SYNTHESIS OF 4-ALKOXYBENZOPYRYLIUM SALTS AND CHROMONES

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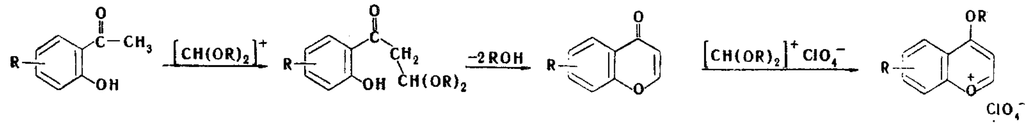
The reaction of substituted o-hydroxyacetophenones with ethyl orthoformate in the presence of 70% perchloric acid gave 4-alkoxybenzopyrylium salts, which were converted to the corresponding chromones in almost quantitative yield on refluxing with water.

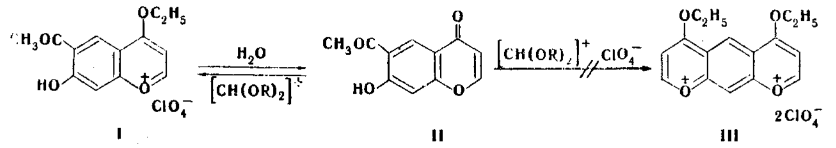
o-Hydroxyaryl alkyl ketones react with ethyl orthoformate in the presence of 70% perchloric acid [1] or other acid catalysts [2] to give good yields of 4-ethoxychromylium or 4-ethoxyisoflavylium salts [3], which have been used to obtain several natural chromones.

To further study the range of application of this method, we investigated the condensation of a number of o-hydroxyacetophenones with ethyl orthoformate in the presence of 70% perchloric acid. As expected, this reaction gave 4-ethoxychromylium salts (Table 1) in good yields.

$$CH(OR)_3 + HClO_4 \longrightarrow [CH(OR)_2]^+ClO_4^- + ROH$$



The reaction of resodiacetophenone with ethyl orthoformate proceeds peculiarly. In this case, one obtains the difficult-to-purify 4-ethoxy-6-acetyl-7-hydroxybenzopyrylium perchlorate (I), which is converted to 6-acetyl-7-hydroxychromone (II) on treatment with water:



When attempts were made to subsequently condense I and II with ethyl orthoformate in order to obtain bispyrylium salt III, starting salt I was isolated in both cases.

All of the synthesized 4-alkoxybenzopyrylium salts are readily converted to the corresponding chromones (Table 2) in almost quantitative yields on heating with water. Considering the high yields and simplicity of this method, it can be assumed that this method for the preparation of chromones is one of the most convenient of the previously known methods.

The IR spectra of the 4-alkoxybenzopyrylium salts contain intense absorption bands of the pyrylium cation (1620-1630, 1530-1540, and 1460-1500 cm^{-1}), the benzene ring (1590-1610 cm^{-1}), alkoxy groups (1240-1260 cm^{-1}), hydroxyl groups (3410 cm^{-1}), and the ClO_4^- ion (1080-1090 cm^{-1}). The IR spectra of the synthesized chromones also are in agreement with the literature data [1].

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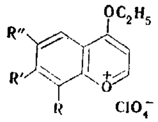
TABLE 1



R	R′	R″	mp, °C[a]	Empirical formula	Found, %			Calculated, %			IR spectrum, cm^{-1}	UV spectrum (in dichloroethane)		Yield, %
					C	H	Cl	C	H	Cl		λ_{max}, nm	lg ε	
H	OCH$_3$	H	121	$C_{12}H_{13}ClO_7$	47,5	4,3	11,3	47,3	4,3	11,6	1625, 1600, 1530, 1465, 1380, 1255, 1090	270 305 330	3,81 4,07 3,75	85
H	H	OH	175	$C_{11}H_{11}ClO_7$	46,2	3,6	11,9	45,5	3,8	12,1	3380—3410, 1630, 1600, 1530, 1460, 1090, 1260	270[b] 305 370	4,11 3,89 3,69	90
H	CH$_3$	H	131	$C_{12}H_{13}ClO_6$	50,2	4,6	12,1	50,0	4,5	12,3	1625, 1600, 1530, 1460, 1250, 1090	310 420	4,09 2,90	70
H	H	CH$_3$	160	$C_{12}H_{13}ClO_6$	50,2	4,6	11,9	50,0	4,5	12,3	1620, 1600, 1540, 1460, 1250, 1090	300 340	3,95 3,53	65
CH$_3$	CH$_3$	H	143	$C_{13}H_{15}ClO_6$	51,3	5,2	11,4	51,6	5,0	11,7	1620, 1590, 1540, 1460, 1330, 1260, 1090	320	3,92	30
H	CH$_3$	i-C$_3$H$_7$	119	$C_{15}H_{19}ClO_6$	54,7	5,9	10,8	54,5	5,7	10,7	1623, 1600, 1530, 1460 1325, 1260, 1080	280, 320	3,87 3,82	50

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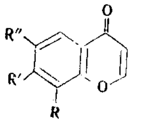
[a] All of the compounds were obtained as colorless or pale-yellow crystals and were purified by reprecipitation from glacial acetic acid by the addition of ether. [b] The spectrum of this compound was obtained with an acetic acid solution.

