# REACTION OF 4-METHOXY-1-BENZOPYRYLIUM, -BENZOTHIAPYRYLIUM, AND -BENZOSELENAPYRYLIUM SALTS WITH SOME NUCLEOPHILIC AGENTS

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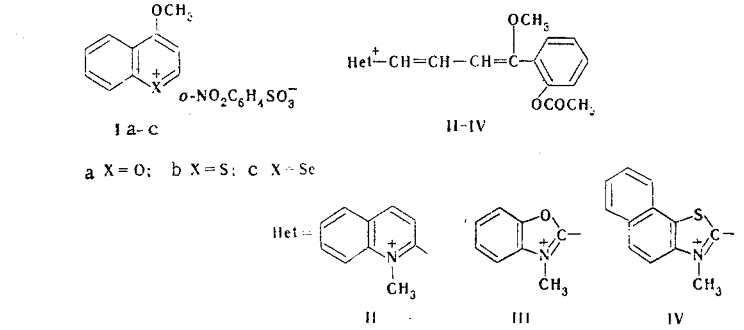
The direction of the reaction of 4-methoxy-1-benzopyrylium salts and their 1-thia and 1-selena analogs with methylene bases formed from methyl-substituted heterocyclic onium salts is qualitatively determined by the nature of the heteroatom. In contrast to the 4-methoxy-1-benzopyrylium salt, which reacts with a nucleophilic agent primarily in the 2 position with cleavage of the O—C bond, the 4-methoxy-1-benzothiapyrylium salt condenses at the 4 position, whereas the 4-methoxy-1-benzoselenapyrylium salt undergoes oxidative condensation at the 2 position. All of the salts react in the same way with dimethylaniline with oxidative condensation at the 2 position.

It has previously been shown [1] that 4-methoxy-1-benzopyrylium o-nitrobenzenesulfonate (Ia) reacts with 2-methylene-3-alkylbenzothiazolines primarily in the 2 position, during which the benzopyrylium ring undergoes reversible cleavage. In addition to this, salt Ia also undergoes condensation at the 4 position. Compounds II-IV were obtained in the present research by reaction of Ia with 1-methylquinaldinium, 2,3-dimethylbenzoxazolium, and 2,3-dimethylnaphtho[2,1-d]thiazolium salts. Consequently, salt Ia reacts in the 2 position with opening of the benzopyrylium ring also with different nucleophilic agents. The reaction to prepare II-IV was carried out in acetic anhydride and was accompanied by acylation of the phenolic hydroxyl group. 4-Methoxy-substituted benzopyrylium salts can also undergo condensation at the 4 position with methylene bases formed from methyl-substituted benzopyrylium salts. A monoethylidynecyanine (V), which was also obtained by alternative synthesis from 4-methyl-7-methoxy-1-benzopyrylium perchlorate and 4-thioflavone, was synthesized by reaction of 4,7-dimethoxy-1-benzopyrylium o-nitrobenzenesulfonate with 4-methylflavylium perchlorate.

