Russian Journal of Organic Chemistry, Vol. 40, No. 5, 2004, pp. 668–674. Translated from Zhurnal Organicheskoi Khimii, Vol. 40, No. 5, 2004, pp. 701–708.

Transformations of 2-(3-Hydroxy-3-methyl-1-butynyl)adamantan-2-ol Catalyzed by Acids

S.S. Koval'skaya, N.G. Kozlov, and E.A. Dikusar

Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Minsk, 220072 Belarus
e-mail: loc@ifoch.bas-net.by

Received February 20, 2003

Abstract—Reaction of 2-(3-hydroxy-3-methyl-1-butynyl)adamantan-2-ol with acetonitrile under Ritter reaction conditions is accompanied by isomerization and partial hydration where the water addition to the triple bond occurs nonselectively. As a result of reaction carried out in the presence of 8 equiv of sulfuric acid a mixture was obtained of N^2-[4-(1-acetylamino-2-adamantyl)-2-methyl-3-butyn-2-yl]acetamide, N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-2-oxo-3-butyl]-acetamide, and N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-1-oxo-3-butyl]acetamide in ~10:3:2 ratio. In the presence of 2 equiv of the acid the mixture obtained consisted of N^2-[4-(1-acetylamino-2-adamantyl)-2-methyl-3-butyn-2-yl]acetamide, N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-2-oxo-3-butyl]acetamide, and 1-(1-acetylamino-2-adamantyl)-3-methyl-2-buten-1-one in the same ratio. In Rupe reaction conditions we obtained instead of the expected α,β-unsaturated ketones a mixture of 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-1-one and 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-2-one in a 5 : 3 ratio.

We established formerly that the ethynyl group in the 2-ethynyladamantan-2-ol remained virtually intact in the process of the Ritter reaction, and 2-acetamido-2-ethynyladamantane formed as a principal product [1]. Unlike that monocyclic butynedioles under the same conditions suffered partial hydrolysis because of Meyer–Schuster rearrangement; therewith the water addition occurred stereoselectively at the acetylene carbon atom located in the α-position with respect to alicycle [2].

We report here on an investigation of transformations under acid catalysis (in Ritter reaction and Rupe rearrangement) occurring with a polycyclic analog of the mentioned diols, 2-(3-hydroxy-3-methyl-1-butynyl)adamantan-2-ol (**I**). Under Ritter reaction conditions the triple bond of diol **I** underwent partial hydration due to mesomer effects similar to those in the monocyclic diols. However the initial compound suffered here more complicated transformations. The reaction of diol **I** with acetonitrile carried out in the presence of 8 equiv of sulfuric acid afforded a mixture of N^2-[4-(1-acetylamino-2-adamantyl)-2-methyl-3-butyn-2-yl]acetamide (**II**), N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-2-oxo-3-butyl]-acetamide (**III**), and N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-1-oxo-3-butyl]acetamide (**IV**) in ~10:3:2 ratio. Thus in the course of the reaction the hydration occurred both at the α- and β-acetylene carbon atoms. Besides 2,2-disubstituted adamantine isomerized into a 1,2-disubstituted compound.

The mixtures of amides **II–IV** were separated by fractional crystallization (see EXPERIMENTAL). The structure of compounds obtained was established from the data of ^{1}H NMR, IR, and mass spectra. The IR spectrum of diamide **II** contained an absorption band at 1655 cm^{-1} characteristic of carbonyl group vibrations in amides, bands at 3400 and 1550 cm^{-1} corresponding to NH group vibrations, and also a very weak band from the triple bond vibrations (2240 cm^{-1}). The mass spectrum of the compound contained the molecular ion peak $[M]^+$, *m/z* 316 (I_{rel} 2%). In the ^{1}H NMR spectrum appear the singlet signals belonging to acetyl groups of amides (δ 1.99 and 2.02 ppm, 3H each), and also downfield signals from NH groups (5.88 and 6.10 ppm). The structure of the compound as 1,2-disubstituted adamantine is proved by the presence in the spectrum of two nonequivalent singlet signals of methine protons located at δ 2.35 ppm (from the proton in the α-position with respect to the triple bond) and δ 2.08 ppm (from the bridghead proton H^3). It is clear that the molecule of 2,2-disubstituted adamantine derivative should possess a mirror plane going through C^2, C^5, C^6, and C^7 carbon atoms of the ring, and in the

