2-BENZOPYRYLIUM SALTS.

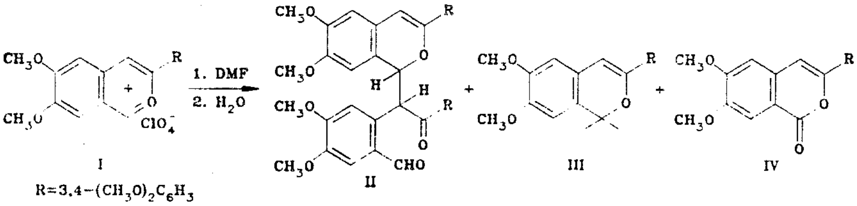
36.* DISPROPORTIONATION OF 2-BENZOPYRYLIUM SALTS THROUGH PRIOR 4—1' DIMERIZATION

S. V. Verin, E. V. Kuznetsov,
and Yu. A. Zhdanov

UDC 547.814.1.04:541.124

It was observed that the disproportionation of 2-benzopyrylium salts proceeds through prior dimerization. Intermediates were isolated and identified. Assumptions regarding the mechanism of the transformation are expressed.

Continuing our study of the recently observed 4—1'dimerization of 2-benzopyrylium salts [2] we have accomplished this transformation for 1-unsubstituted salt I. It was found that dimer II, which, according to the PMR spectral data, is liberated primarily in the form of one diastereomer, and chromatographically detectable trace amounts of isochromene III and isocoumarin IV [3] — products of disproportionation of starting salt I — are formed when salt I is dissolved in the cold in DMF with subsequent precipitation with water.



At the same time, when we heated salt I in acetonitrile with morpholine or N-morphinocyclohexene** (i.e., with nucleophiles that, like DMF, do not give rise to intramolecular recyclization of 2-benzopyrylium salts), instead of colorless dimer II, we obtained an orange reaction product in 7% and 40% yields, respectively (See Fig. 1). The same compound is formed when dimer II is heated with morpholine perchlorate. The doubled number of signals of methoxy groups in its PMR spectrum indicates that salt I has undergone dimerization; in addition, we recorded two multiplet signals of protons of a morpholine residue centered at 2.25 and 3.40 ppm and a multiplet of 11 protons at 6.25-7.57 ppm. Weak carbonyl absorption at 1670 cm^{-1} and two bands at 1633 and 1640 cm^{-1}, which we assigned to vibrations of the C=C bonds of a divinyl ether fragment, are recorded in the IR spectrum. Isocoumarin IV and nitrogen derivation V, which can also be formally regarded as products of disproportionation of salt I, are formed in quantitative yield in the acidic hydrolysis of the compound obtained. The spectral data enumerated above and the character of the formation and decomposition make it possible to assign unsaturated dimer structure VIa to the colored product.

The formation of isocoumarin IV and nitrogen derivative V in the hydrolysis of dimer VIa is explained by hydration of the double bond with its subsequent cleavage in analogy with the known decomposition of β-diketones [4].

---

*See [1] for Communication 35.

**The use of precisely this compound is explained by the specific characteristics of 4—1' dimerization, which will be described in subsequent publications.

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 750-754, June, 1989. Original article submitted December 16, 1987.

