Palladium- and copper-catalyzed synthesis of triarylamines in an aqueous-organic emulsion

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The Ullman synthesis of triarylamines is normally carried out in a high-boiling solvent in the presence of a base and specially prepared copper powder.[1,2] To continue the study of classical organic reactions conducted in water in the presence of metallocomplex catalysts,[3] we studied the reactions of diarylamines with a number of aryl iodides in an alkaline aqueous-ethanolic emulsion in the presence of cetyltrimethylammonium bromide as an emulsifying agent.

Previously[2] the best results concerning the synthesis of triarylamines were achieved when diphenylamines and aryl iodides were boiled for a long period in dichlorobenzene in the presence of an equivalent amount of electrolytically derived copper, potash, and crown ether. Our attempts to realize this procedure under the conditions chosen or by using $Pd(OAc)_2$ as a catalyst were unsuccessful. However, when $Pd(OAc)_2$ and CuI were simultaneously introduced into the reaction mixture, we observed a reaction that finally gives the desired triarylamines in high yields (80—90 %).

$$Ar_2NH + Y{-}C_6H_4{-}I \xrightarrow[H_2O,\ BuOH,\ CTMAB, T]{Pd(OAc)_2,\ K_2CO_3,\ CuI} Ar_2NC_6H_4Y\text{-}p$$

$Ar_2NH = Ph_2NH$, carbasole; Y = H, *p*-Cl, *p*-Me, *p*-MeO

The attempts to use this procedure for aliphatic amines or substituted anilines failed.

Thus, the method suggested makes it possible to prepare triarylamines by a catalytic process without using high-boiling organic solvents or the specially prepared copper catalyst.

Typical procedure. Water (9 mL), *n*-butanol (1 mL), cetyltrimethylammonium bromide (5 g), and K carbonate (5 mmol) were placed in a two-necked flask equipped with a magnetic stirrer. The mixture was stirred at 100 °C until a transparent microemulsion formed. Ar_2NH (2.5 mmol), PhI (3 mmol), CuI (0.05 mmol), and $Pd(OAc)_2$ (0.025 mmol) were added to the resulting microemulsion. The reaction mixture was stirred with boiling for 24 h and neutralized with dilute HCl, and butanol was removed. The precipitate was extracted with benzene, dried with Na_2SO_4, and chromatographed through a thin alumina layer. The resulting solution was concentrated and the residue was crystallized from ethanol. The yield of Ph_3N was 90 %, m.p. 61—63 °C. 4-$ClC_6H_4NPh_2$ (82 %), 4-$MeC_6H_4NPh_2$ (80 %), 4-$MeOC_6H_4NPh_2$ (85 %), and *N*-phenylcarbazole (86 %) were prepared in a similar way. The melting points of the compounds obtained correspond to the literature data.[2]

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References

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