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New organosulfur compounds derived by dithioketalization of hydroxyacetone and its tosylate derivative - mechanistic considerations

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ABSTRACT

This paper presents the results of studies on the products of hydroxyacetone and hydroxyacetone tosylate dithioketalization with ethane-1,2-dithiol and propane-1,3-dithiol. The process was carried out in an inert gas atmosphere, argon, or in the air atmosphere and with a variable excess of one of the substrates, here the dithiol reagent. The structure elucidation and the reaction mechanism for the formation of the isolated products have been discussed. Structure products were confirmed using ^{1}H NMR and ^{13}C NMR spectroscopy as well as mass spectrometry. The structure of one of the main products, 1,2-bis((2-methyl-1,4-dithian-2-yl)thio)ethane, was confirmed by single-crystal X-ray diffraction analysis. It was obtained with yield up to 62%. The studied dithioketalization process of selected ketones allows for the efficient synthesis of 2-methyl-1,3-dithiolan-2-yl)methanol, (2-methyl-1,3-dithian-2-yl)methanol and 3-((2-methyl-1,4-dithiepan-2-yl)thio)propane-1-thiol with yields of 63%, 66% and 50% respectively. Furthermore, we disclose an alternative synthesis of 5-methyl-2,3-dihydro-1,4-dithiine, a synthetically useful building block.

Keywords: dithioketalization, hydroxyacetone, hydroxyacetone tosylate, α-hydroxydithioketals, boron trifluoride diethyl etherate, ethane-1,2- and propane-1,3-dithiols

1. Introduction

For the majority of synthetic chemists dithioacetalization and dithioketalization are associated with the protection of the carbonyl group of aldehydes and ketones. The advantage of the resulting dithioacetals and dithioketals is their stability and ease of formation [1]. Other uses of dithioketals include homo/heterobifunctional reactive oxygen species (ROS) linkers [2]. The most comprehensive review regarding application of the ROS-responsive thioketal linker for the production of smart nanomedicines can be found in ref. [3]. In search of

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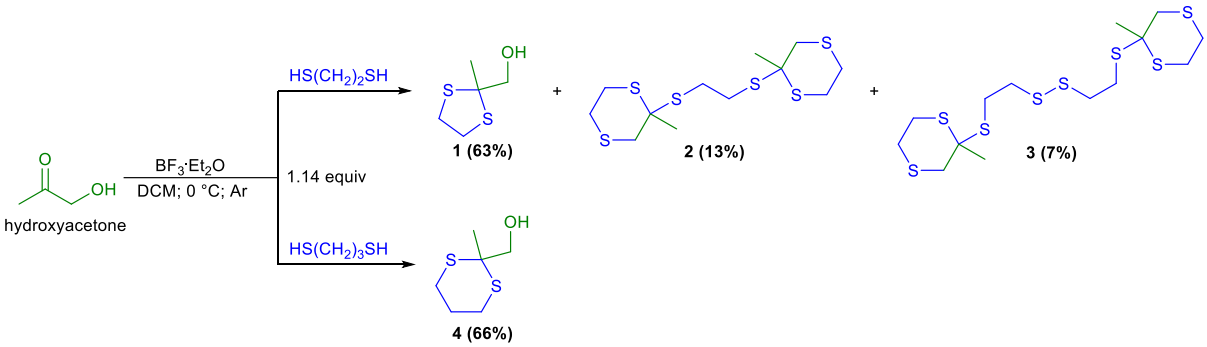
other applications of this group of organosulfur compounds, we found a convenient method to obtain homoallylic thioethers from dithioacetal aromatic derivatives [4]. By exploring this topic, we have developed an efficient method of obtaining cyclic dithioacetals having one functional group in the α position [5]. The resulting products can be useful building blocks in the synthesis of complex chemical structures.

2. Results and discussion

Encouraged by the results of previous research using dithioacetal derivatives [4,5], we took up the research challenge of exploring dithioketal derivatives. The scope of our work concerns the study of dithioketalization reaction products of a model ketone, **hydroxyacetone**, and its **tosylate** derivative. We chose **ethane-1,2-dithiol** and **propane-1,3-dithiol** as dithiol reagents. We propose mechanisms for the formation of isolated products. The mechanism can be radical or ionic (electrophilic, nucleophilic).

2.1 Dithioketalization of hydroxyacetone with ethane-1,2- or propane-1,3-dithiols

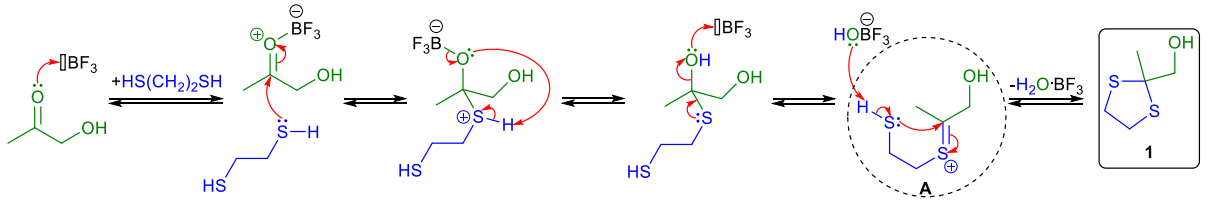
Our first experiments involved the reaction of **hydroxyacetone** with **ethane-1,2-dithiol** or **propane-1,3-dithiol** in the presence of boron trifluoride diethyl etherate as a catalyst. Scheme 1. shows the isolated products.



Scheme 1. Dithioketalization of **hydroxyacetone** with **ethane-1,2-dithiol** or **propane-1,3-dithiol** in the presence of a catalyst and in an argon atmosphere.

Our major goal was to obtain a cyclic dithioketals having a hydroxyl group in the α position. In both cases of the performed transformation, we obtained the expected products **1** and **4** with satisfactory yields of 63% and 66%, respectively. The use of 1.14 equiv of the dithiol reagent guarantees the formation of hydroxydithioketal. Spectral data and synthetic use of product **1** were described by Afonso *et al.* [6]. The usefulness of product **1** was also reported by Jang and Do [7] in polymer chemistry.
Product **4** has not yet been described in the literature. All physicochemical data of product **4** are provided in *SI*.

