2-BENZOPYRYLIUM SALTS.

39.* RECYCLIZATION OF 2-BENZOPYRYLIUM SALTS UPON REACTION WITH VINYL ETHYL ETHER AND COMPOUNDS WITH AN ACTIVE METHYLENE GROUP

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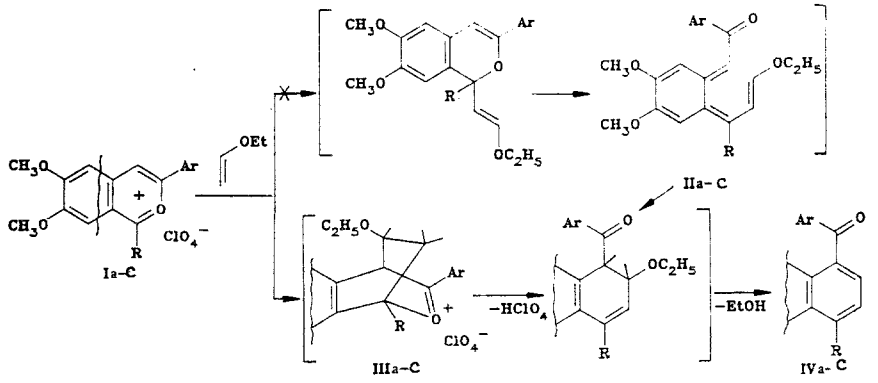
The reaction of 2-benzopyrylium salts with vinyl ethyl ether, ethyl acetoacetate, malonodinitrile, and nitromethane gives variously substituted naphthalene derivatives. It is proposed that the reaction with vinyl ether proceeds through [4+2] cycloaddition, while the reaction with the compounds with an active methylene group proceeds either through the ANRORC mechanism or through the formation of bridged intermediates, depending on the conditions.

The transformation of 2-benzopyrylium salts to derivatives of chrysene [2] and benz[*a*]anthracene [3] involves two major steps: dimerization of the salts, proceeding through the reaction of the cation of one molecule with the vinyl fragment of the anhydro or pseudobase of the other, and intramolecular recyclization of the dimers, which may be seen as adducts of 2-benzopyrylium salts with compounds with an active methylene group. In order to find a model for these steps, we studied the reaction of 2-benzopyrylium salts with vinyl ethyl ether and compounds with an active methylene group.

We should note that the reaction of pyrylium salts with vinyl ethers has not yet been studied and doubt has been cast on the recyclization of C-adducts of 2-benzopyrylium salts [4].

In contrast to the dimerization reaction proceeding at room temperature, the reaction of salts Ia-Ic with vinyl ethyl ether begins only upon heating and leads directly to acylnaphthalenes IVa-IVc. It is unlikely that this reaction proceeds through an ANRORC mechanism involving the dearomatization of the fused benzene ring in open intermediates IIa-IIc.



Ar=3,4-$(CH_3O)_2C_6H_3$; I—IV a R=H; b R=CH_3; c R=C_6H_5

In our opinion, this transformation is analogous to the Bradsher—Folk reaction [5], which has been extensively studied for benzo[b]quinolisinium and isoquinolinium salts and proposed as a concerted but not synchronous [4+2] cycloaddition with inverted electronic

*For Communication 38, see [1].

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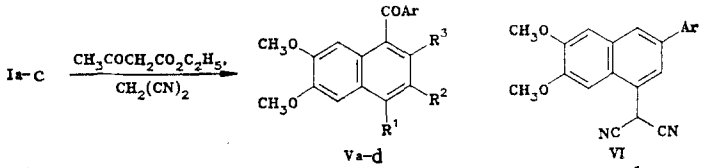
requirements [6]. Such reactions have recently been termed para-cyclization or para-bridging reactions [7].

The replacement of a heteroatom in the substrate affects certain specific features in the reaction course. For example, opening of the heterocycle in bridged intermediates IIIa-IIIc and subsequent aromatization occur under the reaction conditions, while such processes in isoquinolinium salts and their benzo analogs either take place under more vigorous conditions or require several steps [8].

