Short Note

N,N,N-Triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium Perchlorate

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Abstract: Polypyrroles attract significant attention as the promising class of conductive polymers for the organic electronics, electrochemical energy-storage, photovoltaics, sensing and light-emitting devices due to their electrochemical and electrical properties. The attachment of the charged fragments to the pyrrole monomeric unit opens the route to a water-soluble polypyrrole for improved solution processability. Here we report a scalable multigram synthesis of the N-substituted cationic pyrrole, N,N,N-triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium perchlorate, which can be used for the preparation of the water-soluble cationic polypyrrole, in two steps with 81% overall yield. The resulting product was characterized by the ^{1}H and ^{13}C, nuclear magnetic resonance (NMR), ESI-high-resolution mass spectrometry (ESI-HRMS) and Fourier-transform infrared spectroscopy (FTIR).

Keywords: pyrrole; linker; ion exchange; alkylation; solubilization

1. Introduction

Conductive polymers, combining the chemical and mechanical properties of polymers with the electrical behavior of metals, attract attention as functional materials due to their corrosion resistance, easy synthesis, highly tunable structure, good mechanical and optical properties, high flexibility and electrical conductivity [1–5]. Conductive polymers are beneficial due to the reach functionalization chemistry, which allows us to append different active fragments to the main chain of the polymer [6,7]. Derivatives of the polypyrrole, one of the most popular conducting polymers, meet their application in organic electronics [8], electrochemical energy-storage [9], photovoltaics [10], sensing [11] and light-emitting devices [12]. However, common conductive polymers including polypyrroles are poorly processible due to their insolubility in water and organic solvents. One of the ways to overcome this issue is to attach solubilizing fragments to the monomeric units of the conductive polymers. For instance, a variety of water-soluble and easily solution-processable polythiophenes [13], polyanilines [14] and polypyrroles [15] were obtained using the monomers functionalized with charged fragments.

Here we report the synthesis of the novel cationic pyrrole, N,N,N-triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium perchlorate, which can serve as the monomer for the synthesis of the water-soluble polypyrrole. The proposed synthetic procedure is economical and highly scalable, affording the monomer with non-oxidizable counter-ion, which is crucial for further oxidative polymerization. The obtained product was characterized by nuclear magnetic resonance (NMR), high-resolution mass spectrometry (HRMS) and Fourier-transform infrared spectroscopy (FTIR) spectra.

2. Results

Starting 1-(4-bromobutyl)-1H-pyrrole **1** was prepared following the modified literary procedure [16]. Bromide 1 was used for the alkylation of the triethylamine in refluxing acetonitrile (Scheme 1), producing the N,N,N-triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium bromide **2** in 98% yield. The resulting product contained a water-soluble impurity which cannot be separated by crystallization, so it proceeded to the next step without further

purification. The bromide ion in the resulting tetraalkylammonium salt was replaced with the perchlorate ion using the precipitation-aided ion exchange with $NaClO_4$ in acetone (Scheme 1). The crystallizations from CH_2Cl_2 and then from H_2O produced the title compound *N,N,N*-triethyl-4-(1*H*-pyrrol-1-yl)butan-1-aminium perchlorate **3** in 82% yield. The reactions were carried out under an inert atmosphere or in sealed vessels to prevent the oxidation of pyrrole.
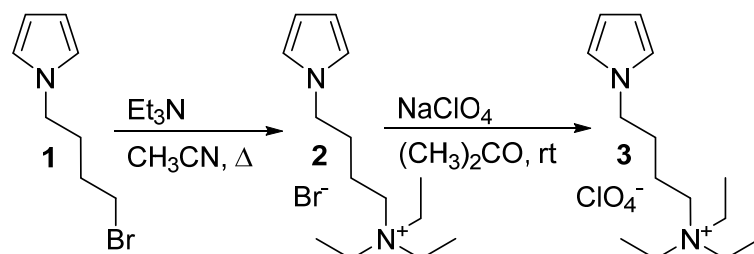
Scheme 1. Reaction conditions for the alkylation of triethylamine with 1-(4-bromobutyl)-1*H*-pyrrole **1** and ion exchange of the resulting bromide with sodium perchlorate.

