Special feature of kinetics of ZcE isomerization of β-*N*-methylaminovinyl trifluoromethyl ketone in Ar matrix exposed to UV radiation and spontaneous E ⇌ Z isomerization of α-methyl-β-*N*-methylaminovinyl trifluoromethyl ketone.

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Although it is well known that reactivity of α,β-unsaturated enaminoketones is closely associated with spatial and electronic structure but until now little attention was devoted to quantitative investigation of interconversion of different stereoisomeric forms of enaminoketones. In present work we studied peculiarities of kinetics of Z⇌E isomerization of enaminoketone 4-(N-methylamino)-1,1,1-trifluorobut-3-en-2-one F3C-COCHCHNH(CH3) (1) in Ar-matrix exposed to UV-radiation (λ=340nm) with IR Fourier and 2D correlation spectroscopy and we found that Z-s-Z-s-trans isomer transforms primarily into two E-isomers, E-s-E-s-trans and E-s-Z-s-trans which further turn into the E-s-E-s-cis and E-s-Z-s-cis conformers all interconversion rate constants being comparable in magnitude. Along with this process long-term exposure to the UV-radiation results in proton transfer from nitrogen of methylamino group to carbonyl oxygen with simultaneous isomerization of 'cyclic' iminoenol form into 'linear'one. In solution of enaminoketone 4-(N-methylamino)-1,1,1-trifluoro-3-methylbut-3-en-2-one F3C-CO-C(CH3)CH-NH(CH3) (2) we observed reversed process, namely, spontaneous interconversion of the E-s-E-s-trans and E-s-Z-s-trans conformers into the Z-s-Z-trans isomer. It was found that rate constants of the dimeric forms of the E-s-E-s-trans and E-s-Z-s-trans conformers are higher than those of the monomers and are independent on total enaminoketone concentration. Addition of highly polar HMPA promotes proton transfer from nitrogen to oxygen in the Z-s-Z-s-trans isomer of 2 with subsequent isomerization into the linear imino-enol product but the rate constant of this transformation is ten-fold smaller than that for 1 in the Ar matrix exposed to UV radiation.

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