

2-BENZOPYRYLIUM SALTS.

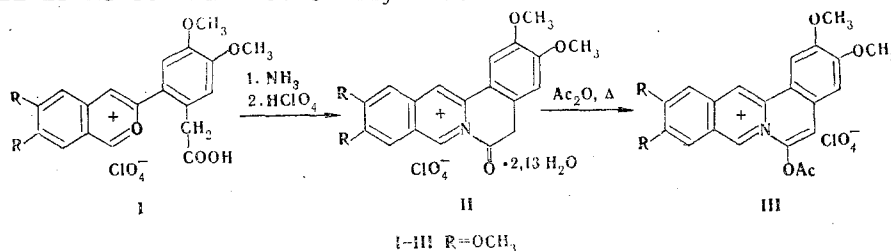
27.* SOME TRANSFORMATIONS OF 6-OXODIBENZO[a,g]-QUINOLIZINIUM SALTS

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The synthesis of 6-oxodibenzo[a,g]quinolizinium perchlorate — an analog of the alkaloid berberine — and a number of its derivatives, including mesoionic compounds, was accomplished on the basis of a 1-unsubstituted 3-(2-methylenecarboxyaryl)-2-benzopyrylium salt. The interconversions of the compounds obtained in this research were studied.

Like 1-alkyl-substituted 3-(2-methylenecarboxyaryl)-2-benzopyrylium salts [2], 1-unsubstituted salt I [3], as a result of successive treatment with ammonia and 70% HClO₄, forms 6-oxodibenzo[a,g]quinolizinium perchlorate (II), which, with respect to its IR, UV, and PMR spectral characteristics, is similar to the previously obtained salts [2]; acetate III is also formed when II is heated in acetic anhydride.



However, in contrast to 8-alkyl-substituted salts [2], which crystallize from acetic acid without undergoing any structural change, colorless unsubstituted salt II upon heating in this solvent forms a yellow substance, in the IR spectrum of which a band appears at 1650 cm⁻¹ in place of the band at 1680 cm⁻¹. We found that the same compound can be obtained by heating salt II above 100°C in aprotic solvents, from its suspensions in high-boiling hydrocarbons, and even in the case of careful heating of crystals of II. The changes in the electronic spectrum of this substance as compared with the starting compound, as well as the undoubted similarity of its spectrum to the spectrum of 8-ethyl-6-oxodibenzo[a,g]quinolizinium acetate[‡] (see Fig. 1) definitely indicate the formation of a more extensive π system, which may occur in the case of enolization of the isoquinolone fragment in salt II.

This slow conversion of keto form II to enol form V cannot be explained by the existence of an equilibrium between them but rather is more likely determined by the occurrence of a chemical reaction. Crystallization water, the presence of which is attested to by the presence in the IR spectrum of a broad double band with maxima at 3290 and 3480 cm⁻¹, may be a possible initiator for this transformation. This sort of absorption is ascribed to the vibrations of the water molecules that participate in the formation of hydrogen bonds and electrostatic interaction with the cationoid center [4]. According to the calculated data obtained by the Pariser-Parr-Pople (PPP) method, the greatest positive charge (except for the

*See [1] for communication 26.

[†]Deceased.

[‡]The extremely low solubility of acetate III in alcohol and acetonitrile made it impossible to record its electronic spectrum.

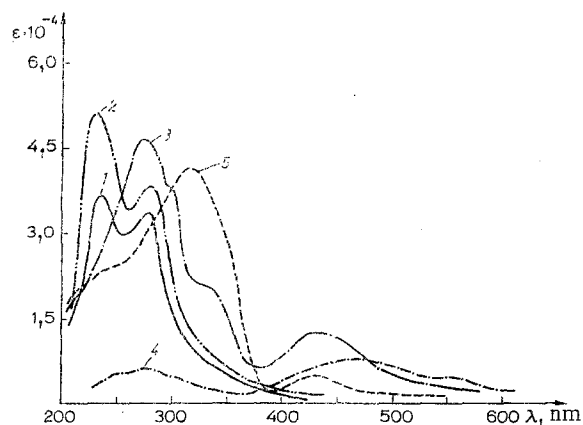
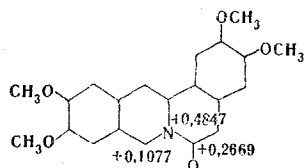
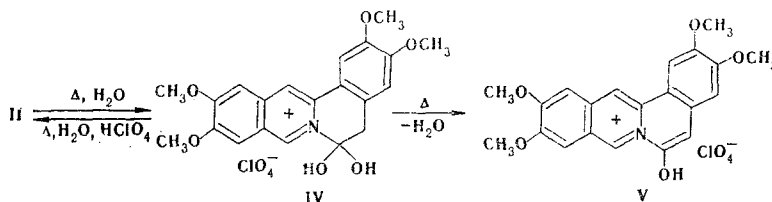