The mechanism of dithioketals **1** and **4** formation is analogous to the mechanism of acetal/ketal formation, with the difference that intermediate product is a **thiocarbenium cation A** instead of oxonium cation for acetal/ketal formation (Scheme 2.) [8].



Scheme 2. Mechanism of dithioketal formation of **1**.

The analog of **cation A** is formed in the reaction of **hydroxyacetone** with **propane-1,3-dithiol**, and the main product is hydroxydithioketal **4**. In this sequence of reactions we did not isolate any by-products despite using several chromatographic columns (see details in *SI*).

Surprisingly, in the reaction of **hydroxyacetone** with **ethane-1,2-dithiol**, we isolated two by-products **2** and **3**, the structures of which were confirmed by the analysis of their NMR spectra, and by HRMS analysis (see *SI*). Moreover, the structure of product **2** was confirmed by single-crystal X-ray diffraction analysis (Figure 1.) [9].

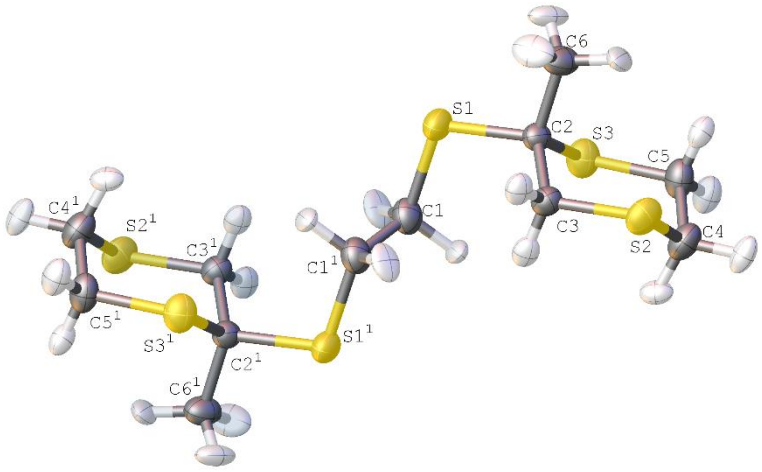
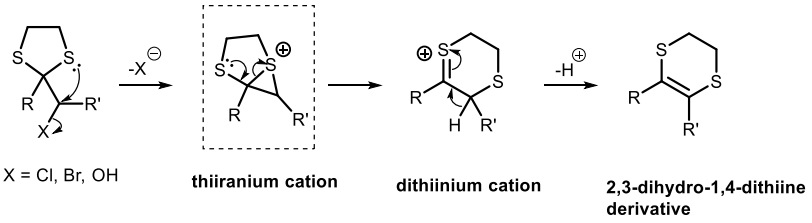


Figure 1. Molecular structure of compound **2**. Thermal ellipsoids are drawn at the 50% probability level. [1]= 1 − *x*, 1 − *y*, −z.

Products **2** and **3** have six-membered 1,4-dithiane rings in their structure. The precursor of this structural fragment could be the five-membered cyclic hydroxyacetone dithioketal.

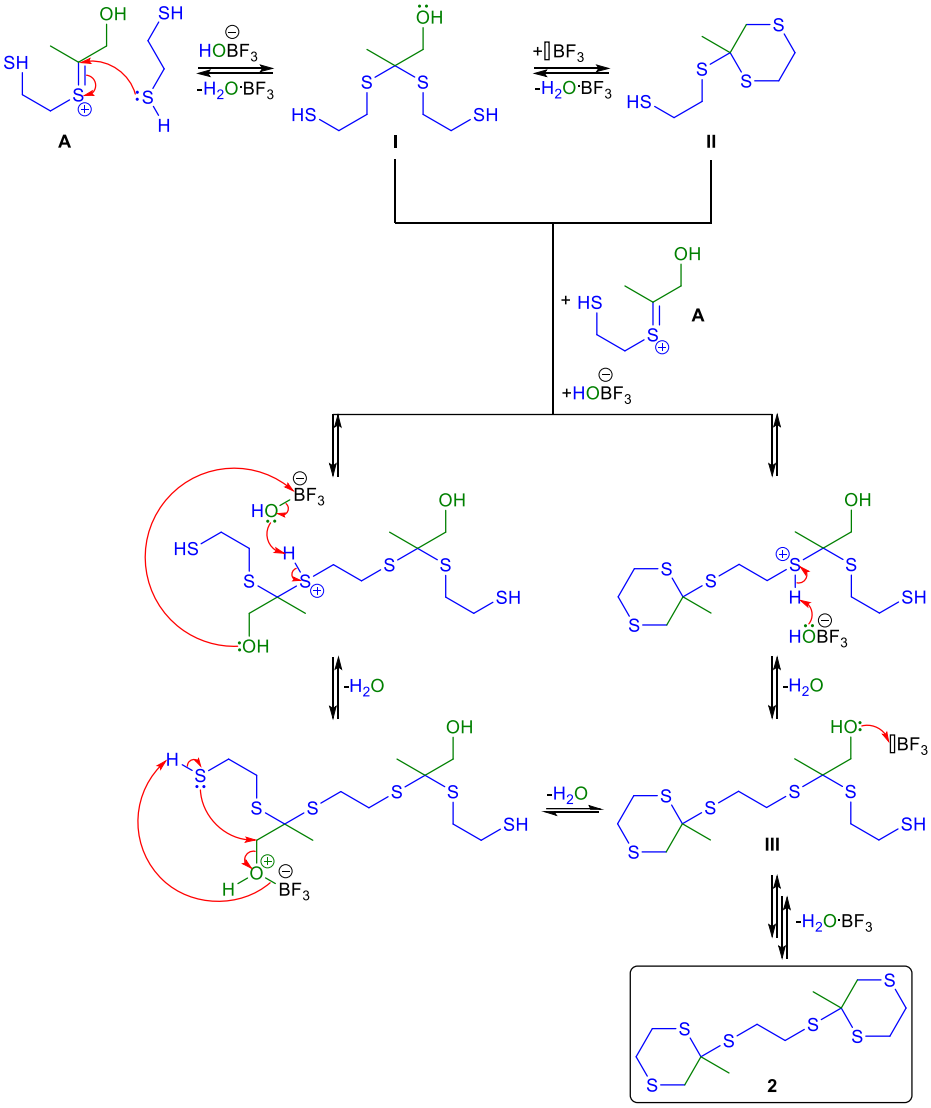
The mechanism of ring expansion accepted in the literature for derivatives of cyclic dithioacetals/dithioketals goes *via* the **thiiranium cation** [10] to finally give the 2,3-dihydro-1,4-dithiine derivative (Scheme 3.).



