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Dimolecular Reduction of Nitrophenols

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Dimolecular reduction of nitrophenols in basic media have been investigated, m- and p-azoxyphenols are obtained in this way. It has been shown that some reducing agents able to produce aminophenols in basic conditions. Cupric, cobaltous and nickel salts of p-azoxyphenol have been made and their propertied. studied.

INTRODUCTION

Genaral ways to synthesize azo- compounds are condensation of an aromatic amine with an aromatic nitroso compound; coupling a phenol, an amine or their derivatives with a diazonium cation; reduction of an aromatic nitro compound in basic conditions; disproportion of a hydrazo- compound. For synthesizing azoxy- compounds, condensation of an aromatic hydroxlamine derivatives with an aromatic nitroso compound or reduction of an aromatic nitro compound have mostly been used. Reduction of nitrophenols in basic conditions have been carried out by some authors, e.g. Ruggli and Hinowker have reduced m-nitrophenol by means of zinc dust in basic contions and obtained m-azoxyphenol or m-azophenol, depending on the conditions [1]. Meier and Böhler have reduced the same compound by means of metallic silicon in basified methanolic solutions to m- azoxyphenol or m-azophenol [2]. Galbrait, Degeriing and Hitch have reduced o-nitrophenol to azoxyphenol or azophenol, depending on the reaction condition [3]. Weselsky and Benedict have melted p-nitrophenol with solid potassium hydroxide in an open dish (in air) and obtained p-azophenol [4].

Nobuyoshi and Kaneniwa have investigated some properties of cupric, cobaltous, nickel, zinc, manganese and cadmium salts of o-azoxyphenol [5]. Tesumaki, Yamaguchi and Schimisu have pyrolized cupric salt of o-azophenol [6], Uemura and his coworkers have studied absorbtion spectra of cobaltous and cromium salts of o-azophenol [7], [8]. Jonassen and Gonzales have studied conductimetric behaviour of cupric salt of o-azophenol.

In this work, faesibility of reduction of o-nitrophenol to 2,2'-dihydroxyazoxybenzene (o-azoxyphenol) or 2,2'-dihydroxyazobenzene (o-azophenol); m-nitrophenol to 3,3'-dihydroxyazoxybenzene (m-azoxyphenol) or 3,3'-dihydroxyazobenzene (m-azophenol); p-nitrophenol to 4,4-dihydroxyazoxybenzene (p-azoxyphenol) or 4,4'-dihydroxyazobenzene (p-azophenol). For this purpose following materials have been used as reducing agents: methanol, isopyl alcohol, arsenic trioxide, glucose, paraformaldehyde, amalgamated magnesium and aluminum, zinc dust, aluminunum dust, stannous chloride, potassium hydrosulphide. Sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate in aqueous solutions; sodium isopropoxide in ethanol have been used as basic reagents. Each reaction has been carried out in calculated amount of reducing agents either azo- /or azoxy– compound, temparature and pH of reaction media controlled. In these reactions only m– and p-nitrophenols were reduced to correspondig azoxyphendols and no azo-phenols were obtained. In mild conditions no reaction took place, and starting materials isolated from the reaction mixture. However in vigorous conditions (namely strong reducing agents and high temperature) aminophenols were isolated.

Reduction of o-aminophenol. Paraformaldehyde, glucose, arsenic trioxide in presence of any basic condensing agents, did not reduced o-nitrophenol at reflux temperature. However, refluxing of o-nitrophenol with zinc dust and alcoholic potassium hydroxide gave o-aminophenol. Aqueous sodium stannite solution also gave the same compound.

Reduction of m-nitrophenol. Reduction of m-nitrophenol with hot methanolic sodium hydroxide solution gave m-azoxyphenol in 11 % yield. Hot methanolic sodium methoxide (17 % yield), sodium isopropoxide in hot isopropyl alcohol (19 % yield), stannous chloride in sodium hydroxide (sodium stannite soluti on) (15 % yield) also gave m-azoxyphenol. However, arsenic trioxide and glucose in hot sodium hydroxide solution, amalgamated magnesium and paraformaldehyde and acetaldehyde in aqueous sodium hydroxide and potassium hydrosulphide did not reduced m-nitrophenol.

