Supporting Information
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The mechanism of formation of derivative 5 was not proved unequivocally and only intermediate I was identified by HPLC in the reaction mixture. Based on our results and on the reactivity of similar compounds described in the literature we believe that intermediate stage I is formed by the reaction of amine 1 and compound 4. There are two possibilities of stabilization - breaking of the bond between the carbonyl group and the nitrogen of nitroamino group or between the carbon of the carbonyl group and the NH group. Compound 5 is formed in the first case. In the second case formation of compound II is likely. Since the isolated product corresponds to product 5, the nitro group would migrate to the NH₂ group. Migrations of nitro group are known, mostly for aromatic compounds in acidic conditions. Among aliphatics linear recyclization of molecules is known. But in the case of compound II intermediate I must be formed. Another possibility is attack on the carbon of the carbonyl group by the nitrogen of the nitroamino group. Nitroamino group is mostly in an aci-form and the basicity of nitrogen is quite low. In any case, migration of one or two groups in the aqueous solution of sodium hydroxide would be necessary to yield 5 in the next step. Thus, we believe that it is not the relevant course of the reaction.

The mechanism and kinetics of similar reactions of aliphatic amines with N-nitroalkylurethane has been studied; only substitution of the nitroamino group was observed. The low stability of the bond between the carbonyl C of the group and nitroamino group is not surprising due to the low basicity of the nitroamino group. This is confirmed in our results, when the reaction of compound 4 with nucleophilic compounds also demonstrates the low stability of this bond.

For these reasons we believe that compound 5 is formed directly through intermediate I.

References: