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REACTION OF 2-METHYLENE-3-OXOQUINUCLIDINE WITH PHENOL AND NAPHTHOLS

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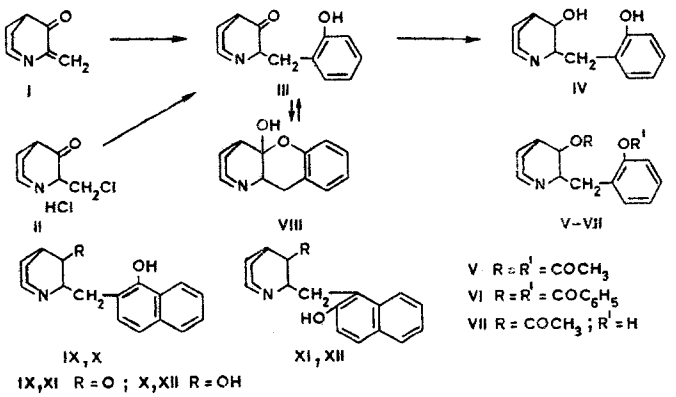
C-Alkylation in the ortho position of phenol and naphthols occurs in the reaction of 2-methylene-3-oxoquinuclidine with sodium phenoxide and sodium derivatives of naphthols. The structures of the products were confirmed by IR, PMR, and mass spectroscopic data.

In a previous communication we described the reaction of 2-methylene-3-oxoquinuclidine (I) and its salts and quaternary derivatives with some nucleophilic reagents (water and alcohols) [1], during which we discovered a substantial difference in the reactivities of base I and its salts.

In a continuation of this research we studied the reaction of I with aromatic hydroxy derivatives – phenol and α- and β-naphthols.

In the reaction of ketone I with sodium phenoxide and sodium derivatives of α- and β-naphthols, instead of the normal Michael reaction – addition of hydroxyl-containing compounds to the olefinic bond of I – we observed C-alkylation in the ortho position of phenol and the naphthols to give 2-(2'-hydroxybenzyl)-3-oxoquinuclidine (III), 2-(1'-hydroxy-2'-naphthylmethyl)-3-oxoquinuclidine (IX), and 2-(2'-hydroxy-1'-naphthylmethyl)-3-oxoquinuclidine (XI). Under similar conditions ketone I does not react with 3-hydroxypyridine. As a result of heating 2-chloromethyl-3-oxoquinuclidine hydrochloride (II) [1] with phenol we also obtained III. It is possible that in this case the initial step in the reaction is thermal dehydrohalogenation of chloride II and subsequent reaction of the resulting reactive 2-methylene-3-oxoquinuclidine hydrochloride with phenol.



The structures of III, IX, and XI were confirmed by chemical transformations and by IR, PMR, and mass spectral data. The IR spectra of these compounds contain, in addition to absorption in the region corresponding

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to carbonyl groups (1725-1730 cm^{-1}), a broad band at 2480-2630 cm^{-1}, which attests to salt formation through the phenolic hydroxyl group and the nitrogen atom of the quinuclidine ring. A quartet of a 2-H proton at 3.42 ppm, a 4-H quintet with a spin–spin coupling constant (SSCC) of 2.5 Hz at 2.56 ppm, and complex multiplets of 5,8-H_2 protons are observed in the PMR spectrum of III; this confirms the presence of a quinuclidine ring with a carbonyl group in the 3 position and a CH_2R group in the 2 position [1]. The magnitude of the chemical shift of the protons of the methylene group of this substituent (~ 3.07 ppm) makes it possible to exclude the possibility of its addition to the phenolic oxygen atom and indicates replacement by this group of one of the protons of the phenyl ring. The overall intensity of the signals of the aromatic ring protons [4 proton units (pu)] is in agreement with this conclusion. The character of the multiplicity of the indicated signals, namely, the absence of a symmetrical spectrum of the A_2B_2 type (which is characteristic for p-disubstituted benzenes) and of a multiplet with an intensity of 1 pu with constants that do not exceed 3 Hz (which is characteristic for m-disubstituted benzenes), makes it possible to conclude that both substituents in the phenyl ring of III are in the ortho position. This sort of character of the substitution of the phenyl ring has also been unambiguously established during a study of the PMR spectrum of VIIt.

