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## Thermolysis of 3,3,5,5-Tetramethyl-1,2,4-trithiolane 1-Oxide: First Matrix Isolation of the HOSS<sup>-</sup> Radical

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Dedicated to Professor Dr. Helge Willner on the occasion of his 65th birthday

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Flash vacuum pyrolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide performed at 700 °C yields the 1-oxatrisulfan-3yl radical (HOSS') along with disulfur monoxide (S<sub>2</sub>O) and diisopropyl sulfide, which were isolated in argon matrices at 10 K. Upon irradiation with UV light, the 1-oxatrisulfan-3yl radical undergoes isomerization to the 1-oxatrisulfan-1-yl radical (HSSO'). Both radicals were identified by comparison of their computed and experimental IR and UV/Vis spectra. In addition, density functional theory (DFT) computations of-

#### Introduction

Sulfur-rich heterocycles with diverse ring sizes are common in nature. In this group of compounds, 1,2,4-trithiolanes as well as their *S*-oxides were isolated from *Shitake* mushrooms,<sup>[1a,1b]</sup> red algae *Hondria californica*,<sup>[1c]</sup> hyperthermophilic archea,<sup>[1d]</sup> and other sources.<sup>[1e-1g]</sup> In a series of recent papers we described thermal reactions of 1,2,4trithiolanes **1a,b** as well as their 4-oxides **2a,b** and 1-oxides **3a,b** (Scheme 1).



Scheme 1. 1,2,4-Trithiolanes 1 and their S-oxides 2 and 3.

We demonstrated that gas-phase thermolysis of **1a** occurs through [3+2] cycloreversion leading to thioformaldehyde

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fer a plausible explanation of the most likely reaction mechanism, suggesting that the initial step is a 1,3-H shift with simultaneous ring opening. A 1-oxatrisulfane derivative formed thereby undergoes fragmentations via a radical and a competitive concerted pathway leading to the observed final products. The same mechanism also governs the thermal fragmentation of di-*tert*-butyl disulfide *S*-oxide. Its pyrolysis at 700 °C affords an analogous set of products, including the 1-oxatrisulfan-3-yl radical (HOSS') as the key intermediate.

S-sulfide (thiosulfine) (4a) and thioformaldehyde (5a). The parent thiosulfine 4a was converted into dithiirane (6a) upon photolysis with  $\lambda > 385$  nm. Prolonged irradiation eventually led to a mixture s-cis and s-trans rotamers of dithioformic acid (7) (Scheme 2).<sup>[2a]</sup> A similar pathway was observed for the thermolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane (1b) in the gas phase at 500–700 °C. In this case, the initially formed thioacetone S-sulfide (4b) underwent cyclization yielding 3,3-dimethyldithiirane (6b), which was found together with a mixture of isomeric products identified as s-cis- and s-trans-isopropenyl disulfane (8) (Scheme 2).<sup>[2b]</sup>



Scheme 2. Thermal fragmentation of 1,2,4-trithiolanes 1 leading to thiosulfines 4 and dithiiranes 6.

When 1,2,4-trithiolane 4-oxide (2a) was used as a substrate for the thermolysis reaction performed in the gas phase at 650 °C, the products collected in the matrix were identified as a mixture of thioformaldehyde *S*-oxide (9a) and thiosulfine **4a** as the major components. These results can also be explained by invoking a [3+2] cycloreversion of the starting material **2a**. In this case, **9a** can be recognized as a dipolarophile, and **4a** is the corresponding 1,3-dipole.<sup>[2c]</sup> The same reaction pathway was observed for 3,3,5,5-tetramethyl-1,2,4-trithiolane 4-oxide (**2b**). The matrix-isolated thioacetone *S*-oxide (**9b**) was subsequently used as a substrate to generate 3,3-dimethyloxathiirane (**10b**) (Scheme 3).<sup>[2d]</sup>



Scheme 3. Thermal fragmentation of 1,2,4-trithiolane 4-oxides 2 leading to sulfines 9 and formation of oxathiiranes 10.

