2-BENZOPYRILIUM SALTS.

30.* SYNTHESIS AND PROPERTIES OF 2-BENZOPYRILIUM SALTS WITH THE 2,6-DI-t-BUTYLPHENYL SUBSTITUENT IN POSITION 3

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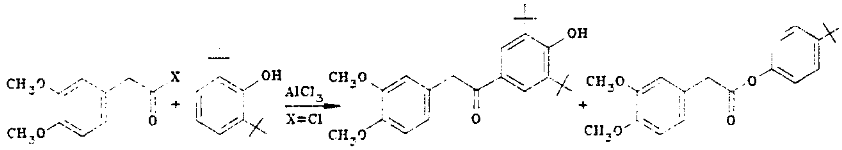
We achieved the synthesis of 2-benzopyrilium salts with a 2,6-di-t-butylphenyl substituent in position 3 by acylation of 3,5-di-t-butyl-4-hydroxy-3',4'-dimethoxydesoxybenzoin. We carried out a comparison of the concurrent deprotonation of 1-methylene and hydroxyl groups in these salts and obtained the corresponding isoquinoline bases.

The association in one molecule of functions responsible for various types of biological activity is one of the prospective ways of seeking new pharmaceutics. Derivatives of isoquinoline, structurally resembling papaverine and containing sterically hindered phenols as substituents, are of particular interest – they are powerful and effective antioxidants [2]. In the present work, an attempt is made to find synthetic approaches to these compounds.

One of the convenient methods of synthesis of isoquinoline derivatives is by replacement of the oxygen atom in 2-benzopyrilium salts by nitrogen using ammonia [3]. However, such salts with sterically hindered phenolic substituents were previously unknown. Therefore, we investigated the possibility of synthesizing 2-benzopyrilium salts with 2,6-di-t-butylphenol substituents in position 3 by methods given in [4, 5]. A general method is known for the synthesis of 3-aryl-2-benzopyrilium salts by the catalytic acylation of the corresponding desoxybenzoins [6], obtained in turn on acylation of substituted benzenes by homoveratric acid in polyphosphoric acid [4]. However, the use of 2,6-di-t-butylphenol in this reaction, even under mild conditions, leads only to resinous products evidently connected with decomposition of the phenol by phosphoric acid [7].

The target ketone (III) was obtained by acylation of 2,6-di-t-butylphenol with homoveratric acid chloride in the presence of $AlCl_3$ [8], with an overall yield, however, of 15%.



Ia,b II III (15%) IV (10%)

Ia X=Cl; b X=OH

The PMR spectrum in $CDCl_3$ completely accords with structure (III). A second product which could be isolated proved to be homoveratric acid p-t-butylphenyl ester (IV). Its structure was demonstrated by x-ray crystallographic analysis since the IR, PMR, and mass-spectroscopic data did not permit location of the position of the t-butyl group (instead of resolved signals for aromatic protons which might be expected for such a structure, the PMR spectrum showed a complex multiplet at 6.83-7.33 ppm).

The structure of molecule (IV) is shown in Fig. 1. The bond lengths and bond angles are listed in Tables 1 and 2, respectively. The central fragment of the molecule $C_{(1)}C_{(2)}$-$O_{(1)}O_{(2)}$ is planar to an accuracy of 0.01 Å (plane A). The planes of the benzene rings

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*For Communication 29, see [1].

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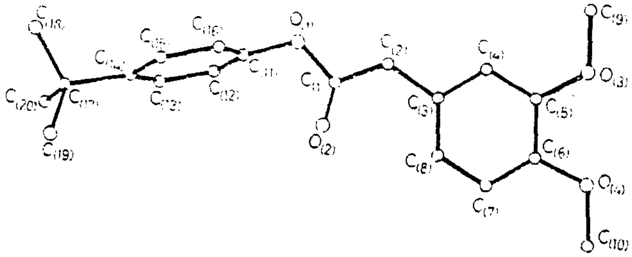


Fig. 1. Structure of molecule (IV) (hydrogen atoms are not shown).