In the PMR spectrum of IX, which, on the whole, is similar to the spectrum of III, a quartet of the AB type with δ_A = 7.10, δ_B = 7.17, and $J_{AB} \approx 8.2$ Hz corresponds to the protons of the substituted naphthyl ring. The magnitude of the SSCC, which is characteristic for the protons in the ortho position, makes it possible to conclude that the CH_2–Quin (quinuclidine) group is attached to the β carbon of the naphthalene ring, i.e., in the ortho position relative to the hydroxyl group.

Ketone III reacts with hydroxylamine to give an oxime, and when it is heated with aqueous potassium hydroxide solution it is converted to a four-ring compound – 7-hydroxy-4,5-benz-6,1-oxazatricyclo[4.2.2.$0^{2,7}$]-dodecane (VIII). The structure of the latter follows from the results of elementary analysis, the absence in the IR spectrum of an absorption band of a carbonyl group, and cleavage of the hemiacetal grouping with regeneration of the starting ketone III when VIII is heated with hydrochloric acid.

The keto group in III, IX, and XI was reduced to a hydroxy group with lithium aluminum hydride and sodium borohydride. In this case we obtained 2-substituted 3-hydroxyquinuclidines (IV, X, and XII) in the form of a mixture of two diastereomeric forms. Individual trans isomer IVt was isolated by crystallization. We were unable to accomplish the catalytic hydrogenation of base III and its hydrochloride in the presence of platinum.

The IR spectrum of IV contains bands at 3370 cm^{-1} (aliphatic OH group) and a broad band at 2340-2550 cm^{-1}, which, as in the case of ketone III, is associated with salt formation through the phenolic hydroxyl group and the quinuclidine nitrogen atom.

2-(2'-Hydroxybenzyl)-3-hydroxyquinuclidine (IV) is acylated at the phenolic and alcohol hydroxyl groups to give diacyl derivatives (V, VI). In the reaction of 2-(2'-acetoxybenzyl)-3-acetoxyquinuclidine with an alcohol solution of hydrogen chloride at room temperature one observes removal of one acetyl group, evidently due to transacylation, to give 2-(2'-hydroxybenzyl)-3-acetoxyquinuclidine (VII).

According to the PMR spectral data, IVt, which is isolated by crystallization of the mixture of diastereomers, and its acylation products Vt, VIt, and VIIt are individual compounds. The substances obtained from the mother liquors are a mixture of diastereomers IVc and IVt, which is converted to a mixture of diastereomeric acyl derivatives V-VII. The configuration of diastereomers IV-VII was established on the basis of the J_{23} and J_{34} vicinal SSCC.

We have previously shown [2, 3] that the relationships $J_{23cis} > J_{23trans}$ and $J_{34cis} > J_{34trans}$ (I) are valid for 2,3-disubstituted quinuclidines. In conformity with these relationships, individual IVt, Vt, VIt, and VIIt were assigned to the trans series.

It follows from the data in Table 1 that the relationship $J_{34cis} > J_{34trans}$ is strictly observed for all of the investigated compounds, and the effect of the substituents on these constants and on the J_{23cis} constant is only slight. The substituents have a much stronger effect on the $J_{23trans}$ SSCC, and in the case of the IVt and VIIt isomers this constant practically reaches the J_{23cis} value; this is probably associated with the considerable deformation of the molecule in the indicated isomers. For all of the investigated pairs of compounds the 3-H signal of the cis isomer is observed at weaker field (~ 0.4-0.5 ppm) as compared with the trans isomer.

