

UDC 66.09

*Maia GLUSHKO\* and Guido RAJALO\****PRENOLSYNTHESIS BY PTC***Maia GLUSKO, Guido RAJALO. PRENOOLI SUNTEES FAASIDEVAHELISE MASSIULEKANDE KATALUSAATORI ABIL**Майя ГЛУШКО, Гуйдо РАЯЛО. СИНТЕЗ ПРЕНОЛА С ПРИМЕНЕНИЕМ КАТАЛИЗАТОРА МЕЖ-ФАЗНОГО ПЕРЕНОСА*

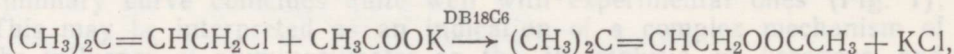
Prenol (3-methyl-2-buten-1-ol) is an initial substance for the synthesis of several insecticides and fragrances. A well-known way to get prenos is the hydrolysis of 1-chloro-3-methyl-2-butene (prenylchloride). Both the isomeric chlorides prenylchloride and 3-chloro-3-methyl-1-butene are contained in the isoprene hydrochlorination product, from which pure (99%) prenylchloride can be produced by catalytic isomerization and rectification of isomeric compounds [1]. Prenylchloride can be hydrolysed easily with any alkaline, but in the course of hydrolysis undesirable isomerization of primary chloride to tertiary one will take place. So, the hydrolysis of prenylchloride with sodium bicarbonate solution yields a product consisting of only 20% prenos, 80% being 2-methyl-3-buten-2-ol [2]. By the hydrolysis with sodium hydroxide solution the simultaneous formation of ether is observed. A more promising method of synthesis seems to be the esterification of prenylchloride followed by saponification of ester. By acetylation of prenylchloride in a solution of glacial acetic acid a product consisting of 70% prenylacetate and 30% tertiary acetate can be achieved. The ratio of isomeric acetates can be retained by the subsequent saponification [3].

We have investigated the possibility of carrying out the acetylation reaction using phase transfer catalysis (PTC). The process was realized in an anhydrous medium to avoid the unadvisable isomerization reaction and to get a high yield of the product desired. Dibenzo-18-crown-6 (DB18C6) was used as catalyst. In an unpolar or slightly polar medium DB18C6 transfers the acetate ion into a soluble complex anion, which is a strong nucleophile, and directs thus the reaction mainly to acetate formation. The activation of the acetate ion by crown ether increases strongly the rate of the acetylation reaction. This effect is more remarkable in polar but at the same time aprotic solvents [4]. Nevertheless the activity of the anion is notably suppressed by water, even in trace quantities. Crown ethers have a tendency to carry water even into unpolar solvents [5]. PTC can also be applied for the saponification of prenylacetate with anhydrous potassium hydroxide in an unpolar solvent. The potassium acetate formed can be used for acetylation of prenylchloride.

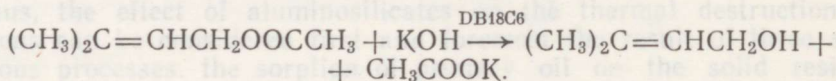
\* Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences). Akadeemia tee 15, EE0026 Tallinn, Estonia.

The synthesis of prenol is in our work realized in two stages:

(1) acetylation of prenylchloride with potassium acetate



(2) saponification of ester



## Experimental

Both the stages of the synthesis were carried out in an anhydrous medium using benzene, dimethylsulphoxide, or acetonitrile as solvents. As stock an industrial product consisting of primary and tertiary chlorides with the ratio of 9:1 and purified by distillation was used. All reagents and solvents used were analytically pure according to specifications of Sojuzreactiv, USSR. As catalyst a chemically pure DB18C6 (Reakhim, USSR, TU 6-09-20-19-83) was used without further purification. Stock and reaction solutions were analysed by GLC on a LHM-8MD chromatograph using a flame ionization detector, Polychrom-1 carrier, polyester 5FIA as stationary phase, and helium as carrier gas.