Scheme 3. The mechanism of ring expansion involving α leaving groups [10].

Plausible mechanism of formation product 2 (Scheme 4.).

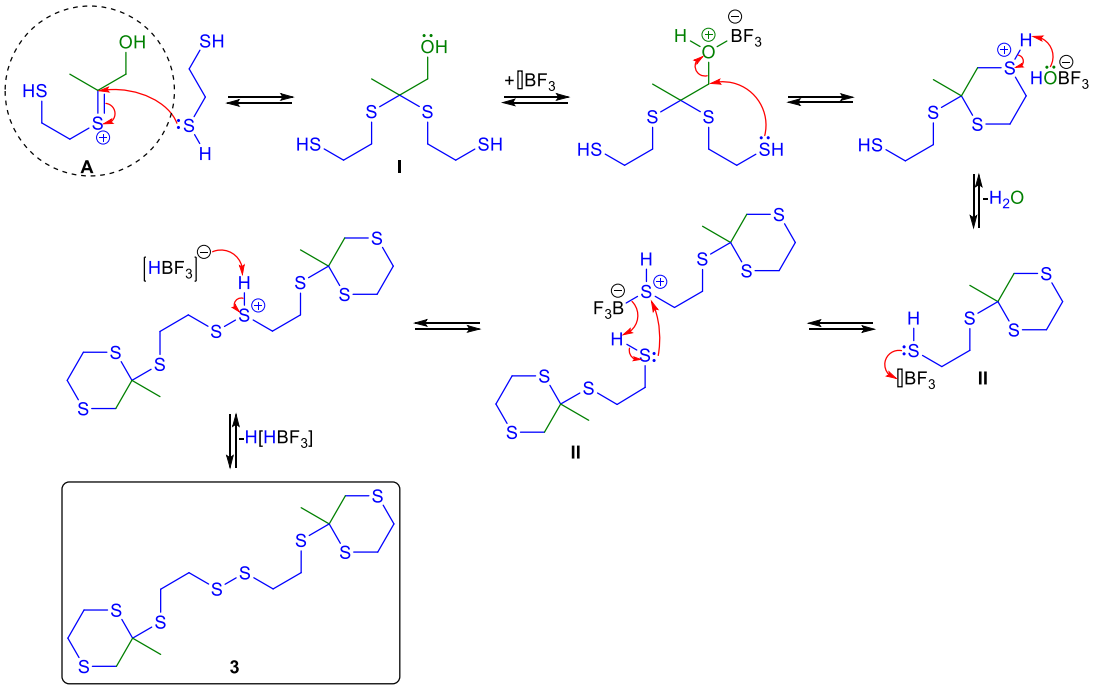
The **thiocarbenium cation A** is also a precursor for the formation of product **2**, although there are two ways of its formation. Scheme 4. shows such possibilities. Intermediates **I** and **II** react with **thiocarbenium cation A** to form intermediate **III**, which gives product **2** via water molecule elimination.



Scheme 4. Plausible mechanism of formation product **2**.

Plausible mechanism of formation product 3 (Scheme 5.).

We propose a mechanism for the formation of product **3** through the **thiocarbenium cation A** as a key intermediate (Scheme 4.). Condensation of the dithiol reagent with **thiocarbenium cation A**, supported by proton abstraction by anion $[HOBF_3]^{\ominus}$, leads to the formation of intermediate **I**. Activation of the terminal hydroxyl group in intermediate **I** by BF_3 promotes its elimination, supported by the attack of an electron pair from a free thiol group. As a result, a six-membered ring is formed – intermediate **II**. Then, the thiol group in **II** activated by BF_3 is susceptible to nucleophilic attack of the parent molecule, which ultimately leads to the formation of product **3** with a disulfide bridge. This is supported by the abstraction of the hydrogen atom by $[HBF_3]^{\ominus}$. The formation of such species was described by Van *et al.* [11].



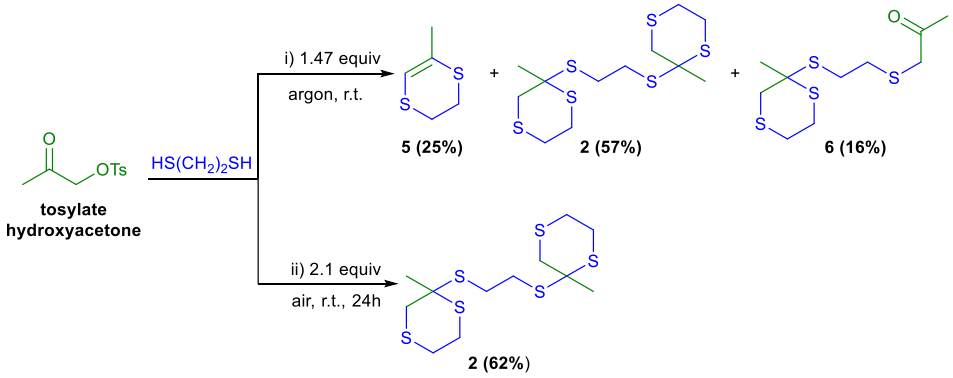
Scheme 5. Plausible mechanism of formation product **3**.

Summing up, the reaction of **hydroxyacetone** with **ethane-1,2-dithiol** or **propane-1,3-dithiol** in the presence of a catalyst, such as boron trifluoride diethyl etherate, and in an inert gas atmosphere yields hydroxydithioketals as the dominant products.