The spectrum of VIIt was also studied by means of a shift reagent – tris(dipivaloylmethanato)europium $Eu(DPM)_3$. When the ratio of the molar concentration of the reagent to the substrate is ~ 0.2, a first-order

TABLE 1. Chemical Shifts of the Protons (δ, ppm)

Compound	2H	3H	4H	5,8H₂	6,7H₂	2'H₂	R₂1(A₂)	R₃	Solvent
III	3,42		2,56	1,95—2,30	3,0—3,25	3,07	6,7—7,2		$CDCl_3$
IVt	~2,85*,† $J_{23}\approx 6,7$ Hz	3,58 $J_{34}\approx 2$ Hz	1,86	1,5—1,95	2,5—3,0	—*	6,65—7,15		$CDCl_3$
IVc‡	$J_{23}\approx 7,0$ Hz*	3,99 $J_{34}\approx 5$ Hz	2,05	1,3—1,8	2,6—3,1	—*	6,7—7,15		$CDCl_3$
Vt	~2,90*,† $J_{23}\approx 4,5$ Hz	4,55 $J_{34}\approx 2$ Hz	1,90	1,2—1,8	2,5—3,1	2,76	7,0—7,3 2,27 (OAc)	1,82	$CDCl_3$
Vc‡	$J_{23}\approx 7,5$ Hz*	4,94 $J_{34}\approx 5$ Hz		1,2—1,65	2,5—3,2	—*	6,85—7,2 2,24 (OAc)	1,97	CCl_4
VIt‡	$J_{23}\leqslant 3$ Hz*	4,70 $J_{34}\leqslant 2,5$ Hz	1,99	1,2—1,9	2,5—3,3	2,86	7,0—8,2	7,0—	CCl_4
VIc‡	$J_{23}\approx 7$ Hz*	5,12 $J_{34}\approx 5$ Hz						8,2	CCl_4
VIIt	$J_{23}=6,5$ Hz*	4,64 $J_{34}\approx 2$ Hz	2,05	1,4—1,9	2,6—3,4	—*	6,6—7,1	2,06	$CDCl_3$
VIIc‡	$J_{23}=7$ Hz*	5,11 $J_{34}\approx 5,5$ Hz						2,13	$CDCl_3$
IX	3,5	—	2,15	1,35—1,70	2,40—2,75	3,05	7,10—8,5 7,10 (A), 7,17 (B) $J_{AB}\approx$ ≈8,2 Hz		$C_6D_5B_2$
Xt‡	$J_{23}\approx 5$ Hz*	3,35 $J_{34}\leqslant 3$ Hz	1,90	1,1—1,8	2,40—3,60	—*	6,8—8,10		$CDCl_3$
Xc‡	$J_{23}\approx 7$ Hz*	3,84 $J_{34}\approx 5$ Hz							$CDCl_3$
XIIt	—*	3,66	1,75	1,3—1,9	2,6—3,4	—*	7,05—8,1 7,08 (A), 7,67 (B) $J_{AB}\approx$ ≈8 Hz		d_6-DMSO

*The signals are superimposed on the signals of the α protons of the quinuclidine ring.
†The position of the signals was determined by means of double resonance.
‡Studied in a mixture of isomers.

spectrum consisting of two doublets and two triplets with a splitting of ≈ 7-8 Hz corresponds to the aromatic protons; this once again confirms the data presented above on ortho substitution in the phenyl ring.

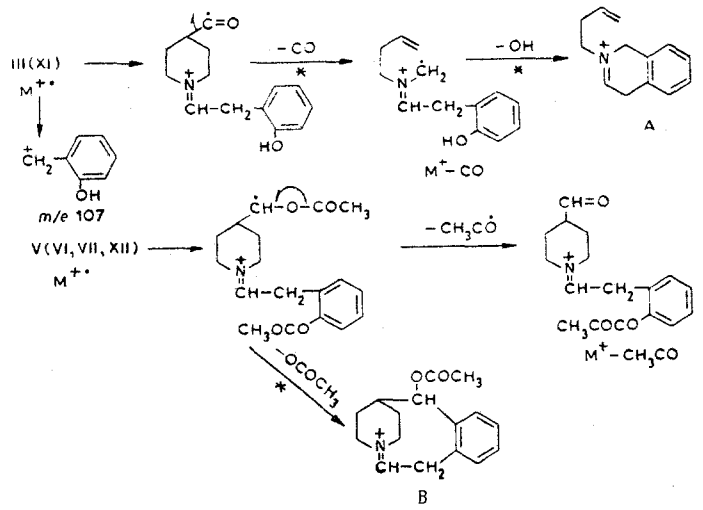
The assignment of the configuration of isomers X and XII was made from relationships (I) and in analogy with the phenyl derivatives IVt and IVc.

