

Synthesis of di- and trialkenylsubstituted aromatic amines

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Keywords: aromatic amines, allyl chloride, 4-chloro-2-pentene, alkenylation, rearrangement of Claisen.

Abstract

Inventing the Claisen rearrangement in aromatic amines series has led to bio-active 2-alkenyl-substituted arylamines availability and their wide usage in the synthesis of heterocyclic compounds. The presence of several reaction centers in the allyl aniline molecule makes it possible to carry out their further transformations in the nitrogen atom, the alkenyl unit, or two centers simultaneously. The preparative value of these compounds can be further strengthened by adding active functional groups or a double bond to the molecule. In this paper, the possibility of introducing an alkenyl group into the composition of aromatic amines with an allyl-type substituent in the nucleus or at the nitrogen atom has been considered. Continuous boiling (20-30 h) of 2-(1-methyl-2-butenyl)arylamines with 4-chloro-2-pentene in a triethylamine solution leads to their *N*-substituted derivatives. The same reaction with 3-chloropropene and 3-chloro-2-methylpropene is completed in 8 hours. The introduction of the second alkenyl group along the nitrogen atom of *N*-(1-methyl-2-butenyl)aniline is under harder conditions (150 °C, autoclave), with 4-chloro-2-pentene forming *N*,2-di-(1-methyl-2-butenyl)aniline (**I**). By heating **I** under ZnCl₂ in nitrobenzene, 2,6-di-(1-methyl-2-butenyl)aniline (**II**) with 78% yield and a small amount of 2,4,6-tri-(1-methyl-2-butenyl)aniline (**III**) were obtained. The same products were obtained by direct 4-chloro-2-pentene and a twofold excess of 2-(1-methyl-2-butenyl)aniline reaction with 10% **III** yield. Both schemes have been implemented to get 2,6-di-(1-methyl-2-butenyl)-4-methylaniline (**IV**). *N*,2-Di-(1-methyl-2-butenyl)-4-methylaniline prepared by the method described, is rearranged under ZnCl₂ in **IV** with 82% yield. The same result was obtained by heating 4-chloro-2-pentene at 150 °C with a twofold excess of 2-(1-methyl-2-butenyl)-4-methylaniline. To synthesize 2,4-di-(1-methyl-2-butenyl)-6-methylaniline (**V**) according to the scheme developed, *N*,2-di-(1-methyl-2-butenyl)-6-methylaniline (**VI**) under equimolar amount of ZnCl₂ in nitrobenzene leads to the amine **V** desired. The catalysis of the Claisen **VI** rearrangement with an equimolar amount of *ortho*-toluidine hydrochloride at 140-150 °C also leads to **V**, but the yield is low, since the splitting process predominates under these conditions. Direct reaction **II** with 4-chloro-2-pentene is not feasible due to the steric inhibition of the *N*-alkenylation step by volume substituents in the *ortho*-positions. The structure of poly-substituted arylamines is established by spectral methods and elemental analysis. The compounds obtained are of interest for the nitrogen-containing heterocycle synthesis.

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