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REACTION OF 2- AND 4-ALKOXY-1-BENZOPYRYLIUM SALTS WITH METHYLENE BASES OF HETEROCYCLIC CATIONS

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668.819.45:542.953

2-Alkoxy- and 2-alkylthio-1-benzopyrylium salts condense in the 2 position with methylene bases formed from methyl-substituted heterocyclic onium compounds. The 4-methoxy-1-benzopyrylium salt also reacts primarily in the 2 position, during which the benzopyrylium ring is cleaved. In addition, condensation also takes place in the 4 position with splitting out of the methoxy group.

We have previously shown that 4-methoxy-1-benzopyrylium salt I undergoes reaction in the 4 position with methylene bases formed from methyl-substituted heterocyclic oniom compounds to give unsymmetrical monomethylidynecyanines [1]. However, it was subsequently observed that products with a different structure are also formed in addition to the monomethylidynecyanines. The aim of the present research consisted in ascertaining the directions of the reaction of 4-methoxy-1-benzopyrylium salt I and of 2-ethoxy- and 2-ethylthio-1-benzopyrylium salts IIa, b with methylene bases of heterocyclic cations – 2-methylene-3-methylbenzothiazoline and its 3-ethyl analog. Although these compounds exist in solution primarily in the form of dimers, the latter exist in solution in equilibrium with the monomers [2], which also undergo reaction [3].

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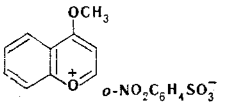

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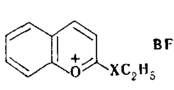
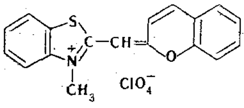


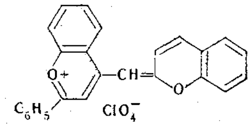
II a, b

a X = O; b X = S

The molecular diagrams of the 2- and 4-hydroxy-1-benzopyrylium cations (A, B), calculated by the MO LCAO method within the Huckel approximation [4], are presented in Fig. 1. A similar electron-density distribution should also be observed in the cations of salts IIa and I. It is apparent from Fig. 1 that the positive π-electron charge is a maximum in the 2 position of both the cations under consideration. Since the positive charge in cation A in the 2 position, to which is attached an easily displaceable group, substantially exceeds the charge in the 4 position (by 0.135), it was natural to expect that salt IIa would react with nucleophilic reagents exclusively in the 2 position. In fact, a (thia)(1-benzo-2-pyrylo)monomethylidynecyanine (III) was obtained in the condensation of IIa, b with 2-methylene-3-methylbenzothiazoline, whereas a (flavylo)(1-benzo-2-pyrylo)monomethylidynecyanine (IV) was obtained in the reaction of IIb with 4-methylflavylium perchlorate. The condensation of salts IIa, b is accompanied by dealkylation, and monomethylidynecyanines of this sort are more conveniently obtained by means of coumarin diethylacetal [5]. The effective positive charge in the 2 position in cation B only slightly exceeds the charge in the 4 position (by 0.037), to which an easily displaceable group is attached. It could therefore be assumed that 4-methoxy-1-benzopyrylium o-nitrobenzenesulfonate (I),