The PMR spectrum of XII is in good agreement with the expected structure. An AB system with $\delta_A(H_\alpha)$= 7.67 and $\delta_B(H_\beta)$ = 7.08 Hz is affiliated with the protons of the substituted phenyl ring. This makes it possible to conclude that the CH_2–Quin group in XII (as in ketone XI) is attached to the α carbon of the naphthalene ring in the ortho position relative to the OH group.

The mass spectroscopic confirmation of the structure of III-XII was based on the use of previously obtained data on the mass spectral characteristics of various functional substituted quinuclidines [3-5].

All of the investigated compounds (III-VII, and XI) are characterized by distinct molecular ion peaks, the intensities of which are determined by the nature of the functional group in the 3 position. In the case of 3-oxo derivatives III and XI the principal (in intensity) peak in the spectra at 70 and 12 eV corresponds to the $M^+ - CO$ fragment (m/e 203 for III and 253 for XI). The usual detachment of an OH group from $M^+ - CO$ in the case of III and XI (m^* = 170.5 for III) is evidently due to the "ortho effect" and the formation of stable cyclic fragment a (see the fragmentation scheme below). In the fragmentation of III and XI one does not observe detachment of the substituent in the form of a neutral particle, but extremely intense formation of a fragment of the benzylium type with m/e 107 (III) and 157 (XI) is observed. As in the case of III and XI, the spectrum of IV contains a peak of a fragment of the benzylium type with m/e 107. However, in contrast to III and XI, detach-

ment of the substituent in the molecular ion from the 2 position leads to a fragment with m/e 126, the peak of which is second in intensity after the M^+ peak. We have previously discussed the mechanism of this process [4].



The characteristic process in the fragmentation of 3-acyloxyquinuclidines is detachment of the acyl group from the M^+ ion [5]. An intense peak of an $M^+ - OCOCH_3$ fragment is present in the spectrum of diacyloxy derivative V along with the $M^+ - CH_3CO$ peak. However, only an $M^+ - COCH_3$ fragment is observed in the fragmentation of VII. It may be assumed that the formation of an $M^+ - OCOCH_3$ ion for V is due to the "ortho effect" with detachment of an acyloxy group from the benzene ring to give fragment b. It is interesting to note that an extremely intense peak of a similarly constructed $M^+ - OH$ ion is also observed in the spectrum of VII. These peculiarities in the fragmentation of V and VII make it possible to determine, from the mass spectra, the number and position of the $OCOCH_3$ or OH groups. The fragmentation mechanisms characteristic for V and VII are also typical for VI. The overall scheme of the fragmentation of III-XII can be briefly represented by the diagram given above.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-10 spectrometer. The PMR spectra were recorded with a JNM-4H-100 spectrometer (100 MHz) with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with an MKh-1303 mass spectrometer with introduction of the samples into the ion source. The sample input temperature was 20°C, and the temperature of the ionization chamber was 125°C. The ionizing voltages were 70 and 12 eV, and the emission current was 75 mA.

