



Study Of The Effect Of Antiseptics Based On Organic Sulfur Compounds In Improving The Efficiency Of Wooden Materials

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Citation: A.I.Kholboeva et al. (2024) Study Of The Effect Of Antiseptics Based On Organic Sulfur Compounds In Improving The Efficiency Of Wooden Materials. *Educational Administration: Theory and Practice*, 30(5), 7719-7736

Doi: 10.53555/kuey.v30i5.4229

ARTICLE INFO ABSTRACT

Nowadays, Wooden construction materials are unique natural ones, which has valuable complex properties necessary for the buildings and structures to be constructed, and the need to protect unique objects containing these materials from the effects of harmful insects has become critical in the world. Buildings and structures can be protected by treating these materials with special antiseptics in order to increase the biological effectiveness of wooden building materials against fire-causing insects. Therefore, it is important to obtain synthetic oligomeric antiseptics to improve the physico-chemical and mechanical properties of materials used in the biological efficiency of wooden building materials and to improve the process of structure formation. Scientific and research activities aimed at the development of biologically effective materials by obtaining oligomeric antiseptics containing sulfur and deep soaking them in wooden construction materials are currently being carried out all around the world. In this regard, special attention is paid to obtaining sulfur-containing polysulfides, disulfides and other sulfur-containing oligomeric adducts, determining their fire resistance and bioefficiency properties of wooden materials, researching the physico-chemical properties of antiseptics, improving their production technology and simplifying the method of application.

Key words. antiseptic, oligomer, sulfur, sulfides, dehydrogenation, mannix reactions, microbe, termite, wooden building materials.

Introduction

Sulfur producers are leading gas processing enterprises, accounting for 90% of their production globally. Modern oil and gas processing plants are becoming large producers of sulfur per year, but the process of extracting sulfur in the process of oil and gas production is technically complex, and special technical requirements are usually imposed by the fact that sulfur compounds accelerate metal corrosion, and that a mixture of various gases released into the environment increases environmental damage [1].

Currently, the main consumers of sulfur are the chemical and tire industries. In this regard, sulfur, which is used on a large scale in the extraction of organic polysulfides, is mainly used as hermetics. In addition, there is an increasing trend for applications in organic synthesis, production of polymer composite materials, agriculture, paper industry, antiseptics protecting wooden building materials, medicine and other industries. It is worth noting that the main sectors of sulphur consumption are the production of agricultural products and the chemical industry [2].

While 70% of the world's sulfur production belongs to the United States, Canada, Poland, Mexico, Iraq, France, and Russia, large global consumers of sulfur raw materials are China, South Africa, India, Brazil, Australia, and North Africa [3]. As a result of numerous scientific research works in order to reduce large

amounts of excreted sulfur raw materials in the process of oil and gas processing, today there are opportunities for the widespread use of building materials as herbicides and bactericides to protect plants in the agricultural sector (polysulfide hermitages, wood construction materials from various insects and bacteria). The fact that many sulfur-based composite materials are water-stable and not impactful to the external environment makes these materials work efficient for the long-term.

The mechanisms of interaction of sulfur-based organic compounds to date have not been sufficiently studied. The reaction that occurs with sulfur makes it difficult to study the structure of sulfur, which has the ability to generate a reaction in several different ways. As we can see as an example, several different reaction processes (coupling, hydrogenation, condensation, polymerization) can be formed by the release of hydrogen sulfide and polysulfones. In addition, the formation of intermediate products in reaction processes, which go with many sulfur, affects the continuation of the reaction. Despite more than a century of scientific research on the use of sulfur to improve the properties of organic binders and mixtures based on them, the weight of controlling the mechanism of interaction of sulfur-bound reactions indicates that there is still a lot of research to be done in this direction [4].

The processes of formation of carbon disulfide bonds by the attachment of organic tar to sulfur compounds consist in the interaction of unsaturated hydrocarbon-based alkenes with sulfur, which produce a very low amount of oil-gas components. Organic tar structures are compounds with a functional property that can interact with sulfur, as they consist mainly of aromatic and heterocyclic rings connected by short aliphatic bonds [5].

The processes of interaction of sulfur with organic binders can proceed through Ionic and radical mechanisms by the decomposition of sulfur at high temperatures. In the first case, when the ring is opened, the electron pairs can remain in the sulfur atom, resulting in a lack of electrons at the other end of the resulting chain. In the latter case, each sulfur atom can attach one electron [6]. As a result of sulfur-based reactions, a decrease in the amount of organic tar is observed and leads to an increase in the dispersion phase of high molecular compounds, which makes it important to increase the role of coagulation walls in the formation of properties of oil-sulfur binders. Hydrogen sulfide is obtained by the interaction of sulfur with oil, followed by the formation of various sulfur-containing organic compounds (first mercaptans, later with their decomposition and conversion to sulfides) that form [7].

In addition to allowing the theoretical research carried out to assess the sufficient complexity of this mechanism, the interaction of sulfur with organic binders and the areas of application of the compounds obtained are an important area of research. Based on these studies, the possibilities of applying polysulfide and sulfur composites obtained as a result of the reaction of interaction of sulfur-containing organic compounds and sulfur-containing organic compounds obtained directly in the process of processing petroleum products have been analyzed [8].

Reactions of elementary sulfur with aliphatic hydrocarbons. Elementary sulfur has the property of reacting with organic compounds to form various elementorganic compounds [9]. Reactions that go with organic substances in the presence of sulfur have been cited in several literatures, which can produce organic compounds that hold sulfur by forming an active reaction process simultaneously in several directions [10]. Synthesis of SH-functional derivatives of hydrocarbons [11] is carried out on the basis of favorable and elementary sulfur. At the same time, the possibility of obtaining valuable products that contain a wide potential sulfur is an important direction in modern organic chemistry (Figure 1) [12].