^{1}H NMR spectra of N^2-[4-(1-acetylamino-2-adamantyl)-2-methyl-3-butyn-2-yl]acetamide (**II**), N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-2-oxo-3-butyl]acetamide (**III**), N^3-[1-(1-acetylamino-2-adamantyl)-3-methyl-1-oxo-3-butyl]acetamide (**IV**), 1-(1-acetylamino-2-adamantyl)-3-methyl-2-buten-1-one (**V**), 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-1-one (**XX**), and 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-2-one (**XXI**) (δ, ppm)

Compd. no.	CH_3, side chain	CH_2, side chain	H^2	H^3	Other adamantane H	NH, OH	$COCH_3$
II	1.44 s	–	2.35 s	2.08 br.s	1.96 m (4H), 1.88 br.s (2H), 1.72 m (4H), 1.65 m (2H)	5.88 br.s, 6.10 br.s	1.99 s, 2.20 s
III	1.53 s	2.32 m	2.10 t (*J* 6 Hz)	2.02 br.s	1.92 m (4H), 1.86 br.s (2H), 1.72 m (4H), 1.62 m (2H)	5.80 br.s, 6.20 br.s	2.02 s
IV	1.40 s	3.36 s	2.87 s	2.09 br.s	1.98 m (4H), 1.90 br.s (2H), 1.72 m (4H), 1.62 br.s (2H)	5.90 br.s, 6.12 br.s	2.00 s, 2.03s
V	1.88 d, 2.10 d (^{W}*J* 1.6 Hz)	6.24 m (^{W}*J* 1.6 Hz)	3.03 s	2.06 br.s	1.96 m (4H), 1.86 br.s (2H), 1.78 m. (4H), 1.64 br.s (2H)	6.22 br.s	1.96 s
XX	1.35 s	3.34 s	2.80 s	2.12 br.s	2.02 m (4H), 1.89 br.s (2H), 1.74 m (4H), 1.62 br.s (2H) 1.95 m (4H), 1.88 br.s (2H),	3.60 br.s, 3.75 br.s	
XXI	1.53 s	2.45 m	2.18 t (*J* 6.5 Hz)	2.06 br.s	1.75 m (4H), 1.66 br.s (2H)	3.10 br.s, 3.55 br.s	

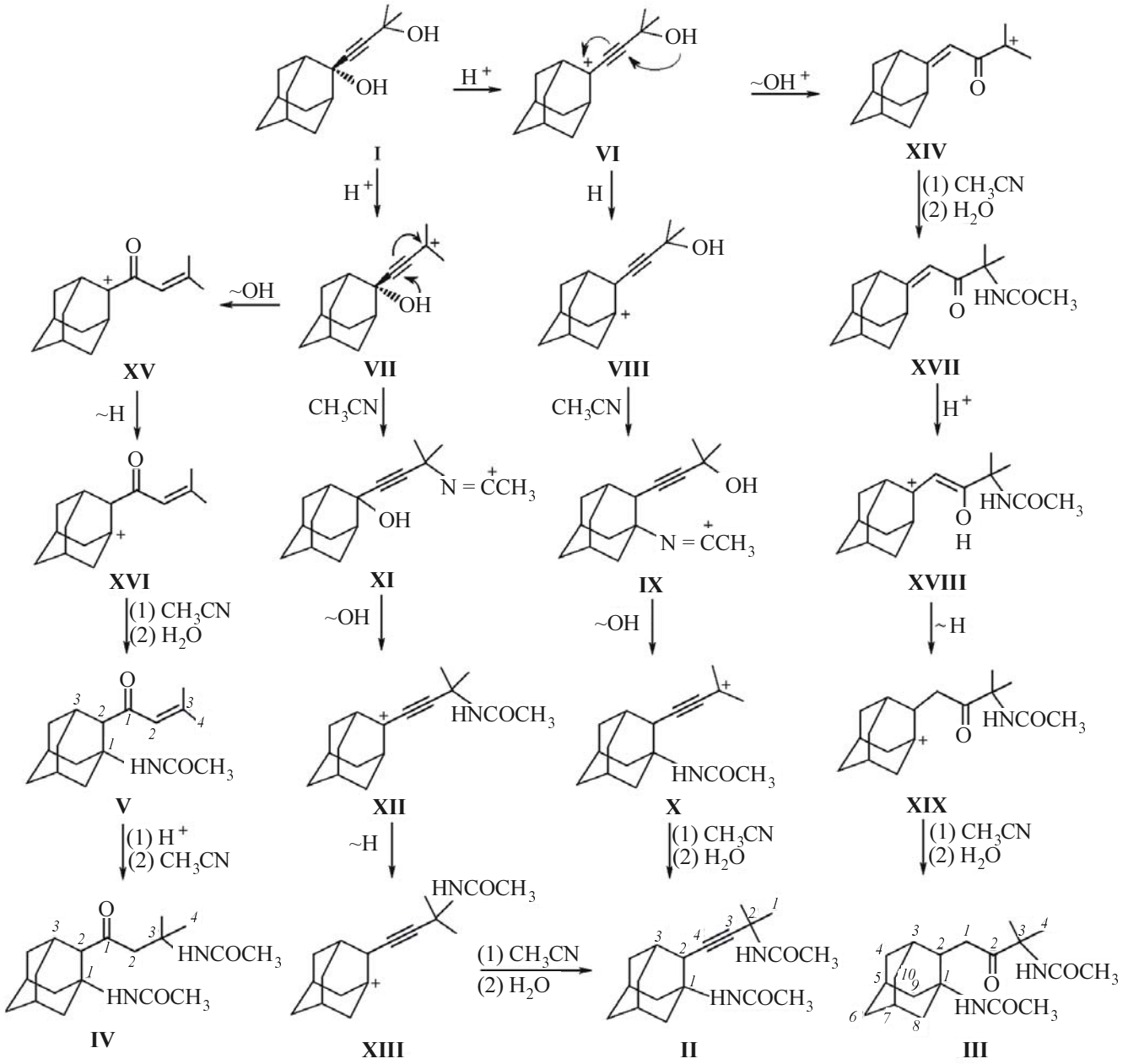
spectrum should have appeared a common signal from equivalent protons H^1 and H^3.

