2-BENZOPYRYLIUM SALTS.
43.* CONVERSION OF DIMERS OF 2-BENZOPYRYLIUM SALTS TO BENZOFURAN DERIVATIVES

S. V. Verin and E. V. Kuznetsov

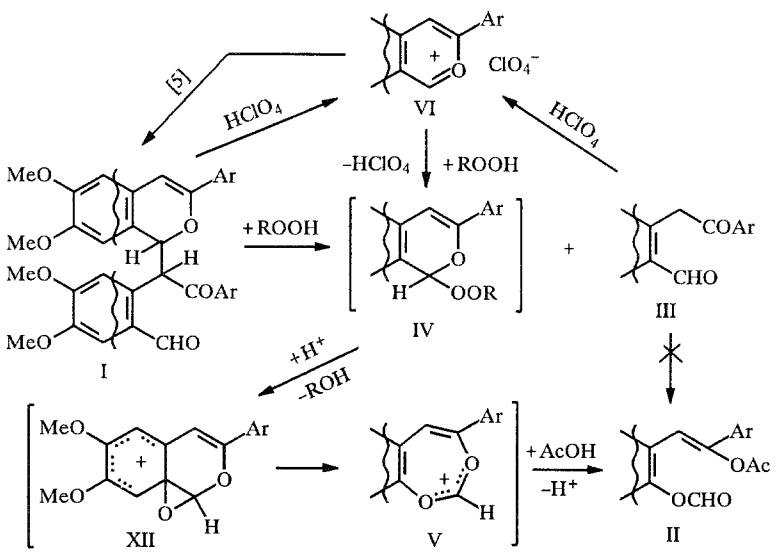
In the acid-catalyzed interaction of dimers of 2-benzopyrylium salts with peracetic acid and hydrogen peroxide, the oxidation products that are formed are readily converted to benzofuran derivatives.

As we had reported previously [2-4], dimers of 2-benzopyrylium salts, as a result of intramolecular condensations, form various derivatives of chrysene, benz[*a*]anthracene, and naphthalene. These conversions proceed in either an alkaline medium or in the presence of acetic or formic acid. The action of strong acids on the dimers regenerates the original 2-benzopyrylium cations.

Now we have found that cleavage of the C—C interfragment bond of the dimer I [5] takes place even when it is held in acetic acid solution for one day in air. This results in formation of the diester II and the aldehydoketone III [6].

The conversion that we have observed (Scheme 1) probably represents replacement of the aldehydoketone fragment III in position 1 of the isochromene ring of the dimer I by peracetic acid that is formed by oxidation of the acetic acid by atmospheric oxygen. Then, a rearrangement of the Baeyer—Villiger type takes place in the adduct IV, as well as the addition of 2 moles of acetic acid to the 7-membered cationic intermediate V and opening of the ring (path C in Scheme 2).

Scheme 1



I-VI Ar=3,4-$(MeO)_2C_6H_3$; R=H, Ac

As expected, when the dimer I is oxidized by a specially prepared acetic acid solution of peracetic acid, the time required for formation of the diester II is shortened: within only 1 h, the dimer is obtained in a 35% yield. The second fragment of the molecule of the dimer I, the aldehydoketone III, as confirmed by a model experiment, is not oxidized under these conditions and can be isolated.

*For Communication 42, see [1].

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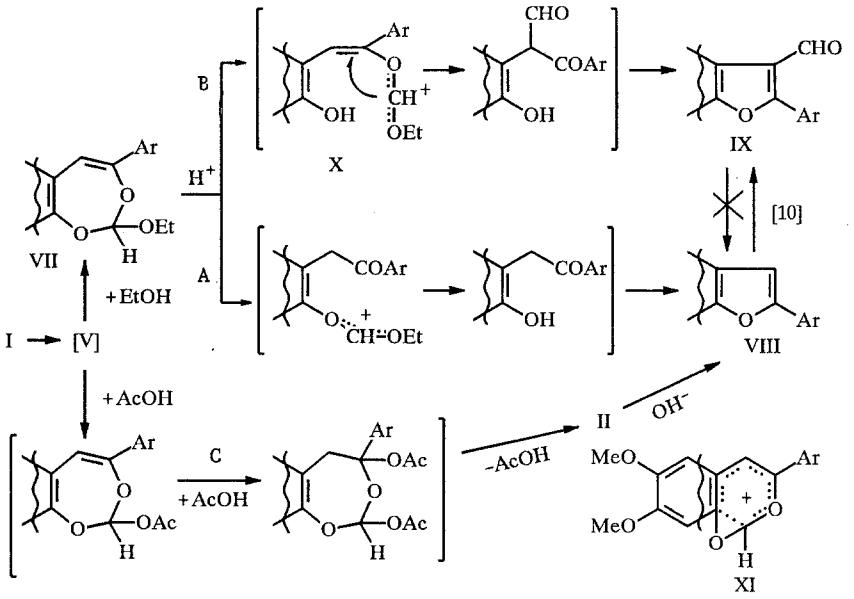
Scheme 2