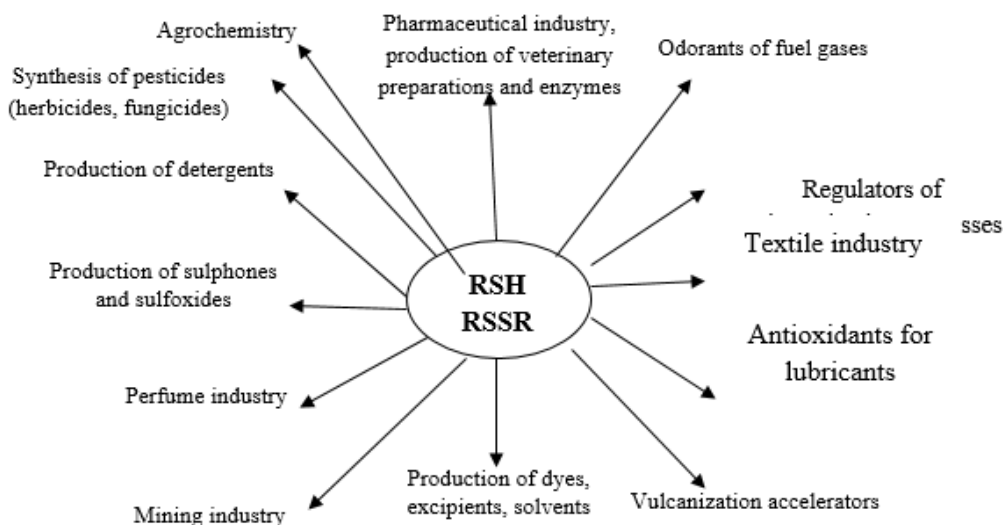
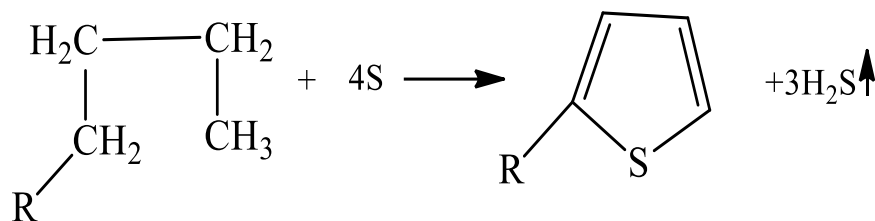
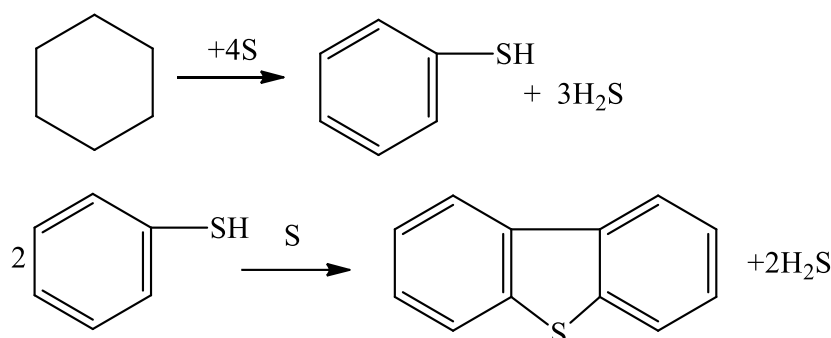


Figure 1. Application of mercaptan (RSH) and disulphides (RSSR).

Sulfur exchange, coupling, dehydrogenation and condensation reactions. Sulfur compounds react with alkanes C_1-C_4 using high temperature, pressure and catalysts based on Al_2O_3 and C (coal) to form thiols, sulfides, disulfides and CS_2 . The reaction process is accelerated by HCl or HBr. The formation of sulfur-containing compounds of C_5H_{12} is 85-90% [13]. Reaction processes proceed with the exchange of hydrogen atoms with small molecule alkanes at a temperature of about $570^\circ C$ to form hydrogen sulfide and thiophene (Scheme 1) [14]. At temperatures $240-280^\circ C$, sulfur is coupled by reacting with cyclohexane to form thiophenol and dibenzothiophene (Scheme 2) [15].

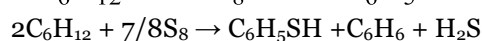
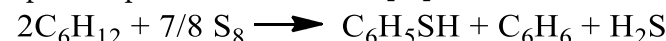


Scheme 1

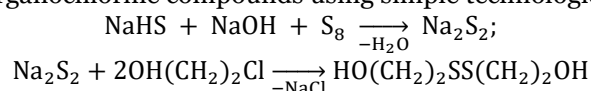


Scheme 2

Dehydrogenation of cyclohexane to benzene (41-50%) was carried out in low yield by A.A.Dudinov and others. As a result of the interaction of cyclohexane and sulphur at a temperature of $350-360^\circ C$, compounds up to thiophenol were obtained [16].

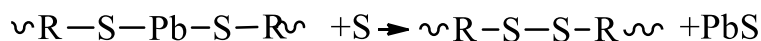


Sulfur-containing high molecular weight compounds. Khalikova G.R. and others synthesized polysulfide oligomers from organochlorine compounds using simple technologies [17].

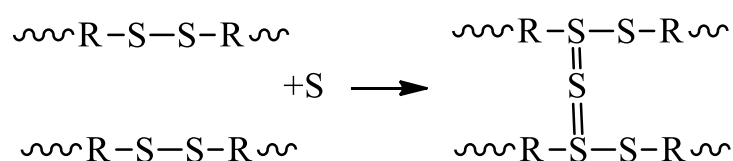


As a result of literature analysis [18], there are some shortcomings in the industrial method of synthesizing polysulfide oligomers [19]. Selectivity of polycondensation of aqueous solutions of sodium tetrasulfide (Na_2S_n) with organic compounds. large amounts of wastewater are produced.

Considering these problems, as a result of the analysis of alternative methods, the authors changed the molecular mass and composition of functional groups as a result of exchanging chlorine atoms for SH-groups, creating modification processes at the synthesis stage and other changes. The role of sulfur in polysulfide oligomers is to harden it under the influence of $\sim R-SH$ groups, and it is oxidized by forming sulfur bonds with vulcanizing agents (metal oxides).

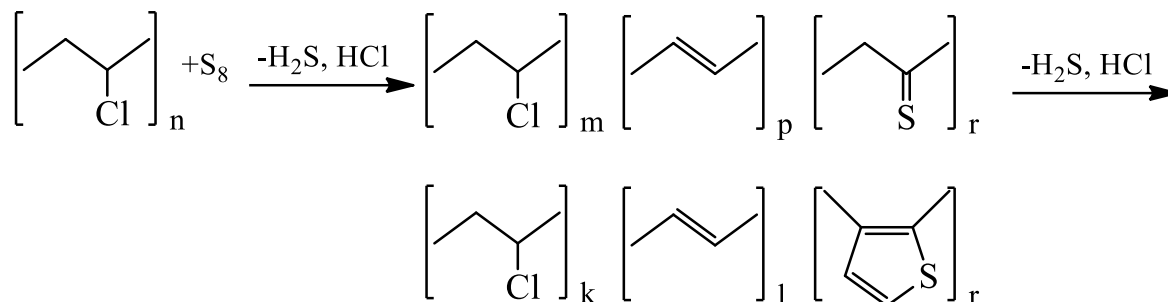


a

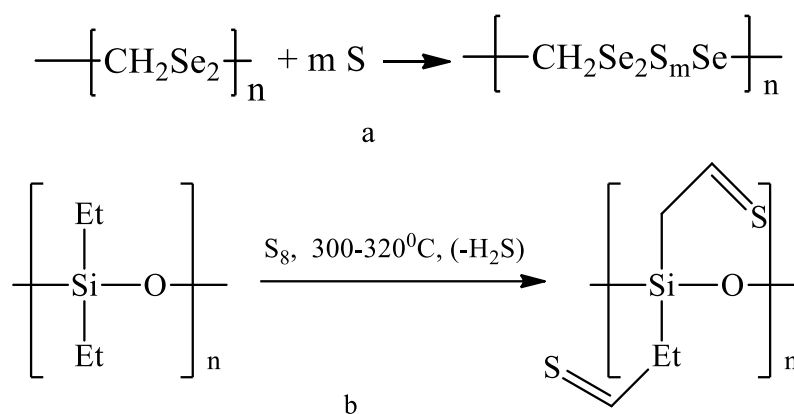


b

Depending on the conditions of the modification of polyvinyl chloride with sulfur, oligomers with a sulfur content of 2 to 57% of the total mass can be obtained at a temperature of 210-230°C (scheme) [20]. Synthesized oligomers are heat resistant (30-40°C) compared to PVC; their electrical conductivity is in the order of 10⁻⁹ cm/cm. [21].



