2-BENZOPYRYLIUM SALTS

XIX.* SYNTHESIS OF OXABENZO[c]PHENANTHRENIUM SALTS

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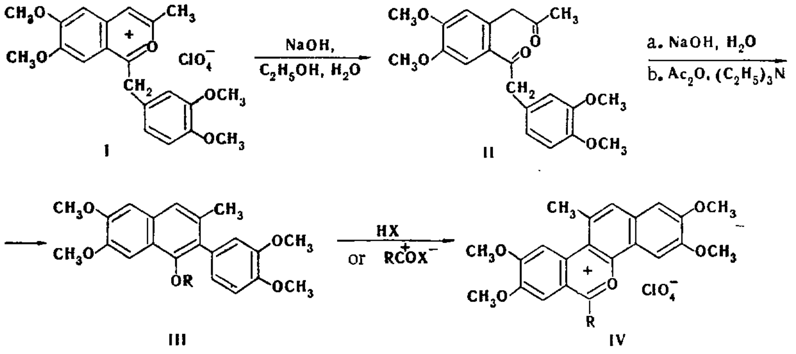
The previously unknown oxabenzo[c]phenanthrenium salts were synthesized from β-veratryl-α-naphthol and its acetate.

Despite the fact that o-arylphenols (naphthols) in a number of cases display the properties of the corresponding unsaturated cyclic ketones [2], up until now they have not been used in the synthesis of 2-benzopyrylium salts. One of the reasons for this is apparently the lack of reliable methods for the synthesis of the starting arylated phenols and naphthols [2].

In our opinion, a method for their synthesis based on the well-known (in the chemistry of pyrylium salts) alkaline condensation [4] of α-benzyl-substituted pyrylium salts may be of definite preparative value.

In the present paper we describe the synthesis of β-veratryl-α-naphthol (IIIa) by condensation of the open form of 1-(3,4-dimethoxybenzyl)-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate and the preparation from it of the previously unknown polycyclic 2-benzopyrylium salts — oxabento[c]phenanthrenium salts (IV).



IIIa R=H; b R=COCH$_3$; IVa R=CH$_3$; b R=C$_2$H$_5$; c R=CH$_2$C$_6$H$_5$; d R=H

The acylation of α-naphthol IIIa with aliphatic anhydrides in the presence of perchloric acid or polyphosphoric acid (PPA) and phenylacetic acid in PPA made it possible to obtain salts IVa-c in high yields.

Attempts to synthesize the 6-unsubstituted salt by the Riehe [5] and Vilsmeier–Haack [6] methods for direct formylation in the ring were unsuccessful. However, we were able to isolate salt IVd in 75% yield by treatment of the naphthol with excess 98% formic acid in PPA. In this case the O-formyl derivative is probably formed initially and then undergoes cyclization to the salt.

Cyclization to naphthol acetate IIIb, which can be obtained either by reaction of the open form of II with acetic anhydride in the presence of triethylamine or, in quantitative yield, by heating naphtol IIIa with acetic anhydride without a catalyst, occurs just as smoothly on treatment with PPA.

As in the acylation of enol acetates [1], treatment of the naphthol acetate with a mixture of propionic anhydride and perchloric acid or PPA led to salts with an ethyl group in the 6 position.

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*See [1] for communication XVIII.

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TABLE 1. Conditions for the Preparation of 2,3,8,9-Tetramethoxy-6,11-dimethyl-5-oxabenzo[c]phenanthrenium Perchlorate (IVa)*

No.	Starting compound	Acylating agent	Catalyst	Conditions	Yield, %
			acylating agent/ catalyst		
1	Naphthol	$(CH_3CO)_2O$	PPA, tenfold excess	1 h, 75–80°	Quantitative
2	Naphthol	$(CH_3CO)_2O$	$HClO_4$, 11 : 1	For a few seconds at 100° and for 24 h at room temperature	51
3	Naphthol acetate	—	PPA, tenfold excess	25 min, 130°	83
4	Naphthol acetate	$(CH_3CO)_2O$	$HClO_4$, 11 : 1	For 24 h at room temperature	67

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*This compound had mp > 310° (from nitromethane). PMR spectrum: δ 2.85 (s, CH_3); 3.13 (s, CH_3); 3.73, 3.80, 3.85, and 4.00 (four CH_3O groups): and 7.05-8.20 ppm (m, 5H). Found: C 57.8: H 5.2; Cl 8.0%. $C_{23}H_{23}ClO_9$. Calculated: C 57.6; H 4.8; Cl 7.9%. IR spectrum: 1610, 1505, 1255, 1100 cm^{-1}.

An indirect proof for the occurrence in this case of intermolecular acylation is the extreme stability of naphtol acetate IIIb under various conditions of acidic and basic hydrolysis.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71 IR 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.