Ar=3,4-$(MeO)_2C_6H_3$

The yield of the diester II is much higher (55%) when the dimer I is oxidized by a solution of peracetic acid in acetic acid in the presence of catalytic quantities of perchloric acid. Under these conditions, the above-described process of substitution in the dimer I is evidently accompanied by direct cleavage as a result of protonation of the interfragment C—C bond by perchloric acid [3, 7]. The resulting 2-benzopyrylium salt VI (the aldehydoketone III under the action of $HClO_4$ is also converted to the cation VI [8]), in contrast to its open form III, is now capable of oxidation. At the same time, the molar quantity of perchloric acid that is released upon direct oxidation of the perchlorate VI initiates side conversions that we have not been able to identify, thus lowering the yield of the diester II.

If the $HClO_4$ catalyzed oxidation of the dimer I is performed with hydrogen peroxide in ethanol, a 60% yield of the cyclic ortho ester VII is obtained; probably by addition of a solvent molecule to the cationic intermediate V (see Scheme 2).

The ortho ester VII is stable against bases; in an acidic medium (in the presence of HCOOH, CF_3COOH, HCl, or $HClO_4$, in the cold and upon heating) it is converted to a mixture of the furan VIII and its formyl derivative IX; however, conditions can be selected so as to form primarily one product or the other (see Experimental). The furan VIII has also been obtained by heating the diester II in aqueous alcoholic caustic, in an analogous manner [9].

The structure of the aldehyde IX is supported by its spectral characteristics and also by its synthesis from the furan VIII by formylation in accordance with Rieche [10]. It has also been shown that the conversion IX → VIII is not realized even under the action of perchloric acid, and hence we can eliminate the possibility that the furan VIII is formed by this path when the ortho ester VII is treated with acids.

The ambidentate behavior of the ortho ester VII in an acidic medium is evidently related to the possibility of its protonation at different positions of the heterocycle. The path that leads to the formation of the furan VIII is most probably proton attack on the vinyl fragment or the oxygen atom in position 3 of the dioxepine ring, leading to rupture of the C_2—O_3 bond (path A). At the same time, the initial protonation of the O_1 atom, initiating rupture of the O_1—C_2 bond, is ultimately concluded in the formation of the aldehyde IX (path B). In the latter case, the intermediate X, before cyclization, must undergo a rearrangement analogous to that known in a number of complex vinyl ethers [11].

Unfortunately, even in the chamber of an NMR spectrometer at —70°C, with trifluorosulfonic acid acting on a solution of the ortho ester VII in SO_2, we were unable to register the third possible direction of protonation (at the exocyclic oxygen atom); i.e., we were unable to regenerate the intermediate V, which may also be presumed to exist in the form of the 2-benzohomopyrylium cation XI.

In conclusion, we must emphasize that the isolation of the adduct VII confirms the hypothesis of intermediate formation of the cation V, as we had suggested previously in order to explain the character of the interaction of 1-aryl-2-benzopyrylium salts with hydrogen peroxide [12]. And this in turn suggests that in a number of 2-benzopyrylium salts, oxidation by peroxides does not proceed through the traditional ANRORC scheme that is characteristic for analogous conversions of monocyclic pyrylium salts [13], but rather along a path of so-called *ortho*-bonding [14], where the opening of the old ring is preceded by the formation

of the new ring (intermediate XII). Quite recently, we had proposed an essentially similar mechanism of *para*-bonding in order to interpret the character of the recyclization reaction for adducts of 2-benzopyrylium salts with methylene-active compounds [15].

EXPERIMENTAL

The IR spectra were taken in a Specord IR 75 spectrophotometer in white mineral oil, the PMR spectra in a Tesla BS-487 instrument (80 MHz) at 20°C in $CDCl_3$ solution, with HMDS as an internal standard. The mass spectra were obtained in a Finnigan MAT-4615 instrument with 70-eV ionizing radiation and direct introduction of the sample into the source.

Elemental analyses of compounds II, VII, VIII, and IX for C and H contents were in agreement with the calculated values.

