

Development of Vinyl Ether Synthesis

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Abstract:

The article discusses the development of vinyl ether synthesis and the contribution of Russian scientists to this field. Particular attention is paid to the research of Academician A. E. Favorsky and his student M. F. Shostakovsky, who developed an original method for obtaining vinyl ethers without diluting acetylene with inert gases. The key stages of the technology's development are described, from laboratory research to industrial implementation. Shostakovsky's achievements in the field of medical chemistry are also covered, including the development of the well-known drugs "Vinilin" and "Gemodez", which played an important role in the treatment of wounds and intoxications. The article emphasizes the importance of the scientists' work for the development of organic chemistry and polymeric materials.

Keywords: vinyl ethers, Favorsky, Shostakovsky, synthesis, polymers, medicinal chemistry, Vinilin, Hemodez.

Introduction

Russian scientist, academician Alexey Evgrafovich Favorsky was a true statesman of Russia and organizer of science. He created new scientific institutes, was engaged in the training of highly qualified scientific personnel. A. E. Favorsky cared about the development of science and carried out a number of practical works that were useful to society. Under his leadership, many industries were created, including those related to the use of synthetic rubber, as well as scientific institutions.

One of his closest students, who worked at these institutes, was Mikhail Shostakovsky, who remained faithful to the requirements set by his great mentor.

Mikhail Fyodorovich Shostakovsky was born on May 24, 1905 in the village of Novoselytsia in the Kherson region (now Ukraine) to a poor peasant family.

In 1924, after finishing school, he entered the Irkutsk State University, Faculty of Medicine, Department of Biochemistry. Mikhail Fyodorovich studied well, was one of the best students.

In 1929, after graduating from the university, he stayed on to study in graduate school. However, due to the conflict between the USSR and China, he was mobilized into the Red Army, where he

served until 1930. At the request of the Irkutsk State University, he lectured on organic chemistry at the Medical Institute and at a meat and dairy plant.

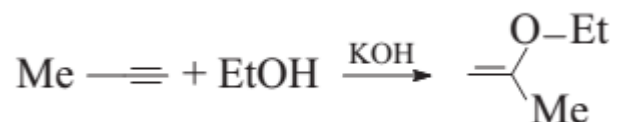
After working at this institute for two years, he entered graduate school at the chemistry department of the Leningrad Research Institute of the USSR Academy of Sciences. At that time, Aleksey Evgrafovich became interested in studying cycloalkynes. He was interested in the conditions of their stability. To solve this problem, he commissioned Mikhail Fedorovich Shostakovsky and Nikolay Aleksandrovich Domnin to conduct research on this topic. Their goal was to study the changes in carbocyclic molecules of various sizes containing an intracyclic triple bond, their stability, possible isomers, and oligomerization pathways. [1-2]

M. F. Shostakovsky studied the five-membered cycle, and N. A. Domnin studied the seven-membered cycle. In the course of his research, M. F. Shostakovsky established that cyclopentene is unstable and prone to polymerization, forming mainly complex composite polymers and mixtures of 1,3-dienes.

Methods. Cycloheptene was partially converted into oligomeric products, and its other part was isomerized into a seven-membered cycle with an allene group. Subsequently, cyclopentene synthesized by N. A. Domnin turned out to be the first stable molecule among cyclic acetylenes.

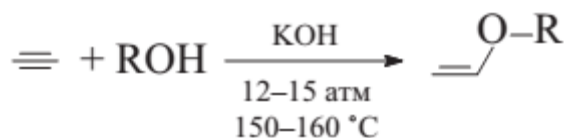
Based on these studies, cyclic polyynes containing six triple bonds are currently synthesized. [3]

At that time, reports began to appear in the scientific literature about innovations created by Voltaire Reppe in the field of synthesis of vinyl ethers and their use in industry as polymers. However, in reality this was a development of Alexei Evgrafovich's work on the synthesis of ethyl isopropenyl ether (the first vinyl ether), which he obtained by heating allylene (methylacetylene) with ethyl alcohol in the presence of potassium hydroxide.



Due to insufficient laboratory conditions, the reaction of direct vinylation of alcohols with acetylene, discovered by Alexey Evgrafovich, could not be realized. For about half a century, this reaction, which had important industrial significance, awaited the attention of researchers.

On behalf of Alexey Evgrafovich, Mikhail Fedorovich directed his research to the synthesis of vinyl ethers from local raw materials. Independently of the classified work of V. Reppe in Germany, M. F. Shostakovsky established that by heating acetylene or methylacetylene with any alcohol in an autoclave (at 150–160°C) in the presence of KOH and under a pressure of 12–15 atm, vinyl ethers can be obtained with a yield of about 96%.

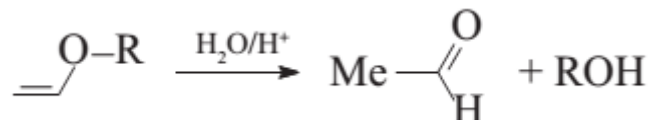


The uniqueness of the Favorsky-Shostakovsky method is that pure acetylene (not diluted with an inert gas) was used for the first time for the vinylation of alcohols. V. Reppe diluted acetylene with nitrogen for this purpose.