Reactions to obtain Se-protected oligomeric polysulfides from methylenediselenide and diethylsiloxane at different temperatures. (145-148°C) and (300-320°C) - reaction scheme [22]:



These sulfur-containing polymers obtained are thermally and chemically resistant oligomers and polymers that are stable to oxidation-reduction processes as well as chemical reagents [22].

Sulfoxides and sulfones based on sulfur and oxygen. Sulfoxides are colorless liquid or solid substances that liquefy at low temperature [23]. For instance, dimethylsulfoxide is widely used as a solvent in various production processes with low toxicity. These solvents are mainly used in the development of polyacrylonitrile fibers, pesticides and aromatic hydrocarbons.

These types of sulfoxides are used in the activation of enzymes and in the widespread distribution of metals and in the decomposition of radioactive substances [24]. Figure 1 shows the formulas of some sulfoxides that contain sulfonyl groups that are characteristic of biologically active compounds. In addition, several sulfoxide-containing compounds are widely used as veterinary drugs and lubricants, in the production of pharmaceuticals, agrochemicals, and polymer materials. [25].

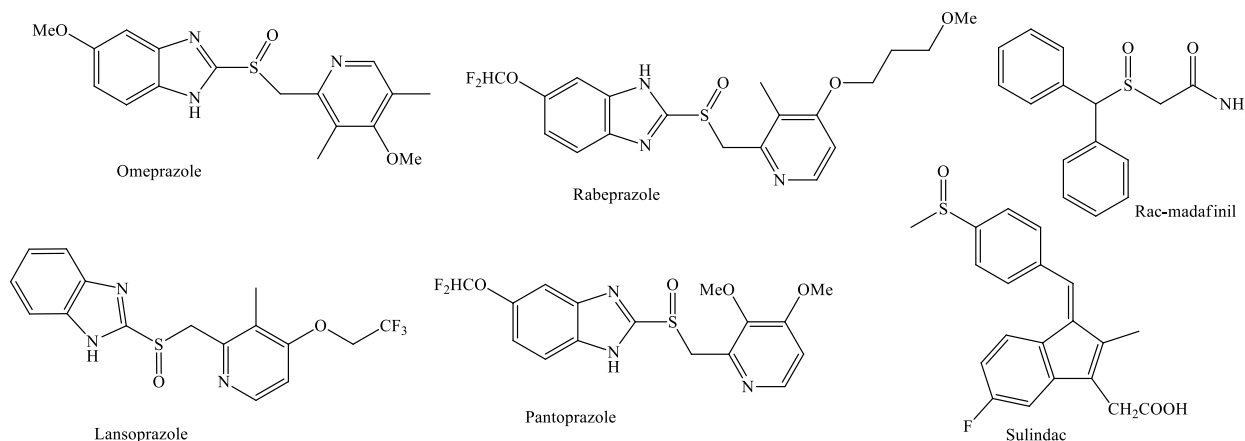


Figure 2. Structure of sulfur-containing compounds.

Arylsulfones also have pharmacological properties, protective properties against ferments, and inhibiting properties of other types of bacteria [26]. Compounds containing the "sulfone" group obtained on the basis of organic synthesis shown in Figure 2 are widely used in medicine. [27].

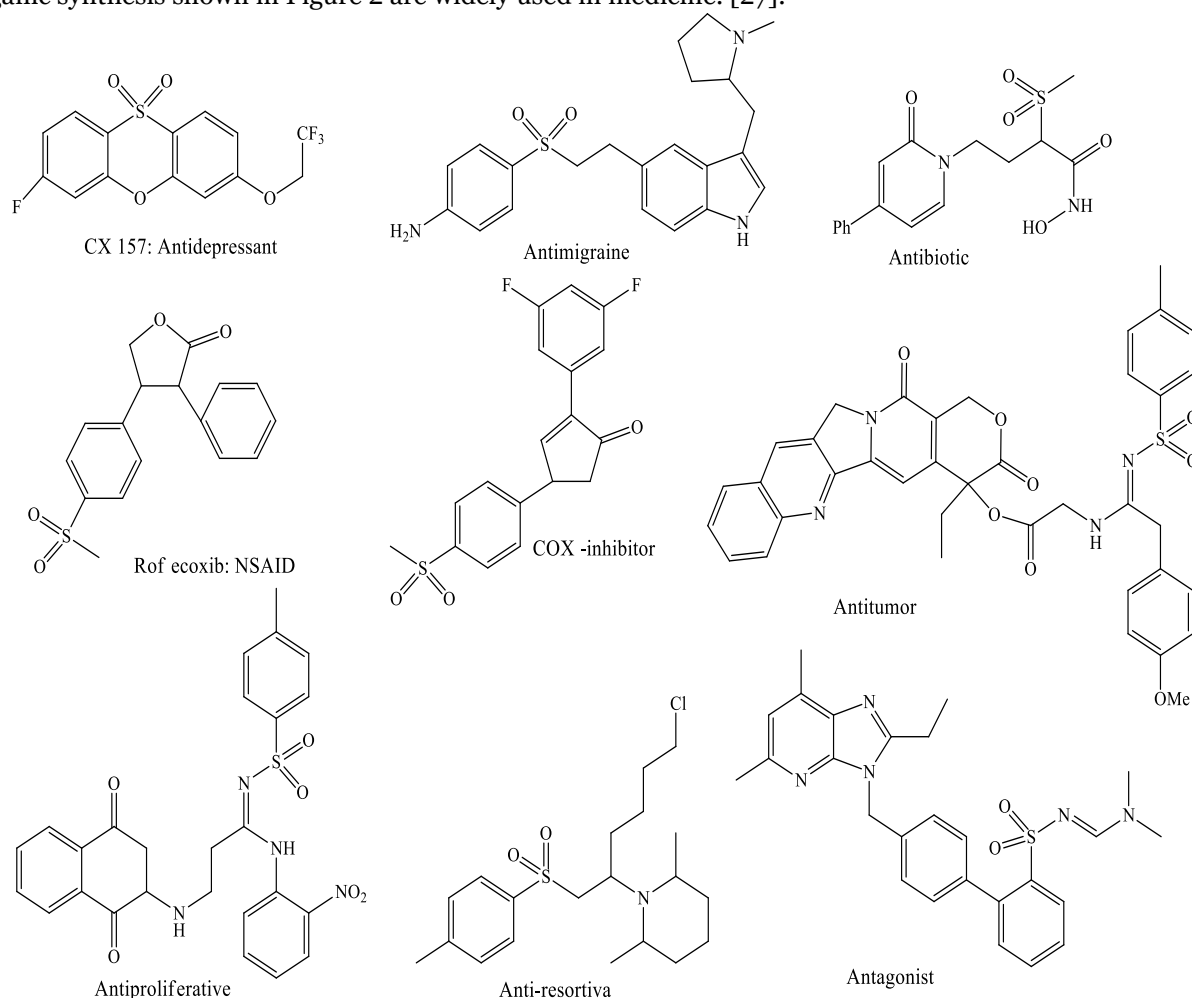


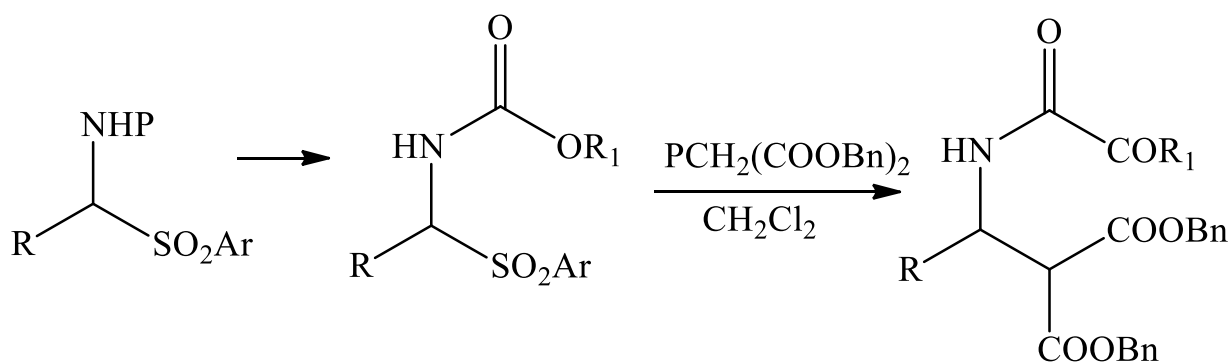
Figure 3. Structure of sulfur-containing compounds.