2-(2'-Hydroxybenzyl)-3-oxoquinuclidine (III). A) A 1.7-g (74 mg-atom) sample of sodium was added to a solution of 15 g (160 mmole) of phenol in 30 ml of xylene, and the mixture was refluxed with stirring until the sodium dissolved. A 10-g (73 mmole) sample of 2-methylene-3-oxoquinuclidine (I) was added to the resulting sodium phenoxide solution, and the mixture was refluxed for 10 h. It was then cooled and treated with 50 ml of water, and the xylene layer was separated. The aqeuous layer was extracted with chloroform, the solvents were removed by distillation, and the residue was triturated with ethyl acetate to give 11 g (65.5%) of III with mp 137-139°C (from ethyl acetate). IR spectrum: 1725 (C = O), 2480-2630 cm^{-1} ($\overset{+}{N}H\cdots OC_6H_5$). Found: C 72.7; H 7.3; N 6.4%. $C_{14}H_{17}NO_2$. Calculated: C 72.7; H 7.4; N 6.1%.

B) A mixture of 3 g of 2-chloromethyl-3-oxoquinuclidine hydrochloride was heated at 120-130°C (bath temperature) for 6 h. At the start of the heating period, hydrogen chloride evolution was observed. The mixture was dissolved in 30 ml of water, and the aqueous solution was made alkaline with 40% sodium hydroxide solution and extracted with chloroform. The residue was triturated with ether and recrystallized from ethyl acetate to give 2 g (57.5%) of a product with mp 137-139°C.

trans-2-(2'-Hydroxybenzyl)-3-hydroxyquinuclidine (IVt). A) A solution of 2.3 g (10 mmole) of ketone III in 50 ml of dioxane was added to a suspension of 1.9 g (50 mmole) of lithium aluminum hydride in 25 ml of ether, and the mixture was refluxed with stirring for 10 h. It was then cooled and treated with 4 ml of water, and the resulting precipitate was removed by filtration and washed thoroughly with chloroform. The combined extracts were evaporated, and the residue was triturated with ether. Workup gave 1.6 g (69.5%) of a mixture

of diastereomeric IVc and IVt with mp 130-140°C. Recrystallization of the mixture from acetone gave 0.66 g of trans isomer IVt with mp 169-171°C. IR spectrum: 3370 (OH), 2340-2550 cm^{-1} ($\overset{+}{N}H\cdots OC_6H_5$). Found: C 72.2; H 8.0; N 5.9%. $C_{14}H_{19}NO_2$. Calculated: C 72.1; H 8.2; N 6.0%. The acetone mother liquor was evaporated, and the residue was recrystallized from ethyl acetate to give 0.6 g of a mixture of IVc and IVt (mp 138-142°C) containing ~ 80% IVc. Found: C 72.3; H 8.1; N 6.2%. $C_{14}H_{19}NO_2$. Calculated: C 72.1; H 8.2; N 6.0%.

B) A 10-g (262 mmole) sample of sodium borohydride was sprinkled in the course of 1 h into a solution of 15 g (65 mmole) of ketone III in 200 ml of methanol, and the mixture was stirred at room temperature for 20 h. It was then evaporated, 70 ml of water was added, and the mixture was extracted with chloroform. Workup of the extract gave 9.5 g (63%) of a mixture of IVc and IVt, from which 4.3 g of carbinol IVt, with mp 169-171°C, was isolated by crystallization from acetone.

trans-2-(2'-Acetoxybenzyl)-3-acetoxyquinuclidine (Vt). A solution of 2.33 g (10 mmole) of IVt in 20 ml of acetic anhydride was heated at 100°C for 6 h, after which the excess acetic anhydride was removed by vacuum distillation, and the residue was treated with a 25% solution of potassium carbonate. The alkaline mixture was extracted with chloroform, and the extract was worked up to give 2.68 g (84.5%) of a product with bp 163-165°C (0.5 mm). IR spectrum: 1724 ($OCOCH_3$) and 1756 cm^{-1} ($C_6H_4OCOCH_3$). Found: C 68.4; H 7.3; N 4.4%. $C_{18}H_{23}NO_4$. Calculated: C 68.1; H 7.3; N 4.4%.

