

## DEDIAZONIATION OF 2,4,6-TRIMETHYLBENZENEDIAZONIUM TETRAFLUOROBORATE (TMD) IN MIXED SOLVENTS

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**INTRODUCTION AND AIMS.** 2,4,6-Trimethylbenzene diazonium ion, TMD, spontaneously decomposes generating a phenylic cation, which rapidly and unselectively reacts with any nucleophile. Our previous results show that the product ratios of diazotiation of TMD in varying alcohol(s)/water mixtures and acetonitrile/water are not ideal. The selectivity for the reaction of TMD with Br<sup>-</sup> and Cl<sup>-</sup> is also solvent dependent. The aim here is to study the TMD reaction in methanol/water (HCl 0.001M) mixtures in the presence of the organic solvent-soluble tetraethylammonium bromide (TEABr). **RESULTS.** We studied the reaction of TMD with methanol, water and halides in methanol/water mixtures. Products were quantified by HPLC. The increase in the methanol/water molar fraction produced 2,4,6-trimethylphenol (TMF) and 2,4,6-trimethylanisole (TMA<sub>n</sub>), from the reaction of TMD with water and methanol. The TMF/TMA<sub>n</sub> molar ratio was proportional to the nucleophile molar ratio (ideal behavior) except at high methanol ratios, where the TMD reduction product, mesitylene, was favored. The reaction between TMD and TEABr showed that the TMF and TMA<sub>n</sub> formation are nearly constant for low TEABr concentrations while the ratio of 2-bromo-mesitylene (TMBr), the product between TMD and Br<sup>-</sup>, increases with increasing TEABr concentration. The ratio of TMBr/TMA<sub>n</sub> and TMBr/TMF at 0.1 M TEABr varies from more than 10% in methanol to less than 5% in water, respectively, showing that the reaction between TMD and Br<sup>-</sup> is preferential in high methanol/water ratio mixtures. **CONCLUSION:** the increase in methanol/water ratio increases the concentration of the ion pair between TMD and Br<sup>-</sup> leading to preferential formation of TMBr.

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