In the IR spectrum of diamidoketone **III** alongside the absorption bands from amide groups vibrations a band is present at wavenumber 1720 cm^{-1} corresponding to the keto carbonyl vibrations. The molecular ion peak appeared in the mass spectrum $[M]^+$, *m/z* 334 (I_{rel} 3%). In the ^{1}H NMR spectrum signals are observed from two amide groups (see table), and a two-proton resonance with the chemical shift δ 2.32 ppm characteristic of protons from a methylene group adjacent to the carbonyl. The multiplicity of the signal indicates the nonequivalence of the methylene group protons and consequently the restricted conformational mobility in the side chain of the compound that may originate from either hydrogen bonds formation or from steric effects. The signal from the proton at C^2 atom of the adamantane skeleton appeared as a triplet at 2.10 ppm; coupling constants of 6 Hz correspond to the coupling with the protons of the above-mentioned methylene group. The signal of methane proton H^3 is observed at 2.02 ppm The presence in the spectrum of the latter of two signals like it happened with diamide **II** demonstrated the vicinal position of the two substituents in the adamantane ring.

IR and mass spectra of the minor component of the reaction mixture, diamidoketone **IV**, are similar to those of compound **III**. In the ^{1}H NMR spectrum alongside the signals from amide groups is present a two-proton singlet at δ 3.36 ppm. The chemical shift indicates that this methylene group is neighboring both to keto and amide groups. Signals from two methine protons are observed at δ 2.87 and 2.09 ppm (H^2 and H^3 of adamantane skeleton respectively).

Monocyclic butynediols in Ritter reaction carried out in the presence of 2 equiv of sulfuric acid gave rise to a mixture of butynediamide and amidoenone [2]. From compound **I** under the same conditions we obtained a mixture of diamide **II**, diamidoketone **III**, and 1-(1-acetylamino-2-adamantyl)-3-methyl-2-buten-1-one (**V**). The mixture was separated by fractional crystallization (see EXPERIMENTAL). The structure of amidoenone was also established from ^{1}H NMR, IR, and mass spectra. The absorption bands present in the IR spectrum of this compound correspond to vibrations of amide group (see EXPERIMENTAL), and to vibrations of a carbonyl and a double C=C bond in α,β-unsaturated ketones (bands at 1680 and 1620 cm^{-1}). A molecular ion peak $[M]^+$, *m/z* 275 (I_{rel} 6%) appeared in the mass spectrum of the compound. In the ^{1}H NMR spectrum of monoamide **V** alongside the signals of amide group (see table) doublets of methyl groups were observed at the chemical shifts 1.88 and 2.10 ppm characteristic of methyl groups attached to a conjugated double bond. The value *J* 1.6 Hz corresponds to allyl coupling with an olefin proton (δ 6.24 ppm, multiplet). The signals of two methine protons of adamantane skeleton appear at δ 3.03 (H^2) and 2.06 ppm (H^3). The enone fragment of compound **V** like that in the monocyclic analogs has *s-cis*-configuration as indicates the practi-

Scheme 1.



cally equal integral intensity of the bands at 1680 and 1620 cm^{-1} in the IR spectrum of this compound. This conclusion is also supported by the significantly different chemical shifts of the methyl groups attached to the double bond demonstrating that one of them is spatially close to a carbonyl group (deshielding $\Delta\delta$ 0.22 ppm).

