

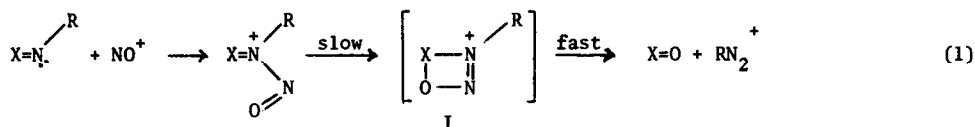
NITROSATIVE CLEAVAGE OF BENZALAZINE AND RELATED ALDEHYDE AZINES.  
 PRODUCTION, DECOMPOSITION AND TRAPPING  
 OF IMINODIAZONIUM IONS<sup>1</sup>

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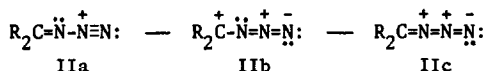
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Nitrosonium halides and stable nitrosonium salts effect cleavage of the C=N bond in imines,<sup>3</sup> isocyanates, thioisocyanates, and sulfinylamines.<sup>4</sup> These reactions are thought to proceed with rate limiting formation of an N-substituted oxadiazetene compound (I) to the observed carbonyl and diazonium ion products (eq 1, x = R<sub>2</sub>C, O=C, S=C, O=S).<sup>3</sup> We have been interested in testing the generality of C=N bond cleavage by nitrosonium salts and in determining the general utility

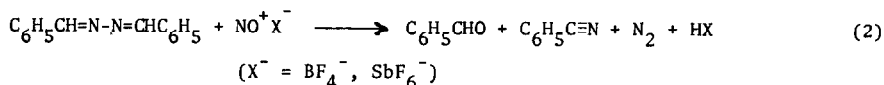


of this reaction. In this regard we have examined the reactions of azines with stable nitrosonium salts. Unlike imines and related compounds which produce aryldiazonium ion salts or alkyl cations (eq 1), azines would be expected to react with nitrosonium salts to form iminodiazonium ion intermediates (II).<sup>5</sup> We wish to report the production, decomposition and trapping of iminodiazonium



ions formed from aldehyde azines.

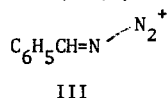
When benzalazine is added to an equivalent amount of NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> in anhydrous acetonitrile or nitromethane at room temperature, immediate gas evolution is observed and both benzaldehyde and benzonitrile can be detected by pmr and ir spectroscopy as well as by glpc analysis. Nitrogen is the sole gaseous product. The amount of benzaldehyde produced under these anhydrous conditions is equal within experimental error to the amount of benzonitrile; and the yield of nitrogen is the same as that of the aldehyde or nitrile (eq 2). However, only one-half of the initial benzalazine



reacts with the nitrosonium salt to produce the observed products. The same results, a 50% yield of benzaldehyde, benzonitrile, and nitrogen from benzalazine, are observed when 0.5, 1.0, 1.5 and 2.0 equiv. of  $\text{NO}^+\text{BF}_4^-$  are used. Only when less than 0.5 equiv. is added to benzalazine does the yield of products fall below 50%. Protonated benzalazine, which accounts for the unreacted azine, is formed from benzalazine and the acid generated in eq 2<sup>6</sup> and is resistant to subsequent attack by the nitrosonium ion. Neither the reverse addition of  $\text{NO}^+\text{BF}_4^-$  to the azine nor heating the reaction solution at 65° for over two hours changes the products or yields of products. Identical results are obtained when  $\text{NO}^+\text{SbF}_6^-$  is used.

*p*-Anisalazine yields equal amounts of *p*-anisaldehyde and *p*-anisonitrile when treated with nitrosonium salts. However hydrogen abstraction at the methoxy group by the nitrosonium ion<sup>7</sup> competes with nitrosative cleavage and lowers the yield of aldehyde and nitrile from 50% to 30%. In a separate control experiment using the same reaction conditions, a similar limited loss of *p*-anisaldehyde was observed when that compound was treated with  $\text{NO}^+\text{BF}_4^-$ . Salicylaldazine gave less than 5% aldehyde and nitrile when treated with nitrosonium salts.

