1-Methyl-4-[5-(1-methyl-4,6-diphenyl-1,2-dihydropyridin-2-ylidene)-1,3-pentadienyl]-2,6-diphenylpyridinium Perchlorate (IX). This compound was obtained from 0.11 g (0.175 mmole) of pyrylocyanine III by a method similar to that used to prepare VII.

LITERATURE

1. A. I. Tolmachev, N. A. Derevyanko, and A. A. Ishchenko, Khim. Geterotsikl. Soedin., No. 9, 1173 (1982).
2. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 898 (1980).
3. M. A. Kudinova, N. A. Derevyanko, G. G. Dyadyusha, A. A. Ishchenko, and A. I. Tolmachev, Khim. Geterotsikl. Soedin., No. 7, 903 (1980).
4. M. Simalty, H. Strzelecka, and H. Khedija, Tetrahedron, 27, 119 (1971).
5. G. van Allan and L. Reynolds, J. Heterocycl. Chem., 14, 119 (1977).
6. A. Katritzky, Tetrahedron, 36, 679 (1980).
7. G. G. Dyadyusha, A. A. Ishchenko, N. A. Derevyanko, E. F. Karaban, and A. I. Tolmachev, Ukr. Khim. Zh., 46, 1186 (1980).
8. G. G. Dyadyusha, A. A. Ishchenko, N. A. Derevyanko, M. A. Kudinova, and A. I. Tolmachev, Teor. Éksp. Khim., 15, 412 (1979).
9. A. A. Ishchenko, N. A. Derevyanko, M. A. Kudinova, G. G. Dyadyusha, and A. I. Tolmachev, Teor. Éksp. Khim., 13, 828 (1977).

2-BENZOPYRYLIUM SALTS.

26.* RECYCLIZATION OF 2-BENZOPYRYLIUM SALTS TO α-NAPHTHOLS

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The behavior of 2-benzopyrylium salts with a CH_2 group in the 1 position at pH $\leqslant 7$ was studied, and it was established that they undergo recyclization to α-naphthols under these conditions. A mechanism for the conversion is proposed. One of the intermediates, viz., 3-hydroxy-1-tetralone, was isolated.

It has been proposed [2, 3] that an equilibrium between the cationic form of the pyrylium salt and its anhydro and pseudo bases, which has been studied at pH $\geqslant 7$ [4-6] and determines its reactivity, may also exist in an acidic medium.

We have observed that, probably owing to this equilibrium, irreversible recyclization of 2-benzopyrylium salts to α-naphthols is possible at pH $\leqslant 7$. This transformation takes place to give the products in 75-90% yields when 2-benzopyrylium salts with a CH_2 group in the 1 position are heated in ethanol or water both with and without acidification.

The recyclization evidently takes place due to reaction of the pyrylium salt with water, which can add immediately to the cation, acting as a nucleophile (pathway A), or initially as a base to deprotonate it (pathway B).

The anhydro bases (benzylideneisochromenes III) formed by pathway B are derivatives of vinyl ethers, which, as is known [7], are readily hydrated in acidic media; protonation of the β-cation atom of the vinyl fragment (hydration of the exocyclic double bond is more likely) takes place with simultaneous attack by the nucleophile at the α-position, i.e., in this case the I → III transformation is irreversible. Pseudo bases IVa-i undergo subsequent recyclization to naphthols VIIa-i (R^3 = H) through 1,5-dicarbonyl compounds V.

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*See [1] for communication 25.

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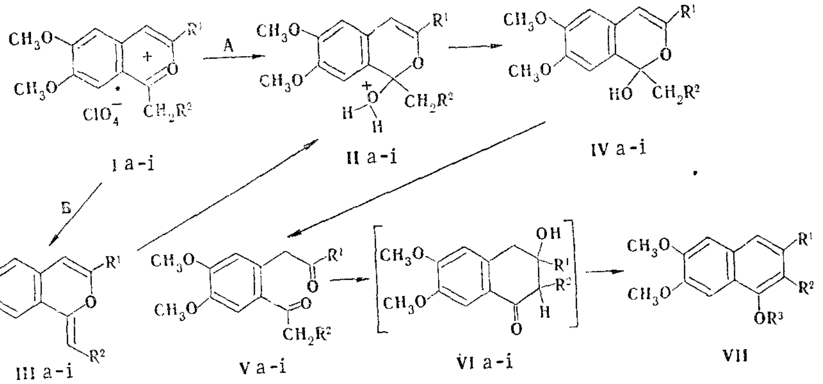

