

## Reaction of Nitrosonium (NO<sup>+</sup>) with Schiff Bases

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**Abstract:** The reaction of nitrosonium (NO<sup>+</sup>) with Schiff bases produced diazonium salts and aldehydes in good yield. The reaction is assumed to be an electrophilic reaction of nitrosonium with imines *via* a four-member ring intermediate.

**Keywords:** Nitrosonium, Schiff bases, electrophilic.

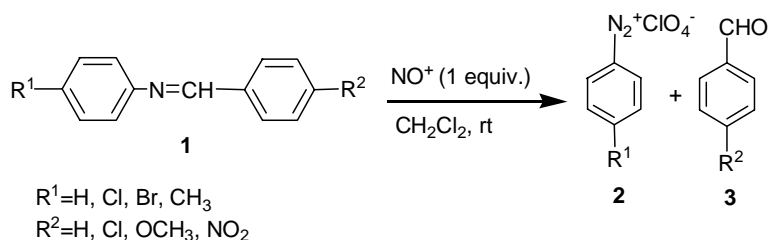
Nitrosonium (NO<sup>+</sup>) is a superior electron transfer (ET) agent with a rather high reduction potential of  $E_{\text{red}}^0 = 1.50 \text{ V vs. SCE}^1$ . It was also found that NO<sup>+</sup> could attack hetero-atoms such as nitrogen<sup>2</sup>, iodine<sup>3</sup>, sulfur<sup>4</sup>, *etc.* as an electrophile. It even reacted with a carbon-carbon double bond initiated by a NO<sup>+</sup> electrophilic addition to the double bond of the partner molecule<sup>5</sup>. These facts imply that NO<sup>+</sup> acts as either an oxidant or an electrophile. In addition, the oxidative cleavage of oximes and dimethylhydrazones<sup>6</sup> by NO<sup>+</sup> led to obtain carbonyl compounds. The electrophilic addition of NOCl<sup>7</sup> to imines and NO<sup>+</sup> to imines<sup>8</sup> in the presence of the carboxylate anion were reported too. Furthermore, Joseph<sup>9</sup> reported that the reaction of nitric oxide (NO), a redox partner NO<sup>+</sup>, with the imine double bond of some Schiff bases *via* an electrophilic addition of NO to the nitrogen atom of a carbon-nitrogen double bond. In the present work, we tried to perform the reaction of NO<sup>+</sup> with a number of Schiff bases, instead of NO. The main aim is to learn that NO<sup>+</sup> acts in these reactions, as an oxidant or an electrophile.

In a representative experiment, the powder of NO<sup>+</sup> perchlorate (0.5 mmole) and 2 mL dry dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) were placed in a flask. 10 mL of dry CH<sub>2</sub>Cl<sub>2</sub> solution of N-*p*-nitrobenzylidene-*p*-chloroaniline (**1a**, 0.5 mmole) was added slowly to the flask under stirring at room temperature for a duration of about 1 hour. Off-white precipitate formed and the solution turned orange. The precipitate was then filtrated and recrystallized from acetone and petroleum ether. The petroleum ether was added dropwise, giving purple needle crystals. The product was identified to be diazonium perchlorate<sup>10</sup> **2a** in 94% yield. Benzaldehyde<sup>10</sup> **3a** was obtained by column chromatography on silica-gel from the mother liquid in 77% yield. The reaction of a number of N-*p*-substituted benzylidene-*p*-substituted anilines with NO<sup>+</sup>ClO<sub>4</sub><sup>-</sup> was conducted by the same way. It is outlined in **Scheme 1** and the results are collected in

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Scheme 1



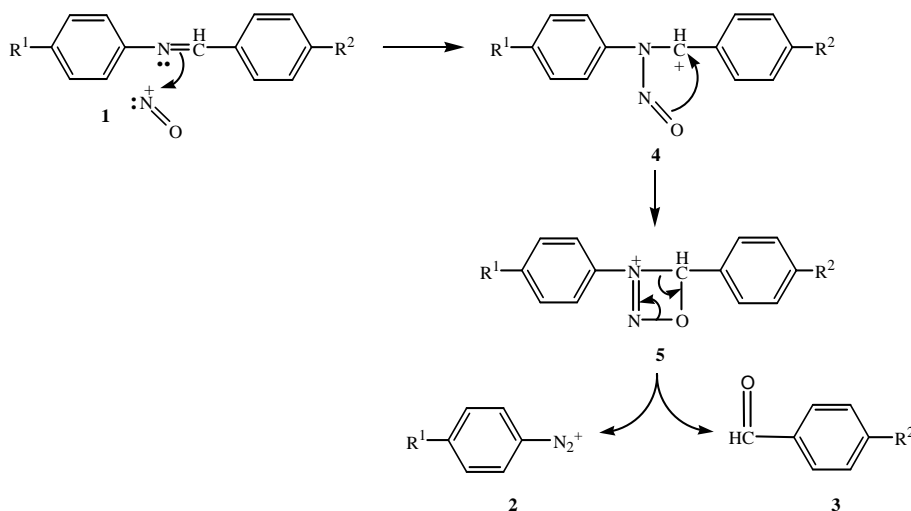
**Table 1.** The products revealed that the carbon-nitrogen double bond of Schiff bases was cleaved. The stoichiometry study showed a 1:1:1:1 quantitative relationship between Schiff base,  $\text{NO}^+$ , diazonium salt and benzaldehyde. Very similar results were also obtained in the absolute absence of oxygen. Neither  $\text{NO}$  nor  $\text{NO}_2$  were detected in the reaction gas phase. We carried out the reaction using nitrosonium tetrafluoroborate in stead of nitrosonium perchlorate. Similar results were obtained, which implied that the oxidant, perchlorate anion, does not interfere with the reaction proceeding. The yield of **2** seems to be somewhat decreased with the rising electron withdrawing character of substituents  $\text{R}^1$  and  $\text{R}^2$ . The yield of the non-substituted benzenediazonium was also low, because it was rather instable in the presence of other chemicals. But the pure benzenediazonium salt was quite stable.

