ABSTRACT BOOK

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P-0840

KINETIC INVESTIGATION OF PHENYLSELENOETHERIFICATION OF SOME ?4-ALKENOLS IN PRESENCE OF CATALYTIC AMOUNT OF $COCL_2$

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The phenylselenoetherification of unsaturated alcohols is the one of the most rapid and convenient methods for formation of THF and THP type of rings. The convenient position of a double bond and a hydroxyl group in an alkenol can easily lead to formation of corresponding cyclization product. The reaction of selenium electrophiles with alkenols is a stereospecific *anti* addition where the nucleophile (pendant hydroxyl group) attacks usually at higher substituted carbon atom (Markownikoff stereoselectivity).[1] Despite the established synthetic utility of these selenofunctionalization reactions, there is no many report on a detailed kinetic investigation of these transformations.[2] In previous work it was found that in the presence and absence of various additives these reactions follow the mechanism of bimolecular nucleophile substitution S_N2 pathway.[2c]

In this work we reported the kinetic study of the cyclization of some Δ^4-alkenols with PhSeX (X=Cl, Br) in presence of catalytic amount of $CoCl_2$. We investigated the influence of olefinic and carbinol substitution pattern in some Δ^4-alkenols on the rate constants of the cyclization under the *pseudo*-first order conditions, in the presence and absence of $CoCl_2$, by UV-VIS spectrophotometry. Reactions were carried out in the THF as a solvent. The obtained values for rate constants have shown that the reactions with phenylselenenyl bromide are slower then with chloride. Reactions with $CoCl_2$ present are faster then without one. Values for rate constants strongly depend on a substitution pattern of used alkenol.

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2-(METHYLAMINO)PYRIDINE AS A LIGAND PRECURSOR FOR THE TI-CATALYZED HYDROAMINOALKYLATION OF ALKENES AND STYRENES

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Due to its direct and highly atom-efficient conversion of simple starting materials into more complex molecules by C–C bond formation the hydroaminoalkylation of alkenes[1,2] and styrenes[1c,2b] must be regarded as a very promising alternative to the industrial synthesis of amines. While reactions of 1-alkenes performed with group 5 metal catalysts (Ta, Nb) exclusively deliver the branched hydroaminoalkylation product[1] mixtures of the branched and the linear product are obtained with Ti-catalysts.[2] However, in this context, it must be noted that even with Ti-catalysts, the branched product is always formed as the major product and successful hydroaminoalkylations of styrenes can only be achieved with *N*-methyl anilines. Herein, we report the first intermolecular hydroaminoalkylation reactions of styrenes with *N*-alkyl anilines and dialkyl amines. The reactions are catalyzed by a 2-aminopyridinato Ti-complex[3] that is generated in situ from $Ti(NMe_2)_4$ and the ligand precursor 2-(methylamino)pyridine. Most importantly, it is possible for the first time to obtain the industrially more interesting linear product as the major product of the reaction.

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