

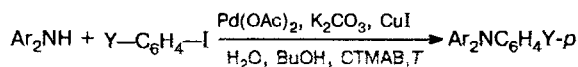
Palladium- and copper-catalyzed synthesis of triaryl amines in an aqueous-organic emulsion

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The Ullman synthesis of triaryl amines 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 diaryl amines with a number of aryl iodides in an alkaline aqueous-ethanolic emulsion in the presence of cetyltrimethylammonium bromide as an emulsifying agent.

Previously² the best results concerning the synthesis of triaryl amines were achieved when diphenyl amines 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 triaryl amines in high yields (80–90 %).



Ar₂NH = Ph₂NH, 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 triaryl amines 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. Ar₂NH (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 Na₂SO₄, and chromatographed through a thin alumina layer. The resulting solution was concentrated and the residue was crystallized from ethanol. The yield of Ph₃N was 90 %, m.p. 61–63 °C. 4-ClC₆H₄NPh₂ (82 %), 4-MeC₆H₄NPh₂ (80 %), 4-MeOC₆H₄NPh₂ (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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