

Cleavage of different ether bonds in butyl glycidyl ether and allyl glycidyl ether by K^- , $K^+(15\text{-crown-5})_2$

Zbigniew Grobelny^a, Andrzej Stolarzewicz^{a,*}, Adalbert Maercker^b,
Stanisław Krompiec^c, Tadeusz Bieg^d

^a Centre of Polymer Chemistry, Polish Academy of Sciences, 34, Marie Curie-Skłodowska Street, 41-819 Zabrze, Poland

^b Institut für Organische Chemie, Universität Siegen, D-57068 Siegen, Germany

^c Institute of Chemistry, Inorganic Technology and Electrochemistry, Silesian Technical University, 44-101 Gliwice, Poland

^d Institute of Chemical Technology of Coal and Petroleum, Silesian Technical University, 44-101 Gliwice, Poland

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Abstract

The kind of substituent in alkyl glycidyl ethers affects the course of their reaction with K^- , $K^+(15\text{-crown-5})_2$. The cyclic oxirane ring is exclusively cleaved in the case of butyl glycidyl ether whereas the presence of the unsaturated allyl group in the glycidyl ether molecule unexpectedly prefers the scission of the linear ether bond. In both the systems organometallic intermediates are formed. They react with crown ether causing its ring opening. Allylpotassium formed from allyl glycidyl ether reacts also with another glycidyl ether molecule; the oxirane ring is opened in this case.

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1. Introduction

Glycidyl ethers, $\text{CH}_2\text{-CH-CH}_2\text{-O-R}$, where R is an alkyl or an aryl group, possess two kinds of ether bonds, i.e. the cyclic and linear ones. Under basic conditions the scission of the strained cyclic oxirane ring is preferred. A nucleophile attacks its less hindered carbon atom and the opening occurs in the β -position, i.e. between the CH_2 group and oxygen [1].

In our previous work [2] a system containing potassium anions was used for the reaction with phenyl glycidyl ether. Potassium alkali K^- , $K^+(15\text{-crown-5})_2$ (**1**) in tetrahydrofuran solution was selected for that study. It was found that also in this case the cyclic ether bond namely in the β -position was cleaved. An organometallic intermediate was formed in this reaction. That underwent γ -elimination resulting in potassium cyclo-

propoxide and potassium phenoxide. Crown ether ring opening occurred in a side reaction under the influence of the organometallic intermediate. The process was very fast at ambient temperature as it was already earlier observed using alkali solutions [2–4].

In the present work we describe results of further investigations in this field. Glycidyl ethers possessing an aliphatic substituent, i.e. butyl glycidyl ether and allyl glycidyl ether were selected in this case. They were model systems for our studies of the initiation step of glycidyl ethers polymerization. The reaction conditions, therefore, were the same as in the polymerization process, i.e. glycidyl ethers were used in the excess in relation to **1**.

2. Results and discussion

The reaction of **1** with butyl glycidyl ether was investigated in the first series of experiments. After mixing of substrates the reaction mixture was treated with benzyl bromide or methyl iodide to transform non-volatile reaction products into volatile compounds. The

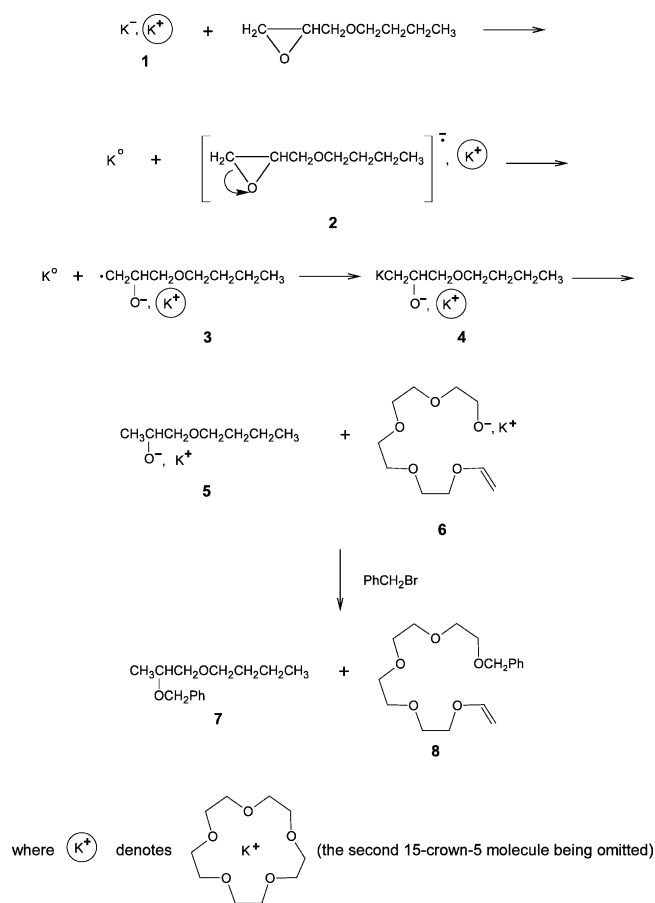
* Corresponding author. Tel.: +48-32-271-6077; fax: +48-32-271-2969

