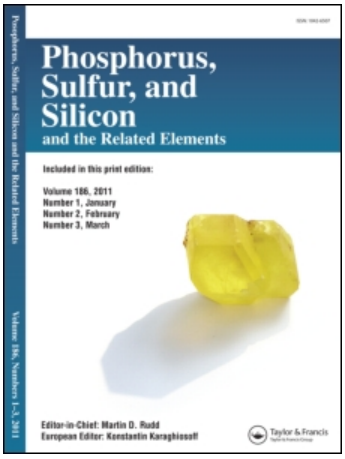

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Catalytic Activity of Amines Hydrochlorides, Intramolecular Catalysis and Stereoselectivity of Phosphorylation of Hydroxylcontaining Nucleophiles with P(III)-N-Ethylanilines

Sergei Yu Burmistrov[a]; Mikhail K. Gratchev[a]; Galina I. Kurochkina[a]; Larisa K. Vasyanina[a]; Edward E. Nifantyev[a]
[a] Moscow Pedagogical State University, Moscow, Russia

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CATALYTIC ACTIVITY OF AMINES HYDROCHLORIDES, INTRAMOLECULAR CATALYSIS AND STEREOSELECTIVITY OF PHOSPHORYLATION OF HYDROXYLCONTAINING NUCLEOPHILES WITH P(III)-N-ETHYLANILINES

SERGEI YU.BURMISTROV, MIKHAIL K.GRATCHEV, GALINA I. KUROCHKINA, LARISA K. VASYANINA AND EDWARD E. NIFANTYEV

Moscow Pedagogical State University, 1M. Pirogovskaya, Moscow 119882, Russia

Key words: Phosphorylation; aminophosphines; alcoholysis; acid catalysis.

The effect of acid-base properties of amines hydrochlorides (AH) on their catalytic activity in methanolysis of P(III)-N-ethylaniline has been studied. The analysis of Brönsted correlation equation was indicative of *general acid catalysis* and it was thus confirmed, that general regularities had place during alcoholysis of P(III)-amines under catalysis with AH. In addition, the increasing of alcohol polarity leads to the increasing of proton transfer degree (α) from acid catalysts to phospho(III)amine substrate and to the increasing of the positive charge at the phosphorus in the transition state.Besides, the comparison of α values indicates that in more polar methanol (in comparison with t-butanol) the catalysis is more sensitive to the acidity change of used catalysts.

$$>P\text{-}NEtPh + ROH \xrightarrow{\overset{+}{HN}<} >P\text{-}OR + HNEtPh$$

As it was shown earlier[1] the application of optically active catalysts may lead to the stereoselectivity during phosphorylation with P(III)-amines. At present this fact was used to attain a more effective "contact" between P(III)-amine and AH forming part of this molecule, which ensured effective *intramolecular catalysis* resulting in a sharp increase in rates of phosphorylation (in 150-300 times) and in a significant stereoselectivity of the process following the inclusion of a chiral fragment in the molecule of the "catalytic" part of P(III)-amine. The stereoselectivity thus revealed was used for the enrichment of racemic mixtures of protonodonor nucleophiles.

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