Compounds **II–V** form from the adamantine diol **I** under Ritter reaction conditions apparently through the following conversions. Under the action of acid catalyst one of hydroxy groups is eliminated to afford carbocations **VI** and **VII**. Each of the latter can undergo transformations along two different pathways. Ion **VI** may convert into 1-adamantyl cation **VIII** via 1,2-hydride shift. The addition thereto of a nucleophile (nitrile) results in intermediate **IX**. This by hydroxy group migration to the cation center provides ion **X** that takes up the second nitrile molecule and with subsequent hydration affords the main reaction product, acetylene diamide **II** (Scheme 1).

This compound may also arise through analogous conversions of cation **VII** via intermediates **XI–XIII**.

An alternative pathway of cations **VI** and **VII** transformations is Meyer–Schuster rearrangement [3]. In the course of the process due to the conjugation of the cation center with the multiple bond and to the hydroxy group migration to the carbon atom which acquires an effective positive charge enone carbocations **XIV** and **XV** are formed. The latter via a hydride shift converts into 1-adamantyl cation **XVI** that by adding the nucleophile affords amidoenone **V**. In reaction carried out under mild conditions this compound is among the final products. Under more stringent conditions monoamide **V** converts into diamidoketone **IV**. The nucleophilic stabilization of cation **XIV** should have resulted in amidoenone **XVII** but as we already mentioned we failed to obtain compound of this structure even under mild reaction conditions. This fact is apparently due to the high strain in the hydrocarbon skeleton caused by bond angles distortion at formation of a semicyclic double bond. Consequently intermediate **XVII** transforms into diamidoketone **III** through the stages of cations **XVIII** and **XIX** formation at a very high rate in the presence of even small amounts of acid catalyst.

It should be noted that Ritter reaction with 2-ethynyladamantanol afforded a compound with amide group attached to C^2 atom [1]. The lack of analogous compound among reaction products of diol **I** is apparently caused by bulky substituent as compared to ethynyl group at the C^2 atom in cations **VI, XII, XV**, and **XVIII** which hampers the geminal addition of a nucleophile. We previously observed a rearrangement in the course of Ritter reaction of 2-adamantyl cation into 1-adamantyl one induced by analogous spatial effects during transformations of 2-acetyladamantan-2-ol [4].

