

Novel reactions of aryldiazonium salts. A method for the generation of electrophiles

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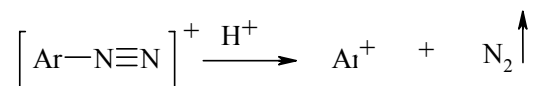
Abstract

Aryldiazonium salts decomposed in alkaline medium in the presence of starch. The hydroxide anions accompanying aryldiazonium cations were complexed by starch. Naked aryldiazonium cations decomposed into molecular nitrogen and arylum cations. The latter reacted into phenols. Since decomposition of aryldiazonium cations was slow, phenols which were formed were coupled by non-decomposed aryldiazonium cations to form arylazophenols.

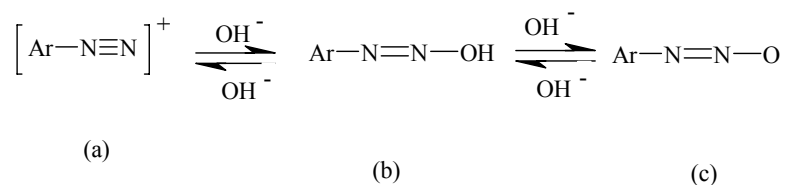
Keywords: Aryldiazonium salts, aryldiazonium cations, phenols

Introduction

Aryldiazonium salts are known for their instability, particularly under acidic conditions.¹⁻⁴ In aqueous solutions, preferably at elevated temperature, the hydroxyl anion attacks the aryl cation resulting from elimination of molecular nitrogen from the aryldiazonium cation.

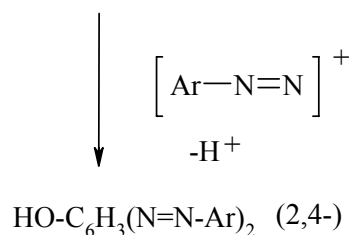
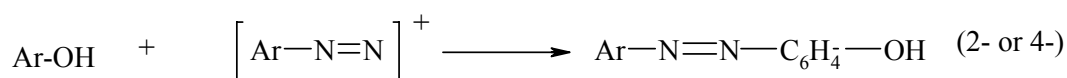
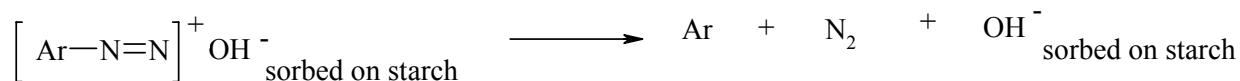


In alkaline solutions three species (a-c) reside in equilibrium:⁵⁻⁷



The position of the equilibrium depends, among other things, on the pH and the effects of substituents residing on the Ar moiety.⁵⁻⁸

This paper describes the facile, spontaneous, decomposition of aryldiazonium cations under alkaline conditions in the presence of starch. A slow evolution of nitrogen takes place, and phenols, which are formed as intermediates couple with the non-decomposed diazonium salts to form azodyes.



Results and Discussion

As anticipated, aryldiazonium salts introduced to aqueous alkali did not decompose as deduced from a lack of evolution of nitrogen and unchanged color of the reaction mixture. Also, pouring an aqueous, acidic solution of aryldiazonium salts into an aqueous suspension of starch produced no reaction of the diazonium salt. However, noticeable changes could be observed at $\text{pH} > 7$ when an aqueous suspension of starch was maintained on introducing of solution of aryldiazonium salts. Slow evolution of nitrogen begun and the color of the reaction mixture changed from dark yellow or red to brown depending on the decomposing aryldiazonium salt. The decompositions were stopped when the reaction mixtures were acidified. Thus, evidently starch under basic conditions catalyzes the decomposition of aryldiazonium salts.

It is commonly known¹⁻⁴ that aryldiazonium salts are stabilized by resonance and electrical field of the counter anions. Our observation leads to the conclusion that starch forms complexes with hydroxyl anions of aryldiazonium hydroxides formed in alkaline solutions. Destabilized aryldiazonium cations lost molecular nitrogen, generating in this manner arylum cations accepting hydroxyl anions to form phenols. The decomposition of aryldiazonium cations was slow and the phenols formed in this manner coupled with the non-decomposed aryldiazonium cations into arylazophenols. The formation of complexes of starch⁹⁻¹⁰ and cyclodextrins¹¹ preferably with anions rather than cations was already suggested and the behavior of aryldia-

zonium salts in alkaline solutions of starch can serve as additional prove of this ability of poly- and oligosaccharides. In this manner one may assume that starch could be potentially utilized in organic synthesis for generation of electrophiles from ionizing compounds.

