STEREOCHEMISTRY OF NITROGEN HETEROCYCLES.

49.* SYNTHESIS AND TRANSFORMATIONS OF STEREOISOMERIC 4-KETO-2-METHYL-N-CHLORO-trans-DECAHYDROQUINOLINES

G. S. Litvinenko and L. A. Voronenko

UDC 541.634'547.831.3

Epimeric (with respect to the methyl group) stereoisomers of 4-keto-2-methyl-1-chloro-trans-decahydroquinoline were obtained, and their transformations under the influence of triethylamine were investigated. It was shown that the direction of the transformations depends on the steric orientation of the methyl group and the molar ratio of the N-chloroamine and triethylamine. The N-chloroamine isomer with an equatorial methyl group undergoes dehydrochlorination in the presence of excess triethylamine to give 2-methyl-4-hydroxy-trans-5,6,7,8,9,10-hexahydroquinoline. With an equimolar amount of triethylamine in solution in CCl_4 the principal reaction pathway becomes dehydrochlorination and subsequent chlorination to give 2-methyl-4-hydroxy-3-chloro-trans-5,6,7,8,9,10-hexahydroquinoline. The N-chloroamine isomer with an axial methyl group in the presence of both excess and, in particular, equimolar amounts of triethylamine undergoes, in addition to dehydrochlorination and chlorination in the β position of the piperidine ring, cis-trans isomerization and subsequent dehydrogenation with the primary formation of 2-methyl-4-hydroxy-3-chloro-5,6,7,8-tetrahydroquinoline. The mechanism of the transformations is examined.

Although chloroamines as a class of organic compounds have been known for a long time, the chemistry of thse compounds has undergone its most intensive development in the last 15-20 years. It has been shown that the high and diverse reactivities of chloroamines make it possible to use them to prepare compounds that are difficult to obtain by other methods [2-5].

Up until now, functionally substituted N-chloropiperidines have remained almost completely uninvestigated. In this connection it seemed of interest to us to investigate the transformations of stereoisomeric α,α'-disubstituted N-chloro-γ-piperidones — N-chloroderivatives of 4-keto-2-methyldecahydroquinoline, the stereoisomerism of which we have previously studied [6, 7]. In the present paper we describe the synthesis of spatial isomers of 4-keto-2-methyl-N-chloro-trans-decahydroquinoline that differ with respect to the orientation of the methyl group in the α position and their transformations under the influence of basic agents, particularly triethylamine.

The synthesis of isomeric N-chloroamines III and IV was accomplished by chlorination of 4-keto-2-methyldecahydroquinoline isomers I and II with sodium hypochlorite in a dipotassium phosphate buffer [8].

Both N-chloroamines III and IV are viscous colorless oils that are quite soluble in many organic solvents. When they are heated to 60-70°C, they undergo rapid decomposition (with foaming and resinification) to give, as shown by thin-layer chromatography (TLC), complex mixtures of compounds. Of the two N-chloroamines, isomer III with an equatorial methyl group in the 2 position is the more stable isomer. Although a spot of the starting amino ketone I appears at room temperature after 2 days, at 0-5°C III crystallizes completely and does not display signs of decomposition upon storage for 3 months, whereas the isomeric N-chloroamine IV with an axial methyl group displays a spot of starting amine II when it is stored in a refrigerator for a month. On the basis of the assignment of the frequencies of the IR spectrum for N-chloropiperidine [9] (νN—Cl 680 cm^{-1}) it may be assumed that N-chloroamines III and IV

*See [1] for communication 48.

