UNUSUAL HYDRATION OF STEREOISOMERIC trans-1,2-DIMETHYL-4-VINYLETHYNYLDECAHYDRO-4-QUINOLOLS

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The hydration of stereoisomeric trans-1,2-dimethyl-4-vinylethynyldecahydro-4-quinolols and their acetates under the conditions of the Kucherov reaction was studied. The reaction proceeds ambiguously; the character of the products depends on the three-dimensional structure of the starting vinylethynyl alcohol or ether. The formation of spirodihydro(tetrahydro)furan and spirotetrahydropyran derivatives of the decahydroquinoline series is characteristic for all of the stereoisomeric vinylethynyldecahydroquinolols. A Favorskii–Nazarov retroreaction, as well as epimerization at the C_2 center of the decahydroquinoline ring, is observed in individual cases during the hydration of the vinylethynyldecahydroquinolols. The hydration of the O-acetates of the vinylethynyldecahydroquinolols proceeds more rapidly and more unambiguously than the hydration of the corresponding alcohols. The structures of the synthesized compounds were proved by a combination of the results of elementary analysis and data from the Raman, IR, PMR, and mass spectra.

The literature data on the hydration of carbocyclic and heterocyclic vinylethynyl alcohols are fragmentary and involve only the addition of water to the triple bond to give α-keto alcohols with isolated [1] or conjugated [2] C=C and C=O bonds. Isomerization of the starting vinylethynyl alcohols to dienyl ketones was noted under the conditions of this reaction [3, 4].

Continuing our study of the chemical transformations [5, 6] of vinylethynylcarbinols of the decahydroquinoline series obtained in [7], we studied their hydration under the conditions of the Kucherov reaction. It was established that the hydration of vinylethynyldecahydroquinolols proceeds in a complex and ambiguous manner and that the addition of the elements of water occurs both at the double bond and at the triple bond. The character of the products depends on the three-dimensional structure of the starting vinylethynylcarbinol. The formation of spiro derivatives is characteristic for all of the stereoisomers. A Favorskii–Nazarov retroreaction, as well as epimerization at the C_2 center of the decahydroquinoline ring, occurs in individual cases.

In the present communication we describe the results of the hydration of stereoisomeric 1,2-dimethyl-4-vinylethynyldecahydro-4-quinolols (Ia-c) and their O-acetates XIVa-c, the configurations of which were established in [5, 8, 9].

The hydration of the alcohols and ethers cited above in 80% acetic acid in the presence of mercuric oxide led to pronounced resinification, whereas the reaction did not take place at all in 80% methanol in the presence of mercuric sulfate. The optimum conditions were obtained with 10% sulfuric acid in the presence of mercuric sulfate. However, partial resinification and polymerization of the starting substances lower the yields of the final products in this case also.

The addition of water to 1,2e-dimethyl-4e-vinylethynyldecahydro-4-quinolol (Ia) under the conditions indicated above takes place even at room temperature; II, IIIa,b, and IV were isolated from the mixtures of reaction products by chromatography. (Scheme, top, following page.)

The principal reaction product, viz., II, was identified as the known 1,2e-dimethyldecahydro-4-quinolone [10]. Compound IIIa has the following spectral characteristics: Raman spectrum: 1625 cm^{-1} (C=C); IR spectrum: 3600 cm^{-1} (OH); mass spectrum: $[M - CH_2OH]^+$ m/e 220

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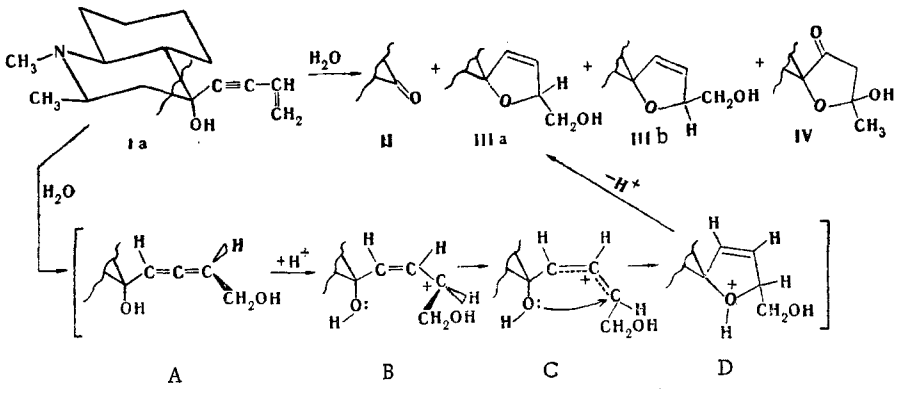


