

PREPARATION AND NOVEL REARRANGEMENTS OF *N*-ARYLOXYPYRIDINIUM SALTS.

A [3,5] SHIFT LEADING TO PYRIDO[2,3-*b*]BENZOFURANS

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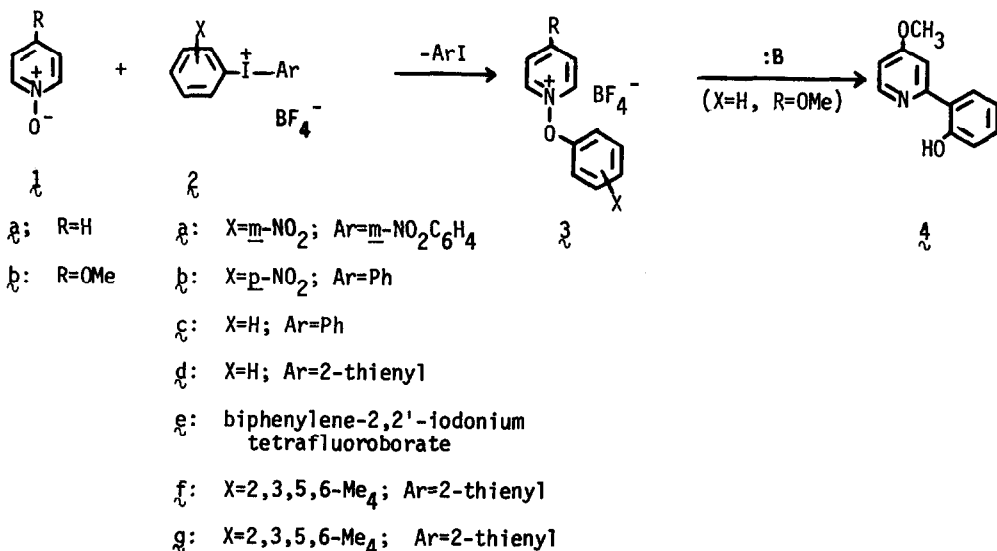
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The preparation of *N*-aryloxy pyridinium tetrafluoroborates (useful in the synthesis of 2-*o*-hydroxyarylpyridines^{1a} and for the generation of aryloxonium ions^{1b,c}) from pyridine 1-oxides and aryldiazonium tetrafluoroborates bearing an electron-withdrawing substituent in the aryl ring has been described.^{1a} 2-Aryloxy pyridine 1-oxides rearrange to give *N*-aryloxy-2-pyridones.² In view of limitations of these syntheses an alternate method of achieving *O*-arylation of pyridine 1-oxides is now described together with some novel and useful transformations of the salts.

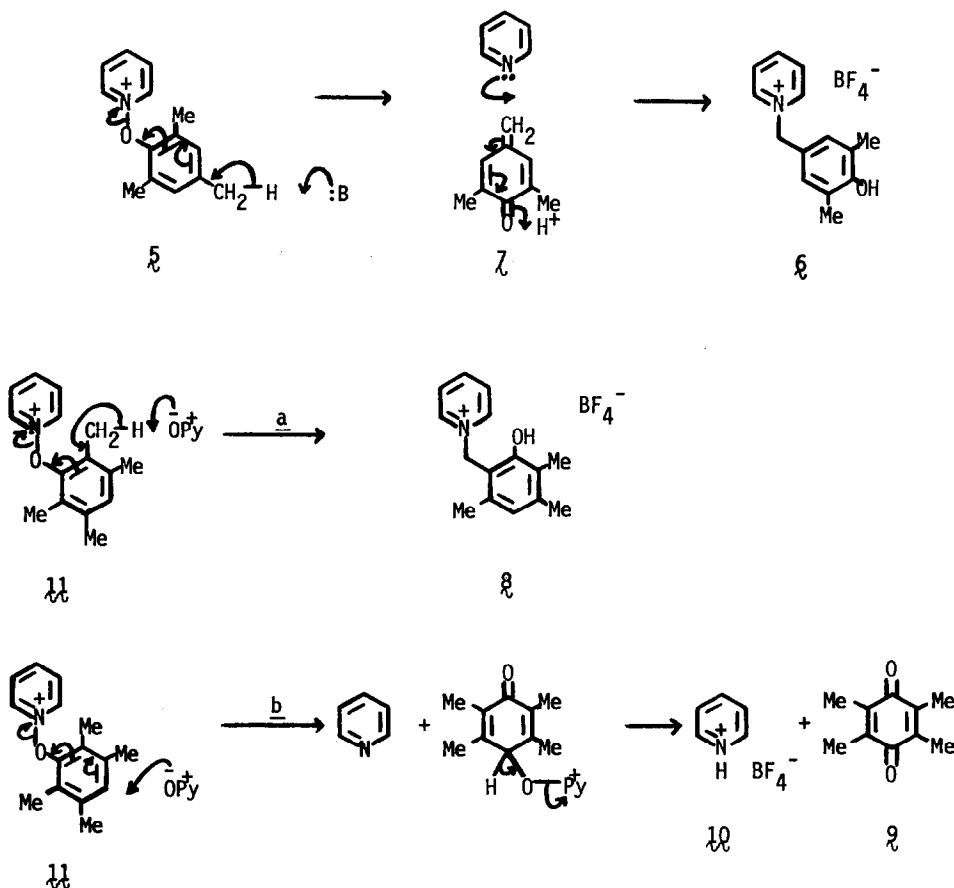
Treatment of λ^a with pyridine 1-oxide (λ^b) in boiling acetonitrile for 1 hr gave *N*-(3-nitrophenoxy)pyridinium tetrafluoroborate (λ^c ; X=*m*-NO₂, R=H) in high yield.³ Similarly, λ^a and λ^b afforded λ^d (X=*p*-NO₂, R=H), in accordance with the known preferential attack of the nucleophile on the more electron-poor aryl ring of the iodonium salt.^{5b}