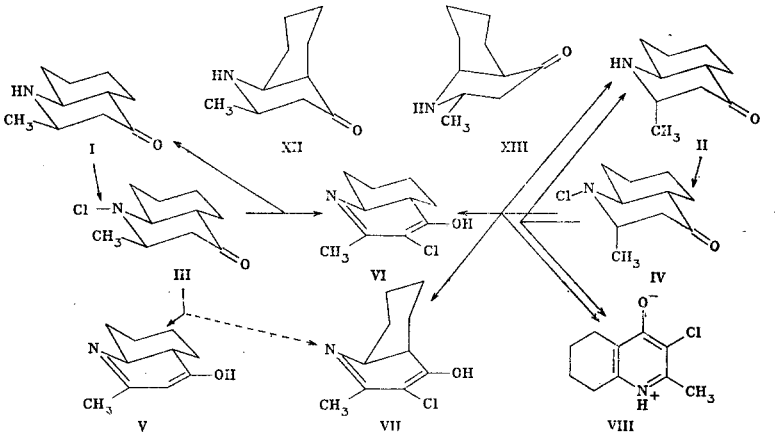
Institute of Chemical Sciences, Academy of Sciences of the Kazakh SSR, Alma-Ata 480100.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 792-798, June, 1984. Original article submitted July 11, 1983.

0009-3122/84/2006-0643$08.50

exist primarily in a conformation with an equatorial N—Cl bond (685 and 790 cm^{-1}, respectively).

Attempts to carry out the dehydrochlorination of N-chloroamines III and IV by means of aqueous and alcoholic alkali by the method described for 2,5-dimethyl-N-chloro-4-piperidone [10] gave complex markedly resinified mixtures of products. In this connection we investigated milder conditions; in particular, triethylamine was used as the agent to tie up the hydrogen chloride. The experiments were carried out with excess triethylamine (it was used as the solvent in this case), as well as with an equimolar amount in CCl_4 solution. We found that these two variants led to different results, depending on the structure of the N-chloroamines.

The principal reaction product in the action of excess triethylamine on 4-keto-2e-methyl-N-chloro-trans-decahydroquinoline (III) is 2-methyl-4-hydroxy-trans-5,6,7,8,9,10-hexahydroquinoline (V).



The molecular mass of V (by mass spectroscopy) is 165, i.e., it contains two fewer protons than starting amino ketone I. Intense bands at 1580, 1610, and 3290 cm^{-1} are observed in the IR spectrum, but the absorption band of a carbonyl group at 1700 cm^{-1} is absent. This provides a basis for the assumption that the compound obtained does not exist in the keto form but rather in the enol form with a conjugated system of N=C and C=C bonds. The PMR spectrum confirms the presence of a hydroxy group and makes it possible to unambiguously determine the position of the double bonds [$N{=}C_{(2)}(CH_3)C_{(3)}{=}C_{(4)}{-}OH$] and trans fusion of the cyclohexane and piperidine rings. Thus the broad, singlet, one-proton signal at 5 ppm, which is shifted to strong field when the solution is diluted, demonstrates the presence of a hydroxy group. The narrow signal of a proton attached to a double bond with a chemical shift of 4.85 ppm constitutes evidence that the double bond of the enol form is located in the $C_{(3)}{-}C_{(4)}$ position, and its singlet form demonstrates the absence of a proton attached to the vicinal $C_{(2)}$ atom and, consequently, $N{=}C_{(2)}$ orientation of the second double bond; the latter is also confirmed by the fact that the signal of the 2-CH_3 group is not split, and its large chemical shift (1.9 ppm) indicates its allylic character. The pattern of the splitting of the signal of the 9-H proton (3.13 ppm, t, J = 12.5 Hz; d, J = 4 Hz) constitutes evidence for a diaxial orientation of the 9- and 10-H protons and, consequently, a trans fusion of the rings.

The mass spectrum, which shows fragmentation to give [M − 1], [M − CH_3], [M − OH], [M − $(CH_2)_2$], and [M − $(CH_2)_3$] ions, rearranged [M − $(CH_2)_4$ + 1] ion, combinations of these ions, and a maximum ion with m/z 84, which is $\overset{+}{N}{=}C(CH_3)CH{=}CH{-}OH$, also confirms the structure of V.

The formation of V from chloroamine III may occur via both dehydrochlorination and disproportionation of the amine radical. The formation of 0.59 mole of V from 1 mole of chloroamine III by the action of excess triethylamine on the latter constitutes evidence in favor of dehydrochlorination [reaction (1)]; of course, the possibility of the partial formation of V via disproportionation also cannot be completely excluded.