Thus, the reaction of 2-benzopyrylium salts in Ia-Ic with vinyl ethyl ether may be the first example of a hetero-Diels-Alder reaction [9] involving an oxonium oxygen atom.

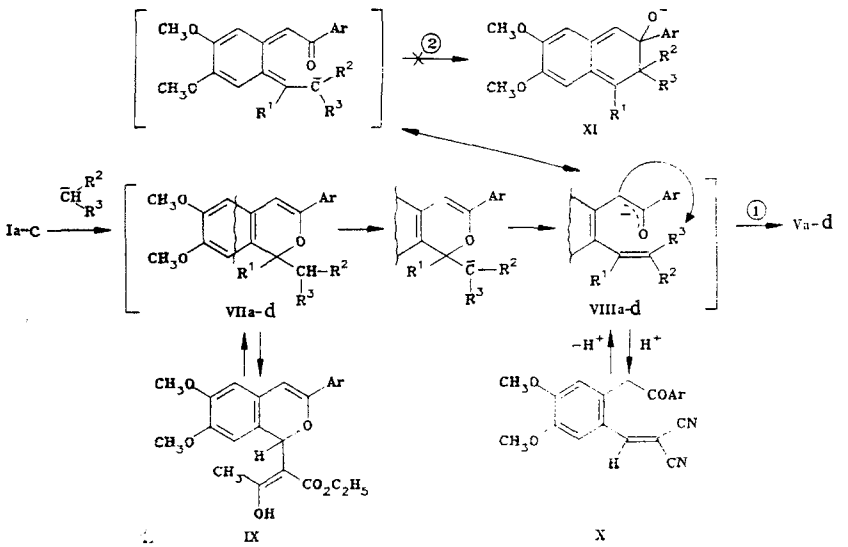
In a study of the reaction of 2-benzopyrylium salts Ia-Ic with ethyl acetoacetate and malonodinitrile under phase transfer conditions [10] or in the presence of sodium tert-butylate, we discovered that it leads to 1-acylnaphthalene derivatives Va-Vd.



Va–d, VI Ar=3,4-$(CH_3O)_2C_6H_3$; Va, c R^1=H, b R^1=C_6H_5, d R^1=CH_3; a, b R^2=$CO_2C_2H_5$, R^3=CH_3; c, d R^2=CN, R^3=NH_2

The hypothesis that anions of compounds with an active methylene group react in the enol form by [4+2] cycloaddition, by analogy to the reaction with vinyl ethyl ether, is not in accord with the observations that cyclic (IX) and open-chain intermediates (X) were isolated starting from Ia. In alkaline medium, these intermediates are converted to acyl-naphthalenes Va and Vc, respectively.

These results as well as the parallel formation of naphthalene VI from salt Ib, when the α-methyl substituent already present on the heterocycle is involved in the formation of a new ring by analogy to the data of Gompper and Christmann [11], indicate that the reaction proceeds through an ANRORC mechanism [12, 13].



VII, VIIIa–d Ar=3,4-$(CH_3O)_2C_6H_3$; a, c R^1=H, b R^1=C_6H_5, d R^1=CH_3; a, b R^2=$CO_2C_2H_5$, R^3=$COCH_3$; c, d R^2=$COCH_3$, R^3=CN

However, in contrast to monocyclic pyrylium salts, in which the opening of the heterocycle occurs as an electrocyclic process [13], the opening in this case is preceded by deprotonation of the added nucleophile, which prevents the dearomatization of the fused ring in resonance form VIIIa-VIIId by analogy to that described in the formation of benz[a]anthracenes [3].

