CYCLIZATION OF p,p'-DISUBSTITUTED DIPHENYLAMINES TO 1-ARYL-3-ACETYLLEPIDINIUM SALTS

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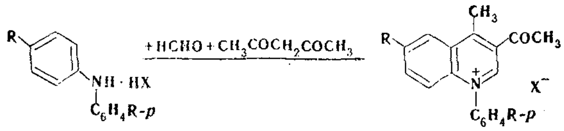
The effect of several substituents in the p,p' positions of diphenylamine on the cyclization of these amines with formaldehyde and acetylacetone in acid media was investigated.

The reaction of diphenylamine with formaldehyde and acetylacetone in perchloric acid was described in communication [1]. It was established that the reaction product is 1-phenyl-3-acetyllepidinium perchlorate (Ia).

In the present paper we present the results of an investigation of the reaction of p,p'-dimethyl-, p,p'-dihydroxy-, p,p'-dimethoxy-, p,p'-dibrom-, and p,p'-dinitrodiphenylamines with formaldehyde and acetylacetone in acid media. The first three amines quite readily undergo the condensation to give high yields of the corresponding 1-aryl-3-acetyllepidinium salts.



IIa R=CH_3, X=ClO_4; IIIa R=OH, X=Cl; IVa R=OCH_3, X=ClO_4

As in the case of diphenylamine [1], the use of nitrobenzene as the oxidizing agent increases the yield of IIa and IVa. As for IIIa, in this case nitrobenzene induces resinification of the reaction mass, and as a result of this, the yield and purity of the product are markedly lowered. In addition, the yield of IIIa in the absence of nitrobenzene is quite high (66%).

An acetyl group in the 3 position of the quinoline ring in IIa-IVa considerably lowers their basicity, as a result of which the compounds undergo partial hydrolysis with an attendant change in color when they are recrystallized from water. The tendency of these compounds to undergo hydrolysis was the reason for the impossibility of obtaining a quaternary salt in pure form from p,p'-dibromodiphenylamine, since it hydrolyzes even in strongly acid solutions during its synthesis.

p,p'-Dinitrodiphenylamine does not react with the indicated carbonyl compounds under the conditions that we investigated and was isolated unchanged from the reaction mass.

In order to ascertain the effect of an acetyl group and other substituents (CH_3, OH, OCH_3) on the spectra of the synthesized IIa-IVa, they were compared with one another, with the spectrum of Ia, and also with the spectra of lepidinium salts without an acetyl group (Ib-IVb).

The UV spectra of all of the acetyl-containing salts Ia-IVa are characterized by three absorption bands, while there are only two bands [2] in the spectra of their analogs without a $COCH_3$ group. The introduction of an acetyl group into the 3 position of the quinoline ring of 1-aryllepidinium salts causes a decrease in the excitation energy of the compounds, which is manifested in a bathochromic shift of the two long-wave absorption maxima. In addition, an intense band, which is not present in the UV spectra of Ib-IVb, appears in the spectra of Ia-IVa at ~210-230 nm.

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TABLE 1. Characteristic Frequencies (cm^{-1}) in the IR Spectra of Lepidinium Salts[a]

Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb	Assignment of the frequencies
1718vs		1731vs		1730 w		1731 m		$\nu_{C=O}$
	1616sh		1622sh		1636 m		1650 sh	
1640 s	1609m	1643m	1611m	1628s	1624 sh	1637m	1642 s	
		1618 sh						
1616m	1585m	1607 sh	1587 m	1607 m	1599sh	1613sh	1605 s	
1573m		1576sh	1576 sh		1585 w	1585 w		$\nu_{C=C}$, $\nu_{C=N}$
1538vs	1525m	1550 s	1533 vs	1530vs	1530 vs	1549m	1550 s	
1510m		1529 s	1518vs			1529vs	1527s	
	1398m							
1365sh	1347sh	1351sh	1361sh	1351sh	1351 sh	1354sh	1339 w	
1328sh	1320m	1325sh	1325 s	1334 w	1308 w	1313w	1313 w	$\nu_{C\,phenyl-N^+}$
1294m	1305 w	1296w	1297 w			1294 w		
	1293sh		1267 m		1283 m		1282 m	
1259vs		1273s		1288 s		1275sh		Aromatic ketone [6]
	1238 w		1241 m					
					1264 m	1266 s	1265 s	
				1248 s	1255 m	1250 s	1250 s	$\nu_{C\,aryl-O}^{as}$
				1229 vs	1222 m	1235 sh	1239sh	
	1200 w		1217w		1208sh			
1204vs		1208s		1192sh		1208m		Aromatic ketone [6]
1183m	—	1204 m	1191m	1183m	1178m	1194 s	1183 m	β_{C-H}[b]
1176m	1162sh							β_{C-H}[c]
1165vw								
	1154sh	1199 m	1173m	1175sh	1163m	1177 m	1170 m	β_{C-H}[d]
1133m		1159m		1130m		1149m		Ketone [6]
					1109m		1110 vs	ν_{C-O}
1092vs	1091s	1091vs	1092vs			1091vs	1091 vs	ClO_4^-
				1075 w	1063 sh			
					1050 w			1-, 2-, 1,4-, and 1,2,4-substituted rings
1033m	1020w	1033 s	1024sh	1039 w	1027vw			
				1015 w	1015 w	1016 s	1024 s	$\nu_{C\,aryl-O}^{s}$
1009 w	1004sh	996sh	1000 w				999 sh	Ring ?
974m	974 w	976 m	974 w	979 w	979sh	982m		γ_{C-H}
		861 sh	959 w	946 w	950 w		959sh	
			948 w					
940m	937w	937 w	933 w	931 w	941 w	935 w	926 w	
			911 w					
915m		907 w	898 w	861sh	865 m	908 sh	864s	γ_{C-H}[b]
858vw								
842vw								
	870w							
	853w							
		843m	846s	849 s	852 m	858 s	850 vs	γ_{C-H}[d]
	828vs	823s	829 vs	836m	841 m	841vs	829vs	γ_{C-H}[d]
	816vw	813 m			827 m	815 m	807 w	
			799 sh		818 m			
786vs	778w							γ_{C-H}[e]
		772 vw	765sh	783 w	786sh	770 w	780vw	
				771vs	776vw		767 w	
747s	773s							γ_{C-H}[c]
		735w	731 w	741 sh	744 w	740 w	739w	
	719w	723 s	715m	724 m	725 m	727 m	729 m	
	706sh		708m	708w				
698vs	695 m							γ_{C-H}[c]

