

## 2-BENZOPYRILIUM SALTS.

### 28.\* CONVERSION OF 1-METHYL-2-BENZOPYRILIUM SALTS INTO SUBSTITUTE CHRYSENES IN BASIC MEDIA

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It is shown that the conversion of 1-methyl-2-benzopyrilium salts into chrysenes in basic media occurs via an intermediate dimeric pseudobase. The properties of this have been examined, and mechanisms are proposed for its formation and conversion into chrysenes.

We have previously [1] described the conversion of 1-methyl-2-benzopyrilium salts into substituted chrysenes, and shown that 1,5-diketones, which are often considered as the main intermediates in a variety of recyclizations of the pyrilium ring, are not involved in this reaction, at least in basic media. The formation of 1,5-diketones such as (III) occurs by the direct attack of the pyrilium cation on water or the hydroxide anion followed by ring opening in the intermediate pseudobase.

Under these conditions, however, there is an alternative for 1-alkyl-2-benzopyrilium salts, namely initial deprotonation to give the anhydro-base (V). The latter types of compound are analogs of vinyl ethers which are known not to be hydrated in basic solution, and therefore the pseudobase (II) and the diketone (III) cannot be formed.

On the other hand, since a negative charge is centered on the exo-methylene group in the anhydro-base (V), if screening alkyl or aryl groups are absent it can interact with electrophiles present in the reaction mixture. The unreacted pyrilium salt (I) can function as such an electrophilic entity in this reaction.

It has been found that treatment of the salt (I) with aqueous sodium acetate at 20°C affords, in addition to the diketone (III) [1], a product the PMR spectrum of which shows the presence of four methoxy-groups, evidence that dimerization of the initial salt has occurred. In addition, the spectrum contains signals for three methyl groups, four aromatic and two vinyl protons. The broadened one-proton signal at 5.82 ppm, which disappears on deuteration, is assigned to a tertiary OH group, which absorbs in the IR spectrum at 3350  $\text{cm}^{-1}$ . The absorption at 1660  $\text{cm}^{-1}$  is due to the presence of isochromene moieties. The splitting of the methylene group signal at 2.60 ppm in the PMR spectrum is explicable in terms of the chirality of the molecule formed.

On the basis of the spectral data, the molecular mass (454), and the elemental analysis, the product obtained is assigned the pseudobase structure (VII), formed as shown in the diagram below.

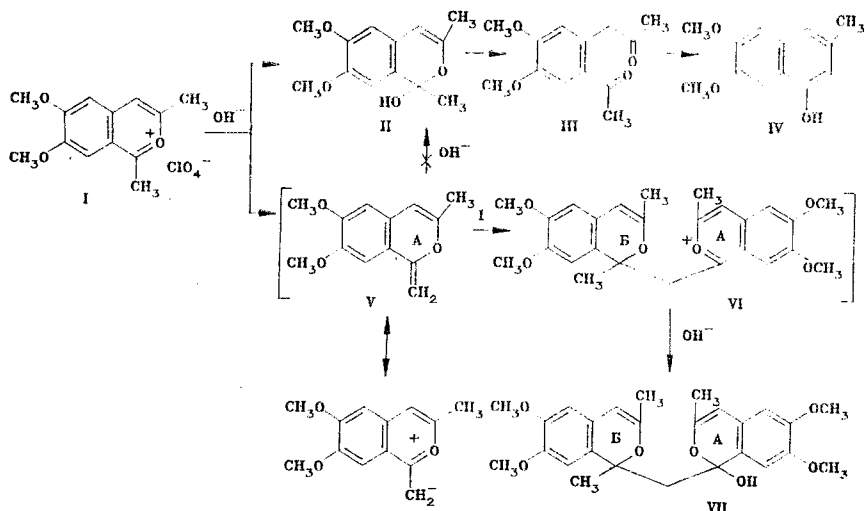
That the reaction proceeds via the intermediate anhydro-base (V) is shown indirectly by the fixation of the pseudobase (VII) in the reaction mixture of the salt of (I) with bis-1,8-dimethylaminonaphthalene (a "proton sponge"), which is known to display strongly basic properties [3]. The participation of methylene anhydro-bases of heteroaromatic cations in dimerization reactions is known to occur in monocyclic pyrilium salts [4], benzopyrilium salts [5], and their nitrogen analogs [6], but these reactions are not completed by recyclization of the heterocycles.