TABLE 1. Bond Lengths

Bond	d, Å	Bond	d, Å	Bond	d, Å
$O_{(1)}—C_{(1)}$	1.370(4)	$C_{(3)}—C_{(4)}$	1.398(5)	$C_{(13)}—C_{(14)}$	1,379(5)
$O_{(1)}—C_{(11)}$	1.428(4)	$C_{(4)}—C_{(5)}$	1.381(5)	$C_{(14)}—C_{(15)}$	1,397(5)
$O_{(2)}—C_{(1)}$	1.185(4)	$C_{(5)}—C_{(6)}$	1.402(5)	$C_{(15)}—C_{(16)}$	1.391(5)
$O_{(3)}—C_{(5)}$	1.373(4)	$C_{(6)}—C_{(7)}$	1,377(5)	$C_{(16)}—C_{(11)}$	1.364(5)
$O_{(3)}—C_{(9)}$	1.427(4)	$C_{(7)}—C_{(8)}$	1.405(5)	$C_{(14)}—C_{(17)}$	1.543(5)
$O_{(4)}—C_{(6)}$	1.376(4)	$C_{(8)}—C_{(3)}$	1,385(5)	$C_{(17)}—C_{(18)}$	1.534(6)
$O_{(4)}—C_{(10)}$	1.434(4)	$C_{(11)}—C_{(12)}$	1.374(5)	$C_{(17)}—C_{(19)}$	1.534(6)
$C_{(1)}—C_{(2)}$	1.502(5)	$C_{(12)}—C_{(13)}$	1,397(5)	$C_{(17)}—C_{(20)}$	1,519(6)
$C_{(2)}—C_{(3)}$	1,524(5)				

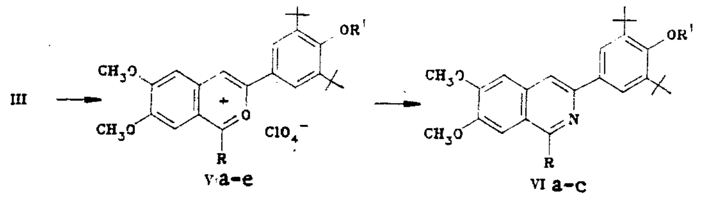
TABLE 2. Bond Angles

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(1)}O_{(1)}C_{(11)}$	116,1(3)	$C_{(5)}C_{(6)}C_{(7)}$	119,7(4)	$C_{(13)}C_{(14)}C_{(15)}$	117,9(4)
$C_{(5)}O_{(3)}C_{(9)}$	116.6(3)	$C_{(6)}C_{(7)}C_{(8)}$	120.3(4)	$C_{(14)}C_{(15)}C_{(16)}$	121,5(4)
$C_{(6)}O_{(4)}C_{(10)}$	116.8(3)	$C_{(7)}C_{(8)}C_{(3)}$	120,2(4)	$C_{(15)}C_{(16)}C_{(11)}$	118.8(4)
$O_{(1)}C_{(1)}O_{(2)}$	122,9(3)	$O_{(3)}C_{(5)}C_{(4)}$	124,6(3)	$C_{(13)}C_{(14)}C_{(17)}$	122.5(4)
$O_{(1)}C_{(1)}C_{(2)}$	108,5(3)	$O_{(3)}C_{(5)}C_{(6)}$	115,6(3)	$C_{(15)}C_{(14)}C_{(17)}$	119,6(4)
$O_{(2)}C_{(1)}C_{(2)}$	128.6(4)	$O_{(4)}C_{(6)}C_{(5)}$	115,2(3)	$C_{(14)}C_{(17)}C_{(18)}$	108,7(4)
$C_{(1)}C_{(2)}C_{(3)}$	116.0(3)	$O_{(4)}C_{(6)}C_{(7)}$	125,1(4)	$C_{(14)}C_{(17)}C_{(19)}$	108.2(3)
$C_{(2)}C_{(3)}C_{(4)}$	118.6(3)	$O_{(1)}C_{(11)}C_{(12)}$	117,9(3)	$C_{(14)}C_{(17)}C_{(20)}$	112.3(3)
$C_{(2)}C_{(3)}C_{(8)}$	122,2(3)	$O_{(1)}C_{(11)}C_{(16)}$	120,3(4)	$C_{(18)}C_{(17)}C_{(19)}$	108,8(4)
$C_{(8)}C_{(3)}C_{(4)}$	119.0(4)	$C_{(16)}C_{(11)}C_{(12)}$	121,6(4)	$C_{(18)}C_{(17)}C_{(20)}$	109.7(4)
$C_{(3)}C_{(4)}C_{(5)}$	120,9(4)	$C_{(11)}C_{(12)}C_{(13)}$	119,1(4)	$C_{(19)}C_{(17)}C_{(20)}$	109,1(4)
$C_{(4)}C_{(5)}C_{(6)}$	119,8(4)	$C_{(12)}C_{(13)}C_{(14)}$	121,1(4)		