TABLE 2



R	R′	R″	mp, °C	Empirical formula	IR spectrum, cm^{-1}	UV spectrum (in alcohol)		Yield, %
						λ_{max}, nm	lg ε	
H	CH_3	H	95[a]	$C_{10}H_8O_2$	1630, 1600, 1460, 1375, 1340, 1245	243 250 308	3,90 3,88 3,65	85
H	H	CH_3	88[b]	$C_{10}H_8O_2$	1650, 1620, 1570, 1460, 1375, 1240	245 306	3,95 3,76	90
H	H	OH	244[c]	$C_9H_6O_3$	1640, 1610, 1460, 1380	250 330	3,93 3,72	80
H	OCH_3	H	110[d]	$C_{10}H_8O_3$	1630, 1600, 1460, 1370, 1240	240 248 305	4,14 4,16 3,97	85
CH_3	CH_3	H	152[e]	$C_{11}H_{10}O_2$	1630, 1590, 1460, 1370, 1240	244 252 305	4,13 4,12 3,87	80

[a] According to [4], mp 72°. Found: C 75.1; H 5.0%. $C_{10}H_8O_2$. Calculated: C 75.0; H 5.0%. [b] According to [4], mp 88-89°. [c] According to [5], mp 243°. [d] According to [6], mp 110°. [e] Found: C 75.9; H 5.8%. $C_{11}H_{10}O_2$. Calculated: C 75.9; H 5.7%.

There is an intense absorption band at 300-320 nm, which corresponds to a $\pi^* \rightarrow \pi$ transition, in the UV spectra of all of the benzopyrylium salts obtained.

There are short-wave (240-245 nm) and long-wave (300-325 nm) absorption bands in the UV spectra of the chromones. The long-wave band in the spectrum of 7-hydroxy-6-acetylchromone is shifted to 375 nm as a consequence of an increase in the conjugation chain.

EXPERIMENTAL

o-Hydroxyaryl Alkyl Ketones. The starting substituted acetophenones were obtained by acetylation of the appropriate phenols with acetic anhydride in the presence of 70% perchloric acid at reagent ratios of 1 : 3 : 1 and 1 : 3 : 0.5, regarding which we will additionally communicate in greater detail.

Resodiacetophenone. A 0.5-ml (0.005 mole) sample of 70% perchloric acid was added with cooling to a solution of 1.1 g (0.01 mole) of resorcinol in 3.06 ml (0.03 mole) of acetic anhydride, and the mixture was refluxed for 10-12 min. The reaction mixture began to crystallize when it was cooled. The resodiacetophenone was removed by filtration and washed with 50% ethanol to give 0.82 g (42%) of a product with mp 182° (from alcohol) [4].

2-Hydroxy-4-methoxyacetophenone. A 7-ml (0.07 mole) sample of 70% perchloric acid was added with cooling to a solution of 12.4 g (0.1 mole) of m-methoxyphenol in 30.18 ml (0.3 mole) of acetic anhydride, and the mixture was refluxed gently for 4-5 min and diluted with ether. The mixture was filtered, and the ether solution was washed with ice water and dried with anhydrous sodium sulfate. The solvent was removed by distillation, and the residue was steam-distilled to give 6.6 g (40%) of 2-hydroxy-4-methoxyacetophenone as colorless crystals with mp 50° [4].

4-Ethoxy-7-methoxychromylium Perchlorate. A 0.5-ml (0.005 mole) sample of 70% perchloric acid was added all at once to a solution of 0.83 g (0.005 mole) of 2-hydroxy-4-methoxyacetophenone and 4.4 ml (0.03 mole) of freshly distilled ethyl orthoformate, and the mixture was allowed to stand for 10-15 min. It was then diluted with ether, and the resulting precipitate was removed by filtration and reprecipitated from glacial acetic acid by the addition of ether to give 1.29 g (85%) of product. The other 4-alkoxybenzopyrylium salts (Table 1) were similarly obtained.

Chromones. A total of 10-15 ml of water was added to 0.01 mole of substituted 4-ethoxychromylium perchlorate, and the mixture was boiled for 1-2 min. The resulting colorless precipitate was removed by filtration, air-dried, and crystallized from aqueous alcohol or water (Table 2).

6-Acetyl-7-hydroxychromone. A 2-ml (0.02 mole) sample of 70% perchloric acid was added to a solution of 0.97 g (0.005 mole) of resodiacetophenone and 16 ml of ethyl orthoformate, and the mixture was allowed to stand for 15-20 min. It was then diluted with a threefold amount of ether, and the resulting oil was treated with 30-40 ml of water. The aqueous mixture was boiled for 2-3 min, and the resulting precipitate was removed by filtration and air-dried to give colorless crystals with turquoise luminescence in UV light and mp 169° (from alcohol). IR spectrum: 1660, 1630, 1610, 1460, 1380 cm^{-1}. UV spectrum, nm ($\log \varepsilon$): 255 (4.31), 284 (4.47), 373 (3.84). Found: C 64.6; H 4.0%. $C_{11}H_8O_4$. Calculated: C 64.7; H 3.9%.

The IR spectra of mineral oil pastes of the compounds were recorded with a UR-20 spectrophotometer. The UV spectra were recorded with a Specord uvv is spectrophotometer.

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