(78%); PMR spectrum: 3.28 (d, $J_{5',5'} = 6$ Hz, 5'-CH_2OH), 4.80 (m, 5'-H), 5.64 (dd, $J_{4',3'} = 7$ Hz, $J_{4',5'} = 2.2$ Hz, 4'-H), and 5.80 ppm (dd, $J_{3',5'} = 1.4$ Hz, 3'-H). The spin–spin coupling constants (SSCC) were confirmed by double homonuclear resonance. The combination of the spectral data presented and the results of elementary analysis made it possible to assign the 1,2e-dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyl-$\Delta^{3'}$-dihydrofuran) structure to IIIa. Compound IIIb, which has the spectral characteristics of IIIa, differs from the latter with respect to its melting point. According to the PMR data, isomerization at the C_2 center and ring fusion do not occur, and it therefore must be assumed that IIIa,b are epimers with respect to the $C_{5'}$, center. However, it is not possible to unambiguously assign one of them to a pseudoequatorial orientation and the other to a pseudoaxial orientation of the hydroxymethyl group because of the slight difference in the constants of spin–spin coupling of the 3'-H and 5'-H protons (0.3 Hz) for the two compounds.

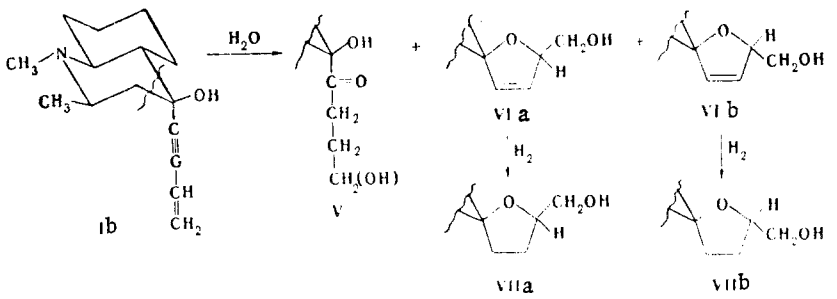
The proposed mechanism for the formation of IIIa suggests the addition of the elements of water to alcohol Ia in the 1 and 4 positions of the vinylethynyl substituent with the formation of allene A, which under the reaction conditions undergoes protonation at the central atom of the allene grouping to give carbonium ion B. Ion B is stabilized due to charge delocalization with the participation of the π electrons of the adjacent double bond and the formation of coplanar carbonium ion C, which subsequently undergoes cyclization to oxonium ion D. The latter splits out a proton and is converted to spirofuran derivative IIIa. The formation of IIIb in addition to IIIa is most likely explained by the possibility of 90°C rotation about the $C_{2'}$–$C_{3'}$ bond in both directions in carbonium ion B.

Characteristic bands at 1765 (C=O in a five-membered ring [11]) and 3580 cm^{-1} (OH) are observed in the IR spectrum of IV, but absorption bands of multiple bonds are absent. A sharp solitary signal at 1.42 ppm, which corresponds to the protons of the 5'-CH_3 group, is observed in the PMR spectrum. The singlet character of this signal constitutes evidence that the hydroxy group is attached to the $C_{5'}$ atom. The signals of the nonequivalent protons of the methylene group of the tetrahydrofuran ring appear in the spectrum in the form of an AB quartet (δ_{AB} 2.40 ppm). The spectral data and the results of elementary analysis make it possible to identify IV as 1,2e-dimethyldecahydroquinoline-4-spiro-2'-[5'-hydroxy-5'-methyltetrahydro-3'(4')-furanone].