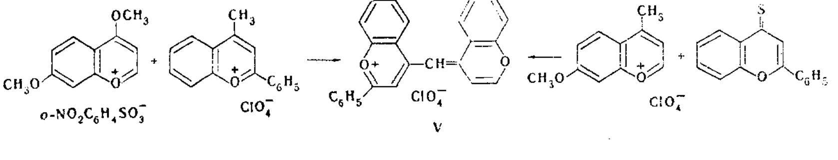


I a-c

II-IV

a X = O; b X = S; c X = Se

II III IV



V

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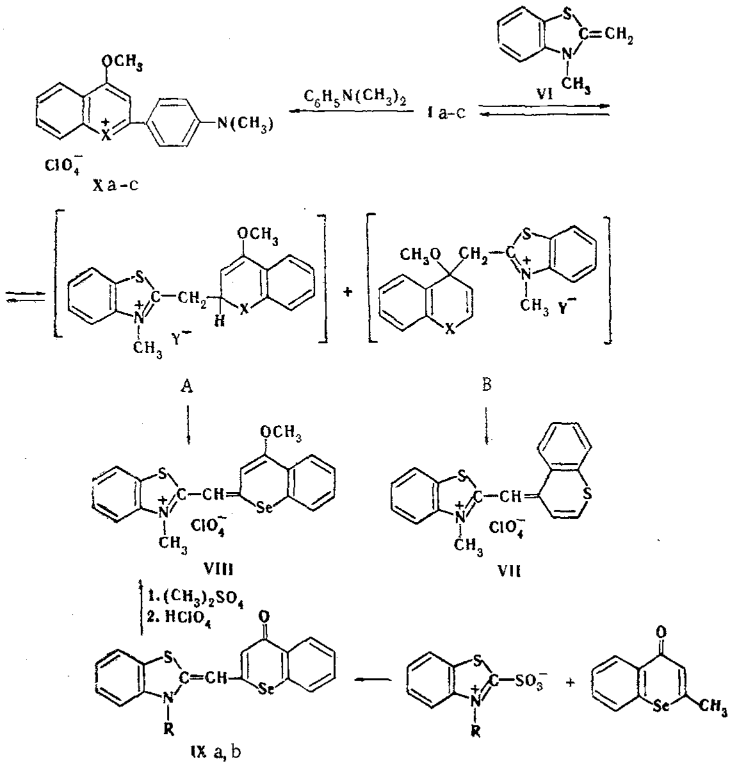
One can also assume attack by the nucleophilic agent [for example, 2-methylene-3-methylbenzothiazoline (VI)] at the 2 and 4 positions for 4-methoxy-1-benzothiapyrylium salt Ib. However, owing to the high stability of the thiapyrylium ring, an intermediate of the A type is not formed. The chief substance formed in the reaction is therefore thiapyrylomonomethylidynecyanine VII [2].

We also investigated the reaction of 4-methoxy-1-benzoselenapyrylium o-nitrobenzenesulfonate (Ic) with 2-methylene-3-methylbenzothiazoline. Salt Ic was obtained by the method used to prepare Ia, b [3] by addition of methyl o-nitrobenzenesulfonate to selenachromone. It was found that the reaction of salt Ic with VI gives a product of a different type than the reaction of salts Ia, b with the same nucleophilic agent. Because of the high tendency of the selenium derivatives to undergo oxidation, an intermediate of the A type, which is formed in the reaction of Ic with VI, is oxidized to a methoxy-substituted monomethylidynecyanine (VIII). The structure of this dye was confirmed by alternative synthesis, which was accomplished as presented in the scheme below. A product of condensation of salt Ic at the 4 position is also evidently formed in addition to monoethylidynecyanine VIII. However, the former could not be isolated in the individual state.



IX a $R=CH_3$; b $R=C_2H_5$

It follows from the data presented above and in [1] that the direction of the reaction of 4-methoxy-1-benzopyrylium salts and their 1-thia and 1-selena analogs with methylene bases formed from methyl-substituted heterocyclic onium salts depends on the nature of the heteroatom. However, the character of the products of the reaction of salts Ia-c also depends on the nature of the nucleophilic agent. It was found that all salts Ia-c react in the same way with dimethylaniline to give, depending on the character of X, products of oxidative condensation at the 2 position (Xa, b [4] and Xc). The reason for the latter apparently consists in the tendency for the formation of compounds maximally stabilized by conjugation, which would be sterically hindered in the case of substitution in the 4 position.

## EXPERIMENTAL

The electronic spectra of ethanol solutions of II-IV and VIII and acetonitrile solutions V and Xc were measured.

4-Methoxy-1-benzoselenapyrylium o-Nitrobenzenesulfonate (Ic). A mixture of 0.522 g (2.5 mmole) of selenachromone [5] and 0.542 g (2.5 mmole) of methyl o-nitrobenzenesulfonate was fused at 100° for 2 h, after which the cooled mass was triturated successively with anhydrous acetone and ether and worked up to give Ic, with mp 120° (from $CH_2Cl_2$), in 70% yield.

