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SYNTHESIS OF THIOETHERS BASED ON THIOL-EN AND THIOL-IN COMPOUNDATION REACTIONS

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Abstract: This article focuses on the synthesis of sulfur-containing organic compounds based on thiol-en and thiol-in addition reactions, their physicochemical properties, international scientific research, as well as their applications in industry, pharmaceuticals, and agriculture. In particular, the reactivity and importance of thiols, thioethers, sulfides, and sulfonic compounds in their applications are highlighted. At the same time, it serves as an important scientific-theoretical and practical basis for the further development of the synthesis of organic sulfur compounds and the development of environmentally friendly and effective technologies. The theoretical and practical results of the research lay the foundation for the further development of the chemistry of sulfur-containing organic compounds, the development and practical application of methods for the synthesis of new sulfur-containing compounds.

Key words; thiols, sulfur compounds, synthesis, thioethers, reactivity, biological activity

INTRODUCTION

Currently, organic sulfur compounds are becoming increasingly widespread in the chemical industry and biological systems. This is due to the fact that such compounds are found in the organisms of plants and animals in important biological processes, such as the structure of medicines, the structure of enzymes, and the composition of catalysts. They consist of organic molecules containing a sulfur atom and are divided into such types as thiols (R-SH), thioethers (R-S-R′), sulfides, sulfons, and sulfonamides. The intermolecular thiol-en reaction (hydrotylation reaction) is highly effective with free radical mediation, with various applications in biofunctionalization and materials science[1]. Organic compounds containing sulfur atoms are widely used in biology, pharmaceuticals, materials science, agriculture, and the oil industry. At the same time, the presence of organosulfur compounds in the antibiotics and pharmaceutical industry, their significance in medicine

LITERATURE REVIEW

The biological activity of thiols and thioethers has been repeatedly emphasized in the scientific literature, especially as a means of combating cancer cells. For example, E.Block in his book "Garlic and Other Alliums" (2009) showed the anticarcinogenic activity of sulfur-containing substances in garlic. He scientifically substantiated the anti-cellular oxidation activity of the sulfur atom due to its high biological adaptability.[2]

Huseynov, Gasanov, and Kurbanova (Baku State University, 2017-2022) developed methods for conducting the synthesis of thioethers in an environmentally friendly, water-based environment. They developed a methodology based on the principles of green chemistry and achieved effective results without chemical waste.[3]

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Prof. In the works of Klaus Müllen (Max Planck Institute), the use of aromatic sulfur compounds as semiconductor and optoelectronic materials is highlighted. In his opinion, "Thiol-en and sulfide structures are very promising in increasing electron conductivity."

Prof. Charles Drain (Hunter College) studied the possibilities of using organic sulfur compounds in artificial photosynthesis systems and substantiated the role of sulfur ligands as catalysts in the formation of complexes with metals.

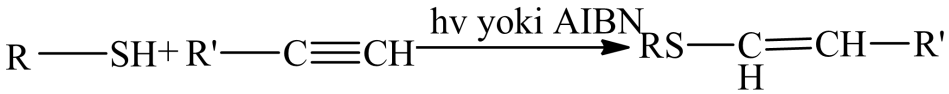
METHOD

In thiol-ene addition reactions, the addition of alkene and thiol occurs primarily through a radical mechanism, and this reaction is considered one of the important "click" reactions in chemistry.

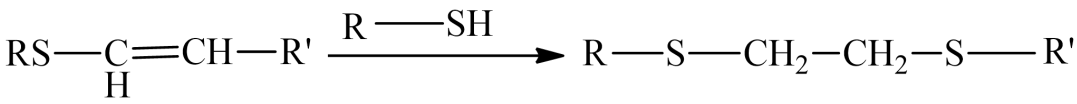
Radical mechanism: in this mechanism, the reaction is initiated by the initiator AIBN (2,2-azobitsisubutyronitrile) or UV radiation (λ = 365 nm).

Thiol-in addition reactions proceed similarly to thiol-ene reactions, but the reaction proceeds in two stages. In the first stage, thiol molecules combine with alkyne to form vinyl sulfide (R-S-CH=CH-R). In the second stage, vinyl sulfide reacts with a molecule of thiol to form bis-thioether (R-S-CH2-CH2-S-R).

Stage 1



Stage 2



Reagents used.

1-propantiol, 1-hexene, 1-hexine, UV rays (λ = 365 nm), nitrogen for creating an inert medium.

In a clean, dry flask with a volume of 25 ml, 1.66 g of 1-hexene is added, weighed on a 0.02 mol analytical balance. In the same flask, 0.02 mol 1.5 g of 1-propanethiol is measured. To create an inert environment, nitrogen is sprayed into the flask 3-4 times. After this, the flask is placed under UV-LED (365 nm).The magnetic stirrer is started, the reaction is carried out at room temperature for 30-60 minutes.To increase the intensity, the flask can be slightly heated.