We were unable to accomplish the acid hydrolysis of IV, which is a cyclic hemiacetal, in order to unambiguously assign the position of the keto group. However, IV undergoes partial decomposition to give decahydroquinolone II during elution with a column filled with acidic aluminum oxide (pH ~ 6). It may be assumed that this sort of transformation also occurs under the reaction conditions. Compounds IIIa,b are stable during chromatography on aluminum oxide.

In contrast to the hydration of its equatorial epimer with respect to C_4 (Ia), the hydration of 1,2e-dimethyl-4a-vinylethynyldecahydro-4-quinolol (Ib) in 10% sulfuric acid in the presence of mercuric sulfate occurs only when the mixture is heated. Individual V and VIa,b were isolated from the mixture of products.

The Raman spectrum of V does not contain absorption bands of double and triple bonds. The IR spectrum contains the following characteristic bands: a band at 1720 cm^{-1} (C=O) and a broad band with a maximum at 3300 cm^{-1} (OH), the position and intensity of which are constant in the crystalline state and in solution (0.005 g-mole/liter), which constitutes evidence for the presence of an intramolecular hydrogen bond. The principal peak with m/e 182 in the mass

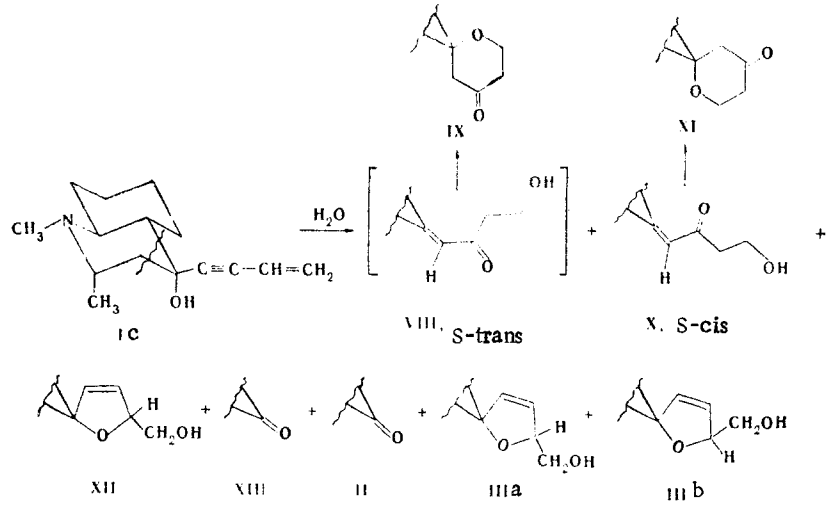


spectrum of this compound corresponds to the peak of an $[M - COCH_2CH_2CH_2OH]^+$ ion. The PMR spectrum contained peaks at 2.68 (t, 2'-CH_2) and 3.56 ppm (t, 4'-CH_2). The protons of these groups couple with the protons of the 3'-CH_2 group with a constant of 6 Hz (this was confirmed by double homonuclear resonance). The multiplet of protons of the 3'-CH_2 group falls in the "methylene exaltation" region and is not analyzable. The character of the multiplet splitting of the signals of the protons of the side chain excludes an alternative structure with a keto group attached to the C_2' atom.

With respect to their spectral characteristics, VIa,b are similar to IIIa,b and differ from them only with respect to the spatial orientation of the spirofuran rings. This difference was reflected in the chemical shifts of the signals of the 3'-H and 4'-H protons (5.94 and 6.14 ppm, respectively). In this case the signal of the 3'-H proton is found at stronger field than the signal of the 4'-H proton. The reverse relationship is observed for IIIa,b.

The hydrogenation of VIa,b with 1 mole of hydrogen in the presence of $Pd/CaCO_3$ leads to the corresponding 1,2e-dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyltetrahydrofurans) (VIIa,b), in the Raman spectra of which multiple bonds were not observed. The character of the fragmentation of these compounds is similar to the fragmentation of their unsaturated analogs, and the $[M - CH_2OH]^+$ ion peaks with m/e 222 have the maximum intensity.

