LETTERS TO THE EDITOR

NEW TYPE OF RECYCLIZATION OF 2-BENZOPYRYLIUM SALTS

V. G. Brovchenko and E. V. Kuznetsov

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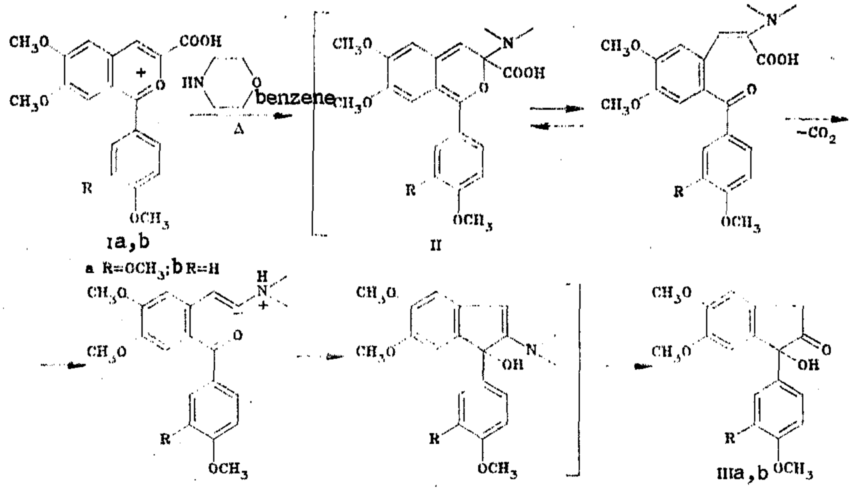
Decarboxylation of monocyclic α-carboxy-substituted pyrylium [1], pyridinium salts [2], pyridine and its bezologs [3] proceeds with the retention of the heterocyclic structure.

We found that when heated with a twofold excess of morpholine in benzene for 2.5 h, 1-aryl-3-carboxy-2-benzopyrylium salts Ia, b convert into ketols IIIa, b. It is probable that the formation of ketols IIIa, b takes place as the result of opening the heterocyclic ring in adduct II, decarboxylation of the intermediate enamine, in a similar way as described in [4], an attack by the anion formed on the benzophenone carbonyl group carbon atom, and subsequent hydrolysis of the enamine.



Ketols IIIa,b were isolated after column chromatography on aluminum oxide (eluent—chloroform).

Ketol IIIa. mp 97-98°C (from benzene); yield 68%. IR spectrum ($CHCl_3$): 35.25, 1755, 1590, 1240 cm^{-1}. PMR spectrum ($CDCl_3$): 3.70, quart., J_{AB} = 5 Hz, CH_2); 3.82 (s, 3OCH$_3$); 3.92 (s, OCH$_3$); 6.42-7.42 ppm (m, 5H); M$^+$ 344.

Ketol IIIb. mp 150-152°C (from benzene); yield 46%. IR spectrum ($CHCl_3$): 3545, 1755, 1600, 1235 cm^{-1}. PMR spectrum ($CDCl_3$): 3.31 and 3.36 (Ch, 2s, CH_2); 3.62 (s, OCH$_3$); 3.72 (s, OCH$_3$); 3.80 (s, OCH$_3$); 6.52-7.20 ppm (m, 6H).

The initial, previously unknown salts Ia,b were obtained by the reaction of 3,4-dimethoxyphenylpyruvic acid with veratraldehyde or anisaldehyde in polyphosphoric acid.

Salt Ia. mp 296°C (from acetic acid); yield 20%. IR spectrum: 3500, 1725, 1600, 1110 cm^{-1}. PMR spectrum (CF_3COOH): 3.55 (s, 3OCH$_3$); 3.80 (s, OCH$_3$); 6.95 (d, 1H); 7.30 (s, 2H), 7.50 (d, 1H); 7.70 (s, 1H); 8.20 ppm (s, 1H).

Salt Ib. mp 290-291°C; yield 23%. IR spectrum: 3500, 1715, 1600, 1095 cm^{-1}.

For all the compounds studied, the elemental analysis corresponds to the calculated values.

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REACTION OF FLAVYLIUM PERCHLORATE WITH CARBON MONOXIDE

I. M. Gavrilyuk

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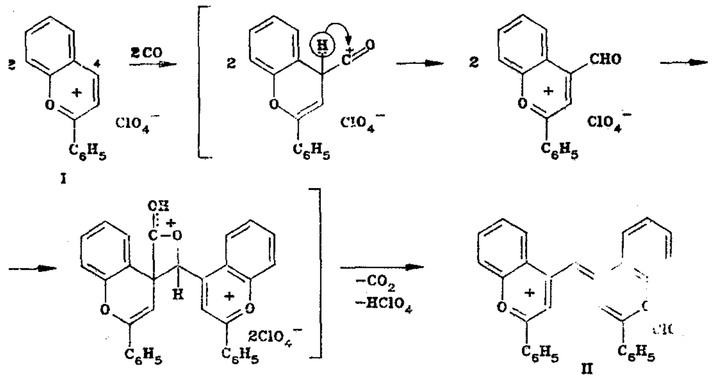
It is known that pyrylium and benzopyrylium salts, unsubstituted at the 4-position, react with nucleophilic reagents, such as triphenylphosphine [1], or for example malonodinitrile in the presence of triethylamine [2]. It could be expected that a similar reaction will proceed also with carbon monoxide, although such examples were not reported in the literature. In fact, it was found that when CO is passed for a long time into a hot solution of flavylium perchlorate I in glacial acetic acid, a small amount of blue dye is formed. The latter was isolated in individual state, and was identified as flavylomonomethinecyanine II, previously described in [3] (6% after heating for 6 h and passing CO). The initial salt I, contaminated by unidentified impurities, was also isolated from the reaction mixture.

The above described reaction is a new reaction in the series of pyrylium salts, a complex redox process, whose mechanism is still unknown. However, it can possibly be stated that at the first stage a nucleophilic addition of CO takes place at the 4-position of salt I, and the following mechanism can be suggested for this reaction:



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Institute of Organic Chemistry of the Ukrainian SSR, Kiev, 252660. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, p. 126, January, 1986. Original article submitted April 15, 1985.