A mixture of acetyl derivatives Vc and Vt was similarly obtained from a mixture of diastereomeric carbinols IVc and IVt.

trans-2-(2'-Hydroxybenzyl)-3-acetoxyquinuclidine (VIIt). An alcohol solution of hydrogen chloride was added at room temperature to a solution of 1.9 g (6 mmole) of Vt in 20 ml of ethanol until the mixture was acidic with respect to Congo Red. The resulting precipitate was removed by filtration and washed with acetone to give 1.4 g (75.2%) of the hydrochloride of VIIt with mp 287-288°C. IR spectrum: 1730 ($OCOCH_3$), 3150 (OH), and 2510-2570 cm^{-1} ($\overset{+}{N}H$). Found: C 61.9; H 7.3; Cl 10.8%. $C_{16}H_{21}NO_3 \cdot HCl$. Calculated: C 61.6; H 7.1; Cl 11.4%.

Treatment of the hydrochloride of VIIt with aqueous potassium carbonate solution and subsequent extraction with chloroform yielded base VIIt with mp 151-153°C (from a mixture of acetone and ethanol). IR spectrum: 1740 ($OCOCH_3$) and 2580-2740 cm^{-1} (associated OH group). Found: C 69.6; H 7.8%. $C_{16}H_{21}NO_3$. Calculated: C 69.8; H 7.7%.

2-(2'-Benzoyloxybenzyl)-3-benzoyloxoquinuclidine (VIc and VIt). A 1.05-g (7.5 mmole) sample of benzoyl chloride and 10 ml of pyridine were added to a mixture of 1 g (3.7 mmole) of the hydrochlorides of diastereomeric IVc and IVt, and the mixture was refluxed for 10 h. The resulting solution was vacuum evaporated, and the residue was made alkaline with 25% potassium carbonate solution and extracted with chloroform. The chloroform was removed from the extract, and the residue was distilled to give 1.2 g (73.8%) of a product with bp 252-254°C (0.3 mm). IR spectrum: 1708 ($OCOC_6H_5$) and 1732 cm^{-1} ($C_6H_4OCOC_6H_5$). Found: C 76.3; H 6.1%. $C_{28}H_{27}NO_4$. Calculated: C 76.2; H 6.2%.

2-(2'-Hydroxybenzyl)-3-oxoquinuclidine Oxime. A mixture of 3 g (13 mmole) of ketone III, 0.9 g (13 mmole) of hydroxylamine hydrochloride, and 30 ml of ethanol was refluxed for 10 h, after which it was cooled, and the resulting precipitate was removed by filtration and recrystallized from methanol to give 1.8 g (49%) of the oxime hydrochloride with mp 173-174°C. To isolate the base, the oxime hydrochloride was treated with 50% potassium carbonate solution, and the mixture was extracted with chloroform. The chloroform solution was evaporated, and the residue was recrystallized from ethyl acetate to give the oxime with mp 146-148°C. Found: C 68.4; H 7.5; N 11.4%. $C_{14}H_{18}N_2O_2$. Calculated: C 68.3; H 7.4; N 11.4%.

7-Hydroxy-4,5-benz-6,1-oxazatricyclo[4.2.2.$0^{2,7}$]dodecane (VIII). A mixture of 7 g (30 mmole) of III and 70 ml of 25% aqeuous potassium hydroxide solution was refluxed for 16 h, after which the alkaline solution was extracted with chloroform, and the chloroform solution was vacuum evaporated. The residue was recrystallized from isopropyl alcohol to give 5.8 g (83%) of a product with mp 151-153°C. IR spectrum: 2650-3030 cm^{-1} (associated OH group); no absorption was observed in the carbonyl group region. Found: C 73.0; H 7.7; N 5.9%. $C_{14}H_{17}NO_2$. Calculated: C 72.7; H 7.4; N 6.1%.