$C_{(3)}$—$C_{(8)}$ (plane B) and $C_{(11)}$—$C_{(16)}$ (plane C) form with plane A dihedral angles of 41.4(2) and 79.1(2)°, and with each other – an angle of 100.6(2)°. The t-butyl substituent is oriented symmetrically with respect to place C: one of the C—C(Me) bonds is in the plane of the phenyl ring [the torsion angle $C_{(13)}C_{(14)}C_{(17)}C_{(20)}$ is equal to 0.3(3)°]. Both CH_3O groups are in the plane of the benzene ring B as is noted in the overwhelming majority of methoxy-substituted aromatic compounds [9] whose structure has been investigated. Bonds C(Ar)—O [$C_{(5)}$—$O_{(3)}$ 1.373(4), $C_{(6)}$—$O_{(4)}$ 1.376(4) Å] as usual are shortened by comparison with distances C(Alk)—O [$C_{(9)}$—$O_{(3)}$ 1.427(4), $C_{(10)}$—$O_{(4)}$ 1.434(4) Å] and are close to those found in bis(3,4-dimethoxyphenyl) sulfide [10]. [The average distances C(Ph)—O and C(Me)—O are 1.364 and 1.432 Å, respectively.] The remaining geometrical parameters of the molecule also have the expected values. In particular, the marked inequality of the endocyclic bond angles in the benzene ring C can be noted: an increase to 121.6(4) for $C_{(11)}$ and decrease to 117.9(4) for $C_{(14)}$ under the influence of the electron-accepting ether substituent and electron-donating t-butyl substituent, respectively.

The best method of synthesis of ketone (III) (yield 60%) proved to be acylation of phenol (II) by homoveratric acid in polyphosphoric ester at 85°C.

2-Benzopyrilium salts (Va-d) were obtained on acylation of ketone (III) by acetic anhydride in the presence of 70% $HClO_4$, and also by benzoic acid or phenylacetic acid in polyphosphoric ester.



V, VI a $R=CH_3$, $R'=COCH_3$; b $R=CH_2Ph$, $R'=H$; c $R=CH_2Ph$, $R'=COCH_2Ph$; d $R=Ph$, $R'=H$; e $R=Ph$, $R^1=COCH_3$

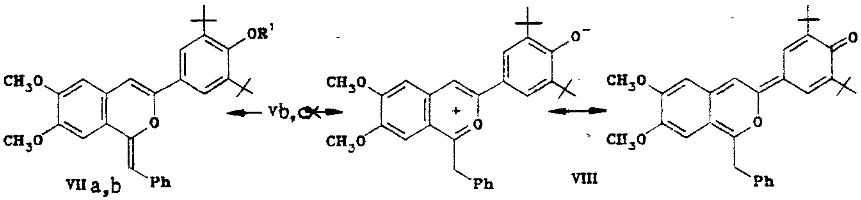
Salt (Vb) forms using equimolar proportions of ketone to phenylacetic acid. With a twofold excess of acid, the phenolic hydroxyl group acylates as well with formation of salt (Vc). Only salt (Vd) forms in the case of benzoic acid, irrespective of its quantity. This result is evidently governed by steric factors – the bulky phenyl substituent hinders acylation of the hydroxyl function shielded by t-butyl groups. This is also confirmed by the fact that the less bulky acetyl cation (acetic anhydride + 70% $HClO_4$) easily interacts with the bright-red salt (Vd), converting it into a yellow salt (Vc) having an acetoxy group.

One of the characteristic properties of para-substituted sterically hindered phenols is the capacity to form stable methylenequinonoid (quinoloid) compounds. The conversion to a methylenequinone by the action of bases [11] proceeds equally readily when the phenol is conjugated with a carbocationic center [12].

It is also known that pyrilium salts containing methyl and methylene groups in ortho and para positions can be deprotonated by bases forming methylenepyrans [13, 14]. In this connection, it was of interest to study the action of bases on the salts obtained – especially (Vb) for which, in principle, concurrent deprotonation is possible.