According to thin-layer chromatography (TLC), a small amount of 2-methyl-4-hydroxy-3-chloro-cis-5,6,7,8,9,10-hexahydroquinoline (VII), the structure and the pathways of the formation of which will be discussed below, is present in the mother liquor after isolation of 2-methyl-4-hydroxy-trans-5,6,7,8,9,10-hexahydroquinoline (V).

The reaction of N-chloroamine III with an equivalent amount of triethylamine in CCl_4 proceeds considerably more slowly, and the chief reaction products are 2-methyl-4-hydroxy-3-chloro-trans-5,6,7,8,9,10-hexahydroquinoline (VI) (54% yield) and 4-keto-2e-methyl-trans-decahydroquinoline (I) (84% yield).

The IR spectrum of chloro derivative VI is very similar to the spectrum of the analogous V, which does not contain chlorine. New bands of prominent intensity that could have been ascribed to the C—Cl vibration do not appear at 600-800 cm^{-1}; however, the presence of chlorine in VI is demonstrated reliably by the results of elementary analysis and the characteristic isotopic ions in the mass spectrum. The molecular mass of VI (found by mass spectrometry) is 199, which corresponds to replacement of a hydrogen atom in V by a chlorine atom.

The PMR spectrum makes it possible to determine the position of the double bonds and the chlorine atom and the ring fusion. The absence in the spectrum of resonance signals that are characteristic for protons attached to a double bond and the singlet character of the signal of the protons of a methyl group, as well as their large chemical shift (2.06 ppm), demonstrate the $N{=}C_{(2)}(CH_3){-}C_{(3)}Cl{=}C_{(4)}{-}OH$ orientation of the double bonds and the chlorine atom. The character of the splitting of the 9-H signal (δ 2.93 ppm, t with J = 12 Hz, d with J = 4 Hz) constitutes evidence for the axial orientation of the 9-H and 10-H protons and, consequently, trans fusion of the rings.

The presence of $[M - H]$, $[M - CH_3]$, $[M - OH]$, $[M - Cl]$, $[M - (CH_2)_2]$, and $[M - (CH_2)_3]$ ions, rearranged $[M - (CH_2)_4 + 1]$ ion, and particularly the ions with m/z 117 (119) $[N{=}C(CH_3){-}CCl{=}C{-}OH]$ and 118 (120) $[N{=}C(CH_3){-}CCl{=}CH{-}OH]$ corresponding to the unsaturated part of the molecule in the mass spectrum also constitutes evidence in favor of structure VI.

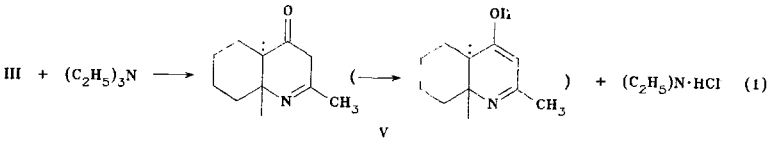
The mechanism of the formation of the unsaturated chlorine-containing amino ketone, which exists in enol form VI, can, in conformity with investigations of the mechanisms of the transformation of dibutylchloroamine in CCl_4 [11], be represented as follows. The first step in the reaction is the formation of 2-methyl-4-hydroxy-trans-5,6,7,8,9,10-hexahydroquinoline (V). The high yield (84%) of amino ketone I shows that unsaturated compound V is formed under the conditions of a slightly basic medium primarily via a mechanism involving disproportionation of amino radicals IX [Eqs. (2) and (3)]. The reaction of a chlorine radical with the active hydrogen of unsaturated ketone V gives radical X with an unpaired electron in the 3 position, which reacts with starting N-chloroamine III to give 2-methyl-4-hydroxy-3-chloro-trans-5,6,7,8,9,10-hexahydroquinoline (VI) and regenerates amino radical IX [Eqs. (4) and (5)]. The overall reaction is expressed by Eq. (6).

