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Synthesis and Reactivity of 1-Methyl-4-ethynylpyridinium Triflate

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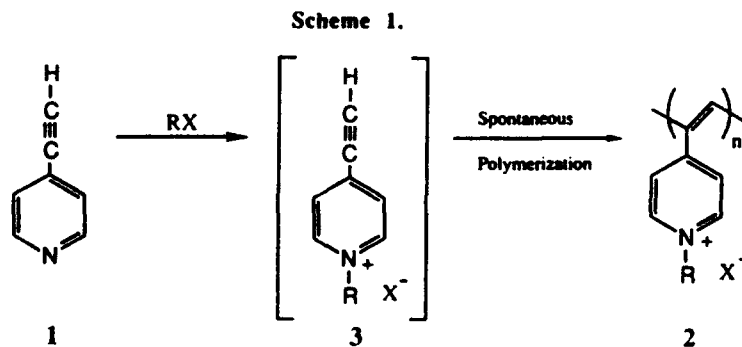
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Key Words: Ethynylpyridine; alkylation; ethynylpyridinium triflate; trimerization; polyacetylenes

Abstract: 1-Methyl-4-ethynylpyridinium triflate has been prepared by treatment of 4-ethynylpyridine with methyl triflate in methylene chloride. This new active acetylenic monomer trimerized to *tris*-1,3,5-(1-methylpyridinium-4-yl)benzene triflate when heated in aqueous solution. The new compounds were isolated and characterized.

Widespread interest in polyacetylenes is a consequence of the possibility that these materials may be used as lightweight, easily fabricated replacements for semiconductor chips, wiring, electrode materials in fuel cells and batteries, and components in a wide variety of optoelectronic devices.^{1,2,3} Substituted polyacetylenes have received much attention because of their greater stability to oxidation and better processability relative to their unsubstituted analogues.⁴ Recently Blumstein reported that 4-ethynylpyridine (1) and its derivatives undergo spontaneous polymerization to polyacetylenes (2a) during quaternization at pyridine nitrogen⁵ (Scheme 1). *N*-Alkylated ethynylpyridinium salts (3a) were proposed as unstable intermediates.



- a. R = C₂H₅, C₁₂H₂₅; X = Br⁻, I⁻
b. R = H; X = OSO₂CF₃⁻
c. R = CH₃; X = OSO₂CF₃⁻

The literature on the synthesis of stable N-alkylated ethynylpyridinium salts is limited to derivatives of bis(pyridyl)acetylenes.^{6,7} Stable N-alkyl-4-ethynylpyridinium salts (3) have not been reported prior to this investigation. Recently, we developed a general method for the synthesis of N-alkyl-4-vinylpyridinium ions and described their conversion to polymers with regular structure.^{8,9} Using the analogy to vinylpyridine, we examined reactions of 1 with triflic acid and methyl triflate. We now wish to describe the first time synthesis of stable salts of 4-ethynylpyridine: the N-protonated (3b) and N-methylated (3c) analogues. These compounds may serve as precursors to poly(4-ethynylpyridinium) and poly(1-methyl-4-ethynylpyridinium) salts (2).

4-Ethynylpyridinium triflate (3b) was prepared from 1 and triflic acid in CH_2Cl_2 at 0 °C. After addition of ethyl ether to the reaction mixture, the salt precipitated from solution as a white powder in 92% yield. Compound 3b was fully characterized. IR (KBr; cm^{-1} , assign): 3239, $\equiv\text{C-H}$ str; 2779, N-H str; 2123, $\text{C}\equiv\text{C}$ str; $^1\text{H-NMR}$ (D_2O ; δ , mult, J (Hz), area, assign): 4.34, s, 1H, $\equiv\text{C-H}$; 8.03, d, 7, 2H, Py^{3,5}; 8.68, d, 7, 2H, Py^{2,6}; $^{13}\text{C-NMR}$ (D_2O ; δ , assign): 80.36, $\equiv\text{C-H}$; 93.5, $\equiv\text{C}$; 131.5, Py^{3,5}; 142.7, Py⁴; 142.8, Py^{2,6}; UV (D_2O): 257nm, $\epsilon = 17230$; Anal: Found (Calc), C, 37.9 (37.9); H, 2.33 (2.37); N, 5.47 (5.53); m.p. (DSC) = 84.5 °C.

