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2-AZAPHENALONE HYDROCHLORIDE

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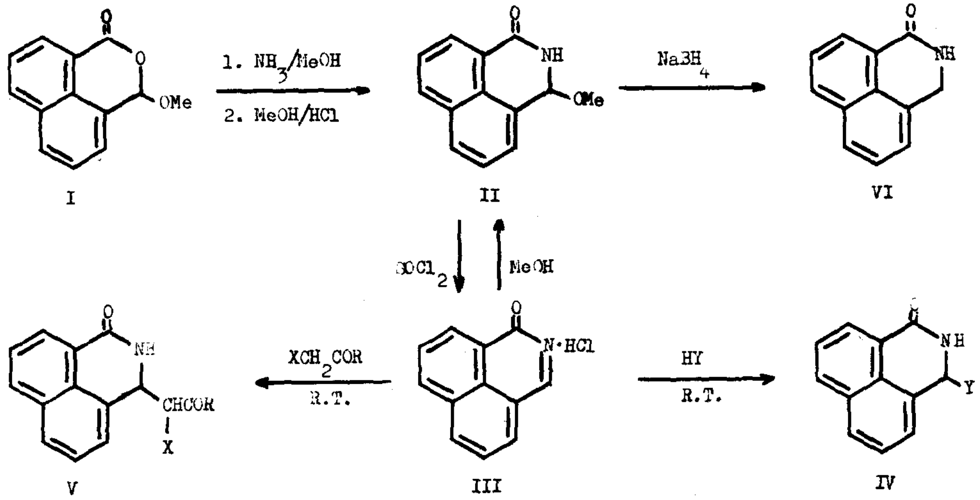
Protonated acylimines were suggested as intermediates in the acid catalyzed amidoalkylations of compounds containing reactive methylene or methine groups(1). We would like to report the synthesis and some of the properties of 2-azaphenalone hydrochloride (III), a protonated cyclic acylimine.

The pseudo methyl ester of 1,8-naphthaldehydic acid (I, 3-methoxynaphthalide) was converted on amidation, followed by treatment with methanolic hydrogen chloride, to 3-methoxy-2-azadihydrophenalone (II). The crystalline product melted at 175°, solidified and melted again with decomposition at 314°. It showed a strong NH band at 3410 cm^{-1} and a carbonyl absorption at 1680 cm^{-1} in the infrared ($CHCl_3$). The N.M.R. spectrum ($CDCl_3$) showed apart from the aromatic absorptions (1.7-2.8 τ), a doublet (1H) at 4.02 τ and a sharp singlet (3H) at 6.98 τ.

Treatment of the methoxyazaphenalone (II) with thionyl chloride, in benzene solution at room temperature, afforded a yellow non-hygroscopic solid (III, m.p. 230°) which did not dissolve in the ordinary organic solvents. The infrared spectrum of the 2-azaphenalone hydrochloride (KBr) showed a broad ammonium band at 2400 cm^{-1}, two bands in the triple bond region at 2120 and 1990 cm^{-1} and a doublet in the carbonyl region at 1710 and 1700 cm^{-1}. The ultra-violet spectrum (conc. sulfuric acid) showed absorptions at 440 mμ (log ε 4.11), 419 mμ (log ε 4.11), 310 mμ (log ε 3.35) and 234 mμ (log ε 4.28). In the N.M.R. (conc. sulfuric acid) apart from the aromatic absorptions (0.8-2.0 τ) only one sharp singlet (1H) appeared at 0.4 τ.



	X	R	M.p. (°C)
a.	CH_3CO	CH_3	297 d
b.	CH_3CO	OC_2H_5	135
c.	C_2H_5OCO	OC_2H_5	167
d.	CN	OC_2H_5	191
e.	H	CH_3	141
f.	H	C_6H_5	176
g.	$(CH_2)_4$		164
h.	$COCH_2C(CH_3)_2CH_2$		255

	Y	M.p. (°C)
a.	OC_2H_5	168
b.	$OCH(CH_3)_2$	164
c.	SC_7H_7	172
d.	NC_5H_{10}	218
e.	$HNCOC_6H_5$	365
f.	$HNCO_2C_7H_7$	224

The 2-azaphenalone hydrochloride showed unusual chemical reactivity towards nucleophiles possessing an active hydrogen e.g. alcohols, amides, and towards compounds having active methylene groups. It reacted at room temperature, within seconds to a few hours, with the various reagents described above to give crystalline products in 75 - 97% yield. During the reaction the insoluble hydrochloride went into solution and in many cases the product precipitated out. With the liquid nucleophiles the reagent itself was used as solvent. Sodium borohydride reduction of the hydrochloride or its precurser, the methanol addition product (II), yielded 2-aza-dihydrophenalone (VI, m.p. 208°) in good yields.

Attempts to obtain the free azaphenalone from the hydrochloride (III) or from the methanol addition product (II) led to an insoluble white solid (m.p. 336° d.). This product is probably a s-triazine which depolymerized in concentrated sulfuric acid to give the same U.V. and N.M.R. spectra as the hydrochloride. The infrared spectrum (KBr) agreed best with a tertiary amide structure, it showed a carbonyl band at 1660 cm^{-1} and did not have any NH absorptions. The open chain acylimines described in the literature do not polymerize readily(2,3,4,5).

Satisfactory elemental analyses, infrared and N.M.R. spectra have been obtained for all the new compounds mentioned above.

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