2.2 Dithioketalization of hydroxyacetone tosylate with ethane-1,2-dithiol at room temperature in argon or air atmosphere

The dithioketalization is in principle catalyzed by Lewis or Brönsted acids [1]. In the next experiment, we took into account the acidic nature of the thiol used, and, therefore, the possibility of an autocatalytic process of dithioketalization, as well as the possibility of a subsequent ring expansion reaction to form 2,3-dihydro-1,4-dithiins derivative. We took the idea of such a solution from the paper by Afonso *et al.*[6].

We choose **hydroxyacetone tosylate** as the substrate. The process of dithioketalization with **ethane-1,2-dithiol** was carried out at room temperature, both in an inert gas and an air atmosphere. The scheme below shows isolated products (Scheme 6.).



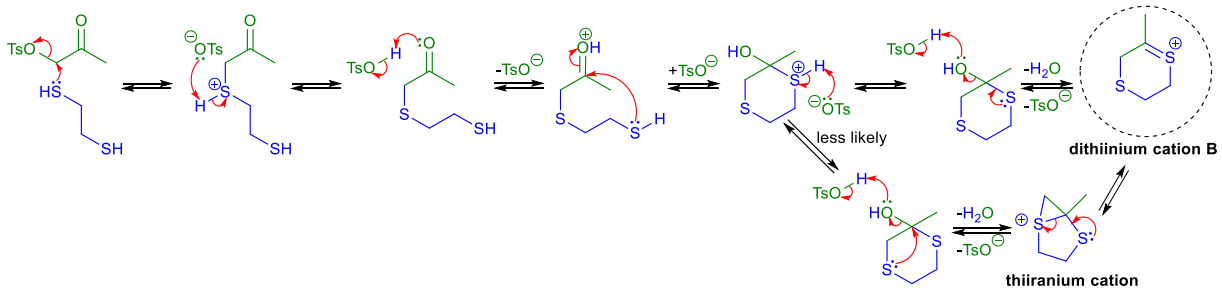
Scheme 6. Dithioketalization of **hydroxyacetone tosylate** with **ethane-1,2-dithiol** in an atmosphere of argon or air and excess of dithiol reagent.

In both variants of the performed transformation, the main isolated product was compound **2**, obtained with a yield of 57% and 62%, respectively. Only in variant i) did we isolate also compound **5** with a yield of 25% and by-product **6** with a yield of only 16%. Carrying out this transformation in an inert gas atmosphere allows to obtain

the synthetically useful heterocyclic product **5**. The synthetic utility of dihydrodithiin **5** has recently been reviewed by Winne *et al*. [12]. We did not optimize this transformation to obtain product **5**, which was first synthesized and described by Bottini and Böttner [13]. Also, Afonso *et al*. [6] propose getting ene **5** *via* ring expansion of (2-methyl-1,3-dithiolan-2-yl)methanol, **1**, with *p*-toluenesulfonyl chloride in pyridyne and catalytic amount of DMAP in argon atmosphere. The authors postulate a mechanism for the formation of product **5** *via* the **thiiranium ion** [10]. They „assume a mechanism in which the activated hydroxyl group is displaced by one of the sulfur atoms of the dithioacetal to form a thiiranium ion which then rearranges to a sulfur stabilised carbocation and this subsequently loses a proton to form the double bond". The authors declare yield of the process to be 72-96%.

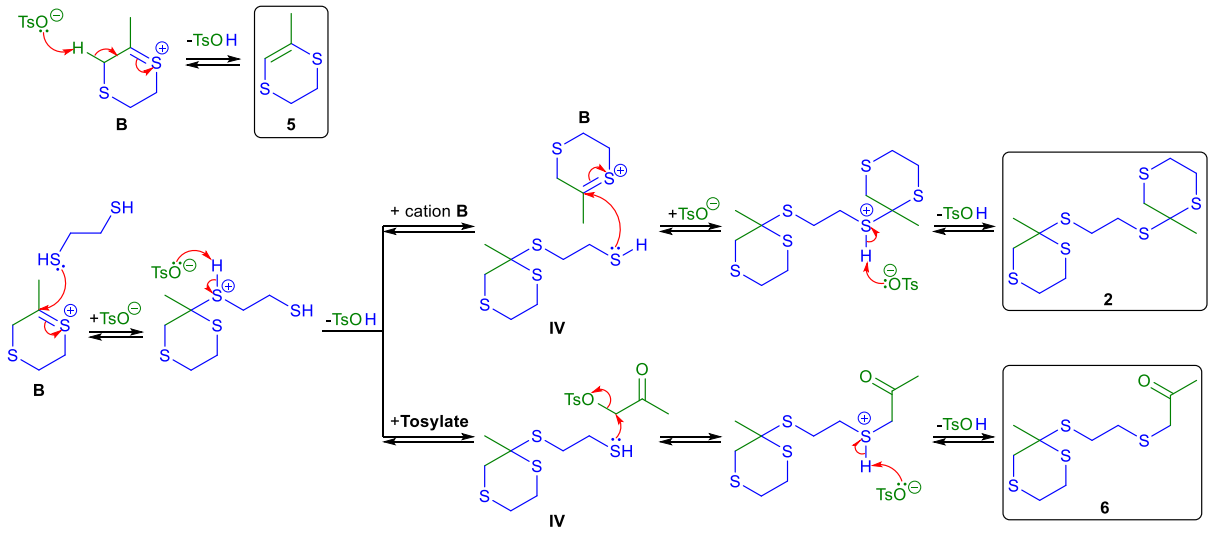
The isolation of the three products **2**, **5,** and **6** led us to propose a different mechanism for their formation, without the necessity to form the **thiiranium ion** as a precursor for 6-membered rings with two sulfur atoms in positions 1,4 (see Scheme 3.). Moreover, the proposed mechanism does not involve the **thiocarbenium cation A**. The key intermediate of the considered mechanism is the formation of a **dithiinium cation B** (Scheme 7.), which is a precursor to the formation of three isolated products (Scheme 6. in route i) and Scheme 8.). In an air atmosphere with 2.1 equiv of dithiol reagent, we isolated only product **2** with a moderate yield of 62% (Scheme 6. route ii)).

However, the precursor of a **dithiinium cation B** may be the **thiiranium cation**. The difference in the proposed formation of product **2** in this sequence of transformations results from the chemical nature of the used substrate, **hydroxyacetone tosylate**.



