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C→N migration of methoxycarbonyl and acetyl groups in reactions of functionally substituted carbanions with aryl isocyanates. Kinetics and mechanism of the reactions

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Abstract

The kinetics and mechanism of C→N migrations of methoxycarbonyl and acetyl groups in the reactions of the sodium derivative of methyl (2-cyano-2-phenyl)acetate and 1,1-diacetyl-2-phenyl-2-tributylphosphonioethanide with aryl isocyanates were studied by spectrophotometry. The reactions afford a prereaction complex via a concerted mechanism, according to which the nucleophilic attack of the carbanionic center to the carbon atom of the isocyanate group and the subsequent nucleophilic attack of the nitrogen atom to the carbonyl carbon atom, resulting in the C-C bond cleavage, occur almost simultaneously in the framework of the same transition state. © Springer Science+Business Media, Inc. 2006.

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Keywords

Aryl isocyanates, Kinetics, Migrations of methoxycarbonyl and acetyl groups, Phosphorus-containing zwitterions, Reaction mechanism