Reduction of p-nitrophenol. Reduction of p-nitrophenol by means of arsenic trioxide in boiling aqueous sodium hydroxide gave p-azoxphenol in 85% yield. Bigelow and Palmer have used arsenic trioxide in basic solutions in order to reduce nitrobenzene to azoxybenzene [10]. Glucose reduced p-nitrophenol to p-azoxyphenol in hot aqueous sodium hydroxide solution (This method has been used to reduce o-nitrophenol to o-azoxyphenol [3]). Reduction of p-nitrophenol by means of paraformaldehyde in hot aqueous sodium bicarbonate gave p-azoxyphenol in 50 % yield. The same reducing agent in hot aqueous sodium carbonate gave 56 % ,in hot aqueous sodium hydroxide 68 % yield. Boiling isopropyl alcohol-sodium hydroxide solution reduced p-nitrophenol to p-azoxyphenol in 87 % yield. Boiling sodium ethoxide gave 88 % yield. All experiments in which used the same reducing agent but excess amount, did not give p-azophenol, but always p-azoxyphenol was obtained. Either amlgamated magnesium or aluminium in aqueous basic solutions did not give a definite and separable reaction mixture but some tary materials were formed. Zinc dust in ethanolic potassium hydroxide solution, reduced p-nitrophenol to p-aminophenol.

Cupric, nickel and cobaltous saltous of p-azoxyphenol. Cupric salt of p-azoxyphenol was formed mixing an aqueous solution of p-azoxyphenol with cupric acetate. This salt was found to be $C_{12}H_8O_3N_2CuCu\ (OH)_2$ (a basic salt). Nickel and cobaltous salt of p-azoxyphenol were prepared in the same manner, using nickel and cobaltous acetate. These salts also were found to be basic salts: $C_{12}H_8O_3N_2NiNi\ (OH)_2$ and $C_{12}H_8O_3N_2CoCo\ (OH)_2$.

Result: In basic conditions, powerful reducing agents reduce nitrophenols to aminophenols. Mild reducing agents give azoxxyphenols rather than azophenols.

EXPERIMENTAL

Reduction of p-nitrophenol with arsenic trioxide in basic condition. In a 250 ml thre neck round bottom flask, fitted with reflux condenser, mechanical strirrer and a stopper, were introduced a mixture of 6 .20 g (30 a mmoles) of arsenic trioxide dissol ved in 20 ml of water containing 7 .5 g of sodium hydroxide and 5 .55 g (40 mmoles) of p-nitrophenol. Mechanical stirrer was started and flask heated on an oil bath at temperature 110-120 °C for half hours, was allowed to cool to room temperature. Reaçtion mixuture which was solidified as a dark yellow mass, was triturated with a small amount of water and filtered on a Büchner funnel. Recrystallization of this from water containing 1 % of acetic acid (heating up the solution to 80 °C) gave 3 .92 g (17 mmoles, 85 %) of p-azoxyphenol. Melting point was 224–229 ° (decomposed). No depression in melting point was observed mixing this substance with an authentic sample.

Reduction of p-nitrophenol by means of glucose. In a 250 ml three neck round bottom flask, fitted with reflux condenser, mechanical stirrer and a stopper were introduced 5 .55 g (40 mmoles) of p-nitrophenol and 100 ml of sodium hydroxide solu tion containing 1 .20 g of solid NaOH. After dissolving all of p-nitrophenol, 5 .4 g (30 mmoles) of glucose was added. Stirrer started, flask heated on an oil bath (temperature 100-105 °C) for two hours. Light yellow reaction mixture was changed to a darker yellow, finally become red brown. Flask was allowed to cool to room temporature, separated cryctals were filtered. Recrystallization of crude procduct from 1 % aqueous acetic acid gave 3 .2 g (14 mmoles. 70 %) orange needle crystalline material, m.p. 225 °-230 °C (decomposed). No depression in melting point was observed mixing this substance with p-azoxyphenol.

