A new method for the synthesis of dry diazonium nitrates in nonaqueous condition

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Amines react with PEG-NO2 adduct in nonaqueous condition to give dry arenediazonium nitrates in high purity and excellent yields.

As classical but ever-lasting synthetic intermediates, diazonium salts have long been used in dyes and pharmaceutical industry. Recently, diazonium salts have also found new application in recording, imaging, copying and printing sciences. Because they are so valuable, extensive studies on the synthesis of diazonium salts have been reported. The common synthesis of diazonium salts is carried out in aqueous medium at low temperature and usually the resultant diazonium salt is not isolated from the solution. The frequently synthesized diazonium salts are arenediazonium chlorides, tetrafluoroborates, hydrosulfates and dihydrophosphates. However, the synthesis of arenediazonium nitrates have seldom been studied because of the strong oxidising ability of nitric acid. To avoid the oxidation of aromatic amines by nitric acid, N2O4 in CHCl3 was treated with phenyl isocyanates by Backman to obtain diazonium nitrates. The synthesis of arenediazonium nitrates have seldom been studied because of the strong oxidising ability of nitric acid. To avoid the oxidation of aromatic amines by nitric acid, N2O4 in CHCl3 was treated with phenyl isocyanates by Backman to obtain diazonium nitrates. Recrystallization with DMF-Et2O gave dry and pure diazonium nitrates. The IR peaks at 2252-2293 cm⁻¹ confirmed the existence of ArN₂⁺, while the peaks at 1384 cm⁻¹ and 825-826 cm⁻¹ were assigned to the nitrate ions. The microanalysis and ¹H NMR data of the diazonium nitrates are summarized in Table I.

The arenediazonium nitrates with electron-withdrawing substituents have been proved to be very
<table>
<thead>
<tr>
<th>Product</th>
<th>Yield (%)</th>
<th>$^1$H NMR (δ, ppm)</th>
<th>Calcd (%) (Found)</th>
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<tr>
<td></td>
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<td><strong>C</strong></td>
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<td><strong>Calcld</strong></td>
</tr>
<tr>
<td>$\text{H_2C=C-NO}_3$</td>
<td>75</td>
<td>8.41(s,1H,H) 8.66(d,1H,H) 7.68(m,2H,H +Hd) 2.83(s,3H,CH)</td>
<td>46.40</td>
</tr>
<tr>
<td>$\text{H_3C-C-NO}_3$</td>
<td>78</td>
<td>8.32(s,2H,H +Hb) 8.07(s,1H,H) 7.73(s,1H,H) 2.45(s,3H,CH)</td>
<td>46.40</td>
</tr>
<tr>
<td>$\text{Cl-N_2-NO}_3$</td>
<td>81</td>
<td>8.75(d,1H,H) 8.47(d,1H,H) 8.23(m,1H,H) 7.80(m,1H,H)</td>
<td>35.75</td>
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<tr>
<td>$\text{Br-N_2-NO}_3$</td>
<td>80</td>
<td>8.58(d,1H,H) 8.15(m,2H,H +Hd) 7.84(t,1H,H)</td>
<td>29.29</td>
</tr>
<tr>
<td>$\text{H_2C=C-NO}_3$</td>
<td>84</td>
<td>8.77(s,1H,H) 8.53(d,1H,H) 8.43(d,1H,H) 7.82(t,1H,H)</td>
<td>29.29</td>
</tr>
<tr>
<td>$\text{Br-N_2-NO}_3$</td>
<td>82</td>
<td>8.44(d,2H,H) 8.12(d,2H,H)</td>
<td>29.29</td>
</tr>
<tr>
<td>$\text{COOH-NO}_3$</td>
<td>88</td>
<td>8.56(d,1H,H) 8.25(d,1H,H) 8.18(t,1H,H) 7.94(t,1H,H)</td>
<td>39.82</td>
</tr>
<tr>
<td>$\text{COOH-NO}_3$</td>
<td>91</td>
<td>9.08(s,1H,H) 8.67(m,2H,H +Hd) 7.98(t,1H,H)</td>
<td>39.82</td>
</tr>
<tr>
<td>$\text{HOOC-NO}_3$</td>
<td>86</td>
<td>8.59(d,2H,H) 8.38(d,1H,H)</td>
<td>39.82</td>
</tr>
</tbody>
</table>

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stable and could be stored at room temperature for half a year without any change. These salts were prepared at 10-40°C in excellent yield. While the diazonium nitrates without electron-withdrawing substituents (compounds 1-9) can be stored in refrigerator. On storage at room temperature these salts gradually darken. These salts can be obtained at lower reaction temperatures (10-15°C) in good yield. Higher reaction temperature leads to the formation of tar. Furthermore, when heated to about 65°C, struck or ignited, all these diazonium salts explode. The diazonium nitrates have advantages of dryness and high purity compared with other diazonium salts prepared as an aqueous solution. This may make the diazonium nitrates more versatile synthetic intermediates in different reaction medium. Further studies on the reaction of the diazonium nitrate are under investigation.

Experimental Section
Starting materials were of reagent grade and used without further purification. All products were characterized by IR and 'H NMR spectroscopy and elemental analyses. IR spectra were obtained on a FTIR-410 infrared spectrophotometer, and 'H NMR spectra on a Bruker DPX-400 spectrometer using TMS as an internal standard. Elemental analyses were carried out on a PE-2400 microelemental analyser.

PEG-NO\textsubscript{2} adduct. To a three-necked round bottom flask containing 21.1 g (0.3 mole) of sodium nitrate (98%), was added dropwise 30 g (0.3 mole) of conc. sulfuric acid (98%) at room temperature. The evolved gases were blown by a stream of oxygen into condenser (NO was converted into NO\textsubscript{2} at the same time), then into a drying tower (packed with the mixture of phosphorous pentaoxide and quartz sand, P\textsubscript{2}O\textsubscript{5}:SiO\textsubscript{2}; 1:1 in wt, an oxidizing tower (packed with quartz sand carrying chromium trioxide, CrO\textsubscript{3}:SiO\textsubscript{2}; 5:95 in wt) and finally reached the bottom of an absorption tower (high 300 mm, inside diameter 15 mm, packed with glass ring). From the top of the absorption tower, 30 mL of PEG was dropped through a pressure-equalized dropping funnel. The counterface absorption of NO\textsubscript{2} by PEG gave the adduct PEG-NO\textsubscript{2}.

Arenediazonium nitrates. To 5 mmoles of aromatic amine in 10 mL PEG was added 4 mL of PEG-NO\textsubscript{2} (containing NO\textsubscript{2}, 40 mmoles) in one portion with vigorous stirring. Gases evolved immediately. Then 20 mL of diethyl ether was added to the reaction mixture in 5 min. The solution was stirred until the diazonium salt precipitated completely. The diazonium nitrate was filtered and washed with Et\textsubscript{2}O, then dissolved in DMF. Addition of Et\textsubscript{2}O to the DMF solution gave crystals. The crystals were filtered through suction, washed with Et\textsubscript{2}O and dried in vacuo to give pure diazonium nitrate.

References
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