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The interaction of piperylene and its chlorine derivatives with aromatic amines

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Abstract

The article considers the possibility of introducing a pentenyl radical into the structure of aromatic amines by the interaction of the latter with piperylene and its chlorine derivatives, 4-chloro-2-pentene and 3,4-dichloro-2-pentene. Direct alkenylation of aniline with piperylene in the presence of Lewis acids leads to *C*-alkenyl arylamines. The most effective catalyst is $AlCl_3$. Along with the expected 2- and 4-(1-methyl-2-butenyl) anilines, the formation of 2,4-di- and 2,4,6-tri-(1-methyl-2-butenyl) anilines is observed, the latter being virtually the only product in the reaction with a 5-fold excess of piperylene. In addition to Lewis acids, H_3PO_4 deposited on kieselguhr or silica gel, as well as polyphosphoric acid, were used to catalyze this reaction. Under the action of these catalysts, *ortho*- and *para*-alkenylated anilines are mainly formed, and the yield of the *ortho*-isomer, reaching 34%, always exceeds the yield of the *para*-product. It is possible that, under these conditions, *N*-alkenylation occurs simultaneously with direct *C*-alkenylation followed by an amino rearrangement. The yield of the 2,4-dialkenyl product does not exceed 8%, and trialkenylated aniline is completely absent. The optimal reaction temperature is in the range of 180-200 °C, at higher temperatures the yield of the target products decreases due to the polymerization of piperylene. Various aniline derivatives are also involved in the reaction with piperylene. When one of the *ortho* positions in the arylamine molecule is occupied, as in *ortho*-toluidine or in 2-chloroaniline, a mixture of the three products is formed in comparable amounts. The reaction of *meta*-toluidine with piperylene also leads to the mixture of three products, and the substitution does not affect the 2-position between the amino and methyl groups. If both *ortho*-positions are occupied, as in 2-methyl-6-ethylaniline, the reaction is quite successfully under way in the *para*-position (yield is 61%). To increase the selectivity of the process, the alkylation of aromatic amines is best carried out not by piperylene, but by its chlorine derivatives. The reaction of aniline with 4-chloro-2-pentene takes place in the environment of triethylamine and leads to *N*-(1-methyl-2-butenyl) aniline with a yield of 80%. Other primary and secondary arylamines react in the same way. The reaction with 3,4-dichloro-2-pentene proceeds under more severe conditions. If the reaction of aromatic amines with 4-chloro-2-pentene is carried out not in triethylamine medium, but in an excess of arylamine itself as a solvent, then not *N*- but *C*-substituted products are formed. The reaction proceeds as a consequitive-simultameous process. In the first stage, *N*-alkenylation occurs with the formation of *N*-(1-methyl-2-butenyl) arylamine followed by an amino rearrangement of Claisen under the catalytic action of evolved HCl. Alongside with the obvious predominance of *ortho*-substituted arylamine (64-82%), *para*-isomers and, in some cases 5-12% of 2,4- or 2,6-disubstituted compounds were found in the reaction products. The amino rearrangement in the interaction of arylamines with 3,4-dichloro-2-pentene proceeds with exceptional *ortho*-selectivity. Alkyl groups at nitrogen and *ortho* positions accelerate, and *ortho*-chloro, *para*-methyl, 2,4-dimethyl substituents slow down the process, while the *meta*-methyl group has no significant effect. The same dependence was observed in the case of 4-chloro-2-pentene. Thus, pentenyl fragment can be introduced in various ways into the structure of aromatic amines: by direct interaction with piperylene in the presence of catalysts, *N*-alkenylation of 4-chloro-2-pentene and 3,4-dichloro-2-pentene in triethylamine medium and reaction of arylamines with chlorine derivatives of piperylene, accompanied by an amino rearrangement of Claisen.

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