A. E. Favorsky and M. F. Shostakovsky proved that low-boiling alcohols can be safely used for vinylation without diluting acetylene. This indicates that non-vinylated alcohol and, in particular, vinyl ether vapors are reliable phlegmatizers of acetylene, preventing its explosiveness.

Undoubtedly, this method ensured high productivity and made the process more convenient for industrial use. [4-5]

Results. In 1935, M. F. Shostakovsky defended his PhD thesis, in which he presented a wide range of vinyl ether homologues, methods for their synthesis, and the most important transformations. Mikhail Fedorovich noted that one of the key characteristics of simple vinyl ethers is acid-catalytic hydrolysis: even in the presence of a 1% solution of acetic acid, they decompose to form acetic aldehyde and restore the original alcohol.



After defending his candidate's dissertation in 1936, under the direction of A. E. Favorsky, M. F. Shostakovsky began working at the Institute of Organic Chemistry at the USSR Academy of Sciences in Moscow. Here he first headed the department, and then until 1962 he headed the laboratory of vinyl compounds.

After the start of the war, the laboratory of vinyl compounds was evacuated to the Kazan Chemical Institute named after A. M. Butlerov. There, the scientist continued research on the synthesis of the substance "Vinipol".

Despite working in wartime conditions, in 1944 M. F. Shostakovsky successfully defended his doctoral dissertation.

During the war, he also took up a new direction — "medical chemistry." One of his students, Doctor of Chemical Sciences F. P. Sidelkovskaya, recalled those events: "In Kazan, one of the heads of health care came to Mikhail Fedorovich and asked a question that was then addressed to all chemists: "Is it possible to create drugs against inflammation, burns, and antipyretics in your laboratory?" We had never worked with medications before, but when the doctors listed the drugs needed for the army, Shostakovsky noted that he was already working on polymers similar to a well-known natural remedy — Peruvian balsam, used for burns and inflammation. He said that he was ready to try to study them.

Until that time, synthetic polymers had never been used in medicine in world practice. We began to synthesize substances with different molecular weights. Each fraction obtained was given to physiologists working at the university, who immediately conducted experiments on frogs. The results were obtained quickly: fractions with a molecular weight of one and a half to two thousand accelerated the healing of burns and promoted the regeneration of epithelial tissue. Moreover, when testing on other animals, it turned out that these substances were completely non-toxic." After the most suitable fraction for medical purposes was determined, the industrial plant in Sverdlovsk began optimizing the production of the new drug. Six months later, the drug began to be sent to the front.

This is how the famous Favorsky-Shostakovsky balm was created, which later received the name "**Shostakovsky Balm**". Today in pharmacies you can find a reliable wound-healing agent, tested for decades - "**Vinilin**". Thanks to this drug, the lives of thousands of wounded and burned people were saved. Thus, Mikhail Fedorovich, engaged in medical chemistry, quickly became one of the leading scientists in this important field. However, antibiotics and wound-healing balm are far from the only drugs created under his leadership.

Conclusions. In parallel with the development of **Vinilin**, the first production of **polyvinylpyrrolidone** (now known as Hemodez) was launched in the USSR. For many years, this drug was used as a plasma substitute and an effective detoxifier. During the war, it saved thousands of lives. In some countries, it is still used to treat patients with massive blood loss and poisoning. [6]



2. «Винилин» — бальзам Шостаковского (а); препарат «Гемодез» (б)

In 1957, at the invitation of the Chairman of the Siberian Branch of the USSR Academy of Sciences, Academician M. A. Lavrentiev, Mikhail Fedorovich Shostakovsky organized the Institute of Organic Chemistry in Irkutsk.

For Mikhail Fedorovich, moving to Irkutsk was not an easy decision. Exchanging a fully equipped laboratory at the Moscow Institute of Organic Chemistry for an unfinished institute in Siberia was not an easy choice. However, it was in Irkutsk that he spent his student years, which played an important role in making this decision.

Combining the management of his own laboratory in Moscow with the creation of a new institute, he managed to gather around himself a team of dedicated and proactive scientists. Among them was Doctor of Chemical Sciences Alexander Spiridonovich Ataving, who became deputy director for research and founded the laboratory of organic chemistry synthesis.

Atavin was responsible for the main organizational tasks related to the selection of personnel, construction and equipment of the institute. In his laboratory, the direction of vinyl ether chemistry was actively developed, in particular the synthesis of vinyl ethers of polyhydric alcohols. The reactions of electrophilic and radical addition of vinyl ethers to water, alcohols, carboxylic acids, hydrogen halides, halogens, hydrogen sulfide, mercaptans, halogen alkanes, phosphites, phosphorus chloride and other reagents were studied in detail. Currently, this institute is headed by Doctor of Chemical Sciences, Academician B. A. Trofimov. [7]

During their scientific work, Mikhail Fedorovich Shostakovsky and his students created more than 220 inventions, most of which were put into practice. Remaining true to the ideas of his teacher, Academician A. E. Favorsky, he continued his work and made a huge contribution to the development of science and industry. For his services to the country, Mikhail Fedorovich was awarded numerous state awards.

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