SYNTHESIS AND CONVERSIONS OF POLYHEDRAL COMPOUNDS

19.* OPENING OF RING OF 1,3,6-TRIAZOHOMOADAMANTANE BY ELECTROPHILIC REAGENTS

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A new method has been developed for obtaining 8-nitro-1,3,6-triazahomoadamantane. By the action of electrophilic reagents on this compound, N-C bonds of the methylenediamino fragment are ruptured, forming derivatives of 1,4,8-triazabicyclo[4.3.1]decane. Depending on the conditions in reactions of 8-nitro-1,3,6-triazohomoadamantane with benzoyl chloride and nitrous acid, derivatives of either 1,4,8-triazabicyclo[4.3.1]decane or hexahydro-1,4-diazepine may be obtained. The formation of the latter proceeds through the above-mentioned derivatives of 1,4,8-triazabicyclo[4.3.1]decane.

We have developed a new method for obtaining 8-nitro-1,3,6-triazahomoadamantane (I) in high yields by the interaction of nitromethane with ethylenediamine and urotropin in a 1:1:1 ratio in dilute acetic acid (see [2, 3] regarding the preparation of the triazahomoadamantane I by other methods). It was established that in the absence of acetic acid or water, the triazahomoadamantane I is not formed. The best yields of the triazahomoadamantane I are obtained when using 50% acetic acid in a fourfold excess.

Nothing is reported on the literature on the interaction of 1,3,6-triazahomoadamantane with any sort of electrophilic reagent, or on rupture of the N-C bonds of the methylenediamino fragment. With the aim of investigating the possibility of opening a ring of 1,3,6-triazahomoadamantane, and also studying the properties of the resulting products, 8-nitro-1,3,6-triazahomoadamantane I was subjected to the action of a number of electrophilic reagents of different classes, in particular acetic anhydride, acetyl chloride, benzoyl chloride, p-toluenesulfonyl chloride, and nitrous acid.

Upon heating the triazahomoadamantane I in acetic anhydride, 4,8-diacetyl-6-nitro-1,4,8-triazabicyclo[4.3.1]decane (II) is formed; i.e., the action of acetic anhydride results in rupture of the N-C bonds of one methylenediamino fragment of the triazahomoadamantane ring, forming the diacetyl derivative of the previously unknown 1,4,8-triazabicyclo[4.3.1]decane. Interaction of the triazahomoadamantane I with acetyl chloride or p-toluenesulfonyl chloride in a ratio from 1:2.5 to 1:3 in a mixture of water with an organic solvent, in the presence of bases, leads to the formation of (respectively) 4,8-diacetyl- (II) and 4,8-ditosyl-6-nitro-1,4,8-triazabicyclo[4.3.1]decane (III). At the same time, upon interaction of the triazahomoadamantane I with benzoyl chloride in the presence of bases, the product obtained, depending on the reaction conditions and the reactant ratio, may be either 4,8-dibenzoyl-6-nitro-1,4,8-triazabicyclo[4.3.1]decane (IV) or 6-benzoylaminomethyl-6-nitro-1,4-dibenzoylhexahydro-1,4-diazepine (V).

Thus, when the reaction is carried out in a mixture of water with ether (reactant ratio 1:2.2, 1.5 h), the dibenzoyltriazabicyclodecane IV precipitates from the reaction mixture. In contrast, when the same reaction is carried out at a mixture of water with ethyl acetate (reactant ratio 1:3.5, 3 h), the dibenzoyldiazepine V is recovered from the ethyl acetate solution.

Analogously, upon interaction of the triazahomoadamantane I with nitrous acid, depending on the reaction conditions, either of two different substances may be formed. When the reaction is carried out in acetic acid, 4,8-dinitroso-6-nitro-1,4,8-triazabicyclo[4.3.1]decane (VI) is formed, and in sulfuric acid, 6-nitro-6-chloromethyl-1,4-dinitrosohexahydro-1,4-diazepine (VII).

*For Communication 18, see [1].

It was established by means of TLC that the hexahydrodiazepines V and VII are obtained through the intermediate formation of the corresponding triazabicyclodecanes IV and VI. This conclusion was further supported by the fact that, under the conditions that we found for the formation of diazepines, compounds IV and VI, when subjected to the action of benzoyl chloride and nitrous acid are converted to the respective hexahydrodiazepines V and VII.

Thus, interaction of the triazahomoadamantane I with carboxylic and arylsulfonic acid chlorides, and also with nitrous acid, leads to rupture of N–C bonds of one methylenediamino fragment of the 1,3,6-triazahomoadamantane, forming the corresponding 4,8-disubstituted 1,4,8-triazabicyclo[4.3.1]decane. (See [4-6] regarding the rupture of N–C bonds of one methylenediamino fragment of 7-nitro-1,3,5-triazaadamantane under the action of these electrophilic reagents, forming the corresponding 3,7-disubstituted 1,3,7-triazabicyclo[3.3.1]nonane.) On the other hand, the action of benzoyl chloride or nitrous acid may also lead to rupture of N–C bonds of the NCH₂NCOR and NCH₂NNO fragments in compounds IV and VI, forming derivatives of hexahydro-1,4-diazepine. (See [7] regarding rupture of N–C bonds of these fragments in derivatives of 1,3,7-triazabicyclo[3.3.1]nonane to form derivatives of hexahydropyrimidine.) The molecular weights of the synthesized compounds, as determined by mass spectrometry, matched the calculated values. In the IR spectra of compounds II, IV, and V, bands are observed corresponding to absorption by the CO of the amide group in the 1630-1650 cm⁻¹ region; for compound III, absorption of the N–SO₂ group is observed at 1170-1180 cm⁻¹; for compounds VI and VII, absorption of the N–NO group is observed in the 1460-1480 cm⁻¹ region. The PMR spectra of the triazahomoadamantanes II, IV, and VI and the dinitrosohexahydrodiazepine VII are complex and difficult to interpret.