In the case of benzenediazonium cation a trace of 2,4-di-(phenylazo)phenol was also formed. With *meta*-substituted anilines the main products from the coupling of the diazo-component to the *para*-position (with respect to the hydroxyl group of phenol) were contaminated by minute amounts of products resulting from coupling to the *ortho*-position as well. Sucs subtle non-selectivity in azocoupling to phenols was already formerly observed.¹² Another side-reaction was the formation of formazanes, in which the anomeric carbon atoms of the terminal D-glucose units were involved, resembling the behavior of aldehydes in reactions with aryldiazonium salts.¹³ Consequently, the starch left after extraction of the reaction mixture never recovered its colorless appearance. This side reaction as well as the sorption of dyes on starch¹⁴ influenced the reaction yields.

Conclusions

Starch complexes with anions rather than with cations. Therefore, starch could be potentially useful in organic synthesis for generation of electrophiles from ionizing compounds.

Experimental Section

General Procedures. Either aniline or its derivative (Table) (0.05 mole) was placed in solution prepared from conc. hydrochloric acid (12 mL) diluted with water (15 mL) (0.128 mole of HCl) and cooled to 0–5 °C. An aqueous solution containing 0.05 mole of sodium nitrite was added dropwise with agitation and temperature control until excess of nitric acid was reached as indicated by starch-iodine paper. This solution was then added dropwise with stirring into a suspension of either granular (Niechlów Potato Enterprise, Poland) or potato soluble starch (Sigma, St. Louis, Missouri, U.S.A.) (10–20 g) in water (150 mL) to which aq. 30% NaOH solution was added until pH 10 was reached. As NaOH was neutralized by addition of the acidic solution of aryldiazonium salt, a pH of 8.5–10 of the reaction mixture was maintained by addition of 30% aq. NaOH solution. Nitrogen was liberated as proved by passing its stream through a very diluted aqueous solution of KMnO₄ (solution did not decolorize). Simultaneously, a colored solid separated from the suspension (a temperature between 5 and 15 °C was maintained). When the evolution of nitrogen had ceased, the solid was filtered off, dried in the air and subjected to continuous extraction with diethyl ether, ethanol or acetone. The composition of extracts was controlled with thin-layer chromatographic plates (Merck DC Fertigplatten, Kieselgel 60 F₂₅₄).

The azodyes prepared in the reaction under study are characterized in the Table.

Table 1. Results of decomposition of aryldiazonium chlorides in alkaline suspension of potato starch^a

| Substituent in aryl moiety | Elemental analysis, % C | | | | H | | M.p. °C Lit. | | Yield ^d % |
|----------------------------|-------------------------|-------|--------|-------|--------|-------|---------------------|------------------|-------------------------|
| | N Calcd. | Found | Calcd. | Found | Calcd. | Found | Dtd. | | |
| None | 72.71 | 72.40 | 5.08 | 5.40 | 14.13 | 14.26 | 152 ¹⁵ | 149 | < 53 |
| | | | | | | 4.40 | 83 ¹⁶ | 80 ^b | trace |
| | | | | | 18.5 | 19.4 | 131 ¹⁷ | 129 ^C | trace |
| 4-Me | 74.31 | 74.81 | 6.24 | 6.15 | 12.39 | 12.03 | 112–3 ¹⁸ | 112 | 37 |
| 3-Me | | | | | | 13.06 | 106–7 ¹⁹ | 104 | n.d. ^e |
| 2-Me | | 74.78 | | 5.80 | | 12.60 | 132 ²⁰ | 130 | 54 |
| 4-NO₂ | 50.01 | 49.60 | 2.80 | 3.10 | 19.45 | 20.16 | 205–7 ²¹ | 201 | 62 |
| 2-NO₂ | | 50.35 | | 2.56 | | 19.90 | 186 ²² | 184 | n.d. ^e |

^a For the compounds mono-coupling was assumed in the *para*-position to the hydroxyl group whenever available and in the *ortho*-position to the hydroxyl group if the *para*-position was blocked. ^b The *ortho*-isomer. ^c 2,4-Di-(phenylazo)phenol. ^d For crude products. ^e Not determined.

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