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LETTERS TO THE EDITOR

FRIEDEL–CRAFTS ACYLATION OF 2,5-DIMETHYLTHIOPHENE IN THE PRESENCE OF PYRIDINE

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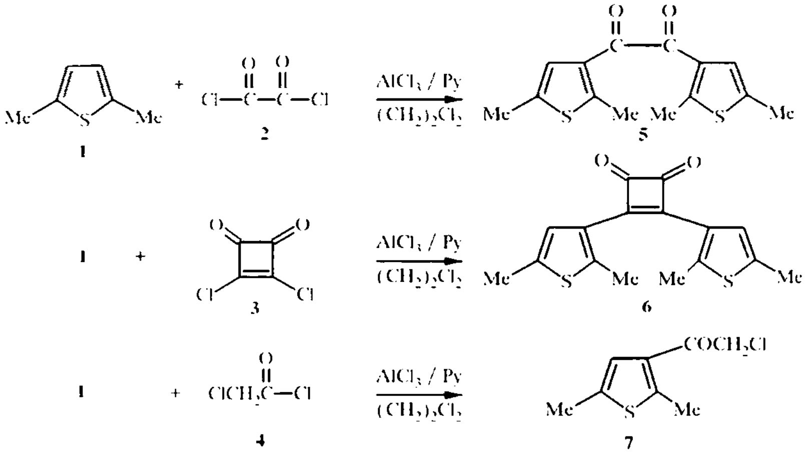
When acylating thiophene and its homologs in the presence of AlCl, about half of the initial compound is bound as a stable σ-complex, the product of α-C-protonation of the thiophene ring, as a result of which the yields of the desired ketones are comparatively low [1]. We have found that the use of pyridine as an acceptor of hydrogen chloride in the Friedel–Crafts acylation of 2,5-dimethylthiophene (**1**) by various acylating agents **2-4** in the presence of aluminum chloride, enabled the synthesis of the corresponding 2,5-dimethylthiophene derivatives in good yield (63-90%).



The role of pyridine evidently includes the destruction of the σ-complex referred to and the possibility of increasing the yields of the desired products. Compounds **5-7** were formed in yields of 18, 22, and 57% respectively under the usual conditions of the Friedel–Crafts reaction without using pyridine. The structure of products **5,6** was confirmed by the results of elemental analysis, mass spectra, and ^{1}H NMR spectra. The ^{1}H NMR spectrum of diketone **6** differs from that given in the patent [2], where there were no data other than the ^{1}H NMR spectrum. The structure of compound **6** was also confirmed by X-ray structural analysis (the data will be published later). Ketone **7** was identical in melting point with that described previously.

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Acid chloride **2-4** (0.105 mol) in dichloroethane (20 ml) was added with stirring and cooling to a suspension of $AlCl_3$ (14 g, 0.105 mol) in 1,2-dichloroethane (30 ml) in a stream of nitrogen. The resulting solution was cooled to -20 to -30°C and 2,5-dimethylthiophene **1** (11.2 g, 0.1 mol) was added dropwise. The reaction mixture was maintained at the same temperature for a further 0.5-1 h, then anhydrous pyridine (0.5 mol) was added, and the reaction mixture was stirred for 1 h. The reaction mixture was brought to room temperature and then processed in the usual way.

Di(2,5-dimethylthienyl)ethanedione (5). Yield 38%; mp 64.5-65.5°C. Mass spectrum, *m/z* (I_{rel}, %): M^+ 278 (100). ^1H NMR spectrum ($CDCl_3$): 2.38 (6H, s, CH_3); 2.73 (6H, s, CH_3); 6.92 ppm (2H, s, $2H_{Het}$). Found, %: C 60.55, 60.58; H 5.20, 5.36; S 22.79, 22.71. $C_{14}H_{14}O_2S_2$. Calculated, %: C 60.40; H 5.07; S 23.03.

1,2-Di(2,5-dimethylthien-3-yl)cyclobutenedione (6). Yield 63%; mp 130-131°C. Mass spectrum, *m/z* (I_{rel}, %): M^+ 302 (100). ^1H NMR spectrum ($CDCl_3$): 2.42 (6H, s, $2CH_3$); 2.50 (6H, s, $2CH_3$); 6.88 ppm (2H, s, H_{Het}). The ^1H NMR spectrum given for compound **6** in patent [2]: 2.41 (6H, s, $2CH_3$); 2.78 (6H, s, $2CH_3$); 7.01 ppm (2H, s, H_{Het}). Found, %: C 63.53; H 4.66; S 20.97. $C_{16}H_{14}O_2S_2$. Calculated, %: C 63.55; H 4.66; S 21.20.

2,5-Dimethyl-3-chloroacetylthiophene (7). Yield 90%; mp 55-56°C. Literature mp 54.5-55°C [1].

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