

REARRANGEMENTS OF O-PHENYLHYDROXYLAMINE DERIVATIVES

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Nitrogen-oxygen bond cleavage of O-arylhydroxylamine derivatives initiates several new reactions in the field of aromatic chemistry. Now, we report several new rearrangements of O-aryl-N-acylhydroxylamines (1).

1. O-Aryl-N-benzoylhydroxylamines (2) were treated with $\text{CF}_3\text{COOH}-\text{CF}_3\text{SO}_3\text{H}$ at room temperature to give 2-hydroxyaryl benzoates (3) in yields of 49-78% (6 examples).
2. N-Alkyl-N'-phenoxyureas (4) were treated with CF_3COOH in CH_2Cl_2 at room temperature to give 2-(N-alkyl-N-carbamoyl)aminophenol (5) (51-85%) (7 examples).
3. N-Aryl-N'-aryloxyureas (6) were treated with CF_3COOH in CH_2Cl_2 at room temperature to give N-(4'-hydroxy-2-biphenyl)ureas (7) and N-carbamoyl-2-hydroxydiphenylamines (8) as major products (7 examples).
4. O-Aryl-N-acetoacetylhydroxylamines (9) were treated with $\text{CF}_3\text{COOH}-\text{CF}_3\text{SO}_3\text{H}$ at room temperature to give 2-methylbenzofuran-3-carboxamides (10) in yields of 34-79% (6 examples).

The mechanisms of key steps of the rearrangements are accounted by the acid catalyzed [3,3] or [5,5] rearrangements involving nitrogen-oxygen bond fission of O-arylhydroxylamines.

