2-BENZOPYRYLIUM SALTS. 42.* ORTHO-QUINOID INTERMEDIATES IN RECYCLIZATION REACTIONS OF 2-BENZOPYRYLIUM SALTS

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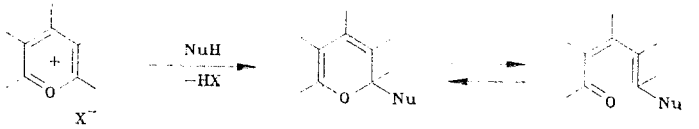
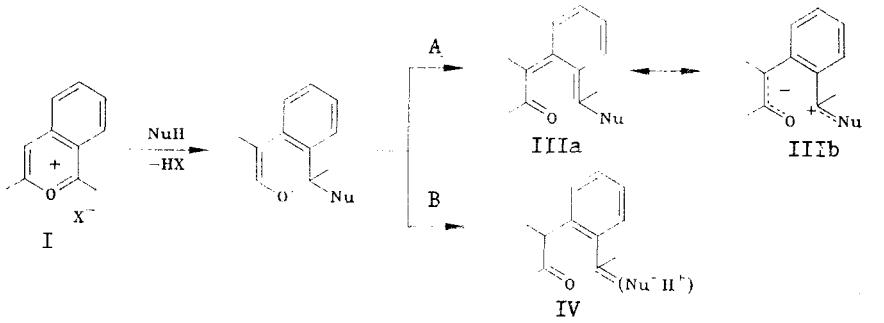
The interaction of 1-styryl-substituted 2-benzopyrylium salts with morpholine, methylamine, and malononitrile is highly stereoselective in forming cis-3,4-dihydronaphthalenes; this can be taken as evidence that ortho-quinoid intermediates participate in these conversions.

It is generally accepted [2, p. 67] that the opening of the hetero ring in adducts of monocyclic pyrylium salts with various nucleophiles, which proceeds quite readily even under thermal conditions, is accomplished through an electrocyclic mechanism.



If an analogous process is realized in the series of benzo[c]annelated pyrylium salts I (2-benzopyrylium salts), the reaction must be accompanied by an energetically unfavorable breakdown of aromaticity of the annelated ring (path A):



On this basis, Dimroth and Odenwalder [3] stated that for 2-benzopyrylium salts under thermal conditions, the only possible recyclization reactions are those in which it is possible to avoid the formation of *ortho*-quinoid intermediates of the type of III. In their opinion, this can be achieved if the nucleophile that has been added contains a mobile hydrogen atom (path B). Unfortunately, possible mechanisms for the formation of type IV intermediates were not examined in [3] or in similar studies [4, 5].

The above statement is contradictory to the known smooth course of the recyclization reaction of 2-benzopyrylium salts with secondary amines [6], which includes the formation of the adducts II (Nu = NR^1R^2), which are incapable of deprotonation. From these data we could postulate that formation of *ortho*-quinoid intermediates of the type of III is still possible not only under exposure to radiation [7], but also under thermal conditions, if their resonance stabilization is favored by an unshared electron pair on the α-atom of the added nucleophile (IIIb). Also, this pair will obviously facilitate the opening of the isochromene ring in the adducts II.

*For Communication 41, see [1].

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TABLE 1. Characteristics of Compounds V-XIV

