

Influence of the features of the spatial and electronic structure of α -substituted β -ethoxyvinyl trifluoromethyl ketones and secondary amines on their reactivity.

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Streszczenie

Spatial and electronic structure of possible isomers/conformers of three α -substituted β -ethoxyvinyl trifluoromethyl ketones with general formula $F_3CCO-CR=CH-OC_2H_5$, where $R = H$ (**I**), $R = F$ (**II**), and $R = CH_3$, (**III**), their ability to form H-bonds with two secondary amines, namely, diethyl amine (**1**) and *bis*(methoxyethyl)amine (**2**) have been studied. It was shown that all studied α -substituted enones are *E*-isomers forming predominantly three conformers, *viz* *E*-*s*-*E*-*s*-*E*-*trans*, *E*-*s*-*Z*-*s*-*E*-*trans*, and *E*-*s*-*Z*-*s*-*E*-*gosh*, percentage of separate conformer depending not only on environment but also on steric and/or special (repulsion) interaction between α -substituent and trifluorocarbonyl group. Hydrogen bonding ability evaluated in thermodynamic scale of hydrogen bond basicity revealed that pK_{HB} values of each conformer strongly depends on steric and/or effective charge change on carbonyl oxygen due to influence of α -substituent. Formation of H-bonded ternary complex between enone conformer and secondary amine changes electron density distribution in conformer conjugated chain, reducing positive charge on C_β and thus changing conformer electrophilicity. On the other hand cooperativity effect in amine dimer increases net charge on amine nitrogen thus enhancing amine nucleophilicity.

Słowa kluczowe

Conformers, α -substituted β -ethoxyvinyl trifluoromethyl ketones, Secondary amines, Hydrogen bond, Cooperativity effect, Electrophilicity, Nucleophilicity

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