow needles of 2,2′,5,5′-tetrachloroazoxybenzene, m.p. 147° C. alone or with an authentic sample, yield, 37%. Treatment of extract XIII with carbon dioxide gave a red precipitate which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C., yield, 0.5%, and yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C., yield, 0.2%. The trichlorotrihydroxydihydrophenazine prepared was very soluble in methanol and glacial acetic acid and insoluble in water. The total yield was 3.2%. The trichlorodihydroxydihydrophenazine had similar solubilities, except that it was only moderately soluble in ethanol. The total yield was 0.3%. As for chlorotrihydroxydihydrophenazine, the two phenazine derivatives obtained here were degraded to phenazine by zinc dust distillation and their structures will be discussed in a forthcoming publication. The analyses are given in Table VI.

Reduction on a large scale.—Several reductions were carried out on a larger scale. The experimental details of a typical example are mentioned in Table I. As indicated, the yield of 2,2′,5,5′-tetrachloroazoxybenzene was raised to 78%, but the yields of the phenazines were not greatly changed.

Effect of alcohol.—A series of reductions of 2,5-dichloronitrobenzene (50.0 g., 0.26 mole) was carried out using sodium arsenite solution containing arsenic trioxide (50.0 g., 0.25 mole) and sodium hydroxide (70 g., 1.75 mole) in water (300 ml.), in the presence of various alcohols. The reaction mixtures were refluxed for 2 hours. The results are shown in Table IV.

Reduction of 2,5-Dichloronitrobenzene with Dextrose

A mixture of sodium hydroxide (30.0 g., 0.75 mole), water (270 ml.), and 2,5-dichloronitrobenzene (32.0 g., 0.17 mole) was heated to 60° C. with efficient stirring. A sirup of dextrose (23.0 g., 0.13 mole) in water (15 ml.) was slowly added in small portions. The reaction mixture was heated to 75° C. for 40 minutes and was then steam distilled until the amount of solid coming over in the steam distillate was negligible. The residue was recovered 2,5-dichloronitrobenzene, m.p. 69° C. Yield, 34%. The filtrate was made basic with sodium hydroxide and a light precipitate of 2,5-dichloroaniline was obtained, m.p. 50° C. alone or with an authentic sample. Yield, 1.6%.

The solution remaining in the flask after steam distillation contained brown crystals of 2,2′,5,5′-tetrachloroazoxybenzene, which were removed by filtration. The filtrate was discarded. The azoxy compound obtained was treated with large volumes of hot water until all water soluble substances were removed. The crude azoxy compound was recrystallized from ethanol as bright yellow needles, m.p. 147° C. alone or with an authentic sample. Yield, 23%.

The red colored solution containing water soluble materials was cooled and carbon dioxide was bubbled through it for about 10 minutes. A pale brown flocculent precipitate was obtained, which was recrystallized from ethanol as red needles of trichlorotrihydroxydihydrophenazine, m.p. 127–128° C. Yield, 1.5%. Calculated for $C_{12}H_7O_3N_2Cl_3$: C, 43.20%; H, 2.12%; N, 8.39%; Cl, 31.89%. Found: C, 43.30%; H, 2.09%; N, 8.33%; Cl, 32.17%.

The alcoholic mother liquor was found to contain another compound, which was purified by fractional crystallization and obtained as bright yellow needles of trichlorodihydroxydihydrophenazine, m.p. 154° C. Yield, 0.3%. Calculated for $C_{12}H_7O_2N_2Cl_3$: C, 45.38%; H, 2.23%; N, 8.82%; Cl, 33.49%. Found: C, 45.50%; H, 2.25%; N, 9.08%; Cl, 33.65%.

Effect of sodium hydroxide.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (15 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water. The water contents varied from 70 to 400 ml. and the reaction mixtures were refluxed at 80° C. for 40 minutes.