However, when 1,2,4-trithiolane 1-oxide (**3a**) was thermolyzed in the gas phase at 700 °C, a different reaction was observed. Spectroscopic analysis of the matrix-isolated products led to the identification of thioformaldehyde *S*oxide (sulfine) (**9a**) formed together with dithioformic acid (**7**) (Scheme 4). The reaction mechanism was elucidated by DFT computations at the B3LYP/6-311+G(3df,3pd) level of theory (see Experimental Section for details), and – in this case – the initial step is an allowed 1,4-H shift leading to open-chain intermediate **11**, which spontaneously splits into a mixture of final products **7** and **9a** (Scheme 4).<sup>[2c]</sup> Structure **3a** can also be considered as a cyclic thiosulfinate, and the initial step of the observed fragmentation corresponds to the typical reactivity of *S*alkyl alkanethiosulfinates under pyrolytic conditions.<sup>[3]</sup>



Scheme 4. Mechanism of thermal fragmentation of 1,2,4-trithiolane 1-oxide (3a).

The goal of this study was to investigate the behavior of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (**3b**), which can also be considered as a type of an *S*-alkyl alkanethiosulfinate with  $\beta$ -hydrogen atoms. In addition, di-*tert*-butyldisulfane *S*-oxide (**12**) was included in this study as an easily available model representative for thiosulfinates with a similar substitution pattern (Scheme 5).

Although experimental and theoretical studies on the fragmentation of **12** leading to 1-oxatrisulfane (**13**) have been reported,<sup>[4]</sup> this process has never been investigated by



Scheme 5. Formation of 1-oxatrisulfane through thermolysis of disulfane *S*-oxide **12**.

means of vacuum pyrolysis in combination with matrix isolation. Moreover, there are no reports available on the thermal fragmentations of this type of thiosulfinates by using matrix-isolation spectroscopy. This approach is a powerful tool for studying reactive intermediates involved in this type of thermal transformation of thiosulfinates.

### **Results and Discussion**

Oxidation of 3,3,5,5-tetramethyl-1,2,4-trithiolane (1b) with *m*-chloroperbenzoic acid (*m*-CPBA) in dichloromethane solution at room temperature leads to a mixture of *S*-oxides **2b** and **3b** that can be easily separated by chromatography.<sup>[5]</sup> Analytically pure **3b** was used for the pyrolysis experiments described in this paper.

In a typical experiment, an evaporated sample of **3b** was pyrolyzed in high vacuum at 500-800 °C (empty quartz tube; inner diameter: 8 mm; heated zone: 5 cm). The pyrolysis products, diluted with a large excess of argon, were condensed on the cooled spectroscopic window (BaF<sub>2</sub> or CsI) of the cryostat at 10 K. The matrices formed thereby were investigated by means of FTIR (4000–300 cm<sup>-1</sup>) and UV/ Vis spectroscopy (850-200 nm). The FTIR spectrum recorded after a typical pyrolysis experiment carried out at 700 °C is presented in Figure 1. Two absorption bands located at 1157 and 673 cm<sup>-1</sup> are attributed to disulfur oxide S<sub>2</sub>O (14).<sup>[6]</sup> Another band at 1275 cm<sup>-1</sup> indicates the presence of a moderate amount of thioacetone (5b).<sup>[7]</sup> Another set of bands with the most intense absorption located at  $893 \text{ cm}^{-1}$  is attributed to diisopropenyl sulfide (15). Because this compound is unknown, we also independently prepared it by conducting large-scale vacuum pyrolysis and subsequently identified it by high-resolution mass spectrometry and NMR spectroscopy. A sample of 15 was condensed with Ar at 10 K, and the recorded IR bands were identical to those found in the original pyrolysate of **3b**. Four other bands observed in the IR spectrum at 3540, 1092, 729, and 659 cm<sup>-1</sup> can be assigned to 1-oxatrisulfanyl radical [HO-S-S<sup>-</sup>] (16) by comparison with the computed IR spectrum (vide infra).

