2-BENZOPYRYLIUM SALTS.

41.* INTRAMOLECULAR TRANSFORMATIONS OF 4-1'-DIMERS OF α-UNSUBSTITUTED 2-BENZOPYRYLIUM SALTS

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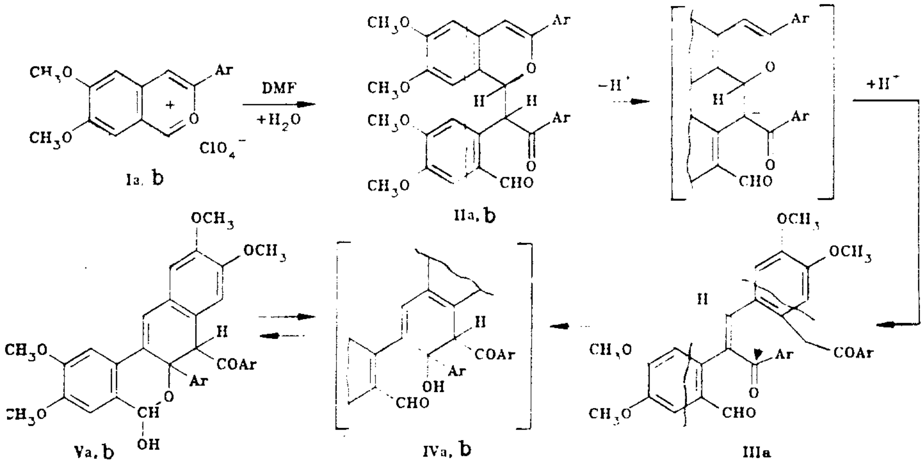
Recyclization reactions of 4-1'-dimers of 2-benzopyrylium salts leading to naphthalene derivatives are described. A new variant of the intramolecular Cannizzaro rearrangement has been discovered.

In previous work on the dimerization of 2-benzopyrylium salts we found that intramolecular transformation of the dimers can yield derivatives of chrysene [2, 3] and benz[*a*]anthracene [4]. With the aim of preparing new carbocyclic systems we have studied recyclization reactions of the 4-1'-dimers IIa, b obtained from the 1-unsubstituted salts Ia, b. It is known [5] that the dimers undergo intramolecular disproportionation under perchloric acid catalyzed thermolysis.

It was found that the transformation of the above compounds under the action of bases was not as unambiguous as the behavior of the 4-1'-dimers which form benz[*a*]anthracenes [4]. Establishing the nature of the transformations described was facilitated in many ways by the studies undertaken earlier on the recyclization reactions of type-II dimer analogs — adducts of 2-benzopyrylium salts with active methylene compounds [6].

As in the case of the dimers mentioned [6], reactions of dimers IIa, b with bases results first in deprotonation of an α-methyl group giving rise to rupture of the isochromene ring. Under relatively mild conditions it is possible to stop the reaction at this stage, isolating the intermediate chalcone of type IIIa.

It should be noted that, according to their PMR spectra, the initial dimers IIa, b are formed from salts Ia, b predominantly in the form of one diastereoisomer. The chalcone IIIa was also isolated by us in the form of a single diastereoisomer and, although the absolute configuration was not determined, in further intramolecular aldol condensation reactions it participated in its Z-form.



I—V a Ar=3,4(CH$_3$O)$_2$C$_6$H$_3$; I, II, IV, V b Ar=C$_6$H$_5$

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*For communication 40, see [1].