Reduction of p-nitrophenol with paraformaldeyhde in presence of aqueous sodium bicarbonate. In a 250 ml three neck round bottom flask equipped with reflux condenser, machanical stirrer and a stopper, were introduced 2 .78 g (20 mmoles) of nitrophenol and 100 ml of 3 % equeous sodium bicarbonate solution. After dissolution was comlete (clear yellow solution) 1 .20 g (30 mmoles) of paraformaldehyde was added into this solution.

Mechanical stirrer was started and flask heated on an oil bath having temperature 100–105 °C for four hours. Reaction mixture was allowed to stand overnight, next day was filtered. Filtrate was acidified adding a few drops of conc. hydrochloric acid carefully*. Precipotate which was formed filtered and recrystallized from water**, gave 1 .22 g (5 .3 mmoles, 53 %) of p-azoxyphenol, m.p. 225 °–230 °C (decomposed). No melting point lowering was observed mixing this compound with an authentic sample.

Reduction of p-nitrophenol with p-formeldehyde in presence of aqueous sodium carbonate. Experiment was performed as above, using same amount of p-nitrophenol and paraformaldehyde and 100 ml of 2 % sodium carbonate solution instead of sodium bicarbonate (foaming was observed during the reaction), and 1 .28 g (5 .6 mmoles, 56 %) p-azoxyphenol was obtained, m.p. 225–230 °C. No depresseion in melting point was observed mixing this compound with an authentic sample.

Reduction of p-nitrophenol with paraformaldehyde in presence of aqueous sodium hhydroxide. Experiment was performent as above, using, the same amount of p-nitrophenol and paraformaldehyde and 100 ml of 1 .5 % aqueous sodium hydroxide. Foaming was observed in this reaction also. 1 .56 (6 .8 mmoles. 68 %) of p-azoxyphenol was obtained, m. p. 225–230 °C, no depression in melting point was observed mixing this compound with an authentic sample.

Reduction of p-nitrophenol by means of isopropyl alcoholic sodium hydroxide solution. In a 100 ml three neck round bottom flask, equipped with reflux condenser, mechanical and a stopper, were introduced a solution of 2.78 g (20 mmoles) of p-nitrophenol in 40 ml of basified isoproyl alcohol with sodium hydroxide (2 .0 g NaOH /40 ml isopropyl alcohol). Mechanical stirrer was started and flask was heated on a water bath for one and half hours. Excess of isopropyl alcohol and aceton which is formed, were distilled off and a yellow solid material was remained. This was

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* Because of p–azoxyphenol is unstable in strong acidic media, it was avoided to add excess of hydrochloric acid.

** p–Azoxyphenol in aquenous solutions was decomposed in temperatures higher than 80 °C.

triturated with warm water (60–70 °C), was cooled to room temperature, and conc. acetic acid was added to get a complete percipitation, mixture was heated up and was allowed to crystallize for two hours, was filtered and washed to get 2 .01 g (87 mmoles, 87 %) of p-azoxyphenol, m.p. 225–230 ° (decomposed). No depression in melting point was observed mixing this material with an authentic sample.

Reduction of p-nitrophenol by means by ethanolic sodium ethoxide solution. In a 100 ml three neck round bottom flask, fitted with reflux condenser, mechanical stirrer and a stopper, were introduced 25 ml of absolute ethanol (99.9 %) and 1 .5 g of sodium in small portions. Flask was heated to 40–50 °C for a short period to dissove all sodium. Into this solution 2 .78 g (20 mmoles) of p-nitrophenol was added and heated at 70–80 °C on a water bath for two hours. Excess of alchohol (and acetaldehyde which is formed) was distilled off, a dark yellow residue was remained. This was triturated with small amount of water to dissolve, 3 % acetic acid was added until to get a complete precipitation. Mixture was heated and was allowed to crystallize for two hours, and filtered, washed to get 2.03 g (8.8 mmoles 88 %) of p-azoxyphenol, m.p. 225–230 ° (decomposed). No depression in melting point was observed mixing this, with an authentic sample.