The corresponding UV/Vis spectrum revealed two strong absorption bands located at  $\lambda_{max} = 290$  and 385 nm (Figure 2). The first absorption displays a resolved vibrational structure that belongs to **14**, whereas the second band can be assigned to radical **16**, the existence of which in the gas phase was previously proven by neutralization-reionization mass spectrometric measurements.<sup>[8]</sup> The absorption band



Figure 1. Matrix-isolated pyrolysis products of 3,3,5,5-tetramethyl-1,2,4,trithiolane 1-oxide (**3b**) (argon matrix, 10 K, pyrolysis temperature 700 °C).



Figure 2. UV/Vis spectra of matrix-isolated pyrolysis products of 3,3,5,5-tetramethyl-1,2,4,trithiolane 1-oxide (**3b**) (argon matrix, 10 K, pyrolysis temperature 700 °C) before (full line) and after (dashed line) photolysis ( $\lambda = 405$  nm). Inset: Computed [TD-UB3LYP/6-311+G(3df,3pd)] electronic transitions for **16**.

of 16 observed experimentally was in good agreement with the most intense computed electronic transitions at  $\lambda_{\text{max}} =$  377 nm (f = 0.0294).

To gain more information on the photochemical reactivity of the matrix-isolated pyrolysis products, the mixture was photolyzed at 10 K with monochromatic light of different wavelengths. Thus, irradiation with  $\lambda = 290$  nm resulted in the disappearance of the corresponding UV and IR absorption bands of 14 and the parallel formation of new IR absorption bands of the cyclic  $S_2O$  isomer 17.<sup>[6c]</sup>

Photolysis of the matrix with wavelengths corresponding to the broad absorption band of **16** either at  $\lambda = 366$  or at 405 nm induced a 1,3-H shift leading to the isomeric radical [HS–S–O'] (**18**). This photoisomerization is reversible, and radical **16** can be regenerated upon irradiation at  $\lambda =$ 546 nm (Scheme 6).



Scheme 6. Thermolysis of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (3b) and subsequent photolysis of matrix-isolated products.

Comparison of computed and experimental IR absorption bands of isomeric radicals 16 and 18 allowed their unambiguous identification (Figure 3). Whereas in the case of **16** the O–H stretching frequency appears at  $3540 \text{ cm}^{-1}$ , **18** displays a weak S-H stretching band at 2560 cm<sup>-1</sup>. Moreover, the strongest absorption at 730 cm<sup>-1</sup> is attributed to the S–O stretching vibration in 16, and the corresponding S-O stretching band in 18 was found at 1091 cm<sup>-1</sup>. The observed large wavenumber difference of 361 cm<sup>-1</sup> proves a significant enhancement of the SO bond order in 18. The latter absorption overlaps with the SOH deformation mode in isomer 16, resulting in diminished intensities of both bands in the experimental difference spectrum. However, replacement of argon as the matrix material with nitrogen leads to a characteristic shift of the corresponding absorption bands, and both bands can be observed undisturbed in the difference spectrum (see the Supporting Information, Figure S1).

The characteristic absorption attributed to the S–S stretching vibration in 16 appears at  $653 \text{ cm}^{-1}$ . In the case of 18, the position of the corresponding absorption was found at  $458 \text{ cm}^{-1}$ . Structures of isomeric radicals 16 and

**18** were computed at the UB3LYP/6-311+G(3df,3pd) and CCSD(T)-FC/cc-pVTZ level of theory (Figure 4).

In accordance with earlier theoretical studies of the isomeric radicals **16** and **18**,<sup>[8]</sup> the CCSD(T)-FC/cc-pVTZ-optimized geometry shows a planar ( $C_s$ ) *cisoid* structure for **16** as an energy minimum. Computation of the internal rotation energy profile identified the planar *transoid* conformation as a transition structure associated with a barrier of ca. 2 kcalmol<sup>-1</sup> (see the Supporting Information, Figure S2). In contrast to **16**, computations indicate a  $C_1$  minimum structure for **18** with a torsional angle of 63°. In addition, the computed S–O bond in radical **18** is shorter, and the S–S bond is longer than in the case of **16**. The latter displays an approximate 2:1 spin density distribution between the two sulfur atoms. Approximately the same amount of delocalization of the unpaired electron between the S and O atoms is computed for radical **18** (Figure 4).