The hydration of 1,2a-dimethyl-4e-vinylethynyldecahydro-4-quinolol (Ic) is the most complicated process. A multicomponent mixture, from which we were able to isolate eight individual compounds, viz., IX-XIII, II, and IIIa,b, is formed in this case. This decidely ambiguous reaction of vinylethynyl alcohol Ic is due mainly to epimerization at the C_2 center, as evidenced by the formation in this reaction of II and IIIa,b, which were obtained in the hydration of vinylethynyl alcohol Ia.



Three groups of signals belonging to the protons of the side chain, viz., signals at 2.70 (t, 2'-CH_2), 3.86 (t, $J_{1',2'}$ = 6 Hz, 1'-CH_2), and 6.02 ppm (s, 4'-H), can be isolated in the PMR spectrum of X. The principal peak in the mass spectrum of this compound is due to the $[M - CH_3]^+$ ion, which is formed by ejection of the 2-CH_3 group. The peak of the $[M - CH_2O]^+$ ion with m/e 221, which is due to elimination of a terminal hydroxymethylene group, and the peak of the ion with m/e 206, which is formed by cleavage of the C–C bond adjacent to the carbonyl group and elimination of a $\cdot CH_2CH_2OH$ radical from the $[M]^{+\cdot}$ ion, have appreciable intensities. The IR spectrum contains characteristic bands at 1615 (C=C) and 1680 cm^{-1} (C=O),

the ratio of the intensities of which is 1.3:1 [12, 13]. On the basis of the spectral data presented above we feel that X has the 1,2a-dimethyldecahydro-$\Delta^{4,4'}$-quinolylidene-1'-hydroxy-3'-butanone structure in the S-cis conformation of the side chain. The formation of X can be explained by isomerization [14, 15] of vinylethynyl alcohol Ic to a dienone with the subsequent addition of water to the double bond.

The IR and mass spectra of IX and XI are identical; characteristic bands are observed in the IR spectra at 1720 cm^{-1} (C=O), whereas absorption bands of OH groups and multiple bonds are absent. The peaks of $[M - CH_3]^+$ ions with m/e 236 are the principal peaks in the mass spectra. The PMR spectrum of XI contains a well-resolved multiplet at 4.00 ppm (6'-CH_2). The protons of the 6'-CH_2 group couple with the protons of the 5'-CH_2 group and constitute the AB part of an ABXY spin system* (δ_A 3.38 and δ_B 4.10 ppm), which is characterized by the following constants: $^2J_{AB}$ = −11.2 Hz, $^3J_{A,Y}$ = 11.2 Hz, $^3J_{A,X}$ = 3.7 Hz, $^3J_{B,Y}$ = 8 Hz, and $^3J_{B,X}$ = 2.2 Hz (found from the spectrum within the AMXY approximation and confirmed by double homonuclear resonance). We assigned the doublet at 2.76 ppm to the equatorial proton attached to C_3'; the signal of the axial proton attached to C_3', andthe signals of the protons of the 5'-CH_2 group lie at 1.8-2.3 ppm and are overlapped by other lines of the spectrum. The observed constants are characteristic for the SSCC of the vicinal protons in a six-membered ring in the chair conformation. To confirm the reliability of our conclusions regarding the structure of XI we carried out deuterium exchange of the protons in the α position relative to the keto group. As expected, the PMR spectrum of XI became considerably simpler after this: the doublet at 2.76 ppm vanished, while the multiplet at 4.00 ppm took on the form of two doublets with δ_A 3.38 and δ_B 4.80 ppm with $^2J_{A,B}$ = − 11.2 Hz.

