

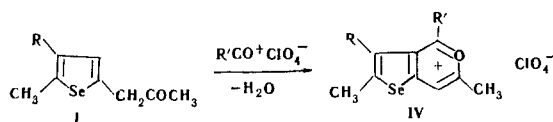
THE SELENOPHENO[3,2-c]PYRYLIUM CATION -
A NEW HETEROAROMATIC SYSTEM

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UDC 547.739.3'812'821

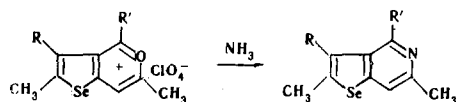
The preparation of thieno-, furano-, and indolopyrylium salts by acylation of the acetyl derivatives of five-membered heterocycles with subsequent cyclization of the diketones formed was recently described in [1-3]. We have shown that this method is also applicable in the selenophene series.

Selenopheno[3,2-c]pyrylium salts (IV), isolable as stable perchlorates, are obtained by the acylation of 5-methyl-2-acetyl derivatives of selenophene (I) with carboxylic acid anhydrides (II) in the presence of equimolecular amounts of perchloric acid (III):



When R = H, the yield of perchlorates is 30-40%. The low yields of products can be explained by the fact that the acylation proceeds equally at the 3- and 4-positions. A confirmation of this assumption is the increase in the yield (65-75%) of selenopheno[3,2-c]pyrylium salts on introduction of an alkyl substituent into the 4-position of the selenophene ring (R = CH₃). The reaction to form IV is carried out at room temperature by the addition to I of a previously prepared mixture of an equivalent amount of III with excess II. The structures of the synthesized IV were confirmed by a study of their IR spectra. The intense band at 1616-1620 cm⁻¹ belongs to the symmetrical stretching vibrations of the pyrylium cation, which served as a proof of the presence of the latter in molecules of the investigated compound. Two intense bands at 1100 and 625 cm⁻¹ are related to the vibrations of the ClO₄⁻ anion.

The selenopheno[3,2-c]pyrylium cation is a new heteroaromatic system that is apparently capable of the conversions characteristic for pyrylium salts [4]. In fact, the previously undescribed selenopheno[3,2-c]pyridines are obtained in good yield by the action of ammonia on the selenopheno[3,2-c]pyrylium salts:



EXPERIMENTAL

2,3,4,6-Tetramethylselenopheno[3,2-c]pyrylium Perchlorate. This was obtained in 70% yield and had mp 163° (from alcohol). Found %: C 39.11; H 4.02; Cl 10.4; Se 23.41. C₁₁H₁₃ClO₅Se. Calculated %: C 38.88; H 3.83; Cl 10.45; Se 23.56.

2,4,6-Trimethylselenopheno[3,2-c]pyrylium Perchlorate. This was obtained in 37% yield and had mp 151° (from n-butanol). Found %: C 36.98; H 3.55; Cl 11.01; Se 23.91. C₁₀H₁₁ClO₅Se. Calculated %: C 36.86; H 3.37; Cl 10.90; Se 24.26.

Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR, Donetsk. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 7, pp. 997-998, July, 1971. Original article submitted September 2, 1970.

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2,3,4,6-Tetramethylselenopheno[3,2-c]pyridine. This was obtained in 69% yield and had mp 81-82° (from hexane). Found %: N 6.12. $C_{11}H_{13}SeN$. Calculated %: N 5.88. The picrate had mp 203-204° (from alcohol). Found %: N 12.36. $C_{17}H_{16}N_4O_7Se$. Calculated %: N 11.99. The hydrochloride was obtained in 91% yield and had mp 315-316° (from acetone). Found %: N 5.02. $C_{11}H_{14}ClSeN$. Calculated %: N 5.1.

2,4,6-Trimethylselenopheno[3,2-c]pyridine. This was obtained in 61% yield and had mp 59-60° (from hexane). Found %: N 6.37. $C_{10}H_{11}SeN$. Calculated %: N 6.25. The picrate had mp 205° (from alcohol). Found %: N 12.41. $C_{16}H_{14}N_4O_7Se$. Calculated %: N 12.36.

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