To extend the study of 3b, an analogous high-vacuum pyrolysis experiment was carried out with di-*tert*-butyldisulfane S-oxide (12) at 500 and 700 °C. The 500 °C experiment led to the formation of 3-*tert*-butyl-1-oxatrisulfane (19), which was postulated in an earlier paper based on



Figure 3. Comparison of the computed [UB3LYP/6-311+G(3df,3pd)] and experimental IR spectra of radicals 18 (top) and 16 (bottom). The experimental spectrum refers to a difference of spectra taken before and after radiation with 366 nm light.

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Figure 4. Geometry and spin densities (numbers in italic) of isomeric radicals 16 and 18 computed at the UCCSD(T)-FC/cc-pVTZ level of theory [UB3LYP/6-311+G(3df,3pd) in parentheses]. Bond lengths are given in Å, angles in °.

trapping experiments with methyl propiolate.<sup>[4a]</sup> Its existence was also postulated as an intermediate that undergoes further conversion in the gas phase yielding 1-oxatrisulfane (13). The structure of 13 was elucidated by analysis of its rotational spectrum as well as that of its isotopologues.<sup>[4b,4c]</sup> Recently, the mechanism of thermolysis of 12, leading to 13 and S<sub>2</sub>O (14), was studied by means of computational methods.<sup>[9]</sup> In accordance with earlier reported results,<sup>[4a,4b]</sup> the experiment conducted at 500 °C leads to elimination of isobutene (20) and the formation of 1-oxatrisulfane derivative 19 (Scheme 7).



Scheme 7. Thermolysis of disulfane S-oxide 12 at different temperatures.

The experimental and computed IR spectra are in good agreement, thus lending confidence to the correct assignment of the postulated structure 19. It is worth noting that, in the experimental IR spectrum, bands of the radical 16 and disulfur oxide (14), which were formed in trace amounts, were also observed (see the Supporting Information, Figure S3).

When the thermolysis experiment was carried out at 700 °C, only a very small amount of **19** formed. Instead, the most intense absorption bands evidenced the formation of **14** and radical **16** as the major products. In addition, *tert*-butyl radical **(21)** and 1-oxatrisulfane **(13)** were present in the mixture. Radical **21** could be identified by its characteristic IR absorption bands.<sup>[10]</sup> The absorption bands assigned to **13** are in agreement with their reported gas-phase

values.<sup>[4]</sup> In addition, the IR absorption bands of matrixisolated **13** correspond closely to the computed IR spectrum (Figure 5). The computed IR-band intensities of **14**, **16**, **21**, and **13** allow an approximate molar ratio of these compounds in the matrix to be estimated as 6:2:2:1.

The IR absorption bands of matrix-isolated parent 1oxatrisulfane (13), which are very close to those of radical 16, deserve a short comment. In the case of 13, the OH absorption band is found at 3560 cm<sup>-1</sup>, which is close to the analogous absorption of 16 (3540 cm<sup>-1</sup>). The S–O stretching vibration (13: 736 cm<sup>-1</sup>) is also only slightly shifted to a higher value (16: 730 cm<sup>-1</sup>). Furthermore, the S–S stretching in 13 (511 cm<sup>-1</sup>) is significantly lower than that of 16 (653 cm<sup>-1</sup>). In addition, two new absorption bands attributed to the torsional mode of the HOSS fragment were observed at 386 and 416 cm<sup>-1</sup>. However, due to the very low intensity, the S–H stretching absorption band in 13 could not be detected.