Mannix reactions involving chiral catalysts. Optically active forms of organic sulfur compounds obtained on the basis of these reactions are currently produced as drugs, aromatizers, preparations for use in agriculture and pharmaceuticals [28]. Physiologically active compounds obtained on the basis of the Mannix reaction have been widely used since 2000. Currently, the total cost of the production of chiral drugs exceeds 100 billion dollars [29].

Among the general reactions of classical and organic chemistry, Mannix reactions (MR) are the reactions that have different properties. These reactions are distinguished by their useful properties as well as by the simplicity of the process of obtaining substances.

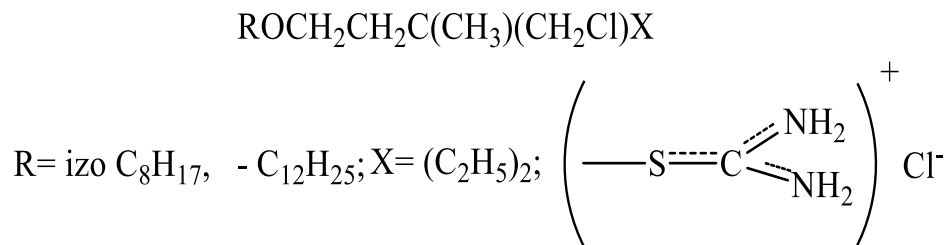
According to the researchers, as a result of hydroxyacetone and ultrasound examination, chiral pyrroline in the presence of propanol has high enantomers with a total yield of up to 90% [30].

Studies have been conducted on the use of ethers as universal substrates for multifunctional MRs [31]. The study of chiral alkylamines containing carbonate, which have optical activeness during MR operation, continues [32].



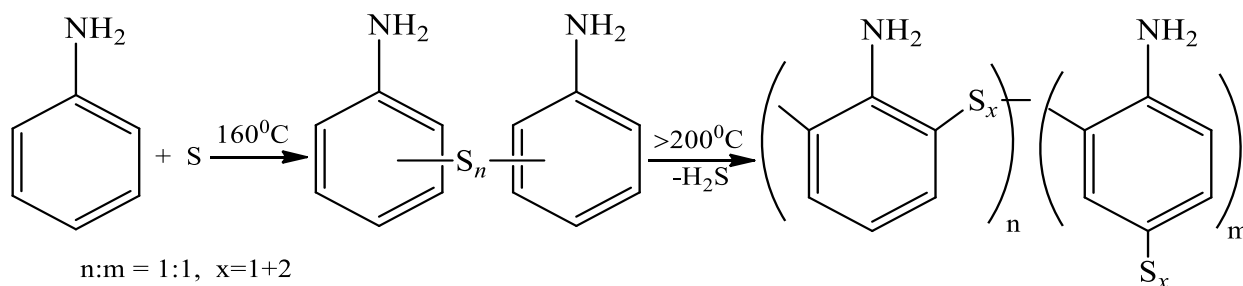
In this reaction, the reaction of forming optically active aryl and alkyl- β -amino acids from aromatic and aliphatic aldehydes is considered to be one of the most efficient methods. In another reaction, asymmetric MR involving chiral catalysts was studied [33].

Alkoxymethylchlorobutane-based compounds containing nitrogen and sulfur. New methods for synthesizing organic compounds containing nitrogen and sulfur with the participation of α -chloromethylisooctyl, α -chloromethylundecyl ether and metal chlorides are presented in the literature [34].



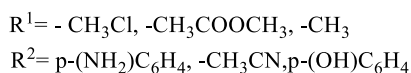
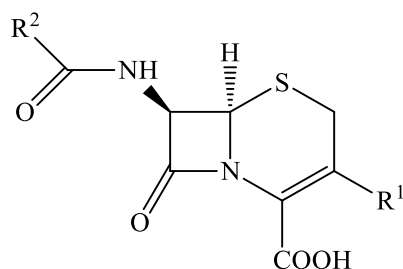
These organic compounds containing nitrogen and sulfur are of great importance in preventing metal corrosion caused by hydrogen sulfide in oil and gas processing. At the same time, the protection of metals from the effects of various bacteria has also been studied [35].

Reactions of amines and aromatic nitro compounds with sulfur. V.A.Sergeyev and V.I.Nedelkin [36] studied the reactions of aniline with sulfur using catalysts and solvents in two stages under normal conditions: the first stage is carried out by boiling until the aniline is exhausted, and the second stage is carried out at temperatures above 200°C (scheme).



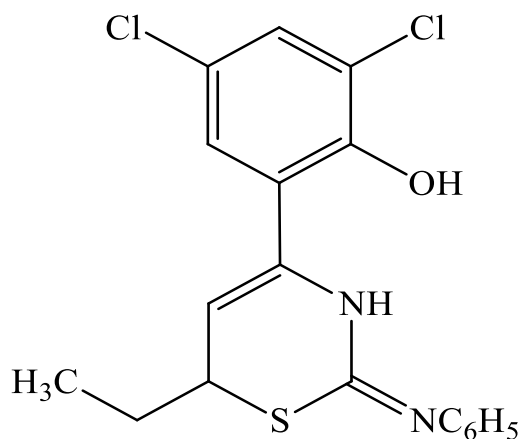
As the temperature rises to 300°C and the sulfur content decreases, the foamy viscous liquid monosulfide compounds contain about 9-11% of NH_2 -groups [37]

Antimicrobial properties of sulfur-containing heterocyclic compounds. Currently, due to the pharmacological and biological properties of heterocyclic compounds and their derivatives, positive results have been achieved in the field of medical research. It is of great importance that many products contain antibiotics, vitamins and hormones from heterocyclic compounds with a natural structure. Several scientists have studied the properties of heterocyclic compounds with activeness against various types of microbes and their structures are presented below. These reviews are mainly based on thiazines and their derivatives with antimicrobial activeness [38].



