

ARYLOXENIUM IONS FROM *N*-ARYLOXYPYRIDINIUM SALTS AND ARYLOXYAMINE DERIVATIVES

Rudolph A. Abramovitch,\* Gerard Alvernhe, and Muthiah N. Inbasekaran

*Department of Chemistry, University of Alabama, University, AL. 35486*

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The thermolysis of *N*-aryloxyppyridinium salts ( $\text{X}$ ; including substituents other than  $\text{NO}_2$ ) in aromatic solvents has given a variety of substitution products in which new C-O and C-C bonds were formed.<sup>1</sup> Two possible mechanisms were retained:<sup>1</sup> (i) heterolytic N-O cleavage of  $\text{X}$  to give pyridine and an aryloxenium ion ( $\text{ArO}^+$ ),<sup>2</sup> the latter then attacking the aromatic solvent; (ii) a concerted nucleophilic attack by solvent upon the developing positive charge simultaneous with the departure of the pyridine, so that a free aryloxenium ion is not formed. Though the first mechanism was favored it was not possible at that time to rule out the concerted process. Two probes are now used which support the intermediacy of free aryloxenium ions in these reactions.

The effect of substituents in the pyridine ring of an *N*-*p*-nitrophenoxypyridinium tetrafluoroborate upon the isomer ratios in the substitution of anisole under otherwise identical conditions was studied quantitatively. In a stepwise process, once singlet  $\text{p-NO}_2\text{C}_6\text{H}_4\text{O}^+$  is formed, the ratio of products formed by its attack on anisole will be independent of the nature of the substituent in the pyridine ring provided formation of the  $\sigma$ -complex is the rate-determining step in the substitution process and there is no selective removal of individual  $\sigma$ -complexes or products. In a concerted process the substituent will influence the electrophilicity of the oxygen or the ortho carbon atoms resulting in a probable change in the isomer ratios of substitution products.

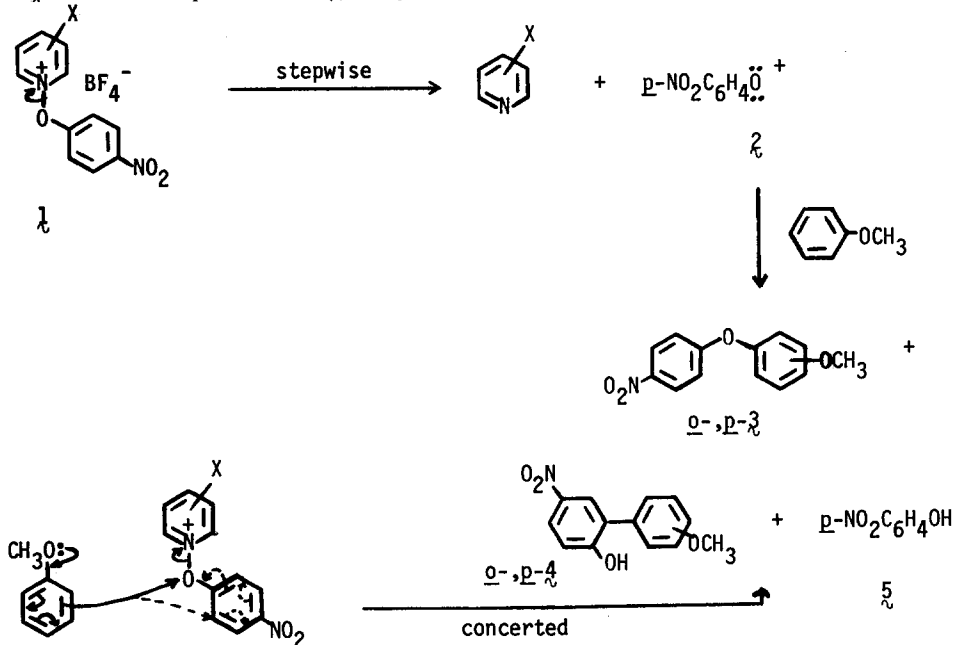
Table I Yields and Isomer Ratios of Products in the Thermolysis of  $\text{X}$ <sup>4</sup> in Anisole.<sup>a</sup>

$\text{X}$	% <sub>3</sub> <sup>b</sup>	<i>o</i> -/ <i>p</i> - <sub>3</sub> <sup>c</sup>	% <sub>4</sub> <sup>b</sup>	<i>o</i> -/ <i>p</i> - <sub>4</sub> <sup>c</sup>	% <sub>5</sub>
H	43.4	29:71 <sup>e</sup>	9.2	74:26	26.7
4-Me	42.5	28:72	8.5	77:23	27.2
4-OMe	43.0	30:70	8.0	76:24	26.0
4-Ph	44.7	26:74	9.3	75:25	25.4
4-Cl	57.4	37:63	10.5	77:23	5.0
3-CO <sub>2</sub> Me	53.2	28:72	10.9	76:24	3.6
2-OH <sup>d</sup>	5.1	29:71	-	-	17.8