The presented data show that the distributions of products 16, 13, and 14 are very similar in both experiments performed either with 3b or with 12. This important finding allows us to conclude that, in both cases, the reaction pathways are governed by analogous mechanisms in which sulfur radicals play a key role. The appearance and role of the sulfur radical 16 was not considered in either experimental or computational works focusing on the thermolyses of thiosulfinates.<sup>[4,9]</sup>

Based on the experimental findings and computational results, we suggest a fragmentation mechanism of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (**3b**), as presented in Scheme 8. The first step is an electrocyclic ring opening with a simultaneous H-shift yielding 1-oxatrisulfane derivative **22**. It corresponds to the mechanistic pathway postulated on the basis of computations carried out for **12**.<sup>[9]</sup> In both cases, the computed activation energies are below 30 kca1mol<sup>-1</sup>. The reaction is slightly endothermic, with  $\Delta H_r = 3.3$  kca1mol<sup>-1</sup>. In contrast to **19**, formation of **22** results from an intramolecular reversible process, which is very likely the reason why the latter intermediate cannot be detected in the matrix. We assume that **22** undergoes very



Figure 5. Matrix-isolated pyrolysis products of 12 (700 °C, Ar, 11 K); bands of isobutene (20) have been subtracted for clarity. Top: Computationally simulated IR spectrum [B3LYP/6-311+G(3df,3pd)] of a mixture consisting of S<sub>2</sub>O (14), radical 16, *tert*-butyl radical (21), and 1-oxatrisulfane (13) in a molar ratio of 6:2:2:1.



Scheme 8. Proposed mechanism of the thermal fragmentation of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (**3b**) based on the results of B3LYP/6-311+G(3df,3pd) computations.

fast fragmentation through two competitive pathways presented as "A" and "B" (Scheme 8).

Whereas pathway A leads to the formation of radical 16 and very likely to its cofragment radical 23, the IR bands of which – according to DFT computations – overlap with those of sulfide 15 and therefore could not be assigned unambiguously, pathway B follows a concerted H-shift of a retro-ene fragmentation, yielding diisopropyl sulfide (15) and parent thiosulfinic acid (24). Both processes require comparable activation energies and reaction enthalpies (Scheme 8). However, product 24 could not be detected in the matrix and, very likely, in the gas phase, immediately undergoes conversion into 1-oxatrisulfane (13), which was found in the matrix in trace amounts. The route through which disulfur oxide (14) is formed is not completely clear. One of the possible pathways could be a synchronous H<sub>2</sub> elimination from *cis*-conformer of 13. However, the computed activation energy for this type of H<sub>2</sub> elimination is rather high ( $\Delta H^{\ddagger} = 61.0 \text{ kcal mol}^{-1}$ ). Alternative formation of radical 16 either from 24 or from 1-oxotrisulfane (13) by homolytic cleavage of the corresponding S–H bonds are energetically less favorable processes, with bond dissociation energies (BDEs) of 40.4 and 62.8 kcal mol<sup>-1</sup>, respectively.

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It should be noted that the alternative pathway **B** corresponds to that computed for the fragmentation of 19.<sup>[9]</sup> However, competitive homolytic fragmentation corresponding to pathway **A** (Scheme 8) has not been considered in this report.<sup>[9]</sup> The results of the experiment conducted at 700 °C (Scheme 7) underscores the importance of the "radical" pathway **A**.

### Conclusions

The present study shows that thermal fragmentations of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (3b) and ditert-butyldisulfane S-oxide (12) occur in a similar manner to other S-alkyl alkanethiosulfinates with β-hydrogen atoms. The initial step of the observed fragmentation is a synchronous H-shift, resulting in the formation of the corresponding 1-oxatrisulfane derivative together with an olefinic fragment. The intermediates formed thereby undergo further fragmentation, yielding 1-oxatrisulfan-3-yl radical (16) in both cases. For the first time, vacuum pyrolysis in combination with matrix isolation allowed the detection and spectroscopic characterization of this type of sulfurcontaining radicals. These findings lead to the final conclusion that, besides a concerted reaction pathway postulated in earlier reports,<sup>[4,9]</sup> a competitive radical process does play an important role. For the first time, the key intermediate 16 was isolated in an argon matrix and identified spectroscopically.