The whole reaction sequence starting from 1*H*-pyrrole is chromatography free, atom-economic and produces the title product in very high yield. Purification of **1** was carried out by fraction distillation under reduced pressure, **2** was used after a simple extraction workup without further purification and **3** was purified by dissolving in CH_2Cl_2, filtration and evaporation, followed by recrystallization from aqueous ethanol. Compound **2** appears as highly hygroscopic gum, while the **3** is crystalline material relatively insensitive to moisture. The synthetic procedure was carried out on a multigram scale and may be easily scaled up, which makes it highly suitable for the mass production of cationic pyrrole monomer.

In the ^{1}H NMR spectrum of compound **2** in $CDCl_3$ (Figure S1), the aromatic signals appear as a pair of triplets at 6.70 and 6.11 ppm with the coupling constant of 2.1 Hz instead of the anticipated pair of doublets, which is typical for *N*-alkylpyrroles [17]. The set of signals of the butyl linker is situated at 4.02, 3.06–3.28, 1.93 and 1.66–1.77 ppm, and the pair of ethyl signals, quartet at 3.39 and triplet at 1.30 ppm. The ^{13}C NMR of the **2** in $CDCl_3$ (Figure S2) contains the signals at 120.7, 108.5, 57.2, 53.5, 48.5, 28.2, 19.4 and 8.1 ppm. Both spectra contain a set of minor signals which belongs to an unknown contaminant. The ^{1}H NMR spectrum of compound **3** in DMSO-d$_6$ (Figure S3) contains a pair of triplets 6.77 and 6.00 ppm with the coupling constant of 2.1 Hz, set of butylene signals at 3.92, 3.03–3.13, 1.74 and 1.48–1.58 ppm, and the pair of ethyl signals, quartet at 3.19 and triplet at 1.15 ppm. The ^{13}C NMR of the **3** in DMSO-d$_6$ (Figure S4) contains the signals at 120.4, 107.6, 55.6, 52.0, 47.7, 27.9, 18.3 and 7.1 ppm. HRMS of both compounds (Figures S5 and S6) lies within 5 ppm error from the calculated value of 223.2169 Da. The FTIR spectrum of **3** (Figure S8) shows the presence of the strong band at 1090 cm^{-1}, which is characteristic of the asymmetric stretching of Cl=O bonds ClO_4^- anion. At the same time, the spectrum of **2** (Figure S7) contains the broad strong band around 3435 cm^{-1}, while in the spectrum of **3**, only a minor band appears at the same position, indicating that the **3** is nearly non-hygroscopic when compared to **2**.

The resulting cationic pyrrole may be used for the preparation of the cationic polypyrroles, which may be easily processed from aqueous solutions. This option allows the development of green procedures for the fabrication of organic electronics, energy storage devices, sensors, etc. A simple and scalable synthetic approach makes the resulting compound a promising candidate for the implementation in industrial production of conductive polymers.

3. Materials and Methods

3.1. General Consideration

Reagents of "reagent grade" purity were purchased from Sigma–Aldrich (Europe). The starting 1-(4-bromobutyl)-1*H*-pyrrole 1 was prepared following the modified literary procedure [16]. The Fourier-transform infrared spectra were recorded on the Shimadzu

IRaffinity-1 FTIR spectrophotometer (Shimadzu Europa GmbH, Kyoto, Japan) in KBr pellets. ^{1}H and ^{13}C-NMR spectra were acquired on a Bruker Avance 400 spectrometer (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) at 400 and 101 MHz, respectively, in CDCl$_3$ and DMSO-d$_6$. The HRMS spectrum was recorded using electrospray ionization on a Bruker microTOF apparatus (Bruker Analytische Messtechnik GmbH, Rheinstetten, Germany) in positive mode.