Scheme 7. Formation of **dithiinium cation B**.

Plausible mechanism of formation products 2, 5 and 6 (Scheme 8.).



Scheme 8. Plausible mechanism of formation products **2**, **5** and **6**.

The TsO group in the substrate acts as a good leaving group. In the presence of lone pair of electrons from a nucleophile, such as a dithiol reagent, the **tosylate hydoxyacetone** loses the condensation-formed *p*-toluenesulfonic acid (as Brönsted acid), which catalyzes the formation of the six-membered **dithiinium cation B**. In the reaction with the anion $TsO^{\ominus}$ **cation B** loses a proton to form the product **5**.

What is more, **cation B** is prone to nucleophilic attack by the electron pair of the dithiol reagent forming intermediate **IV**. This one is consumed by **cation B** or by the substrate, **hydroxyacetone tosylate**, which leads to the formation of products **2** and **6** respectively.

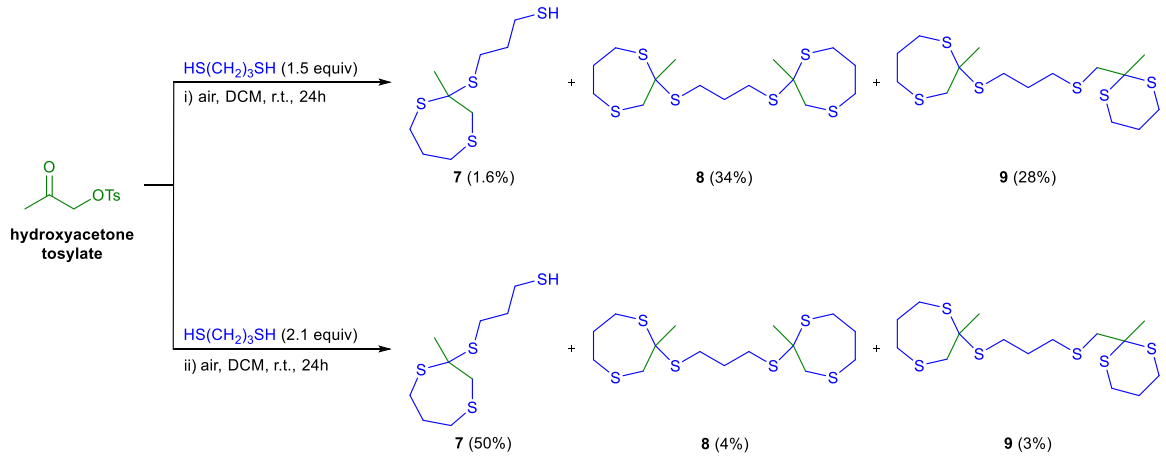
In conclusion, **hydroxyacetone tosylate** in the reaction with **ethane-1,2-dithiol** under inert atmosphere allows one to obtain the synthetically useful product **5** with moderate yield. The presence of air favors the formation of product **2**.

2.3. Dithioketalization of hydroxyacetone tosylate with propane-1,3-dithiol in an atmosphere of air

The dithioketalization reaction of **hydroxyacetone tosylate**, using **propane-1,3-dithiol**, gave us quite different results.

We planned the transformation of **hydroxyacetone tosylate** with **propane-1,3-dithiol** in an air atmosphere. Scheme 9 illustrates the structures of the isolated products. We carried out the reactions using 1.5 and 2.1 equiv dithiol. Three products - **7**, **8** and **9** - were isolated with different yields depending on the amount of dithiol reagent used. Using twice the excess of dithiol preferably affords product **7** with a yield of 60% (path ii)). On the other hand, reducing the amount of dithiol reagent favors the formation products **8** and **9** at the cost of the formation of product **7** (path i)), which is justified by the reaction stoichiometry.

Increasing the excess of dithiol reagent from 1.5 equiv to 2.1 equiv quantitatively reverses the yields of isolated products.

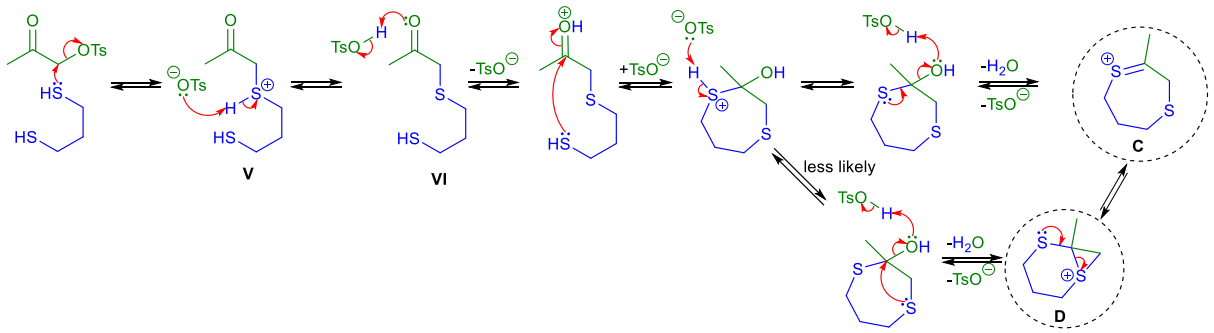


Scheme 9. Dithioketalization of **hydroxyacetone tosylate** with **propane-1,3-dithiol** in an atmosphere of air.

The proposed isolated products formation mechanism proceeds through the **dithiepinium cation C** (Scheme 10.), an analogue of the **dithiinium cation B** (see Scheme 7.). The condensed by-product of the tested process *p*-toluenesulfonic acid, PTSA, acts as a process catalyst.

