ALLYL-VINYLIC ISOMERIZATION IN THE SERIES OF NITRO GROUP CONTAINING THIOLENE-1,1-DIOXIDES.

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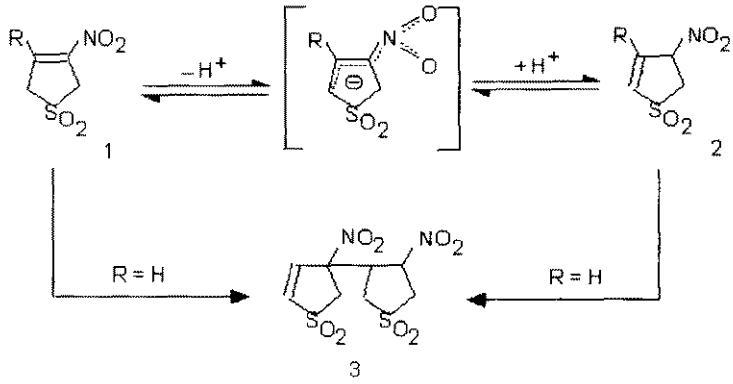
Allyl-vinylic isomerization of the representatives of nitrosulfolene - 4-nitro-2- and 3-thiolene-1,1-dioxides (1,2) series have been studied by us for the first time. The nitro group insertion into thiolene-1,1-dioxide cycle is shown to decsrease the energy barrier between Δ2- and Δ3-isomers (1 ⇌ 2). A research conducted shows the complicative dependence of the isomerization conditions upon steric and electronic effects of substitutents attached at the double bond.



R = H, CH_3, Cl, Ar, ArNH, ArNHNH, morpholino, piperidino

In the case of small substitutents (R = H, CH_3, Cl) the process proceeds under the action of proton accepting solvents or weak bases, as well as under the heating or UV-irradiation. In this case unsubstituted 4-nitro-3-thiolene-1,1-dioxide isomerizes into Δ2-form (2) in the alcohol, acetone or dimethylformamide solutions and immediately forms dimer (3). Strong n-donor substitutents (R = ArNH) tending to form H-bond with nitro group make more difficult the double bond migration in the nitroethene Δ3-isomer (3). Bulk substitutents (R = Ar, morpholino etc) stabilize nitroallylic Δ2-form (2). The process proceeding is controlled by means of IR, UV and H^1 NMR techniques.