O_{63}

DYNAMIC PERTURBATION OF *CIS*-S-*CIS*-FIXED β-AMINOVINYLKETONES AND β-AMINOVINYLTHIONES

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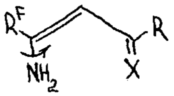
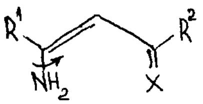
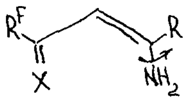
Retarded rotation of H_2N-group about C-N-bond has been shown for the first time by means of dnmr techniques to be typical not only for β-aminovinylketones and β-aminovinylthiones I, II with gem-position of R^F and H_2N-groups, but it is a common process for alicyclic *cis*-S-*cis*-fixed compounds of hydrocarbon series (III, IV) and their fluorinated analogs with γ-position of R^F and H_2N-groups (V, VI).



I, II



III, IV



V, VI

I, III, V : X = O ; II, IV, VI : X = S.

The retarded rotation about C-N-bond with the activation energies of 12-21 kcal/mol has been established. The influence of the substituent structures and positions and of the heteroatom nature (O or S) on the dynamics of the process has been investigated. As distinct from amides and thioamides it was shown that steric factors of the substituents in investigated vinylogs exercise weak influence on the value of $\Delta G_k^{\neq}$. The most important factor determining the change of the activation energy and degree of n-π-conjugation is position and electronic nature of substituents and nature of the heteroatom in β-dicarbonyl system. It was found that gem-position of R^F and H_2N-groups is generally highly effective in reducing the barrier to the rotation and γ-position of R^F and H_2N-groups leads to increase of the barrier comparatively to aliphatic analogs. The transition from O to S has been shown to cause the rise of the barrier to rotation by approximately 1-2 kcal/mol.