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SHORT COMMUNICATIONS

Tetrakispyridinium Derivative of Perfluorosuccinic Acid Dimer

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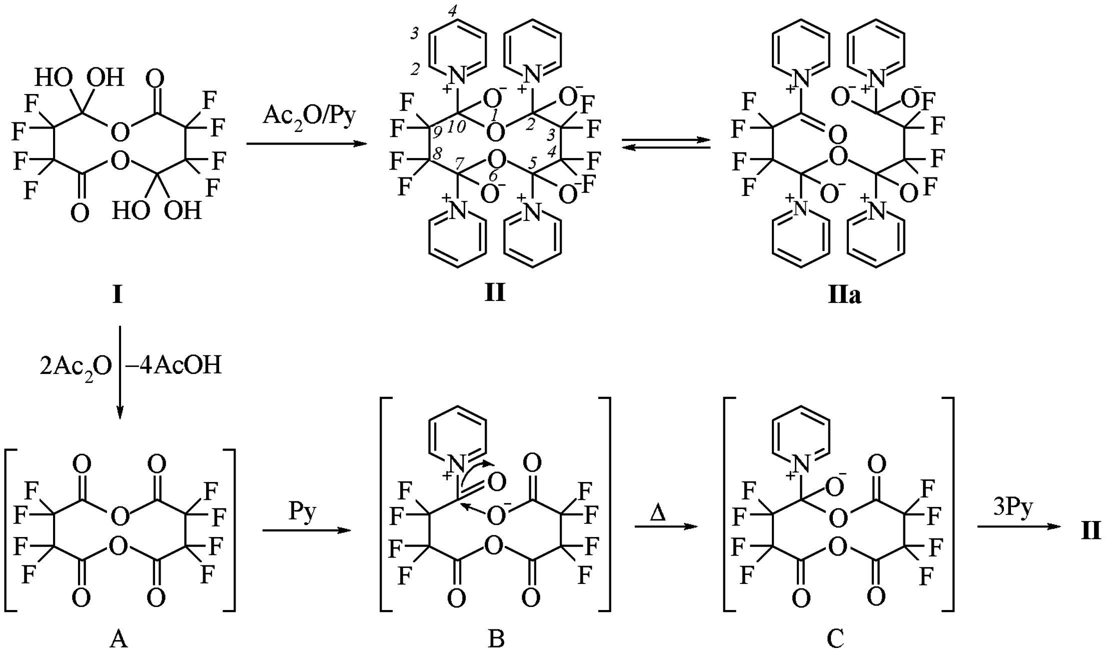
We reported [1] on synthesis of 2.7-dioxo-5,5,10,10-tetrahydroxy-3,3,4,4,8,8,9,9-octafluoro-1,6-dioxacyclodecene (**I**) by ozonolysis of 1-methoxyperfluorocyclobutene dissolved in Freon-113. Compound **I** is a hydrated form of the dimeric anhydride of perfluorosuccinic acid.

It was established that the reaction of compound **I** with acetic anhydride in pyridine yielded its tetrakispyridinium derivatives with the structure of 2,5,7,10-tetrapyridinio-3,3,4,4,8,8,9,9-octafluoro-1,6-dioxacyclodecane-2,5,7,10-tetraoxide (**II**) (see the Scheme).

The structure of compound **II** is confirmed by ^{13}C NMR spectrum containing only two signals from the carbon carcass [triplet of triplets from CF_2 groups (δ_C 111.40 ppm, $^1J_{CF}$ 263.4, $^2J_{CF}$ 30.0 Hz), and a triplet (δ_C 165.14 ppm, $^2J_{CF}$ 26.7 Hz) from the other four carbons of the cycle] that evidences a symmetry in the molecule. The pyridinium groups of compound **II** appear as 3 signals of carbon atoms in the region δ_C 128.20, 144.12, and 146.48 ppm characteristic of the pyridinium cation (cf. [2]). In the ^{1}H NMR spectrum of compound **II** are present 3 signals (2 : 1 : 2) corresponding to the protons of pyridinium groups (8.86 d, J 5.1 Hz; 8.04 d.d, J 5.1 and 7.9 Hz; 8.59 d, J 7.9 Hz). In the IR spectrum of compound **II** appear a strong absorption band in the region ν 1665 cm^{-1} and a less strong at 1750 cm^{-1}. It is presumable that the presence of the latter band evidences the possibility of a reversible conversion of compound **II** into a tautomeric form **IIa** containing a carbonyl group. The increased frequency of the stretching vibrations of the carbonyl group is characteristic of α-halosubstituted amides [3].

Scheme.



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It is presumable that the first stage in compound **II** formation consists in generation of bis-anhydride A that reacts with pyridine to afford *N*-acylpyridinium carboxylate B similarly to the reaction between anhydrides of carboxylic acids with pyridine [4]. Next apparently follows the intramolecular attack of the carboxylate-anion on the carbonyl group to form a cyclic system C. Four-fold succession of this process results in the final reaction product **II**.

To 5 ml of a mixture (2 : 3) of acetic anhydride and pyridine at room temperature was added while stirring 0.73 g (1.92 mmol) of compound **I**. The reaction mixture was stirred for 5 h and left standing for 48 h. The separated precipitate was filtered off and washed with ethyl ether. We obtained 0.99 g (78%) of compound **II**, mp 92–94°C. IR spectrum, cm^{-1}: 3400 (*W*/2 400), 3060 (*W*/2 130), 2980–2400, 2300–2000, 1750, 1665, 1540, 1480, 1380, 1205, 1120, 1100, 970, 800, 750, 710, 700, 680, 630, 595, 530. ^1H NMR spectrum, (300.13 MHz, CD_3OD), δ, ppm (*J*, Hz): 8.04 d.d (8H, $H^{3'}$, *J* 5.1 and 7.9), 8.59 d (4H, $H^{4'}$, *J* 7.9), 8.86 d (8H, $H^{2'}$, *J* 5.1). ^{13}C NMR spectrum (75 MHz, CD_3OD), δ_C, ppm, (*J*, Hz): 111.40 ($C^{3,4,8,9}$, $^1J_{CF}$ 263.4, $^2J_{CF}$ 30.0), 128.20 (8C, $C^{3'}$), 144.12 (8C, $C^{2'}$), 146.48 (4C, $C^{4'}$), 165.14 ($C^{2,5,7,10}$, $^2J_{CF}$ 26.7). Found, %: C 50.48, 50.59; H 3.25, 3.19; N 8.18, 8.34. $C_{28}H_{20}F_8N_4O_6$. Calculated, %: C 50.91; H 3.05; N 8.48.

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