I—VII a $R^1 = CH_3$, $R^2 = 3,4\text{-}(OCH_3)_2C_6H_3$; b $R^1 = CH_3$, $R^2 = C_6H_5$; c $R^1 = R^2 = 3,4\text{-}(OCH_3)_2C_6H_3$; d $R^1 = CH_3$, $R^2 = 2\text{-I-}4,5\text{-}(OCH_3)_2C_6H_2$; e $R^1 = CH_3$, $R^2 = 2\text{-Br-}4,5\text{-}(OCH_3)_2C_6H_2$; f $R^1 = 3\text{-}OCH_3C_6H_4$, $R^2 = C_6H_5$; g $R^1 = R^2 = C_6H_5$; h $R^1 = R^2 = CH_3$; i $R^1 = 3,4\text{-}(OCH_3)_2C_6H_3$, $R^2 = CH_3$; VII $R^3 = H$, $COCH_3$

In an alkaline medium, in which vinyl ethers are stable, the formation of naphthols is possible only through nucleophilic attack by a water molecule or the oxide anion of the pyrylium ring. In fact, benzylideneisochromene IIIb, which was obtained by the method in [8], remained unchanged after refluxing for 1 h in aqueous alkali but underwent smooth recyclization to naphthol VIIb (R^3 = H) upon treatment with aqueous or alcohol solutions of acids.

It must be noted that in acidic media naphthols are obtained only from 2-benzopyrylium salts that have a CH_2 group in the 1 position; salts with a methyl group form different compounds (their structure is currently being elucidated), although this sort of recyclization takes place in 40% yield in an alkaline medium [9]. This difference can be explained by the degree of stabilization of the intermediately formed benzylideneisochromenes or by the peculiarities of the aldol-crotonic condensation of 1,5-dicarbonyl compounds V (R^2 = H).

The observed transformation pertains essentially to the "isomerizational recyclization of heteroaromatic cations" [10]; however, according to our data, this is the first example of such processes that take place in an acidic medium. Recyclization in an acidic medium possibly is general in character and can be realized for both one-ring pyrylium salts and pyridinium salts.

1-Benzyl-3-methyl-2-benzopyrylium salt Ib undergoes recyclization to naphthol VIIb (R^3 = H) upon brief heating in aqueous solutions of HCl and $HClO_4$ or simply in water. In the latter two cases, in addition to the naphthol, the reaction gives a product, in the IR spectrum of which absorption bands at 1660 and 3200 cm^{-1} (C=O and OH groups, respectively) are recorded. Naphthol VIIb (R^3 = H) is formed when it is heated in aqueous alkali or an inert solvent, whereas the acetate of naphthol VIIb ($R^3 = COCH_3$) is formed in acetic anhydride. A singlet at 1.1 ppm (3H), for which a methyl group bonded to the alicycle is responsible, singlets at 3.00 (CH_2), 3.73 (1H), 3.83 (OCH_3), and 3.90 (OCH_3), and a multiplet at 6.90-7.55 ppm (aromatic 7-H) were observed in the PMR spectrum of the product obtained. On the basis of this, as well as the results of elementary analysis, we assigned a hydroxytetralone structure (VIb) to the compound obtained.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71 IR spectrometer, while the PMR spectra of solutions in CF_3COOH, d_4-CH_3OH, and d_6-DMSO were recorded with a Tesla BS-467 spectrometer (60 MHz) at 20°C with hexamethyldisiloxane as the internal standard.

