

1-NITRO-2-THIO(SULFONYL)ALKENES IN NUCLEOPHILIC REACTIONS WITH AMINES AND THIOLES

Kuzmina N.V., Lipina E.S., Pavlova Z.F., Kropotova T.U.

*Russian State Pedagogical University named after A.I.Hertsen,
191186, Russia, St. Petersburg, The River Moika emb., 48,
Department of Organic Chemistry*

e-mail: chemis@herzen.spb.ru, berest@mail.admiral.ru

The reactions of nucleophilic vinylic substitution are characteristic for the 1-nitro-2-thio(sulfonyl)alkenes containing two conjugated nucleofuge groups. A wide range of new nitroenamines were synthesized in searching the reactions of nitrothio(sulfonyl)alkenes with different types of amines and the following stereochemical regularities were developed: primary amines gave the products in Z-form while secondary amines gave preferably the E-products no matter of the configuration of starting nitroalkene. The studied nitroalkenes reacted with thiolates to give the products of the sulfocontaining group substitution. For the first time the intermediates - products of addition of nucleophile (α -nitro- β -thioacetals) were isolated. These nitrothioacetals were transformed into the substitution products at 20°C temperature. That fact proves that the S_N vin reactions proceed via addition – elimination. Some regulations of these reactions nitrothioalkenes with thiolates were developed: 1) Alkylthiolates displace aryl- and heterylthiogroups but the back reactions do not proceed. 2) Electron withdrawing substituents in leaving group speed on the reaction and electron donating ones slow down the reaction according to the transformation of the nucleofugality of leaving group. Reaction of transthiolation may be recommended as a preparative method for 1-nitro-2-alkylthioalkenes. The reactions of nitrothioalkenes with thiolates under the increased temperature lead to the products of unusual substitution of nitrogroup to give bisarylthioalkenes.