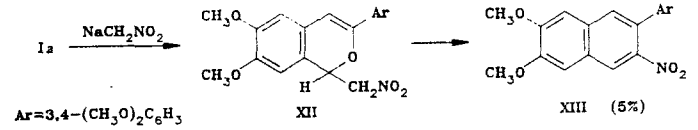
TABLE 1. Physicochemical Indices of Compounds Synthesized

Compound	Chemical formula	mp, °C*	R_f	IR spectrum, cm^{-1}	Yield, %
IVa	$C_{21}H_{20}O_5$	155	0,85	1650, 1595, 1130, 1020	70
IVb	$C_{22}H_{22}O_5$	167	0,85	1640, 1595, 1120	75
IVc	$C_{27}H_{24}O_5$	199	0,80	1636, 1600, 1135	65
Va	$C_{25}H_{26}O_7$	167	0,80	1715, 1635, 1580	90 (A), 92 (B), 95 (C)
Vb	$C_{31}H_{30}O_7$	154	0,77	1725, 1645, 1585	86
Vc	$C_{22}H_{20}N_2O_5$	196	0,45	3460, 3353, 2207, 1620	73
Vd	$C_{23}H_{22}N_2O_5$	198	0,45	3393, 2207, 1620	33
VI	$C_{23}H_{20}N_2O_5$	223	—	2206, 1610, 1020	60
IX	$C_{25}H_{28}O_8$	202	0.65	3393, 1660, 1620, 1580	88
X	$C_{22}H_{20}N_2O_5$	250	0,80	2213, 1660, 1570	52
XII	$C_{20}H_{21}NO_7$	164	0,70	1633, 1606, 1066	95
XIII	$C_{20}H_{19}NO_6$	162	0,80	1625, 1606, 1013	5
XV	$C_{16}H_{18}O_4$	107	0,85	1700, 1620, 1060	83

*The recrystallization solvent was ethanol for IVa, IVb, Va-Vd, IX, XII, and XIII, acetic acid for IVc and X, dioxane for VI, and 50% aqueous ethanol for XV.

Despite the possibility of a second direction for the reaction through an ANRORC mechanism (pathway 2), in which the new ring is formed after opening of the heterocycle due to the nucleophile atom previously directly involved in formation of the adduct, products of this type were not observed in the reaction mixtures under various conditions. In a number of monocyclic pyrylium salts, there is equal possibility for the existence of two alternative reaction directions in the framework of the ANRORC scheme [13].

On the other hand, realization of pathway 2 is difficult for 2-benzopyrylium salts, even if a type-1 reaction is impossible. Thus, the recyclization of salt Ia with nitromethane, despite the almost quantitative formation of adduct XII, leads to nitronaphthalene XIII in less than 5% yield and is accompanied by the formation of a complex mixture of byproducts, while the analogous transformation proceeds readily with monocyclic pyrylium salts [14].

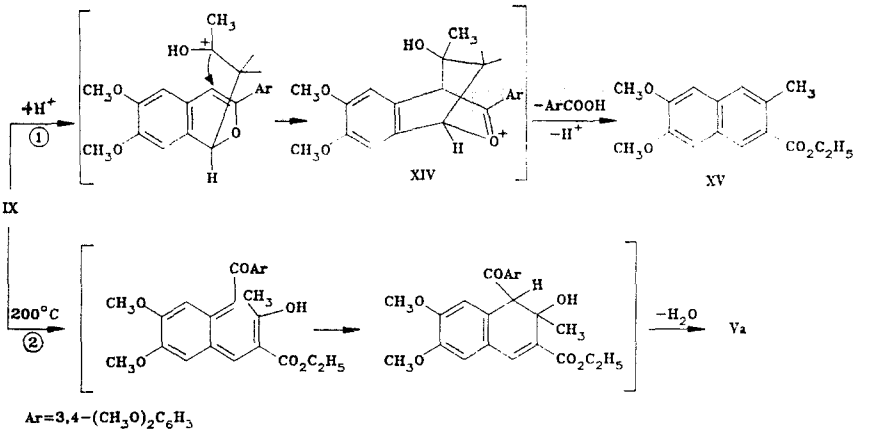


The difficulty for pathway 2 apparently lies in the complications related to the necessity of forming intermediate XI with fixed ortho-quinoid structure.

On the other hand, adduct IX, which exists in the enol form, is capable of converting to acylnaphthalene Va not only in alkaline media but also upon thermolysis, while naphthalene XV is formed upon the action of acids.

