3250 (broad, NH and OH), 1655, 1725 (CO). Found: C 62.2; H 4.8; N 3.1%. $C_{25}H_{23}NO_7S$. Calculated: C 62.4; H 4.8; N 2.9%.

1,2-Dimethyl-3-acetyl-4-(p-tolylsulfonyl)-5-hydroxyindole (XIII) and 3-[2-p-Tolylsulfonyl)-3,6-dihydroxyphenyl]acetyl acetone (XIV). A solution of 2.26 g (0.02 mole) of 4-methylamino-3-penten-2-one (X) [7] was added with stirring to a suspension of 5.25 g (0.02 mole) of Ib in 80 ml of glacial acetic acid, and the mixture was allowed to stand at room temperature for 2 days. The solvent was then vacuum evaporated to a residual volume of 10 ml, and the precipitate was separated and washed with methanol to give 2.65 g (37%) of XIII with mp 209-210° (from methanol) and $R_f$ 0.84. IR spectrum, $\nu_{max}$, $cm^{-1}$( 3190-3340 (OH, NH) and 1625 (CO). Found: C 63.9; H 5.4; N 4.3%. $C_{19}H_{19}NO_4S$. Calculated: C 63.8; H 5.4; N 3.9%. The mother liquor remaining after separation of hydroxyindole XIII was diluted with water, and the resulting precipitate was removed by filtration to give 1.55 g (21%) of XIV with mp 146-148° (from methanol) and $R_f$ 0.70. IR spectrum, $\nu_{max}$, $cm^{-1}$: 3250 (OH) and 1725 and 1755 (CO). Found: 59.6; H 4.9%. $C_{18}H_{18}O_6S$. Calculated: C 59.7; H 5.0%.

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# 2-BENZOPYRLIUM SALTS.

## XVIII.* SYNTHESIS OF 2-BENZOPYRYLIUM SALTS BASED ON SOME ENOL ACYLATES

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The fundamental possibility of the synthesis of 2-benzopyrylium salts by intramolecular cyclization of enol acylates of suitable structure is shown. An assumption is made regarding the mechanism of the formation of pyrylium salts from enol acetates in the presence of acylating agents.

The possibility of primary acylation of the carbonyl oxygen atom and, in analogy with the Pictet–Gams reaction [2], subsequent cyclization of the resulting enol acylate to a 2-benzopyrylium salt exists in the preparation of 2-benzopyrylium salts by acylation with various benzyl ketones.

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*See [1] for communication XVII.

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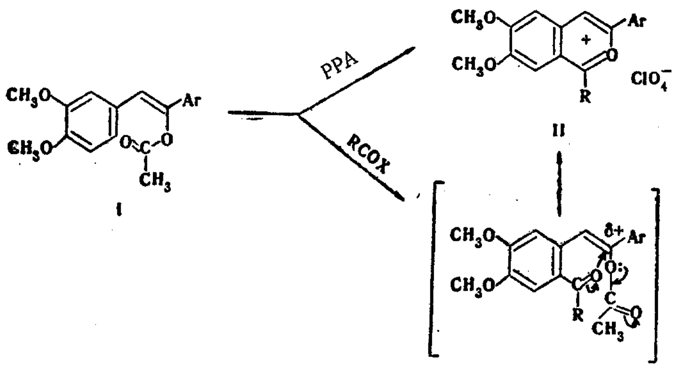
A preliminary verification of this assumption showed that the enol acetate of phenylacetaldehyde forms either polymeric products or 4-hydroxypyrylium salts [3], depending on the reaction conditions.

One should have expected that the probability of successful intramolecular cyclization would be considerably higher when donor substituents are present in the ring of the enol acetate of the benzyl ketone under attack.

In fact, salts IIa, c, d, which, according to the IR spectroscopic data and melting points, are completely identical to the previously described compounds [4], are smoothly formed in 56-75% yields on treatment of enol acetates (Ia-c) of desoxybenzoins with polyphosphoric acid (PPA)



I a $Ar=3,4\text{-}(OCH_3)_2C_6H_3$; b $Ar=3\text{-}OCH_3C_6H_4$; c $Ar=3\text{-}OC_2H_5C_6H_4$; II a $Ar=3,4\text{-}(OCH_3)_2C_6H_3$, $R=CH_3$; b $Ar=3,4\text{-}(OCH_3)_2C_6H_3$, $R=C_2H_5$; c $Ar=3\text{-}OCH_3C_6H_4$, $R=CH_3$; r $Ar=3\text{-}OC_2H_5C_6H_4$, $R=CH_3$

It was noted that the yield of salt IIa is raised to 80% when Ia is treated with acetic anhydride in the presence of perchloric acid.

In order to determine the character of the action of the reagent used in the reaction we established the structure of the salts formed during the reaction of enol acetate Ia with a mixture of propionic anhydride and perchloric or polyphosphoric acid, i.e., with an acylating agent with a different structure. In both cases we isolated identical salts, in the PMR spectra we observed the signal of an ethyl group, whereas the singlet at $\delta$ 2.95 ppm characteristic for an $\alpha$-methyl group vanished.