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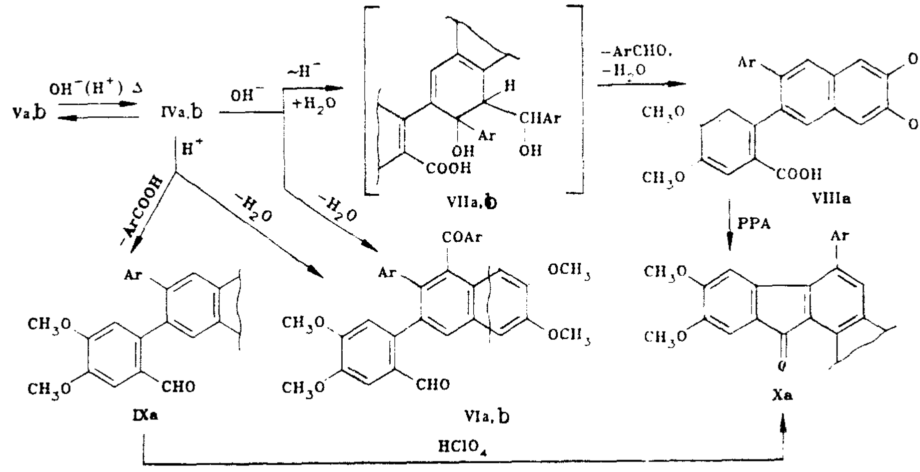
The product of condensation in a mixture of dioxane and aqueous alkali in the cold is the cyclic hemiacetal Va which is evidently formed by intramolecular reaction of the formyl and hydroxyl groups of the aldol IVa [7]. The product Va and its analog Vb can also be formed directly from the dimers IIa, b. As with their precursors, the hemiacetals Va, b are isolated in the form of a single diastereoisomer notwithstanding the existence of three chiral centers in the molecule. The proton of the hemiacetal ring in compound Vb appears in the form of a doublet at 5.49 ppm, degenerating to a singlet after deuteration of the hydroxyl group which was previously a broad singlet at 1.77 ppm. Signals from the tertiary and olefinic protons were recorded at 5.16 and 6.33 ppm, respectively.

Heating the hemiacetals Va, b in strongly basic media leads to rupture of the heterocycle and aromatization as a result of splitting off of water to yield naphthalenes VIa, b, the formation of which is also possible under the same conditions directly from dimers IIa, b. In their PMR spectra, run at room temperature, there is considerable broadening of the proton signals from one of the methoxy groups and the aldehyde and certain aromatic protons. Each of them is resolved into singlet signals on cooling to −30°C which most probably points to a slowing down of the rotation of the bulky substituents on the naphthalene ring. For the same reason, compound VIa can be obtained in two modifications, depending on the conditions of crystallization. They are readily converted one into the other and are distinguished by their melting points and, very slightly, by their IR spectra.

It was found that the naphthalenes VIa, b were not the sole products of these conversions. On acidification of the mother liquor in the case of compound Va the acid VIIIa was isolated. Evidently its formation is preceded by an intramolecular hydride shift between aldehyde and ketone groups in the intermediate aldol IVa



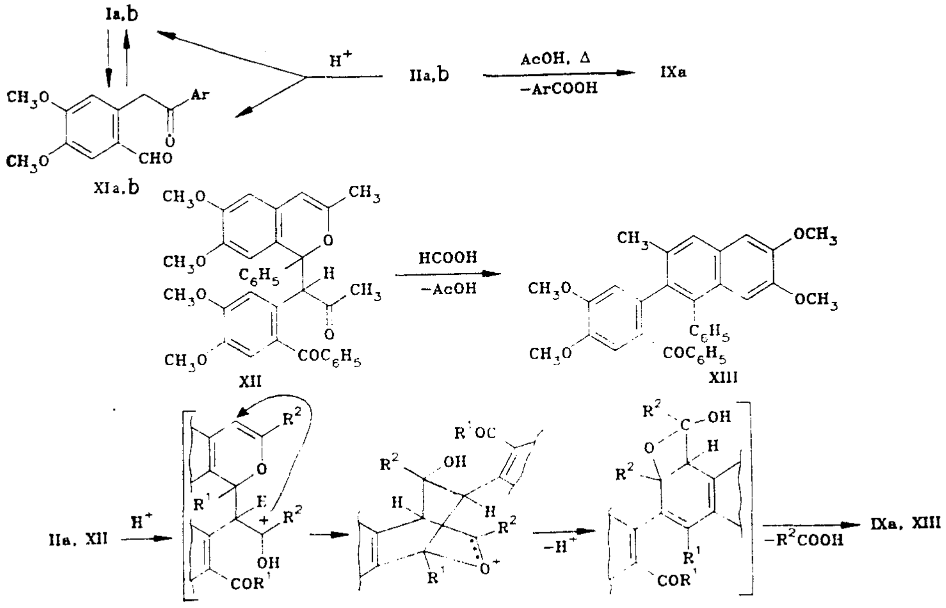
VI—X a Ar=3,4(CH$_3$O)$_2$C$_6$H$_3$; VI, VII b Ar=C$_6$H$_5$