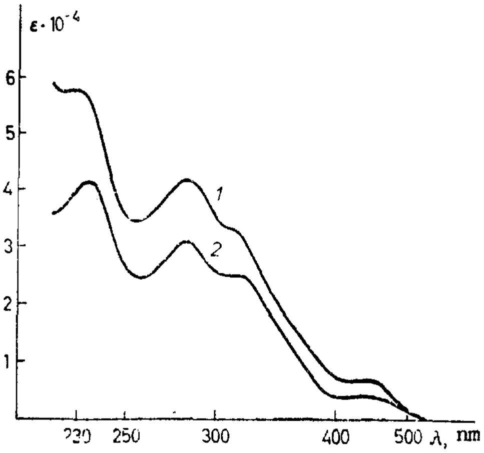
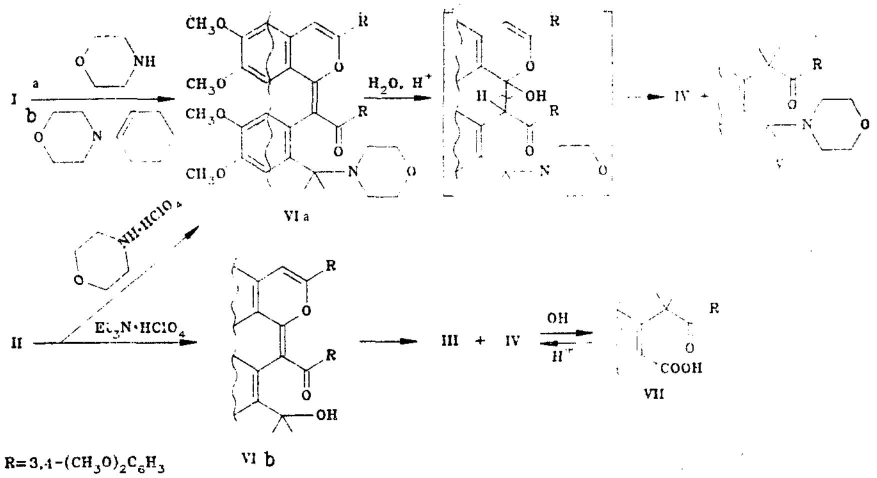
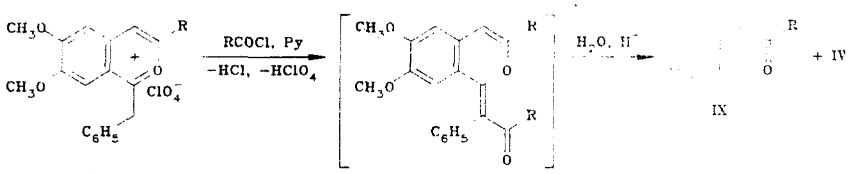


Fig. 1. UV absorption spectra (in methanol): 1) VIa: 2) VIb.



The results of a model experiment, the first step of which is known in series of monocyclic pyrylium salts [5], may serve as an indirect confirmation of the proposed scheme of the transformation.

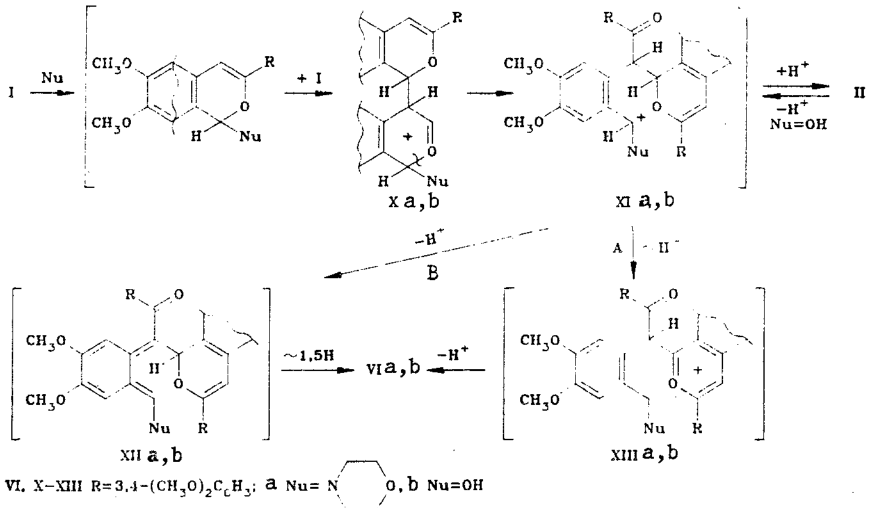


Thus under conditions of neutral hydrolysis of the reaction mixture we visually noted the formation of a red substance, which probably has structure VIII, whereas under conditions of acidic hydrolysis we detected the formation of products of a similar decomposition — deoxybenzoin IX [6] and isocoumarin IV — by TLC and GLC.

Thus it may be asserted that the observed disproportionation of salt I is preceded by its dimerization.

Intermolecular hydride-ion transfer from the geminal node of the anion of the monomeric pseudobase to the α or γ position of the monomeric cations is considered to be the generally accepted mechanism of the disproportionation of heterocyclic cations [7]. However, prior dimerization allows for the possibility of intramolecular hydride transfer. Neverthless, in the only study [8] in which the disproportionation of 7-hydroxyflavylium salts, which is preceded by dimerization due to attack on the 7-hydroxy group of one molecule with respect to the γ position of another (which occurs in the case of maintenance of these salts in solution in acetic acid for many days), the monomeric starting salt that is present in solution is considered to be the transferrer of hydride ion from the geminal node of the pseudobase fragment of the original dimer to the cationic fragment. It should be noted that Jurd [8] was able to isolate only a dimer in which disproportionation had already occurred; its decomposition to the oxidized and reduced forms of the starting salt was not realized.

