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Synthesis of Seroorganic Compounds Based on the Reactions Tiol-En and Tiol-In

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Annotation

The mechanism of radical reaction and addition processes were analyzed, and their significance in polymer, pharmaceutical, agricultural, and other fields was presented. The research investigated the conditions and mechanism for obtaining sulfur-containing organic compounds, such as thioethers and sulfides, formed as a result of reactions of alkenes and alkynes with substances with thiol groups. At the same time, this serves as an important scientific-theoretical and practical basis for the further development of the synthesis of sulfur-containing organic compounds and the development of environmentally friendly and effective technologies.

Keywords: thiol-ene reaction, thiol-in reaction, organosulfur compounds, thioether, radical mechanism, addition reaction.

ENTRY

Sulfur-containing organic compounds play an invaluable role in modern organic chemistry, biology, materials science, and other fields. Due to the presence of such bonds as C-H, C-C, C-C in the composition of these compounds, sulfurous compounds have high thermal stability, reactive, catalytic, and biological activity properties. undefined The term "click chemistry," first introduced by K. B. Sharples, refers to a complex of simple, highly productive, non-producing by-products, and environmentally friendly reactions. Thiol-ene addition reactions are radical substitution reactions between thiol (R SH) and olefins (R'-CH=CH2). As a result of such reactions, thioethers are formed. In thiol-yne reactions, disulfide or thioalkenes are formed by adding thiol to alkynes instead of alkenes. These two reactions occur under normal conditions, in a short time, in the presence of a photoinitiator, or under the influence of heat.

The addition reactions of thiol-ene and thiolin are important not only in modern organic chemistry but also in the production of functional polymers, drug transfer systems, and surfactants. Especially, photochemical reactions of thiol-ene addition using ultrasonic radiation have opened up new possibilities in the synthesis of composite materials. Nevertheless, the mechanism, selectivity, and applications of these reactions have not yet been fully studied.

The purpose of this study is to study the mechanism of the addition reactions of thiol-ene, thiol-ene, and to synthesize new sulfur-containing organic compounds based on them, as well as to determine the physicochemical properties of these compounds and the possibilities of their practical application.

METHOD

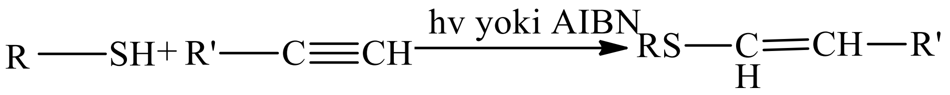
In thiol-ene addition reactions, the addition of alkene and thiol occurs primarily through a radical mechanism, and this reaction is considered one of the important "click" reactions in chemistry.

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

$$R{-}SH + R'{-}\overset{H}{C}{=}CH_2 \xrightarrow{hv,AIBN} R{-}S{-}CH_2{-}CH_2{-}R'$$

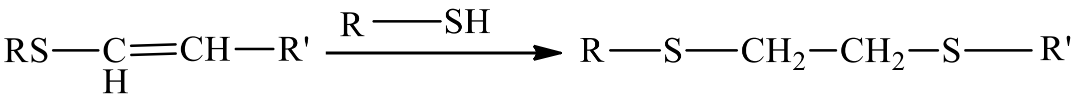
Thiol-in addition reactions proceed similarly to thiol-ene reactions, but the reaction proceeds in two stages. In the first stage, thiol molecules combine with alkyne to form vinyl sulfide (R-S-CH=CH-R). In the second stage, vinyl sulfide reacts with a molecule of thiol to form bis-thioether (R-S-CH2-CH2-S-R).

Stage 1



$$R{-}SH + R'{-}C{\equiv}CH \xrightarrow{hv\ yoki\ AIBN} RS{-}\underset{H}{C}{=}CH{-}R'$$

Stage 2



$$RS{-}\underset{H}{C}{=}CH{-}R' \xrightarrow{R{-}SH} R{-}S{-}CH_2{-}CH_2{-}S{-}R'$$

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.

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.

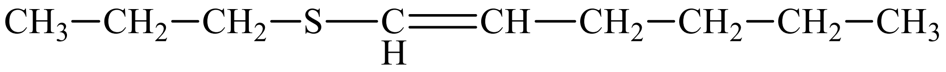
$$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_2{-}CH_3 + CH_3{-}CH_2{-}CH_2{-}SH \xrightarrow{hv}$$

$$CH_3{-}CH_2{-}CH_2{-}S{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

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

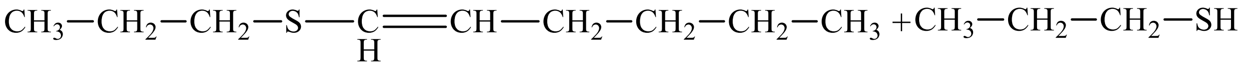
$$HC\equiv C-CH_2-CH_2-CH_2-CH_3 + CH_3-CH_2-CH_2-SH \xrightarrow{hv}$$



$$CH_3-CH_2-CH_2-S-\underset{H}{C}=CH-CH_2-CH_2-CH_2-CH_3$$

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.



$$CH_3-CH_2-CH_2-S-\underset{H}{C}=CH-CH_2-CH_2-CH_2-CH_3 + CH_3-CH_2-CH_2-SH$$

$$\xrightarrow{hv} CH_3-CH_2-S-CH_2-(CH_2)_4CH_2-S-CH_2-CH_3$$

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.

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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