Taken together these results suggest a mechanism for the nitrosative cleavage of aldehyde azines consistent with the intermediacy of an iminodiazonium ion. Loss of nitrogen and elimination of a proton from the benzaliminodiazonium ion (III) yields the corresponding nitrile. The formation

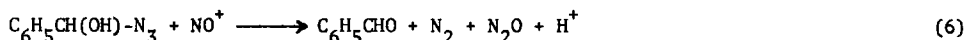
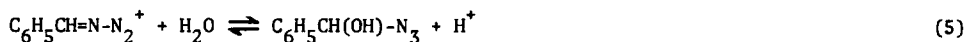
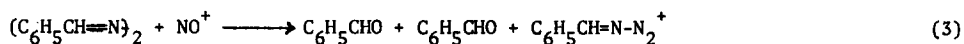


of nitriles in the Schmidt reaction of aldehydes with hydrazoic acid<sup>8</sup> can be similarly explained as resulting from the elimination of nitrogen and a proton from an iminodiazonium ion.

In the only previous report of the reaction of nitrosonium compounds with azines, Franzen and Zimmerman found that benzal chloride, benzaldehyde, nitrogen, and nitrous oxide were produced from benzalazine and nitrosyl chloride under anhydrous conditions.<sup>9</sup> Although no yields were given, these early results suggest that the iminodiazonium ion may be trapped by suitable nucleophiles to form  $\alpha$ -substituted alkyl azides. Production of  $\alpha$ -chlorobenzyl azide followed by reaction of the azide with nitrosyl chloride would explain the observed results. We have previously reported that alkyl azides react with nitrosonium salts to give alkyl cations, nitrogen and nitrous oxide.<sup>10</sup>

Treatment of benzalazine (5.0 mmol) with  $\text{NO}^+\text{BF}_4^-$  (5.4 mmol) in acetonitrile containing water

(1.5 mmol) gave benzaldehyde (2.9 mmol), protonated benzalazine (3.4 mmol), benzonitrile (0.2 mmol) and 3.4 mmol of gaseous products consisting of both nitrogen and nitrous oxide. Benzonitrile was not produced in reactions in which more than 0.33 equiv. of water (based on azine) was used; however, the yields of benzaldehyde (3.4-4.0 mmol), protonated azine (3.2-2.9 mmol), and gaseous products (3.6-3.9 mmol) did not change greatly in experiments using 5.0 mmol of benzalazine and 1.8, 2.7 and 5.0 mmol of water. When  $\text{NO}^+\text{BF}_4^-$  was replaced in a separate experiments by equivalent amounts of  $\text{HBF}_4$ , less than 5% of the benzalazine hydrolyzed to benzaldehyde during reaction times twice as long as those used for the nitrosation reaction. These results are consistent with a mechanism involving formation of benzaldehyde and III (eq 3-6). Water reacts with III to form an  $\alpha$ -hydroxyazide (eq 5) which eliminates hydrazoic acid, subsequently reacting with the nitrosonium



ion to form nitrogen and nitrous oxide,<sup>11</sup> or reacts directly with the nitrosonium ion to form the same reaction products (eq 6).<sup>10</sup> Since 2 equiv. of protons are produced for each equiv. of reacted water (eq 5 and 6), and since protonated benzalazine is resistant to nitrosation, two-thirds of the benzalazine will not be nitrosated when more than one-third equiv. of water is used. With less than one-third equiv. of water, benzonitrile (eq 4) is also formed.

Benzyl azide was produced when triethylsilane (5-fold molar excess) was added to the reaction mixture of benzalazine and  $\text{NO}^+\text{BF}_4^-$  in acetonitrile after gas evolution had commenced (1-2 min). The identity of this product, formed by hydride transfer to III, was confirmed by glpc retention times and peak enhancement and by ir and pmr spectral analysis. The maximum yield of benzyl azide (8%) was obtained when the nitrosation and quenching reactions were run at  $-22^\circ$ . Lower yields of benzyl azide (2-6%) were observed when the nitrosation reaction occurred at  $-15^\circ$  or  $-35^\circ$  or when triethylsilane was added more than three minutes after gas evolution had commenced. Triethylsilane rapidly reacted with  $\text{NO}^+\text{BF}_4^-$  to give nitric oxide and a small amount of nitrous oxide. Under the reaction conditions employed, benzaldehyde was reduced to benzyl alcohol and dibenzyl ether. Benzonitrile and benzalazine were unaffected by triethylsilane under these conditions.

Since reduction is in competition with both nitrosative cleavage of the azine and elimination of nitrogen and a proton from the iminodiazonium ion, the production of benzyl azide by silane reduction supports the intermediacy of a relatively stable iminodiazonium ion. Other attempts to

trap III as an  $\alpha$ -substituted azide, including the addition of methanol, tetrapropylammonium chloride and tetrapropylammonium iodide, were unsuccessful.

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#### REFERENCES AND NOTES

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