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SYNTHESIS AND ALKYLATION OF TRIETHYLAMMONIUM 3,5,5-TRICYANO-4,6-DI(2-THIENYL)-1,4,5,6-TETRAHYDRO-PYRIDINE-2-SELENOLATE

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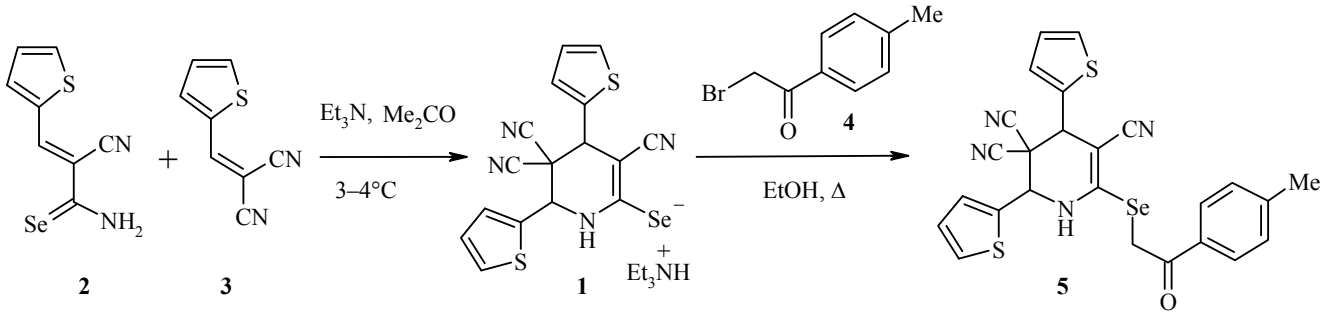
Partially hydrogenated pyridines with selenium substituents form a small class of organic compounds [1, 2]. In the course of our study of cyanoselenoacetamide derivatives [3–5], we have developed a method for the synthesis of a new selenium heterocyclic system, namely, triethylammonium 3,5,5-tri-cyano-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridine-2-selenolate (**1**). 2-Cyano-2-(2-thienyl)methylideneselenoacetamide (**2**) [6, 7] was found to react with (2-thienyl)methylidenemalononitrile (**3**) in the presence of excess triethylamine to give 1,4,5,6-tetrahydropyridine-2-selenolate **1** in 71% yield. This selenolate obtained is readily alkylated by bromide **4** at the selenium atom to give 2-aroylmethylselanyl-1,4,5,6-tetrahydropyridine **5** in 62% yield.



The IR spectra were obtained on an IKS-29 spectrophotometer for samples in vaseline mull. The ^{1}H NMR spectra were taken on a Bruker Avance II 400 spectrometer at 400 MHz in DMSO-d_6 with TMS as internal standard. The elemental analysis was carried out on a Perkin-Elmer C,H,N-analyzer. The purity of the compounds obtained was monitored by thin-layer chromatography on Silufol UV-254 plates with 1:1 acetone–hexane as the eluent with development by iodine vapor and a UV detector. The melting points were determined on a Koffler block and not corrected.

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Triethylammonium 3,5,5-Tricyano-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridine-2-selenolate (1). A mixture of 2-cyano-2-(2-thienyl)methylideneselenoacetamide **2** (0.68 g, 2.8 mmol), (2-thienyl)methylidenemalononitrile **3** (0.45 g, 2.8 mmol), and excess triethylamine (0.58 ml, 4.2 mmol) in acetone (3 ml) was stirred with cooling (3–4°C) under argon until the starting reagents dissolved (about 2–3 min) and left for 24 h at this temperature in an argon atmosphere. The precipitate formed was filtered off and washed with ethanol, acetone, and hexane to give selenolate **1** in 71% yield; mp 139–141°C. IR spectrum, ν, cm^{-1}: 2235, 2175 (C≡N), 3460, 3312, 3257 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.14 (9H, t, ^3J = 6.4, $N(CH_2C\underline{H}_3)_3$); 2.79 (6H, q, ^3J = 6.4, $N(C\underline{H}_2CH_3)_3$); 5.20 (1H, s, H-4); 5.56 (1H, br. s, H-6); 7.10–7.12 (2H, m, 2H-3 thienyl); 7.30 (1H, m, H-4 thienyl); 7.39 (1H, m, H-5 thienyl); 7.51 (1H, m, H-4 thienyl); 7.57 (1H, m H-5 thienyl); 8.10 (1H, br. s, NH). Found, %: C 52.23; H 5.04; N 14.08. $C_{16}H_9N_4S_2Se{\cdot}C_6H_{16}N$. Calculated, %: C 52.58; H 5.01; N 13.94.

3,5,5-Tricyano-2-{[2-(4-methylphenyl)-2-oxoethyl]selanyl}-4,6-di(2-thienyl)-1,4,5,6-tetrahydropyridine (5). A mixture of 1,4,5,6-tetrahydropyridine-2-selenolate **1** (0.4 g, 0.8 mmol) and bromide **4** (0.17 g, 0.8 mmol) in 70% aqueous ethanol (20 ml) was heated at reflux under argon until the starting compounds dissolved (~2–3 min), rapidly filtered through a paper filter, and left for 24 h at room temperature in an argon atmosphere. The precipitate formed was filtered off and washed with ethanol and hexane to give 0.26 g (62%) tetrahydropyridine **5**; mp >358°C (dec.) (1:1 ethanol–acetic acid). IR spectrum, ν, cm^{-1}: 1638 (C=O), 2208, 2248 (C≡N), 3422, 3310, 3242 (NH). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.43 (3H, s, 4-$C\underline{H}_3C_6H_4$); 4.65 (2H, br. s, $SeC\underline{H}_2$); 5.07 (1H, s, H-4); 5.44 (1H, d, ^3J = 1.9, H-6); 6.53 (1H, m) and 6.48 (1H, m, 2H-3 thienyl); 6.79 (1H, m) and 6.58 (1H, m, 2H-4 thienyl); 7.28 (2H, d, ^3J = 8.1, H Ar); 7.62 (1H, m, H-5 thienyl); 7.71 (1H, m, H-5 thienyl); 7.80 (2H, d, ^3J = 8.1, H Ar); 8.17 (1H, br. s, NH). Found, %: C 55.92; H 3.42; N 10.57. $C_{25}H_{18}N_4OS_2Se$. Calculated, %: C 56.28; H 3.40; N 10.50.

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