In contrast, on heating the pseudobase (VII) in alcoholic alkali for 2-3 h, it is nearly completely converted into the acetylchrysene (IXa) [1], with only trace amounts of the product previously detected chromatographically in the reaction of the salt (I) under similar conditions.

\*For No. 27, see [1].

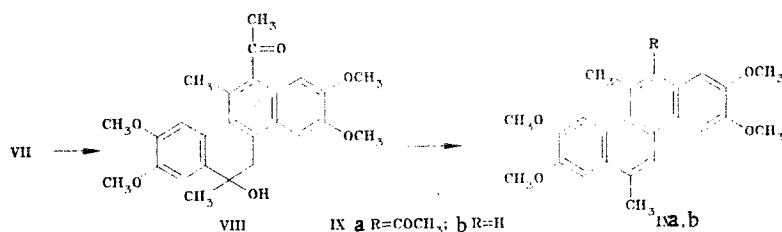
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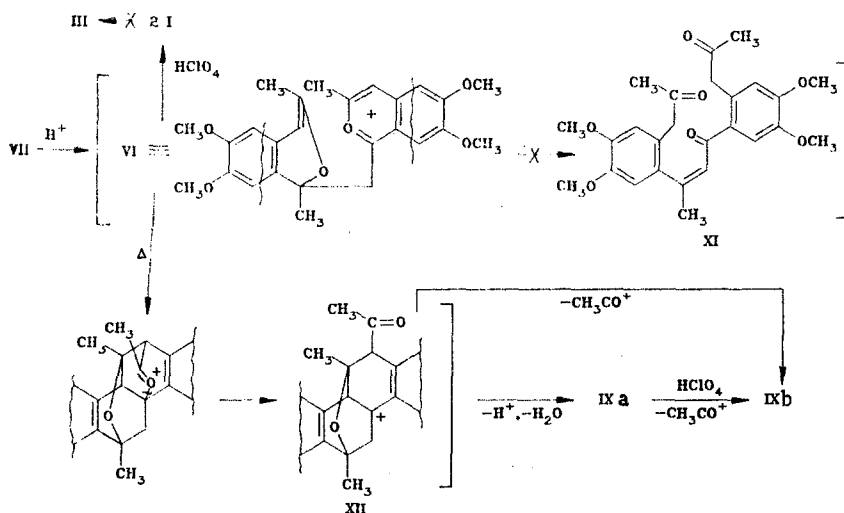
If the reaction is stopped after 10-15 min, this is the only product. Its IR spectrum, which is highly reminiscent of that of the acetylchrysene (IXa), shows absorption at  $3425\text{ cm}^{-1}$  for the OH group. The PMR spectrum of this compound contains signals for four aromatic protons [there are five in the acetylchrysene (IXa)], a broad signal for the OH proton at 4.85 ppm which disappears on deuteration, and signals for three methyl groups, one of these being shifted to higher field, typical of alkyl groups attached to an aliphatic ring. The signals at 3.50-3.75 ppm for four methoxy groups partly overlap the multiplet signal for the methylene group, which is split as a result of the proximity of the asymmetric center. The mass spectrum of this compound contains, in addition to the molecular ion peak (436), peak with  $m/z$  418, which is equal to the molecular mass of acetylchrysene (IXa). The subsequent fragmentation of these two compounds is completely identical.

The hypsochromic shift of the long-wavelength absorption of the compound obtained as compared with the acetylchrysene (IXa) may be regarded as evidence of the partial disruption of the conjugated system in this compound. On the basis of the data obtained, the structure (VII) is assigned to this product.