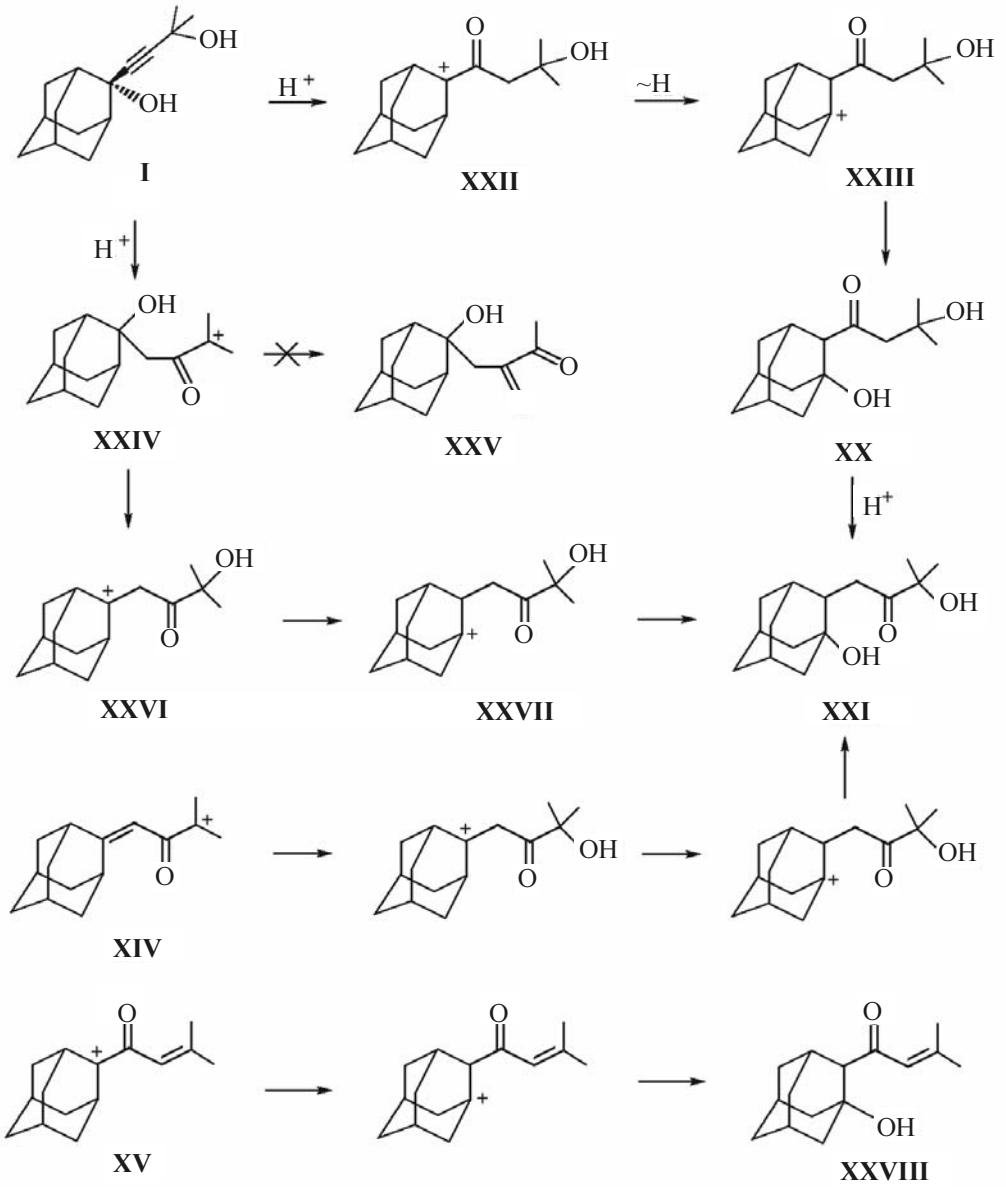
The other distinction of the reaction under study from the transformations of the monocyclic diols is the nonselectivity of triple bond hydration. Here the products of the β-hydration **III** in the reaction mixture surpass the amount of the α-hydration **IV** or **V**, whereas with monocyclic butynediols the derivatives with the 2-oxo group were lacking [2]. We suggested that the lack of the β-hydration products among the reaction products obtained from monocyclic butynediols is governed by the thermodynamic feasibility of cation stabilization with a positive charge in the ring by proton ejection resulting in conjugated enyne as compared to Meyer–Schuster rearrangement affording enone with a semicyclic double bond. This assumption is consistent with a relative readiness of dehydration of the corresponding diols [2]. The transformations of diol **I** observed in the present study testify to the validity of the previous assumptions: inasmuch as cation **VI** cannot undergo stabilization by proton ejection to form an endocyclic double bond, the generation of 2-oxodiamide **III** becomes possible, and its predominance over the α-hydration products **IV** or **V** is due apparently to relative feasibility of cation **VI** than **VII** formation since the positive charge in the former is more delocalized.

Hence certain distinctions in the spatial structure of 2-(3-hydroxy-3-methyl-1-bytynyl)adamantan-2-ol (**I**) and 1-(3-hydroxy-3-methyl-1-butynyl)cycloalkan-1-ols result in significant difference in the direction of their transformations in the course of Ritter reaction.

We mentioned in [2] that the Ritter reaction of butynediols is accompanied by intermolecular Tillmans-Ritter reaction [5] giving rise to a large amount of polymer products. To suppress the polymerization we carried out the reaction in a diluted solution. In Ritter reaction of diol **I** to avoid the above unwanted process we added to the acetonitrile solution a little water (10–15% with respect to acetonitrile). The concurrent water molecule addition to iminium cation arising in the course of the reaction reduced the possibility of its attack on the hydroxy group of the "foreign" molecule and thus hampered the polymerization. However a significant decrease in the reaction rate was also observed. Note that increased content of water in the reaction mixture did not result in larger relative content of compounds **III** and **IV**. This fact evidences that these compounds form exclusively as a result of intramolecular rearrangement. The ratio of hydrated and nonhydrated products is governed entirely by the rates ratio of Meyer–Schuster rearrangement and nucleophile addition and is virtually independent of the reaction conditions.