Compound*	Empirical formula	mp, °C*	IR spectrum, cm^{-1}	PMR spectrum, ppm (J, Hz)**	Yield, %
V	$C_{24}H_{19}ClO_6$	194...196	1620, 1605, 1100	3,25 (m OCH_3); 6,33...6,49 (m 2H); 6,77...7,97 (m 14H arom.)	68
Va	$C_{27}H_{25}ClO_9$	290...293	1620, 1600, 1100	3,17 (s, $2OCH_3$); 3,37 (s, OCH_3); 3,45 (s, OCH_3); 6,32...7,07 (m, 2H and 11H arom.)	96
Vb	$C_{28}H_{27}ClO_9$	226...228	1620, 1600, 1100	2,35 (s, CH_3); 3,57 (s, OCH_3); 3,60 (s, OCH_3); 3,65 (s, OCH_3); 3,82 (s, OCH_3); 6,70...7,90 (m, 1H and 11H arom.)	65
VIb	$C_{32}H_{35}NO_6$	171...172	1633, 1605, 1585	1,75 (s, CH_3); 2,77...2,95 (m, $2CH_2$); 3,57...3,77 (m, $2CH_2$); 3,82 (s, $3OCH_3$); 3,87 (s, OCH_3); 6,12 (s, 1H); 6,57 (s, 1H); 6,67...7,42 (m, 10H arom)	92
VIIa	$C_{31}H_{33}NO_6$	165...168	1665, 1620, 1590	2,77...3,07 (m, $2CH_2$); 3,60...3,75 (m, $2CH_2$); 3,65 (s, OCH_3); 3,67 (s, OCH_3); 3,72 (s, OCH_3); 3,80 (s, OCH_3); 4,20 (d.d 3-H, $J_{3,4}=7,0$; $J_{3,2}=3,0$); 4,80 (d, 4-H, $J_{4,3}=7,0$); 5.12 (d, 2-H, $J_{2,3}=3,0$); 6,56 (s, 1H arom); 6,58 (d 1H, $J=9,0$ arom.); 6,99...7,15 (m, 8H arom.)	90
VIIb	$C_{32}H_{35}NO_6$	203...205	1670, 1625, 1595	1,86 (s, CH_3); 3,12...3,21 (m $2CH_2$); 3,54 (d, 3-H, $J_{3,4}=7,0$); 3,72 (s, OCH_3); 3,81...3,91 (m $2CH_2$); 3,93 (s, OCH_3); 3,99 (s, $2OCH_3$); 5,43 (d, 4-H, $J_{4,3}=7,0$); 6,81...7,74 (m, 10H arom.)	82
VIIc	$C_{24}H_{27}NO_4$	197...198	1700, 1625, 1605, 1580	1,80 (s, CH_3); 2,55...2,79 (m, CH_2); 3,00...3,24 (m, CH_2); 3,69...3,87 (m, $2OCH_3$, $2CH_2$ and 4-H); 4,18 (d.d, 3-H, $J_{3,4}=7,0$; $J_{3,2}=2,5$); 5,25 (d, 2-H, $J_{2,3}=2,5$); 6,51 (s, 1H arom.); 7,11 (s, 1H arom.); 7,23 (s, 5H arom.)	73
VIIIa	$C_{31}H_{33}NO_6$	115...117	1670, 1620, 1590	2,73...2,97 (m, $2CH_2$); 3,70 (s OCH_3); 3,90 (s, OCH_3); 3,93 (s, OCH_3); 3,96 (s, OCH_3); 3,81...4,11 (m, $2CH_2$ and 3-H); 4,80 (d, 4-H, $J_{4,3}=7,0$); 5,10 (d, 2-H, $J_{2,3}=5$); 6,46 (s, 1H arom.); 6,91 (d, 1H, $J=9,0$, arom.); 7,18...7,25 (m, 6H arom.); 7,53 (s, 1H arom.); 7,71 (d, 1H, $J=9,0$, arom.)	90
VIIIb	$C_{32}H_{35}NO_6$	177...179	1670, 1625, 1595	1,75 (s, CH_3); 3,10...3,22 (m, $2CH_2$); 3,65 (m, OCH_3); 3,67...3,80 (s, $2CH_2$); 3,85 (s, OCH_3); 3,90 (s, $2OCH_3$ and 3-H); 4,55 (s, 4-H); 6,37 (s, 1H arom.); 6,92 (d, 1H, $J=9,0$, arom.); 7,12 (s, 5H arom.); 7,35 (s, 1H arom.); 7,50 (s, 1H arom.); 7,67 (d, 1H, $J=9,0$, arom.)	85
IXa	$C_{27}H_{26}O_6$	223...224	1665, 1660, 1595	2,57 (d.d, 2-H, $J_{2,2'}=16,0$; $J_{2,3}=2,5$); 3,52...3,90 (m, $4OCH_3$, 2-H and 3-H); 5,02 (d, 4-H, $J_{4,3}=4,0$); 6,38 (s, 1H, arom.); 6,50 (d, 1H, $J=9,0$, arom.); 6,98...7,05 (m, 7H arom.); 7,50 (s, 1H arom.)	78