It was found that the corresponding benzylideneisochromene (VIIa) is formed by the action of triethylamine on salt (Vb) in dry benzene, while the phenolic fragment of the molecule remains unchanged.

Benzylideneisochromene (VIIb) also proved to be the sole product of the interaction of salt (Vc) with triethylamine. The 1-phenyl substituted salt (Vd), under the conditions described, forms a dark-green oil which was not identified due to its instability. This compound rapidly and irreversibly lightens in the air and readily gives the initial salt on addition of an excess of 70% $HClO_4$ to its ethanolic solution. The possibility of formation of quinoloid structures of type (VIII) in this case is being investigated.



VIIa $R'=H$; b $R'=COCH_2Ph$

Heating salts (Va, c) with ammonium acetate in acetic acid leads to the formation of isoquinolines (VIa, c), in which the substituent in position 3 is unchanged.

EXPERIMENTAL

The IR spectra were recorded (in Vaseline oil) on a Specord-71 IR instrument; the PMR spectra on a Tesla BS-467 (60 MHz) instrument at 20°C in CF_3COOH, CCl_4, and $CDCl_3$ (internal standard HMDS). The mass spectra were obtained on a Varian MAT-112 instrument at an ionization energy of 70 eV with direct introduction of the sample into the source.

X-Ray Crystallographic Analysis of Homoveratric Acid 3-t-Butylphenyl Ester (IV). Crystals of composition $C_{20}H_{24}O_4$ were grown from isopropanol and were triclinic; at –120°, $a = 7.319(4)$, $b = 11.122(9)$, $c = 11.641(8)$ Å, $\alpha = 93.09(6)$, $\beta = 104.65(5)$, $\gamma = 100.47(6)°$, $d_{calc} = 1.222$ g/cm³, $z = 2$, space group $P\bar{1}$. The parameters of the unit cell and the intensities of 1753 independent reflections with $F^2 \geq 3\sigma$ were measured on a Syntex $P2_1$ automatic four-circle diffractometer (–120°, $\lambda_{MoK\alpha}$ radiation, where $\theta \leq 28°$). The structure was analyzed by a direct method and refined by the method of least squares, initially in an isotropic approximation and then in an anisotropic approximation. All the hydrogen atoms appeared in

TABLE 3. Atomic Coordinates ($\times 10^4$, for H $\times 10^3$) and Their Equivalent Temperature Factors

