Chemistry of Heterocyclic Compounds, Vol. 45, No. 5, 2009

UNUSUAL REACTION OF 7-METHYL-1,3,7-TRIAZAPYRENIUM SALTS WITH AQUEOUS $K_3[Fe(CN)_6]$ SOLUTION

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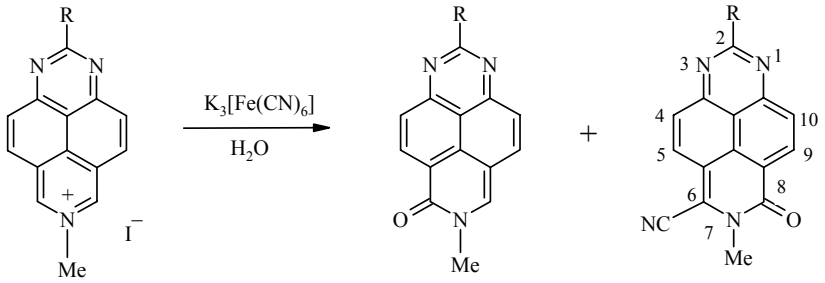
Keywords: 7-methyl-1,3,7-triazapyrenium salts, nucleophilic cyanation, oxidative hydroxylation.

We have previously reported the synthesis and oxidative hydroxylation of 1-alkyl- and 7-alkyl-1,3,7-triazapyrenium salts [1]. In the system KOH–$K_3[Fe(CN)_6]$–H_2O the 2-oxo- and 6-oxo derivatives respectively are formed.

The starting point for this work arose from the fact that dissolving the 7-methyl-1,3,7-triazapyrenium iodide (**1a**) in water was accompanied by a bright-red coloration. A similar characteristic is noted for the products of nucleophilic addition at position 6(8) of 7-alkyl-1,3,7-triazapyrenium salts having a quinoid azadienonamine structure. With the increased π-deficiency of cation **1a** in mind it would be logical to propose that the role of nucleophile is played by water in this case to give the corresponding pseudobase. If so, in the presence of an oxidant the result of the reaction could be the desired product of oxidative hydroxylation, i.e. 7-methyl-6-oxo-6,7-dihydro-1,3,7-triazapyrene (**2a**). In fact compound **2a** was obtained by heating salt **1a** at 75-80ºC with excess aqueous $K_3[Fe(CN)_6]$ solution. However, in addition, the 6-cyano-7-methyl-8-oxo-7,8-dihydro-1,3,7-triazapyrene (**3a**) was also unexpectedly separated from the reaction mass.

The 2,7-dimethyl-1,3,7-triazapyrenium salt (**1b**) reacted similarly to give the amide **2b** and cyanoamide **3b**.



1a,b **2a** (73%), **b** (70%) **3a** (15%), **b** (17%)

1–3 a R = H, **b** R = Me

This indicates that the cyanide ion, present in small concentration but considerable more nucleophilic, competes successfully with the water molecules during the course of addition to the substrate cation. Since it appears that the cyano derivatives **3a,b** are not formed under the same conditions from amides **2a,b** the

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Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 780-782, May, 2009. Original article submitted January 21, 2009.

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formation of these compounds is the result of two parallel processes. The mechanism of the formation of compounds **3a,b** likely includes a stepwise addition of the nucleophiles to the cation **1** and subsequent oxidation, cyanide being added in the first step and water in the second. When MnO_2 is used in place of $K_3[Fe(CN)_6]$ in the reaction of salt **1a** with water the amide **2a** is formed exclusively.

^{1}H NMR spectra were recorded on a Bruker WP-200 (200 MHz) instrument with TMS as internal standard, the signal assignments being carried out using a double resonance method. IR spectra were obtained on a Varian 800 FT-IR (thin film) and mass spectra on an MX-1321A instrument.