[a] Abbreviations: vs is very strong, s is strong, m is medium, w is weak, vw is very weak, and sh is shoulder. [b] Isolated hydrogen atom in the aromatic ring. [c] In a monosubstituted aromatic ring. [d] Two adjacent hydrogen atoms in an aromatic ring. [e] Four adjacent hydrogen atoms in an aromatic ring.

The IR spectra of Ia-IVa (see Table 1) contain a distinct intense band of the stretching vibrations of the carbonyl group ($\nu_{C=O}$ 1718-1731 cm^{-1}), the intensity of which depends markedly on the character of the ring substituents. Thus its intensity increases when methyl groups are introduced (IIa) and decreases considerably when hydroxyl (IIIa) and methoxy (IVa) groups are present in the molecule. Methyl groups thus display an electron-donor effect, while OH and OCH_3 groups display an electron-acceptor effect [3-5].

By comparing the characteristic frequencies of the IR spectra of the corresponding salts of the a and b groups, one can see that the introduction of an acetyl group into the 3 position of the quinoline ring causes a shift of certain bands of the stretching vibrations of the heteroaromatic rings ($\nu_{C=C}$, $\nu_{C=N}$ 1628-1643, 1607-1616, and 1530-1550 cm^{-1}) and of the planar deformation vibrations (β_{C-H} 1183-1204, 1159-1177, and the band at 1033-1039 cm^{-1}) to higher frequencies.

EXPERIMENTAL

1-(p-Tolyl)-3-acetyl-6-methyllepidinium Perchlorate (IIa). A 10 g (0.05 mole) sample of p,p'-ditolylamine, 50 ml (0.5 mole) of acetylacetone, 50 ml (0.5 mole) of nitrobenzene, and 21 ml (0.1 mole) of 42% perchloric acid were placed in a three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a dropping funnel, and the flask was heated on a boiling-water bath. A solution of 1.5 g (0.05 mole based on formaldehyde) of paraformaldehyde, 50 ml (0.54 mole) of n-butyl alcohol, and two drops of hydrochloric acid (sp. gr. 1.19), which was previously heated until the paraformaldehyde had dissolved completely, was added dropwise with vigorous stirring in the course of 2 h from the dropping funnel. The reaction mass was heated with vigorous stirring for another 8 h. The alcohol, nitrobenzene, and unchanged acetylacetone were removed by steam distillation, and the residual aqueous solution in the flask was decanted from the resinous residue and cooled. The precipitated crystals were recrystallized from acidified (with perchloric acid) water to give 3.9 g (51%) of a product with mp 214°. UV spectrum, λ_{max}, nm (log ε): 220, 247 (4.62), 337 (4.06). Found: Cl 9.1; 9.2; N 3.8; 3.7%. $C_{20}H_{20}ClNO_5$. Calculated: Cl 9.1; N 3.6%.

1-(p-Hydroxyphenyl)-3-acetyl-6-hydroxylepidinium Chloride (IIIa). A mixture of 10 g (0.05 mole) of p,p'-dihydroxydiphenylamine, 50 ml (0.5 mole) of acetylacetone, and 10.2 ml (0.05 mole) of hydrochloric acid (sp. gr. 1.19) was heated with stirring on a boiling-water bath, and an aqueous solution of formaldehyde, which was obtained by heating 1.5 g (0.05 mole) of paraformaldehyde, 50 ml of water, and 0.5 ml (0.016 mole) of hydrochloric acid (sp. gr. 1.19) until the paraformaldehyde dissolved, was added in the course of 1 h from the dropping funnel. The reaction mass was heated for another 7 h with stirring, after which it was steam distilled. The aqueous solution in the flask was decanted from the resinous precipitate and evaporated until crystallization began to give 12.5 g (66%) of a product with mp 194-195° [from butanol–benzene (1:10)]. UV spectrum, λ_{max}, nm (log ε): 230 (4.84), 262 (4.86), 430 (3.95). Found: Cl 10.7; 10.9; N 4.4; 4.3%. $C_{18}H_{16}ClNO_3$. Calculated: Cl 10.7; N 4.2%.

1-(p-Methoxyphenyl)-3-acetyl-6-methoxylepidinium Perchlorate (IVa). This compound was obtained in the same way as IIa using the appropriate amount of p,p'-dimethoxydiphenylamine in place of p,p'-ditolylyamine and heating the reaction mixture for 5 h. The yield of product with mp 205-206° (from water acidified with perchloric acid) was 12.9 g (69%). UV spectrum, λ_{max}, nm (log ε): 229 (4.79), 256 (4.67), 354 (4.15). Found: Cl 8.6; 8.3; N 3.3; 3.4%. $C_{20}H_{20}ClNO_7$. Calculated: Cl 8.4; N 3.3%.

The UV spectra of methanol solutions of the preparations were recorded with an SF-4a spectrophotometer. The IR spectra of mineral oil suspensions were recorded with an IKS-14 spectrophotometer.

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