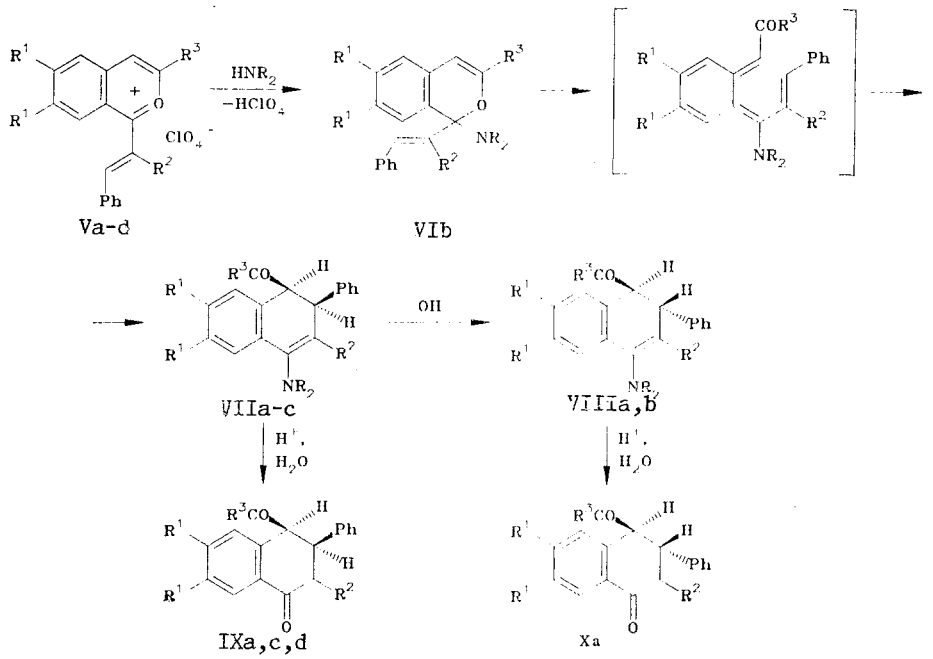
IXc	$C_{20}H_{20}O_4$	123...125	1710, 1675, 1600	1,65 (s, CH_3); 2,67 (d.d. 2-H, $J_{2,2'}=16,5$; $J_{2,3}=4,0$); 3,48 (d.d. 2H', $J_{2',2}=16,5$; $J_{2',3}=14,0$); 3,63...3,87 (m, $2OCH_3$ и 3-H); 4,29 (d, 4-H, $J_{4,3}=4,5$); 6,51 (s, 1H arom.); 7,14...7,29 (m, 5H arom.); 7,56 (s, 1H arom.)	91
IXd	$C_{24}H_{20}O_3$	166...167	1675, 1665, 1600	2,79 (d, 2-H, $J_{2,2'}=14,0$); 3,74...3,90 (m OCH_3, 2-H and 3-H); 5,25 (d, 4-H, $J_{4,3}=4,0$); 6,75 (d, 2H, $J=9,0$, arom.); 7,23 (s, 5H arom.); 7,41...7,53 (m, 3H arom.); 7,62 (d, 2H, $J=9,0$, arom.); 8,22...8,31 (m, 1H arom)	60
Xa	$C_{27}H_{26}O_6$	193...195	1670, 1660, 1595	2.73...3,18 (m, CH_2); 3,60...3,82 (m, $4OCH_3$ 3-H); 5,07 (d, 4-H, $J_{4,3}=8,0$); 6,33 (s, 1H, arom.); 6,77 (d, 1H, $J=9,0$, arom); 7,01...7,07 (m, 6H arom.); 7,37 (d, 1H, $J=9,0$, arom.); 7,50 (s 1H arom.)	80
Xc	$C_{20}H_{20}O_4$	171...172	1710, 1670, 1600	2,04 (s, CH_3); 2,61...3,06 (m, CH_2); 3,57...3,87 (m, $2OCH_3$ and 3-H); 4,17 (d 4-H, $J_{4,3}=8,5$); 6,36 (s, 1H arom.); 7,14 (s, 5H arom.); 7,53 (s, 1H arom.)	55
XII	$C_{28}H_{29}NO_5$	227...229	1675, 1625, 1595	2,88 (d.d 2-H, $J_{2,2'}=16,0$; $J_{2,3}=4,5$); 3,36 (s, CH_3); 3,45...3,93 (m, $4OCH_3$, 2-H' and 3-H); 5,04 (d, 4-H, $J_{4,3}=4,0$); 6,42 (s, 1H arom.); 6,66 (d, 1H, $J=9,0$, arom.); 7,14...7,29 (m, 7H arom.); 7,92 (s, 1H. arom)	87
XIV	$C_{30}H_{26}N_2O_5$	220...222	2206, 1665, 1600	3,15...3,80 (m, $4OCH_3$, CH_2 and 2-H); 4,80 (d, 1-H, $J_{1,2}=4,0$); 6,45 (s, 1H, arom.); 6,62 (d, 1H, $J=9,0$, arom.); 6,98...7,05 (m, 7H arom); 7,81 (s, 1H arom.)	85
XIII	$C_{21}H_{22}ClNO_6$	241...243	1625, 1610, 1563, 1100	2,73 (m, CH_3); 3,84 (d, CH_3); 4,02 (d, OCH_3); 4,11 (s, OCH_3); 7,14 (d, 1H, $J=15,0$); 7,32...7,83 (m, 1H 8H arom.)	35

