STRUCTURE OF THE ANHYDRO BASE OF THE 1-PHENYL-3-ACETYLLEPIDINIUM CATION

B. M. Gutsulyak and P. D. Romanko

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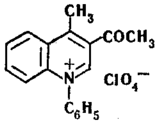
The anhydro base of the 1-phenyl-3-acetyllepidinium cation, which is characterized by increased stability, was isolated, and a structure was proposed for it.

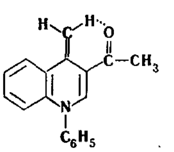
As with other lepidinium salts, the action of aqueous alkali at room temperature on 1-phenyl-3-acetyllepidinium perchlorate (I) [1] gives the almost water-insoluble anhydro base (II). The latter is quantitatively converted to starting salt I by the action of perchloric acid. Both the dry form of the base and an aqueous suspension of it can be preserved for quite a long time at room temperature without any appreciable change, which distinguishes it from analogous bases obtained from leipidinium salts that do not contain a 3-acetyl group.

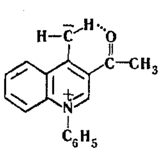

I

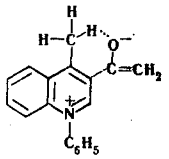
To elucidate the structure of II, we determined its molecular weight by a cryoscopic method and recorded the IR and UV spectra. In contrast to the anhydro bases of lepidinium salts that do not contain a 3-acetyl group, which were isolated as dimers [2], the molecular-weight determination demonstrated that base II is a monomer.

A shift of the $\nu_{C=O}$ band by 67 cm^{-1} (from 1718 to 1651 cm^{-1}) to lower frequencies as compared with $\nu_{C=O}$ of quaternary salt I is observed in the IR spectrum of the anhydro base; this can be explained by the participation of the carbonyl group in an intramolecular hydrogen bond of average strength [3]. The carbonyl group in the 3 position of the quinoline ring can form an intramolecular hydrogen bond with the hydrogen atom of the γ-methylene or methyl group to give a six-membered ring. The latter is apparently the major reason for the increased stability of II.

The structure of anhydro base II can therefore be represented either by a nonpolar 1,4-dihydroquinoline structure with a trivalent nitrogen atom (IIa) or as dipolar ions, which, like quaternary salt I, have a tetravalent positively charged nitrogen atom and a localized negative charge on the γ-methylene group (IIb) or on the oxygen atom of the carbonyl group (IIc).


IIa


IIb


IIc

However, the presence of a very intense band of the stretching vibrations of the carbonyl group ($\nu_{C=O}$) at 1651 cm^{-1} and the absence of an intense band of asymmetrical C−O stretching vibrations [4] in the IR spectrum of II enabled us to assume that structure IIa or IIb is much more likely than IIc.

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TABLE 1. Frequencies (in cm^{-1}) in the IR Spectra of I-III*

I	II	III[5]	Frequency assignment	I	II	III[5]	Fequency assignment
1718 vs			$\nu_{C=O}$	1133 m	1123 sh		Ketone [4]
	1698 w			1092 vs			ClO_4^-
	1651 vs		$\nu_{C=O\cdots H}$		1067 w		
1640 s	1614 vs	1616 sh	$\nu_{C=C}$, $\nu_{C=N}$	1033 m	1029 w	1031 m	β_{CH} 4 H
1616 m	1588 m	1594 s	$\nu_{C=C}$, $\nu_{C=N}$	1009 w	1010 vw	1017 m	Ring?
1573 m	1570 w	1570 s	$\nu_{C=C}$, $\nu_{C=N}$	974 m	979 w	980 w	γ_{CH}
1538 vs	1516 vs	1507 s	$\nu_{C=C}$, $\nu_{C=N}$		965 w		
1510 m	1503 vs			940 m	929 w		
	1388 s			915 m	898 w		γ_{CH} 1 H
1365 sh	1345 sh		$\nu_{C=C}$, $\nu_{C=N}$	858 vw	864 vw		
1328 sh	1320 m		$\nu_{C_{phenyl}-\overset{+}{N}}$	842 vw	846 vw		
1294 m					790 vw		
1259 vs	1251 vs		Aromatic ketone [4]	786 vs	757 s	758 vs	γ_{CH} 4 H
1204 vs				747 s			γ_{CH} 5 H
1183 m	1184 sh		β_{CH} 1 H	698 vs	699 s		γ_{CH} 5 H
1176 m	1170 w		β_{CH} 5 H				
1165 vw							

