SALTS OF HETEROAROMATIC CATIONS AND ANIONIC σ COMPLEXES

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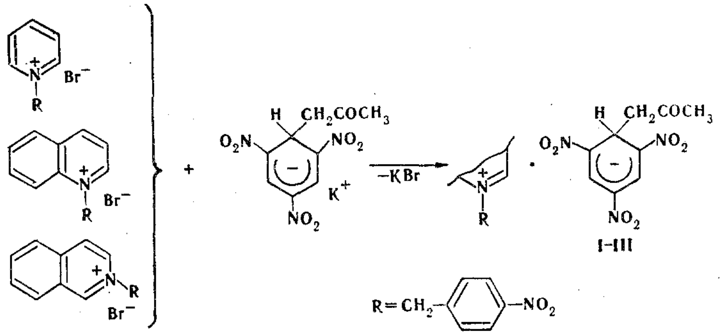
Continuing our study of the nature of the cation–anion reaction in salts of heteroaromatic cations with various anions [1], we obtained the previously undescribed salts of pyridinium and benzopyridinium cations, in which the gegenions are anionic Janovsky σ complexes. Similarly constructed salts of heteroaromatic cations with Meisenheimer hydride complexes were obtained in the reaction of hydride-ion donors, viz., dihydroheteroaromatic compounds, with trinitrobenzene [2]. We have found a more convenient and universal method for the preparation of such compounds by an exchange reaction between salts of heteroaromatic cations and anionic σ complexes:



I-III

Thus by reaction of the Janovsky trinitrobenzene σ complex with 1-(p-nitrobenzyl)-pyridinium bromide at room temperature we obtained the corresponding salt of the Janovsky σ complex with the 1-(p-nitrobenzyl)pyridinium cation (I) with mp 106-107°C and λ_{max} ($\varepsilon \cdot 10^4$) at 260 (2.55), 459 (1.10), and 578 nm (0.90). Salts with the 1-(p-nitrobenzyl)quinolinium cation (II) [mp 69-71°C, λ_{max} ($\varepsilon \cdot 10^4$): 240 (3.92), 265 (2.13), 320 (1.26), 460 (1.09), and 582 nm (0.97)] and the 2-(p-nitrobenzyl)isoquinolinium cation (III) [mp 79-81°C, λ_{max} ($\varepsilon \cdot 10^4$): 233 (3.20), 465 (1.08), and 582 nm (0.84)] were similarly obtained.

The dark-colored crystalline compounds obtained are salts of organic cations and organic anions rather than charge-transfer complexes (CTC), since their UV spectra contain only bands that are characteristic for the pyridinium (260 nm), quinolinium (240, 265, and 320 nm), and isoquinolinium (235 nm) cations and the anionic σ complex (462 and 578 nm) and do not contain any additional charge-transfer bands. Similar electronic spectra were also observed in the case of salts with the Meisenheimer complex [2]. The results of elementary analysis of salts I-III were in agreement with the calculated values.

The formation of salts I-III is the first step in the reaction of heteroaromatic cations with aninoic σ complexes. Farther-proceeding cation–anion interactions with the formation of CTC, ion radicals, covalently bonded adducts of the anions and cations, products of hydride migration, as well as products of nucleophilic alkylation of the heteroaromatic cations by the anionic σ complexes, as we have previously observed in reactions with dinitrobenzene Janovsky σ complexes [3], occur under more severe conditions, depending on the redox potentials of the σ complexes and the heteroaromatic cations.

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NEW METHOD FOR THE PREPARATION OF 2-(1-ADAMANTYL)THIOPHENE

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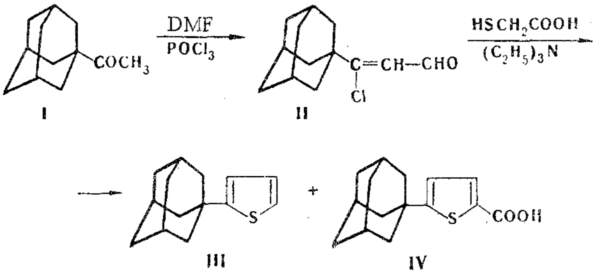
Among the numerous derivatives of adamantane [1] that have been of interest to researchers in the last 20 years owing to their high and diversified biological activity, compounds with a thiophene ring have received rather little study [2, 3]. This is due primarily to the lack of convenient methods for the synthesis of thienyladamantanes. The use of the alkylation of thiophene with bromo-substituted adamantanes in the presence of stannic chloride for this purpose gives a mixture of α- and β-thienyladamantanes in a ratio of 2:1, from which one can isolate individual thienyladamantanes, although additional treatment of the mixture with mercuric chloride and subsequent hydrolysis of the resulting monochloromercuri derivatives are required for this [2].

We have developed a different method for the preparation of individual 2-(1-adamantyl)-thiphene (III), which consists in construction of the thiophene ring on the basis of a functionally 1-substituted adamantane and is illustrated by the following scheme:



A 4.4-g sample of thioglycolic acid was added at 20°C to a solution of 7.5 g of β-(1-adamantyl)-β-chlorovinyl aldehyde (II), obtained in 70% yield by Vilsmeier formylation of 1-acetyladamantane (I), in 30 ml of ethanol, after which 8.7 ml of triethylamine was added at 0-10°C, and the mixture was refluxed for 5 h. It was then worked up, the solvent was removed by distillation, and the residue was subjected to flash chromatography [with a 2 by 25 cm column filled with silica gel (40-100 mesh) by elution with $CHCl_3$—heptane (1:1)] to give 2.67 g (34%) of 2-(1-adamantyl)thiophene (III) with mp 61.5-62°C (mp 62-62.5°C [2]). The aqueous layer, after extraction with ether, was acidified with concentrated HCl to give 0.4 g (4.5%) of 2-(1-adamantyl)thiophene-5-carboxylic acid (IV) with mp 267-269°C (dec., from benzene) (mp 266-268°C [3]). The compositions and structures of II-IV were confirmed by the results of elementary analysis and the IR, PMR, and mass spectra.

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