Fig. 1. Absorption spectra [1), 2), and 4) in ethanol; 3) and 5) in acetonitrile]: 1) II; 2) VIIb; 3) V; 4) VI; 5) 2,3,10,11-tetramethoxy-6-acetoxy-8-ethyl-dibenzo[a,g]quinolizinium perchlorate [2] ($c = 3.10 \cdot 10^{-5}$ mole/liter).

ring heteroatom) is found on the C_6 atom of the carbonyl group, while the order of the $C=O$ bond is 0.8995.

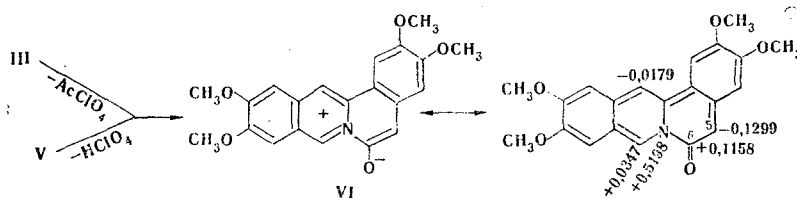


The results of elementary analysis and derivatographic measurements also indicate the presence of crystallization water; this is a property that is extremely characteristic for compounds of the dibenzo[a,g]quinolizinium series [5]. The crystallization water could not be established directly in the mass spectrum of salt II; however, its presence can be confirmed by certain chemical transformations that take place during recording and are recorded in the spectrum, data regarding which will be presented below.



The formation of enol V upon heating is evidently realized due to interaction of the crystallization water with the carbonyl group and the formation of intermediate hydrate IV, which subsequently loses water with splitting out of a proton from the adjacent methylene group. This assumption is confirmed by the formation and isolation of hydrate IV when salt II is heated in water and by its conversion to enol V by heating in an anhydrous medium.

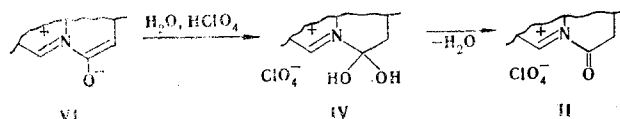
We were unable to accomplish the reversible conversion of enol V to ketone II directly, although this proved to be possible by carrying out a series of successive reactions (see the last scheme). Moreover, enol V, inasmuch as it is a strong acid, ejects a proton under the influence of water even in a markedly dilute aqueous solution of perchloric acid.



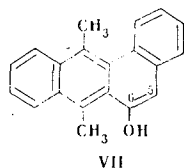
The IR spectrum of the resulting bright-red VI contains a strong band of stretching vibrations at 1653 cm^{-1} , which is related to the absorption of a carbonyl group with a diminished multiple bond (the order of the $C=O$ bond is 0.6638). As compared with the electronic spectrum of enol V, an appreciable bathochromic shift of the long-wave absorption with λ_{max} 550 nm