Atom	x	y	z	B_{iso}^{eq}, Å^2
$O_{(1)}$	1112(4)	5759(3)	8501(3)	2.40(7)
$O_{(2)}$	−1343(4)	6000(3)	6982(3)	3.07(8)
$O_{(3)}$	−9828(4)	2635(3)	6325(2)	2.24(7)
$C_{(1)}$	−732(5)	5434(4)	7776(3)	1.9(1)
$C_{(2)}$	−1714(5)	4271(4)	8146(4)	2.0(1)
$C_{(3)}$	−3888(5)	3903(3)	7610(3)	1.62(9)
$C_{(4)}$	−5050(5)	3519(4)	8361(3)	1.67(9)
$C_{(5)}$	−7013(5)	3099(3)	7910(3)	1.60(9)
$C_{(6)}$	−7861(5)	3050(4)	6680(3)	1.7(1)
$C_{(7)}$	−6732(5)	3442(4)	5935(3)	2.0(1)
$C_{(8)}$	−4732(5)	3852(4)	6396(3)	1.9(1)
$C_{(9)}$	−7455(6)	2845(4)	9846(4)	2.7(1)
$C_{(10)}$	−10760(6)	2633(5)	5083(4)	3.6(2)
$C_{(11)}$	2342(5)	6758(4)	8178(3)	1.9(1)
$C_{(12)}$	3625(5)	6484(4)	7572(4)	2.0(1)
$C_{(13)}$	4932(5)	7443(4)	7314(3)	1.7(1)
$C_{(14)}$	4958(5)	8652(4)	7662(3)	1.7(1)
$C_{(15)}$	3623(5)	8889(4)	8272(4)	2.1(1)
$C_{(16)}$	2311(5)	7942(4)	8530(4)	2.3(2)
$C_{(17)}$	6395(6)	9732(4)	7404(4)	2.3(2)
$C_{(18)}$	7592(7)	10464(4)	8593(4)	3.9(2)
$C_{(19)}$	5236(7)	10570(4)	6652(4)	3.1(2)
$C_{(20)}$	7727(6)	9302(4)	6732(4)	2.9(2)
$H_{(21)}$	−143(5)	437(4)	901(3)	2.0(8)
$H_{(22)}$	−108(5)	363(3)	790(3)	1.7(8)
$H_{(4)}$	−442(5)	352(3)	914(3)	1.3(7)
$H_{(7)}$	−733(5)	351(4)	519(3)	2.4(8)
$H_{(8)}$	−398(5)	404(4)	585(3)	2.2(8)
$H_{(9.1)}$	−853(5)	258(4)	1013(3)	2.3(8)
$H_{(9.2)}$	−641(5)	234(3)	1006(3)	1.2(7)
$H_{(9.3)}$	−697(5)	374(4)	1017(4)	2.9(9)
$H_{(10.1)}$	−1215(6)	237(4)	508(4)	3.4(9)
$H_{(10.2)}$	−1042(6)	344(4)	481(4)	3.9(9)
$H_{(10.3)}$	365(5)	566(3)	731(3)	1.6(7)
$H_{(13)}$	584(5)	719(4)	692(3)	2.8(8)
$H_{(15)}$	352(5)	969(3)	854(3)	2.0(8)
$H_{(16)}$	142(6)	815(4)	890(4)	3.1(9)
$H_{(18.1)}$	842(7)	1108(5)	846(4)	6(1)
$H_{(18.2)}$	677(7)	1094(4)	905(4)	5(1)
$H_{(18.3)}$	840(6)	990(4)	909(4)	3.7(9)
$H_{(19.1)}$	438(6)	1101(4)	704(4)	3.3(9)
$H_{(19.2)}$	608(6)	1125(4)	649(4)	3.7(9)
$H_{(19.3)}$	442(6)	1009(4)	583(4)	4(1)
$H_{(20.1)}$	705(5)	880(4)	598(3)	2.5(8)
$H_{(20.2)}$	860(6)	879(4)	719(4)	5(1)
$H_{(20.3)}$	850(6)	996(4)	660(4)	3.2(9)

a differential synthesis and were refined in an isotropic approximation. The final R-factor was 0.052 (R_w = 0.061). All calculations were carried out on an Eclipse S/200 computer using INEXTL programs [15]. The atomic coordinates and their temperature factors are listed in Table 3.

3,5-Di-t-butyl-4-hydroxy-3,4-dimethoxydesoxybenzoin (III). A. Thionyl chloride (2.2 ml, 30 mmole) is added dropwise with stirring to homoveratric acid (Ib) (1.96 g, 10 mmole). The mixture is set aside for 3 h at 20°C, then the excess of thionyl chloride is distilled off at 75°C. A solution of anhydrous $AlCl_3$ (1.5 g, 12 mmole) in pure nitromethane (10 ml) and a solution of phenol (II) (2.06 g, 10 mmole) in nitromethane (7 ml) is added with stirring and ice-cooling to the acid chloride (Ia) formed. The mixture is stirred with ice-cooling for 2 h, then poured into cold water (100 ml) and extracted with chloroform (3 × 50 ml). The chloroform extract is dried and 100 ml of solvent removed in vacuo. The dark-brown residue is purified using preparative column chromatography ($Al_2O_3/CHCl_3$, dry filling of the column: $R_{f(III)}$ 0.75). After steam distillation of the chloroform, cream-colored crystals (III) (0.38 g, 10%), mp 133°C, are obtained (from ether). IR spectrum: 3560, 1660, 1580, 1240 cm^{-1}. PMR spectrum ($CDCl_3$): 1.38 (s, 6-CH_3), 3.80 (s, 2-OCH_3), 4.10 (s, CH_2), 5.75 (s, OH), 6.83 (s, 3-H-arom.), 7.95 ppm (s, 2-H arom.). Found, %: C 75.1, H 8.3. $C_{24}H_2O_3$. Calculated, %: C 75.0, H 8.3.

On steam distillation of the fraction with R_f 0.85, colorless crystals of homoveratric acid 3-t-butylphenyl ester (IV) (0.5 g, 15%), mp 95°C, were obtained. IR spectrum: 1750, 1600, 1590, 1255 cm^{-1}. PMR spectrum ($CDCl_3$): 1.08 (s, 3-CH_3), 3.58 (s, CH_2), 3.78 (s, 2-OCH_3), 6.83-7.33 ppm (m, 7H arom.). Found, %: C 73.1, H 7.3; M$^+$ 328. $C_{20}H_{24}O_4$. Found, %: C 73.2, H 7.3.