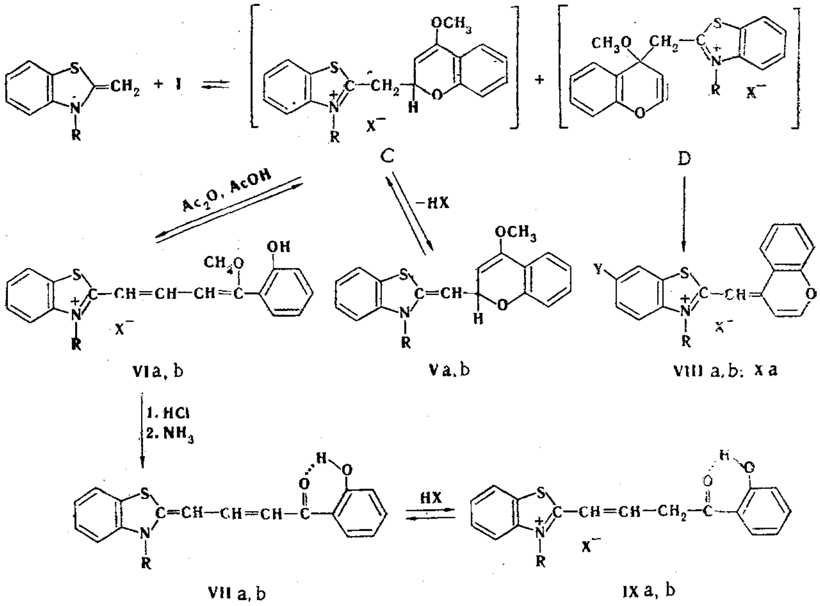


III



IV

in contrast to IIa, would react via two pathways with nucleophilic agents. In fact, it was found that the nature of the products of the reaction between salt I and 2-methylene-3-alkylbenzothiazolines depends on the reaction conditions. Thus if a solution of 2-methylene-3-methylbenzothiazoline in acetic acid is added to a solution of I in acetic anhydride, spontaneous heating is observed, and VIa is isolated. This compound was converted by hydrolysis to dye VIIa, which was previously obtained by reaction of chromone with a 2,3-dimethylbenzothiazolium salt [6]. The UV spectrum of VIa [in ethanol, λ_{max} 433 nm (ε $2.17 \cdot 10^4$)] repudiates the possibility of isomeric structure C. If the same starting compounds are heated at 100° for 1 h in the same mixture of solvents, the only product is monomethylidynecyanine VIIIa [1]. Consequently, the reaction may commence with the approach of the nucleophilic agent at both the 2 and 4 positions of the benzopyrylium cation. In the first case the pyrylium ring is opened to give VIa. In the second case the intermediate (D) splits out a molecule of methanol



V–X a R = CH_3; V–IX b R = C_2H_5; VIII Y = H; X Y = NO_2

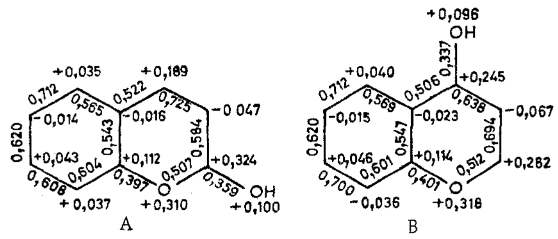


Fig. 1

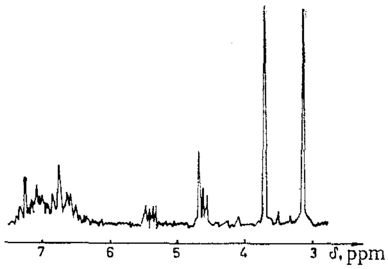


Fig. 2

Fig. 1. Effective π-electron charges and orders of the mobile bonds in the 2-hydroxybenzopyrylium (A) and 4-hydroxybenzopyrylium (B) cations.

Fig. 2. PMR spectrum of 2-[(4-methoxybenzopyran-2-yl)methylene]-3-methylbenzothiazoline (Va) in CCl_4.

and is converted to monoethylidynecyanine VIIIa. The salt (IXb) of base VIIb was isolated in addition to VIb in the reaction between I and 2-methylene-3-ethylbenzothiazoline; the salt is probably formed by dealkylation of VIb and subsequent protonation. Owing to the reversibility of the formation of VIa, b, these compounds are converted to monomethylidynecyanines VIIIa, b when they are heated. The reversibility of the formation of VI is in agreement with a crossover reaction. When VIb was heated in acetic anhydride with 2,3-dimethyl-6-nitrobenzothiazolium o-nitrobenzenesulfonate, a nitro-substituted monomethylidynecyanine (Xa) was formed. Intermediates C, formed by the addition of the nucleophilic agent to the 2 position of salt I, should exist in equilibrium with 2H-chromenes (Va, b). In fact, the latter were isolated by treatment of VIa, b with ammonia. Chromenes Va, b are relatively unstable. A solution of Va in carbon tetrachloride was prepared without heating for the measurement of the PMR spectrum. The PMR spectrum of Va (Fig. 2) contains a multiplet at 7 ppm due to the absorption of aromatic protons and two singlets at 3.10 and 3.65 ppm of the $N-CH_3$ and OCH_3 groups, respectively. In addition, the quartet of a proton in the α position of the chromene ring is observed in the spectrum at 5.32-5.47 ppm. The signal is split owing to coupling with two nonequivalent protons – β-H of the chromene ring and the proton of the CH group connecting the heterocyclic residues. The triplet at 4.55-4.67 ppm is the superimposition of two doublets corresponding to the signals of the protons of β-H and the same CH group. Proceeding from the theoretical relationship between the J_{AB} spin–spin coupling constants (SSCC) and torsion angle φ, for the $>CH_A-CH_B<$ structure [7], it should be concluded that the doublet with J = 4 Hz corresponds to the signal of the β-H proton and the doublet with J = 8 Hz corresponds to the proton of the CH group connecting the heterocyclic rings. On the basis of the same J value of 8 Hz, it can also be concluded that α-H and the hydrogen atom of the CH group connecting the heterocyclic residues are located in the same plane in the cis position to one another and that consequently the heterocyclic residues in the Va molecule are situated in mutually perpendicular planes.