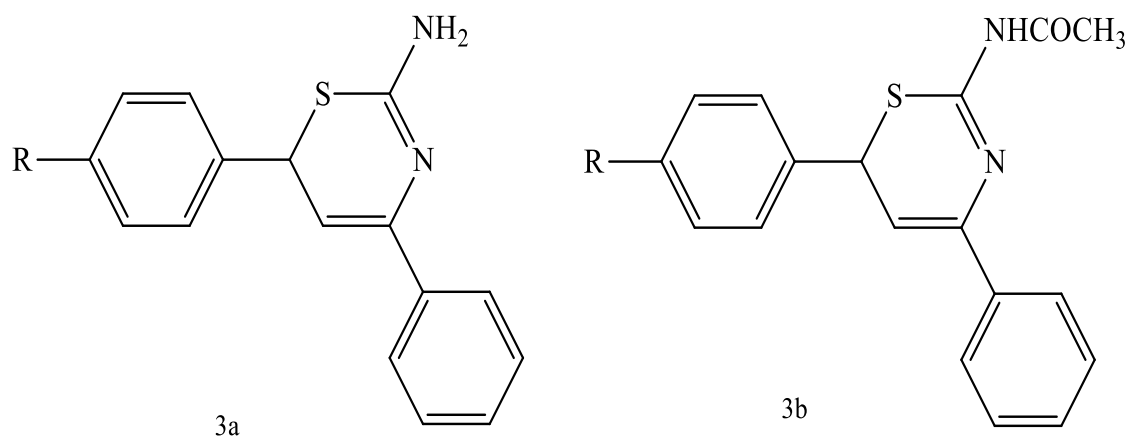
(1)

C.S. Damanjit (2013) studied that 1,3-thiazine has antimicrobial properties [39]. 1,3-thiazines proposed by I.Yavari and Z.Hossaini (2010) found that chalcones derived from chalcones are biologically effective against *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli* and *Pseudomonas aeruginosa* [40].



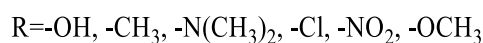
(2)

1,3-thiazine-based compounds proposed by L.P.Bhangale and J.B.Wadekar (2011) are considered acylation-based products, and these substances also have antimicrobial properties [41].

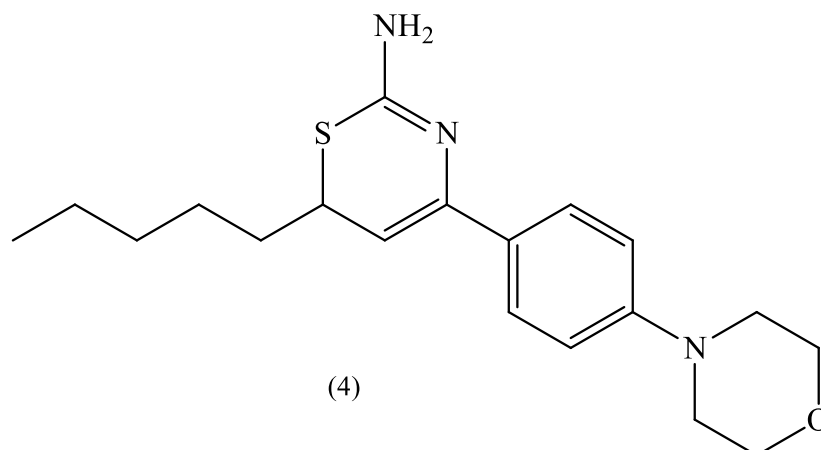


3a

3b

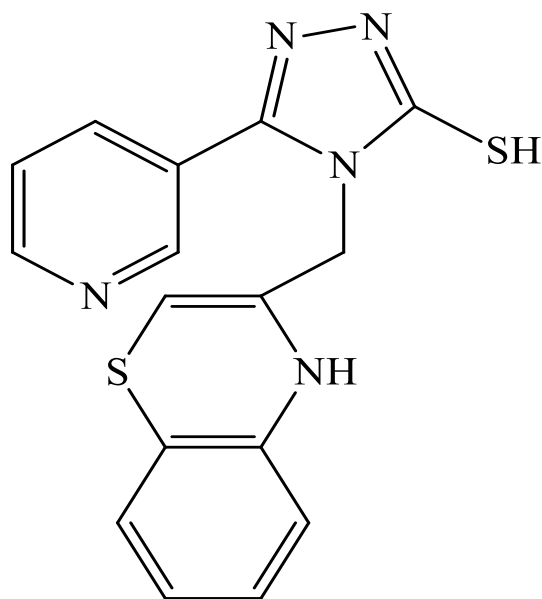


J. Thanusu and M. Gopalakrishnan (2010) studied that the division of morpholine groups in thiazine-containing compounds produced substances with high anti-influenza and antibacterial activeness and actively resisted *Rhizopus* and *Vibrio cholerae* bacteria [42].



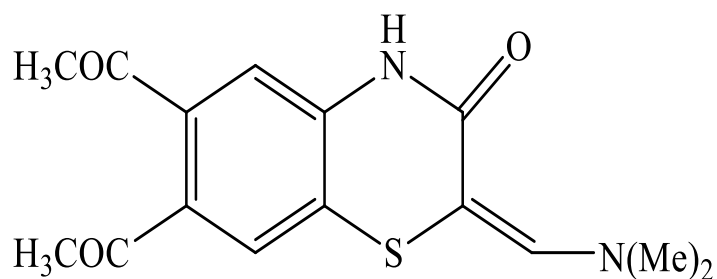
(4)

C.H.Suresh and K.N.Jayaveera (2010) showed that compounds of formula (5) were tested for antibacterial activeness against two different microorganisms, and they confirmed that they have activeness against *E.Soli* and *S.Aureus*, general antibacterials [39].

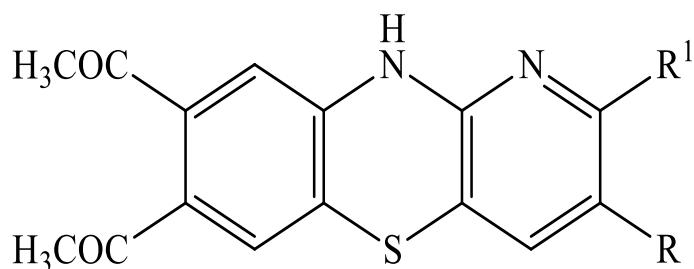


(5)

E.M.Abbas and T.A.Farghaly (2010) proposed that compounds 6, 7a, 7b have antibacterial and anti-influenza activeness against *S.Aureus* and *E.Soli*, in addition to the pathogenic bacteria *Aspergillus flavus* and *Candida* that confirmed their activeness against *albicans* [40].