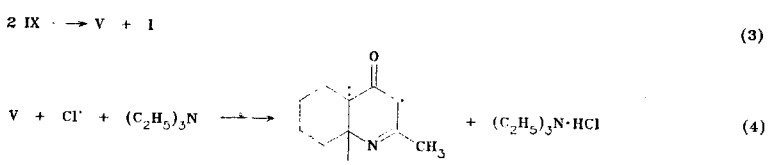
A substantially different pattern is observed in the case of N-chloroamine IV with an axial methyl group. The following four substances can be isolated in the reaction of IV with excess triethylamine: 2-methyl-4-hydroxy-3-chloro-trans- (VI, 2% yield) and -cis-5,6,7,8,9,10-hexahydroquinoline (VII, 6% yield), amino ketone II (50% yield), and 2-methyl-4-hydroxy-3-chloro-5,6,7,8-tetrahydroquinoline (VIII, 25% yield), which is not formed in the case of N-chloroamine III with an equatorial methyl group (see following page).

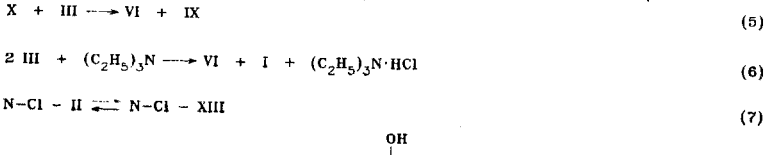
With respect to both its properties and spectral characteristics, VIII differs completely from the previously described substances. It does not melt when it is heated but only carbonizes at 300°C. It is only very slightly soluble in ordinary organic solvents. It remains at the start when it is subjected to TLC. Its molecular weight is two units lower (197) than the molecular mass of amino chloro ketones VI and VII. Both a carbonyl absorption band and a hydroxy absorption band are absent in its IR spectrum. Strong absorption corresponding to $\overset{+}{N}{-}H$ stretching vibrations in ammonium salts is present at 2400-2800 cm^{-1} in addition to vibrations at 1515 and 1620 cm^{-1}, which are similar to the vibrations previously described for V and VI.

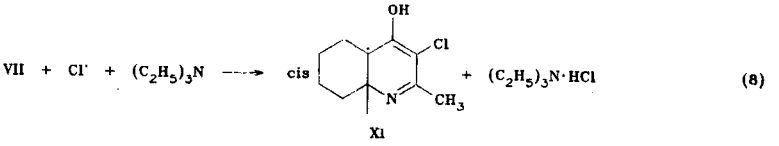
The PMR spectrum of this compound in $(CD_3)_2SO$ (with hexamethyldisiloxane as the external standard) displays an unsplit signal of protons of a methyl group attached to a double bond (2.62 ppm) and a broad signal of an ammonium proton (11.5 ppm). On the basis of all of these data betaine structure VIII, which explains all the peculiarities of its behavior, can be assigned to it.

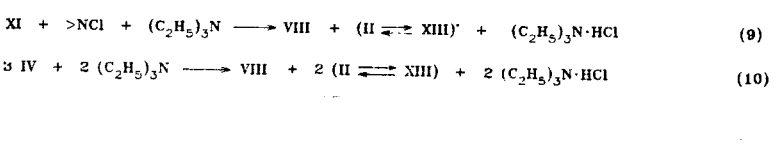
This structure is also confirmed by the mass spectrum, in which high stability of the compound with respect to electron impact is displayed: The maximum peak for it is the molecular-ion peak with m/z 197 (199), and there are small amounts of $[M - H]$, $[M - CH_3]$, $[M - Cl]$, and $[M - (CH_2)_2]$ fragment ions. It is well known [12] that the pyridine ring is very stable and does not form large fragment ions during fragmentation.

