

Doctoral dissertation abstract

„Isomerization of allyl compounds catalyzed by crown ether-base systems”

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The main subject of interest in the doctoral dissertation was the innovative use of the crown ether-base type catalytic systems in isomerization reactions of allyl compounds. Crown ethers complex metal cations of groups I and II selectively, creating ion pairs with a strongly coordinated cation and exposed anion. For the alkoxides, hydroxyl, or amide ions, attractive catalytic systems were obtained for reactions proceeding *via* deprotonation. The following procedures were tested: 12-crown-4/LiOH, 15-crown-5/NaOH, 18-crown-6/KOH or *t*-BuOK, dibenzo-18-crown-6/*t*-BuOK, and others. The literature analysis showed that the isomerization reaction is poorly researched and described concerning super-basic systems of the crown ether-base type. Therefore, the conducted research was aimed at expanding knowledge on this subject.

The leading goal of the work was to obtain a series of 1-propenyl, bis(1-propenyl), and – by regioselective migration of the double bond – allyl-(1-propenyl) compounds under possibly mild conditions and environmentally friendly solvents. The influences of the type and concentration of the crown ether and base, the type and amount of the solvent, as well as the reaction time and the effect of ultrasound on the yield, regio- and stereoselectivity of isomerization, were analyzed. A series of *Z*-, *E*-, or (*E* + *Z*)-(1-propenyl) compounds were obtained *via* isomerization of allyl precursors. A convenient methodology for obtaining a conjugated system of bonds in the glyceride chain of linoleic acid and the methyl ester of linoleic acid was developed. It was shown which of the tested *Q*-allyl systems do not undergo isomerization, and an attempt was made to explain this state of affairs. The activities of the base catalysts used were compared – both the bases themselves and the crown-base complexes; the most active turned out to be the 18-crown-6/*t*-BuOK system. Conditions for fully regioselective isomerization of selected bis(allyl) systems were developed. The reactivity of several allyl compounds was compared using the method of competitive reactions (equimolar mixtures of two different allyl systems were isomerized). It was shown that the results obtained for model systems (mixtures) fully correspond to the effects of individually isomerized bis(allyl) compounds. Procedures for recycling the entire catalytic system and (and recycling) the crown ether from all used catalytic systems were also developed.

As part of the dissertation, 61 *Q*-allyl systems (*Q* = *O*, *S*, *N*, *P* or *C*, ten were synthesized), eight *Q*¹-allyl + *Q*²-allyl systems (competitive reaction method) and seven synthesized allyl-*Q*¹-*Z*-*Q*²-allyl. The structures of the obtained substrates and products were confirmed by: ¹H and ¹³C NMR (¹H-¹H COSY and ¹H-¹³C HMQC for selected derivatives), HRMS, or elemental analysis. Innovative solutions regarding crown ether-base systems have been the subject of nine patents.