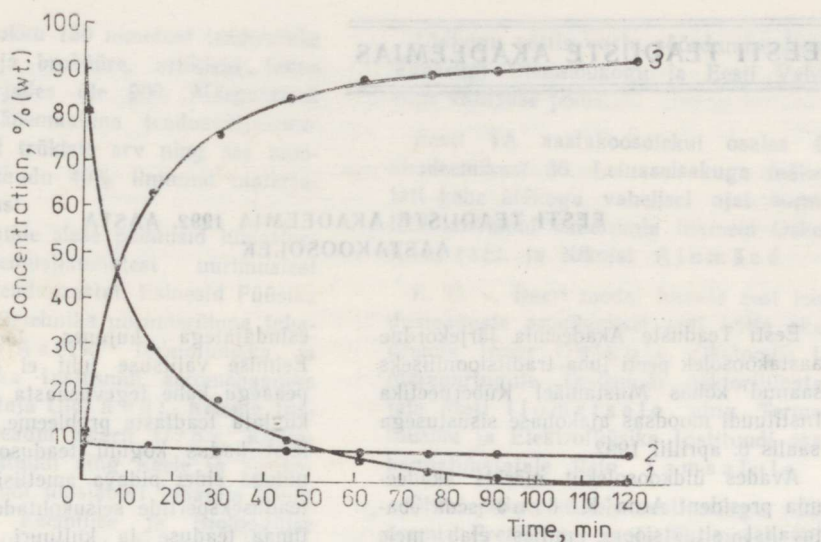
For the esterification a suspension of potassium acetate, DB18C6, and benzene was introduced into a thermostated flask equipped with a stirrer and a Dean-Stark tube connected with a reflux condenser. First the water traces in the form of benzene-water azeotrope were separated. After that prenylchloride was added and the reaction mixture was boiled under a reflux condenser at stirring for 20 h, cooled, and filtered. Benzene was distilled off from the filtrate, the settled DB18C6 filtered, and prenylacetate separated by vacuum rectification. From filtration and distillation residues DB18C6 was separated by benzene extraction and removed to the process.

For the saponification of prenylacetate, a suspension of anhydrous potassium hydroxide and benzene was introduced into the flask already used in the first stage. After dewatering and cooling the prenylacetate was added with careful stirring. The reaction mixture was stirred for 3 h and then filtered. The prenol was separated by vacuum rectification.

## Results

The total yield of prenylacetate in the first stage was 99%, the yield of prenol in the second stage was 95%. The electronegativity of the solvent affects greatly the acetylation rate. So the reaction rate is much higher in an acetonitrile solution than in benzene, and somewhat higher in the dimethylsulphoxide than in acetonitrile. This phenomenon can be explained by the solvation of the cation by the aprotic solvent and the formation of a bare complex anion. The acetylation rate depends on the concentration of acetate—DB18C6 complex, so also on the DB18C6 concentration. A rise in the temperature accelerates the solubility of the complex and raises also the rate of the reaction. In the Figure experimental data and time dependence of the concentrations of reagents and the product are shown. As can be seen, the concentration of the tertiary chloride, 3-chloro-3-methyl-1-butene, remains time-constant. We have established this phenomenon by different initial ratios of isomeric chlorides, as well as by all the above-mentioned solvents. So the acetylation





Kinetics of prenylchloride acetylation in a dimethylsulphoxide solution by the use of PTC (DB18C6). Temp. 40–42°C; DB18C6 concentration 0.07 mol/dm<sup>3</sup>. 1 — prenylchloride, 2 — 3-chloro-3-methyl-1-butene, and 3 — prenylacetate.

reaction by PTC (DB18C6) is selective for prenylchloride only. Probably the reaction of a complex with tertiary chloride is suppressed by steric difficulties. The rate of the saponification reaction by the use of DB18C6 is high, but it decreases rapidly after 93% conversion is attained, probably due to the competition of OH<sup>-</sup> and CH<sub>3</sub>COO<sup>-</sup> ions in the complex formation.

#### REFERENCES

1. Раяло Г. К моделированию и расчету гидрохлоратора типа насадочной колонны. — Ж. прикл. хим., 1984, 57, 4, 820–827.
2. Методы элементоорганической химии. Хлор. Алифатические соединения. Москва, Наука, 1973, 590–597.
3. Назаров И. Н., Азербайев И. Н. Производные ацетилена. 63. Обратимые перегруппировки аллильной системы. III. Действие хлористого водорода на α,γ- и γ,γ-диметилаллилкарбинолы и изомерные превращения α,γ- и γ,γ-диметилаллилхлоридов в реакциях обмена. — Ж. общ. хим., 1948, 18, 3, 414–423.
4. Хираока М. Краун-соединения. Свойства и применение. Москва, Мир, 1986.
5. Демлов Э., Демлов З. Межфазный катализ. Москва, Мир, 1987.

Presented by J. Kann

Received  
July 3, 1992