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DIRECT TRANSFORMATION OF ARYLAMINES TO ALKENYLARENES UNDER PALLADIUM(0) CATALYSIS

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Olefins could be arylated in good yields by the combination of arylamines (substituted anilines: 4-Me, 4-Cl, 4-Br, 2-NO_2, 4-NO_2, and 3-aminopyridine) and *t*-butyl nitrite under palladium(0) catalysis.

Previous papers[1)] revealed that palladium(0) effectively catalyzed the arylation of olefins by arenediazonium salts. The arylation can be adequately applied to olefins bearing either electron-releasing or -withdrawing group(s), but is limited by the unstability of diazonium salts at room temperature. The combination of an arylamine and an alkyl nitrite has been used in Doyle Modification of the Meerwein arylation[2)] and the Sandmeyer halogenation[3)] with significant improvements. Palladium(II) acetate promoted arylation[4)] with an arylamine and *t*-butyl nitrite has been shown to require a stoichiometric amount of $Pd(OAc)_2$ and long reaction time (8 h). Now we wish to report a successful arylation of olefins with arylamines and *t*-butyl nitrite in the presence of palladium(0) catalyst.

In acetonitrile or dichloromethane the reaction of styrene with aniline and *t*-butyl nitrite in the presence of bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$) gave a large amount of tarry material and stilbene only in 11%. When the reaction was carried out in the presence of monochloroacetic acid, the yield increased significantly as high as 53%. Raising of the reaction temperature (from r.t. to 50 °C) and use of acetic acid as solvent gave additional improvements.

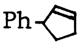
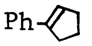
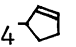
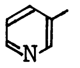
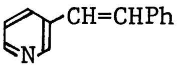
Dropwise addition of *t*-butyl nitrite to a stirred mixture of an arylamine, an olefin, $Pd(dba)_2$ (5 mol%) and monochloroacetic acid in acetic acid resulted in the evolution of nitrogen (eq. 1). Crude product separated from neutralized reaction

$$\underset{(10\ \text{mmol})}{ArNH_2} + \underset{(20\ \text{mmol})}{HC(R^1)=CHR^2} + \underset{(11\ \text{mmol})}{t\text{-}BuONO} + \underset{(0.5\ \text{mmol})}{Pd(dba)_2}$$

$$\xrightarrow[50\ ^\circ\text{C},\ 0.5\ \text{h}]{AcOH(20\ \text{ml})\text{-}ClCH_2COOH(20\ \text{g})} Ar\text{-}C(R^1)=CHR^2 \qquad (1)$$

mixture was purified by column chromatography (silica gel-benzene or CCl_4) followed by recrystallization or distillation. The typical results are summarized in the Table. The good yields of nitro substituted products are notable in view of marked depressing effect of the group on product yields in the arylation with diazonium salts,[1)] and also lower yields due to an *ortho* nitro group in the Meerwein arylation.[5)] The

Table. Alkenylation of Arylamines[a)]

$ArNH_2$	Olefins	Products[b)]	Yields(%)[c)]
Ph-	CH_2=CHPh	(E)stilbene	97
" d)	CH_2=CHCOOEt	(E)ethyl cinnamate	81
"	cyclopentene	 ,  (95:5)	81
4-Me-C_6H_4-	CH_2=CHPh	(E)4-Me-stilbene	84
4-Cl-C_6H_4-	"	(E)4-Cl-stilbene	84
4-Br-C_6H_4-	"	(E)4-Br-stilbene	61
2-NO_2-C_6H_4-	"	(E)2-NO_2-stilbene	73
4-NO_2-C_6H_4-	"	(E)4-NO_2-stilbene	79
"	cyclopentene	4-NO_2-C_6H_4-	67
 e)	CH_2=CHPh		69

a) Unless otherwised noted the reaction conditions were same to those described in eq. 1. b) All products listed here have satisfactory mps and spectral features (IR and NMR) and isomer distribution was determined by GLC.

c) Isolated yields based on arylamines used. d) $ClCH_2COOH$ was not added.

e) CH_2Cl_2 was used in place of AcOH with 10% of $Pd(dba)_2$ at r.t.

successful results obtained with 3-aminopyridine, whose diazonium salt decomposes easily at room temperature, is also favorably compared with the route *via* diazonium salts. The present arylation is free from the formation of addition products and the limitation in starting olefins observed in the Meerwein arylation[2,5)] (eq. 2).

$$ArNH_2 + t\text{-BuONO} + PhCH{=}CH_2 \longrightarrow [ArCH_2CHPh] \xrightarrow{CuCl_2} ArCH_2CH(Cl)Ph \qquad (2)$$

This procedure contains several advantages as a synthetic method in the following respects; 1) high product yields under mild conditions, 2) no substituent effect in both olefinc substrates and arylamines, and 3) adaptability to heteroaromatic amines which frequently raise difficulty in diazotization.

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