1-Benzyl-3-methyl-6,7-dimethoxy-2-benzopyrylium Perchlorate (Ib). A 2-g (10 mmole) sample of 3,4-dimethoxyphenylacetone and 1.5 g (10 mmole) of phenylacetic acid were heated in 20 ml of polyphosphoric acid (PPA) at 100°C with vigorous stirring for 30 min, after which the mixture was hydrolyzed with cold water, and 1 ml of 70% $HClO_4$ was added. The liberated oily product was separated by decantation and crystallized twice from acetic acid with hot filtration to give 1.7 g (45%) of light-green crystals with mp 182°C. IR spectrum: 1640, 1605, 1540, 1535, and 1510 cm^{-1}. PMR spectrum (CF_3COOH): 2.39 (s, CH_3), 3.70 (s, OCH_3),

TABLE 1. 2-R^2-3-R^1-6,7-Dimethoxy-1-naphthols

Compound	Reaction time, h	mp, °C	Found, %		Empirical formula	Calc., %	
			C	H		C	H
VIIa[9]	2	177					
VIIc	4	216	69,9	5,4	$C_{28}H_{28}O_7$	70,3	5,8
VIId[9]	1,5	171					
VIIe[9]	1	162					
VIIf	20	168	77,8	5,6	$C_{25}H_{22}O_4$	77,7	5,7
VIIg	2	186	89,7	6,2	$C_{24}H_{20}O_3$	89,9	6,2
VIIh[9]	2	126					
VIIi	2	104	70,8	6,1	$C_{21}H_{22}O_5$	71,2	6,2

3.85 (s, OCH_3), 4.50 (s, CH_2), 6.95 (s, aromatic 5-H), 7.02 (s, aromatic 1-H), and 7.35 ppm (s, aromatic 2-H). Found: C 57.6, H 4.6, Cl 9.2%. $C_{19}H_{19}ClO_7$. Calculated: C 57.8, H 4.8, Cl 9.0%.

1-Benzylidene-3-methyl-6,7-dimethoxyisochromene (IIIb). A suspension of 0.4 g (1 mmole) of salt Ib in 10 ml of dry benzene with 2 ml of triethylamine was refluxed for 30 min, after which it was cooled, the residual oil was separated by decantation, and the benzene solution was evaporated to dryness to give 0.12 g (40%) of yellow crystals with mp 133°C (from ethanol). IR spectrum: 1665, 1585, 1560, and 1520 cm^{-1}. PMR spectrum (d_6-DMSO): 2.75 (s, CH_3), 3.78 (s, OCH_3), 3.85 (s, OCH_3), 5.78 (s, 1-H), 6.20 (s, 1-H), and 6.65-7.80 ppm (m, aromatic 7-H). Found: C 77.3; H 6.3%. $C_{19}H_{18}O_3$. Calculated: C 77.6, H 6.1%.

2-Phenyl-3-methyl-6,7-dimethoxy-1-naphthol (VIIb). A) A suspension of 0.45 g (1 mmole) of salt Ib in 10 ml of alcohol containing two drops of 36% HCl was refluxed for 2 h, after which the resulting solution was cooled and poured into 50 ml of water. The resulting precipitate was removed by filtration, washed with water, and dried to give 0.27 g (81%) of light-gray crystals with mp 103°C (from ethanol). IR spectrum: 3250, 1610, 1575, and 1500 cm^{-1}. PMR spectrum (CF_3COOH): 1.70 (s, CH_3), 3.58 (s, two OCH_3), and 6.73-7.08 ppm (m, aromatic 8-H). The product had R_f ($Al_2O_3/CHCl_3$) 0.8 with a characteristic yellow-green coloration upon development with iodine vapors. Found: C 77.8, H 6.2%. $C_{19}H_{18}O_3$. Calculated: C 77.6, H 6.1%.

Naphthols VIIa,c-i were obtained by a similar method (Table 1).

B) A reaction product that was identical to the product described in experiment A was obtained in 80% yield when the reaction was carried out in the presence of perchloric acid.

C) A suspension of 0.45 g (1 mmole) of salt Ib was refluxed in 10 ml of 36% HCl for 15 min, during which the salt dissolved, and the solution became turbid. The solution was cooled, and the precipitate was removed by filtration, washed with water, and dried to give 0.26 g (78%) of naphthol VIIb.