Preparation of Compounds 2a,b and 3a,b (General Method). Salt **1a** or **1b** (1 mmol) was added portionwise with stirring over 10 min to an aqueous solution of $K_3[Fe(CN)_6]$ (10%) heated to 75-80ºC. Stirring was continued for 1 h, the mixture was extracted with butanol (3×20 ml), the extract was washed with a small amount of water, and evaporated *in vacuo*. Further separation of the products was carried out using dry flash chromatography [2] on silica gel eluting the first fraction with ethyl acetate and the second with a mixture of ethyl acetate and alcohol (1:1). Evaporation of solvent gave compounds **3a,b** from the first fraction and compounds **2a,b** from the second.

7-Methyl-6-oxo-6,7-dihydro-1,3,7-triazapyrene (2a). Yield 0.171 g (73%). Yellow crystals, mp 260-262ºC (butanol). IR spectrum, ν, cm^{-1}: 1648 (C=O), 1560 (ring). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 3.85 (3H, s, CH_3); 7.41, 7.94 (2H, two d, AB system, ^3J = 9.2, H-9,10); 8.11, 8.64 (2H, two d, AB system, ^3J = 8.9, H-4,5); 8.96 (1H, s, H-8); 9.39 (1H, s, H-2). Found, %: C 71.29; H 3.68; N 17.80. $C_{14}H_9N_3O$. Calculated, %: C 71.48; H 3.86; N 17.86.

2,7-Dimethyl-6-oxo-6,7-dihydro-1,3,7-triazapyrene (2b). Yield 0.174 g (70%). Yellow crystals, mp 280-282ºC (butanol). IR spectrum, ν, cm^{-1}: 1643 (C=O), 1556 (ring). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.84 (3H, s, 2-CH_3); 3.84 (3H, s, N–CH_3); 7.37, 7.88 (2H, two d, AB system, ^3J = 8.9, H-9,10); 8.11, 8.63 (2H, two d, AB system, ^3J = 8.9, H-4,5); 8.93 (1H, s, H-8). Found, %: C 72.37; H 4.49; N 17.00. $C_{15}H_{11}N_3O$. Calculated, %: C 72.28; H 4.45; N 16.86.

6-Cyano-7-methyl-8-oxo-7,8-dihydro-1,3,7-triazpyrene (3a). Yield 0.039 g (15%). Bright-yellow crystals; mp 298-300ºC (ethyl acetate). IR spectrum, ν, cm^{-1}: 2221 (C≡N), 1657 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.13 (3H, s, CH_3); 7.78, 8.17 (2H, two d, AB system, ^3J = 9.6, H-5,4); 8.32, 8.92 (2H, two d, AB system, ^3J = 9.0, H-10,9); 9.69 (1H, s, H-2). Mass spectrum, *m/z* (I_{rel}, %): 261 $[M+H]^+$ (16), 260 $[M]^+$ (100), 231 $(M+H–CH_2O)^+$ (10), 207 (31), 190 (14), 44 (60). Found, %: C 69.44; H 3.49; N 21.59. $C_{15}H_8N_4O$. Calculated, %: C 69.23; H 3.10; N 21.53.

6-Cyano-2,7-dimethyl-8-oxo-7,8-dihydro-1,3,7-triazapyrene (3b). Yield 0.046 g (17%). Bright-yellow crystals; mp 220-222ºC (ethyl acetate). IR spectrum, ν, cm^{-1}: 2223 (C≡N), 1643 (C=O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.92 (3H, s, 2-CH_3); 3.95 (3H, s, N–CH_3); 7.68, 8.13 (2H, two d, AB system, ^3J = 9.2, H-5,4); 8.16, 8.72 (2H, two d, AB System, ^3J = 8.9, H-10,9). Found, %: C 69.79; H 3.51; N 20.64. $C_{16}H_{10}N_4O$. Calculated, %: C 70.07; H 3.67; N 20.43.

Oxidative Hydroxylation of 7-Methyl-1,3,7-triazapyrenium Iodide (1a). MnO_2 (0.87 g, 10 mmol) was added to a solution of salt **1a** (0.35 g, 1 mmol) in water (20 ml) and the mixture was refluxed for 1 h. The precipitate was filtered off and the solution was extracted with butanol (3×20 ml). The extract was evaporated to 5 ml volume and the crystals formed after cooling were filtered off to give compound **2a** (0.178 g, 76%). Its IR spectrum was identical with that of a known sample.

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