1-Methyl-4-ethynylpyridinium triflate (3c) was prepared from 1 and methyl triflate in CH_2Cl_2 at 0 °C. It precipitated from solution as a fine white crystalline powder in 88% yield. This new compound was characterized by spectroscopic methods and elemental analysis. IR (KBr; cm^{-1} , assign): 3236, $\equiv\text{C-H}$ str; 2116 $\text{C}\equiv\text{C}$ str; $^1\text{H-NMR}$ (D_2O ; δ , mult, J (Hz), area, assign): 4.37, s, 3H, CH_3 ; 4.43, s, 1H, $\equiv\text{C-H}$; 8.08, d, 6, 2H, Py^{3,5}; 8.94, d, 6, 2H, Py^{2,6}; $^{13}\text{C-NMR}$ (D_2O ; δ , assign): 50.1, CH_3 ; 79.7, $\equiv\text{C-H}$; 93.8, $\equiv\text{C}$; 131.4, Py^{3,5}; 140.8, Py⁴; 146.9, Py^{2,6}; UV (D_2O): 258nm, $\epsilon = 17300$; Anal: Found (Calcd), C, 40.39 (40.45); H, 2.99 (3.00); N, 4.99 (5.24); S, 12.26 (11.99); m.p. (DSC) = 135.4 °C

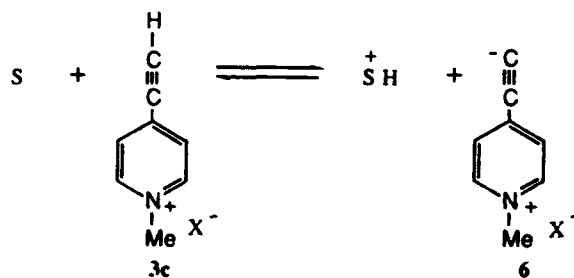
Both materials, 3b and 3c, are stable in the solid state as well as in solutions of water, alcohols, DMSO or acetonitrile at room temperature. Their DSC thermograms show sharp melting points. Both monomers undergo thermal polymerization above the melting point as indicated by a broad exothermic peak. Similar results were obtained by preparative scale experiments in which 3b and 3c were heated at 180 °C for 2 hrs. The resulting materials are black solids which are soluble in polar solvents. The characteristic $\text{C}\equiv\text{C}$ bond absorption at 2120 cm^{-1} disappeared. The $^1\text{H-NMR}$ spectrum of 3b exhibits broad unresolved signals from 7.2 to 9.2 ppm. The spectrum of 3c includes an additional broad multiplet at 4.1-4.6 ppm.

Monomers 3b and 3c are unstable in solution at elevated temperature. The polymerization of these materials was observed during heating in water or DMSO solution at 100 °C for several hrs. Interestingly, compound 3c undergoes trimerization to *tris*-1,3,5-(1-methylpyridinium-4-yl)benzene triflate (4). The benzene derivative 4 was obtained in 50% yield after separation from linear oligomers by repeated precipitation from methanol with ethyl acetate. The structure of 4 was confirmed by spectroscopic characterization and elemental analysis: $^1\text{H-NMR}$ (D_2O ; δ , mult, J (Hz), area, assign): 4.47, s, 9H, CH_3 ; 8.68, d, 6, 6H, Py^{3,5}; 8.79, s, 3H, Ph; 9.02, d, 6, 6H, Py^{2,6}; $^{13}\text{C-NMR}$ (D_2O ; δ , assign): 49.1, CH_3 ; 127.1, Ph; 131.9, Py^{3,5}; 148.6, Py⁴; 147.2, Py^{2,6}; 155.7, Ph; UV (D_2O): 281nm, $\epsilon = 20600$; Anal: Found (Calcd), C, 40.25 (40.45); H, 2.94 (3.00); N, 4.99 (5.24); S, 12.23 (11.99); m.p. (DSC) = 372 °C. The IR spectrum indicates the absence of the $\text{C}\equiv\text{C}$ bond stretching band at 2100 cm^{-1} .