3,4-Dimethoxy-6-homoveratroylphenylacetone (II). A solution of 2.5 g of NaOH in 5 ml of water was added to a suspension of 4 g (0.009 mole) of 1-(3,4-dimethoxybenzyl)-3-methyl-6,7-dimethoxy-2-benzopyrylium perchlorate [7] in 15 ml of ethanol, after which the mixture was refluxed for 2 h. The alcohol was then removed by distillation, and the resulting precipitate was removed by filtration and dried to give 2.5 g (81%) of yellow crystals with mp 187° (from alcohol). Found: C 67.6; H 6.3%. $C_{21}H_{24}O_6$. Calculated: C 67.7; H 6.4%. IR spectrum: 1670, 1610, and 1250 cm^{-1}.

2-(3,4-Dimethoxyphenyl)-3-methyl-6,7-dimethoxy-α-naphthol (IIIa). A suspension of 9.4 g (0.0253 mole) of the open form of II and 25 g of NaOH in 200 ml of water was refluxed for 6 h, after which it was cooled, and 4.8 g (51%) of the unchanged open form of II was removed by filtration. The filtrate was acidified with concentrated hydrochloric acid, and the resulting precipitate was removed by filtration and dried to give 1.7 g (39% based on the converted open form) of light-yellow crystals with mp 177° (from alcohol). IR spectrum: 3520, 1600, and 1565 cm^{-1}. Found: C 71.5; H 6.7%. $C_{21}H_{22}O_5$. Calculated: C 71.2; H 6.4%.

2-(3,4-Dimethoxyphenyl)-3-methyl-6,7-dimethoxy-α-naphthol Acetate (IIIb). A solution of 1.5 g (0.004 mole) of the open form of II and 2 ml of triethylamine in 15 ml of acetic anhydride was refluxed for 24 h, after which it was cooled and poured into water. The excess acetic anhydride was neutralized with sodium carbonate, and the resulting oil, which crystallized rapidly, was washed with water and dried to give 0.5 g (31%) of light-yellow crystals with mp 156° (from alcohol). IR spectrum: 1760, 1605, and 1575 cm^{-1}. Found: C 73.9; H 6.0%. $C_{23}H_{24}O_6$. Calculated: C 73.4; H 6.4%.

2,3,8,9-Tetramethoxy-6-ethyl-11-methyl-5-oxabenzo[c]phenanthrenium Perchlorate (IVb). A) A mixture of 0.2 g (0.001 mole) of naphthol acetate IIIb, 0.3 g (0.002 mole) of propionic anhydride, and 5 g of PPA was heated at 130 g with vigorous stirring for 15 min. The reaction mixture was then hydrolyzed with cold water and acidified with 30% $HClO_4$, and the resulting precipitate was removed by filtration, washed successively with acetic acid and ether, and dried to give 0.2 g (74%) of orange crystals with mp > 310° (from nitromethane). IR spectrum: 1610, 1505, 1255, and 1100 cm^{-1}. PMR spectrum: δ 1.45 (t, CH_3): 2.85 (s, CH_3): 3.57 (q, CH_2); 3.73, 3.80, 3.85, and 4.00 (four CH_3O groups); and 7.03-8.18 ppm (m, 5H). Found: C 58.3; H 5.0; Cl 7.2%. $C_{24}H_{25}ClO_9$. Calculated: C 58.4; H 5.1; Cl 7.3%.

B) Salt IVb was obtained in 40% yield by acylation of IIIb with propionic anhydride in the presence of $HClO_4$.

2,3,8,9-Tetramethoxy-6-benzyl-11-methyl-5-oxabenzo[c]phenanthrenium Perchlorate (IVc). A mixture of 0.5 g (0.0014 mole) of α-naphthol IIIa, 0.19 g (0.0014 mole) of phenylacetic acid, and 7 g of PPA was heated at 70° with vigorous stirring for 1 h. The reaction mixture was then hydrolyzed and acidified with 30% $HClO_4$, and the resulting precipitate was removed by filtration, washed successively with acetic acid and ether, and dried to give 0.65 g (83%) of orange crystals with mp 296° (from nitromethane). IR spectrum: 1610, 1505, 1255, and 1065 cm^{-1}. Found: C 60.9; H 5.2; Cl 6.0%. $C_{29}H_{29}ClO_9$. Calculated: C 60.4; H 4.9; Cl 6.5%.

2,3,8,9-Tetramethoxy-11-methyl-5-oxabenzo[c]phenanthrenium Perchlorate (IVd). A mixture of 0.5 g (0.0014 mole) of α-naphthol IIIa, 3 ml of 98% HCOOH, and 5 g of PPA was heated at 80° for 20 min and at 100° for 40 min, after which it was worked up in the usual way to give 0.5 g (75%) of orange crystals with mp > 300° (from nitromethane). IR spectrum: 1612, 1505, 1250, and 1065 cm^{-1}. PMR spectrum: δ 2.75 (s, CH_3); 3.55, 3.60, 3.80, and 3.98 (four CH_3O groups); and 6.93-8.08 ppm (m, 6H). Found: C 56.6; H 4.5; Cl 7.6%. $C_{22}H_{21}HClO_3$. Calculated: C 56.7; H 4.5; Cl 7.7%.

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