The examined reaction of 4-methoxy-1-benzopyrylium salt I is similar to the reaction of 4-hydroxycoumarin with aniline, which under mild conditions leads primarily to 2-[3-(anilino)malonyl]phenol, which is converted to 4-anilinocoumarin under more severe conditions [8]. We note that instances in which methoxy-substituted aromatic cations react with nucleophilic agents simultaneously in different directions are also known. Thus 1,3-diethoxyphenalenium tetrafluoroborate reacts with 2-methylene-3-ethylbenzothiazoline to give primarily the product of oxidative condensation at the 6 position, in addition to a small amount of product of condensation at the 1 position [2].

EXPERIMENTAL

The electronic absorption spectra of alcohol solutions of the compounds were measured with an SF-4A spectrophotometer. The IR spectra were recorded with a UR-10 spectrometer. The PMR spectra were measured with a Tesla BS 487B spectrometer with an operating frequency of 80 MHz at 20° with tetramethylsilane as the internal standard. The purity of the preparations was monitored by thin-layer chromatography (TLC) on plates with a fixed layer of Silufol UV-254 silica gel and elution with nitromethane.

2-Ethoxy-1-benzopyrylium Tetrafluoroborate (IIa) [9] and 2-Ethylthio-1-benzopyrylium Tetrafluoroborate (IIb). These compounds were obtained by reaction of 1 g (5 mmole) of triethyloxonium tetrafluoroborate [10] with an equimolar amount of coumarin or 2-thiocoumarin in 1.5 ml of methylene chloride at room temperature. After 24 h, the isolated salt was washed with ether by decantation and stored under a layer of the same solvent because of its high tendency to undergo hydrolysis. The IR spectra of IIa, b, which were determined with solu-

TABLE 1. Transformation Products of 2- and 4-Alkoxy-1-benzopyrylium Salts

Compound	mp, °C	Found, %	Empirical formula	Calculated, %	λ_{max}, nm ($\varepsilon \cdot 10^{-4}$)	Yield, %
III	302	Cl 8,6 S 8,4	$C_{18}H_{14}ClNO_5S$	Cl 9,1 S 8,4	440 (3,62) 465 (4,38) 495 (2,6)	28
IV	240	Cl 7,9 C 67,1 H 4,0	$C_{25}H_{17}ClO_6$	Cl 7,9 C 66,9 H 3,8	526 (4,75) 567 (9,62)	26
Va	137	N 4,5 S 9,9	$C_{19}H_{18}NO_2S$	N 4,4 S 9,9		71
Vb	135	S 9,5	$C_{20}H_{19}NO_2S$	S 9,8		77
VIa	239	Cl 8,1 S 7,8	$C_{19}H_{18}ClNO_6S$	Cl 8,4 S 7,6	433 (2,17)	54
VIb	193	C 54,7 H 4,6 Cl 8,1 N 3,3 S 7,4 OCH_3 7,1	$C_{20}H_{20}ClNO_6S$	C 54,9 H 4,6 Cl 8,1 N 3,2 S 7,3 OCH_3 7,1		49

tions in methylene chloride, do not contain the frequencies corresponding to the stretching vibrations of the C = O group of coumarin (1705 cm^{-1}) or the C = S group of 2-thiocoumarin (1205 cm^{-1}). Bands at 1610-1640 and 1000 cm^{-1}, related, respectively to the symmetrical stretching vibrations of the pyrylium ring [11] and the BF_4^- anion, are observed in the spectra of both compounds. In addition, a band at 1240 cm^{-1}, which is related to the vibrations of an ether bond, is observed in the IR spectrum of IIa. UV spectrum of IIb in acetonitrile: λ_{max} 375 nm (ε $1.84 \cdot 10^4$) and a shoulder at 387 nm (ε $1.65 \cdot 10^4$).