B. A mixture of homoveratric acid (Ib) (1.96 g, 10 mmole), 2,6-di-t-butylphenol (II) (2.06 g, 10 mmole), and polyphosphoric acid ester (24 g) is stirred vigorously for 3 h at 85°C, then poured into 100 ml of water, and heated to boiling with stirring and then cooled. After extraction of the oily product with ether (3 × 70 ml) and drying, the excess of solvent (190 ml) is removed in vacuo. The crystalline product which separates on cooling is removed by filtration and carefully washed with n-heptane. The ketone (III) (2.4 g, 60%) is obtained similarly as in A.

1-Methyl-3-(3,5-di-t-butyl-4-acetoxyphenyl)-6,7-dimethoxy-2-benzopyrilium Perchlorate (Va). To the solution of ketone (III) (0.38 g, 1 mmole) in acetic anhydride (5 ml) is added, with cooling, 70% $HClO_4$ (1 ml, 10 mmole). The mixture is diluted with ether until crystallization begins. After 24 h, a yellow salt (0.5 g) (Va) is obtained in quantitative yield, mp 252°C (from acetic acid). IR spectrum, cm^{-1}: 1755, 1620, 1600, 1235, 1090. PMR spectrum (CF_3COOH): 1.05 (s, 6-CH_3), 2.18 (s, CH_3), 4.00 (s, CH_3), 3.83 (s, OCH_3), 3.90 (s, OCH_3), 7.25 (s, 1-H), 7.35 (s, 1-H), 7.80 (s, 2H), 8.00 ppm (s, 1-H). Found, %: C 61.1, H 6.3, Cl 6.2. $C_{28}H_{35}ClO_9$. Found, %: C 61.0, H 6.3, Cl 6.4.

1-Benzyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-6,7-dimethoxy-2-benzopyrilium Perchlorate (Vb). A mixture of ketone (III) (0.38 g, 1 mmole), phenylacetic acid (0.14 g, 1 mmole), and polyphosphoric ester (3 g) is stirred for 30 min at 80°C and poured into 30 ml of cold water. Ether (15 ml) and 70% HClO (1 ml) are added and the mixture stirred vigorously for 15 min. An orange salt begins to crystallize at the ether—water interface. After 3 h the precipitate is removed by filtration, dried, and recrystallized from acetic acid. The salt (Vb) (0.3 g, 50%) mp 237°C (decomp.) is obtained. IR spectrum: 3540, 1600, 1540, 1240, 1090 cm^{-1}. Found, %: C 65.6, H 6.3, Cl 5.9. $C_{32}H_{37}ClO_8$. Calculated, %: C 65.7, H 6.3, Cl 6.1.

1-Benzyl-3-(3,5-di-t-butyl-4-phenacetoxyphenyl)-6,7-dimethoxy-2-benzopyrilium Perchlorate (Vc). A mixture of ketone (III) (0.38 g, 1 mmole), phenylacetic acid (0.35 g, 2.5 mmole), and polyphosphoric acid ester (5 g) is stirred for 1 h at 85°C and worked up as for salt (Vb). A dark-yellow salt (0.4 g, 70%), mp 174°C (from acetic acid), is obtained. IR spectrum: 1730, 1635, 1615, 1240, 1090 cm^{-1}. PMR spectrum ($CDCl_3$): 1.27 and 1.33 (two s, 6-CH_3), 3.93 (s, CH_2), 4.10 (s, 2-OCH_3), 4.93 (s, CH_2), 7.33 (m, 10-H), 7.80 (m, 4-H), 8.60 ppm (s, 1-H). Found, %: C 68.2, H 6.0, Cl 4.9. $C_{40}H_{43}ClO_9$. Calculated, %: C 68.3, H 6.1, Cl 5.1.

