

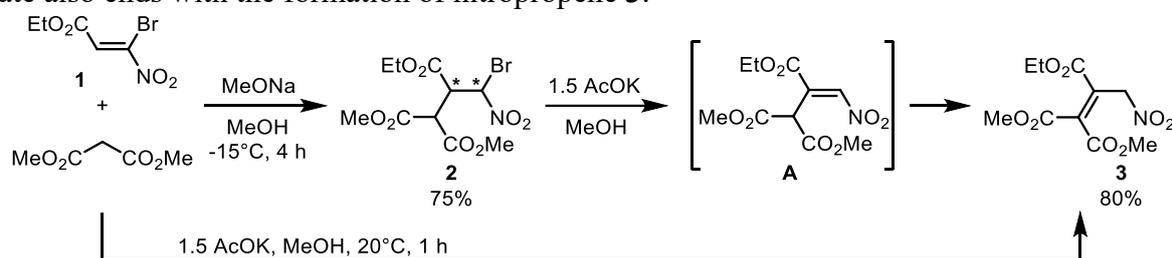
Features of the interaction of ethyl 3-bromo-3-nitroacrylate with dimethyl propanedioate

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Alkyl 3-bromo-3-nitroacrylates are effective substrates in reactions with cyclic CH-acids leading to the formation of fused furan-3-carboxylates [1, 2]. In the case of the reaction with 2,2-dimethyl-1,3-dioxane-4,6-dione and 5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one spiro-fused nitrocyclopropanecarboxylates are formed [3]. It is interesting to study the reactivity of 3-bromo-3-nitroacrylates with acyclic CH-acids. Previously it was shown that the reactions of 3-bromo-3-nitroacrylates with pentane-2,4-dione and methyl 3-oxobutanoate lead to the formation of furan-3-carboxylates [4].

We have studied the interaction of ethyl 3-bromo-3-nitroacrylate **1** with acyclic CH-acid – dimethyl propanedioate. It turned out the reaction in the presence of sodium methoxide (the ratio of bromonitroacrylate : CH-acid : MeONa = 1 : 1 : 1) upon cooling to -15°C in anhydrous methanol for 4 h, the reaction is completed with the formation of the Michael adduct – 2-ethyl 1,1-dimethyl 3-bromo-3-nitropropane-1,1,2-tricarboxylate **2** in 75% yield. Bromonitropropane tricarboxylate **2** undergoes dehydrobromination and subsequent isomerization of the C=C bond of intermediate **A** under the action of fused potassium acetate, turning into 2-ethyl 1,1-dimethyl 3-nitroprop-1-ene-1,1,2-tricarboxylate **3** with the yield 80%. At the same time, carrying out the reaction in the *one pot* mode in the presence of fused potassium acetate also ends with the formation of nitropropene **3**.



Thus, it has been shown that, in contrast to reactions with cyclic enolizable CH-acids, the reaction of 3-bromo-3-nitroacrylates with acyclic CH-acid, dimethyl propanedioate, proceeds along the path of formation of the Michael adduct, which eliminates HBr under basic conditions with the formation of 3-nitroprop-1-en-1,1,2-tricarboxylate.

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References

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