Mendeleev Commun., 2020, **30**, 325–327

Mendeleev Communications

Pyrano[3,4-*c*]pyrandiium dication

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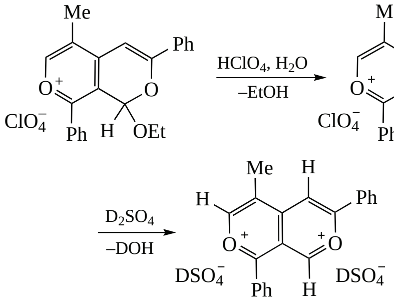
DOI: 10.1016/j.mencom.2020.05.022

Pyrano[3,4-*c*]pyrandiium dication has been detected in anhydrous D_2SO_4 using two-dimensional correlation NMR spectroscopy. The dication is generated as an intermediate in acid-catalyzed hydrolysis of 1-ethoxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyran-7-ium perchlorate, where the action of 70% $HClO_4$ leads to the replacement of ethoxy group by hydroxyl one, and the reaction with $SbCl_5$ affords dimeric bis(hexachloroantimonate) bearing two pyrano[3,4-*c*]pyran-7-ium moieties linked *via* oxygen atom. The crystal structures of both isolated products have been determined.



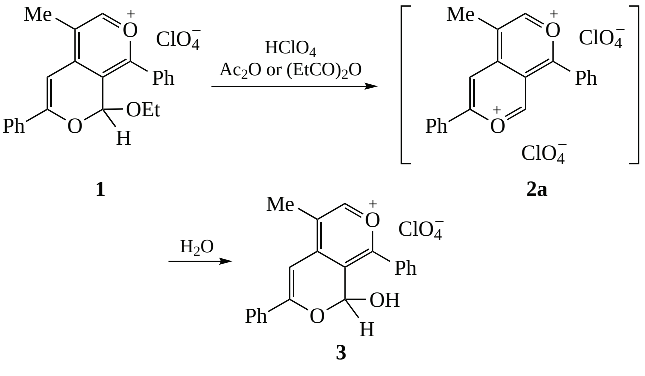
Keywords: dication, pyrylium salts, carbocation chemistry, pyrano[3,4-*c*]pyrandiium.

Reactivity of electrophiles constitutes a driving force for numerous chemical reactions. Typically, an increase in electrophilicity significantly influences the transformation mechanism.[1] Therefore, the search and investigation of new electrophilic reagents and intermediate particles is relevant. Mono-charged carbon electrophiles, namely carbocations and their derivatives, have long been known and used extensively in organic synthesis.[2] However, multi-charged cations have not been examined so widely. According to the known data,[3] di-charged electrophiles, unlike the mono-charged ones, are classified as superelectrophiles and represent intermediates in various transformations. In some cases, the dications can be isolated in stable form,[4] but typically they are generated *in situ* for further interaction with nucleophiles. The high reactivity of dications as superelectrophiles allows them to interact with rather weak nucleophiles, for example a dication formed from 2-acetylpyridine can react with benzene and nitrobenzene.[5] The heterocyclic dications with fused rings have not been sufficiently investigated, although due to their high reactivity they represent useful starting materials or intermediates for organic synthesis. There is little information on the isolation of such dications, a few examples are the preparation of stable cyclic bisurea dications[6] as well as 2,7-naphthyridindium ones.[7] In a recent review,[8] the fused ring dications were pointed out as reaction intermediates. As well, cyclic dicationic species were produced in the cyclization of heterocycle-substituted acetophenones[9] and phenylethyl-substituted pyridinecarboxaldehydes[10] after treatment with triflic acid. Besides, pyrano[3,4-*c*]pyridinediium dication was been supposed as an intermediate in the S_N1 nucleophilic substitution of the leaving ethoxy group in 1-ethoxy-5-methyl-3,8-diphenyl-1*H*-pyrano[3,4-*c*]pyridin-7-ium perchlorate.[11]

This work describes the detection of pyrano[3,4-*c*]pyrandiium dication by NMR spectroscopy as well as our attempts to isolate it. The significance of this heterocyclic system originates from its possibility to be converted into other fused heterocycles through stepwise recyclizations of two oxygen-containing six-membered rings,[11] since it is known that monocyclic pyrylium salts represent universal starting compounds for the synthesis of various carbo- and heterocycles.[12]

Previously, we synthesized compound **1** (Scheme 1) and characterized it using X-ray diffraction. This compound consisted of an uncharged ethoxy-substituted pyran ring and a pyrylium cation.[13] *A priori* its reaction with an acid should lead to protonation of the ethoxy group and formation of pyrano[3,4-*c*]pyrandiium salt **2a**, but its existence remains debatable, since the two fused pyrylium cations in one moiety can reduce drastically the molecule stability and increase the reactivity.