<sup>a</sup>Degassed. Reaction conditions: 5 hr at 180° under dry N<sub>2</sub>. <sup>b</sup>Isolated yields. <sup>c</sup>Determined by gas chromatography. <sup>d</sup>Thermolysis at 154° for 5 hr. The starting material was prepared from

1-(*p*-nitrophenoxy)-2(1*H*)-pyridone and one equivalent of trifluoromethanesulfonic acid.

<sup>e</sup>Compound  $\sigma$ - $\mathfrak{z}$  is thermally unstable (see text).

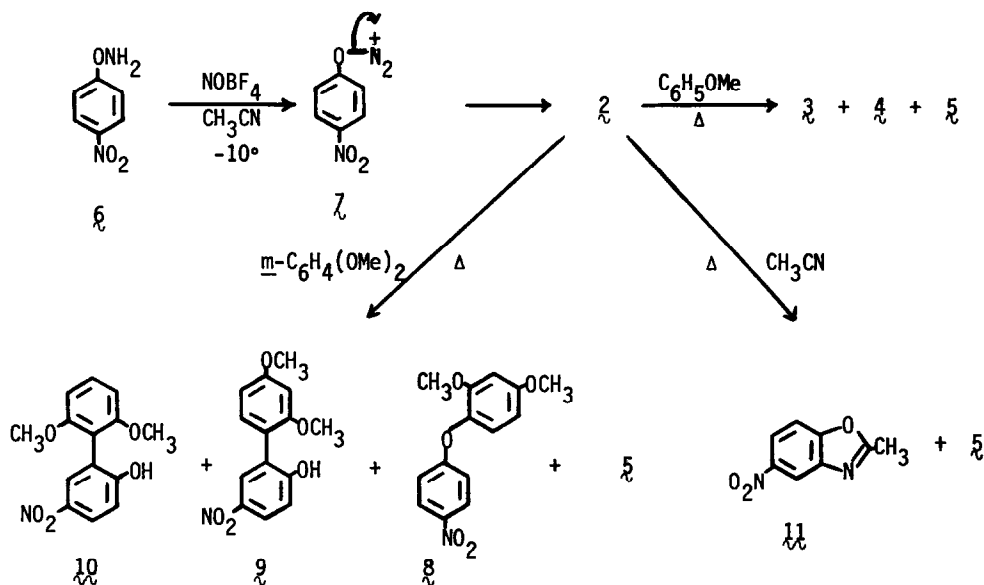


The results are summarized in Table I. The ortho-para ratio in  $\mathfrak{z}$  remains constant at 28:72 ( $\pm 2$ ) for all substituents except  $X = 4\text{-Cl}$ . In the latter case we suspect that selective removal of one of the  $\sigma$ -complexes may be occurring, perhaps by reaction with a nucleophile. The ortho-para ratio of hydroxybiphenyls ( $\mathfrak{4}$ )<sup>5</sup> is constant at 75:25 within experimental error in all cases, except that when  $X = 2\text{-OH}$  the yield of  $\mathfrak{4}$  is too low to be determined. In this case, the yield of the major product  $\mathfrak{z}$  (C-O-C bond formation) is also considerably lower than usual. These results support the stepwise mechanism above. The *p*-nitrophenol may arise either from the triplet oxenium ion or from some competing homolytic N-O bond fission.<sup>1</sup>