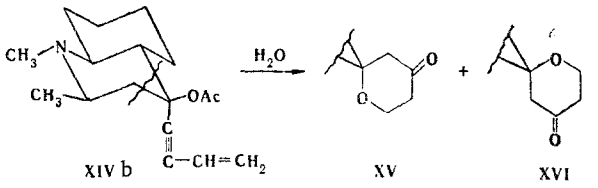
The PMR spectrum of IX differs from the PMR spectrum of XI with respect to the character of the coupling of the protons both in the tetrahydrofuran ring and in the piperidine ring. In the case of IX we observed equivalence of the protons attached to the C_3 atom of the decahydroquinoline ring for the first time in decahydroquinoline derivatives. The signal of the protons of the 3-CH_2 group in the PMR spectrum of IX has the form of a sharp doublet at 1.90 ppm, whereas the signal of the 2-H proton, after irradiation with a strong radiostatic field at the frequency of the protons of the 2-CH_3 group (double resonance), has the form of a triplet at 3.30 ppm with $^3J_{2,3}$ = 4.5 Hz. We assigned the doublet of doublets at 4.06 ppm to the signal of equivalent protons of the 6'-CH_2 group of the tetrahydropyran ring, which couple with the nonequivalent protons of the 5'-CH_2 group and form an A_2XY system with $^3J_{A,X}$ = 3 Hz and $^3J_{A,Y}$ = 10.8 Hz. The signals of the protons of the 5'-CH_2 and 3'-CH_2 groups appear in the spectrum at 2.2-2.8 ppm but overlap with one another and are therefore difficult to interpret. We confirmed the fact of the equivalence of the protons of the 6'-CH_2 group and the assignment of the signals of the protons of the 5'-CH_2 and 3'-CH_2 groups by means of deuterium exchange and double resonance. After deuterium exchange, the doublet of doublets at 4.06 ppm took on the form of a broad singlet, whereas signals of the protons of the 5'-CH_2 and 3'-CH_2 groups were absent in the spectrum. This excludes an alternative structure with a keto group attached to C_3'.

It might be assumed that IX was formed as a result of cyclization of enone VIII, while XI was formed by cyclization of enone X. Attack by the hydroxy group on the double bond in enone X is evidently hindered because of steric hindrance on the part of the axial methyl group attached to C_2, whereas cyclization of the side chain in the S-trans conformation (enone VIII) should occur freely. The latter was evidently the reason for the facile transformation of enone VIII under the reaction conditions. An examination of molecular models provides evidence for the existence in IX of a strong spatial interaction of the protons of the axial 2-CH_3 group of the piperidine ring with the equatorial 3'-H proton of the tetrahydropyran ring. This interaction gives rise to a certain distortion of both rings, which is manifested in the PMR spectrum in the form of equivalence of the protons of the 3-CH_2 and 6'-CH_2 groups. In other words, the $ABMX_3$ spin system of the 3-CH_2, 2-H, and 2-CH_3 protons undergoes degeneration to an A_2MX_3 system, and the ABXY system of the 6'-CH_2 and 5'-CH_2 protons undergoes degeneration to an A_2XY system.

The hydration of 1,2e-dimethyl-4e-vinylethynyl-4a-acetoxydecahydroquinoline (XIVa) proceeds in the same way as the hydration of alcohol Ia and leads to II and IIIa,b. Enone X is formed as the principal product in the hydration of acetate XIVc. Two isomeric 1,2e-dimeth-

*The axial protons attached to C_6' and C_5' are are designated by A and Y, respectively, while B and X pertain to the equatorial protons attached to C_6' and C_5'.

yldecahydroquinoline-4-spiro-2'-tetrahydro-4-pyranones (XV, XVI) were isolated as a result of hydration of acetate XIVb.



XIV b XV XVI

In this case, in addition to acid hydrolysis of the acetoxy group, one observes simultaneous isomerization of the resulting carbinol to the corresponding dienones, which, as a consequence of the absence of steric hindrance, then easily undergo cyclohydration to a mixture of tetrahydropyranones XV and XVI with predominance of XV. The lower yield of pyranone XVI is probably due to the existence in it of a steric interaction between the 2-H and 3'-H atoms. The latter shows up in the PMR spectrum in the form of equivalence of the protons of the 6'-CH_2 group.