In our opinion, the set of data that we obtained, without excluding the possibility of the participation of a molecule of salt I in hydride transfer, makes a mechanism of intramolecular hydride shift that occurs during the formation of unsaturated dimer VIa more preferable. It is evident that the key here is cationic intermediate XIa, which develops directly in the dimerization after opening of the lower ring in dimer Xa. When a morpholine residue, which stabilizes the cationic center, acts as the nucleophile, intermediate XIa immediately undergoes intramolecular transformation; however, if Nu = OH, the XIb cation primarily is deprotonated to dimer II, and unsaturated dimer VIb, which then undergoes decomposition to isocoumarin IV and isochromene III, is formed only in insignificant amounts.



VI, X-XIII R=3,4-$(CH_3O)_2C_6H_3$; a Nu= N◯O, b Nu=OH

This point of view makes it possible to assume that in the regeneration of hydroxybenzyl cation XIb hydride shift may also be realized in saturated dimer II. In fact, when we heated it with triethylamine perchlorate, which was used as a source of catalytic amounts of a strong acid (the free acid cannot be used, since this leads to decomposition of the dimer to starting salt I as in [2]), we obtained unsaturated dimer VIb. It was found to be extremely labile, readily undergoing decomposition to isochromene III and isocoumarin IV on further heating, and we were able to isolate it only in amounts sufficient for recording the UV spectrum (Fig. 1), which was almost identical to the absorption spectrum of unsaturated dimer VIa; this indicates the similarity in their structures. The greater stability of dimer VIa as compared with dimer VIb is probably explained by a transannular interaction between the nitrogen atom of the morpholine residue and the carbonyl group [9]. On the whole, the formation of unsaturated dimer VIb and its subsequent decomposition proceed in high yields, as evidenced by the amount of keto acid VII obtained by treatment of the melt with alkali. Its reverse cyclization to isocoumarin IV proceeds readily under the influence of strong acids. Isochromene III, like the specially obtained sample, undergoes resinification under these conditions.

It must be emphasized that the formation of unsaturated dimers VIa,b is possible not only via direct hydride migration from the geminal node of the C adduct with subsequent deprotonation of the intermediately formed salt XIII (pathway A) but also through the equivalent (with respect to the result) 1,5-sigmatropic rearrangement in o-quinoid form XII [10], which develops in the case of deprotonation of the methylidyne group (pathway B).

In conclusion, let us note that the disproportionation of salt I cannot be carried out under the usual conditions, i.e., by heating with alkalis, since different transformations, which are currently being investigated, are realized in this case.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a Specord 71 IR spectrometer. The UV spectra of solutions in MeOH were recorded with an M-40 spectrometer. The PMR spectra of solutions in $CDCl_3$ and C_5D_5N were obtained with a Tesla BS-487C spectrometer (80 MHz) at 20°C with hexamethyldisiloxane (HMDS) as the internal standard. The purity of the products obtained was monitored by means of TLC on aluminum oxide in $CHCl_3$. The results of elementary analysis of the compounds for C, H, and N were in agreement with the calculated values.

1-[α-(3,4-Dimethoxybenzoyl)(2-formyl-4,5-dimethoxybenzyl)]-3-(3,4-dimethoxyphenyl)-6,7-dimethoxyisochromene (II, $C_{38}H_{38}O_{11}$). A 0.43-g (1 mmole) sample of perchlorate I [11] was dissolved at room temperature in 5 ml of DMF, and the solution was diluted immediately with 50 ml of cold water. After separation and drying, the product was dissolved in 3 ml of glacial acetic acid, and the trace amounts of starting perchlorate I were removed by filtration after 15 min. The mother liquor was again diluted with 50 ml of cold water, and the resulting precipitate was dried and recrystallized from aqueous isopropyl alcohol (1:1) to give 0.24 g (70%) of light-yellow crystals with mp 182°C and R_f 0.65. IR spectrum: 1685, 1680, 1633, 1270 cm^{-1}. PMR spectrum: 3.33 (s, OCH_3), 3.60 (s, OCH_3), 3.72 (s, $5OCH_3$), 3.93 (s, OCH_3), 5.50 (s, 1H), 6.00 (d, 1H, J = 10 Hz), 6.30-7.85 (m, 1H and 10H, arom.), 9.53 ppm (s, 1H, CHO).

