

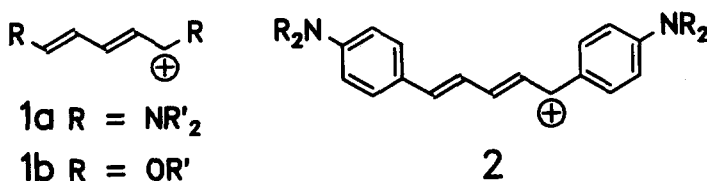
An Isolable Dioxasubstituted Pentadienylium Ion

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Abstract: The condensation of the bis-*ortho*-substituted acetophenone **3** with triethyl orthoformate (**4**) by perchloric acid does not yield a pyrylium salt **5** but a pentadienylium ion **6** which is stabilized by oxasubstituents.

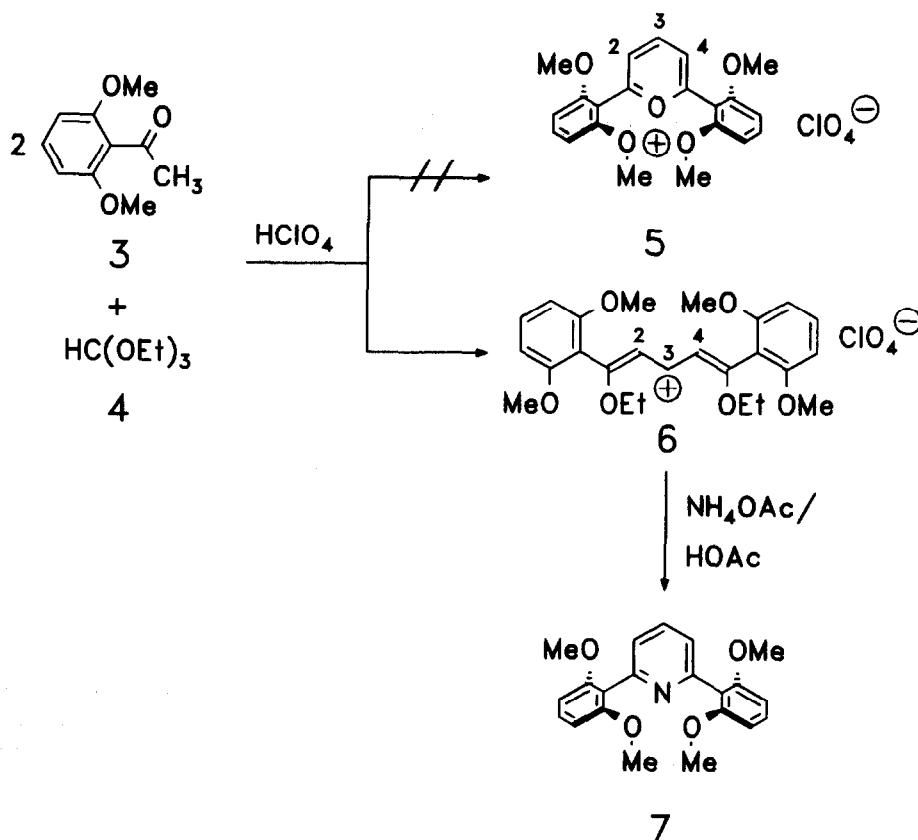
Pentadienylium salts **1** are a class of carbocations which can be isolated when they contain stabilizing substituents R in 1- and 5-position. For photographic processes a variety of 1,5-bis(4-dialkylaminophenyl)pentadienylium ions **2** have been developed¹. The stabilization by aminogroups in 1- and 5-position is also well known², a variety of vinylogous amidinium salts **1a** has been synthesized some of which are used in synthesis^{2e}.



The substitution by oxasubstituents instead of amino groups (**1b**) is not documented, probably because 1,5-dioxa-substituted pentadienylium cations **1b** cyclize to form the more stable, well known³ pyrylium ions.

We have now found that a 1,5-dioxa-substituted, stable pentadienylium ion **6** can be generated when carrying appropriate substituents. These stabilize the positive charge but for steric reasons hinder the cyclization to a pyrylium ion **5**. Such a substituent is the 2,6-dimethoxyphenyl group. In the Scheme the synthesis of the pentadienylium ion **6** is described. This reaction pathway uses the well known methodology^{3, 4} for the synthesis of pyrylium compounds condensating two molecules of an acetophenone with triethyl orthoformate in perchloric acid. But with methoxy substituents in the *ortho*-positions of the acetophenone **3** this reaction formed the orange crystalline pentadienylium ion **6** instead of the pyrylium ion **5**.