Compound 1 does not undergo an analogous cyclo-trimerization reaction even after prolonged heating (i.e., 2 days) in DMSO solution. Thus, quaternization of pyridinyl nitrogen must play an important role in the reaction mechanism. It was shown by Blumstein that 1 undergoes "spontaneous" polymerization to polyacetylenes during quaternization. It is known that the presence of a powerful electron withdrawing group, in this case N-alkylpyridinium, activates the acetylenic bond which then functions as the dienophile in a Diels-Alder reaction.^{6,7}

A cycloaddition mechanism may be ruled out due to the observation that addition of acid to the solution of 3c strongly retards the rate of trimerization. For the same reason and because the presence of free-radical inhibitors does not affect the rate of reaction, a free-radical mechanism can be excluded as well. The effect of acid on the rate of trimerization suggests that nucleophilic addition to the triple bond may be significant. It is known that haloalkynes are "triphilic"; that is, they are susceptible to nucleophilic attack at three sites - at both acetylenic carbons and halogen.¹⁰ The presence of the N-alkylpyridinium substituent makes the acetylenic bond even more vulnerable to nucleophilic attack, especially at the β carbon. This was demonstrated by the addition of pyridine which accelerates the reaction. It is likely, therefore, that the (N-alkylpyridinium)acetylide zwitterion (6), the conjugate base of 3c, may serve as initiating nucleophile (Scheme 2).

Scheme 2

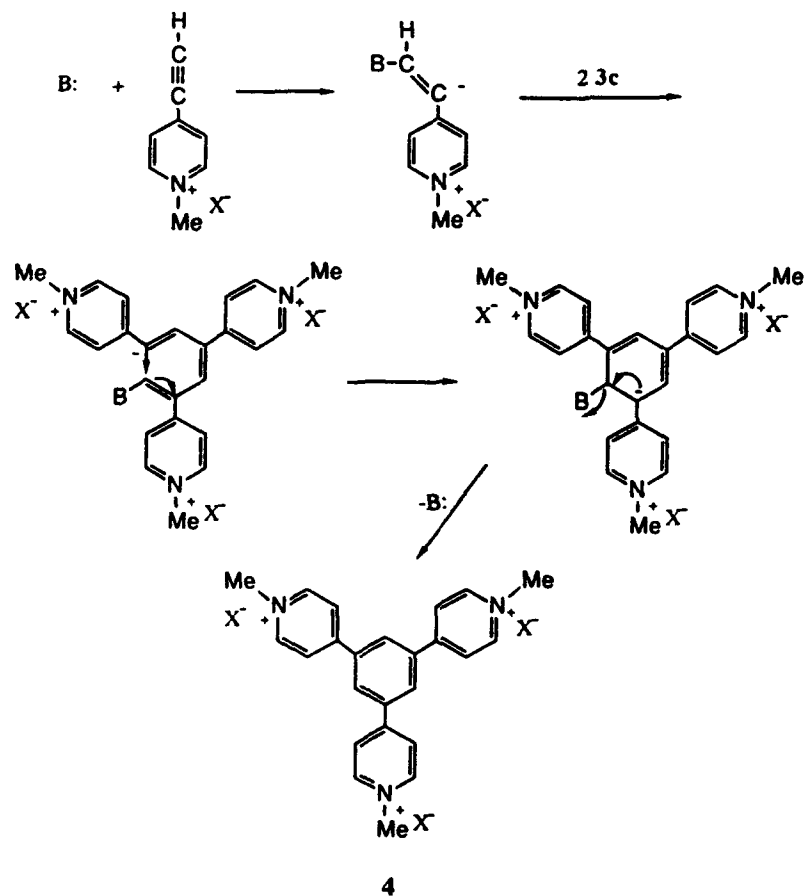


This is supported by the observation that the reaction is much faster in DMSO and water than in acetonitrile. Due to their greater ability to stabilize protons, DMSO and water promote dissociation of 3c and, thus, will increase the concentration of 6. All of our observations are consistent with the mechanism of trimerization of 3c as shown in Scheme 3; i.e., nucleophilic addition of a base B: to the β carbon of 3c which yields a vinyl anion. The vinyl anion then adds to two 3c ions in consecutive steps. A cyclization of the trimeric intermediate and an elimination of base furnish 4.

Further study of the polymerization of N-alkylated ethynylpyridinium salts is currently in progress and the results will be reported elsewhere.

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Scheme 3



4

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