1-[α-(3,4-Dimethoxybenzoyl)(3,4-dimethoxy-6-N-morpholinomethylbenzylidene)]-3-(3,4-dimethoxyphenyl)-6,7-dimethoxyisochromene (VIa, $C_{42}H_{45}NO_{11}$). A 0.43-g (1 mmole) sample of salt I and 5 ml of absolute acetonitrile were added to 0.16 g (1 mmole) of N-morpholinocyclohexene, and the mixture was heated rapidly to the boiling point. After heating for 15 min, the bright-orange solution was evaporated. The residue was chromatographed with a column (Al_2O_3, $CHCl_3$) with collection of the orange-red fraction to give 0.15 g (40%) of an orange oil with R_f 0.4. IR spectrum: 1670, 1640, 1633, 1600 cm^{-1}. PMR spectrum: 2.16-2.35 (m, 4H), 3.20 (s, 2H, $-CH_2-$), 3.39-3.51 (m, 4H), 3.57 (s, OCH_3), 3.77 (s, $7OCH_3$), 6.25-7.57 ppm (m, 11H, arom.).

3,3',4,4'-Tetramethoxy-6-N-morpholinomethyldeoxybenzoin (V, $C_{23}H_{29}NO_6$). A 0.15-g (0.2 mmole) sample of VIa was dissolved in 2 ml of acetic acid, two drops of 70% perchloric acid were added, and the mixture was heated to the boiling point and allowed to stand overnight. It was then filtered to remove the colorless perchlorate, and 0.06 g (80%) of isocoumarin IV, which, with respect to all of its characteristics, coincided with the compound described in [3], was precipitated from the mother liquor by means of water. The colorless perchlorate was treated in the cold with 5% aqeuous NaOH solution to give 0.07 g (80%) of a colorless product with mp 143°C (from alcohol) and R_f 0.45. IR spectrum: 1675, 1600,1145, 1020 cm^{-1}. PMR spectrum: 2.07-2.25 (m, 4H), 3.17-3.35 (m, 2H, $-CH_2-$, and 4H), 3.72 (s, $2OCH_3$), 3.80 (s, $2OCH_3$), 4.18 (s, 2H, $-CH_2-$), 6.60-7.70 ppm (m, 5H, arom.).

1-[α-(3,4-Dimethoxybenzoyl)(3,4-dimethoxy-6-hydroxymethylbenzylidene)]-3-(3,4-dimethoxyphenyl) 6,7-dimethoxyisochromene (VIb). An excess of triethylamine was added to an ether solution of 70% perchloric acid, after which powdered dimer II was moistened with very small amounts of the resulting solution and heated in an argon atmosphere to 170°C. The product was chromatographed on aluminum oxide ($CHCl_3$), and the orange spot with R_f 0.4 was extracted with MeOH (see Fig. 1 for the UV spectrum). Similar results were obtained when crude dimer II was heated to 170°C, since during its isolation it adsorbed a very small amount of an unidentified perchlorate.

2-Carboxy-4,5,3',4'-tetramethoxydeoxybenzoin (VII, $C_{19}H_{20}O_7$). A 0.34-g (0.5 mmole) sample of crude dimer II was heated in an argon atmosphere to 220°C. After cooling, the residue was treated with 5 ml of ethanol and 2 ml of 10% aqueous NaOH solution, and the mixture was heated for 15 min. The cooled solution was diluted with 20 ml of cold water, and the resulting precipitate was separated. The mother liquor was acidified with 20% HCl; after 30 min, the resulting precipitate was removed by filtration and dried to give 0.16 g (90%) of a colorless substance with mp 239°C (from acetic acid). IR spectrum: 1700, 1685, 1605, 1595 cm^{-1}. PMR spectrum (C_5D_5N): 3.59 (s, OCH_3), 3.63 (s, $3OCH_3$), 4.94 (s, 2H, $-CH_2-$), 6.77-7.93 ppm (m, 5H, arom.).