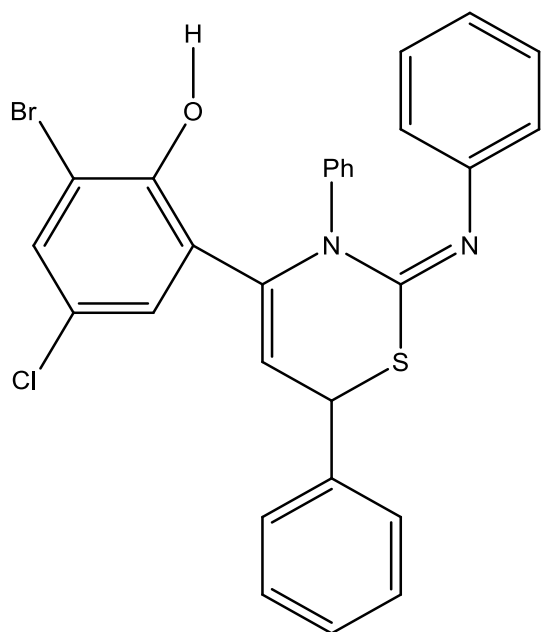
(6)



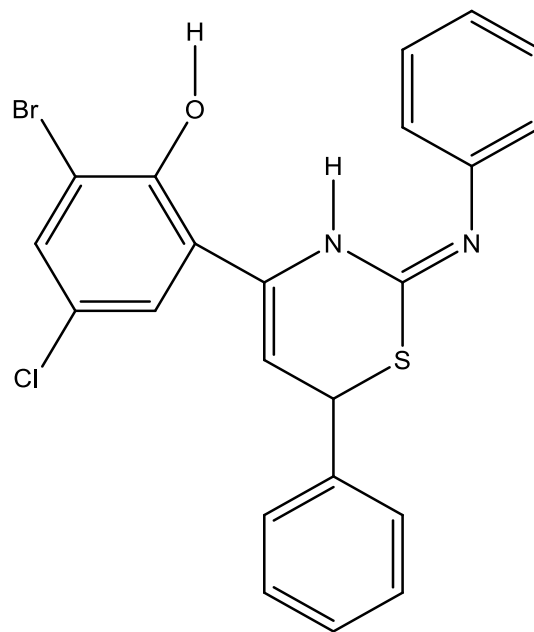
R/R¹; a, COCH₃/CH₃; b, CPh/Ph

(7a-b)

All antibacterial properties of the following substances proposed by S.Jupudi and P.V.Rao (2013) were tested and positive conclusions were obtained [41].

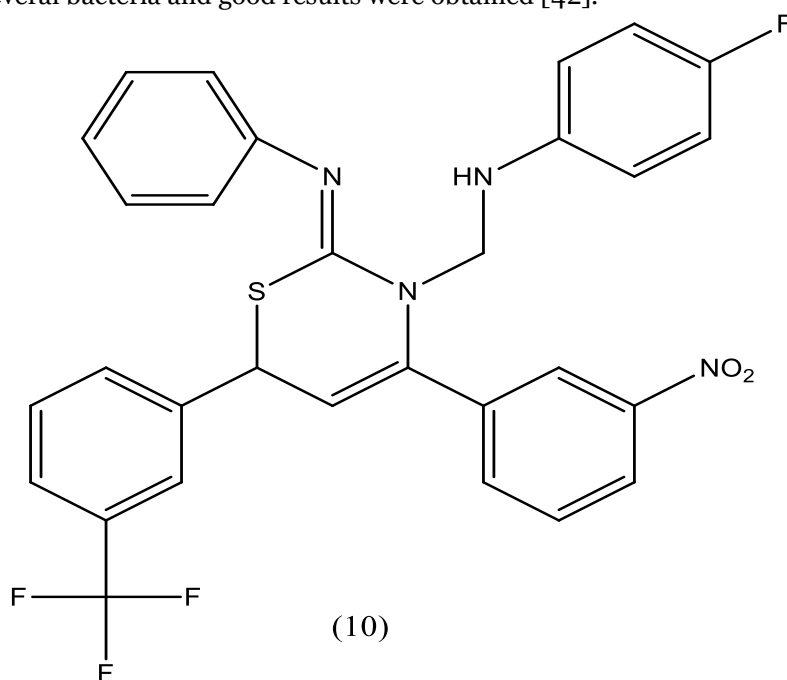


(8)



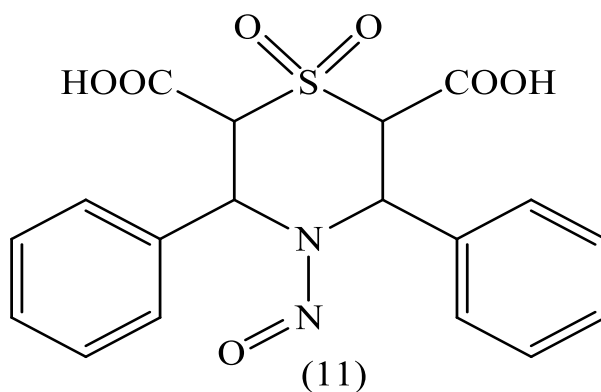
(9)

According to G.S. Dipansu and B.P. Mander (2012), the developed thiazine (10) was tested for antibacterial properties against several bacteria and good results were obtained [42].

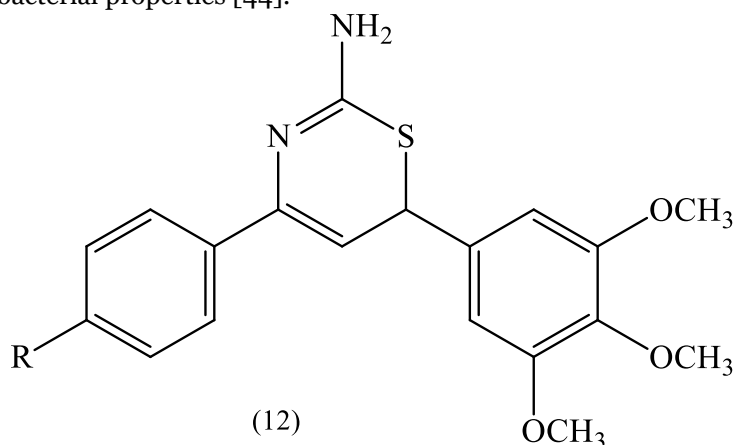


(10)

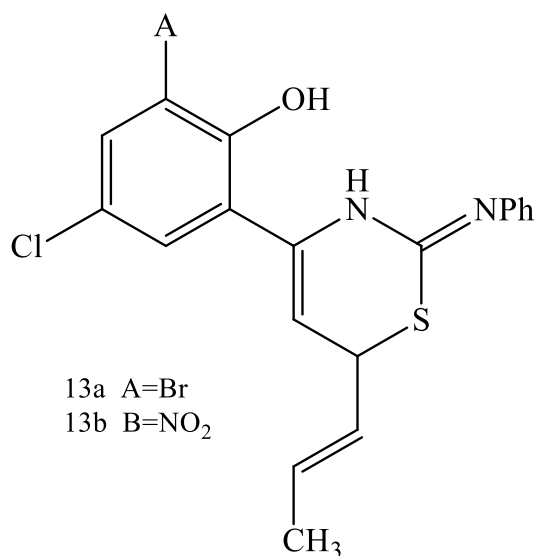
E.Naushad and R. Panugonda (2012) investigated the properties of 1,4-thiazines against influenza and bacteria [43].



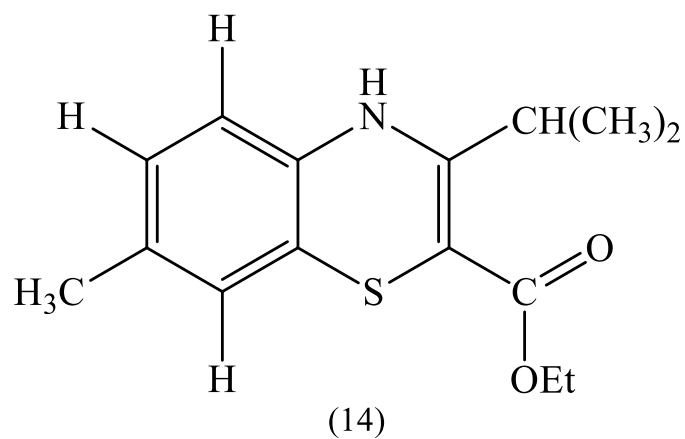
By Varalakshmy Devy and others (2011) were synthesized thiazines with antibacterial properties and found that they had high antibacterial properties [44].