To generate similar electrophilic particles, Brønsted or Lewis acids are typically used. Thus, treatment of compound **1** with a mixture of 70% perchloric acid with acetic or propionic anhydride led to the formation of 1-hydroxypyrano[3,4-*c*]pyran-



Scheme 1

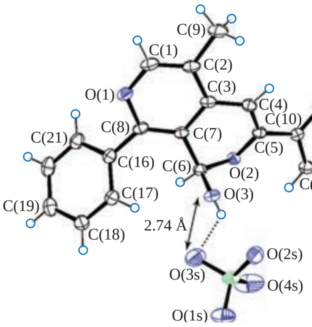
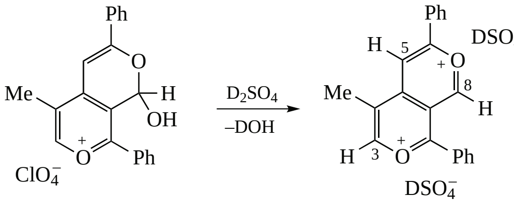


Figure 1 Molecular structure of perchlorate salt **3**.

7-ium salt **3** (see Scheme 1), which was characterized by X-ray diffraction (Figure 1).[†] Note, that in this salt the perchlorate anion has a hydrogen bond with the OH group of pyran ring, the distance O(3)···O(3s) being equal to 2.74 Å. Obviously, the formation of perchlorate salt **3** proceeds through dication **2a**, however, due to its highly electrophilic nature the dication attaches a water molecule from an environment during isolation.

Since it was not possible to isolate pyrano[3,4-*c*]pyrandiium dication as its perchlorate salt **2a** because of its high affinity for water, we attempted to generate this particle in a strongly acidic nonaqueous medium. When yellow compound **3** was dissolved in deuterosulfuric acid, a dark red solution was formed and its NMR spectrum indicated the presence of dicationic salt **2b** (Scheme 2).

In the ^{1}H NMR spectrum of salt **2b** (Figure S3, see Online Supplementary Materials), a significant dislocation of the chemical shifts for ring protons to a downfield area is observed compared with spectrum of the starting compound **3**. This spectral change originates from the presence of two positive charges in the same molecule. The characteristic signals are the H-8, H-3 and H-5 proton peaks of the pyrylium rings, located at 10.67, 9.13 and 9.11 ppm, respectively. The assignment of these signals is based on two-dimensional correlation spectra. The most downfield signal at 10.67 ppm belongs to the H-8 proton, which is confirmed by its cross peak with the δ_C 180.40 ppm peak in two-dimensional HMQC{^{1}H,^{13}C} spectrum (Figure S6). The signal at 9.13 ppm is assigned to the H-3 proton from the corresponding cross peak with δ_C 157.54 ppm. The NOESY{^{1}H, ^{1}H} spectrum demonstrates correlation of the H-3 proton (9.13 ppm) with methyl group at 3.06 ppm, as well as interactions with the protons of phenyl ring in position 1, which have been identified as cross peaks with signals at δ_H 8.74 and 8.76 ppm (Figure S5). Finally, the H-5 proton signal at 9.11 ppm appears as a cross peak with δ_C 113.95 ppm in the two-dimensional HMQC{^{1}H, ^{13}C} spectrum (see Figure S6).



3 **2b**

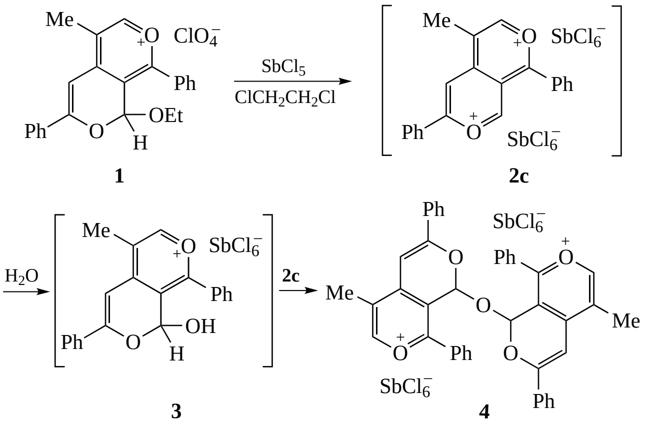
Scheme 2

Note, that only deuterosulfuric acid taken from a freshly opened sealed ampoule is appropriate for these spectral results. Our attempt to use deuterosulfuric acid from a flask with a ground glass stopper led to the NMR spectrum of initial compound **3**, apparently due to the presence of water absorbed from the air during storage or use.