EXPERIMENTAL

The IR spectra of solutions of the compounds in chloroform and of KBr pellets were obtained with a Spex Ramalog Ramalog-4 spectrometer over a $\Delta\nu$ range of 1000 to 2500 cm^{-1} with irradiation of the capillary containing the substance with themonochromatic emission of an Ar laser with a wavelength of 5145 Å. The PMR spectra of 10% solutions of the compounds in $CDCl_3$ were recorded in the TsASI of the Academy of Sciences of the Belorussian SSR with a Jeol PS-100 spectrometer (100 MHz) relative to tetramethylsilane. The mass spectra were obtained with an MKh-1303 mass spectrometer with direct introduction of the samples into the ion source at a vaporization temperature of 70-80°C and an ionizing-electron energy of 70 eV. The melting points were measured with a Koffler apparatus. Thin-layer chromatography (TLC) was carried out on Woelm neutral Al_2O_3 with a chloroform–ethanol system (1:0.1). Brockmann activity II Al_2O_3 was used for column chromatography in all cases; the ratio of the substance to the adsorbent was 1:60.

1,2e-Dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyl-$\Delta^{3'}$-dihydrofurans) (IIIa,b) and 1,2e-Dimethyldecahydroquinoline-4-spiro-2'-[5'-hydroxy-5'-methyltetrahydro-3'(4')-furanone] (IV). A mixture of 4 g (17 mmole) of vinylethynyl alcohol Ia, 4g (13 mmole) of $HgSO_4$, and 2.4 ml of concentrated H_2SO_4 in 36 ml of H_2O was stirred at 20°C for 10 h, after which the catalyst was removed by filtration, and the cooled (to 0°C) reaction mass was treated with small portions of 25% ammonium hydroxide up to pH 7-8. The supernatant base was extracted with ether, the extract was dried over $MgSO_4$, and the solvent was removed to give 3 g of a resinified viscous mixture of products with R_f 0.23, 0.42, 0.50, 0.62, and 0.90. Column chromatography of this mixture (elution with ether) and recrystallization from acetone gave 1.2 g (30%) of amino ketone IIa with mp 193-194°C and R_f 0.50. Found: C 71.8; H 10.2; N 5.4%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251. Also obtained was 0.16g (4%) of alcohol IIIb with mp 153-154°C and R_f 0.42. Found: C 71.9; H 10.1; N 5.5%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251. The purification procedure also gave 0.12 g (3%) of hemiacetal IV with mp 174-175°C and R_f 0.23. Found: C 67.2; H 9.3; N 5.1%; M^+ 267. $C_{15}H_{25}NO_3$. Calculated: C 67.4; H 9.4; N 5.2%; M 267.

Hydrolysis of Hemiacetal IV. A 0.1-g (0.4 mmole) sample of hemiacetal IV was heated in 2 ml (2 mmole) of 4% HCl at 80-90°C for 10 h, after which the mixture was neutralized with potassium carbonate and dried over $MgSO_4$, and the solvent was removed to give 0.06 g of starting hemiacetal IV.

Conversion of Hemiacetal IV to Amino Ketone II. A 0.05-g (0.2 mmole) sample of hemiacetal IV was passed through a column filled with Al_2O_3 (pH ~ 6) by elution with ether. The solvent was removed from the eluate, and the product was converted to 0.04 g of the picrate with mp 173-174°C. No melting-point depression was observed for a mixture of this picrate with the picrate of amino ketone II.