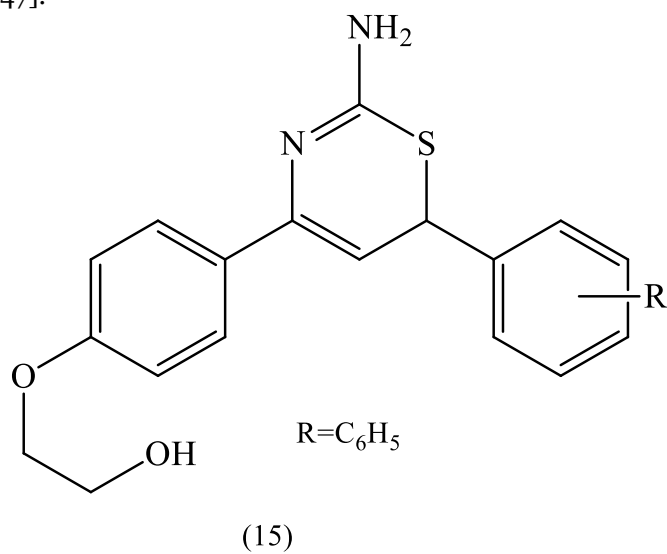
S.G.Ram and V.V.Parhate (2013) studied the antimicrobial activeness of 1,3-thiazines and determined their stability against several bacteria [45].



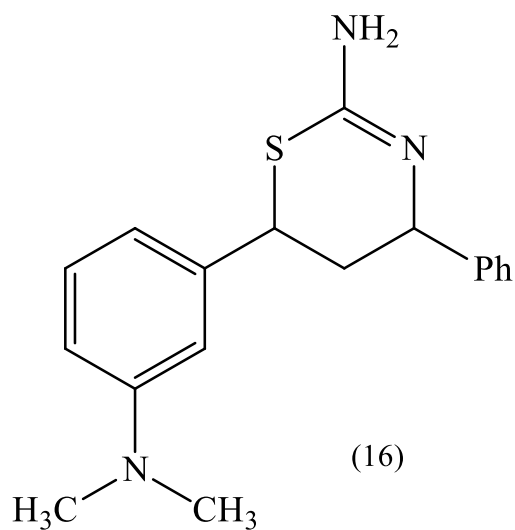
4N-1,4-benzothiazines were efficiently synthetically synthesized in one step through heterocyclization of 2-aminobenzenethiols with β -ketoether by Sharma P.K. and A.Fogla. The structure of the synthesized compounds was confirmed by their analytical and spectral data. The synthesized compounds were evaluated for their activeness against the following bacterial microbial species: *YE.coli* and *Bacillus cereus*. Thiazine components present in the mixture have been proven to have various medicinal effects such as antihypertensive, antimicrobial, antibacterial, anticoagulant, anticancer and antiviral [46].



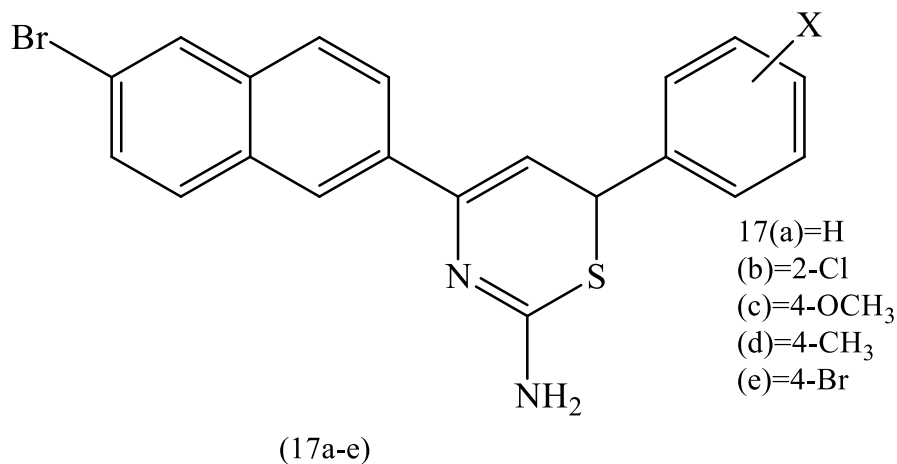
Didwagh va Piste (2013) [47].



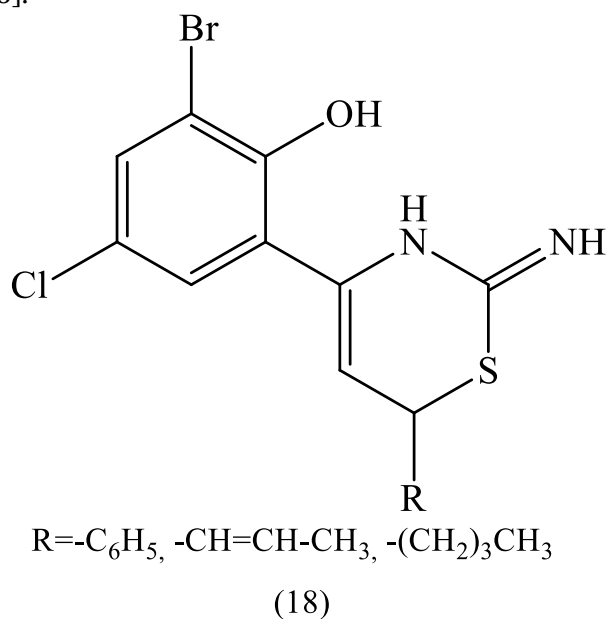
Elarfi va Al-Difa (2012) [48].



Prakash va Ingarsal (2015) [49].



Rathore va Rajput (2013) [50].



In the literature cited above, it is noted that thiazines are a major class of heterocyclic compounds and that their results are in great demand in fighting against infections caused by pathogens.

The study of thiazine-based heterocycles has shown that the thiazine moiety is of great interest to biochemists and medicinal chemists and can be used as an important molecule for creating promising biologically active medicinal compounds. Thus, many substituted thiazine derivatives are potential antimicrobial agents. In addition to antimicrobial activity, thiazine-based heterocycles have also been unusually identified for other chemicals important in agrochemistry and pharmaceuticals [51].

Analysis of residential buildings damaged by termites in our republic and the countries of the world. There is various information about damage caused by termites to residential buildings in Uzbekistan. Among them, as a result of scientific research in 2013, UzA experts reported that about 40 historical monuments in Khiva and about 30,000 residential buildings in other regions of the country are being damaged by termites [52]. According to the information provided by the Republican Center for Combating Termites under Institute of Gene Fund of Plants and Animals of the Academy of Sciences of Uzbekistan, there are about 3,000 species of termites.