While the parent λ^e (X=R=H) could not be isolated from λ^a and λ^c , the more nucleophilic λ^b did give λ^f (X=H, R=OMe), mp 122-122.5°, either with λ^c or with λ^d .⁶ Compound λ^f (X=H, R=OMe) is the first known example of an *O*-phenylpyridinium salt. It underwent base-catalyzed rearrangement^{1a} to give 2-*o*-hydroxyphenyl-4-methoxy pyridine (4), mp 70-71°.⁷ An electron-



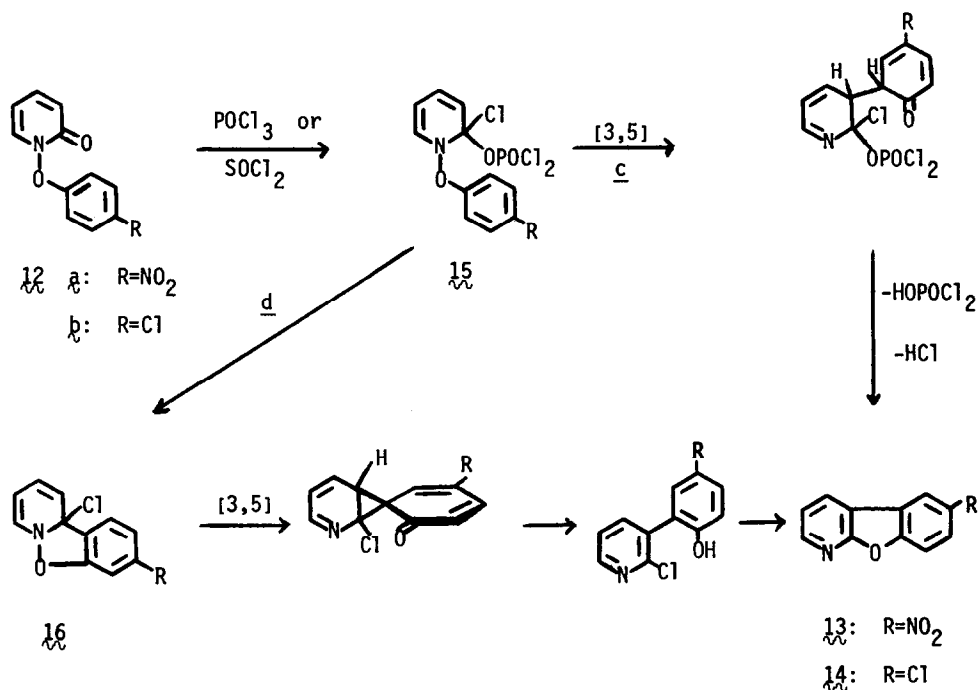
withdrawing substituent in the σ -aryl ring is, therefore, not a prerequisite for the success of this rearrangement. Biphenylene-2,2'-iodonium tetrafluoroborate (λ_e) and λ_b gave λ_c ($X=\sigma\text{-IC}_6\text{H}_4$; $R=\text{OMe}$), mp 128-129°.

The mesityl-2-thienyliodonium cation has been reported to undergo S_N1 -type cleavage⁸ and was, therefore, expected to arylate the less basic λ_a . Indeed, λ_a and λ_c in DMF (100°, 6 hr) gave λ_d -N-(3,5-dimethyl-4-hydroxybenzyl)pyridinium tetrafluoroborate (λ_e) (82.7%),⁷ mp 160-161.5°, probably from the expected λ_f by N-O bond cleavage and (cage?) recombination to form an N-C bond.⁹ A concerted 1,6-shift of the pyridinium ion from O \rightarrow C in an intermediate zwitterion is also conceivable. Similarly, λ_a and λ_g gave λ_h (31%),⁷ mp 131-132°, tetramethylbenzoquinone (λ_i) (40%), and pyridinium tetrafluoroborate (λ_j) (44.2%), all of which can arise from the presumed intermediate λ_k .



In an attempt to prepare 2-chloro-N-p-nitrophenoxypyridinium tetrafluoroborate (needed in ref. 1c) \underline{N} -p-nitrophenoxy-2-pyridone (12a)² was heated with either POCl_3 or with thionyl chloride.

The product obtained instead was 6-nitropyrido[2,3-*b*]benzofuran (13) (70%), mp 276-278°, identical with an authentic sample.¹⁰ Compound 12b^{7,11} similarly gave 14 (42%), mp 150-151°. Two plausible mechanisms (paths c and d) which would account for the formation of 13 and 14 involve a [3,5] shift in a 1,2-dihydropyridine 1-oxide intermediate 15 or 16. Path c (a direct 3,5-shift in a 1,2-dihydro-1-aryloxyppyridine) is the simpler of the two but appears to have no precedent.¹³ Path d (electrophilic aromatic substitution) leads to a 1,2-dihydropyridine 1-oxide derivative (16) of a type which is known¹⁵ to undergo a [3,5]-shift. Aromatization¹⁵ and loss of HCl would then lead to 13 and 14. The driving force would presumably be the large gain in stability on going from a 1,2-dihydropyridine 1-oxide to a 2,3-dihydro derivative.¹⁶



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References and Notes

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- The reaction between pyridine 1-oxide and diphenyliodonium bromide did not yield N-

phenoxypyridinium bromide.⁴ This may be due to interaction between the diaryliodonium cation and nucleophilic counteranions such as bromide.^{5a} For this reason, a non-nucleophilic counteranion, tetrafluoroborate, was used here.

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