With a 7.5% solution of sodium hydroxide, the yield of the azoxy compound was 78%, that of trichlorotrihydroxydihydrophenazine, 1.6%, and that of trichlorodihydroxydihydrophenazine, 1.3%. With a 10% solution, the yield of the azoxy compound was 77%, that of trichlorotrihydroxydihydrophenazine, 3.4%, and that of trichlorodihydroxydihydrophenazine, 0.6%. Only traces of 2,5-dichloroaniline were isolated in these experiments.

Effect of temperature.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.), in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (200 ml.). The reaction mixtures were heated for 40 minutes at varying temperatures (60° to 90° C.). With a temperature of 70° C. the yield of the azoxy compound was 88% and that of trichlorodihydroxydihydrophenazine was raised to 1.9%; 80° C. was the optimum for the best yield of trichlorotrihydroxydihydrophenazine (1.6%).

Effect of Tergitol-08.—2,5-Dichloronitrobenzene (32.0 g., 0.17 mole) was reduced with dextrose (23.0 g., 0.13 mole) in water (25 ml.) in the presence of sodium hydroxide (30.0 g., 0.75 mole) and water (270 ml.). The reaction mixtures were heated to 80° C. for 40 minutes. Tergitol-08 in varying amounts (0.5 to 1.0 ml.) was added. With 0.5 ml. of Tergitol-08, the yield of the azoxy compound was raised by 11%.

Effect of ethanol.—2,5-Dichloronitrobenzene (16.0 g., 0.09 mole) was dissolved in ethanol (40 ml.), and sodium hydroxide (15.0 g., 0.38 mole) and water (100 ml.) were added. The reaction mixture was heated to 60° C. and a paste of dextrose (11.5 g., 0.06 mole) in water (8 ml.) was added slowly. The mixture was then refluxed at 86–87° C. for 2 hours. Unreacted 2,5-dichloronitrobenzene was recovered in 2.5% yield. Other products isolated were 2,5-dichloroaniline (yield, 6.0%), 2,2′,5,5′-tetrachloroazoxybenzene (yield, 60%), and trichlorotrihydroxydihydrophenazine (yield, 2.2%).

Reduction of 2,5-Dichloronitrobenzene with Lactose

2,5-Dichloronitrobenzene was reduced with lactose in alkaline medium and the same procedure as described for the lactose reduction of 2-chloronitrobenzene was employed. The quantities and experimental conditions are given in Table V.

Reduction of 2,5-Dichloronitrobenzene with Maltose

2,5-Dichloronitrobenzene was reduced with maltose using the procedure previously described for 2-chloronitrobenzene. The details of the reduction are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Sodium Hydroxide and Alcohols

The procedure followed was the same as the one described for the 2-chloronitrobenzene reduction, except that the refluxing time was 2 hours instead of 3. The alcohols used were methanol and ethanol. The results are shown in Table V.

Reduction of 2,5-Dichloronitrobenzene with Potassium Hydroxide and Ethanol

2,5-Dichloronitrobenzene was reduced with potassium hydroxide and ethanol using the same procedure as described for the corresponding reduction of 2-chloronitrobenzene. The experimental details and yields of products are given in Table V.

Reduction of 2-Bromonitrobenzene

Reduction with sodium arsenite.—2-Bromonitrobenzene was also reduced with sodium arsenite in alkaline medium. The experimental details are mentioned in Table I. The analysis for the bromotrihydroxydihydrophenazine obtained is given in Table VI.

Reduction with dextrose.—2-Bromonitrobenzene was reduced with dextrose in alkaline medium. The experimental details are given in Table III.

Reduction of 2,4-Dinitrochlorobenzene with Sodium Arsenite

The details of the reduction of 2,4-dinitrochlorobenzene with sodium arsenite in alkaline medium are shown in Table I. 2,2-Dichloro-5,5′-dinitroazoxybenzene, reddish-yellow colored, crystallizing in needles from ethanol, m.p. 163–164° C., was obtained. Calculated for $C_{12}H_6O_5N_4Cl_2$: C, 40.36%; H, 1.69%; N, 15.69%. Found: C, 40.11%; H, 1.80%; N, 15.40%.

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