1-Phenyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)-6,7-dimethoxy-2-benzopyrilium Perchlorate (Vd). A mixture of ketone (III) (0.38 g, 1 mmole), benzoic acid (0.3 g, 3.5 mmole), and polyphosphoric ester (5 g) is stirred for 1.5 h at 85°C and worked up similarly to salt (Vb). A bright-red salt (Vd) (0.25 g, 43%) mp 204°C (from ethanol) is obtained. IR spectrum: 3625, 1620, 1590, 1240, 1090 cm^{-1}. PMR spectrum (CF_3COOH): 1.50 and 1.57 (two s, 6-CH_3), 4.01 (s, OCH_3), 4.30 (s, OCH_3), 7.50-8.23 (m, 9-H arom.), 9.50 ppm (s, 1-H). Found, %: C 65.3, H 6.2, Cl 6.0. $C_{31}H_{35}ClO_8$. Calculated, %: C 65.2, H 6.1, Cl 6.2.

1-Phenyl-3-(3,5-di-t-butyl-4-acetoxyphenyl)-6,7-dimethoxy-2-benzopyrilium Perchlorate (Ve). To a solution of salt (Vd) (0.28 g, 5 mmole) in acetic anhydride (5 ml) is added 70% $HClO_4$ (1 ml, 10 mmole) dropwise with cooling. The red solution becomes yellow. After addition of 100 ml of ether and the solution set aside for 24 h, a yellow salt (Vd) (0.3 g) mp 258° (from ethanol) is obtained in quantitative yield. IR spectrum: 1755, 1620, 1590, 1250, 1100 cm^{-1}. PMR spectrum ($CDCl_3$): 1.40 (s, 6-CH_3), 2.40 (s, CH_3), 4.00 (s, OCH_3), 4.23 (s, OCH_3), 7.20-8.13 (m, 9-H arom.), 8.90 ppm (s, 1-H arom.). Found, %: C 64.8, H 6.2, Cl 6.0. $C_{33}H_{37}ClO_9$. Calculated, %: C 64.7, H 6.0, Cl 5.8.

1-Methyl-3-(3,5-di-t-butyl-4-acetoxyphenyl)-6,7-dimethoxyisoquinoline (VIa) and 1-Benzyl-3-(3,5-di-t-butyl-4-phenacetoxyphenyl)-6,7-dimethoxyisoquinoline (VIc). These are obtained by method [5] in quantitative yield. Compound (VIa), mp 218°C (from ethanol). IR spectrum: 1750, 1620, 1580, 1200 cm^{-1}. PMR spectrum ($CDCl_3$): 1.38 (s, 6-CH_3), 2.35 (s, CH_3), 2.93 (s, CH_3), 4.09 (s, 2-OCH_3), 7.13 (s, 1-H), 7.28 (s, 1-H), 7.78 (s, 1-H), 8.05 ppm (s, 2-H). Found, %: C 74.8, H 7.7, N 3.1. $C_{28}H_{35}NO_4$. Calculated, %: C 74.8, H 7.8, N 3.1. Compound (VIc): mp 200°C (from ethanol). IR spectrum: 1735, 1600, 1590, 1235 cm^{-1}. Found, %: C 80.0, H 7.3, N 2.3. $C_{40}H_{43}NO_4$. Calculated, %: C 79.9, H 7.2, N 2.3.

1-Benzylidene-3-(3,5-di-t-butyl-4-hydroxyphenyl)-6,7-dimethoxyisochromene (VIIa) and 1-Benzylidene-3-(3,5-di-t-butyl-4-benzoyloxyphenyl)-6,7-dimethoxyisochromene (VIIb). These are obtained by the method of [14] in quantitative yield. For compound (VIIa): mp 140-141°C (from ethanol). IR spectrum: 3600, 1630, 1610, 1580, 1250 cm^{-1}. Found, %: C 79.3, H 7.6. $C_{32}H_{36}O_4$. Calculated, %: C 79.3, H 7.4. For compound (VIIb): mp 178°C (from ethanol). IR spectrum: 1735, 1638, 1600, 1580, 1230 cm^{-1}. PMR spectrum (CCl_4): 1.30 (s, 6-CH_3), 3.73 (s, OCH_3), 3.77 (s, OCH_3), 3.85 (s, CH_2), 5.83 (s, 1-H), 6.13 (s, 1-H), 6.43 (s, 1-H), 6.90 (s, 1-H), 7.07 (s, 1-H), 7.23-7.63 ppm (m, 11-H arom.). Found, %: C 79.8, H 7.1. $C_{40}H_{42}O_5$. Calculated, %: C 79.7, H 7.0.

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