3.2. Synthesis of 1-(4-Bromobutyl)-1H-pyrrole 1

Freshly distilled pyrrole (6.95 mL, 6.7 g, 100 mol) was added to an ice-cooled suspension of NaH (4.2 g of 60% suspension in oil, 105 mmol) in dry THF (150 mL) under Ar. Then, 1,4-dibromobutane (36 mL, 65 g, 300 mol) was added dropwise for 5 min. The ice bath was removed, and the reaction mixture was stirred at RT for 16 h, isolated from light. After the completion of the reaction was confirmed by TLC, the reaction mixture was quenched with sat. NH$_4$Cl solution, filtered, THF was removed in vacuo, and an oily residue was fractionally distilled at 0.012 mbar. Excessive 1,4-dibromobutane was isolated as a first fraction (b.p. 30 °C), and product 1 as a second fraction (b.p. 70–74 °C). The fraction containing product 1 was distilled again at 0.012 mbar, producing pure 1 as a slightly brownish oil (14.1 g, 70 mmol, 70%). The ^{1}H NMR spectrum is consistent with literary data [16].

3.3. Synthesis of N,N,N-Triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium Bromide 2

A solution of 1 (5.7 g, 28.2 mmol) and Et$_3$N (5.87 mL, 4.27 g, 42.3 mmol) in dry CH$_3$CN (140 mL) was heated at 80 °C for 48 h under Ar in a sealed vessel. After the completion of the reaction monitored by TLC, the solvent was evaporated in vacuo, the residue was dissolved in 70 mL DCM and extracted with 25 mL of H$_2$O 4 times. The aqueous layer was evaporated, and the orange oily residue was dried in vacuo to the constant mass in 98% yield (8.46 g, 27.7 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ, ppm: 6.70 (t, *J* = 2.1 Hz, 2H), 6.11 (t, *J* = 2.1 Hz, 2H), 4.02 (t, *J* = 6.5 Hz, 2H), 3.39 (q, *J* = 7.3 Hz, 6H), 3.28–3.06 (m, 2H), 1.93 (p, *J* = 6.9 Hz, 2H), 1.76–1.66 (m, 2H), 1.30 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ, ppm: 120.7, 108.5, 57.2, 53.5, 48.5, 28.2, 19.4, 8.1. FTIR (KBr) $\tilde{v}$, cm^{-1}: 3435 (H$_2$O), 2850–3000 (C-H). HRMS (ESI) *m/z* [M]$^+$ calcd for C$_{14}$H$_{27}$N$_2^+$ 223.2169, found 223.2163.

3.4. Synthesis of N,N,N-Triethyl-4-(1H-pyrrol-1-yl)butan-1-aminium Perchlorate 3

Substance 2 (8.46 g, 27.7 mmol) was mixed with a saturated solution of NaClO$_4$ (3.76 g, 30.7 mmol) in acetone (9.2 mL). The mixture was stirred for 1.5 h at RT under Ar, the precipitate was filtered off, the filtrate was evaporated in vacuo and the residue was redissolved in 50 mL CH$_2$Cl$_2$, filtered again and evaporated in vacuo. The resulting brownish solid was recrystallized from 80% aqueous ethanol, producing the desired product 3 as creamy crystals in 82% yield (7.38 g, 22.9 mmol).

^{1}H NMR (400 MHz, DMSO-d$_6$) δ, ppm: 6.77 (t, *J* = 2.1 Hz, 2H), 6.00 (t, *J* = 2.1 Hz, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.19 (q, *J* = 7.3 Hz, 6H), 3.13–3.03 (m, 2H), 1.74 (p, *J* = 6.9 Hz, 2H), 1.58–1.48 (m, 2H), 1.15 (t, *J* = 7.3 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d$_6$) δ, ppm: 120.4, 107.6, 55.6, 52.0, 47.7, 27.9, 18.3, 7.1. FTIR (KBr) $\tilde{v}$, cm^{-1}: 2850–3000 (C-H), 1090 (ClO$_4^-$). HRMS (ESI) *m/z* [M]$^+$ calcd for C$_{14}$H$_{27}$N$_2^+$ 223.2169, found 223.2159.

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