Synthesis of Organic Nitrogen Heterocyclic Salts

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Received 25 September 2003; revised 10 November 2003

Abstract: New (pyrrolyl)-pyridinium and quinolinium salts have been prepared selectively in high yields by reacting (pyrrolyl)-pyridine or -quinoline and their derivatives with CF3SO2CH3 in CH2Cl2. No methylation of the nitrogen of pyrrole was observed. Preliminary investigations revealed that these salts show a good response as nonlinear optics.

Key words: pyrrole, polypyrrole, pyridinium, quinolinium, methylation, SN1, Hyper-Rayleigh Scattering

Organic push-pull molecules, formed with donor and acceptor end groups connected via a π-conjugated system, are well suited for quadratic optical effects.1 Their chemical stability towards optical damage and high nonlinear response make them good candidates for electro-optical devices.2 Among them, para-disubstituted biphenyl compounds such as pyridinium-phenoxide zwitterions and pyridinium-phenol organic salts have drawn special attention.3 Here, we have focused on another family of intramolecular charge transfer compounds based on pyrrole to take advantage of the intrinsic stability of pyrrole, the high conductivity of its corresponding polymer,4 and its availability. Such compounds should therefore be well suited as chromophores for nonlinear optical applications as well as precursors of conducting polypyrroles substituted by charged species.

Herein, we report the synthesis of a new series of pyridinium and quinolinium salts substituted by a pyrrole moiety. The (pyrrolyl)-pyridine and -quinoline precursors (1-4) have been prepared via an electroinduced SN1 reaction in liquid ammonia by reacting the pyrrolyl anion and the corresponding aryl halide, a method described in our previous papers.6 Alkylation of the precursors was achieved by a Menschutkin reaction, using CF3SO2CH3 as quaternization reactant. The synthetic procedure for all pyridinium and quinolinium salts is represented in Scheme 1. Alkylation of pyridine and quinoline rings substituted by a phenol or naphthol group using 1-iodoheptane and 1-bromo-octadecane have been described elsewhere.3a,b Recently, DesMarteau and co-workers described the syntheses of new alkyl pyridinium ionic salts using N-methyl bis(perfluoralkyl)sulfonylimides or trifluoroethyl phenyliodonium bis[(trifluoromethyl)sulfonyl]imide.7 This method required the synthesis of the methylating agent. Speranza and co-workers have reported the electrophilic methylation of pyrrole and N-methylpyrrole by CH3XCH3+ (X = Cl, F) using radiolysis. Their studies led to three isomers in the case of pyrrole (substituted in positions 1, 2, and 3) and two isomers for N-methylpyrrole (substituted in positions 2 and 3).8 They also reported the reaction to be unselective and dependent mainly on the experimental conditions. The electron pair on nitrogen of pyrrole is unavailable because it participates in the electron delocalization rendering it less reactive towards electrophilic attack. In contrast, the electron pair of pyridine is available and more nucleophilic, and should therefore be easily attacked by an electrophile such as CF3SO2CH3. During methylation, pyrrolyl- pyridinium and -quinolinium salts were precipitated. This precipitation is due to the excellent reactivity of CF3SO2CH3 and to the size of CF3SO2–, which is the driving force for the high regioselectivity of the reaction. In all cases, methylation occurred selectively at the pyridine and quinoline nitrogen atoms with no methylation on the nitrogen of pyrrole. In our case using methyl-iodide for alkylation of pyrrolyl-pyridine and -quinoline may affect the solubility of the salts and therefore the regioselectivity of the reaction.

![Scheme 1](image-url) Principle of the synthesis of nitrogen heterocyclic salts.

SYNTHESIS 2004, No. 4, pp 0517–0520
Advanced online publication: 26.01.2004
DOI: 10.1055/s-2004-815931; Art ID: M04103SS
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The $\text{S}_{\text{RN1}}$ reaction was performed according to a previously reported procedure, the yields of the salts are listed in Table 1.

For all salts, the $^1\text{H NMR}$ spectra exhibited a new singlet corresponding to methyl protons in the region $\delta 4.10–4.60$ ppm. Some signals were shifted significantly compared to the precursors, namely the pyrrolic (NH) proton at $\delta 11.30–12.50$ ppm (1 ppm shift), the pyridinium and quinolinium protons (0.5 ppm shift). For salt $5$, the coupling constants of the aromatic pyridinium protons were small and unresolved, therefore they appeared as singlets. In addition, the $^{13}\text{C NMR}$ spectra data concurred with the $^1\text{H NMR}$ assignments, the pyridinium and quinolinium methyl carbon atoms appearing in the region $\delta 44–49$ ppm. A significant difference of about 5–6 ppm was observed in the chemical shifts for all the pyridinium and quinolinium ring carbon atoms compared to those of the precursors.

Also, neither methyl protons nor carbon atoms were observed to suggest methylation had occurred on the pyrrolic nitrogen atom, which proved the high selectivity of the reaction.

With regard to optical properties, hyperpolarizabilities are generally measured by the electric field induced second harmonic generation technique (EFISHG). This method, in which the molecules are oriented in an electric field, can be used to study only dipolar molecules not ionic species. However, another method based on second harmonic scattering called the Hyper-Rayleigh Scattering method (HRS) has been developed for the measurement of hyperpolarizabilities. The main advantage of HRS over EFISHG is that it permits the study of all molecular units: dipolar, octopolar, and ionic species. Moreover, the hyperpolarizability coefficients can be estimated directly without the need of any independent measurement of the dipole moment of the molecules. The HRS method was used to measure the hyperpolarizabilities of the pyridinium and quinolinium salts synthesized.

