

Synthesis of aromatic azo dyes using stable diazonium salts: Influence of the reaction conditions on the mono and disubstituted product ratio

Adrian Kreuz (PG), Gianluca C. Azzellini* (PQ) gcazzell@iq.usp.br

Instituto de Química, Universidade de São Paulo. Av. Profº Lineu Prestes, 748 - Butantã - São Paulo, SP - 05508-000

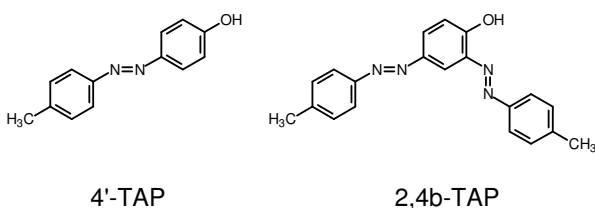
Palavras Chave/Key Words: Azophenols, stable diazonium salts, diazo coupling reactions, microdiffusion process

Abstract

Optimal conditions have been found in the reaction of stable diazonium salt derivative and phenolate yielding exclusively a mono azophenol derivative.

Introduction

Aromatic azo compounds have very important applications in industry as pigments/dyes in textiles and foods, and are components of printing toners.¹ Many other applications include acid-base indicators, sensors for metal ions and the elaboration of photocontrolled advanced materials such as liquid crystals and drug release systems.² Azophenol derivatives are prepared reacting phenolate with an *in situ* generated diazonium salt derivative. This classical coupling reaction has some limitations as the low temperatures required to maintain the unstable diazonium compound and the acid-base conditions to generate and maintain each reactive species¹. To overcome these inconvenient conditions we used stable tosylate diazonium salts. However in this case, the *p*-substituted main product is accompanied by the disubstituted compound at *ortho* and *para* positions.



Scheme 1 4-tolylazophenol (4'-TAP) and 2,4-bis(*p*-tolylazo)phenol (2,4b-TAP).

In the present communication we report on the reaction conditions to reduce the yield of the disubstituted product by using stable diazonium tosylate derivatives.

Results and Discussion

The reaction conditions were studied using 4-tolyldiazonium tosylate as a model compound. The reactions were conducted by dropping a methanolic solution of 4-tolyldiazonium tosylate over an aqueous solution of phenol. Have been tested the

influence of pH and temperature on the yield of mono/disubstituted product ratio. For the reaction of 4-tolyldiazonium and phenol in the pH range 8 – 10 a pronounced decrease of the disubstituted product is observed lowering pH and at pH 8 the disubstituted product is found in less than 2% yield. Regarding the effect of temperature (0 - 60 °C) at 0 °C the yield of disubstituted product reach its minimum (1%). The effect of pH on yields is illustrated in Fig. 1

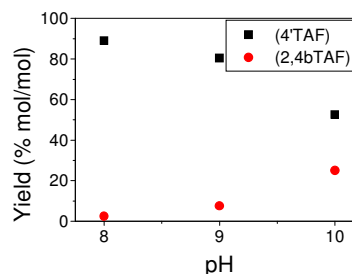


Figure 1. pH effect on the yield of 4'-TAP and 2,4b-TAP at 30°C.

These results can be understood on the basis of microdiffusion process that generates the disubstituted product.³ Lowering pH reflects on the equilibrium concentration of the reactive phenolate specie and lowering the temperature decrease the rate constant of the second coupling reaction with the mono-substituted product.

Conclusions

Taking into account some aspects of the microdiffusion process a simple condition has been established for the synthesis of 4-tolylazophenol (4'-TAP) in high yield and purity. Combining the pH and temperature results has been found that at 20 °C and pH 8, no disubstituted product was generated. Studies with other tosylate diazonium salts with different electronic contributions are in course as well as reaction with 1-naphthol as the nucleophilic specie.

Acknowledgement

CNPq and IQ-USP

¹ Merino, E. *Chem. Soc. Rev.* **2011**, 40, 3835.

² Bandara, H.M.D.; Burdette, S.C. *Chem. Soc. Rev.* **2012**, 41, 1809.

³ Zollinger, H. *Diazo Chemistry I*. Weinheim: VCH, 1994.