TABLE 1. Products of the Reaction of 4-Methoxybenzopyrylium Salts and Their Analogs with Nucleophilic Agents

| Compound | mp, °C (crystallization solvent) | Found, % | Empirical formula | Calculated, % | $\lambda_{max}$, nm ($\varepsilon \cdot 10^{-4}$) | Yield, % |
|---|---|---|---|---|---|---|
| II | 193<br>(methanol) | Cl 7,7<br>N 3,9 | $C_{23}H_{22}ClNO_7$ | Cl 7,7<br>N 3,05 | 422 (3,3) | 30 |
| III | 175<br>(methanol) | Cl 7,9<br>N 3,2 | $C_{21}H_{20}ClNO_8$ | Cl 7,9<br>N 3,1 | 401 (2,9) | 31 |
| IV | 223<br>(ethanol) | Cl 7,0<br>S 6,2 | $C_{25}H_{22}ClNO_7S$ | Cl 6,9<br>S 6,2 | 442 (3,5) | 40 |
| V | 251<br>(acetic acid) | Cl 7,3<br>$OCH_3$ 5,8 | $C_{26}H_{19}ClO_7$ | Cl 7,4<br>$OCH_3$ 6,5 | 571 (6,37) | 58 |
| VIII | 231<br>(acetic acid) | Se 16,3<br>$OCH_3$ 6,2<br>Cl 7,0 | $C_{19}H_{16}ClNO_5SSe$ | Se 16,3<br>$OCH_3$ 6,2<br>Cl 7,3 | 478 (5,0);<br>508 (4,7) | 10 |
| IXb | 175<br>(ethanol–water) | Se 20,1 | $C_{19}H_{16}NOSSe$ | Se 20,6 | — | 25 |
| Xc | 199<br>(nitromethane) | Se 13,7<br>N 5,1 | $C_{24}H_{22}N_2O_6SSe$ | Se 13,8<br>N 5,1 | 564 (3,31) | 10 |

2-[4-Methoxy-4-(o-acetoxyphenyl)-1,3-butadien-1-yl]-1-methylquinolinium Perchlorate (II). A mixture of 0.393 g (1 mmole) of 4-methoxy-1-benzopyrylium o-nitrobenzenesulfonate (Ia) and 0.269 g (1 mmole) of 1-methylquinaldinium methylsulfate was heated in a mixture of 3 ml of acetic anhydride, 3 ml of glacial acetic acid, and 0.3 ml of pyridine at 100° for 1 h. The mixture was diluted with ether, and the liberated salt was converted to the perchlorate in methanol solution. The characteristics of this and the remaining newly synthesized compounds are presented in Table 1.

2-[4-Methoxy-4-(o-acetoxyphenyl)-1,3,-butadien-1-yl-3-methylbenzoxazolium Perchlorate (III) and 2-[4-Methoxy-4-(o-acetoxyphenyl-1,3-butadien-1-yl]-3-methylnaptho[2,1-d]thiazolium Perchlorate (IV). These compounds were obtained by the method used to prepare II.

4-[(7-Methoxybenzopyranyl-4-idene)methyl[-2-phenylbenzopyrylium Perchlorate (V). A) This compound was obtained from 4-methylflavylium perchlorate and 4,7-dimethoxy-1-benzopyrylium o-nitrobenzenesulfonate [6] by the method used to prepare the compound without a methoxy group in the 7 position [2].

B) A mixture of 0.262 g (1 mmole) of 4-methyl-7-methoxy-1-benzopyrylium perchlorate [7], 0.24 g (1 mmole) of 4-thioflavone, and 2.5 ml of acetic anhydride was refluxed for 2 min, after which workup gave V in 77% yield.

2-[(4-Methoxy-1-benzoselenapyranyl-2-idene)methyl]-3-methyl]-3-methylbenzothiazolium Perchlorate (VIII). A) A mixture of 0.28 g (0.66 mmole) of salt Ic, 0.088 g (0.54 mmole) of 2-methylene-3-methylbenzothiazoline, and 8 ml of acetic anhydride was heated at 100° for 3 h, after which it was diluted with ether, and the liberated dye was converted to the perchlorate by the addition of 30% perchloric acid to a solution in methanol.