## **Experimental Section**

**Materials:** 3,3,5,5-Tetramethyl-1,2,4-trithiolane 1-oxide (**3b**) was prepared according to known protocols by oxidation of the corresponding 1,2,4-trithiolane **1b** using *m*-CPBA.<sup>[5b]</sup> An analogous protocol was used for the preparation of **12** from commercially available di-*tert*-butyldisulfane.<sup>[11]</sup>

Matrix Isolation Experiments: The cryostat used for the matrix isolation studies was an APD Cryogenics HC-2 closed-cycle refrigerator system fitted with CsI windows for IR and BaF2 windows for UV/Vis measurements. The matrix temperature was measured and controlled by a Scientific Instruments 9600-1 silicon diode temperature controller. For irradiations, a mercury high-pressure lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used (bandwidth ca. 10 nm). IR spectra were recorded with a Bruker IFS 55 FTIR spectrometer (4500–300 cm<sup>-1</sup>, resolution 0.7 cm<sup>-1</sup>), and UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer. For the combination of high-vacuum flash pyrolysis (HVFP) with matrix isolation, we employed a home-built, water-cooled oven directly connected to the vacuum shroud of the cryostat. The pyrolysis zone consisted of an empty quartz tube (inner diameter 8 mm, length of heating zone 50 mm) resistively heated by a thermo-coax wire. The temperature was controlled by an Ni/CrNi thermocouple. In a typical FVP experiment, a sample of 3,3,5,5-tetramethyl-1,2,4-trithiolane 1-oxide (3b) or di-tert-butyl disulfide S-oxide (12) was evaporated from a precooled (3b: 0 °C, 12: -15 °C) storage vessel and pyrolyzed at 500-700 °C. Pyrolysis products were condensed together with a large excess of argon or nitrogen on a cold spectroscopic window. The obtained matrices were analyzed by means of FTIR and UV/Vis spectroscopy. In some cases, matrices were subjected to irradiation with selected wavelengths (see the Results and Discussion).

Semipreparative Flash Vacuum Pyrolysis of 3,3,5,5-Tetramethyl-1,2,4-trithiolane 1-Oxide (3b): Compound 3b (30 mg) was sublimed at a pressure of 10<sup>-2</sup> mbar from a storage vial at room temperature through an empty quarz tube (outer diameter 12 mm, length of the heated zone 60 mm) heated to 700 °C. The pyrolysis tube was connected to a vacuum line by a U-shaped trap that was cooled to liquid nitrogen temperature during the pyrolysis. After a pyrolysis time of 2 h, the trap was warmed, and the volatile reaction products were transferred to an IR gas cell and checked by IR spectroscopy. At -40 °C, a small amount of acetylene was released. The volatile products at room temperature consisted of mainly diisopropenyl disulfide (15). A part of this fraction was mixed with argon in a ratio of 1:500 and checked by matrix-isolation IR spectroscopy. Another part was checked by high-resolution mass spectrometry; the rest was mixed with CDCl3 and analyzed by NMR spectroscopy.

**Disopropenyl Sulfide (15):** IR (gas phase):  $\tilde{v} = 3114$  (m), 2983–2870 (m), 1606 (m), 1447 (m), 1380 (m), 894 (vs) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 5.04$  (s, 2 H), 4.96 (s, 2 H), 1.90 (s, 6 H) ppm. <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta = 143.4$  (C), 113.0 (CH<sub>2</sub>), 20.6 (CH<sub>3</sub>) ppm. HRMS: calcd. for C<sub>6</sub>H<sub>10</sub>S 114.0503; found 114.0503.

**Computational Methods:** All geometries were fully optimized and characterized as minima or transition structures by means of analytical harmonic vibrational frequency computations at the B3LYP/ 6-311+G(3df,3pd) level of theory.<sup>[12]</sup> In addition, for radicals **16** and **18**, full geometry optimization and harmonic frequency computations were performed at the CCSD(T)-FC/cc-pVTZ level. The Gaussian Program Suite was used for all computations.<sup>[13]</sup>

**Supporting Information** (see footnote on the first page of this article): Spectroscopic data, tables of observed and computed IR spectra, computational results.

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