Then we tried to synthesize and isolate pyrano[3,4-*c*]pyrandiium bis(hexachloroantimonate) **2c**, since non-nucleophilic and weakly coordinated anions typically stabilize the cation species. When antimony pentachloride was added to a solution of pyrano[3,4-*c*]pyran-7-ium perchlorate **1** in absolute dichloroethane, dark-yellow crystals were formed and isolated. This product was insoluble in trifluoroacetic acid, acetone, nitrobenzene and chloroform. Because of its extremely poor solubility, it was not possible to record the ^{1}H or ^{13}C NMR spectrum. An X-ray investigation of the single crystals revealed, that the product represented the structure **4** as a solvate with one molecule of 1,2-dichloroethane.[†] Obviously, in this transformation, like in the reaction with perchloric acid, dication salt **2c** is formed first, then the addition of water from an environment affords hydroxy derivative **3**, which in turn binds to unreacted dication from salt **2c** resulting in compound **4** (Scheme 3).

In the doubly charged molecule **4**, an oxygen atom, which is common to the two symmetric parts, lies on the second-order symmetry axis (Figure 2). The angle C(1)–O(3)–C(1A) is 119.9(9)° and the distance C(1)–O(3) is 1.418(9) Å.

For each doubly charged cation of compound **4** in a single crystal, two SbCl_6^- anions and one dichloroethane molecule are located in such a way, that the second-order symmetry axis simultaneously passes through the middle of the statistically located dichloroethane C–C bond and the O(3) atom.



Scheme 3

[†] *Crystal data for* **3**. $C_{21}H_{17}O_7Cl$ (M = 416.81), monoclinic, space group $P2_1/n$, a = 9.7548(14), b = 17.340(2) and c = 11.5349(16) Å, β = 105.561(3)°, V = 1879.6(5) Å^3, Z = 4, T = 120 K, d_{calc} = 1.473 g cm^{-3}, μ(MoKα) = 0.246 mm^{-1}, $2\theta_{max}$ = 59°, 19220 reflections were collected (5381 independent reflections, R_{int} = 0.0347), R_1 = 0.0466 [$I \geqslant 2\sigma(I)$], wR_2 (all data) = 0.1171, largest difference peak and hole 0.62/–0.46 e Å^{-3}. The datasets were collected using a Bruker SMART APEX II CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, 2θ < 56°].

Crystal data for **4**. $C_{44}H_{36}O_5Sb_2Cl_{14}$ (M = 1382.5), orthorhombic, space group $Fdd2$, a = 34.348(2), b = 25.346(1) and c = 12.0660(5) Å, V = 10504.5(9) Å^3, Z = 8, T = 100 K, d_{calc} = 1.748 g cm^{-3}, μ(MoKα) = 1.784 mm^{-1}, $2\theta_{max}$ = 59°, 8437 reflections were collected (5555 independent reflections, R_{int} = 0.0304), R_1 = 0.0722 [$I \geqslant 2\sigma(I)$], wR_2 (all data) = 0.1484, largest difference peak and hole 1.41/–1.80 e Å^{-3}. The datasets were collected using a Bruker P-4 autodiffractometer [λ(MoKα) = 0.71073 Å, ω-scans, $2\theta \leqslant$ 58°].