B) A solution of 0.37 g (1 mmole) of IXa, obtained by the method used to prepare IXb, and 1 g (8 mmole) of dimethyl sulfate in 20 ml of xylene was refluxed for 5 min, and the precipitated dye was converted to the perchlorate by the addition of sodium perchlorate to a solution in methanol. The perchlorate was obtained in 74% yield.

2-(3-Ethyl-1-benzothiazolinyl-2-idene)methyl-1-selenachromone (IXb). A mixture of 0.18 g (0.18 mmole) of 2-methylselenachromone and 0.292 g (1.2 mmole) of 3-ethylbenzothiazolium 2-sulfobetaine [8] was heated at 160° for 1 h, after which it was cooled and dissolved in methanol. Ammonium hydroxide was added to the solution, and the product was removed by filtration and crystallized from aqueous alcohol.

4'-Dimethylamino-4-methoxyselenaflavylium o-Nitrobenzenesulfonate (Xc). A mixture of 0.426 g (1 mmole) of salt Ic and 0.12 g (1 mmole) of dimethylaniline was heated in 1 ml of acetic anhydride at 100° for 1 h, after which the resulting dye was removed by filtration.

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# SYNTHESIS, STRUCTURE, AND STEREOCHEMISTRY OF 2-ALKYL-4,4,5-TRIMETHYL- AND 2-ALKYL-4,4,6,6-TETRAMETHYL-1,3-DIOXANIUM PERCHLORATES

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A number of 2-alkyl-4,4.5-trimethyl- and 2-alkyl-4,4,6,6-tetramethyl-1,3-dioxanium perchlorates were obtained by acylation of 1,3-diols in the presence of 70% perchloric acid. Acid-catalytic cleavage of the heteroring with subsequent cyclization to 2-alkyl-1,3-dioxanium perchlorates occur in the reaction of 2-aryl(alkyl)-substituted and 2-unsubstituted 1,3-dioxanes with carboxylic acid anhydrides and 70% $HClO_4$. Hypothetical detachment of a hydride ion by means of the acceptor acylium cation does not occur under the investigated conditions. The structures of the synthesized perchlorates were studied by PMR spectroscopy and it was shown that 1,3-dioxanium cations at room temperature exist in a state of rapid conformational isomerization of the "chair—chair" form. The rate of interconversion of the 2,4,4-trimethyl-1,3-dioxanium cation decreases appreciably as the temperature is reduced to −90°, as evidenced by marked broadening of the lines of the protons of the gem-dimethyl groupings.

At present little study has been devoted to the synthesis and stereochemistry of nonaromatic carbonium systems. Up until now most attention has been directed to synthesis of 1,3-dioxolanium cations [1, 2]. There are only several communications [3, 4] in the literature regarding 1,3-dioxanium cations; synthesis without a detailed analysis of the structure is illustrated in these communications. Continuing our studies of the stereochemistry of 1,3-dioxanes [5] we studied methods for the synthesis of alkyl-substituted 1,3-dioxanium perchlorates and some of the problems involved in their dynamic stereochemistry.

For this, we obtained 1,3-dioxanium perchlorates by acylation of 1,3-diols in the presence of 70% perchloric acid by the method in [6]; the physical constants of some of these compounds are presented in Table 1. The structures of the salts were confirmed by their IR spectra and were studied in detail by PMR spectroscopy.

To obtain more proof for the structure of the perchlorates we hoped to obtain them by "alternative" synthesis of the corresponding 1,3-dioxanes using a reaction involving detachment of a hydride ion from the 2 position in analogy with the research previously accomplished for dioxolanium salts [7]. For this, a number of 1,3-dioxanes (Table 2) were obtained by condensation of carbonyl-containing compounds with 1,3-diols. Acyl perchlorates were used as the hydride-ion acceptor. Crystalline 1,3-dioxanium perchlorates were isolated after treatment of the 1,3-dioxanes with a mixture of carboxylic acid anhydrides with 70% perchloric acid. Absorption bands at 1537-1585 and 1490-1510 cm$^{-1}$, which are peculiar to the vibrations of the $O-\overset{+}{C}-O-$

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