Reduction of m-nitrophenol with basic methanol. In a 100 ml three neck round bottom flask equipped with reflux condenser, mechanical stirrer and a stopper, were introduced 2 .78 g (20 mmoles) of m-nitrophenol and 40 ml basic methanol (5 g NaOH in 100 ml methanol). Mechanical stirrer was started and flask heated on a water bath at temperature 80–90 °C, for three hours. Reaction mixture which was yellow in color, was turned to dark red at the end of the reaction. Excess of methanol (and formaldehyde which is formed) was distilled of and remaining dark residue was dissolved in small amount of water and sufficient amount of concentrated acetic acid was aded dropwise while continious stirring to acidify the solution. Acidic aqueous solution was extracted twice with ether, ether layers combined (which red in color), 2 /3 of solvent was removed by distillation, residue was transferred in an evaporating dish and allowed to evaporate. Remaining solid was taken up with water, treated with charcoal and was filtered. Filtrate which gray-yellow in color, was allowed to crystallize at room temperature, seperated crystals was filtered and washed with water to give 0 .25 g (1 .1 mmoles, 11 %) of m-azoxyphenol, m.p. 179–180 °C. No depression in melting point was observed mixing this substance with an authentic sample.

Reduction of m-nitrophenol with sodium methoxide in methanol. In a 100 ml three neck round bottom flask fitted with reflux condenser, machanical stirrer and gas inlet, were introduced 30 ml of absolute methanol and 1 g of metallic sodium in small portions through the condeser, while bubling nitrogen in the solution. Flask was heated in short period to dissolve all of sodium. In this sodium methoxide solution, 2 .78 g (20 mmoles) of m-nitrophenol was added, mechanical stirrer started and flask was heated on an oil bath having temperature 115–125 °C for two hours, under nitrogen atmospher. Methanol (and formaldehyde which is formed) was distilled off and a dark residue was remained. This was taken up with water, treated with charcoal and filtered. Filtrate was acidified adding sufficient amount of concantrated acetic acid dropwise then extracted twice with ether layers were combined and 2 /3 of it was removed by distillartion, residue was transferred in an evaporating dish and was allowed to evaporate dryness. Recrystallization of remaining solid material from water gave 0 .41 g (17 %) of m-azoxyphenol, m.p. 179–180 °C. No depression in melting point was observed mixing this material with an authentic sample.

Reduction of m-nitrophenol with sodium isopriopoxide in isopropyl alcohol In a 100 ml three neck round bottom flask fitted with reflux condenser, mechanical stirrer and a stopper, were introduced 35 ml of absolute isopropanol and 0 .80 g of sodium in small portions. Flask was heated to 40–50 °C in short period to dissolve all of sodium. Mechanical stirrer was started, 2 .78 g (20 mmoles) of m-nitrophenol was added in this solution, and flask was heated on an oil bath for two hours. Reaction mixture which was red in color at the begining of the reaction, was turned to a dark color at the end of the reaction. Excess of isopropyl alcohol and acetone which is formed in the reaction, was distilled off to leave a black residue. This was taken up with water, acidified with concentrated acetic acid adding dropwise and stirring. Acidic solution was extracted twice with ether, ether layers combined, and solvent was removed to dryness. Recrystallization of solid material from water was afforded 0.43 g (1.18 mmoles, 18 %) of m-azoxyphenol, m.p. 179–180 °C. No depression in melting point was observed mixing this compound with an authentic sample.