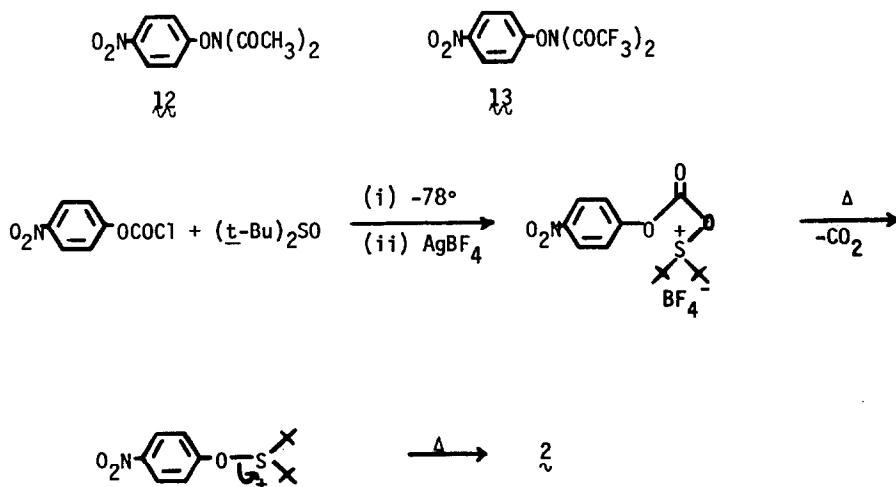
The same aryloxenium ion was generated from a different source than  $\mathfrak{1}$ . If a common intermediate is formed from both sources (thus ruling out the concerted process) product ratios should be the same. *p*-Nitrophenoxamine ( $\mathfrak{6}$ )<sup>6</sup> was diazotized with  $\text{NO}^+\text{BF}_4^-$  in MeCN,<sup>7</sup> anisole was added in excess and the solution heated at 140° to give  $\mathfrak{z}$  (46%),  $\mathfrak{4}$  (18%), and  $\mathfrak{5}$  (23%). Initial concern that the ortho-para ratio in  $\mathfrak{z}$  so obtained (39.5 : 60.5) was higher than that from  $\mathfrak{1}$  was dispelled when it was found that the *ortho*- $\mathfrak{z}$  was thermally unstable and decomposed to uncharacterized tars on heating in anisole, while *para*- $\mathfrak{z}$  was thermally stable. Thus, when *o*- $\mathfrak{z}$  was heated at 230° in anisole only 18% was recovered after 5 hr, whereas *p*- $\mathfrak{z}$  was recovered almost quantitatively. The *o*-hydroxybiphenyls are stable under these conditions and the ortho-para ratio in  $\mathfrak{4}$  formed from  $\mathfrak{6}$  (78.6 : 21.4) is close to that obtained from  $\mathfrak{1}$ . Indeed, thermolysis of  $\mathfrak{1}$  ( $X = \text{H}$ ) in anisole at 160° gave  $\mathfrak{z}$  (22%) (*o/p* = 45.5:54.5),  $\mathfrak{4}$  (6%) (*o/p* = 72:28) and  $\mathfrak{5}$  (27%), whereas at 230° it gave *p*- $\mathfrak{z}$  (27%) (no *o*-isomer),  $\mathfrak{4}$  (14%) (*o/p* = 78:22), and  $\mathfrak{5}$  (22%). The

ortho-para ratio of isomers  $\lambda$  appears, therefore, to be a reasonably good indicator of the intermediacy of free *p*-nitrophenoxenium ions in these reactions.

Compound  $\lambda$  reacted with *m*-dimethoxybenzene (as did also  $\mu$ ) to give  $\delta$  (52%) (only isomer),  $\eta$  (5%),  $\theta$  (traces), and  $\xi$  (29%), and with acetonitrile to give  $\nu$  (32%) and  $\zeta$  (35%). On heating with *sym*-trimethoxybenzene at 140°,  $\lambda$  gave 4'-nitro-2,4,6-trimethoxydiphenyl ether (51%) and  $\xi$  (18%).



Preliminary results indicate that *N,N*-diacetyl-*p*-nitrophenoxamine ( $\mu$ ) and *N,N*-difluoroacetyl-*p*-nitrophenoxamine ( $\nu$ ) may also serve as a source of *p*-nitrophenoxenium ion when heated in the presence of one equivalent of trifluoroacetic acid. When *p*-nitrophenylchloroformate in ether is treated with di-*t*-butyl sulfoxide at 78°, silver tetrafluoroborate added at that temperature and then anisole, and the suspension is heated under reflux  $\lambda$  (13%)



(*o/p* = 31:69), **4** (2.4%) (*o/p* = 72:28), and **5** (25%) are obtained. With *m*-dimethoxybenzene **8** (16%), **9** (4.5%), and **5** (17%) are formed. Again, *p*-nitrophenoxenium ion (**2**) appears to be the intermediate.

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#### References and Notes

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2. Aryloxenium ions, isoelectronic with carbenes, have been implicated as intermediates in some phenolic oxidative coupling reactions.<sup>3</sup>
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4. R. A. Abramovitch, M. Inbasekaran, S. Kato, and G. M. Singer, *J. Org. Chem.*, **41**, 1717(1976), and preceding communication.
5. The *para* isomer of **4** was not reported earlier.<sup>1</sup> It has now been detected, resolved, analyzed and compared with an authentic sample prepared by heating *p*-bromoanisole with 2-bromo-4-nitrophenyl acetate with copper powder at 180° for 24 hr, followed by hydrolysis. All new compounds gave the expected analytical and spectral data.
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7. At -10° a band corresponding to that of a diazonium ion was observed at 2260 cm<sup>-1</sup> in acetonitrile solution.