($\epsilon = 2200$) occurs in the electronic spectrum of VI (see Fig. 1). In the mass spectrum of betaine VI the M^+ peak (365)* has virtually maximum intensity (99.5%), which indicates its high stability with respect to electron impact. The sequence of fragmentation in the mass spectrum of betaine VI is as follows: $M^+ \xrightarrow{-CH_3} (M-CH_3)^+ (350)$; $(M-CH_3)^+ \xrightarrow{-CO} [(M-CH_3)-CO]^+$ (ion A-322); $A^+ \xrightarrow{-CH_3} (A-CH_3)^+ (307)$; $(A-CH_3)^+ \xrightarrow{-CO} [(A-CH_3)-CO]^+ (279)$. Similar fragmentation processes continue further and characterize the presence and amount of methoxy groups in the investigated sample. The direct elimination of a CO particle from the molecular ion (the 337 ion) also constitutes evidence for the presence of a carbonyl grouping with diminished multiplicity of the bond and is characteristic for the fragmentation of compounds of the isoquinolone series [6]. In addition, intense peaks of doubly charged ions with m/z 182.5 (M^{2+}) and 168.5 [$(M-CO)^{2+}$] are recorded in the spectrum. The set of these data confirms the existence of stable betaine structure VI. The same VI is also formed from acetate III but under the influence of stronger bases (Et_3N , NH_4OH).

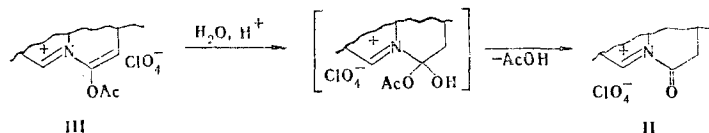
The formation of such mesoionic compounds with a bridged nitrogen atom is characteristic for derivatives of pyridine and its benzo analogs annelated with a five-membered heteroring [7-10]. However, the ability of the resulting betaines to undergo protonation and to produce enol forms has not been noted in these series. Moreover, the five-membered ring was cleaved under the influence of hydrochloric acid [8]. However, when betaine VI was heated in water in the presence of perchloric acid, starting salt II was regenerated. This result can be explained by hydration of the $C_5=C_6$ bond with the subsequent transformations indicated in the scheme



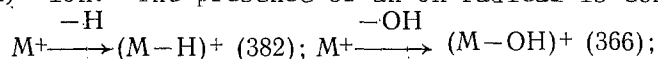
The analogy between the compounds obtained and their carbocyclic analogs such as 6-hydroxybenzanthracene (VII), in which this bond, according to the data from x-ray diffraction analysis, deviates somewhat from the plane and, as a consequence of this, acquires olefinic character [11], makes it possible to disjoin this double bond from the overall conjugation chain.



The assumptions presented above are confirmed by the results obtained in the acidic hydrolysis of acetate III, the product of which is starting quinolizinium salt II. The intermediate formation of brightly colored betaine VI was not observed, i.e., the reaction proceeded via the mechanism of the acidic hydrolysis of vinyl esters [12].

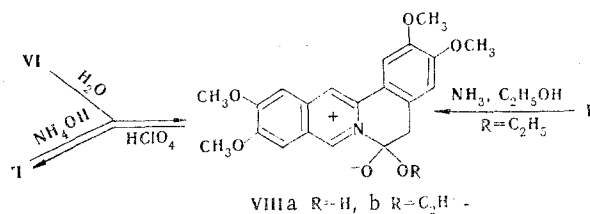


In the absence of acid the hydrolysis of betaine VI leads to the formation of a compound, the PMR spectrum of which recorded in CF_3COOH and its electronic spectrum are virtually identical to the spectra of oxoquinolizinium salt II. However, an M^+ peak (383), the low intensity of which is due to the loss of the aromatic character of the isoquinolonium fragment, is recorded in the mass spectrum. The partial loss of aromatic character is also confirmed by splitting out of ketene from the $(M-OH)^+$ ion. The presence of an OH radical is confirmed by the following fragmentation processes:



*Here and subsequently, the m/z values for the peaks of ions with intensities $>5\%$ are given.

$M^+ \xrightarrow{-H_2O} (M-H_2O)^+$ (365, the B ion). The latter is pseudomolecular, and its subsequent fragmentation therefore proceeds via a scheme similar to that in the fragmentation of VI. Betaine structure VIIIa was assigned to the product thus obtained on the basis of the data enumerated above.