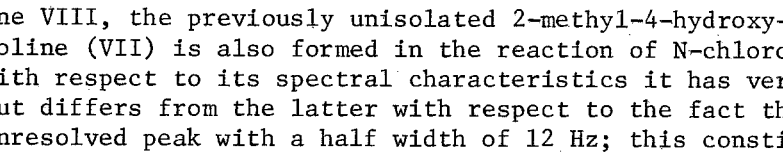


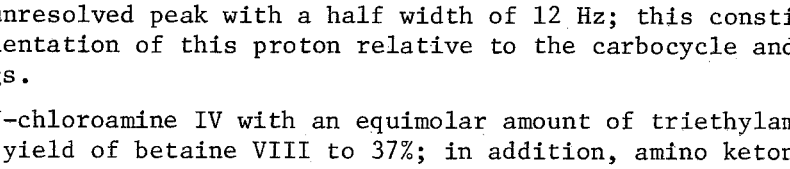












In addition betaine VIII, the previously unisolated 2-methyl-4-hydroxy-3-chloro-cis-5,6,7,8,9,10-hexahydroquinoline (VII) is also formed in the reaction of N-chloroamine IV with excess triethylamine. With respect to its spectral characteristics it has very much in common with trans isomer VI but differs from the latter with respect to the fact that the signal of the 9-H proton is an unresolved peak with a half width of 12 Hz; this constitutes evidence for the equatorial orientation of this proton relative to the carbocycle and, consequently, cis fusion of the rings.

The reaction of N-chloroamine IV with an equimolar amount of triethylamine in CCl_4 led to an increase in the yield of betaine VIII to 37%; in addition, amino ketone II (60%) was isolated, but unsaturated amino ketones V, VI, and VII were not detected even by TLC.

The mechanism of the formation of VIII in the initial stage is similar to the mechanism of the formation of VI and VII. A chlorine radical subsequently attacks the unsaturated amino chloro ketone at the active hydrogen in the 10 position to give a radical with an unpaired electron at the $C_{(10)}$ atom (XI). However, in the next step the N-chloroamine chlorine, instead of adding to $C_{(10)}$, reacts with the adjacent 9-H hydrogen to give diunsaturated ketone VIII with regeneration of the amino radical.

Thus primarily unsaturated amino ketone V (in the enol form) and only traces of 2-methyl-4-hydroxy-3-chloro-cis-5,6,7,8,9,10-hexahydroquinoline (VII) are formed in excess triethylamine in the case of N-chloroamine III with an equatorial methyl group. A decrease in the basicity of the medium leads to radical chlorination of unsaturated amino ketone V with retention of the trans fusion of the rings. In the case of N-chloroamine IV with an axial methyl group an unsaturated ketone is formed only as an intermediate in triethylamine, and the principal products are unsaturated and diunsaturated chlorine-containing trans- and cis-amino ketones VI and VII and diunsaturated amino ketone VIII (in enol forms). A decrease in the basicity of the medium intensifies the radical chlorinating character of the reaction to an even greater extent. This dependence on the orientation of the methyl group is evidently due to the greater tendency of N-chloro ketone IV with an axial methyl group to undergo decomposition into radicals (this also evidently determines its lower stability as compared with N-chloroamine III with an equatorial methyl group) and is the result of the more pronounced electron-donor character of the axial α-methyl group as compared with the equatorial α-methyl

group (the higher basicities of decahydroquinoline derivatives with an axial methyl group as compared with the basicities of those with an equatorial methyl group are also due to this effect [13, 14]).

In connection with the peculiarities of the transformations of N-chloroamines III and IV we should deal with the differences in the behavior of the starting amino ketones I and II themselves as a function of the orientation of the 2-CH_3 group. As we have previously shown [6, 7], both amino ketones have trans fusion of the rings; however, under the influence of alkaline agents they can be converted to isomers with cis fusion of the rings (XII and XIII, respectively) due to keto-enol tautomerism. In the case of a cis orientation of the methyl group attached to the $C_{(2)}$ atom and the methylene group attached to the $C_{(8)}$ atom this equilibrium is shifted markedly to favor trans isomer I; in the case of a trans orientation, however, the fractions of the isomers with cis and trans fusions of the rings are close. Taking this into account, it becomes understandable why primarily unsaturated amino ketone of the trans series V and its chloro derivative VI are formed in the case of chloroamine III, and only traces of cis isomer VII are detected [and only in the case of a high basicity of the medium (excess triethylamine)], whereas in the case of N-chloroamine IV the amounts of the trans and cis isomers are commensurable, and the cis isomer even predominates somewhat.