*Salts Va, b, d and XIII were purified by recrystallization or by washing out from acetic acid, the other compounds from ethanol.

**The PMR spectra of the salts Va, b, d were measured in CF_3COOH, XIII in CD_3CN, other compounds in $CDCl_3$.

In order to confirm the possibility that *ortho*-quinoid intermediates participate in thermal recyclizations of 2-benzopyrylium salts, we investigated conversions of the 1-styryl-substituted derivatives Va-d. Their double bond should play the role of an intramolecular trap for any *ortho*-quinoid intermediate that would appear after opening the hetero ring. The resulting hexatriene fragment, in accordance with the rules of preservation of orbital symmetry [8, p. 82], as a result of disrotator cyclization, would be converted to a derivative of *cis*-dihydronaphthalene.

And, in fact, the interaction of morpholine with the salt Va forms the *cis*-enamene VIIa stereoselectively and with a high yield. The *cis* configuration of the enamene VIIa is confirmed by its facile conversion, upon heating in an alkaline medium (through enolization of the carbonyl group) to the *trans* isomer VIIIa, which is thermodynamically more favorable because of steric considerations (see Table 1).



V—X a $R^1=CH_3O$, $R^2=H$, $R^3=3,4\text{-}(CH_3O)_2C_6H_3$; b $R^1=CH_3O$, $R^2=CH_3$, $R^3=3,4\text{-}(CH_3O)_2C_6H_3$; c $R^1=CH_3O$, $R^2=H$, $R^3=CH_3$; d $R^1=R^2=H$, $R^3=4\text{-}CH_3OC_6H_4$; HNR_2 = morpholine

By means of PMR spectroscopy, specifically on the basis of the SSCC of the 3-H and 4-H protons, it is impossible to assign configurations for the pair of stereoisomeric enamenes VIIa and VIIIa. The two SSCCs are practically identical ($J_{3,4}$ = 7 Hz), corresponding to an angle between the vicinal protons of approximately 25° or 135° [9, p. 337]. As shown by an analysis of molecular models, the 135° value, corresponding to the *trans* isomer, is achieved in a conformation with an equatorial position of the bulky substituents R^3CO and Ph. With axial positions of these substituents, the angle that is of interest to us becomes close to 90°, and the constant $J_{3,4}$ should be quite small. Such a conformation would be preferred if a bulky substituent were present in position 2 of the dihydronaphthalene ring of the enamene VIIIa.

In order to confirm this hypothesis, we carried out analogous conversions with the α-methyl-substituted salt Vb. As had been assumed, the value of $J_{3,4}$ was not changed appreciably for the *cis*-enamene VIIb,* whereas for the trans-isomer VIIIb, the constant could not be registered within the limits of resolution of the instrument.