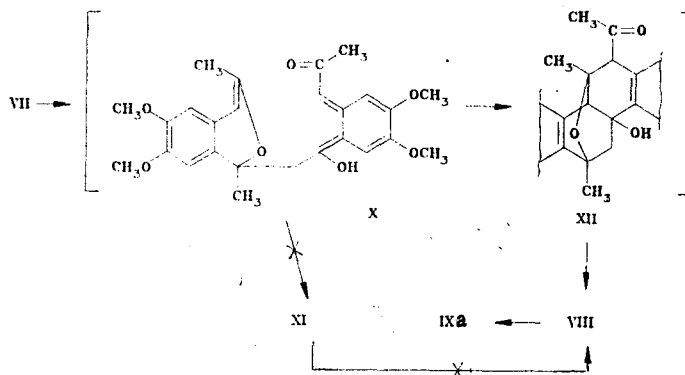
In contrast to basic media, in which removal of water from (VIII) occurs on heating for 2.5-3 h, in acid solution the conversion (VIII)  $\rightarrow$  (IX) is complete on crystallization of (VIII) from acetic acid.

The reaction of the dimeric pseudo-base (VII) in acid solution is more complex. Depending on the temperature and the strength of the acid used, mixtures of varying proportions of the initial salt and the substituted chrysenes (IXa, b) are obtained [1]. For example, on treating a solution of (VII) in acetic acid with 70% perchloric acid in the cold, the salt (I) is obtained in 70% yield, the mother liquors being shown chromatographically to contain small amounts of the acetylchrysene (IXa). Apparently, under these conditions the dimeric salt (VI) is formed, which on treatment with such a strong electrophile as  $\text{H}^+$  undergoes retrodegradation as in [7]. If this mixture is heated rapidly to the boil, the yield of the salt falls to 44%, and that of chrysene (IXb) increases to 33%. On heating in the absence of perchloric acid, the overall yield of chrysenes (IXa, b) reaches 75%. Under these conditions, which exclude the possibility of the opening of both isochromene rings in (VII) and subsequent aldol-type condensation between the acetylonyl fragments formed [compound (XII)] or the formation of two molecules of the diketone (III), the intramolecular heterodiene synthesis mechanism becomes the most likely.



The role of heterodiene similar to that of isoquinolinium salts [8] is played by the 1,4-fragment of the 2-benzopyrilium cation, and that of electron donor dienophile by the vinyl ether fragment of the isochromene ring B, i.e., the reaction takes place in accordance with the inverse of the electron requirements of the Diels-Alder reaction [9].

The formation of the chrysene (IXb) on heating the pseudobase (VII) in acetic acid cannot be rationalized as being due to ipso-protonation of the acetylchrysene (IXa) followed by deacetylation [1], since the latter remains unchanged under these conditions. It is possible that, in addition to ipso-protonation in the presence of strong acid, the deacetylation of (IXa) occurs at an earlier stage in its formation. Cases of the competitive cleavage of an organic acid amide or amine in the aromatization of the primary products of the cycloaddition reaction are known for a number of monocyclic pyrilium salts [10]. The most probable mechanism comprises cycloaddition also in the conversion of the pseudobase (VII) into the acetylchrysene (IXa) in basic media. In this case, the part of the diene is played by the quinodimethane moiety of (X), formed as a result of the electrocyclic opening of the isochromene ring A, rather than isomerization to the dimeric triketone (XI). The dienophile is the same fragment of ring B.



Following cleavage of the heterocycle to the endo-oxide (XII) and partial aromatization, (VIII) is formed, which is then slowly converted into the acetylchrysene (IXa). It is unlikely that the pathway of the reaction under these conditions involves opening of both isochromene rings in the pseudobase (VII) and isomerization to the triketone (XI), followed by interfragmental condensation. First this mechanism would not permit the formation of (VIII), and second the reaction mixture contains no products of intrafragmental cyclization, although, as shown in [1], monomeric triketones such as (III) under these conditions form exclusively the products of intramolecular cyclization. In addition, it has been held to be impossible [11] for ring opening to occur in the products of the addition of C-nucleophiles to 2-benzopyrilium salts (ring B).

It is likely that chrysenes are formed in this reaction in alkaline media from 1-methyl-3-aryl-2-benzopyrilium salts [1], despite the fact that in these cases it has not been possible to isolate intermediates such as (VII) and (VIII). In acid media, the formation of chrysenes is possible both from the dimeric pseudobase (VII) and from the diketone (III) [1], but it is not yet possible to say which of these is the intermediate in the reaction of 1-methyl-2-benzopyrilium salts under these conditions.