Treatment of 2-(3-hydroxy-3-methyl-1-butynyl)-adamantan-2-ol (**I**) in conditions of Rupe rearrangement (boiling with formic acid) instead of expected in keeping with the classic reaction path α,β-unsaturated ketones [3] afforded two isomeric dihydroxyketones in a 5:3 ratio. The products were separated by column chromatography on silica gel(see EXPERIMENTAL). On the strength of ^{1}H NMR, IR, and mass spectra the compounds obtained were assigned structures of 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-1-one (**XX**) and 1-(1-hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-2-one (**XXI**). The IR spectra of both dihydroxyketones contain absorption bands characteristic of hydroxy groups vibrations (~3400 cm^{-1}) and of keto carbonyls (1720 cm^{-1}). In the mass spectra of these compounds molecular ion peaks are present $[M]^+$, *m/z* 252 (I_{rel} ~4%). In the ^{1}H NMR spectrum of prevailing ketodiol **XX** a downfield two-proton

Scheme 2.



signal at 3.34 ppm was identified as belonging to protons of a methylene group neighboring both with a keto and a hydroxy groups. The signals of methine protons attached to C^2 and C^3 of adamantine skeleton were observed at δ 2.80 and δ 2.12 ppm respectively. Signals of similar protons in the spectrum of dihydroxyketone **XXI** appear at δ 2.45 (2H,multiplet), 2.18 (H^2, triplet), and 2.06 ppm (H^3).

The transformation of diol **I** via Rupe rearrangement into hydroxyketones **XX** and **XXI** instead of expected α,β-unsaturated compounds obviously originates from the special features of initial compound **I**. It is commonly assumed that in the course of the rearrangement the acetylene carbon in the β-posution to a hydroxy group gets proptonated. As a result the hydroxyl migrates to the nearest acetylene atom that acquires a positive charge [3]. In our case when a hydroxy group attached to the adamantine skeleton is involved into the reaction the above described transformations afford adamantyl cation **XXII** that cannot be stabilized by proton ejection in keeping with the classic path of Rupe rearrangement. Instead, a hydride shift occurs and further a hydration of cation **XXIII** resulting in formation of dihydroxyketone **XX** as the main reaction product. The protonation of another

acetylene atom leads to migration of the terminal hydroxy group and to formation of carbocation **XXIV** which according to the usual pathway of the rearrangement should have given enone **XXV**. However the presence in the molecule of the second hydroxy group resuls in migration of the latter to the cation center giving rise to adamantyl cation **XXVI**. Apparently the prevalence of this isomerization way of cation **XIV** instead of formation of enone with a terminal double bond is governed by thermodynamic factors. Cation **XXVI** undergoes transformations similar to those described above for intermediate **XXII** affording finally the second dihydroxy ketone **XXI** (Scheme 2).

The ratio of compounds **XX** and **XXI** in the reaction mixture apparently depends on the relative protonation rates at more and less spatially accessible acetylene carbons. It should also be noted that under catalysis with formic acid the protonation of the triple bond is favored and not the elimination of hydroxy groups effected by acid catalyst. In the latter case the Meyer–Schuster rearrangement should occur with formation of earlier described cations **XIV** and **XV**. The former due to the lability already discussed might convert into dihydroxy ketone **XXI**; however the most probable final product of ion **XV** transformations would be 1-(1-hydroxy-2-adamantyl)-2-buten-1-one **XXVIII** for the enone fragment present in this structure is relatively stable and takes up a nucleophile only under effect of high concentration of sulfuric acid. The lack among the reaction products of α,β-unsaturated hydroxy ketone **XXVIII** rules out the reaction via Meyer–Schuster rearrangement under catalysis with formic acid although it is considered to be characteristic of tertiary acetylene alcohols [3].

EXPERIMENTAL

IR spectra were recorded on Fourier spectrometer Nicolet Protege-460, mass spectra on Chrommas GC/MS Hewlett Packard 5890/5972, column HP-5MS (70 eV). ^{1}H NMR spectra were registered on spectrometer Tesla BS-567 (100 MHz) from solutions in $CDCl_3$, internal reference HMDS. The reaction progress was monitored and the purity of products was checked by GLC on chromatograph Chrom-5 with a glass column 2000×2 mm packed with carrier Chromaton-N-AW-DMCS (0.16–0.20), liquid phase Apiezon L.