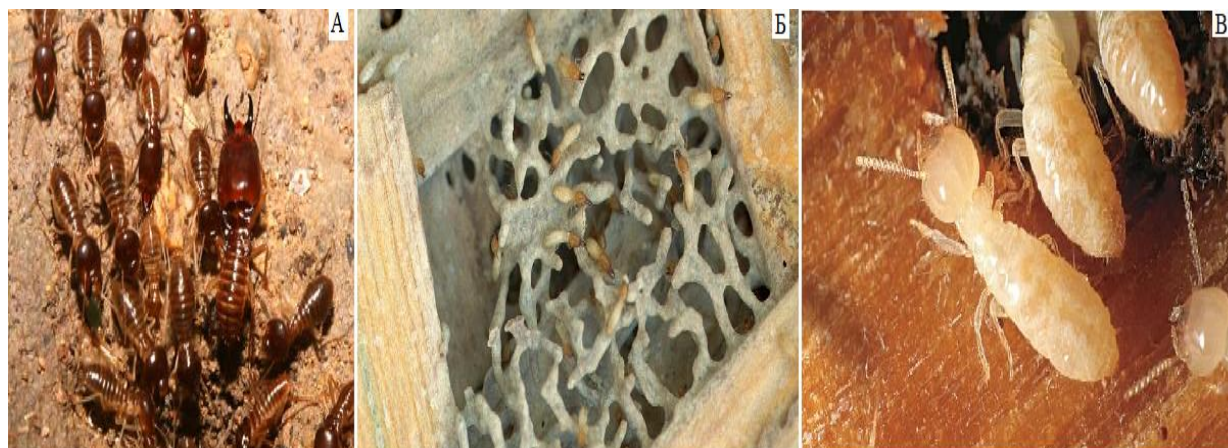


Figure 4. Residential buildings damaged by termites in our republic and the countries of the world.

These insects living in regions with a warm climate feed on plant residues and other waste, and play an important role in ensuring the stability of ecosystems. The large-scale development of steppe zones has led to the modification of termites and the modification of habitats. As a result, they began to live close to people, especially historical monuments [53].

Today, according to the Press service of the Ministry of Emergencies of the Republic of Uzbekistan, a number of measures are being implemented to combat harmful termites and reduce their damage. On July 14-21, 2017, measures for studying the situation of termite infestation in the houses of the population, installing poisonous fodder in the affected houses, preventing the spread of termites in the objects of socio-economic, historical and cultural heritage and for prevention and reduction of damage were implemented in cooperation with the official services in the Republic of Karakalpakstan, Kashkadarya, Surkhandarya, Samarkand, Navoi and Khorezm regions [54]. During these actions, 1,257 poison feeders were installed and chemical treatment was carried out in 589 households and 58 economic-social, 11 cultural and historical objects; 11,430 m² of termite-infested fields and spaces were disinfected. The activities of cleaning, chemical treatment of termite-infested residential areas, cultural-historical monuments, socio-economic objects, and promotion activities among the population are being continued in the above-mentioned areas. [55].

According to the information given in 2019 by the scientists of the Institute of Zoology of the UzAC (Academy of Sciences of Uzbekistan), 2 species belonging to the Anacanthotermes generation, which are Turkestan and large Caspian termites (*A. Turkestanicus* Jacobs., *A. Ahngerianus* Jacobs.), are distributed in Uzbekistan. In almost all regions of our republic and the Republic of Karakalpakstan, people's houses, agricultural buildings and even historical monuments are being severely damaged in recent years, especially for the last 20-30 years. Today, a total of 15,313 houses, 24 social sphere objects, 75 organizations and 772 open land areas (fields, deserts, cemeteries) are affected by termites [56]. The damage caused by termites around the world is increasing year by year. In West Africa, termite damage to buildings accounts for 10% of current repair costs, while termite damage in the United States is \$1.5 billion per year, and \$20 billion worldwide, with some estimates of \$40 billion. A single family of 25,000 termites with a volume of 100 cm³ has been found to consume an average of 50,000 cm³ of cellulose of various forms per year [57].

Analysis of damage caused by termites to historical monuments in Khiva. Historical monuments in the city of Khiva, which is considered the world-famous Eastern jewel of Central Asia, are suffering from tremendous damage caused by termites. As a result of scientific research conducted to study termite activity in the Ancient Arch complex, Juma Mosque, Shergazikhan, Qutlug Murad Inoq and Matpanoboy madrasas under the control of Khiva Ichan-Kal'a State Museum Reserve, it was noted that termites were active in some parts of these monuments in the warm November of 2017. "Ichan-Qala", "Yangi Turmush", "Mevaston" neighborhoods of Khiva city of Khorezm region, Yangiabad town in Gulistan neighborhood, "Yangilik" village of Koshkopir district, 74 houses in "Ayronkol" neighborhood, 14 houses in "Madaniyat" neighborhood of Shavat town in Shavot district, Arab Bobo cemetery, as well as Porsang neighborhood of Qoriqtom village in Yangiariq district, Olaja neighborhood in Khanka district, Hazorasp Castle of Hazorasp town, Chingiz region of Pitnak district were seriously damaged by termites according to analysis in the framework [58].



Figure 5. Observation of termite damage to the cane covering between the main wall and the foundation on the south side of the Matpanaboy madrasa (November 2017).

Due to the extremely high economic damage caused by termites, the protection of cellulose materials from termites is one of the urgent problems that need to be solved worldwide. Therefore, it is important to develop and improve new measures against termites [59]. Currently, there are several chemical, biological, combined and radiological, ultrasonic, thermal, mechanical methods of termite control, which are confined to limiting the number of termites and partially reducing the damage they cause [60]. In current conditions, the chemical method of fighting termites is considered more effective compared to other methods, but if we take into account the negative impact of this method on warm-blooded animals, including human health, it is clear that this method is more harmful than its effectiveness [61].

Khorezm Ma'mun Academy. Scientists of the Khorezm Ma'mun Academy are currently conducting scientific research on improving the fight against termites, one of the most urgent problems in the world. It is known that the fight against termites without thorough study and knowledge of their ecobiology will not give the expected results [62]. Therefore, scientists are studying the composition of the fauna in the nest chambers of termites in the local natural landscape and are conducting research on the use of parasites in the chambers to fight against them [63].



Figure 6. Queen and young termites photographed by research scientists A.Jumaniyazov and B.Palvanov during the study of the composition of the fauna in the chambers [64].

Application of the fungus *Beauveria tenella* BD 85 strain, which is completely harmless to the environment, but has fatal effects only on insects, including amphibians, grasshoppers, and silkworms, was developed and put into practice as a result of scientific research conducted by M.Rakhimova, research scientist of Khorezm Ma'mun Academy [65].

Analysis of residential buildings damaged by termites in Surkhandarya region. According to the data of Vatandosh.uz media in 2013, termites have caused great damage to 70-80% of residential area, as well as paper, books and clothes of the population in the village of Bahoristan, Termez district, Surkhandarya region, for the last few years. It was found that Termez airport, which is adjacent to the village, is also being damaged by termites [66].



Figure 7. Building materials found to be damaged by termites.

Conclusion. The synthesis of sulfur-containing organic compounds, the development prospects and modern problems of their use, as well as the data and analyzes based on the use of antiseptics in the world and in our republic, were studied thoroughly. Modern methods of synthesizing sulfur-containing organic compounds, reaction mechanisms and factors affecting reaction processes were analyzed. The current research works of international and our country's scientists on the active resistance of sulfur-containing organic compounds to bacteria were studied through the analysis of the literature. After studying the above-mentioned fundamental laws, a brief classification of chemical preparations used as wood-protecting antiseptics in the world and in our republic was studied in the next part. Based on these analyses, damage to historical monuments, buildings and structures in our republic, as well as actual problems of their protection, were studied.

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