E-mail address: andrzej.stolarzewicz@cchp-pan.zabrze.pl (A. Stolarzewicz).

samples were then analyzed using preliminarily the gas chromatography–mass spectrometry (GC–MS) technique.

Two main signals were observed in the chromatogram of the benzylated sample. They were identified as of 1-butoxy-2-benzyloxypropane (in 20% yield) and tetraethylene glycol benzyl vinyl ether (18%). It means that potassium 1-butoxy-2-propoxide and potassium tetraethylene glycoxide vinyl ether were the real reaction products. The former was obtained by the oxirane ring opening. The latter is known as the product of crown ring opening by organometallic intermediates [3,4]. In order to analyze side reaction products the reaction mixture was treated with methyl iodide instead of benzyl bromide. Tri- and tetraethylene glycol dimethyl ethers in 4% total yield were found in this case additionally. They were formed in the methylated sample as a result of the reaction occurring between **1** and potassium tetraethylene glycoxide vinyl ether leading to dipotassium tri- and tetraethylene glycoxides [3,4].

Potassium anion is known as two electron transfer species reacting in two steps [5]. In the first one K^0 is obtained from K^+ . Then, after the transfer of the second electron K^+ is finally formed. The same mechanism was supposed in the present work. It was



Scheme 1.

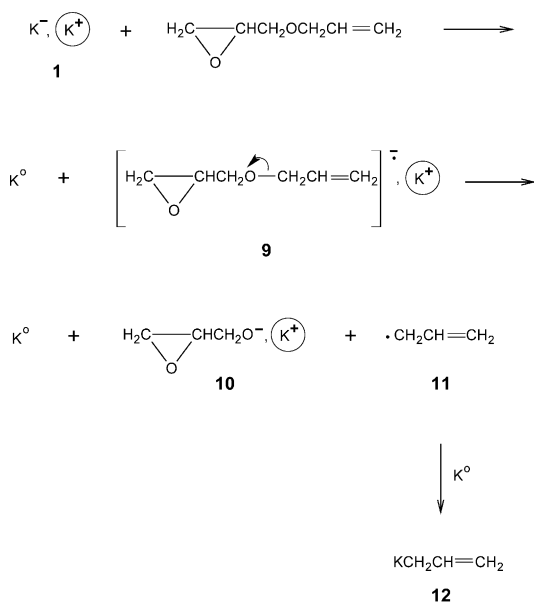
assumed that in the first step of the reaction one electron is transferred from K^+ of **1** to the oxirane ring of butyl glycidyl ether (Scheme 1). Then, the oxirane ring is opened in the β -position giving radical anion **3**. It presumably recombines with K^0 forming an organometallic alkoxide **4**. The latter reacts with crown ether causing its destruction. The final products involve two potassium alkoxides, **5** and **6**, and after benzylation their benzylated derivatives, **7** and **8**, respectively. No products of γ -elimination of **4**, i.e. potassium cyclopropoxide and potassium butoxide, were found in the reaction mixture. As mentioned, such reaction was observed in the case of phenyl glycidyl ether when the resonance stabilized phenoxide anion was formed [2].

It is worth noting that the reaction of butyl glycidyl ether with **1** in tetrahydrofuran solution was presented already in [6]. Methanol was used as the quenching agent in that case. The oxirane ring opening was described to occur in the system resulting in the organometallic alkoxide **4**. However, the latter was assumed to react with methanol giving 1-butoxy-2-propanol found in the mixture after protonation. A possibility of the crown ring cleavage was not taken into account on that stage of investigations. Thus, the use of protonation as the only quenching method can lead to the assumption of a wrong reaction mechanism.