1,2e-Dimethyl-4a-(4'-hydroxy-1'-butanonyl)decahydro-4-quinolol (V) and 1,2e-Dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyl-$\Delta^{3'}$-dihydrofurans) (VIa,b). A mixture of 5 g (21 mmole) of vinylethynyl alcohol Ib, 5 g (16 mmole) of $HgSO_4$, and 3 ml of concentrated H_2SO_4 in 45 ml of water was stirred at 65-70°C for 12 h, after which it was worked up as de-

scribed for alcohol Ia to give 3 g of a mixture of products (R_f 0.16 and 0.46), which was chromatographed with a column (elution with ether) and crystallized from acetone to give 0.47 g (15%) of ketone V with mp 139-140°C and R_f 0.16. Found: C 67.1; H 9.9; N 5.1%; M^+ 269. $C_{15}H_{27}NO_3$. Calculated: C 66.9; H 10.1; N 5.2%; M 269. Also obtained was 0.33 g (11%) of alcohol VIa with mp 132-133°C and R_f 0.46. Found: C 71.9; H 9.9; N 5.7%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251. This procedure also gave 0.21 g (7%) of alcohol VIb with mp 156-158°C and R_f 0.46. Found: C 71.8; H 10.1; N 5.7%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251.

1,2e-Dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyltetrahydrofurans) (VIIa,b). A 0.5-g (2 mmole) sample of alcohol VIa was hydrogenated in the presence of $Pd/CaCO_3$ (with 58 ml of H_2 at 734 mm and 22°C) in methanol, and subsequent crystallization of the product from hexane gave 0.45 g (90%) of alcohol VIIa with mp 101-102°C and R_f 0.40. Found: C 71.3; H 10.8; N 5.6%; M^+ 253. $C_{15}H_{27}NO_2$. Calculated: C 71.1; H 10.7; N 5.5%. Similarly, 0.3 g (1.1 mmole) of alcohol VIb (hydrogenation with 32 ml of H_2 at 741 mm and 23°C) gave 0.24 g (80%) of alcohol VIIb with mp 123-124°C and R_f 0.40. Found: C 71.2; H 10.8; N 5.7%; M^+ 253. $C25H_{27}NO_2$. Calculated: C 71.1; H 10.7; N 5.5%.

1,2a-Dimethyldecahydro-$\Delta^{4,4'}$-quinolylidene-1'-hydroxy-3'-butanone (X), 1,2a-Dimethyldecahydroquinoline-4-spiro-2'-(tetrahydro-4-pyranones) (IX, XI), and 1,2a-Dimethyldecahydroquinoline-4-spiro-2'-(5'-hydroxymethyl-Δ^3-dihydrofuran) (XII). A mixture of 15 g (63 mmole) of vinylethynyl alcohol Ic, 9 ml of concentrated H_2SO_4, and 15 g (48 mmole) of $HgSO_4$ in 135 ml of H_2O was stirred at 60-70°C for 15 h, after which it was worked up as described for alcohol Ia to give 8 g of a resinous viscous liquid with R_f 0.23, 0.42, 0.50, 0.60, 0.70, 0.75, 0.86, and 0.90. This product was chromatographed with a column by elution with petroleum ether to give a substance with R_f 0.70-0.90, after which elution was continued with ether. Chromatography and crystallization from acetone gave 0.6 g (7%) of amino ketone XIII with R_f 0.86, the picrate of which had mp 193-194°C and did not depress the melting point of the picrate of 1,2a-dimethyldecahydro-4-quinolone [10]; 0.4 g (5%) of amino ketone II (R_f 0.90); 0.24 g (3%) of enone X (mp 99-100°C and R_f 0.50. Found: C 71.7; H 10.1; N 5.4%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251); 0.2 g (3%) of ketone XI (mp 87-88°C and R_f 0.60. Found: C 71.5; H 10.2; N 5.4%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7· H 10.0; N 5.6%; M 251); 0.38 g (5%) of ketone IX (mp 129-130°C and R_f 0.60. Found: C 71.5; H 10.1; N 5.5%; M^+ 251. $C_{15}H_{25}NO_2$. Calculcated: C 71.1; H 10.0; N 5.6%; M 251); 0.24 g (3%) of alcohol XII (mp 115-116°C and R_f 0.50. Found: C 71.8; H 9.9; N 5.7%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.1; H 10.0; N 5.6%; M 251); 0.15 g (2%) of alcohol IIIa; 0.18 g (2%) of alcohol IIIb.