In the latter case, in our opinion, the opening of the heterocycle preceding formation of the carbocycle, i.e., the reaction in accord with the ANRORC scheme, is unlikely. A more favorable mechanism involves protonation of the enol fragment of ethyl acetoacetate and attack of the hydroxycarbenium ion generated on the nucleophilic $C_{(4)}$ atom of the heterocycle. Naphthalene XV is formed after opening of the ring in intermediate XIV and elimination of veratric acid occurs under these conditions by analogy to our previous results [2] (see scheme on following page).

The possibility of electrocyclic opening of the heterocycle with temporary loss of aromaticity of the fused benzene ring (pathway 2), as shown in the thermolysis of 3-hydroxyisochromenes [15], and subsequent electrocyclic closure to an acylnaphthalene Va (pathway 2) is not excluded upon thermolysis along with the above-mentioned variant (but with attack of the vinyl fragment of the isochromene ring by the carbonyl group instead of the hydroxycarbenium ion).



Thus, it is not excluded that the transformation of 2-benzopyrylium salts into substituted naphthalenes upon reaction with vinyl ethyl ether and compounds with an active methylene group is possible not only in the framework of the ANRORC scheme but also through the intermediate formation of bridged intermediates.

EXPERIMENTAL

The IR spectra were taken on a Specord 75 spectrophotometer for vaseline mulls. The PMR spectra were taken on a Tesla 487C spectrometer at 80 MHz and 26°C with HMDS as the internal standard. The frequency of the products obtained was monitored using thin-layer chromatography on alumina with chloroform as the eluent.

The physical indices of the products obtained are given in Tables 1 and 2. The elemental analysis data for C, H, and N corresponded to the calculated values.

1-(3,4-Dimethoxybenzoyl)-6,7-dimethoxynaphthalene (IVa). A sample of 0.1 ml (10 mmoles) vinyl ethyl ether was added to a suspension of 0.43 g (1 mmole) salt Ia in 2.5 ml ethanol and 2.5 ml acetonitrile and heated for 2 h. After cooling, the reaction mixture was poured into 70 ml cold water and maintained for a brief period. The precipitate formed was separated, dried, and purified by passage through an alumina column with chloroform as the eluent, taking the fraction with R_f 0.85.

1-(3,4-Dimethoxybenzoyl)-4-methyl-dimethoxynaphthalene (IVb) was obtained by analogy using only acetonitrile as the solvent in the presence of calcium carbonate. The product obtained did not require chromatographic purification.

1-(3,4-Dimethoxybenzoyl)-4-phenyl-6,7-dimethoxynaphthalene (IVc) was obtained by analogy using DMF as the solvent. The heating time was 10 min.

1-(1-Carboxyethyl-2-hydroxypropen-1-yl)-3-(3,4-dimethoxyphenyl)-6,7-dimethoxyisochromene (IX). A sample of 0.26 g (1 mmole) ethyl acetoacetate, 0.43 g (1 mmole) salt Ia was added to a suspension of 0.1 g (1 mmole) sodium tert-butylate in 3 ml tert-butyl alcohol and heated until dissolved. Adduct IX slowly separated after the addition of 2 ml ethanol.

1-Nitromethyl-3-(3,4-dimethoxyphenyl)-6,7-dimethoxyisochromene (XII). A sample of 0.17 g (2 mmoles) sodium salt of nitromethane was added to a suspension of 0.43 g (1 mmole) salt (Ia) in 2 ml nitromethane and heated until the salt was dissolved. After cooling, 5 ml water was added and the reaction mixture was extracted with three 7-ml portions of ether. The organic layer was dried and evaporated.

2-(2,2-Dicyanoethylenyl)-3',4,4',5-tetramethoxydesoxybenzoin (X). A mixture of 0.13 g (2 mmoles) malonodinitrile, 0.1 g (1 mmole) sodium tert-butylate, and 0.43 g (1 mmole) salt Ia was suspended in 8 ml tert-butyl alcohol and heated until the color of the salt disappeared. After cooling, the reaction mixture was diluted with 30 ml water and the precipitate formed was separated.