The hyperpolarizability coefficient $\beta$ was determined experimentally under laser light; it depends on the excitation radiation (here, $\lambda = 1.06 \, \text{um}$) and the wavelength of the molecule charge transfer band ($\lambda_{0}$). Assuming that only the ground and the first excited states of the molecule have

<table>
<thead>
<tr>
<th>Aryl-pyrrole</th>
<th>Salt</th>
<th>Yield (%)$^a$</th>
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<tbody>
<tr>
<td><img src="image1" alt="Aryl-pyrrole 1" /></td>
<td><img src="image2" alt="Salt 1" /></td>
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<tr>
<td><img src="image3" alt="Aryl-pyrrole 2" /></td>
<td><img src="image4" alt="Salt 2" /></td>
<td>6</td>
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<tr>
<td><img src="image5" alt="Aryl-pyrrole 3" /></td>
<td><img src="image6" alt="Salt 3" /></td>
<td>7</td>
</tr>
<tr>
<td><img src="image7" alt="Aryl-pyrrole 4" /></td>
<td><img src="image8" alt="Salt 4" /></td>
<td>8</td>
</tr>
</tbody>
</table>

$^a$ Isolated yield.
an influence on its quadratic hyperpolarizability, the normalized hyperpolarizability coefficients, $\beta^0$, was estimated from Equation 1.11a
\[
\beta = \beta^0 \frac{x_i^2}{(\lambda^2 - \lambda_d^2)(\lambda^4 - 4\lambda_d^4)}
\]
Equation 1 $\lambda = 1.06 \, \mu m$. $\lambda_d$: salt absorption wavelength (nm).

The apparatus for HRS experiments require a calibration with a reference that has a known $\beta$. In our experiments, the reference chosen was para-nitroaniline (pNA) dissolved in methanol. The $\beta$(pNA) was found to be 34.5 $\times 10^{-30}$ esu.11

Table 2 presents our preliminary investigations of $\beta$ and $\beta^0$ in methanol, which correlate well with literature values for analogous unsymmetrical biaryl salts.3b

| Table 2 Optical Hyperpolarizability Measurements by HRS of Different Salts |
|-------------------|-----|-----|
| Salt             | $\lambda_d$ (nm) | $10^4 \times \beta^0$ (esu) | $10^6 \times \beta^0$ (esu) |
| 5                | 328 | 23  | 13  |
| 6                | 426 | 64  | 19  |

Based on these promising results, further measurements are underway of the other salts and their corresponding zwitterions. The latter can be directly obtained in the HRS device via deprotonation of the corresponding salts.

Pyridinium and Quinolinium Salts; General Procedure

Liquid NH$_3$ (220 mL), 4,4'-dipyridyl (4.00 mmol, 0.636 g), pyrrole (104 mmol, 7.05 g) and 2,5-dichloropyridyl (20.3 mmol, 3.00 g) were dissolved in CH$_2$Cl$_2$ (10 mL) at r.t., then CF$_3$SO$_2$CH$_2$NH$_2$ (0.320 g, 1.95 mmol) was added dropwise to the solution and the mixture was stirred for 1 hour. A yellow precipitate formed, which after filtration was washed with CH$_2$Cl$_2$ (10 mL), pentane (100 mL), and dried overnight. Products were characterized by $^1$H, $^{13}$C NMR spectroscopy and elemental analysis.

5

Mp 247 °C.

$^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta = 4.30$ (s, 3 H), 6.31 (m, 1 H), 7.03 (m, 1 H), 7.20 (m, 1 H), 8.80 (s, 1 H), 9.80 (s, 1 H), 9.25 (s, 1 H), 11.85 (br s, 1 H).

$^{13}$C NMR (DMSO-$d_6$, 75 MHz): $\delta = 6.6$ (CH$_3$), 112.6 (CH), 116.6 (CH), 119.2 (CH), 124.4 (C), 125.9 (CH), 127.8 (CH), 128.5 (C), 134.6 (CH), 139.2 (C), 146.7 (C), 147.6 (CH).

Anal. Calcd for C$_{13}$H$_{15}$N$_2$O$_3$F$_3$S: C, 44.98; N, 6.60; H, 2.78. Found: C, 44.98; N, 6.60; H, 2.78.

6

Mp 141 °C.

$^1$H NMR (DMSO-$d_6$, 300 MHz): $\delta = 4.45$ (s, 3 H), 6.55 (m, 1 H), 7.05 (m, 1 H), 7.55 (m, 1 H), 7.90 (s, 1 H), 8.00 (dt, $J_1 = 1.1$ Hz, $J_2 = 7.7$ Hz, 1 H), 8.20 (dt, $J_1 = 1.2$ Hz, $J_2 = 7.9$ Hz, 1 H), 8.79 (dt, $J_1 = 8.5$ Hz, 1 H), 9.40 (d, $J = 6.5$ Hz, 1 H), 12.35 (br s, 1 H).

$^{13}$C NMR (DMSO-$d_6$, 75 MHz): $\delta = 44.3$ (CH$_3$), 112.6 (CH), 116.6 (CH), 119.2 (CH), 124.4 (C), 125.9 (CH), 127.8 (CH), 128.5 (C), 134.6 (CH), 139.2 (C), 146.7 (C), 147.6 (CH).

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Acknowledgment

This work was partially supported by the Centre National de la Recherche Scientifique and by the Ecole Supérieure de Physique et Chimie Industrielles de Paris. Dr. Gregoire Mathey is gratefully acknowledged for HRS measurements.

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