2-[2(2H-Chromen-2-ylidene)methyl]-3-methylbenzothiazolium Perchlorate (III). A solution of 0.8 g (5 mmole) of 2-methylene-3-methylbenzothiazoline [12] and 1.4 g (5 mmole) of salt IIb in a mixture of 4 ml of acetic anhydride and 0.8 ml (13 mmole) of glacial acetic acid was heated at 100° for 1 h, after which a solution of sodium perchlorate in acetic acid was added, and the dye was removed by filtration and washed with water, alcohol, benzene, and ether.

The characteristics of this compound and the remaining newly synthesized compounds are presented in Table 1.

2-Phenyl-4-[(2H-chromen-2-ylidene)methyl]-1-benzopyrylium Perchlorate (IV). A solution of 0.6 g (2.1 mmole) of IIb and 0.64 g (2 mmole) of 4-methylflavylium perchlorate in 10 ml of acetic anhydride was heated at 100° for 1 h, after which the dye was removed by filtration, reprecipitated twice from methanol by the addition of 30% perchloric acid, and washed with glacial acetic acid.

Reaction of 4-Methoxy-1-benzopyrylium o-Nitrobenzenesulfonate (I) with 2-Methylene-3-ethylbenzothiazoline. A solution of 2 g (11 mmole) of 2-methylene-3-ethylbenzothiazoline in 3.3 ml (55 mmole) of glacial acetic acid was added to a heated (on a water bath) solution of 4.9 g (15 mmole) of salt I in 17 ml of acetic anhydride. The product was removed by filtration without cooling, recrystallized from methanol, and converted to the perchlorate in the same solvent. 2-[4-Methoxy-4-(o-hydroxyphenyl)-1,3-butadien-1-yl]-3-ethelbenzothiazolium perchlorate was isolated in this way. After separation of VIb from the reaction mixture, the mother liquor was cooled to 0°, and the precipitated 2-[3-(o-hydroxybenzoyl)-1-propen-1-yl]-3-ethylbenzothiazolium o-nitrobenzenesulfonate (IXb) was removed by filtration and recrystallized from acetic anhydride – glacial acetic acid to give a product with 189° in 16% yield. The perchlorate, [mp 198° (dec.)], obtained from this compound in acetic acid solution, was identical to the perchlorate obtained by the addition of perchloric acid to an acetic acid solution of base VIIb [6].

Compound VIa was obtained in the form of the perchlorate by the method used to prepare VIb.

2-[(4-Methoxy-2H-chromen-2-yl)methylene]-3-methylbenzothiazoline (Va). A 0.34-g sample of VIa was shaken in a separatory funnel with a mixture of 30 ml of benzene and 30 ml of water containing 8 ml of concentrated ammonium hydroxide, after which the benzene solution was separated and washed with water. The benzene was removed by vacuum distillation with a water aspirator at room temperature, and the residue was triturated successively with ether and methanol, and the solid material was removed by filtration.

Compound Vb was obtained by the method used to prepare Va.

2-[3-(o-Hydroxybenzoyl)allylidene]-3-ethylbenzothiazoline (VIIb). A 0.54-g sample of VIb was heated in a mixture of 4 ml of methanol and 2 ml of 10% hydrochloric acid for 5 min, after which the mixture was cooled and neutralized with ammonia. The product was removed by filtration to give a material with mp 188° in 50% yield. No melting point depression was observed for a mixture of this product with the compound obtained by reaction of chromone with 2-methyl-3-ethylbenzothiazolium p-toluenesulfonate [6].

2-[(4H-Chromen--4-ylidene)methyl]-3-ethylbenzothiazolium Perchlorate (VIIIb) [1]. A) This compound was obtained in 46% yield from I and 2-methylene-3-ethylbenzothiazoline by the method in [12].

B) A 0.6-g (12 mmole) sample of o-nitrobenzenesulfonate IVb was heated in a mixture of 4 ml of acetic anhydride and 0.8 ml (13 mmole) of glacial acetic acid at 100° for 2 h. The mixture was worked up as in [12] to give VIIIb in 32% yield.

2-[(4H-Chromen-4-ylidene)methyl]-3-methyl-6-nitrobenzothiazolium o-Nitrobenzenesulfonate (Xa). This compound was obtained in 65% yield by reaction of 0.6 g (12 mmole) of VIb with 0.6 g (15 mmole) of 2,3-dimethyl-6-nitrobenzothiazolium o-nitrobenzenesulfonate under conditions similar to those in the preparation of VIIIb by method B. With respect to its electronic absorption spectrum and decomposition temperature the dye was identical to the dye obtained in [1].

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