It should be noted that we recently discovered the previously unknown Cannizzaro 1,5-rearrangement in the aldehyde-ketones XIa, b [8] (ring-opened forms of the initial salts Ia, b) which undoubtedly results from favorable steric factors. Examination of a molecular model of compound IV shows that in one of its possible configurations the reaction centers also prove to be adjacent. After transfer of the hydride ion, elimination of veratric aldehyde takes place; the presence of this in the reaction mixture was recorded by chromatography. In the quite rigid molecules of the aromatic naphthalenes VIa, b the proximity of aldehyde and ketone groups is not possible, and hence they undergo heating with alkali without change of any sort.

It is also possible to convert the hemiacetal Va into the naphthalene VIa in an acid medium, but under these conditions veratric acid (which was isolated) is split off parallel to the elimination of water, which leads to the formation of naphthalene IXa.

We were able to prepare naphthalene IXa in ~30% yield by the thermolysis of dimer IIa in the presence of a catalytic quantity of acetic acid. It is thus possible to bring about the intramolecular transformation of 4-1'-dimers of 2-benzopyrylium salts not only in alkaline but also in acid media. However, in the latter case, a special set of conditions is required since dimers IIa, b and others [4] normally break down to the original salts or their ring-opened forms under the influence of acids. Dimer XII behaves in a similar way in alkaline solution, forming a benz[*a*]anthracene derivative [4]. On keeping this in a solution of formic acid a quantitative yield of XIII is obtained, this being related to naphthalene IXa. Both reactions are accompanied by the splitting off of the corresponding carboxylic acid. We consider the mechanism below as the most probable; it was proposed for the reaction of the adduct of salt Ia with acetoacetic ester in acid solution [6] (see scheme on following page).

It is interesting to note that the behavior of dimer IIa and chalcone IIIa during electron bombardment under the conditions of a mass spectrometry experiment is similar to the transformation described above. Thus, they are both converted to the naphthalenes VIa and IXa, the presence of these in the mass spectra being shown by ion



XI a Ar=3,4$(CH_3O)_2C_6H_3$; b Ar=C_6H_5

peaks at m/z 652 and 488, which correspond to the molecular weights of these naphthalenes, together with a molecular ion peak for veratric acid at m/z 182.

The presence of functional groups in the naphthalenes obtained from dimers IIa, b makes further conversions possible. For example, oxidative cyclization of the aldehyde group on the activated naphthalene nucleus readily takes place with the formation of the benzofluorenone Xa. This product can also be prepared in quantitative yield from the acid VIIIa.

Thus, because of the possibility of varying the substituents and the conditions of further conversion of the dimers formed, dimerization of 2-benzopyrylium salts can be considered as a new approach to the synthesis of various polycondensed aromatic compounds.

EXPERIMENTAL

IR spectra were run on a Specord 75 spectrophotometer in mineral oil and PMR spectra on Tesla 487C (80 MHz) and Tesla 567A (100 MHz) instruments at 20°C in $CDCl_3$ and a mixture of C_5D_5N and DMF-D_7 as solvents with HMDS as internal standard. A Finnigan MAT-4615 spectrometer was used for the mass spectra at an ionization energy of 70 eV with direct introduction of the sample into the source. Purity of the compounds prepared was monitored by TLC on alumina in $CHCl_3$.

1-[α-Benzoyl(2-formyl-4,5-dimethoxybenzyl)]-3-phenyl-6,7-dimethoxyisochromene (IIb, $C_{34}H_{30}O_7$). At room temperature, 0.37 g (1 mmole) Ib perchlorate [8] was dissolved in 5 ml DMF and immediately diluted with 50 ml cold water. The precipitate was isolated and dried to yield 0.26 g (95%) of a colorless material shown to be a single substance by TLC and PMR spectroscopy and decomposing on recrystallization. R_f 0.70. IR spectrum (cm^{-1}): 1685, 1680, 1630. PMR spectrum (ppm): 3.35 (s, OCH_3), 3.80 (s, $2OCH_3$), 3.92 (s, OCH_3), 5.57 (s, 1H), 6.07 (d, 1H, J = 9 Hz), 6.42-8.02 (m, 1H and $14H_{arom}$), 9.60 (s, 1H, CHO).