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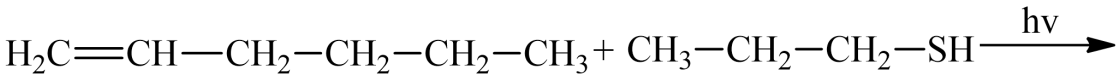
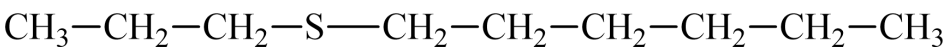
The reaction should be carried out in a fume hood, observing safety regulations.

RESULTS AND DISCUSSION

The research results show that the addition reactions of thiol-ene and thiol-ine are highly effective and productive.

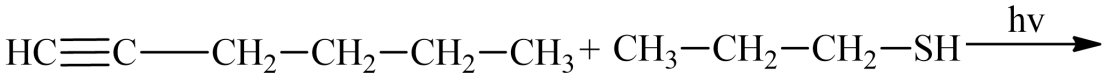
As a result of the reaction of 1-propanethiol and 1-hexene, a hexylpropyl sulfide with a yield of 92% was obtained.

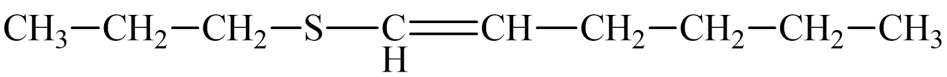




Образование гексилпропилсульфида при соединении 1-гексена и 1-пропантиола

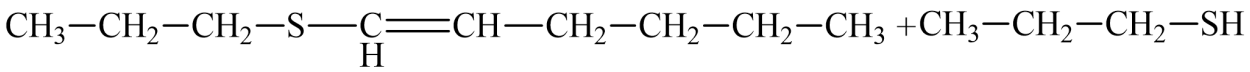
The thioline addition reaction also proceeds according to the method described above. According to the reaction results, 1-hexine and 1-propanethiol are attached to each other, first 1-isopropylsulfanyl-hex-1-ene

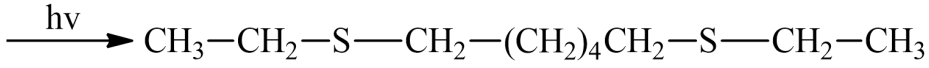




Formation of 1-isopropylsulfanyl-hex-1-ene upon addition of 1-hexine and 1-propanethiol

As a result of the reaction with the released 1 molecule of isopropylsulfanyl-hex-1-ene thiol, 1,2-bis (propylthio) hexane is formed.





The yield in this reaction is 85-88%. When the obtained samples are examined in the IR spectrum, it is evident that a C-S bond is formed. This indicates that the reaction proceeds completely.

Conducting addition reactions of thiol-ene and thiol-ine under the influence of UV radiation is energy-saving, and it can be seen that the yield of the reaction with the catalyst increased.

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To prevent the formation of disulfides in the addition reactions of thiol-ene and thiol-yne, the following measures must be taken.

• In the reaction medium, it is necessary to create an inert medium using gaseous nitrogen. With excess oxygen, the formation of disulfides can be observed.

• High temperatures can also stimulate the formation of disulfides.

• If excess thiol (R-SH) is present in the process, the resulting thioether can react with excess thiol to form disulfides.

PRACTICAL APPLICATION

Thioethers are useful synthetic intermediate products in many aspects of the organic and pharmaceutical industries. Sulfides are used as antioxidants and motor stabilizers, solvents for medicines, fuels, and lubricants. Many biologically active compounds contain thiophers. undefined Thioesters are strong ligands because the S atom has a high affinity for metallic centers. undefined Used as an antioxidant and anti-corrosion additive in lubricating oils.

CONCLUSION

Due to the high efficiency and environmental friendliness of the addition reactions of thiol-en and thiol-in, it is considered one of the important directions of modern organic synthesis. This direction is distinguished by its simplicity and proceeds under "soft conditions." The studied research conditions show that photoinitiated thiolene reactions allow obtaining the purest and most productive thioethers in an inert atmosphere. Thiol-innine reactions are a promising direction for the synthesis of multifunctional products due to the double addition of alkynes. The obtained thiophores have high heat resistance and stability and are widely used in pharmaceuticals, organic synthesis, agriculture, and other fields.

In general, sulfur compounds obtained based on the addition reactions of thiol-en and thiol-in are practically and theoretically significant substances with high potential for application in various fields. In this direction, further in-depth study of the reaction mechanism and the development of new initiator systems remains an important task for future scientific research.

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