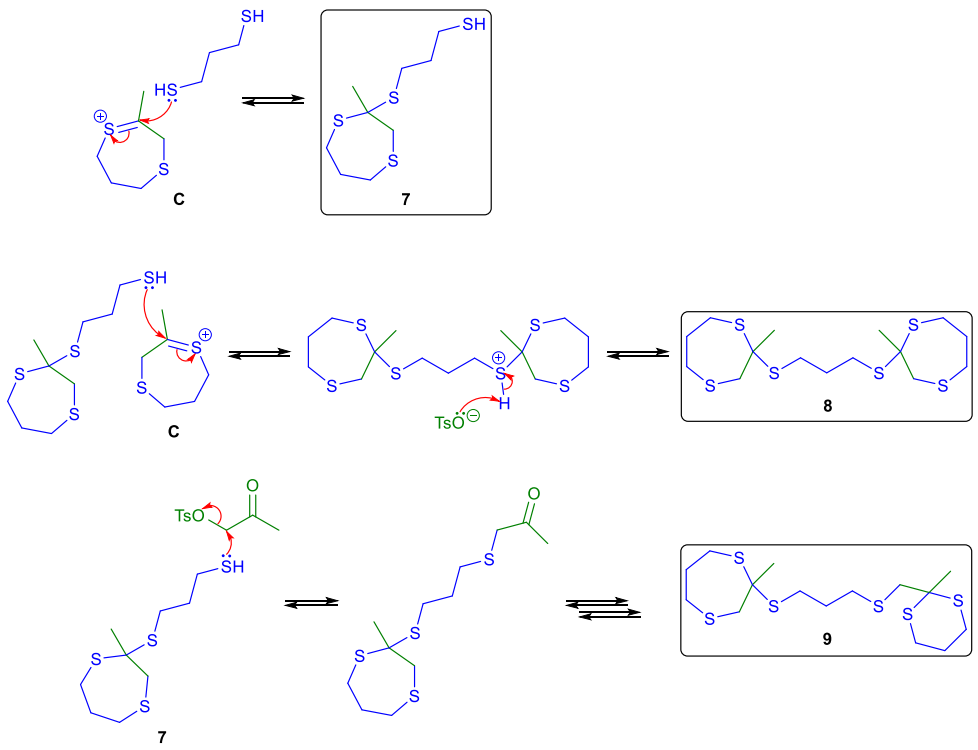
The **dithiepinium cation C** reacts with the dithiol reagent to form product **7**. This is a precursor of products **8** and **9**. If product **7** comes across **cation C** on its synthetic path, it leads to the formation of product **8**, and if it encounters substrate (tosylate), we will get product **9** after subsequent dithioketalization with dithiol.

It seems that if the molar ratio of substrates is one to two (tosylate : dithiol), this has an effect on the yield of the product **7**, which is not surprising, given the stoichiometry of if the reaction.



Scheme 10. Formation of **dithiepinium cation C** and **cation D**.

Plausible mechanism of formation products 7-9 (Scheme 11.).

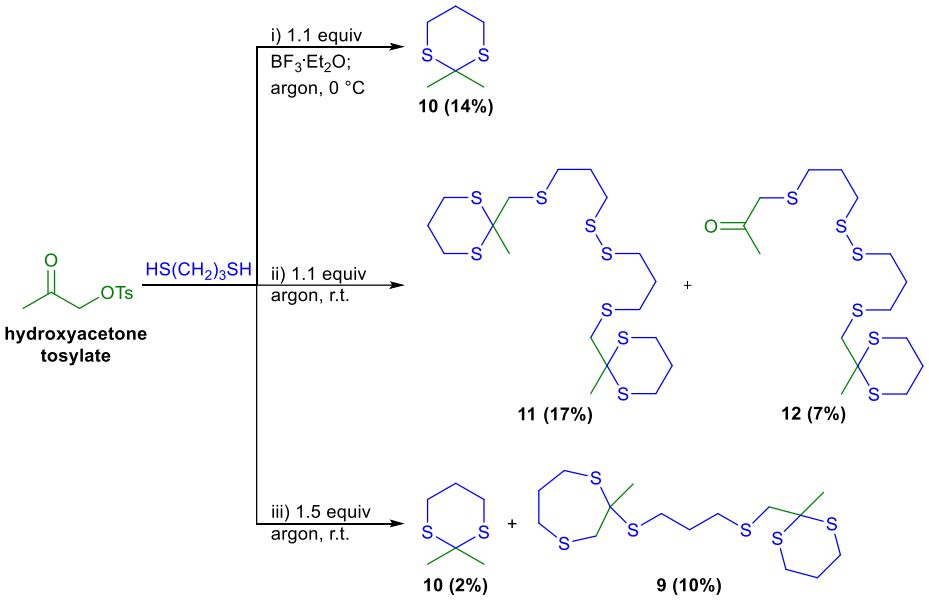


Scheme 11. Plausible mechanism of formation products **7-9**.

In conclusion, it is possible to obtain products **7-9** in the reaction of **hydroxyacetone tosylate** with **propane-1,3-dithiol** in an air atmosphere. The yield of the products maybe controlled by stoichiometric ratio of the substrates, used in the reaction.

2.4. Dithioketalization of hydroxyacetone tosylate with propane-1,3-dithiol in an atmosphere of argon

The dithioketalization reaction of **hydroxyacetone tosylate** using **propane-1,3-dithiol** also were carried out in an inert gas atmosphere, both in the presence of a catalyst, boron trifluoride etherate adduct, and without its presence, and in various stoichiometric ratios of the dithiol reagent (Scheme 12.).

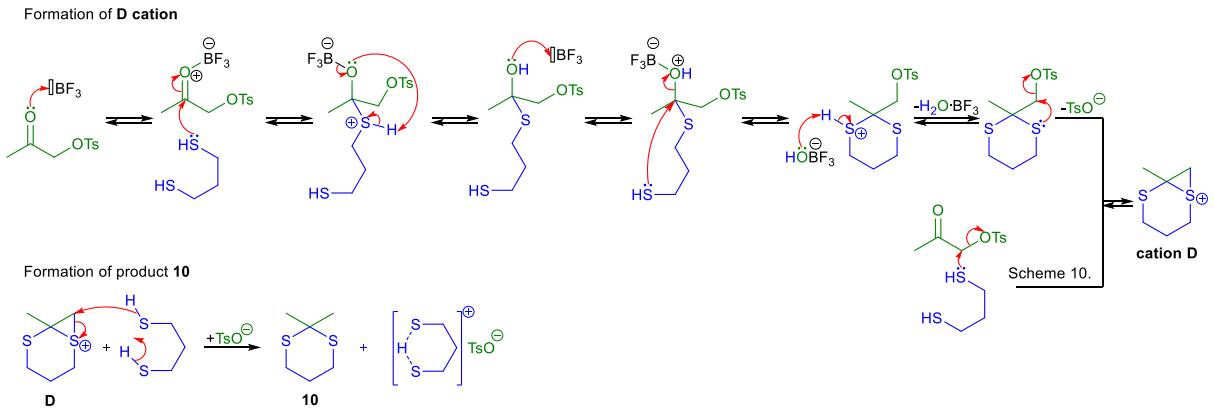


Scheme 12. Dithioketalization of **hydroxyacetone tosylate** with **propane-1,3-dithiol** in an atmosphere of argon.