Dimer IIa [5]. Mass spectrum, m/z (I %):* 137 (7), 151 (3), 165 (100), 166 (16), 167 (3), *182 (4)*, 327 (3), 344 (6), *488 (4), 652 (0.7)*.

1-(3,4-Dimethoxybenzoyl)-1-(2-formyl-4,5-dimethoxyphenyl)-2-[2-(3,4-dimethoxyphenyl)-4,5-dimethoxyphenyl]ethylene (IIIa, $C_{38}H_{38}O_{11}$). A suspension of 0.33 g (0.5 mmole) dimer IIa and 0.3 g sodium acetate in 10 ml isopropanol was heated for 3 h and filtered hot. After washing the precipitate with water 0.16 g (50%) of light yellow crystals was obtained, mp 204°C (from acetic acid), R_f 0.45. IR spectrum (cm^{-1}): 1675, 1630, 1595. PMR spectrum (ppm): 3.32 (s, OCH_3), 3.84 (s, $3OCH_3$), 3.87 (s, $3OCH_3$), 3.96 (s, OCH_3), 4.27 (s, 2H), 6.45 (s, 1H), 6.57-7.68 (m, $10H_{arom}$), 10.08 (s, 1H, CHO). Mass spectrum, m/z (I, %): 137 (6), 149 (4), 165 (100), 166 (22), *182 (25), 488 (19)*, 489 (4), *652 (2)*.

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*Here and below, peaks with intensities >3% are quoted; signals mentioned above are in italics.

2,3,9,10-Tetramethoxy-5-hydroxy-6*a*-(3,4-dimethoxyphenyl)-7-(3,4-dimethoxybenzoyl)-5,6,7,15-tetrahydro-6-oxoniabenz[*a*]anthracene (Va, $C_{38}H_{38}O_{11}$). A. To a suspension of 0.33 g (0.5 mmole) chalcone IIIa in 5 ml dioxane was added 3 ml 5% aqueous KOH and the mixture stirred in the cold for 30 min. After diluting the reaction mixture with water, separation and drying of the precipitate yielded 0.30 g (90%) of a light yellow product.

B. To a solution of 0.33 g (0.5 mmole) dimer IIa in 3 ml dioxane was added 3 ml 5% aqueous KOH and after 20 min the reaction mixture was diluted with cold water. Separation and drying of the product yielded 0.28 g (85%), mp 165°C (from dioxane). R_f 0.40. IR spectrum (cm^{-1}): 3390, 1675, 1635, 1595. PMR spectrum (ppm): 1.77 (br.s, 1H, OH), 3.57 (s, OCH_3), 3.67 (s, $2OCH_3$), 3.75 (s, $3OCH_3$), 3.87 (s, $2OCH_3$), 5.00 (s, 1H), 5.42 (d, 1H, j = 12 Hz, CHOH), 6.27 (s, 1H), 6.60-7.92 (m, $10H_{arom}$).

2,3,9,10-Tetramethoxy-5-hydroxy-6*a*-phenyl-7-benzoyl-5,6,7,15-tetrahydro-6-oxoniabenz[*a*]anthracene (**Vb**, $C_{34}H_{30}O_7$) was prepared in a similar manner to Va, method B. mp 159°C (from ethanol), R_f 0.40. IR spectrum (cm^{-1}): 3325, 1680, 1635, 1605. PMR spectrum (ppm): 1.77 (br.s, 1H, OH), 3.57 (s, OCH_3), 3.72 (s, OCH_3), 3.78 (s, OCH_3), 3.90 (s, OCH_3), 5.16 (s, 1H), 5.49 (d, 1H, J = 12 Hz, CHOH), 6.33 (s, 1H), 6.75 (s, $1H_{arom}$), 6.90 (s, $1H_{arom}$), 7.29-7.77 (m, $10H_{arom}$), 8.19-8.34 (m, $2H_{arom}$). Yield 90%.