2-(3-Hydroxy-3-methyl-1-butynyl)adamantan-2-ol (I) was obtained by treating adamantanone with dilithium derivative of 2-methyl-3-butyn-2-ol along a previously described procedure [6].

Ritter reaction with adamantylbutynediol **I** was carried out analogously to the method described for monocyclic butynediols [2], but to reduce the amount of polymer formation a small portion of water was added to the initial solution (10–15% with respect to the used quantity of acetonitrile). Nonetheless, the reaction product obtained on evaporation of the extract contained some polymer. To remove the latter the residue was dissolved in ethanol, and the insoluble part was rejected. The ethanol solution containing diamides **II–IV** resulting from reaction in the presence of 8 equiv of sulfuric acid was evaporated to dryness, and a little ether was added to the residue. The most soluble diamide **II** predominantly dissolved. The ether solution was evaporated, and the residue was recrystallized from ethanol. After two recrystallization a practically pure ***N*^{2}-[4-(1-acetylamino-2-adamantyl)-2-methyl-3-butyn-2-yl)acetamide (II)** was obtained, mp 147–148°C. IR spectrum, cm^{-1}: 3400 (NH), 2930, 2900, 2850 (CH), 240 (v.w, C≡C), 1655 (C=O, amide), 1550 (NH). Mass spectrum, *m/z* (I_{rel}, %): 316 (2) $[M]^+$, 301 $[M^+ - CH_3]$, 286 $[M^+ - 2CH_3]$, 273 $[M^+ - COCH_3]$, 258 $[M^+ - NHCOCH_3]$, 243 $[M^+ - CH_3–NHCOCH_3]$, 228 $[M^+ - 2CH_3–NHCOCH_3]$, 199 $[M^+ - CH_3–COCH_3–NH_2COCH_3]$, 184 $[M^+ - CH_3–NHCOCH_3–NH_2COCH_3]$, 158, 144, 137, 117, 115, 91, 77, 65, 52, 43 (100).

We met the greatest difficulties in separating the mixture of diamidoketones **III** and **IV** for their solubility in all available solvents was close. They were separated by fractional crystallization from ethanol. At slow evaporation of a solution first precipitated a mixture with a higher content of the minor component **IV**. Repeating this procedure many times we succeeded in getting a mixture enriched with diamide **IV** to ~85%. A sample of ***N*^{3}-[1-(1-acetylamino-2-adamantyl)-3-methyl-1-oxo-butyl]-acetamide (IV)** fit for recording spectra was obtained by two-fold recrystallization of the mixture from anhydrous acetone. mp 172–173°C. IR spectrum, cm^{-1}: 3420 (NH), 2930, 2900, 2850 (CH), 1720 (C=O, ketone) 1650 (C=O, amide), 1550 (NH). Mass spectrum, *m/z* (I_{rel}, %): 334 (3) $[M]^+$, 319 $[M^+ - CH_3]$, 304 $[M^+ - 2CH_3]$, 291 $[M^+ - COCH_3]$, 276 $[M^+ - NHCOCH_3]$, 261 $[M^+ - CH_3–NHCOCH_3]$, 246 $[M^+ - 2CH_3–NHCOCH_3]$, 234, 218, 208, 202, 196, 181, 153, 139, 135, 122, 107, 93, 91, 77, 65, 43 (100).

The alcoholic mother liquor was evaporated to 1/5 of the initial volume, the separated crystals were filtered off, and the solvent was evaporated to dryness. Two-fold recrystallization of the residue from THF afforded virtually pure (~96%) **N^3-[1-(1-acetylamino-2-adamantyl)-3-**

methyl-2-oxo-3-butyl]acetamide (III). mp 196–198°C. IR spectrum, cm^{-1}: 3430 (NH), 2930, 2900, 2850 (CH), 1720 (C=O, ketone) 1650 (C=O, amide), 1550 (NH). Mass spectrum, *m/z* (I_{rel}, %): 334 (4) $[M]^+$, 319 $[M^+ - CH_3]$, 304 $[M^+ - 2CH3]$, 291 $[M^+ - COCH_3]$, 276 $[M^+ - NHCOCH_3]$, 261 $[M^+ - CH_3–NHCOCH_3]$, 246 $[M^+ - 2CH_3–NHCOCH_3]$, 234, 220, 218, 202, 192, 177, 149, 135, 122, 107, 93, 91, 77, 65, 43 (100).