#### EXPERIMENTAL

IR spectra were obtained on a Specord IR-71 (in Vaseline oil), UV spectra on a Specord UV-VIS spectrophotometer (in alcohol), and PMR spectra on a Varian XL-100 (100 MHz) at 20°C (in C<sub>5</sub>D<sub>5</sub>N), internal standard HMDS. Mass spectra were obtained on a Varian MAT-112, ionizing electron energy 70 eV, with direct introduction of the sample into the source. The purity of the compounds obtained was determined by TLC on alumina in the system chloroform-n-hexane, 1:1.

1-Hydroxy-1(1,3-dimethyl-6,7-dimethoxyisochromenen-1-yl)methyl-6,7-dimethoxyisochromene (VII). A suspension of 2 g (6 mmole) of the salt (I) and 2.5 g of sodium acetate in 50 ml of water was stirred for one day at 20°C. The solid was filtered off, washed with water, dried, and crystallized from benzene (filtered hot) to give 1 g (70%) of pale gray crystals, mp 216°C. R<sub>f</sub> 0.38. IR spectrum 3350, 1660, 1230 cm<sup>-1</sup>. PMR spectrum: 1.16 (s, CH<sub>3</sub>), 1.72 (s, CH<sub>3</sub>), 1.96 (s, CH<sub>3</sub>), 2.60 (q, CH<sub>2</sub>), 3.10 (s, OCH<sub>3</sub>), 3.30 (s, OCH<sub>3</sub>), 3.56 (s, OCH<sub>3</sub>), 3.68 (s, OCH<sub>3</sub>), 5.11 (s, 1H), 5.72 (s, 1H), 5.82 (s, 1H), 6.21 (s, 1H), 6.49 (s, 1H), 6.89 (s, 1H), 6.92 ppm (s, 1H). Found, %: C 68.3, H 6.9. C<sub>26</sub>H<sub>30</sub>O<sub>7</sub>. Calculated, %: C 68.7, H 6.6.

6,11-Dimethyl-6-hydroxy-12-acetyl-2,3,8,9-tetramethoxy-5,6-dihydrochrysene (VIII). To a solution of 0.45 g of sodium hydroxide in 6 ml of alcohol and 2 ml of water was added 0.45 g (1 mmole) of (VII), and the mixture was boiled for 10 min. As solution proceeded, a voluminous white solid began to separate. The solution was cooled, and the solid filtered off, washed with water, and dried to give 0.4 g (92%) of colorless crystals, mp 273°C (from benzene), R<sub>f</sub> 0.19. IR spectrum: 3425, 1690, 1225 cm<sup>-1</sup>. PMR spectrum: 1.56 (s, CH<sub>3</sub>), 2.60 (s, CH<sub>3</sub>), 2.64 (s, CH<sub>3</sub>), 3.66, 2.70 (2s, 4-OCH<sub>3</sub>, 1-CH<sub>2</sub>), 4.85 (s, 1H), 6.90 (s, 1H), 7.12 (s, 1H), 7.34 (s, 1H), 7.56 ppm (s, 1H). Found, %: C 71.2, H 6.1. C<sub>26</sub>H<sub>28</sub>O<sub>6</sub>. Calculated: C 71.6, H 6.4.

Reactions of the Pseudobase (VII) in Acid Solution. A. To 5 ml of acetic acid containing 5 drops of perchloric acid was added in small portions at 10°C 0.3 g (6.7 mmole) of (VII). A solid began to separate almost immediately. After the mixture had been kept at this temperature for 1 day, the product was filtered off, and the filtrate diluted with ether, to give a total yield of 0.29 g (70%) of the original salt (I). TLC on the combined filtrates showed the presence of small amounts of the acetylchrysene (IXa).