3-(3,4-Dimethoxyphenyl)-6,7-dimethoxyisochromene (III, $C_{19}H_{20}O_5$). A 0.1-g sample of sodium borohydride was added in small portions in the cold to a suspension of 0.43 g (1 mmole) of salt I in 2 ml of $CHCl_3$ and 2 ml of CH_3CN until the salt had dissolved completely and the solution had become colorless, after which the inorganic impurities were removed by filtration, and the solution was evaporated. Crystallization of the residue from alcohol gave 0.23 g (70%) of colorless crystals with mp 149°C and R_f 0.9. IR spectrum:

1630, 1610, 1600, 1140 cm^{-1}. PMR spectrum: 3.80 (s, $3OCH_3$), 3.82 (s, OCH_3), 5.05 (s, 2H), 6.15 (s, 1H), 6.62-7.17 ppm (m, 5H, arom.). The isochromene III obtained was unstable during chromatography with a column (Al_2O_3, $CHCl_3$, SiO_2, $CHCl_3$), and a large part of it underwent resinification during fusion under the conditions used to obtain keto acid VII.

LITERATURE CITED

1. I. V. Shcherbakova, S. V. Verin, and E. V. Kuznetsov, Khim. Prir. Soedin., No. 1, 75 (1989).
2. Yu. A. Zhdanov, S. V. Verin, I. V. Korobka, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 9, 1185 (1988).
3. E. V. Kuznetsov, D. V. Pruchkin, A. I. Pyshchev, and G. N. Dorofeenko, Khim. Geterotsikl. Soedin., No. 10, 1320 (1978).
4. V. M. Vlasov, Zh. Vses. Khim. Obshch., 15, 708 (1978).
5. A. T. Balaban, Tetrahedron Lett., 599 (1978).
6. M. G. Farooq, W. Rahman, and M. Ilyas, Chem. Ber., 92, 2555 (1959).
7. J. W. Bunting, Adv. Heterocycl. Chem., 25, 1 (1979).
8. L. Jurd, Tetrahedron, 28, 493 (1972).
9. T. Omoto, J. Pharm. Soc. Jn., 80, 137 (1960).
10. J. M. Hornback, J. Org. Chem., 45, 3524 (1980).
11. G. N. Dorofeenko, G. P. Safaryan, and E. V. Kuznetsov, Khim. Geterotsikl. Soedin., No. 8, 1013 (1970).

SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 2,7-DIAMINOBENZOPYRYLIUM TETRAFLUOROBORATES

M. A. Kirpichënok, S. K. Gorozhankin,
D. S. Yufit, Yu. T. Struchkov, P. B. Kurapov,
and I. I. Grandberg

UDC 547.587.51'816:543.
422.25:548.737

Stable 2,7-diaminobenzopyrylium tetrafluoroborates were obtained by the successive treatment of 7-diethylaminocoumarin, 4-methyl-7-diethylaminocoumarin, and 9-methyl-1H,5H-quinolizino[9,9a,1-gh]coumarin with triethyloxonium tetrafluoroborate and amines, viz., diethylamine, piperidine, morpholine, benzylamine, and aniline. The spectral-luminescence characteristics of the synthesized compounds were investigated. The data from the ^{13}C NMR spectra and x-ray diffraction analysis confirm the greater participation of the 2-amino group as compared with the 7-amino group in stabilization of the positive charge of the pyrylium system.

In [1] we demonstrated that the successive treatment of 7-dialkylaminocoumarins with triethyloxonium tetrafluoroborate and C nucleophiles — sodium derivatives of compounds that have an active methylene group — leads to the synthesis of substituted 2-alkylidene-7-dialkylaminobenzopyrans; the reactions proceed through a step involving the formation of unstable 2-ethoxybenzopyrylium salts.

In the present research we studied the reactions of a number of 7-dialkylaminocoumarins — 7-diethylaminocoumarin (I), 4-methyl-7-diethylaminocoumarin (II), and 9-methyl-1H,5H-quinolizino[9,9a,1-gh]coumarin (III) — with triethyloxonium tetrafluoroborate and N-nucleophilic reagents — primary and secondary amines (diethylamine, piperidine, morpholine, benzylamine, and aniline). 2,7-Diaminobenzopyrylium tetrafluoroborates are formed as a result of these reactions. The interest in benzopyrylium salts was due to their potential luminescence properties [2, p. 335]. In addition, it seemed of interest to ascertain the electron and geometrical structures of aminobenzopyrylium salts, including the question of the delocalization of the positive charge in the molecules.

K. A. Timiryazev Moscow Agricultural Academy, Moscow 127550. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 755-766, June, 1989. Original article submitted December 16, 1987.