Transesterification ("transvinylation") evidently does not occur in this case, inasmuch as, first, this process requires, as a rule, specific catalysis by divalent mercury salts [5], and, second, it would lead to the formation of an ester, the cyclization of which to a salt would be energetically somewhat less favorable as compared with starting enol acetate Ia.

Thus it may be assumed that in the cyclization of enol acetates the presence of acyl cations in the reaction mixture makes intermolecular acylation with subsequent splitting out of acetic acid fragments to give salt IIb preferable.

Despite the fact that in this case the method of synthesis of 2-benzopyrylium salts by cyclization of enol acetates Ia-c is inferior to the general method for their synthesis on the basis of acylation of benzyl ketones, it will undoubtedly have definite advantages when difficult-to-obtain starting carbonyl compounds of the homoveratraldehyde type are used.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71IR spectrometer. The PMR spectra of $CF_3COOH$ solutions of the compounds were recorded with a Tesla spectrometer with an operating frequency of 80 MHz at 60° with hexamethyldisiloxane as the internal standard.

Desoxyveratroin Enol Acetate (Ia). A solution of 0.63 g (0.02 mole) of desoxyveratroin and 0.34 g (0.02 mole) of p-toluenesulfonic acid monohydrate in 75 ml of acetic anhydride was refluxed slowly until the bulk of the anhydride was removed by distillation (4-5 h), after which the mixture was cooled and diluted with water, and the resulting precipitate was removed by filtration, washed with sodium carbonate solution and water, and dried to give 0.3 g (42%) of light-yellow crystals with mp 140° (from alcohol). Found: C 66.9; H 6.0%. $C_{20}H_{22}O_6$. Calculated: C 67.0; H 6.1%. IR spectrum: 1765, 1605, and 1585 $cm^{-1}$.

3'-Methoxydesoxyanisoin Enol Acetate (Ib). A similar method was used to obtain this compound, with mp 110° (from alcohol), in 50% yield. Found: C 69.3; H 5.9%. $C_{19}H_{20}O_5$. Calculated: C 69.5; H 6.1%. IR spectrum: 1760, 1605, and 1580 $cm^{-1}$.

3'-Ethoxy-3,4-dimethoxydesoxybenzoin Enol Acetate (Ic). This compound, with mp 113° (from alcohol), was similarly obtained in 53% yield. Found: C 70.1; H 6.2%. $C_{20}H_{22}O_5$. Calculated: C 70.2; H 6.4%. IR spectrum: 1763, 1610, and 1580 $cm^{-1}$.

1-Methyl-3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (IIa). A) A mixture of 0.3 g (0.001 mole) of desoxyveratroin enol acetate and 3 g of PPA was heated at 130° with vigorous stirring for 40 min, after which the mixture was hydrolyzed with cold water and acidified with 30% $HClO_4$. The precipated crystals were removed by filtration, dried, and recrystallized from nitromethane—acetic acid (1:1) to give 0.2 g (56%) of orange crystals with mp 250° (dec.). IR spectrum: 1624, 1602, 1544, and 1512 $cm^{-1}$. No melting point depression was observed for a mixture of this product with a sample obtained by the method in [4] and the IR spectra of the compounds coincided completely. PMR spectrum: $\delta$ 2.95 (s, $CH_3$), 3.65, 3.70, 3.80, and 3.90 (four $CH_3O$ groups), and 6.78-7.93 ppm (m, 6H).

1-Methyl-3-(3-methoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (IIc) and 1-Methyl-(3-ethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (IId). These compounds were similarly obtained in 75 and 65% yields from enol acetate Ib and enol acetate Ic, respectively.

B) A 0.3-ml sample of 70% $HClO_4$ was added dropwise to a solution of 0.3 g (0.001 mole) of desoxyveratroin enol acetate in 3 ml of acetic anhydride, after which the mixture was allowed to stand for 24 h. Workup gave 0.29 g (81%) of a product, which, according to the IR spectrum and melting point, was identical to the product described in method A.

1-Ethyl-3-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-benzopyrylium Perchlorate (IIb). A) A mixture of 0.2 g (0.0006 mole) of deoxyveratroin enol acetate, 0.2 g (0.002 mole) of propionic anhydride, and 2 g of PPA was heated with vigorous stirring at 100° for 40 min. The usual workup gave 0.2 g (80%) of red crystals with mp 260°. IR spectrum: 1625, 1602, 1540, and 1512 $cm^{-1}$. No melting-point depression was observed for a mixture of this product with a sample obtained by the method in [4], and the IR spectra of the compounds coincided completely. PMR spectrum: $\delta$ 1.33 (t, $CH_3$), 3.39 (q, $CH_2$), 3.65, 3.70, 3.80, and 3.90 (four $CH_3O$ groups), and 6.83-7.95 ppm (m, 6H).

B) Reaction of 0.2 g of desoxyveratroin enol acetate, 2 ml of propionic anhydride, and 0.2 ml of 70% $HClO_4$ by the usual method gave 0.2 g (80%) of a salt, which, according to its melting point and IR and PMR spectra, was completely identical to the product described in method A.

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