Two issues could be approached from the above experimental results: (a) an electron transfer (ET) process did not take place in the present cases, otherwise  $\text{NO}$  or  $\text{NO}_2$  would be detected in the absence or presence of oxygen and the stoichiometry would not be 1:1:1:1; (b)  $\text{NO}^+$  most likely initiated an electrophilic attack on the nitrogen-atom of the imine double bond of Schiff bases, giving a carbonium ion **4** as shown in **Scheme 2**. An oxadiazetium-like four-membered ring (**5** in **Scheme 2**) formed as an intermediate, which proceeded ring opening to give diazonium (**2** in **Scheme 2**) and benzaldehyde **3**<sup>11-13</sup>.

**Table 1** Reaction of Schiff bases with  $\text{NO}^+\text{ClO}_4^-$  in  $\text{CH}_2\text{Cl}_2$ 

Substrate	$\text{R}^1$	$\text{R}^2$	Yield of <b>2</b> (%)	Yield of <b>3</b> (%)
<b>1a</b>	Cl	$\text{NO}_2$	94	77
<b>1b</b>	Cl	H	98	79
<b>1c</b>	Br	H	92	81
<b>1d</b>	H	$\text{NO}_2$	78	80
<b>1e</b>	H	Cl	76	89
<b>1f</b>	H	H	76	85
<b>1g</b>	H	$\text{OCH}_3$	78	86
<b>1h</b>	$\text{CH}_3$	Cl	86.5	82

Scheme 2



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10. Data for products: (a) benzenediazonium perchlorates: m.p. 101-102 °C; purple needles; <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>, ppm) 8.11(t, 2H, J=7.8Hz, PhH-3,5), 8.41(t, 1H, J=7.8Hz, PhH-4), 8.88(d, 2H, J=7.8Hz, PhH-2,6); HRMS *m/z* Calcd. For C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>: 105.0447, Found: 105.0444(M<sup>+</sup>); (b) 4-chlorobenzenediazonium perchlorate: m.p. 134-135 °C; off-white needles; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, ppm) 7.82(d, 2H, J=8.7Hz, PhH-3,5), 8.38(d, 2H, J=8.7Hz, PhH-2,6); HRMS *m/z* Calcd. For C<sub>6</sub>H<sub>4</sub>ClN<sub>2</sub>: 139.0058, Found: 139.0053(M<sup>+</sup>), 141.0023(M<sup>+</sup>); FABMS *m/z* Calcd. For C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>4</sub>+H: 238.9, Found: 238.9(M+H)<sup>+</sup>; (c) 4-bromobenzenediazonium perchlorate: m.p. 131-132 °C; yellow needles; <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>, ppm) 8.33 (d, 2H, J=9.0Hz, PhH-3,5), 8.79 (d, 2H, J=9.0Hz, PhH-2,6); HRMS *m/z* Calcd. For C<sub>6</sub>H<sub>4</sub>BrN<sub>2</sub>: 182.9552, Found: 182.9559(M<sup>+</sup>), 184.9538(M<sup>+</sup>); (d) 4-methylbenzenediazonium perchlorate: m.p. 109-110 °C; off-white needles; <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>, ppm) 2.68(s, 3H, CH<sub>3</sub>), 7.92(d, 2H, J=8.4Hz, PhH-3,5), 8.74(d, 2H, J=8.4Hz, PhH-2,6); HRMS *m/z* Calcd. For C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>: 119.0604, Found:

119.0602(M<sup>+</sup>); (e) benzaldehyde: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) 7.52(t, 2H, *J*=6.6Hz, PhH-3,5), 7.62(t, 1H, *J*=6.6Hz, PhH-4), 7.87(d, 2H, *J*=6.6Hz, PhH-2,6), 10.01(s, 1H, CHO); EIMS *m/z* 106(M<sup>+</sup>), 105(M-1)<sup>+</sup>, 77(M-29)<sup>+</sup>; (f) 4-chlorobenzaldehyde: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) 7.52(d, 2H, *J*=8.4Hz, PhH-3,5), 7.83(d, 2H, *J*=8.4Hz, PhH-2,6), 9.98(s, 1H, CHO); EIMS *m/z* 142 (M<sup>+</sup>), 141(M-1)<sup>+</sup>, 140(M<sup>+</sup>), 139(M-1)<sup>+</sup>, 111(M-29)<sup>+</sup>, 75(M-65)<sup>+</sup>; (g) 4-nitrobenzaldehyde: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) 8.07(d, 2H, *J*=9.0Hz, PhH-2,6), 8.39(d, 2H, *J*=9.0Hz, PhH-3,5), 10.15(s, 1H, CHO); EIMS *m/z* 151(M<sup>+</sup>), 150(M-1)<sup>+</sup>, 105(M-46), 104(M-47)<sup>+</sup>; (h) 4-methoxybenzaldehyde: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) 3.79(s, 3H, OCH<sub>3</sub>), 6.91(d, 2H, *J*=8.7Hz, PhH-3,5), 7.74(d, 2H, *J*=8.7Hz, PhH-2,6), 9.79(s, 1H, CHO); EIMS *m/z* 136(M<sup>+</sup>), 135(M-1)<sup>+</sup>, 107(M-29)<sup>+</sup>, 92(M-44)<sup>+</sup>.

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