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ACETYLPYRIDINIUM ANILIDES AND A PYRIDINIUM QUINOLONE ENOL-BETAINE

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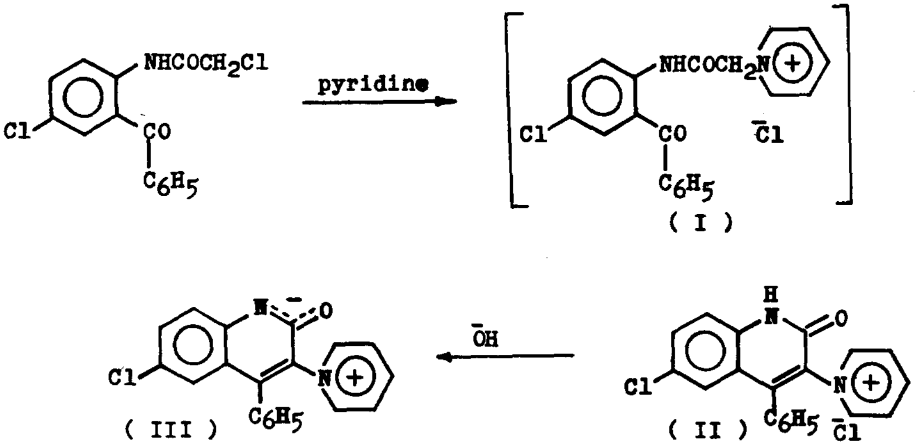
We wish to report the synthesis of 3-pyridinium-6-chloro-4-phenyl-2-quinolone-enol-betaine (III), obtained in the course of our investigation of the acetylpyridinium function as an amino group protector. It was obtained by the action of alkali on the pyridinium chloride (II) which resulted from the interaction of an excess of boiling pyridine and 2-chloroacetamide-5-chloro-benzophenone:



TABLE

Compd.	m.p.	Yield %	Cryst.solvent	Calcd. % C	H	N	Found % C	H	N
II	375°	90	ethanol-benzene	65.1	3.52	7.59	65.3	3.78	7.56
III	307°	92	xylol-methanol	72.1	3.90	8.42	72.1	4.50	8.40

The cyclization proceeds by a Knoevenagel reaction of the phenacyl-pyridinium compound[1,2], and is of the type observed in the reaction between 2-amino-5-chlorobenzophenone and glycyl chloride hydrochloride[3].

The N.M.R. spectrum of III (in $AsCl_3$ solution / TMS) shows three multipletts; a) $\delta = 5.5$ to 6.1, attributed to hydrogens of the pyridinium ring, b) $\delta = 6.2$ to 6.6, of the 4-phenyl group and c) $\delta = 6.8$ to 7.1 of the quinolone ring. The infrared spectrum of II shows a strong carbonyl band at 1660 cm^{-1} and NH hydrogen band at 3000 cm^{-1}; the compound III (betaine) did not show these bands.

The compound II is soluble in water and by adding 20% NaOH the betaine is precipitated immediately; the same test was made with the following compounds similar to I;

a) $C_6H_5NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ * b) $p\text{-}CH_3C_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ (mp 250°)
c) $m\text{-}NO_2C_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ * d) $(C_6H_5)_2NCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ *
e) $p\text{-}NO_2C_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ (mp 280°) f) $m\text{-}CF_3C_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ (mp 215°)
g) $p\text{-}HOC_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ (mp 264°) h) $p\text{-}C_6H_5COC_6H_4NHCOCH_2\overset{+}{N}C_5H_5.\overset{-}{Cl}$ (mp 258°)

Note: the compounds marked * were described by Svetkim[4].

None produced a stable betaine (phenacyl-pyridinium salts produce enol-betaines[1]), but in contrast they afforded quantitatively the corresponding amines in a few minutes. In these products the acetyl-pyridinium group performs as an easily removed amino protector group in 0.1 N NaOH solution which is stable in concentrated or diluted acid solution at room temperature.

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