Turning again to the mechanism of the formation of diunsaturated amino chloro ketone VIII one may now note that the transformations of N-chloroamine IV are preceded by its isomerization via Eq. (7) with subsequent preferred formation of a radical with a cis orientation of the unpaired electron at $C_{(10)}$ and the hydrogen atom attached to $C_{(9)}$ [Eq. (8)]; instead of the addition of N-chloroamine chlorine to $C_{(10)}$ therefore, one observes capture by chlorine of the closely located (cis) extremely active hydrogen atom attached to $C_{(9)}$, as a result of which the diunsaturated enol of the amino chloro ketone, which takes on betaine structure VIII [Eq. (9)], is formed. The overall reaction of the formation of VIII from IV is expressed by Eq. (10).

EXPERIMENTAL

The IR spectra of KCl pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra were obtained with a BS-487 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The mass spectra were recorded with an MKh-1305 mass spectrometer. Thin-layer chromatogrpaphy (TLC) was realized on activity III aluminum oxide in an ether–benzene system (4:1); the chromatograms were developed with iodine vapors (the spots of the N-chloroamines were bright violet).

4-Keto-2e-methyl-1-chloro-trans-decahydroquinoline (III). A 160-ml sample of an aqueous solution of NaOCl containing 0.13 equivalents of the OCl^- ion was added dropwise in the course of 40 min at 0-5°C to a mixture of a solution of 8.35 g (50.6 mmole) of 4-keto-2e-methyl-trans-decahydroquinoline (I) (mp 41-42°C) and 21.7 g of $K_2HPO_4 \cdot 5H_2O$ in 150 ml of water and 60 ml of benzene, after which the mixture was stirred at 0-5°C for 1 h. The benzene layer was separated, the pasty lower layer was diluted with water, and the N-chloroamine was extracted with ether. The combined organic layer was dried with sodium sulfate, and the solvent was removed by vacuum distillation at a bath temperature of no higher than 30°C to give 10.02 g (99%) of a colorless viscous oil that crystallized in the condenser and had R_f 0.93. IR spectrum (thin layer): 1713 (C=O) and 685 cm^{-1} (N–Cl).

4-Keto-2a-methyl-1-chloro-trans-decahydroquinoline (IV). An 80-ml sample of an aqueous solution of NaOCl containing 0.065 equivalent of the OCl^- ion was added dropwise in the course of 30 min at 0-5°C to a mixture of a solution of 4.2 g (25 mmole) of 4-keto-2a-methyl-trans-decahydroquinoline (II) (mp 62-63°c) and 10.9 g of $K_2HPO_4 \cdot 5H_2O$ in 70 ml of water and 30 ml of benzene, and the mixture was stirred at 0-5°C for 1 h. The N-chloroamine was extracted with ether, and the solvent was removed by distillation to give 5 g (99%) of a slightly yellow viscous oil with R_f 0.91. IR spectrum (thin layer): 1713 (C=O) and 790 cm^{-1} (N–Cl).

Transformation of N-Chloroamine III in Triethylamine Solution. A solution of 4.01 g (19.9 mmole) of N-chloroamine III in 50 ml of triethylamine was maintained at room temperature until the spot of the chloroamine vanished on the thin-layer chromatogram (1 month). The precipitate (5.18 g) was removed by filtration and dissolved in 25 ml of chloroform, and the solution was washed with water (15 ml). The chloroform solution was dried, the solvent was removed, and the residue (2.18 g) was recrystallized from acetone to give 1.94 g (59%) of 2-methyl-4-hydroxy-trans-5,6,7,8,9,10-hexahydroquinoline (V) in the form of colorless crystals with mp 198-199°C (from acetone); the product was quite soluble in ethanol and meth-

anol, less soluble in benzene, chloroform, acetone, and water, and only slightly soluble in ether. IR spectrum (KBr pellet): 3280 (OH); 3110 (=C–H); 1610, 1580, 1540 cm^{-1} (C=C, N=C). PMR spectrum ($CDCl_3$): 1.9 (3H, s, 2-CH_3), 3.13 (1H, t, J = 12.5 Hz; d, J = 4 Hz, 9-H), 4.85 (1H, s, 3-H), and ~5 ppm (1H, broad s, OH). Found: C 72.6; H 8.9; N 8.5%; M 165. $C_{10}H_{15}NO$. Calculated: C 72.7; H 9.1; N 8.5%; M 165.