The mixture of amides **II**, **III**, and **V** obtained in reaction performed in the presence of 2 equiv of sulfuric acid after removal of polymers was less difficult to separate because of stronger difference in the structure of products. The least soluble in ether was here monoamide **V**, and we succeeded in its isolation by gradual addition of ether to the mixture. On decanting the solution the residue was subjected to crystallization from ethanol to obtain an individual **1-(1-acetylamino-2-adamantyl)-3-methyl-2-buten-1-one (V).** mp 212–213°C. IR spectrum, cm^{-1}: 3420 (NH), 3050 (=CH), 2920, 2900, 2850 (CH), 1680 (C=O, conjug. ketone), 1650 (C=O, amide), 1620 (C=C conjug.), 1550 (NH). Mass spectrum, *m/z* (I_{rel}, %): 275 (6) $[M]^+$, 260 $[M^+ - CH_3]$, 232 $[M^+ - COCH_3]$, 217 $[M^+ - NHCOCH_3]$, 202 $[M^+ - CH_3–NHCOCH_3]$, 189, 165, 162, 135, 122, 107, 93, 91, 77, 65, 43 (100).

The mixture of diamides **II** and **III** was separated as described above.

Rupe rearrangement with 2-(3-hydroxy-3-methyl-1-butynyl)adamantan-2-ol (I). Diol **I** (3.0 g) was heated at reflux with 10 ml of 85% HCOOH till the completion of reaction. Then the mixture was poured into excess aqueous ammonia, the reaction products were extracted into a large volume of ether, the extract was dried on $MgSO_4$. On distilling off the solvent the obtained mixture of dihydroxyketones **XX** and **XXI** looking as a thick oil was subjected to chromatography on silica gel (Chemapol L 40/100), eluent a mixture of anhydrous acetone and ethanol, 10 : 1. The prevailing isomer **XX** possessed higher chromatographic mobility. **1-(1-Hydroxy-2-adamantyl)-3-hydroxy-3-tone)methylbutan-1-one (XX).** mp 70–72°C. IR spectrum, cm^{-1}: 3420 (OH, v.s), 2930, 2900, 2850 (CH), 1720 (C=O, ketone). Mass spectrum, *m/z* (I_{rel}, %): 252 (4) $[M]^+$, 235 $[M^+ - OH]$, 220 $[M^+ - CH_3–OH]$, 202 $[M^+ - CH_3–OH–H_2O]$, 189, 175, 161, 133, 121, 108, 92, 77, 68, 55 (100).

(1-Hydroxy-2-adamantyl)-3-hydroxy-3-methylbutan-2-one (XXI). mp 56–58°C. IR spectrum, cm^{-1}: 3400 (OH, v.s), 2930, 2900, 2850 (CH), 1720 (C=O, ketone). Mass spectrum, *m/z* (I_{rel}, %): 252 (4) $[M]^+$, 235 $[M^+ - OH]$, 220 $[M^+ - CH_3–OH]$, 202 $[M^+ - CH_3–OH–H_2O]$, 189, 175, 148, 134, 121, 107, 91, 77, 68, 55 (100).

REFERENCES

1. Koval'skaya, S.S., Dikusar, E.A., Kozlov, N.G., and Popova, L.A., *Zh. Org. Khim*., 2001, vol. 37, p. 1292.
2. Koval'skaya, S.S., Kozlov, N.G., and Dikusar, E.A., *Zh. Obshch. Khim*., 2004, vol. 74, p. 972.
3. Vatsuro, K.V. and Mishchenko, G.L., *Imennye reaktsii v organiche-skoi khimii* (Personal Reactions in Organic Chemistry), Moscow: Khimiya, 1976, vol. 276, p. 364.
4. Koval'skaya, S.S., Kozlov, N.G., and Dikusar, E.A., *Zh. Org. Khim.,* 2002, vol. 38, p. 518.
5. Zil'berman, E.N., *Reaktsii nitrilov* (Nitril Reactions), Moscow: Khimiya, 1972, p. 251.
6. Kozlov, N.G., Dikusar, E.A., Zelenkovskii, V.M., Potkin, V.I., Shirokii, V.L., Murashko, V.L., Khrustalev, V.N., and Antipov, M.Yu., *Zh. Obshch. Khim.,* 2004, vol. 74, p. 965