1-(3,4-Dimethoxybenzoyl)-2-methyl-3-carboxyethyl-6,7-dimethoxynaphthalene (Va). A. A sample of 0.52 g (5 mmoles) ethyl acetoacetate and 0.43 g (1 mmole) salt Ia were added to a mixture of 3 ml 50% aqueous NaOH, 5 ml benzene, and 10 mg TEBAC and stirred for 2 h. Then, 10 ml water was added. The organic layer was separated, dried, and evaporated.

TABLE 2. PMR Spectra of Products in $CDCl_3$*

Compound	Chemical shifts, ppm
IVa	3,79 (s OCH_3); 3,82 (s, 2OCH_3); 3,91 (s OCH_3); 6,67...7,85 (m, 8H_{arom})
IVb	2,65 (s CH_3); 3,85 (s, 3OCH_3); 3,97 (s OCH_3); 6,72...7,62 (m 7H_{arom})
IVc	3,67 (s, OCH_3); 3,77 (s, 2OCH_3); 3,83 (s OCH_3); 6,65...7,60 (m, 12H_{arom})
Va	1,41 (t, CH_3); 2,49 (s CH_3); 3,78 (s, OCH_3); 3,93 (s OCH_3); 3,97 (s OCH_3); 4,02 (s OCH_3); 4,44 (q, CH_2); 6,78...8,46 (m, 6H_{arom})
Vb	0,80 (t, CH_3); 2,17 (s CH_3); 3,57 (s OCH_3); 3,62 (s, OCH_3); 3,77 (s, OCH_3); 3,85 (q, CH_2); 3,87 (s, OCH_3); 6,70...7,70 (m 10H_{arom})
Vc	3,52 (s OCH_3); 3,80 (s, 3OCH_3); 4,85 (s, 2H, NH_2); 6,53...7,87 (6H_{arom})
Vd	2,75 (s CH_3); 3,47 (s, OCH_3); 3,80 (s, 2OCH_3); 3,87 (s, OCH_3); 4,95 (s 2H, NH_2); 6,53...7,45 (m 5H_{arom})
VI	3,82 (s OCH_3); 3,87 (s, OCH_3); 3,92 (s 2OCH_3); 5,52 (s, 1H); 6,82...7,87 (m, H_{arom})
IX	1,22 (t, CH_3); 1,50 (s CH_3); 3,67 (s, OCH_3); 3,75 (s 2OCH_3); 3,80 (s, OCH_3); 4,15 (q, CH_2); 4,75 (s 1H); 5,25 (s, 1H, OH); 6,45 (s 1H, CH=C—O); 6,77...7,77 (m 5H_{arom})
X	3,50 (s 2OCH_3); 3,52 (s, 2OCH_3); 4,22 (s, 2H, CH_2); 6,52...7,45 (m 5H_{arom}); 7,67 (s 1H)
XII	3,75 (s 4OCH_3); 4,07...4,82 (m, 2H, CH_2NO_2); 5,82...6,00 (m, 1H); 6,17 (s, 1H); 6,52...6,92 (m 5H_{arom})
XIII	3,80 (s 3OCH_3); 3,85 (s, OCH_3); 6,10...7,21 (m 7H_{arom})
XV	1,30 (t, CH_3); 2,57 (s, CH_3); 3,82 (s 2OCH_3); 4,27 (q CH_2); 6,85 (s 1H_{arom}); 7,00 (s, 1H_{arom}); 7,32 (s, 1H_{arom}); 8,20 (s 1H_{arom})

*Product X was taken in CF_3CO_2H.

B. Naphthalene Va was obtained by heating adduct IX in tert-butyl alcohol in the presence of sodium tert-butylate.

C. Naphthalene Va was obtained by maintaining adduct IX at 200°C for 10 min.

1-(3,4-Dimethoxybenzoyl)-2-methyl-3-carboxyethyl-4-phenyl-6,7-dimethoxynaphthalene (Vb) was obtained by analogy to procedure A from salt Ic and ethyl acetoacetate.