Transformation of N-Chloroamine III in a Solution of Triethylamine in CCl_4. A solution of 6.0 g (3 mmole) of N-chloroamine III and 5 ml of triethylamine in 75 ml of CCl_4 was maintained at room temperature until the spot of the starting chloroamine vanished on the thin-layer chromatogram (3 months). The precipitate (5.3 g) was isolated from the reaction mixture and treated with 30 ml of water. The undissolved precipitate was washed with water, dried (2.02 g), and recrystallized from ethanol to give 1.61 g (54%) of 2-methyl-4-hydroxy-3-chloro-trans-5,6,7,8,9,10-hexahydroquinoline (VI) in the form of colorless crystals with mp 197-198°C and R_f 0.54. IR spectrum: 3280 (OH); 1618, 1500-1555 cm^{-1} (C=C, C=N). PMR spectrum (d_5-pyridine): 2.06 (3H, s, 2-CH_3) and 2.93 ppm (1H, t, J = 12 Hz; d, J = 4 Hz, 9-H). Found: C 60.0; H 5.0; Cl 17.8; N 6.9%; M 199. $C_{10}H_{14}ClNO$. Calculated: C 60.2; H 5.0; Cl 17.8; N 7.0%; M 199. The mother liquor and the wash waters were combined, and the solvent was removed. Thin-layer chromatography of the residue (3.2 g) revealed a spot with R_f 0.69 (I) and a weak spot with R_f 0.54 (VI). Crystallization from water gave 2.11 g (84%) of 4-keto-2e-methyl-trans-decahydroquinoline (I) with mp 41-42°C; no melting-point depression was observed for a mixture of a sample of this product with a genuine sample [6].

Transformation of 4-Keto-2a-methyl-N-chloro-trans-decahydroquinoline (IV) in Triethylamine Solution. A solution of 2.6 g of N-chloroamine IV in 30 ml of triethylamine was maintained at room temperature until the spot of the starting N-chloroamine disappeared on the thin-layer chromatogram (1 month). The precipitate (1.71 g; TLC revealed spots with R_f 0.54 and 0.34 and an intense spot at the start) was removed by filtration and washed with 30 ml of water and 20 ml of chloroform. The insoluble residue (TLC revealed only a spot at the start) was recrystallized from ethanol to give 0.21 g (25%) of 2-methyl-4-hydroxy-3-chloro-5,6,7,8-tetrahydroquinoline (VIII) in the form of colorless fine needles. The product carbonized but did not melt when it was heated to 300°C and was insoluble in organic solvents and water. It was slightly soluble in $(CH_3)_2SO$ and ethanol. IR spectrum: 2400-2800 (N–H); 1640 w; 1618, 1515 (C=C, C=N); 687 cm^{-1} (C–Cl). PMR spectrum [$(CD_3)_2SO$]: 2.29 (3H, s, 2-CH_3) and 11.5 ppm (N–H). Found: C 61.1; Cl 18.0; N 7.2%; M 197. $C_{10}H_{12}ClNO$. Calculated: C 60.7; Cl 17.9; N 7.1%; M 197. The mother liquors (aqueous and chloroform) were evaporated to dryness (0.31 g, R_f 0.34 and 0.54), and the residue was separated by preparative TLC on Al_2O_3 [elution with diethyl ether–benzene (1:1)]. Separation was incomplete but gave 30 mg (2%) of pure 2-methyl-4-hydroxy-3-chloro-trans-5,6,7,8,9,10-hexahydroquinoline in the form of colorless crystals with mp 196-197°C and R_f 0.54 (no melting-point depression was observed for a mixture with a previously described sample) and 80 mg (6%) of 2-methyl-4-hydroxy-3-chloro-cis-5,6,7,8,9,10-hexahydroquinoline (VII) with mp 184-185°C (from acetone) and R_f 0.34. IR spectrum: 3250 (OH); 1615, 1560, 1525 cm^{-1} (C=C, C=N). PMR spectrum ($CDCl_3$): 5.7 (1H, s, OH), 2.11 (3H, s, 2-CH_3), and 3.68 ppm (1H, unresolved, broad, J = 12 Hz, 9-H). Found: C 60.5; H 5.3; Cl 17.9; N 7.0%; M 199. $C_{10}H_{14}ClNO$. Calculated: C 60.1; H 5.0; Cl 17.8; N 7.0%; M 199. The triethylamine mother liquor was evaporated to dryness, and the residue (1.32 g; R_f 0.23) was distilled *in vacuo*. Crystallization from petroleum ether, as described previously, gave 1.1 g (76%) of 4-keto-2a-methyl-trans-decahydroquinoline with mp 62-63°C; no melting-point depression was observed for a mixture of a sample of this product with a genuine sample [6].