The structures were solved by direct method and refined by the full-matrix least-squares technique against F^2 in the isotropic–anisotropic approximation. The positions of hydrogen atoms were calculated from geometrical point of view and refined with the riding model. All calculations were performed using a SHELXTL v.6.14 software package.[14]

CCDC 1963425 and 1963763 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

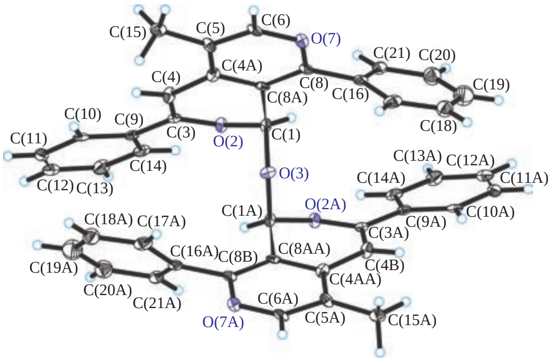


Figure 2 The relative position of the two parts of a doubly charged cation in compound **4**.

The statistical position of the solvent moiety requires the following clarification. In fact, two molecules of 1,2-dichloroethane are combined in the central part of Figure 3, namely Cl(8B)–C(22B)–C(22A)–Cl(7A) and Cl(8A)–C(22A)–C(22B)–Cl(7B), and all their atoms have a population of 1/2. The populations of carbon atoms add up resulting in a total value equal to one, while the corresponding values for chlorine atoms remain 1/2. Thus, for half of the molecules, the contacts Cl(1A)···Cl(8B) = 3.16 Å and Cl(7A)···O(3A) = 3.19 Å occur at the same time, while for another half the contacts Cl(1B)···Cl(8A) and Cl(7B)···O(3A) occur simultaneously, distance values being the same. In other words, Figure 3 represents the superposition of two dichloroethane moiety conformations, for one of them chlorine atoms are marked in blue, for another they are marked in red, and each conformation has a population of 1/2. The dihedral angle Cl–C–C–Cl for an independent dichloroethane molecule, as is seen in the Newman projection along the C–C bond, is close to a right angle (90.6°).

We also performed quantum chemical calculations for the structures of unsubstituted dication **5** (Figure 4) as well as dication **2d** with methyl group and two phenyl substituents, both as bis(hydrogen sulfates). According to the results, the existence of the organic part of molecule in the form of dication **5** is not realized. Obviously, the hypothetical unsubstituted dication **5**, due to its highly electrophilic nature, binds the nucleophilic hydrosulfate anion, affording 1-(sulfooxy)-1*H*-pyrano[3,4-*c*]pyran-7-ium hydrogen sulfate **6**. Nevertheless, structure **2d** is able to exist as dication due to the stabilizing effect of phenyl substituents. The global electrophilicity indices[15] ω for structures **2d** and **6** (see Figure 4) have been calculated. As a result, dication **2d** with ω = 4.64 eV can be classified as a superelectrophilic system, since some nitrofuroxans with ω = 4.5–4.8 eV are known as superelectrophiles.[16]

In summary, the existence of pyrano[3,4-*c*]pyrandiium dication **2** in a strongly acidic medium has been proved using NMR spectroscopy. The structures of its hydrolysis products **3** and **4** also indicate an intermediate formation of the dication.

This work was supported by Southern Federal University (internal grant no. VnGr-07/2017-11). X-ray diffraction investigation was supported by the State Task (registration no. 0089-2019-0013). We are grateful to Dr. O. N. Burov for carrying out the quantum chemical calculations.

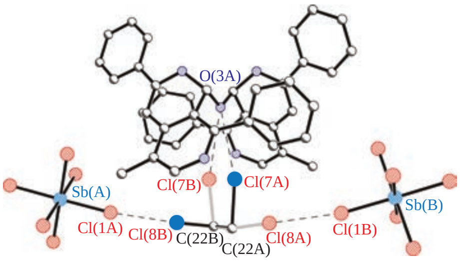
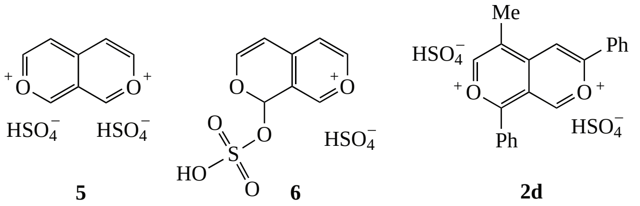


Figure 3 Arrangement of SbCl$_6^-$ anions and dichloroethane molecule in compound **4**.



5
does not exist

6
ω = 4.83 eV

2d
ω = 4.64 eV

Figure 4 Calculation results for the hydrosulfate structures of unsubstituted cations **5**, **6** and substituted dication **2d**.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.05.022.

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Received: 21st November 2019; Com. 19/6063