Scheme:



The structure of 6 was proven by ¹H and ¹³C NMR, MS, IR and elemental analysis ⁵. The mass spectra, the NMR spectra and the elemental analysis showed the additional ethoxy groups in compound 6 (in comparison to the expected pyrylium salt 5), the large coupling constants between the protons in 2-, 3- and 4-position argued for a *trans*- rather than a *cis*-orientation of these protons, and the chemical shifts in the NMR spectra differed enormously from those expected for pyrylium salts (e. g. ¹H NMR shifts of pyrylium ions: ≥8.2 ppm ⁶, here: 6.91 and 7.27 ppm).

The formation of the open-chain pentadienylium ion 6 instead of the cyclic pyrylium ion 5 may be explained by the fact that in the pentadienylium ion 6, the positive charge can be stabilized by conjugation with the electron-rich aryl rings and the ethoxy groups. In the pyrylium ion 5, however, there would be repulsions between the two bis-methoxy substituted phenyl rings. This would lead to a large twist between the planes of the pyrylium ring and the phenyl rings, thus inhibiting a mesomeric stabilization of the positive charge by the bis(methoxy)phenyl groups.

A further proof of the structure of 6 was its reaction to the sterically hindered diarylpyridine 7, a precursor for a new class of concave pyridines ⁷. This cyclization of 6 was only possible with ammonium acetate in acidic media. With ammonia itself, no pyridine formation was found ^{7b}. Pyrylium

salts, in contrast, may be transformed to pyridines either by reaction with ammonia or in an acidic ammonium buffer^{3, 8}.

References and Footnotes

1. E. g. 1,5-Bis[4-dimethylaminophenyl]pentadienylium perchlorate, *Beilsteins Handbuch der Organischen Chemie*, 4. ed., 4. Ergänzungswerk, vol. 13, p. 2262, Springer, Berlin - Heidelberg - New York - Tokyo, 1985. A huge number of related compounds were cited in patents during the past two decades, see *Chem. Abstr.*, *Subject Index*: "Pentadienylium....".
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5. 1,5-Bis(2',6'-dimethoxyphenyl)-1,5-diehoxy-pentadienylium perchlorate (**6**): 3.55 ml (ca. 42 mmol) of HClO₄ (70 %) was added to a solution of 6.20 g (34.4 mmol) of 2,6-dimethoxyacetophenone⁹ (**3**) in 28.60 g (172.2 mmol) of freshly distilled (b. p. 68°C / 20 Torr) triethyl orthoformate. An exothermic reaction occurred and the mixture turned red. After 1.5 h at room temp. and 30 min at reflux temp., the mixture was cooled to 0°C and 100 ml of diethyl ether and ca. 2 ml of water were added yielding a brown to orange precipitate which was washed with iccold diethyl ether and dried in vacuo (8.2 g). Recrystallization from diethyl ether which contained some acetone yielded 5.60 g (62 %) of orange **6**, m. p. 162 - 168°C (dec.). - IR (KBr): $\nu = 3080, 3040, 3000, 2970, 2925, 2830 \text{ cm}^{-1}$ (C-H), 1610 - 1530, 1470 (br., C=C, arom.), 1170 - 1050 (C-O). - MS (EI) : m/z (%) = 398 (M⁺ -Et, 30), 353 (M⁺ -Et -OEt, 36), 156 (100). - High resolution-MS of signal 398 (C₂₃H₂₆O₆, M⁺ - Et): calcd.: 398.1727, found: 398.1732. - High resolution-MS of signal 353 (C₂₁H₂₁O₅, M⁺ - Et - OEt): calcd.: 353.1387, found: 353.1401. - ¹H NMR (250 MHz, CDCl₃) : $\delta = 1.46$ (t, $J = 7$ Hz, 6 H), 3.66 (s, 12 H), 4.48 (q, $J = 7$ Hz, 4 H), 6.50 (d, $J = 8.0$ Hz, 4 H), 6.91, 7.27 (ABA', $J = 14$ Hz, $J = 12.5$ Hz, 2 H, 1 H), 7.39 (t, $J = 8.0$ Hz, 2 H). - ¹³C NMR (100 MHz, CDCl₃) : $\delta = 14.2, 56.1, 70.7, 103.9, 108.4, 114.4, 134.0, 157.4, 174.6, 188.9$.
C₂₅H₃₁O₆·ClO₄ (526.97) Calcd. C, 56.98; H, 5.93. Found C, 56.81; H, 5.88 %.

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