We found that VIIIa is also formed when salt II is treated with ammonium hydroxide. If, however, gaseous ammonia is passed through a suspension of starting 2-benzopyrylium salt I in refluxing ethanol with subsequent refluxing of the solution for 1 h to remove the ammonia, one can isolate VIIIb, which has IR and UV spectral characteristics that are virtually identical to those of betaine VIIIa. However, an M^+ peak (411) is recorded in its mass spectrum. The presence of an ethyl group in the molecule is confirmed by the presence of the following

fragment ions: $M^+ \xrightarrow{-C_2H_5} (M-C_2H_5)^+$ (382); $M^+ \xrightarrow{-OC_2H_5} (M-OC_2H_5)^+$ (366); $M^+ \xrightarrow{-C_2H_5OH} (M-C_2H_5OH)^+$ (365, the B ion). In other respects, the fragmentation of M^+ proceeds via the same scheme as that observed for VIIIa.

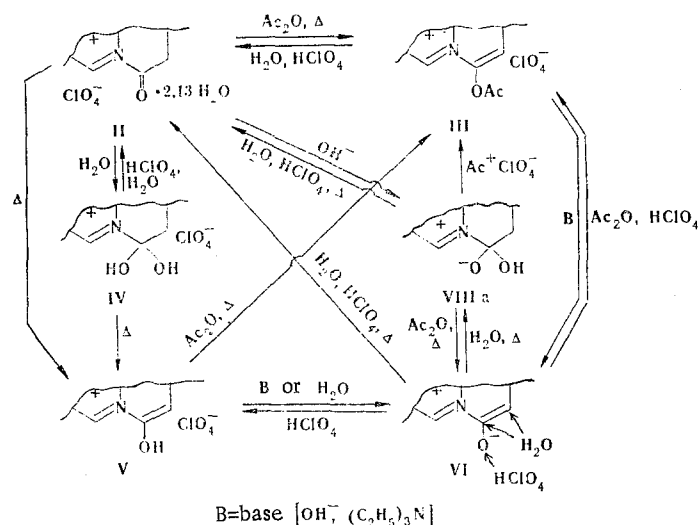
The formation of VIIIa,b takes place by attack by hydroxide and ethoxide anions in alcoholic and aqueous media on the carbon atom of the carbonyl group. The shielding effect of the resulting anion and its inductive effect, which cancels the positive charge on this carbon atom, probably hinder further attack by the nucleophile on the C₈ atom. In this connection, we must mention the studies of Simanek and co-workers [13, 14], who showed that pseudo-protuberberines (of which betaines VIIIa,b are derivatives) that have a methoxy group in the 11 position do not react with solutions of alkalis. This fact is explained by the authors by means of the strong electron-donor effect of the methoxy substituent, which decreases the activity of the 8 position of the heteroring with which it is in conjugation.

When betaines VIIIa,b are heated in acetic acid or acetic anhydride in the presence of 70% HClO₄, they form enol V or its acetate III, whereas starting quinolinizinium salt II is obtained in aqueous perchloric acid.

It is interesting that in obtaining the mass spectrum of quinolinizinium salt II one can record a peak with m/z 383, which is the molecular-ion peak for betaine VIIIa, which is formed after removal of the perchloric acid from hydrate IV — the product of the reaction of the crystallization water, during recording, with the carbonyl group of starting salt II. Nevertheless, the molecular ion of salt II, which should be represented as $(M-HClO_4)^+$ (365), which is characteristic for ionic compounds, is recorded distinctly in the spectrum. The presence of HClO₄ is confirmed by the 100:102 ion (3:1).

Thus it may be asserted that oxoquinolinizinium salt II that is formed initially from 2-benzopyrylium salt I during the reaction undergoes attack by the nucleophile to give betaines VIIIa,b and that the isolation of the desired salt II is possible only after acidification of the mixture with perchloric acid.

In general form, the transformations of unsubstituted 6-oxoquinolinizinium salt II can be represented by a scheme in which only the altered fragments of the molecule are designated:



Certain similar transformations, viz., the formation of acetates (of the III type) and betaines (of the VI and VIII type), are characteristic for 8-alkyl-substituted salts. However, the formation of an enol from the oxo form does not occur; this is possibly explained by the inductive effect of the alkyl groups, which changes the distribution of the charges in the cation, and also by the increased steric hindrance.

