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NOVEL HETEROAROMATIC SYSTEM: THE THIENO[3',4':4,5]THIENO-[2,3-*c*]PYRYLIUM CATION

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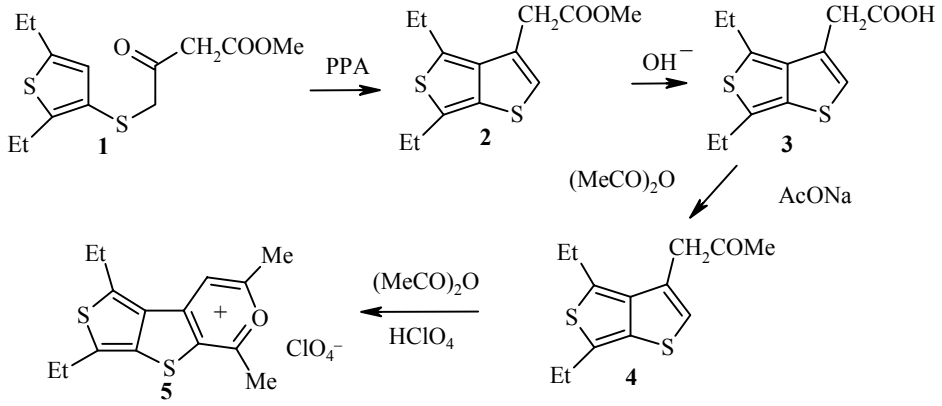
In continuing our work on synthesis of condensed pyrylium salts, we have obtained a novel heterocyclic system: thieno[3',4':4,5]thieno[2,3-*c*]pyrylium perchlorate. To synthesize it, we used an approach that was successfully used earlier for synthesis of thieno[2',3':4,5]thieno[2,3-*c*]- and thieno[2',3':5,4]thieno[3,2-*c*]-pyrylium cations [1]. By cyclization of the methyl ester of γ-(2,5-diethyl-3-thienylmercapto)acetoacetic acid (**1**) in polyphosphoric acid (PPA), we obtained the methyl ester of thieno[3,4-*b*]thiophene-3-acetic acid (**2**). Ester (**2**) was successively converted to thieno[3,4-*b*]-thiophene-3-acetic acid (**3**) and the acetonyl derivative **4**. Heterocyclization of 3-acetonyl-4,6-diethylthieno[3,4-*b*]thiophene (**4**) in the system acetic anhydride – 70% perchloric acid leads to a novel heteroaromatic system: thieno[3',4':4,5]thieno[2,3-*c*]pyrylium perchlorate.



Methyl Ester of γ-(2,5-Diethyl-3-thienylmercapto)acetoacetic Acid (1) was obtained from 2,5-diethyl-3-mercaptothiophene and the methyl ester of γ-chloroacetoacetic acid by the method in [1]. Yield 64%; bp 170-175°C/2 mm Hg. ^{1}H NMR spectrum (DMSO-d_6, 200 MHz), δ, ppm: 1.20 (3H, t, 5-$CH_2\underline{CH_3}$); 1.27 (3H, t, 2-$CH_2\underline{CH_3}$); 2.43 (2H, q, 2-$\underline{CH_2}CH_3$); 2.60 (2H, q, 5-$\underline{CH_2}CH_3$); 3.36 (2H, s, SCH_2); 3.56 (3H, s, $COOCH_3$); 5.55 (1H, s, =CH of the enol form); 6.93 (1H, s, 4-H). Found, %: C 54.3; H 6.4; S 22.1. $C_{13}H_{18}O_3S_2$. Calculated, %: C 54.5; H 6.3; S 22.4.

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Methyl Ester of 4,6-Diethylthieno[3,4-*c*]thiophene-3-acetic Acid (2) was obtained by cyclization of the methyl ester **1** in PPA. Yield 49%; bp 160-165°C/2 mm Hg. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.35 (6H, m, 4-$CH_2\underline{CH_3}$ and 6-$CH_2\underline{CH_3}$); 2.41 (2H, q, 4-$\underline{CH_2}CH_3$); 2.74 (2H, q, 6-$\underline{CH_2}CH_3$); 3.48 (3H, s, $COOCH_3$); 3.60 (2H, s, CH_2); 7.10 (1H, s, 2-H). Found, %: C 58.0; H 6.3; S 24.1. $C_{13}H_{16}O_2S_2$. Calculated, %: C 58.2; H 6.0; S 23.9.

4,6-Diethylthieno[3,4-*c*]thiophene-3-acetic Acid (3) was obtained by hydrolysis of methyl ester **2**. Yield 86%; mp 140-141°C (heptane). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.35 (6H, m, 4-$CH_2\underline{CH_3}$ and 6-$CH_2\underline{CH_3}$); 2.41 (2H, q, 4-$\underline{CH_2}CH_3$); 2.74 (2H, q, 6-$\underline{CH_2}CH_3$); 3.67 (2H, s, CH_2); 7.10 (1H, s, 2-H); 12.10 (1H, s, COOH). Found, %: C 56.5; H 5.4; S 25.5. $C_{12}H_{14}O_2S_2$. Calculated, %: C 56.7; H 5.6; S 25.2.

3-Acetonyl-4,6-diethylthieno[3,4-*c*]thiophene (4) was obtained from acid **3** according to the procedure in [1]. Yield 46%; bp 150-155°C/1 mm Hg. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.35 (6H, m, 4-$CH_2\underline{CH_3}$ and 6-$CH_2\underline{CH_3}$); 2.15 (3H, s, CH_3); 2.41 (2H, q, 4-$\underline{CH_2}CH_3$); 2.74 (2H, q, 6-$\underline{CH_2}CH_3$); 3.66 (2H, s, CH_2); 7.10 (1H, s, 2-H). Found, %: C 61.6; H 6.5; S 25.7. $C_{13}H_{16}OS_2$. Calculated, %: C 61.9; H 6.4; S 25.4.

1,3-dimethyl-5,7-diethylthieno[3',4':4,5]thieno[2,3-*c*]pyrylium Perchlorate (5) was obtained by acylation of **4** with acetic anhydride in the presence of 70% perchloric acid. Yield 64%; mp 180°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.28 (6H, m, 4-$CH_2\underline{CH_3}$ and 6-$CH_2\underline{CH_3}$); 2.65 (2H, q, 4-$\underline{CH_2}CH_3$); 2.85 (2H, q, 6-$\underline{CH_2}CH_3$); 2.90 (3H, s, 3-CH_3); 3.15 (3H, s, 1-CH_3); 7.44 (1H, s, 4-H).

REFERENCES

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