1-Acetoxy-1-(3,4-dimethoxyphenyl)-2-(3-formyloxy-4,5-dimethoxyphenyl)ethylene (II, $C_{21}H_{22}O_8$). A. To a solution of 0.34 g (0.5 mmole) of the dimer I [5] in 4 ml of acetic acid, one drop of a 16% solution of perchloric acid in acetic acid was added (obtained by cautious addition, with cooling, of 6.8 ml of 57% $HClO_4$ to 24.4 ml of acetic anhydride), and also 0.7 ml (1.5 mmole) of a 6% solution of AcOOH in AcOH (obtained by mixing 1 ml of 30% H_2O_2 and 4 ml of Ac_2O); the mixture was stirred for 2 min and poured into 50 ml of cold water. The filtered and dried precipitate was recrystallized from 3 ml of ethanol, obtaining 0.22 g (55%) of the colorless product II, mp 185-187°C. IR spectrum: 1755, 1635, 1605 cm^{-1}. PMR spectrum: 2.23 (s, CH_3), 3.84 (s, $2OCH_3$), 3.91 (s, OCH_3), 3.94 (s, OCH_3), 6.03 (s, —C<u>H</u>=), 6.66-7.29 ppm (m, 5H arom. and OC<u>H</u>O). Mass spectrum, m/z (I_{rel}, %): M^+ 402 (48), $[M - CH_2CO]^+$ 360 (31), $[M - CH_2CO—CO]^+$ 332 (20), $[M - CH_2CO—CO—OH]^+$ 315 (17), HOCO—Ar—C^+ 193 (32), $ArCO^+$ 165 (100).

B. A 0.34-g quantity (0.5 mmole) of the dimer I was dissolved at 20°C in 10 ml AcOH and held in an open flask for 1 day at 20°C. The reaction mixture was diluted with 50 ml of cold water; the precipitate was filtered off, washed with 20 ml of water, and, after drying, was separated in a column (diameter 10 mm, length 40 mm) in a system consisting of Al_2O_3 (No. IV activity according to Brockman) and $CHCl_3$, obtaining 0.12 g (30%) of the diester II (R_f 0.85) and 0.09 g (25%) of the aldehydoketone III (R_f 0.65), with all property indexes matching those reported in [6].

C. To 0.34 g (0.5 mmole) of the dimer I, 4 ml of AcOH was added, along with 0.7 ml (1.5 mmole) of a 6% solution of AcOOH in AcOH; the mixture was stirred for 1 h at 20°C. The reaction mixture was diluted with 40 ml of cold water; the precipitate was filtered off, washed with 20 ml of water, and, after drying, was separated in a column as described in method **B**. Obtained 0.14 g (35%) of the diester II and 0.11 g (32%) of the aldehydoketone III.

2-Ethoxy-4-(3,4-dimethoxyphenyl)-2H-benzo[*b*]-1,3-dioxepine (VII, $C_{21}H_{24}O_7$). To a suspension of 0.34 g (0.5 mmole) of the dimer I in 6 ml of absolute ethanol, one drop of an $HClO_4$ solution was added (solution obtained by mixing 1 ml of ethanol and 0.1 ml of 70% $HClO_4$), along with 0.15 ml (1.5 mmoles) of a 30% solution of H_2O_2; the reaction mixture was stirred for 1 h at 20°C. The precipitate was filtered off and washed with 2 ml of ethanol, obtaining 0.23 g (60%) of a colorless product with mp 154-156°C. IR spectrum: 1640, 1613, 1580 cm^{-1}. PMR spectrum: 1.27 (t, CH_3), 3.67-3.92 (m, $4OCH_3$ and $—CH_2—$), 5.87 (s, —C<u>H</u>= and —C<u>H</u>—O),* 6.77-7.17 ppm (m, 5H arom.). Mass spectrum, m/z (I_{rel}, %): M^+ 388 (100), $[M - C_2H_5OH]^+$ 342 (6), $[M - C_2H_5OCHO]^+$ 314 (39), $[M - C_2H_5OCHO—CH_3]^+$ 299 (63), 243 (20), $[M - ArCO]^+$ 223 (37), $[M - ArCO—CO]^+$ 195 (27), $[M - ArCO—C_2H_5O\cdot]^+$ 178 (16), $ArCO^+$ 165 (97).

