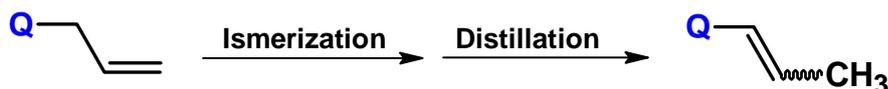


# PROCESS FOR OBTAINING LOW AND HIGH BOILING 1-PROPENYL AND BIS(1-PROPENYL) ETHERS AND SULPHIDES TOWARDS RENEWABLE CATALYTIC SYSTEMS

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Isomerization reactions are widely used in organic chemistry, often being one of the first and/or key stages of cascade reactions. In case of compounds such as allyl ethers or sulphides, an interesting group of compounds are both short and long chaines derivatives. Complexing properties of the heteroatoms (especially sulphure) determine the course of the isomerization reaction - the target product or presence of competitive reactions. In the case of low boiling compounds, the limitations associated with high volatility make it difficult to select an isomerization catalyst (transition metal complex), solvent and reaction conditions – it is difficult to obtain and isolate the 1-propenyl or bis(1-propenyl) target system without losses. The experiments were based on concentration range, temperature and time of reaction for different substrates, efficiency of mixing and distillation, yield and purity of products. A method for the isomerization of 2-propenyl and bis(2-propenyl) precursors for the targeted 1-propenyl and bis(1-propenyl) ethers and sulphides with high 96-98% yield was developed.



**Q = alkylS, alkylO, allylS, allylO**

Thanks to the applied catalytic systems: 18-Crown-6/*tert*-BuOK and dibenzo-18-Crown/*tert*-BuOK, followed by vacuum distillation, 1-propenyl or bis(1-propenyl) systems with purity more then 99% were obtained. The limitation of the effectiveness of the method are boiling points of allylic precursors, which can not exceed 150 °C for low boiling compounds and 250 °C for high boiling compounds under atmospheric pressure. The type of used crown ethers allows the maximum boiling temperature of the distillation process to be controlled. The selection of allyl ethers and sulphides undergoing a two-steps isomerization-distillation proces required a minimum of 100 °C difference between the boiling point of the target product and the catalytic system (crown ether). The methods described have been the subject of two patents <sup>[1, 2]</sup>.

Importantly, the distillation residue, i.e. the catalytic system, can be used for the next reaction – at least three times to ten. The solutions developed are unprecedented in the literature – there are unknown basic catalytic systems for the isomerization reaction of allyl compounds that would be recycled.

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[1]. S. Krompiec, B. Marcol, M. Penkala, M. Filapek, G. Benke, K. Leszczyńska-Sejda, C. Pieraszuk, S. Rogalski „*Process for obtaining low boiling 1-propenyl or bis(1-propenyl) ethers and sulphides*” **2015**, patent No **230459**

[2]. S. Krompiec, B. Marcol, D. Zych, A. Kurpanik, K. Leszczyńska-Sejda, „*Process for obtaining 1-propenyl compound type QCH=CHCH<sub>3</sub>, especially high boiling*”, **2015**, patent granted by decision dated 14/12/2018, waiting for the number to be issued