The introduction of the methyl substituent also affects the stability of the adduct VIb, which can be isolated. Its conversion to the enamene VIIb proceeds smoothly upon thermolysis. If no methyl group is present, the analogous product VIIa is formed rapidly, even in the cold.

The enamenes that are obtained, *cis*-VIIa and *trans*-VIIIa, when heated briefly in aqueous acetic acid, are hydrolyzed, while preserving their configuration, to form the corresponding tetralones *cis*-IXa and *trans*-Xa.

It is evident that substituents can affect the energy of formation of *ortho*-quinoid intermediates and hence the realization of the conversions under investigation. In this connection, we brought into reaction with morpholine the salt Vd, which does not contain any methoxyl groups in the annelated ring. As a result, without intermediate isolation of the enamene, after analogous acid hydrolysis of the reaction mixture, we obtained the *cis*-tetralone IXd

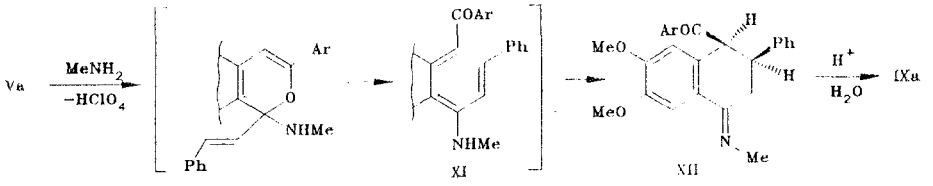
*Any change in conformation of the *cis* isomer is essentially impossible.

with a yield of about 60%. Replacement of the aryl substituent in position 3 of the salt V by a methyl group likewise does not change the course of the reaction. Thus, the salt Vc is converted to the *cis*-enamene VIIc, which is then hydrolyzed to the *cis*-tetralone IXc.

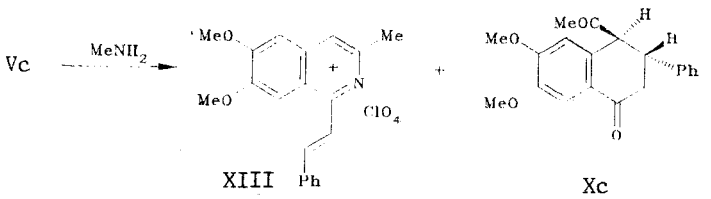
We have also investigated the possibility of forming *ortho*-quinoid intermediates in the interaction of 2-benzopyrylium salts with nucleophiles chosen so that their adducts would contain a hydrogen atom that can be split out. It was considered [3] that the recyclization reactions in this case will proceed without any breakdown of aromaticity of the annelated ring. As such reagents we used methylamine and malononitrile.

The interaction of 1-styryl-3-methyl-2-benzopyrylium salts of the type of V with primary amines had been accomplished previously [10, 11]. In that work, however, only the products of the traditional conversion were recovered — isoquinolinium salts of the type of XIII. The formation of such salts cannot provide any answers to the question that is of interest to us.

In our work, after heating the 3-aryl-substituted salt Va in an aqueous alcohol solution of methylamine, we obtained with a high yield only the product of intramolecular cycloaddition in the imine form XII. In its spectral characteristics this compound is very close to the *cis*-tetralone IXa, to which it is converted by neutral or weakly acetic hydrolysis. The stereoselectivity of formation of the *cis*-imine XII, in our opinion, indicates that closure of the carbocycle, the same as in reactions with morpholine, is a disrotator cyclization of the intermediate XI:



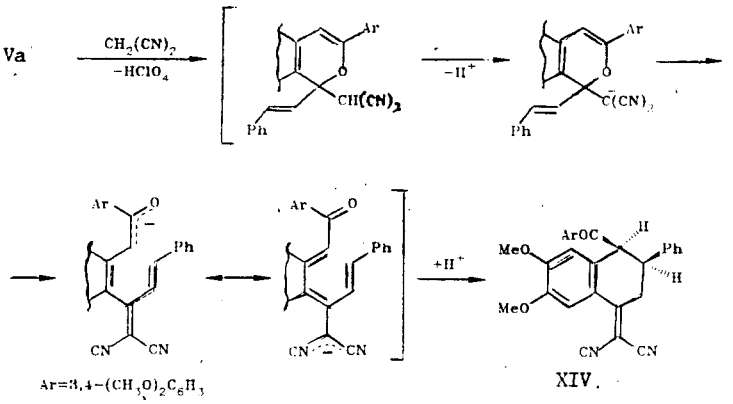
Upon interaction of the 3-methyl-substituted salt Vc with methylamine, regardless of the nature of the solvent, the isoquinolinium salt XIII and the *trans*-tetralone Xc are formed. The recovery of the carbocyclization product in the form of a *trans* isomer with a saponified imino group is probably explained by hydrolysis and inversion of an initially formed compound of the type XII. Since the process of inverting the configuration proceeds through enolization of the endocyclic carbonyl group, its rate will depend on the substituents with this group. Thus, the *cis*-acetyl-substituted tetralone IXc in the presence of methylamine, in the cold, is rapidly converted to its *trans* isomer Xc, whereas the *cis*-tetralone IXa and the *cis*-imine XII do not change their configuration when treated analogously.



The presence of the isoquinolinium salt XIII among the reaction products from the 3-methyl-substituted salt Vc, in contrast to its 3-aryl analog Va, is consistent with an earlier observation [12] regarding the influence of the nature of a substituent in position 3 of 1-alkyl-2-benzopyrylium salts on the predominant course of processes of their carbocyclization and heterocyclization in reactions with ammonia and primary amines. With regard to the structure of the intermediate (III or IV) that participates directly in the heterocyclization process, this must remain an open question.

In adducts of 2-benzopyrylium salts with N-nucleophiles, opening of the hetero ring is favored by even a free electron pair present on the α-heteroatom; in the case of C-nucleophiles, in contrast, in order to realize this process it is necessary to create an anionic center by deprotonation of the added CH-active component by an extraneous base [13, 14]. It has been suggested that the preliminary deprotonation also ensures preservation of aromaticity of the annelated ring in the open intermediate.

However, in the interaction of the salt Va with malononitrile, catalyzed by sodium *tert*-butylate, we recovered the cyclic *cis*-dinitrile XIV. Its configuration indicates that, to a considerable degree, this carbocyclization is likewise an electrocyclic process.



Thus, we have demonstrated the possibility of temporary breakdown of aromaticity of the annelated benzene ring in the course of thermal recyclizations of 2-benzopyrylium salts; this may be used for realization of intramolecular electrocyclic reactions leading to the formation of variously substituted dihydronaphthalenes and α-tetralones.

EXPERIMENTAL

The IR spectra were taken in a Specord IR-75 spectrophotometer in white mineral oil, the PMR spectra in Tesla 487C and 567A instruments (80 and 100 MHz, respectively) at 20°C in CF_3COOH, CD_3CN, and $CDCl_3$, internal standard HMDS. The mass spectra were obtained in a Finnigan MAT-4615 instrument with an ionizing radiation energy 70 eV, with direct introduction of the sample into the source.

Elemental analyses for C, H, Cl, and N matched the calculated values.

1-Styryl-3-(4-methoxyphenyl)-2-benzopyrylium Perchlorate (Vd). To a suspension of 0.18 g (0.5 mmole) of 1-methyl-3-(4-methoxyphenyl)-2-benzopyrylium perchlorate [15, p. 98] in 1.5 ml of acetic acid, 0.16 ml (1.5 mmole) of benzaldehyde was added, and the mixture was heated for 15 min. The precipitate that formed after cooling was separated and washed with 1 ml of acetic acid and ether.

1-Styryl-3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (Va). To a suspension of 0.44 g (1 mmole) of 1-methyl-3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium perchlorate [15, p. 104] in 5 ml of acetic acid, 0.36 g (2 mmole) of benzalaniline was added, and the mixture was heated for 2 min. The precipitate that formed after cooling was separated and washed with 10 ml of acetic acid and ether.

1-(α-Methylstyryl)-3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (Vb). To a mixture of 0.63 g (2 mmole) of desoxyveratroin [15, p. 103] and 0.49 g (3 mmole) of α-methylcinnamic acid, 7 g of polyphosphoric ether was added, and the mixture was heated on a water bath while stirring for 1 h. After cooling, the reaction mixture was poured into 50 ml of cold water, acidified with 6 ml of 57% perchloric acid, and stirred with 30 ml of ether. The resulting precipitate was separated and dried.

