Synthesis of allyl e alkylarenes by Barbier alkylation of diazonium salts in aqueous medium

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Keywords: Barbier alkylation, diazonium salts, Barbier allylation

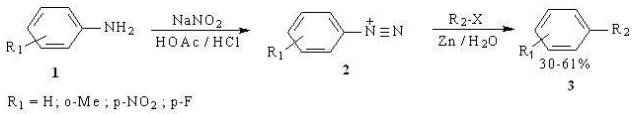
INTRODUCTION

Barbier reactions in aqueous media are mainly performed with allylic halides and carbonyl substrates. This paper presents new a methodology for allylation of ionic substrates in aqueous such as diazonium salts. Getting the first product of allylation as well as of alkylation with halides saturated.
Some allylbenzenes are obtained from sassafras oil extraction. However the propenylbenzene is not obtained from natural sources. During the studies on the allylation of diazoniun salts in water, the propenylbenzene was obtained as a major product in good yields. Due to the good result, we examined the applicability of the method to other saturated halides and different anilines.

RESULTS AND DISCUSSION

Benzene diazonium salt (**2**), generated from nitrous acid and aniline (**1**), was reacted with allylbromide. The reactional media was neutralized by calcium carbonate addition. None co-solvents or catalysts improved the results of the reaction. Applying the method for isopropyl iodide, using the DMSO:H_2O (9:1) mixture, the yielding was 54%. Examining the reaction with the 2-methylaniline, 2-isopropyltoluene (**3**) was formed with 61% of yielding.

Figure 1. Insert the figure caption here



R_1 = H; o-Me ; p-NO_2 ; p-F
R_2-X = allyl-Br; i-Pr-I; t-But-Br

Table 1. Reaction medium

Entry	Solvent	R_1/R_2	Yield (%)
1	H_2O / HCl	H / allyl	56
2	H_2O / HOAc[1]	H / allyl	16
3	H_2O / HOAc[2] / HCl	H / allyl	45

*[1] 2mmol of acetic acid
[2] HOAc (aq) 50% w/w – 2mmol of HCl

Table 2. Alkylarene synthesis

Entry	R_1 / R_2	solvent	Yield
1	H / allyl	H_2O	56
2	H / i-Pr	DMSO:H_2O[1]	54
3	2-CH_3 / allyl	H_2O	54
4	4-F / allyl	H_2O	34
5	4-F / i-Pr	DMSO:H_2O[1]	61
6	2-CH_3 / i-Pr	DMSO:H_2O[1]	61

[1] DMSO:H_20 – 9:1 v/v

CONCLUSION

We have investigated and presented a valuable alternative for one-pot alkylarenes synthesis. Our method proceeds under aqueous conditions, utilizes readily available, inexpensive, amines. Moreover, our one-pot alkylation with isopropyl halides is very innovative.This makes a method economical and regiosseletive.

ACKNOWLEDGEMENTS

FAPESB; UNEB; UFPE Analytical Center

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