D) Naphthol VIIb was obtained in 80% yield by refluxing isochromene IIIb in ethanol in the presence of 70% $HClO_4$ for 2 h.

E) A suspension of 0.4 g (1 mmole) of salt Ib in 50 ml of 30% NaOH was refluxed for 8 h, after which it was cooled, and the undissolved product was removed by filtration. The filtrate was acidified with hydrochloric acid, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.1 g (40%) of naphthol VIIb.

2-Phenyl-3-hydroxy-3-methyl-6,7-dimethoxy-1-tetralone (VIb) and 2-Phenyl-3-methyl-6,7-dimethoxy-1-naphthol (VIIb). A) A suspension of 0.4 g (1 mmole) of salt Ib in 50 ml of water containing five drops of 70% $HClO_4$ was refluxed for 1 h, and 25 min after hot filtration and cooling of the filtrate the resulting precipitate was separated and dried. The mixture was separated by means of preparative column chromatography ($Al_2O_3/CHCl_3$, dry filling of the column: $R_{f(VIb)}$ and $R_{f(VIIb)}$ 0.8). Evaporation of the chloroform gave 0.1 g (36%) of cream-colored crystals of VIb with mp 178°C (from ethanol). IR spectrum: 3200, 1660, 1600, and 1520 cm^{-1}. PMR spectrum (d_4-CH_3OH): 1.10 (s, CH_3), 3.00 (s, CH_2), 3.73 (s, 1H), 3.83 (s, OCH_3), 3.90 (s, OCH_3), and 6.90-7.55 ppm (m, aromatic 7-H). Found: C 72.3, H 6,2%. $C_{19}H_{20}O_4$. Calculated: C 72.7, H 6.4%.

B) Naphthol VIIb was obtained in quantitative yield by heating hydroxytetralone VIb in a solution of 30% NaOH for 4 h. It was also obtained in quantitative yield after hydroxytetralone VIb was allowed to stand for 24 h in a solution of trifluoroacetic acid (with subsequent precipitation by means of ether) or when it was heated in xylene for 10 h.

2-Phenyl-3-methyl-6,7-dimethoxy-1-naphthol Acetate (VIIb, $R^3 = COCH_3$). A) A solution of 0.3 g (1 mmole) of naphthol VIIb in 5 ml of acetic anhydride was refluxed for 4 h, after which it was cooled and poured into water. The aqueous mixture was neutralized with sodium carbonate, and the crystallized oil was separated to give a product with mp 126°C (from ethanol). IR spectrum: 1750, 1640, 1600, and 1580 cm^{-1}. Found: C 78.4; H 6.1%. $C_{21}H_{20}O_3$. Calculated: C 78.8, H 6.3%.

B) Naphthol acetate VIIb ($R^3 = COCH_3$) was isolated in 70% yield when 3-hydroxytetralone VIb was refluxed in acetic anhydride for 12 h with subsequent workup as in experiment A.

LITERATURE CITED

1. G. P. Safaryan, I. V. Shcherbakova, G. N. Dorofeenko, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 12, 1608 (1981).
2. A. T. Balaban, E. Romas, and C. C. Rentia, Tetrahedron, No. 22, 1 (1966).
3. L. Yu. Ukhin, Zh. I. Orlova, V. I. Il'in, A. I. Pyshchev, and G. N. Dorofeenko, Koord. Khim., No. 5, 772 (1978).
4. H. Strzelecka, Ann. Chim., No. 1, 201 (1966).
5. M. Vaida and F. Ruff, Acta Chim. Hung., 40, 225 (1964).
6. A. Williams, J. Am. Chem. Soc., 93, 2733 (1971).
7. A. F. Rekasheva, Usp. Khim., 37, 2272 (1968).
8. E. V. Kuznetsov, D. V. Pruchkin, A. I. Pyshchev, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 10, 1320 (1978).
9. E. V. Kuznetsov, I. V. Shcherbakova, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 6, 745 (1976).
10. R. S. Sagitullin, S. P. Gromov, and A. N. Kost, Dokl. Akad. Nauk SSSR, 236, 6347 (1977).