ELECTROPHILIC AROMATIC SUBSTITUTION WITH N-ALKOXY-N-ACYLNITRENIUM IONS

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A new direct alkoxyamidation to aromatics by the electrophilic aromatic substitution with an N-alkoxy-N-acylnitrenium ion generated from N-chloro-N-alkoxyamides is described.

(I) Intramolecular Aromatic Substitution with an N-Methoxy-N-acylnitrenium Ion

N-Methoxy-N-acylnitrenium ions (1), which are generated by treatment of N-chloro-N-methoxyamides with silver carbonate in trifluoroacetic acid, react with benzene derivatives to give N-phenyl-N-methoxyamides in good yields (eq. 1).

(II) Synthesis of Nitrogen Heterocycles by Intramolecular Cyclization of N-Chloro-N-methoxyamides

Intramolecular cyclization of N-chloro-N-methoxyamides to a suitably situated benzene ring in the molecule provides a convenient synthesis of nitrogen heterocycles having N-methoxy function, which are hitherto difficult to be synthesized (eq. 2). In the case of the cyclization of p-methoxy compounds (2), 1-aza[n,5]-spiranes (3) are obtained in good yields, which have basic skeletons of the cephalotaxus alkaloids and histrionicotoxin groups (eq. 3).