In conclusion, it must be emphasized that the transformations enumerated above are characteristic only for the perchlorates of the salts. An attempt to replace the ClO_4^- ion by a more covalent ion such as Cl^- leads to the formation of different products with possibly dimeric character, the structures of which are currently under investigation.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71-IR spectrometer. The PMR spectra of solutions in CF_3COOH were obtained with a Tesla BS-467 spectrometer (60 MHz) at 20°C with hexamethyldisiloxane as the internal standard. The UV spectra of solutions in ethanol and acetonitrile were recorded with a Specord UV-vis spectrophotometer. The mass spectra were obtained with a Varian MAT-311A spectrometer with an accelerating voltage of 3 kV, a cathode emission current of 300 μA , and an ionizing voltage of 70 eV. The derivatogram was obtained with an MOM apparatus (the heating rate was $5^\circ\text{C}/\text{min}$).

2,3,10,11-Tetramethoxy-5,6-dihydro-6-oxodibenzo[a,g]quinolinizinium Perchlorate (II). A) A 15-ml sample of 25% ammonium hydroxide was added to 0.5 g (1 mmole) of 3-(2-methylenecarboxy-3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate (I) [3]. After 3 days, the markedly darkened solution was diluted with 50 ml of water and acidified with excess perchloric acid to give cream-colored crystals (in quantitative yield) that decomposed when an attempt was made to determine their melting point (from acetonitrile). IR spectrum: 3480, 3290, 1680, 1605, 1260, and 1080 cm^{-1} . PMR spectrum: 3.35 (s, CH_3); 3.65, 3.68 (s, two CH_3O); 3.85 (s, two CH_3O); 6.75-7.83 (m, 5H); 8.83 ppm (s, 1H). UV spectrum (ethanol, $c = 2.4 \cdot 10^{-5}$ mole/liter), λ_{max} (ϵ): 243 (41,110) and 268nm (31,250). Found: C 50.2; H 5.0; Cl 7.1; N 2.7%. $\text{C}_{21}\text{H}_{20}\text{ClNO}_9 \cdot 2.13\text{H}_2\text{O}$. Calculated: C 50.0; H 4.8; Cl 7.0; N 2.8%. According to the data from the derivatogram at $133\text{--}180^\circ\text{C}$, the 0.0090-g loss in mass of the 0.1183-g sample corresponds to the removal of 2.13 mole of H_2O per mole of II. The distinct surge on the differential thermogravimetric curve at 156°C indicates an endothermic chemical reaction involving splitting out of water.

B) Ammonia was passed through a refluxing suspension of 0.5 g (1 mmole) of 3-(2-methylenecarboxy-3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate in 5 ml of 96% ethanol for 30 min. The mixture was then cooled and diluted with 20 ml of water, and excess perchloric acid was added. A compound that was completely identical to the compound described in method A was obtained in quantitative yield.

C) A solution of 0.37 g (1 mmole) of 2,3,10,11-tetramethoxy-6-oxodibenzo[a,g]quinolinizinium betaine (VI) in 20 ml of 30% HClO_4 was refluxed for 12-15 h, after which the refluxing mixture was filtered. The filtrate was cooled and worked up to give a substance (20%) that was completely identical to the compound described in method A.

2,3,10,11-Tetramethoxy-6-acetoxydibenzo[a,g]quinolizinium Perchlorate (III). A) A solution of 0.5 g (1 mmole) of perchlorate II in 3 ml of acetic anhydride was refluxed for 30 min, and the precipitate that formed from the refluxing mixture was removed by filtration, washed with ether, and dried to give 0.44 g (80%) of orange-red crystals with mp 290°C (from nitromethane). IR spectrum: 1790, 1613, 1550, and 1080 cm^{-1} . Found: C 54.2; H 4.3; Cl 7.1; N 2.9%. $\text{C}_{23}\text{H}_{22}\text{ClNO}_{10}$. Calculated: C 54.2; H 4.3; Cl 7.0; N 2.8%.

B) A solution of 0.5 g (1 mmole) of 2,3,10,11-tetramethoxy-6-hydroxydibenzo[a,g]quinolizinium perchlorate (V) in 5 ml of acetic anhydride was refluxed for 5 min, after which it was worked up to give a substance (in quantitative yield) that was identical to the compound described in method A.