Unexpectedly, in an inert gas atmosphere, both in the presence of a catalyst and without it, we isolated product **10** with a yield of 14% and 2%, respectively. In general, product **10** is the result of the dithioketalization process of the carbonyl group of **hydroxyacetone tosylate**, with the simultaneous reductive elimination of the OTs group.

We assume that in the proposed mechanism of product **10** formation **cation D** plays a key role (Scheme 13.). We propose the formation of the **cation D** under conditions of catalyst support and without it.

The use of catalyst, boron trifluoride etherate adduct, favors the formation of **cation D** which results in a product efficiency ratio of **10**.



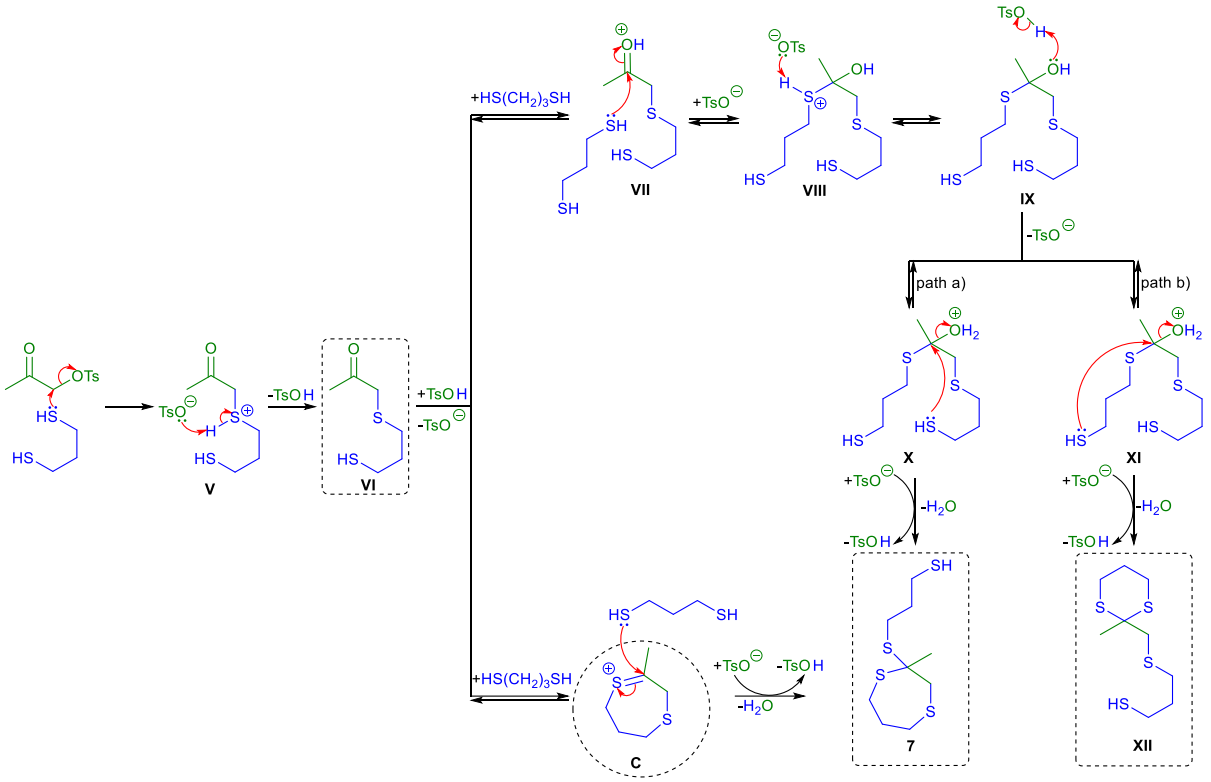
Scheme 13. Plausible mechanism of formation **cation D** and product **10**.

In proposed mechanism for obtaining products **11** and **12**, the formation of an intermediate products **VI**, **C, 7** and **XII** is crucial (Scheme 14.). The condensation-formed PTSA catalyzes subsequent reactions.

The formation of intermediate **VI** is obvious under the selected reaction conditions. It is precursor for remaining key intermediates **C**, **7** and **XII**.

The formation of intermediate **7**, with a seven-membered ring moiety, is the result of the reaction of intermediate **VI** with the **dithiepinium cation C**. However, it is possible to form intermediate **7** by another path *via* intermediate **IX** to **X** (Scheme 14., path a)).

On the other hand, intermediate **IX** can be a precursor for forming of **XII** (Scheme 14., path b)).