1-(3,4-Dimethoxybenzoyl)-2-(3,4-dimethoxyphenyl)-3-(2-formyl-4,5-dimethoxyphenyl)-6,7-dimethoxynaphthalene (VIa, $C_{38}H_{36}O_{10}$) and 2-(3,4-Dimethoxyphenyl)-3-(2-carboxy-4,5-dimethoxyphenyl)-6,7-dimethoxynaphthalene (VIIIa, $C_{29}H_{28}O_8$). **A.** To a solution of 0.67 g (1 mmole) dimer IIa in 8 ml dioxane was added 4 ml 5% aqueous KOH and the solution heated 15 min. After cooling, the reaction mixture was diluted with 20 ml water and the precipitated naphthalene VIa separated and dried. Yield 0.39 g (60%) colorless product. After quickly recrystallizing from ethanol, mp 170°C. IR spectrum (cm^{-1}): 1675, 1655, 1595. After slow recrystallization from ethanol, mp 205°C. IR spectrum (cm^{-1}): 1680, 1645, 1595. It was possible to convert the second crystalline modification into the first by dissolving it in $CHCl_3$ and evaporating the solution. R_f 0.70. PMR spectrum (ppm): 3.45 (br.s, OCH_3), 3.69 (s, OCH_3), 3.84 (s, OCH_3), 3.87 (s, $3OCH_3$), 3.91 (s, OCH_3), 4.05 (s, OCH_3), 6.57-7.89 (m, $11H_{arom}$), 10.00 (br.s, 1H, CHO). Mass spectrum, m/z (I, %): 137 (6), 165 (100), 166 (9), 377 (9), 487 (22), 488 (6), 652 (53).

After separating the naphthalene VIa, the mother liquor was acidified with HCl to yield 0.18 g (35%) colorless precipitate with mp 288°C (from acetic acid) which was soluble in aqueous alkali. IR spectrum (cm^{-1}): 3355, 1660, 1600, 1265. PMR spectrum (in 1:1 C_5D_5N—DMF-D_7) (ppm): 3.50 (s, OCH_3), 3.60 (s, $2OCH_3$), 3.72 (s, OCH_3), 3.82 (s, OCH_3), 3.87 (s, OCH_3), 6.67-7.77 (m, $9H_{arom}$). M^+ 504. The same respective naphthalenes VIa and VIIIa are formed on heating chalcone IIIa (method B) and hemiacetal Va (method B) under similar conditions.

1-Benzoyl-2-phenyl-3-(2-formyl-4,5-dimethoxyphenyl)-6,7-dimethoxynaphthalene (VIb, $C_{34}H_{28}O_6$) was similarly prepared by methods A and B, as for naphthalene VIa. mp 179°C (after slow crystallization from ethanol), R_f 0.70. IR spectrum (cm^{-1}): 1680, 1595, 1045. PMR spectrum (ppm): 3.69 (br.s, OCH_3), 3.81 (s, OCH_3), 3.87 (s, OCH_3), 4.02 (s, OCH_3), 6.60 (br.s, $1H_{arom}$), 6.90-7.92 (m, $14H_{arom}$), 10.02 (br.s, 1H, CHO). Yield 50% (A), 65% (B).

2-(2-Formyl-4,5-dimethoxyphenyl)-3-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene (IXa, $C_{29}H_{28}O_7$). A. A solution was prepared by warming 0.33 g (0.5 mmole) hemiacetal Va in 2 ml acetic acid and on cooling, 0.1 g (40%) colorless crystals, mp 267°C (from acetic acid), were deposited. R_f 0.75. IR spectrum (cm^{-1}): 1693 (w), 1680, 1600. PMR spectrum (ppm): 3.47 (s, OCH_3), 3.70 (s, OCH_3), 3.72 (s, OCH_3), 3.82 (s, OCH_3), 3.92 (s, $2OCH_3$), 6.45-7.70 (m, $9H_{arom}$), 9.60 (s, 1H, CHO). M^+ 488. After diluting the mother liquor with water, 0.18 g (55%) naphthalene VIa was isolated and evaporation of the remaining solution yielded 0.04 g (40%) veratric acid.