Reaction of VIII with Hydrochloric Acid. A solution of 0.3 g (1.3 mmole) of VIII in 3 ml of 17% hydrochloric acid was refluxed for 10 h, after which the mixture was vacuum evaporated, and the residue was made alkaline with potassium carbonate and extracted with chloroform. The chloroform solution was evaporated, and the residue was crystallized from ethyl acetate to give 0.2 g (67%) of III with mp 137-139°C. The IR spectra of ketone III obtained by this method and from 2-methylene-3-oxoquinuclidine (I) coincided. IR spectrum: 1725 (C = O) and 2480-2630 cm^{-1} ($\overset{+}{N}H\cdots OC_6H_5$).

2-(1'-Hydroxy-2'-naphthyl)-3-oxoquinuclidine (IX). A 10-g (70 mmole) sample of α-naphthol and 0.84 g (36 mg-atom) of sodium were heated in 50 ml of anhydrous toluene until the sodium dissolved, after which the mixture was cooled, and 5 g (36 mmole) of ketone I was added. The mixture was then refluxed with stirring for 6 h, after which it was cooled and treated with 160 ml of water. The toluene layer was separated, and the aqeuous layer was extracted with chloroform. The solvents were removed, and the residue was triturated with ethyl acetate to give 8.9 g (87%) of a product with mp 199-201°C (from ethyl acetate). IR spectrum: 1730 (C = O) and 2280-2640 cm^{-1} ($\overset{+}{N}H\cdots OC_6H_5$). Found: C 76.8; H 6.7; N 4.9%. $C_{18}H_{19}NO_2$. Calculated: C 76.8; H 6.8; N 5.0%. The hydrochloride had mp 246-247°C. Found: C 68.0; H 6.4%. $C_{18}H_{19}NO_2 \cdot HCl$. Calculated: C 68.0; H 6.3%.

2-(2'-Hydroxy-1'-naphthyl)-3-oxoquinuclidine (XI). This compound, with mp 190-192°C (from benzene), was similarly obtained in 58.5% yield from 2-methylene-3-oxoquinuclidine (I) and sodium β-naphthoxide. Found: C 76.7; H 6.9; N 5.1%. $C_{18}H_{19}NO_2$. Calculated: C 76.8; H 6.8; N 5.0%.

2-(1'-Hydroxy-2'-naphthyl)-3-hydroxyquinuclidine (Xc and Xt). A 2.2-g (7.1 mmole) sample of IX was added gradually to a suspension of 2 g (52 mmole) of lithium aluminum hydride in a mixture of 25 ml of ether and 50 ml of dioxane, and the mixture was refluxed with stirring for 10 h. It was then cooled and treated with 5 ml of water, and the resulting precipitate was removed by filtration and washed thoroughly with chloroform. The combined extracts were evaporated, and the residue was dissolved in 10 ml of acetone. The acetone solution was treated with an alcohol solution of hydrogen chloride, and the mixture was worked up to give 2 g (87.3%) of the hydrochloride of X in the form of a mixture of the cis and trans isomers with mp 244-245°C (from water). IR spectrum: 3280 (OH) and 2610 and 2660 cm^{-1} ($\overset{+}{N}H$). Found: C 65.7; H 7.0; Cl 10.8%. $C_{18}H_{21}NO_2 \cdot HCl \cdot 1/2H_2O$. Calculated: C 65.7; H 7.0; Cl 10.8%.

trans-2-(2'-Hydroxy-1'-naphthyl)-3-hydroxyquinuclidine (XIIt). A 4.8-g (126 mmole) sample of sodium borohydride was added gradually to a suspension of 4.8 g (17 mmole) of XI in 110 ml of methanol, and the mixture was stirred at room temperature for 20 h, after which the methanol was removed by distillation, 150 ml of water was added to the residue, and the mixture was extracted with chloroform. The chloroform was removed by distillation, and the residue was triturated with a mixture of 20 ml of ether and 10 ml of ethyl acetate to give 2.9 g (60.3%) of a mixture of carbinols XIIc and XIIt. Crystallization from ethanol yielded 0.7 g of individual XIIt with mp 228-230°C. Found: C 76.1; H 7.4; N 4.7%. $C_{18}H_{21}NO_2$. Calculated: C 76.3; H 7.5; N 4.9%.

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