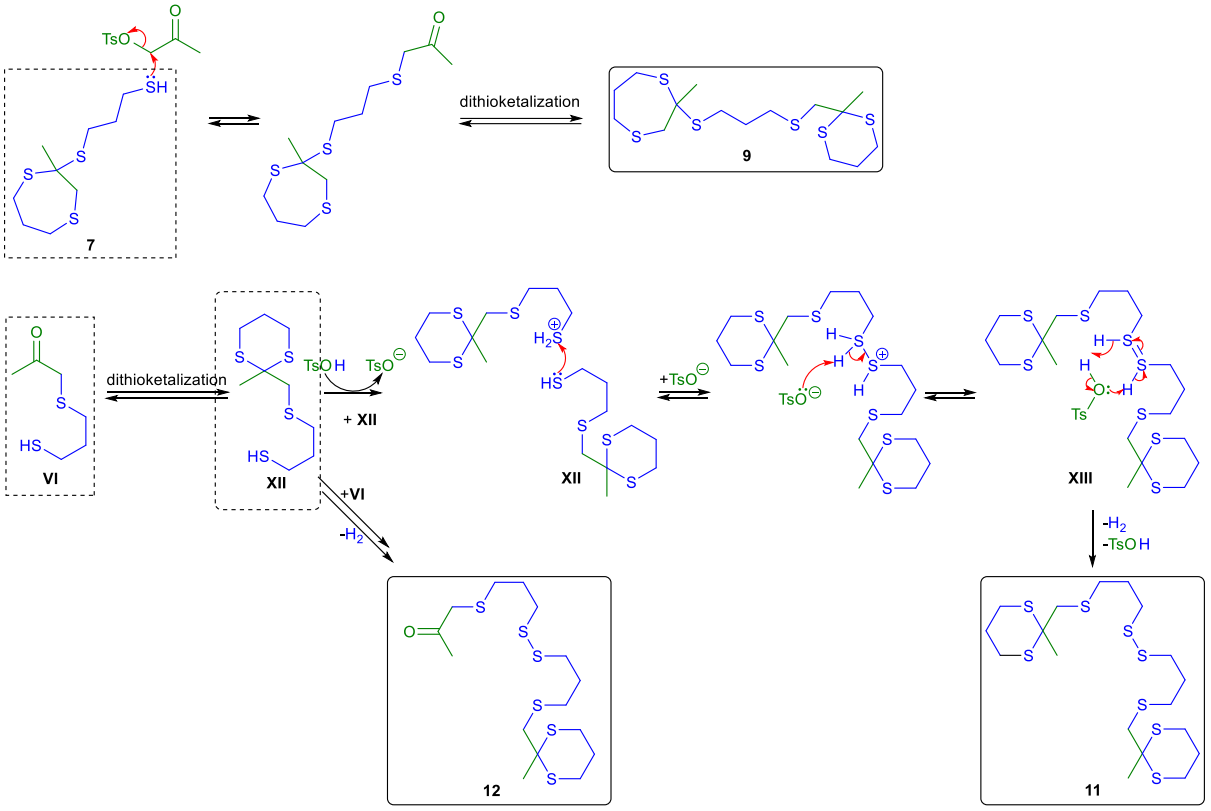
Scheme 14. Formation of intermediates **VI**, **C**, **7** and **XII**.

Plausible mechanism of formation products 9 and 11 and 12 (Scheme 15.).

If intermediate **7** encounters the **hydroxyacetone tosylate** and then the dithiol reagent under acidic conditions, as the result obtaining product **9** takes place.

We postulate the formation of a disulfide bridge in a sequence of steps: a) protonation of the free thiol group in **XII**; b) nucleophilic attack of lone pair electrons of the second **XII** molecule on the electrophilic center of protonated **XII** and the shift of the positive charge to the attacking sulfur atom; c) abstraction of a proton by the $TsO^{\ominus}$ anion with the formation of a π bond between sulfur atoms; d) spontaneous elimination of the hydrogen molecule afforded product **11**, accelerated by low stability of the structure **XIII**.

A similar sequence of steps takes place when **XII** "meets" **VI** what gives product **12**.



Scheme 15. Plausible mechanism of formation products **9** and **11** and **12**.

3. Experimental

General information on the substrates used (materials), analytical techniques used (methods) and the experimental procedures and characterization data for all obtained compounds are given in *SI*.

3.1. Representative experimental protocol with catalyst

Under an atmosphere of argon in heat gun dry a three-necked round-bottom flask (250 mL) equipped with a magnetic stirrer and a dropping funnel with a pressure equalizer the **hydroxyacetone** (29.2 mmol) in dry DCM (15 mL) was added. Reaction mixture was cooled to 0°C in ice bath and **ethane-1,2-dithiol** or **propane-1,3-dithiol** (1.14 equiv) in dry DCM (20 mL) was added dropwise (**Note 1.**). Afterward, **boron trifluoride etherate** (1.0 equiv) in dry DCM (10 mL) was added dropwise (**Note 2.**) and the resulting mixture was stirred for 30 min. The progress of the reaction was monitored by thin layer chromatography (TLC, n-hexane:ethyl acetate, 3:1). Next the cooling bath was removed and the reaction mixture was left for overnight. Then, a mixture of saturated aqueous solution of $NaHCO_3$ (15 mL) and water (30 mL) were added to the reaction mixture and the resulting mixture was stirred for 30 min. After separating the layers, the aqueous phase was extracted with DCM (35 mL). The combined organic layers were dried over anhydrous sodium sulfate. After filtering off the drying agent, volatiles were removed under reduced pressure. The crude reaction mixture was obtained in the form of an oil (5.7 g).

Crude mixture of products was isolated and purified by flash column chromatography on silica gel.

Note:

1. **Dithiol** reagent was added over 35 min.
2. **Boron trifluoride etherate** was added over 40 min.

Author Contribution: Project concept D.T.L.; synthesis W.F., E.E. and G.G.; X-ray analysis P.A.G.; writing-draft preparation D.T.L. and G.G.; writing – visualization of mechanism D.T.L.; writing – review, editing D.T.L., P.A.G., G.G.

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Supporting Information
Included as a separate file.

Conflict of Interest
The authors declare no conflict of interest.

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[9] Crystal data for compound **2**: $C_{12}H_{22}S_6$ (M =358.705 g/mol): triclinic, space group $\boldsymbol{P\bar{1}}$ (no. 2), a = 5.9899(1) Å, b = 7.7228(2) Å, c = 9.8079(3) Å, α = 93.666(2)°, β = 92.363(2)°, γ = 109.581(2)°, V = 425.640(19) Å^3, Z = 1, T = 297 K, μ(Mo Kα) = 0.786 mm^{-1}, ρ = 1.40 g/cm^3, 29994 reflections measured (6.72° ≤ 2Θ ≤ 65.44°), 3011 unique (R_{int} = 0.033, R_{sigma} = 0.019) which were used in all calculations. The final R_1 was 0.026 ($I \geq 2\sigma(I)$), and wR_2 was 0.046 (all data). CCDC 2364133 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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