Hydration of 1,2e-Dimethyl-4e-vinylethynyl-4a-acetoxydecahydroquinoline (XIVa) [5]. A mixture of 3 g (10 mmole) of acetate XIVa, 3 g (9 mmole) of $HgSO_4$, and 1.8 ml of concentrated H_2SO_4 in 27 ml of H_2O was stirred at 50-55°C for 1 h, after which it was worked up as described for alcohol Ia to give 1.7 g of a mixture of substances. Chromatography of the latter with a column (elution with ether) and crystallization from acetone gave 0.5 g (30%) of amino ketone II, 0.16 g (9%) of alcohol IIIa, and 0.12 g (7%) of hemiacetal IV.

Hydration of 1,2a-Dimethyl-4e-vinylethynyl-4a-acetoxydeachydroquinoline (XIVc). A mixture of 3 g (10 mmole) of acetate XIVc, 3 g (9 mmole) of $HgSO_4$, and 1.8 ml of concentrated H_2SO_4 in 27 ml of water was stirred at 50-55°C for 1 h, after which it was worked up to give 2 g of a resinous substance, crystallization of which from hexane-acetone gave 1.1 g (50%) of enone X.

1,2e-Dimethyldecahydroquinoline-4-spiro-2'-tetrahydro-4'-pyranones (XV, XVI). A mixture of 4 g (14 mmole) of acetate XIVb, 4 g (13 mmole) of $HgSO_4$, and 2.4 ml of concentrated H_2SO_4 in 36 ml of water was stirred at 50-55°C for 1 h, after which it was worked up as described for alcohol Ia to give 2.2 g of a mixture of reaction products (R_f 0.73 and 0.81), column chromatography of which yielded 0.75 g (34%) of ketone XV (mp 85-86°C and R_f 0.73. Found: C 71.9; H 10.0; N 5.7%. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%) and 0.3 g (14%) of ketone XVI (mp 103-104°C and R_f 0.81. Found: C 71.9; H 10.1; N 5.4%; M^+ 251. $C_{15}H_{25}NO_2$. Calculated: C 71.7; H 10.0; N 5.6%; M 251).

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STEREOCHEMISTRY OF ETHYNYLATION OF 2,7-DIALKYL- AND 1,2,7-TRIALKYL-trans-DECAHYDRO-4-QUINOLONES*

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The effect of the nature of the acetylide, the temperature, and the character of the solvent on the stereochemistry of ethynylation of isomeric 2,7-dialkyl- and 1,2,7-trialkyldecahydro-4-quinolones was investigated. Acetylenic alcohols that have an axially oriented ethynyl grouping were synthesized. Conditions for the stereospecific synthesis of epimeric (with respect to C_4) acetylenic alcohols were found. The isomers of acetylenic alcohols obtained were incapable of interconversions under the reaction conditions.

We have previously [2] described the stereochemistry of the nucleophilic addition of sodium acetylide in liquid ammonia and of ethynylmagnesium bromide and acetylene in the presence of powdered potassium hydroxide to the carbonyl group of sterically unhindered 2,7-dialkyl- and 1,2,7-trialkyldecahydro-4-quinolones (the 2-CH_3 group is equatorial). These ketones behave unusually: Under the influence of the first two reagents they form only isomers of the acetylenic alcohol with an equatorial orientation of the ethynyl substituent, whereas epimerization of the starting ketones with respect to the C_2 center to give their axial epimers occurs under the conditions of the Favorskii reaction.

In order to synthesize the missing epimers of the acetylenic alcohols that have an axial orientation of the ethynyl group we continued our study of the stereochemistry of the ethynylation of sterically unhindered 2,7- and 1,2,7-alkyl-substituted decahydro-4-quinolones (I-III) with other ethynylating agents under various conditions. The reaction of ketones I and II with lithium, potassium, calcium, and barium acetylides in liquid ammonia, in contrast to the reaction with sodium acetylide [2], proceeds nonstereospecifically with the formation in each case of a mixture of two isomers containing, in addition to alcohols VI and VIII,

*See [1] for our preliminary communication.

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