C) A mixture of 0.37 g (1 mmole) of 2,3,10,11-tetramethoxy-6-oxidodibenzo[a,g]quinolizinium betaine in 3 ml of acetic anhydride and five drops (1.5 mmole) of 70% HClO_4 was heated carefully at 50–60°C for 7–8 min. Workup gave a substance (in quantitative yield) that was identical to the compound described in method A.

2,3,10,11-Tetramethoxy-5,6-dihydro-6,6-dihydroxybenzo[a,g]quinolizinium Perchlorate (IV). A suspension of 0.5 g (1 mmole) of perchlorate II in 5 ml of water was heated at 70°C for 20 min, after which it was cooled, and the colorless precipitate was removed by filtration and dried to give IV, with mp 285°C (dec.), in quantitative yield. IR spectrum: 3600, 1610, 1508, 1260, and 1080 cm^{-1} . Found: C 51.3; H 4.3; Cl 7.6; N 3.0%. $\text{C}_{21}\text{H}_{22}\text{ClNO}_{10}$. Calculated: C 51.2; H 4.1; Cl 7.2; N 2.8%.

2,3,10,11-Tetramethoxy-6-hydroxydibenzo[a,g]quinolizinium Perchlorate (V). A) A solution of 0.5 g of perchlorate II in 5 ml of glacial acetic acid was refluxed for 30 min, after which it was cooled, and the resulting precipitate (some of which also formed from the refluxing solution) was removed by filtration, washed with ether, and dried to give 0.3 g (60%) of dark-yellow crystals with mp 285°C (dec.). IR spectrum: 3130, 1650, 1630, 1565, 1550, 1500, 1210, and 1080 cm^{-1} . UV spectrum (acetonitrile, $c = 1.93 \cdot 10^{-5}$ mole/liter), λ_{max} (ϵ): 298 (46,090) and 434 nm (14,000). Found: C 54.0; H 4.2; Cl 7.9; N 3.1%. $\text{C}_{21}\text{H}_{20}\text{ClNO}_9$. Calculated: C 54.1; H 4.3; Cl 7.6; N 3.0%.

Compound V was also synthesized via the methods listed below.

B) Compound V was obtained by heating suspensions of ketone II in octane, bromobenzene, nitrobenzene, and mineral oil to 115–140°C and also by careful heating of salt II in the crystalline state to 140°C.

C) Perchlorate V was obtained in quantitative yield by refluxing betains VIIa,b in acetic acid with an equimolar amount of 70% HClO_4 for 7–10 min.

D) Compound V was obtained in quantitative yield by refluxing betaine VI in chloroform, acetic acid, or ethanol with an equimolar amount of 70% HClO_4 .

2,3,10,11-Tetramethoxy-6-oxidodibenzo[a,g]quinolizinium Betaine (VI). A) A 15-ml sample of 20% ammonium hydroxide was added with shaking to 0.5 g (1 mmole) of perchlorate III. A bright-red coloration appeared instantaneously, and the III dissolved. After 1–2 min, a bright-red precipitate began to form, and the solution became colorless. After 24 h, the precipitate was removed by filtration and dried to give 0.25 g (69%) of bright-red needles with mp 295°C (from chloroform or acetic anhydride). IR spectrum: 1635, 1565, 1550, and 1430 cm^{-1} . The PMR spectrum recorded in solution in CF_3COOH coincided completely with the spectrum of II. UV spectrum (ethanol, $c = 8.6 \cdot 10^{-5}$ mole/liter), λ_{max} (ϵ): 275 (4994) and 458 nm (5691). Mass spectrum (at a recording temperature of 330°C): 44 (10), 95 (5), 125.5 (7), 132 (5), 138 (8), 145.5 (10), 146 (10), 146.5 (6), 147 (5), 168.5 (10), 182.5 (27), 183 (7), 235 (6), 278 (7), 279 (13), 306.5 (8), 307 (8), 322.5 (43), 323 (9), 337.5 (11), 350.5 (100), 351.5 (23), 352.5 (6), 365 (99). $W_M = 0.94\%$. Found: C 69.2; H 5.0; N 3.8%. $\text{C}_{21}\text{H}_{14}\text{NO}_5$. Calculated: C 69.0; H 5.2; N 3.8%.

