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REACTION OF ANILENIUM ION-RELATED SPECIES AND THEIR SYNTHETIC APPLICATION

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N-Arylhydroxylamines react with benzene in the presence of trifluoroacetic acid to give diphenylamines.[1] In the presence of trifluoromethanesulfonic acid the reaction gives 2- and 4-aminobiphenyls.[2] Dimethylaniline N-oxide reacts with benzene in the presence of the strong acid to give 2- and 4-dimethylaminobiphenyls.[3] Nitrosobenzene, azobenzene, azoxybenzene, nitrobenzene, phenylhydrazine, and N-acyl-N-phenylhydroxylamine give products which can be interpreted by involvement of various immonium-benzenium dications as intermediates.[4,5] These reactions were applied to syntheses of several nitrogen-containing aromatic compounds. Thus, aminoaporphines,[6] apoerysopine dimethyl ether[3], apogaranthamine derivatives[6], and cyclopentenopyridocarbazole(Lys-P-1, a mutagen from lysine pyrolysate) [7] were synthesized.

O-Aryl-N-acylhydroxylamines react with benzenes in the presence of acid with acidity of H_0= -3 ～ -5 to give 2- and 4-hydroxybiphenyls.[8] This reaction was applied to a synthesis of orchinol and loroglossol.[6] O-Aryl-N-acylhydroxylamines rearrange to cathecol derivatives by acid in the absence of nucleophiles, which may be a useful method of introduction of a hydroxyl group to the ortho position of a phenol.[6,8]

Scope and limitation of the reaction which involves N-O bond heterolysis will be discussed.[9,10]

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