Transformation of N-Chloroamine IV in a Solution of Triethylamine in Carbon Tetrachloride. A solution of 2.4 g of N-chloroamine IV and 2.1 ml of triethylamine in 30 ml of carbon tetrachloride was maintained at room temperature until the spot of the chloroamine vanished on the thin-layer chromatogram (3 months). The resulting precipitate (1.62 g) was removed periodically by filtration. The reaction mixture resinified. Chloroform (20 ml) and 10 ml of water were added to the precipitate, and the undissolved residue was washed successively several times with water and chloroform and recrystallized from ethanol to give 0.29 g (37%) of 2-methyl-4-hydroxy-3-chloro-5,6,7,8-tetrahydroquinoline (VIII), which, according to the IR spectrum, was identical to a previously described sample.

Only amino ketone II (R_f 0.23) was detected in the mother liquor and wash waters by TLC. Removal of the solvents, vacuum distillation, and crystallization from petroleum ether gave

1.2 g (90%) of 4-keto-2a-methyl-trans-decahydroquinoline (II) with mp 62-63°C; no melting-point depression was observed for a mixture of this sample with a genuine sample [6].

LITERATURE CITED

1. G. S. Litvinenko, N. Yu. Kuz'mina, and D. V. Sokolov, Khim. Geterotsikl. Soedin., No. 3, 382 (1984).
2. R. S. Neale, M. R. Walsh, and N. L. Marcus, J. Org. Chem., 30, 3683 (1965).
3. F. Minisci, R. Galli, A. Galli, and R. Bernardi, Chim. Ind., 49, 252 (1967).
4. F. Minisci, G. P. Gardini, and F. Bertini, Can. J. Chem., 48, 544 (1970).
5. R. S. Neale, Synthesis, No. 1, 1 (1971).
6. D. V. Sokolov, G. S. Litvinenko, and K. I. Khludneva, Zh. Org. Khim., 29, 1112 (1959).
7. D. V. Sokolov, G. S. Litvinenko, and M. N. Akimova, Izv. Akad. Nauk Kazakhsk. SSR, Ser. Khim., No. 1, 59 (1962).
8. K. W. Baldry and J. T. Robinson, Tetrahedron, 31, 2621 (1975).
9. O. S. Anisimova and Yu. A. Pentin, in: Modern Problems in Physical Chemistry [in Russian], Vol. 7 (1973), p. 295.
10. A. Sh. Sharifkanov and G. M. Mukhametkaliev, Khim. Khim. Tekhnol. Izd. Kazakhsk. Gosudartsv. Univ., No. 11, 147 (1967).
11. S. Wawsonek and J. D. Nordstrom, J. Org. Chem., 27, 3726 (1962).
12. H. Budzikiewicz, C. Djerassi, and D. Williams, Interpretation of the Mass Spectra of Organic Compounds, Holden-Day, San Francisco (1964).
13. D. V. Sokolov, G. S. Litvinenko, V. I. Artyukhin, and A. A. Andrusenko, Izv. Akad. Nauk Kazakhsk. SSR, Ser. Khim., No. 4, 73 (1965).
14. G. S. Litvinenko, V. I. Artyukhin, A. A. Andrusenko, D. V. Sokolov, and K. I. Khludneva, Reakts. Sposobn. Org. Soedin., 5, 263 (1968).