Reduction of m-nitrophenol with aqueous stannite solution. In a 100 ml three neck round bottom flask fitted with reflux condenser, mechanical stirrer and a stopper, were introduced 1.40 g (10 mmoles) of m-nitrophenol and sodium stannite which was prepared from 4.6 g (20 mmoles) of crystalline stannous chloride (tin salt) and aqueous sodium hydroxide solution. Mechanical stirrer was started and flask was heated on an oil bath for four hours. Red reaction mixture was turned to black at the and of the reaction. Reaction mixture was acidified with concentrated acetic acid and a brown precipitate was formed, this dissolved in 2N NaOH solution and was extracted with ether. Ether layer which was red in color. was separated, ether was removed by distilation and a black residue was remained. This was spread on a prous porcelain plate for drying, and a gray solid material was obtained. Recrystalization of this from water gave 0.35 g (1.5 mmoles, 15 %) of m-azoxyphenol, m.p. 179–180 °C No depression in melting point was observed mixing this material with an authentic sample.

Cupric salt of p-azoxyphenol. 0.23 g (1 mmole) of p-azoxyphenol was dissolved in 10 ml of water at 40–50 °C in a 100 beaker. Into this solution, 10 ml of 0.1 M cupric acetate solution was added dropwise and continuous stirring. Yellow-gren precipitate which is formed, was heated at 70 °C for 20 minutes and was filtered as hot. Precipitate washed twice with cold water, 0.10 g (0.34 mmoles, 34 %) of product was obtained, which was decomposed at 325–330 °C. This salt was soluble in 2N HCl, slightly soluble in chloroform and ethanol, insoluble in 2 N NaOH and 1 % ammonium hydroxide.

Analysis, calcld. for $C_{12}H_{10}O_5N_2Cu_2$: Cu, 32 .66; Found Cu, 32.61, 32 .52.

Cobaltous salt of p-azoxyphenol. 0 .23 g (1 mmole) of p-azoxyphenol was dissolved in 10 ml of water at 50-60 °C, in a 100 ml beaker, Into this solution 10 ml of 0 .1 M cobaltous acetate solution was added dropwise and continuous stirring. At the end of the addition no precipitate was formed, istead a red solution was obtained. This solution was heated on a water bath for 30 minutes, stirring occasionally (crystals were started to from at 10 th minute). Reaction mixture was colled to room temperature and separated crystals were filtered and washed twice with cold water to give 0 .04 g (0 .14 mmoles, 14 %) of product, decomposed at 287–290 °C. This salt was soluble in 2N HCl, slightly soluble in chloroform, ethanol and water; insoluble in 2N NaOH and 1 % ammonium hydroxide, ether and kerosene.

Analysis, calcld. for $C_{12}H_{10}O_5N_2Co_2$: Co, 30 .94; Found Co, 30 .81.

Nickel salt of p-azoxyphenol. 0 .23 g (1 mmole) of p-azoxyphenol was dissolved in 10 ml of water, in a 100 ml beaker. Into this solution 10 ml of 0 .1 M nickel acetate solution was added dropwise and continuous stirring at 40–50 °C. At the end of the addition no precipitate was formed (yellow-green solution was obtained) This solution was heatedon a water bath for 30 minutes stirring occasionally (crystals were appeared at 10 th minute). Reaction mixture was cooled to room temperature, was filtered and washed twice with cold water to give 0 .07 g (0 .24 mmoles, 24 %) of material which was decomposed at 315–320 °C. This salt was soluble in 2N HCI, slightly soluble in chloroform ethanol and water. Insoluble. in 2 N NaOH and 1 % ammonium hydroxide.

Analysis, calcld. for $C_{12}H_{10}O_5N_2Ni_2$: Ni, 30 .54; Found Ni, 30 .41.

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ÖZET

Nitrofenollerin bazik ortamlarda dimoleküler indirgenmeleri incelenmiş ve m- ve p-azoksifenoller bu yolla elde edilmiştir. Bazik ortamlarda bazı indirgenlerin amino fenolleri verdikleri gösterilmiştir. p-Azoksifenolün bakır, kobalt-2- ve nikel tuzları elde edilmiş ve özellikleri incelenmiştir.

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