1-(3,4-Dimethoxybenzoyl)-2-amino-3-cyano-6,7-dimethoxynaphthalene (Vc). A sample of 0.38 g (1 mmole) dinitrile X was suspended in 3 ml ethanol and 3 ml 5% aqueous NaOH and heated for 5 min. After cooling, the reaction mixture was diluted with 30 ml cold water and the precipitate formed was separated.

1-(3,4-Dimethoxybenzoyl)-2-amino-3-cyano-4-methyl-6,7-dimethoxynaphthalene (Vd) and 2-(3,4-Dimethoxyphenyl)-4-dicyanomethyl-6,7-dimethoxynaphthalene (VI). A mixture of 0.2 g (3 mmoles) malonodinitrile, 0.19 g (2 mmoles) sodium tert-butylate, and 0.44 g (1 mmole) salt Ib was suspended in 8 ml tert-butyl alcohol and heated until the color of the salt disappeared. After cooling, the reaction mixture was diluted with 30 ml water and the precipitate of Vd was separated. Product VI was obtained upon acidification of the mother liquor.

2-(3,4-Dimethoxyphenyl)-3-nitro-6,7-dimethoxynaphthalene (XIII). A sample of 0.17 g (2 mmoles) sodium salt of nitromethane was added to a suspension of 0.43 g (1 mmole) salt Ia in 5 ml tert-butyl alcohol and heated for 5 min. Then, 0.1 g (1 mmole) sodium tert-butylate was added and the mixture was heated for an additional 30 min. After cooling, the reaction mixture was diluted with 30 ml water. The precipitate formed was separated, dried, and subjected to chromatography on an alumina column with chloroform as the eluent, collecting the fraction with R_f 0.80.

2-Carboxyethyl-3-methyl-6,7-dimethoxynaphthalene (XV). A sample of 0.46 g (1 mmole) isochromene IX was dissolved in 3 ml acetic acid, heated to reflux, and two drops of 70% perchloric acid were added. After cooling, 30 ml water was added and the precipitate formed was separated.

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF AZOMETHINES IN THE COUMARIN SERIES

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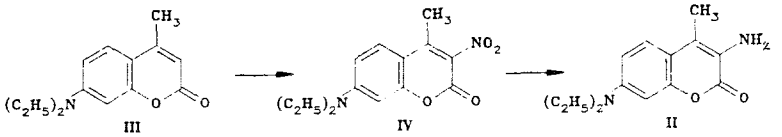
Nitration of 7-diethylamino-4-methylcoumarin and reduction of the resulting 3-nitro derivative gave 7-diethylamino-3-amino-4-methylcoumarin. A series of azomethines have been synthesized based on this material. The spectral-luminescence properties of the products have been investigated.

Substituted coumarins with electron-donating substituents in the 7-position are of interest as organic luminophores and as efficient laser dyes for the blue-green region of the spectrum [1, 2]. Introduction into the 3-position of 7-substituted coumarins of substituent groups which lengthen the conjugation chain leads to a bathochromic shift in their absorption and luminescence spectra; this makes it possible to expand the available selection of fluorescent coumarin dyes [3].

In the present paper we have synthesized and studied azomethines I (Table 1) derived from 7-diethylamino-3-amino-4-methylcoumarin, which was itself prepared by nitration of 7-diethylamino-4-coumarin followed by reduction of the intermediate nitro derivative IV with metallic iron in aqueous ethanol. Optimizing the nitration procedure made it possible to prepare the 3-nitrocoumarin (IV) in 54% yield, since in the nitration of 7-dimethylamino-4-methylcoumarin the 3-nitro derivative was formed in a mixture along with other isomers in equal amounts [4].

The presence of a nitro group in the 3-position in (IV) is indicated by the absence of the 3-H proton signal in the PMR spectrum of compound IV and by the absence of splitting of the 4-CH_3 group signal which is present in the spectrum of compound III due to spin-spin coupling with the 3-H proton.



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