*Abbreviations: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, and sh is shoulder; 1H is an isolated hydrogen atom attached to an aromatic ring, and 4H and 5H are adjacent hydrogen atoms attached to the aromatic ring in the 4 and 5 positions.

To choose between structures IIa and IIb, we used the fact that the appearance of a positive charge on the nitrogen atom of lepidine is accompanied by a shift of the characteristic bands of the stretching vibrations of the quinoline ring ($\nu_{C=N}$ and $\nu_{C=C}$) to higher frequencies [5]. If therefore, the $\nu_{C=N}$ and $\nu_{C=C}$ frequencies of the anhydro base prove to be close to the frequencies of I, the structure of II can be represented by IIb. If, however, the indicated frequencies of II approach the corresponding frequencies of lepidine (III), nonpolar structure IIa is more likely.

As a consequence of this, the IR spectrum of the anhydro base was compared with the spectra of I and III (see Table 1). As seen from the data in Table 1, the characteristic $\nu_{C=C}$ and $\nu_{C=N}$ frequencies of anhydro base II are close to the values of the corresponding frequencies of lepidine and differ from the frequencies of quaternary salt I. In addition, the intensity of the band at 1614 cm^{-1} is augmented considerably and becomes commensurable with the intensity of the $\nu_{C=O}$ band. Proceeding from the above, the structure of the anhydro base in the ground state can apparently be represented by nonpolar structure IIa.

The UV spectrum of II does not differ substantially from the spectrum of I. In both cases, the spectrum is characterized by three absorption bands. The absorption maxima of two of them in methanol (at 226 and 332 nm) in the spectrum of II are shifted hypsochromically as compared with the maxima of I by 4 and 8 nm, respectively. The maxima of the most intense band in the spectra of I and II are found below 220 nm. The maxima of II in hexane are shifted even more to the short-wave region.

EXPERIMENTAL

1-Phenyl-3-acetyl-4-methylidene-1,4-dihydroquinoline (II). A 1.8-g (5 mmole) sample of 1-phenyl-3-acetyllepidinium perchlorate [1] was dissolved by heating in 250 ml of water. The solution was cooled to room temperature, and a solution of 0.4 g of NaOH in 50 ml of water was added dropwise with vigorous stirring until precipitation ceased. The precipitate was removed by filtration, washed with cold water until it was free of alkali, and dried in a desiccator to give 1.16 g (89%) of product. The product was purified by two reprecipitations from ethanol solution by the addition of water to give a light-yellow powder with mp 80-81° that was quite soluble in hydrocarbons, alcohols, ether, chloroform, and pyridine and only slightly soluble in water. Found: C 82.6; H 5.9; N 5.5%; M (cryoscopically in benzene) 262. $C_{18}H_{15}NO$. Calculated: C 82.7; H 5.8; N 5.4%; M 255. UV spectrum, λ_{max}, nm, (log ε): 266 (4.77), 322 (4.68) (in methanol); 260 (4.69); 311 (4.59) (in hexane).

Conversion of II to I. A 5% solution of $HClO_4$ was added with stirring to 1 g (3.8 mmole) of II until the mixture was slightly acidic, and it was then allowed to stand at room temperature for 1 h. The resulting precipitate was removed by filtration and recrystallized from water to give 1.27 g (92%) of colorless crystals with mp 135-146°. This product did not depress the melting point of a sample of 1-phenyl-3-acetyllepidinium perchlorate [1]. The UV and IR spectra of the two preparations were identical.

The UV spectra of I and II were recorded with an SF-4a spectrophotometer. The IR spectra of mineral-oil suspensions were recorded with an IKS-14 spectrophotometer with NaCl prisms.

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