1-N-Morpholino-1-(α-methylstyryl)-3-(3,4-dimethoxyphenyl)-6,7-dimethoxyisochromene (VIb). To a suspension of 0.54 g (1 mmole) of the perchlorate Vb and 3 ml of alcohol, 0.44 ml (5 mmole) of morpholine was added, and the mixture was cautiously heated while stirring until the salt had disappeared. After cooling, 20 ml of water was added to the reaction mixture, and the precipitate was separated.

1-N-Morpholino-3-phenyl-4-(3,4-dimethoxybenzoyl)-*cis*-3,4-dihydro-6,7-dimethoxynaphthalene(VIIa). To a suspension of 0.53 g (1 mmole) of the salt Va in 3 ml of ethanol, 0.44 ml (5 mmole) of morpholine was added, and the mixture was heated until the salt had dissolved. After cooling, the reaction mixture was diluted with 20 ml of water, and the precipitate was separated. Mass spectrum m/z (I_{rel}, %): M^+ 515 (6); $[M - ArCO]^+$ 350 (38), 291 (7), 260 (6), $ArCO^+$ 165 (100), Ar^+ 137 (7), $H_2N^+(CH_2CH_2)_2O$ 88 (33).

The enamene VIIc and the imine XII were obtained analogously, using a 25% aqueous solution of methylamine.

1-N-Morpholino-2-methyl-3-phenyl-4-(3,4-dimethoxybenzoyl)-*cis*-3,4-dihydro-6,7-dimethoxynapthalene (VIIb). A 0.26-g quantity (0.5 mmole) of the adduct VIb was heated for 2 min at 200°C in an argon atmosphere. After cooling, the fused product was heated for 1 min in 1.6 ml of ethanol, and the precipitate that formed upon cooling was separated.

1-N-Morpholino-3-phenyl-4-(3,4-dimethoxybenzoyl)-*trans*-3,4-dihydro-6,7-dimethoxynaphthalene (VIIIa). To 2.5 ml of a 10% NaOH solution, 2.5 ml of ethanol, and 2.5 g (0.5 mmole) of the enamene VIIa were added, and the mixture was heated for 10 min. After cooling, the mixture was diluted with 20 ml of water, and the precipitate was separated.

The enamene VIIIb was obtained analogously.

***cis*-3-Phenyl-4-(3,4-dimethoxybenzoyl)-6,7-dimethoxytetralone-1 (IXa).** A suspension of 0.52 g (1 mmole) of the enamene VIIa in 5 ml of 50% acetic acid was heated for 2 min and then cooled, after which the precipitate was separated.

Tetralones IXc and Xa — obtained in the same manner as the enamenes VIIc and VIIIa.

Tetralone IXd — obtained in the same manner as the salt Vd, pretreating with morpholine as described in the method for obtaining compound VIIa.

***cis*-1-(3,4-Dimethoxybenzoyl)-2-phenyl-1,2,3,4-tetrahydro-4-dicyanomethylene-6,7-dimethoxynaphthalene (XIV).** To a suspension of 0.25 g (0.5 mmole) of the salt Va in 5 ml of *tert*-butanol, 0.09 g (0.6 mmole) of sodium *tert*-butylate, and 0.08 g (1 mmole) of malononitrile were added, and the mixture was heated until the salt had dissolved. After cooling, 20 ml of water and 15 ml of ether were added to the reaction mixture, which was shaken for 5 min and then allowed to settle for 4 h. The resulting precipitate was separated.

1-Styryl-2,3-dimethyl-6,7-dimethoxyisoquinolinium Perchlorate (XIII) and *trans*-3-Phenyl-4-acetyl-6,7-dimethoxytetralone-1 (Xc). To a suspension of 0.20 g (0.5 mmole) of the salt Vc in 2 ml of ethanol, 0.18 ml (1.5 mmole) of a 25% aqueous solution of methylamine was added, and the mixture was stirred for 30 min at 20°C. The precipitated salt XIII was filtered off; from the mother solution, after adding 15 ml of water, the tetralone Xc was recovered.

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