

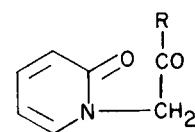
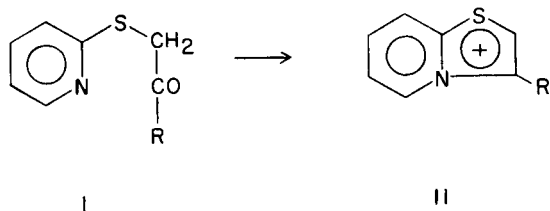
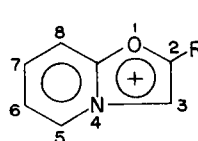
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The Pyrido[2,1-b]oxazolium Cation - A new Aromatic System

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Sir:

Recently (1) the first synthesis of the pyrido[2,1-b]-thiazolium cation (II) was accomplished *via* the cyclization of pyridyl sulfides (I) having a carbonyl function *beta* to the sulfide link. We now wish to report the synthesis of the first derivatives of the analogous pyrido[2,1-b]oxazolium cation (V-VII).

III, R = *p*-BrC₆H₄IV, R = C₆H₅V, R = *p*-BrC₆H₄VI, R = C₆H₅VII, R = CH₃

When 2-methoxypyridine was refluxed in acetone for 48 hours with an excess of *p*-bromophenacyl bromide it afforded a 61% yield of 1-(*p*-bromophenacyl)-2-pyridone (III), m.p. (pure) 168-170°. Concentrated sulfuric acid at room temperature converted III to the 2-(*p*-bromophenyl)pyrido[2,1-b]oxazolium cation, isolated as the perchlorate, m.p. 260-264° (pure), yield 78%, λ max (log ϵ) 265 (4.20), 282.5 sh (4.15), 294 sh (4.14), and 305 sh m μ (4.10). The nuclear magnetic resonance spectrum (trifluoroacetic acid) showed no protons at $>2.14 \tau$.

In the same way phenacyl bromide with 2-methoxypyridine gave 1-phenacyl-2-pyridone (IV) in 54% yield, m.p. 156-158° (2), which was cyclized in 72% yield to afford 2-phenylpyrido[2,1-b]oxazolium perchlorate, m.p. 218-222.5°, λ max (log ϵ) 237.5 (3.97), 285 sh (4.18), and 297 m μ (4.21).

The pyridone formed by reaction of bromoacetone with 2-methoxypyridine could not be obtained in a crystalline condition and was cyclized directly, yielding 2-methylpyrido[2,1-b]oxazolium perchlorate, m.p. 131-132°, in an overall yield of 19%, λ max (log ϵ) 262 (4.08), 270 sh (4.04), and 277 sh m μ (3.91). The spectrum was not altered immediately when measured in 0.001 M NaOH solution, but after the solution had stood for several hours the peak at 262 m μ disappeared and a new one was observed at 305 m μ . The nuclear magnetic resonance spectrum showed a singlet at 7.32 τ assigned to the methyl protons, but no other protons appeared at $>2.2 \tau$. All of the above compounds had the expected composition.

Acknowledgment.

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REFERENCES

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