Compound VI was also synthesized by the methods listed below.

B) Betaine VI was obtained by treatment of enol V with water or ammonium hydroxide and by treatment of enol V and its acetate III with 5% aqueous sodium carbonate solution or by treatment of suspensions of enol V and acetate III in chloroform with triethylamine.

C) Betaine VI was obtained by refluxing solutions of betaines VIIa,b in acetic anhydride or acetic acid for 7–10 min.

2,3,10,11-Tetramethoxy-5,6-dihydro-6-hydroxy-6-oxidodibenzo[a,g]quinolizinium Betaine (VIIa). A) A 0.21-g (50%) sample of colorless needles with mp 295°C (dec.) was obtained (after filtration and washing of the precipitate with water) by treatment of 0.5 g (1 mmole) of II with 2 ml of 25% ammonium hydroxide, heating of the ammoniacal solution at 80°C for 5 h, and cooling of the reaction mixture. IR spectrum: 3480, 1600, 1510, and 1250 cm^{-1} . Mass spectrum (at a recording temperature of 300°C): 44 (6), 89 (6), 95.5 (9), 102 (6), 102.5 (6), 110 (7), 124.5 (8), 125.5 (11), 131.5 (5), 132 (8), 132.5 (8), 138 (14), 138.5 (13), 139 (7), 139.5 (6), 140 (6), 145.5 (14), 146 (16), 146.5 (15), 147 (13), 147.5 (8), 154 (9), 168.5 (47), 169 (14), 178 (10), 182.5 (30), 183 (8), 190 (7), 191 (9), 207 (8), 208 (8), 220 (11), 221 (7), 234 (6), 235 (13), 236 (12), 237 (7), 234 (6), 235 (13), 236 (12), 237 (7), 238 (6), 248 (10), 249 (9), 250 (11), 252 (8), 253 (18), 263 (9), 264 (13), 265 (7), 277 (11), 278 (20), 279 (28), 280 (20), 281 (11), 293 (17), 294 (14), 296 (7), 306 (20), 307 (16), 308 (15), 309 (6), 322 (91), 323 (28), 324 (98), 325 (25), 337 (18), 338 (100), 339 (100), 340 (50), 350 (100), 351 (36), 352 (10), 365 (100), 366 (44), 367 (16), 383 (1). $W_M = 0.05\%$. Found: C 65.9; H 5.5; N 3.8%. $C_{21}H_{21}NO_6$. Calculated: C 65.8; H 5.5; N 3.7%.

B) A substance that was completely identical to the compound described in experiment A was obtained in quantitative yield by refluxing an aqueous suspension of betaine VI until the solid material became completely colorless (for 30-40 h).

2,3,10,11-Tetramethoxy-5,6-dihydro-6-ethoxy-6-oxidodibenzo[a,g]quinolizinium Betaine (VIIb). Ammonia was passed through a suspension of 0.96 (2 mmole) of perchlorate I [3] in 10 ml of 96% refluxing ethanol for 30 min, after which the cooled dark solution was separated from the precipitated NH_4ClO_4 , heated carefully to the boiling point, and refluxed for 40-50 min. The colorless needles that precipitated from the refluxing solution were removed by filtration after cooling, washed with alcohol, and dried to give 0.73 g (90%) of a substance with mp 295°C (dec.). IR spectrum: 3480, 1600, 1505, and 1260 cm^{-1} . UV spectrum (ethanol, $c = 2.5 \cdot 10^{-5}$ mole/liter), λ_{max} (ϵ): 243 (50,800) and 268 nm (38,640). Mass spectrum (at a recording temperature of 250°C): 31 (100), 45.5 (6), 146.5 (8), 322 (10), 324 (34), 325 (7), 338 (71), 339 (71), 340 (16), 350 (18), 365 (20), 366 (6), 411 (1.7). $W_M = 0.027\%$. Found: C 67.1; H 6.0; N 3.2%. $C_{23}H_{25}NO_6$. Calculated: C 67.2; H 6.1; N 3.4%.

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