2-(3,4-Dimethoxyphenyl)-5,6-dimethoxybenzo[*b*]furan (VIII, $C_{18}H_{18}O_5$). A. To a suspension of 0.2 g (0.5 mmole) of the diester II in 2 ml of ethanol, 0.2 ml of a 10% aqueous NaOH solution was added, and the mixture was refluxed for 15 min. After cooling the reaction mixture, 10 ml of H_2O was added, and the solution was acidified with hydrochloric acid to pH 1; the resulting precipitate was filtered off. Obtained 0.14 g (92%) of the furan VIII, mp 197-198°C (from ethanol). IR spectrum: 1615, 1600, 1585, 1560 cm^{-1}. PMR spectrum: 3.82 (s, $3OCH_3$), 3.87 (s, OCH_3), 6.67-7.30 ppm (m, 6H arom.). Mass spectrum, m/z (I_{rel}, %): M^+ 314 (100), $[M - CH_3]^+$ 299 (69), 243 (27), 157 (36).

B. To a suspension of 0.2 g (0.5 mmole) of the ortho ester VII in 3 ml of AcOH at 10°C, 0.1 ml of a 30% HCl solution was added; the mixture was held for 30 min and then diluted with cold water (15 ml). Obtained 0.13 g (85%) of the furan VIII.

2-(3,4-Dimethoxyphenyl)-3-formyl-5,6-dimethoxybenzo[*b*]furan (IX, $C_{19}H_{18}O_6$). A. To 2 ml of 99% HCOOH, heated to 95°C, 0.2 g (0.5 mmole) of the ortho ester VII was added; the resulting solution was heated to boiling and then cooled. After adding 10 ml of H_2O, obtained 0.14 g (80%) of a yellow product IX with mp 137-139°C (from ethanol). IR spectrum: 1660, 1620, 1595, 1545 cm^{-1}. PMR spectrum: 3.84 (s, $4OCH_3$), 6.70-7.60 (m, 5H arom.), 10.22 ppm (s, C<u>H</u>O). Mass spectrum, m/z (I_{rel}, %): M^+ 342 (55), $[M - CH_3]^+$ 327 (12), 80 (90), 64 (84), 48 (100).

B. To a solution of 0.15 g (0.5 mmole) of the furan VIII in 3 ml of chloroform, 0.13 g (1 mmole) of aluminum chloride was added, along with 0.12 ml (0.75 mmole) of dichloromethyl butyl ether. The reaction mixture was held for 2 h at 20°C

*When SO_2 is substituted as the solvent the signals of the protons appear as two singlets.

and poured onto a bed of aluminum oxide that had been moistened with 0.1 ml of H_2O; the colored product was eluted with chloroform. After driving off the solvent, obtained 0.12 g (70%) of the aldehyde IX.

LITERATURE CITED

1. S. V. Verin, D. É. Tosunyan, and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 11, 1468 (1991).
2. I. V. Korobka, Yu. V. Revinskii, and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 7, 910 (1985).
3. Yu. A. Zhdanov, S. V. Verin, I. V. Korobka, and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 9, 1185 (1988).
4. S. V. Verin, D. É. Tosunyan, and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 2, 175 (1991).
5. S. V. Verin, E. V. Kuznetsov, and Yu. A. Zhdanov, *Khim. Geterotsikl. Soedin.*, No. 6, 750 (1989).
6. S. V. Verin and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 8, 1039 (1989).
7. G. A. Olah, D. K. Rakash, and R. E. S. Williams, *Hypercarbon Chemistry*, Wiley, New York (1987).
8. G. N. Dorofeenko, G. P. Safaryan, and E. V. Kuznetsov, *Khim. Geterotsikl. Soedin.*, No. 8, 1013 (1970).
9. M. Lempert-Sreter and A. Muller, *Acta Hung.*,* **41**, 451 (1964).
10. A. Rieche, H. Gross, and E. Holf, *Chem. Ber.*, **93**, 88 (1960).
11. I. V. Machinskaya and V. A. Barkhash, *Reakts. Metody Issled. Org.Soedin. (Khimiya, Moscow)*, **14**, 344 (1964).
12. F. Muller, M. Meszaros, and K. Kormendy, *J. Org. Chem.*, **19**, 472 (1954).
13. A. T. Balaban and S. D. Nenitzescu, *Chem. Ber.*, **93**, 599 (1960).
14. V. N. Charushin and O. N. Chupakhin, *Usp. Khim.*, **53**, 1648 (1984).
15. S. V. Verin, D. É. Tosunyan, E. V. Kuznetsov, and Yu. A. Zhdanov, *Khim. Geterotsikl. Soedin.*, No. 3, 315 (1990).

*As in Russian original — Translator.