

**PALLADIUM(II) CHLORIDE/EDTA-CATALYZED BIARYL
HOMO-COUPLING OF ARYL HALIDES, SOLVOLYSIS OF
DIAZONIUM SALTS IN ETHYLENE GLYCOL ETHERS AND
TRANS-TOSYLATION OF ALCOHOLS WITH 2,2,2-
TRICHLOROETHYL TOSYLATE**

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**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

JULY 2010

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**BY
VIRINDER SINGH**

**Thesis submitted
In fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY
To the**



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
JULY 2010**

Dedicated to my Parents

Certificate

This is to certified that the thesis entitled “Palladium(II) chloride/EDTA-catalyzed biaryl homo-coupling of aryl halides, solvolysis of diazonium salts in ethylene glycol ethers and trans-tosylation of alcohols with 2,2,2-trichloroethyl tosylate”, being submitted by Mr. Virinder Singh, to the Indian Institute of Technology, Delhi, for the award of the degree of “Doctor of Philosophy” in chemistry is a record of bonafide research carried out by him. Mr. Virinder Singh worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which to my knowledge has reached the requisite standard.

The results embodied in this dissertation have not been submitted in part or full, to any other University or Institute for the award of any degree or diploma.

I.I.T Delhi
July, 2010

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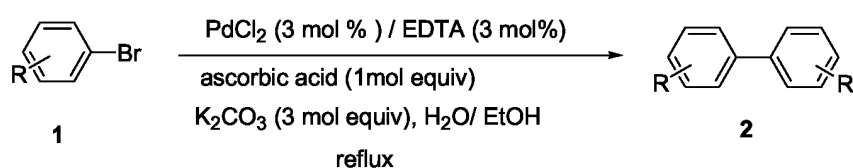
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Virinder Singh

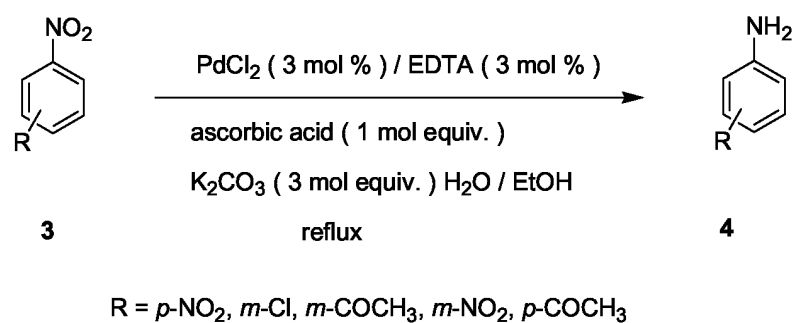
ABSTRACT

In Chapter 1, PdCl₂-EDTA catalyzed homo-coupling of aryl halides in the presence of ascorbic acid in basic (K₂CO₃) aqueous-ethanolic medium has been described. Both electron-rich and electron-deficient bromoarenes **1** underwent homo-coupling to give biaryls **2** in acceptable to good yields.

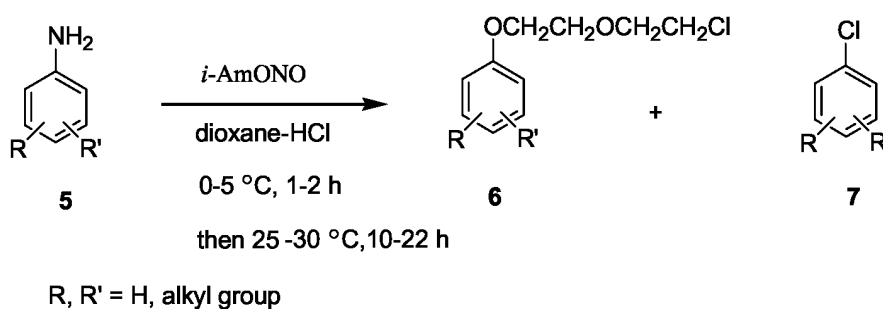


R = H, *p*-CH₃, *p*-CH₃O, *p*-NMe₂, *p*-OH, *p*-PhCO, *p*-Cl, *p*-CH₃O, *p*-COOH, *o*-COOH, *p*-NO₂, *m*-NO₂

Homo-coupling of 4-bromonitrobenzene gave 4-amino-4'-nitrobiphenyl probably due to reduction of one of the nitro groups in the coupling products due to activating effect of the other suitably positioned nitro group. Therefore, it was thought that probably an activated nitro group might be selectively reduced under these conditions. Thus, the reactions of some aromatic nitro compounds **3** activated by another electron-withdrawing and reducible groups, such as nitro, keto, and chloro were performed under similar conditions. It was found that the nitro group was selectively reduced in the presence of these groups to give the amines **4**. Unactivated nitro group as in nitrobenzene and *p*-nitrotoluene was not reduced under these conditions.

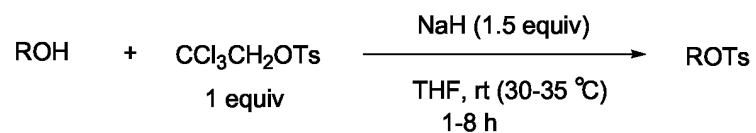


Chapter 2 describes the diazotization of aromatic amines and solvolysis of the corresponding arenediazonium salts in anhydrous dioxane and others ethers of the ethylene glycol saturated with hydrogen chloride gas. Diazotization of the anilines **5** in stock solution of HCl in dioxane with isoamyl nitrite at 0-5 °C followed by stirring at 25-30 °C for 12-18 h gave 2-(2-chloroethoxy)ethyl ary ethers **6** as a result of solvolysis of the diazonium salts. 2,6-Disubstituted anilines yielded chloroarenes **7** as the major products along with the corresponding solvolysis products **6**. The aryl ethers **6** derived from the solvolysis in dioxane are important intermediates for the synthesis of compounds of medicinal value.



In Chapter 3, tosylation of alcohols by a new method involving trans-tosylation with 2,2,2-trichloroethyl tosylate has been described. Primary alcohols on treatment with 2,2,2-trichloroethyl tosylate in the presence of sodium hydride in THF at room temperature underwent trans-tosylation involving S-O bond cleavage to afford alkyl tosylates in good

yields. Phenol was found to be unreactive under similar conditions. Unlike *p*-toluenesulfonyl chloride, the reagent 2,2,2-trichloroethyl tosylate used in the present method is not moisture sensitive.



R = CH₃CH₂, CH₃CH₂CH₂, CH₃CH₂CH₂CH₂, CH₂=CHCH₂, PhCH₂CH₂,
ClCH₂CH₂, CH₃O(CH₂)₂O(CH₂)₂, CH₃OCH₂CH₂O, CH₃(CH₂)₇

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