B. To 0.112 g (2.4 mmole) of (VII) was added 3 ml of acetic acid and two drops of 70% perchloric acid, and the mixture heated to boiling. The solid which separated on cooling was filtered off and crystallized from benzene (filtered hot). The pyrilium salt (I) remained on the filter, and 0.03 g (32%) of the chrysene (IXb) separated from the filtrate. The acetic acid solution was diluted with ether to give a further quantity of (I). Overall yield 0.07 g (44%).

C. A solution of 0.5 g (1.1 mmole) of (VII) in 5 ml of acetic acid was boiled for 5 h. After cooling, 0.2 g of the chrysene (IXb) was filtered off. The filtrate was diluted with water, and the solid which separated was treated as described in [1]. The overall yield of the chrysene (IXa) was 0.03 g.

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HETEROCYCLIZATION OF TRIKETONES OF THE 2-(3-OXOPROPYL)-  
CYCLOHEXANE-1,3-DIONE SERIES

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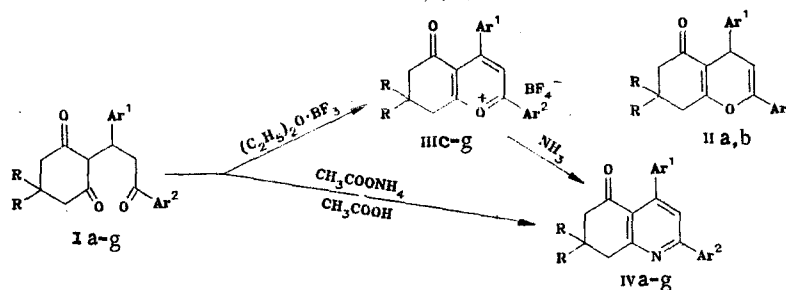
Triketones of the 2-(3-oxopropyl)cyclohexane-1,3-dione series have been shown for the first time to react with boron trifluoride etherate to give the novel 5-oxo-5,6,7,8-tetrahydrochromylum fluoroborates, which in turn react with ammonia to give 5-oxo-5,6,7,8-tetrahydroquinolines. These were also obtained directly from ammonium acetate and 2-(3-oxopropyl)cyclohexane-1,3-diones.

Treatment of 1,5-diketones with acid affords the corresponding pyrilium salts [1-3]. There have, however, been no reports of the reaction of acids with oxo-1,5-diketones, namely, 2-(3-oxopropyl)cyclohexane-1,3-diones.

We have examined the behavior of the oxo-1,5-diketones (Ia-g) with boron trifluoride etherate in glacial acetic acid and acetic anhydride.

Under these conditions, 2-(3-oxopropyl)cyclohexane-1,3-diones (Ia, b), which contain phenyl substituents, cyclize smoothly to give the 5-oxo-5,6,7,8-tetrahydro-4H-chromenes (IIa, b) only, in 70-72% yield.

A feature of phenyl-substituted oxo-1,5-diketones (Ia, b) is their inability to form salts, which is a characteristic of "ordinary" 1,5-diketones, since the initially formed 5-oxotetrahydrochromenes (IIa, b), like their sulfur analogs, are distinguished by the low hydride lability of the hydrogen at C(4). The introduction of electron-donor substituents at this position results in an increase in electron density and the lability of this hydrogen



I, II, IV a, c, e, f R=H; b, d, g, R=CH<sub>3</sub>; a, b Ar<sup>1</sup>=Ar<sup>2</sup>=C<sub>6</sub>H<sub>5</sub>; c, d Ar<sup>1</sup>=C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>-4, Ar<sup>2</sup>=C<sub>6</sub>H<sub>5</sub>; e Ar<sup>1</sup>=C<sub>6</sub>H<sub>5</sub>, Ar<sup>2</sup>=C<sub>6</sub>H<sub>5</sub>-OCH<sub>3</sub>-4; f, g Ar<sup>1</sup>=Ar<sup>2</sup>=C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>-4; III c, e, f R=H; d, g R=CH<sub>3</sub>; c, d, f, g Ar<sup>1</sup>=C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>-4; e Ar<sup>1</sup>=C<sub>6</sub>H<sub>5</sub>; c, d Ar<sup>2</sup>=C<sub>6</sub>H<sub>5</sub>; e-g Ar<sup>2</sup>=C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>-4

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