B. A sample (0.67 g, 1 mmole) of dimer IIa prepared by reprecipitation from acetic acid by the method of [5], but not recrystallized, was heated to 240°C in an atmosphere of argon and the reacted material, after cooling, was dissolved, with heating, in 50% aqueous acetic acid and left to crystallize overnight. The yield of naphthalene IXa was 0.15 g (30%); it was identical in all its characteristics with that obtained by method A.

1-Phenyl-2-(2-benzoyl-4,5-dimethoxyphenyl)-3-methyl-6,7-dimethoxynaphthalene (XIII, $C_{34}H_{30}O_5$). A solution of 0.28 g (0.5 mmole) dimer XII [4] in 3 ml formic acid was left in the cold for a day and then diluted with water. Separation and drying of the precipitate yielded 0.25 g (95%) colorless product, mp 173°C (from ethanol), R_f 0.85. IR spectrum (cm^{-1}): 1650, 1600, 1570. PMR spectrum (ppm): 2.17 (s, CH_3), 3.52 (s, OCH_3), 3.62 (s, OCH_3), 3.72 (s, OCH_3), 3.87 (s, OCH_3), 6.60-7.50 (m, $15H_{arom}$). M^+ 518.

6-(3,4-Dimethoxyphenyl)-2,3,8,9-tetramethoxybenz[*a*]fluorenone (Xa, $C_{29}H_{26}O_7$). A. A solution of 0.24 g (0.5 mmole) naphthalene IXa in 2 ml acetic acid, with the addition of 1 drop of 70% perchloric acid, was heated for 2 min and after cooling the reaction mixture was diluted with water. The precipitate was separated and dried and purified by column chromatography (Al_2O_3, $CHCl_3$), collecting the colored fraction with R_f 0.85. Yield 0.13 g (55%) colored product.

B. A solution of 0.25 g (0.5 mmole) acid VIIIa in 4 g polyphosphoric acid was heated with stirring on a water bath for 40 min and poured onto ice. The precipitate was separated and dried to give 0.22 g (90%) orange crystals, mp 210°C (from ethanol), R_f 0.85. IR spectrum (cm^{-1}): 1680, 1590, 1035. PMR spectrum (ppm): 3.47 (s, OCH_3), 3.80 (s, OCH_3), 3.87 (s, $3OCH_3$), 3.97 (s, OCH_3), 6.17 (s, $1H_{arom}$), 6.85 (s, $1H_{arom}$), 6.95-7.10 (m, $4H_{arom}$), 7.47 (s, $1H_{arom}$), 8.18 (s, $1H_{arom}$). M^+ 486.

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STEREOCHEMISTRY OF THE IONIC HYDROGENATION OF PENTASUBSTITUTED 4H-THIOPYRANS AND STRUCTURES OF THE THIACYCLOHEXANES OBTAINED FROM THEM

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The structure of 3,5-dimethyl-2,4,6-triphenylthiacyclohexane, obtained as a result of the ionic hydrogenation of the corresponding 4H-thiopyran with the $CF_3COOH/HSi(C_2H_5)_3$ *couple, was established. It is shown that the stereochemistry of the ionic hydrogenation of 2,3,4,5,6-pentasubstituted 4H-thiopyrans, both those that disproportionate and those that do not disproportionate under the influence of trifluoroacetic acid, is the same.*

Pentasubstituted 4H-thiopyrans I-III react differently with trifluoroacetic acid. Thus, thiopyrans II and III undergo disproportionation to the corresponding thiopyrylium salts XII and XIII and thiacyclohexanes VII and VIII like di-, tri-, and tetrasubstituted 4H-thiopyrans IV and V, while sulfide I undergoes quantitative conversion to thiopyrylium trifluoroacetate XI with the participation of air oxygen [1]. 3,5-Dimethyl-2,4,6-triphenylthiacyclohexane (VI), which should be formed in the case of disproportionation of thiopyran I, is obtained only as a result of catalytic (H_2, Pd/C) or ionic [$CF_3COOH/HSi(C_2H_5)_3$] hydrogenation of this compound. The ionic hydrogenation of substituted 4H-thiopyrans can be regarded as a model of their disproportionation under the influence of protic

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