The reaction of **1** with allyl glycidyl ether was studied in the second series of experiments. Signals of 6-allyloxy-5-benzyloxy-1-hexene (17%), benzyl glycidyl ether (19%) and tetraethylene glycol benzyl vinyl ether (12%) were observed as the main ones in the chromatogram of the benzylated sample. It means that potassium alkoxide with two double bonds and potassium glycidoxide as well as potassium tetraethylene glycoxide vinyl ether was formed in this process. Propylene (6.5 cm^3) was found in the liquid phase and in the gas phase before and after benzylation. Signals of low intensities of triethylene and tetraethylene glycol dimethyl ether present in the chromatogram of the methylated sample has shown that also in this case the side reactions occurred.

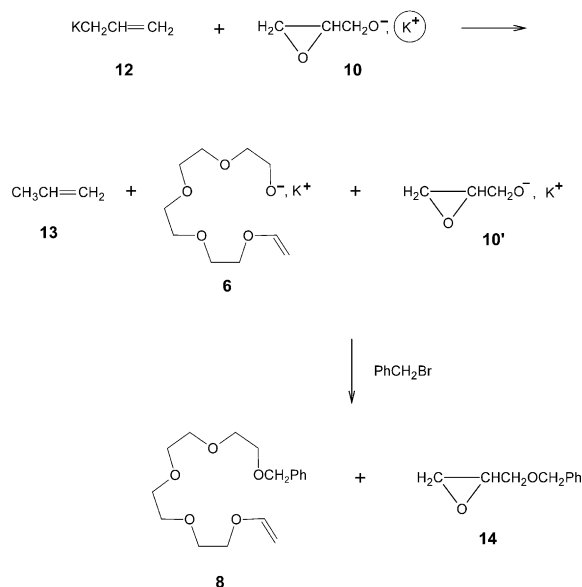
Potassium glycidoxide and propylene were assumed to be the products of the linear ether bond scission in the allyl glycidyl ether molecule. The presence of potassium tetraethylene glycoxide vinyl ether showed the crown ring opening [3,4]. Potassium 6-allyloxy-1-hexene-5-oxide seemed to be the product of the oxirane ring opening.

Thus, introduction of the allyl group into the glycidyl ether molecule instead of the saturated one fundamentally changes the course of the reaction with **1**. The cleavage of the linear ether bond takes place in this case whereas the oxirane ring remains undisturbed. It is suggested that initially one electron transfer occurs from K^+ to the double bond of allyl glycidyl ether (Scheme 2). The neighboring linear ether bond is opened and potassium glycidoxide **10** and an allyl radical **11** are

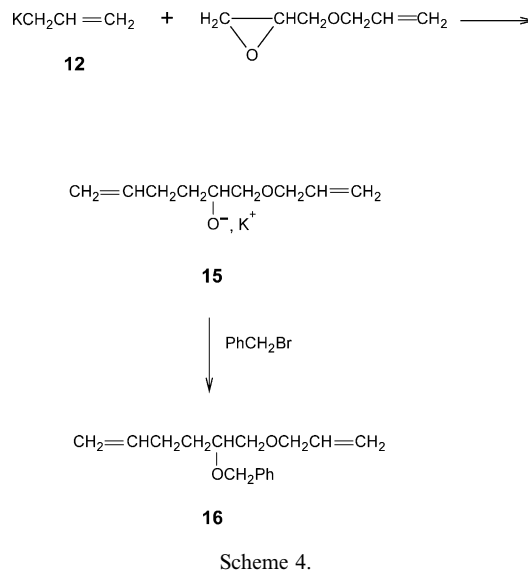


Scheme 2.

formed. Then, **11** recombines with K^0 giving allylpotassium **12**. It reacts with crown ether of **10** which results in propylene **13** and potassium tetraethylene glycoxide vinyl ether **6** with one crown ether in the complex (Scheme 3). Allylpotassium reacts also with another allyl glycidyl ether molecule (Scheme 4). The oxirane ring is opened in this case in the β -position. It leads to potassium alkoxide with two double bonds **15** and after benzylation to its benzyl derivative **16**. It should be mentioned that potassium anions do not take part in such a process. An expected product of the oxirane ring opening by **1**, i.e. potassium 1-allyloxy-2-propoxide, was not observed in the reaction mixture.



Scheme 3.

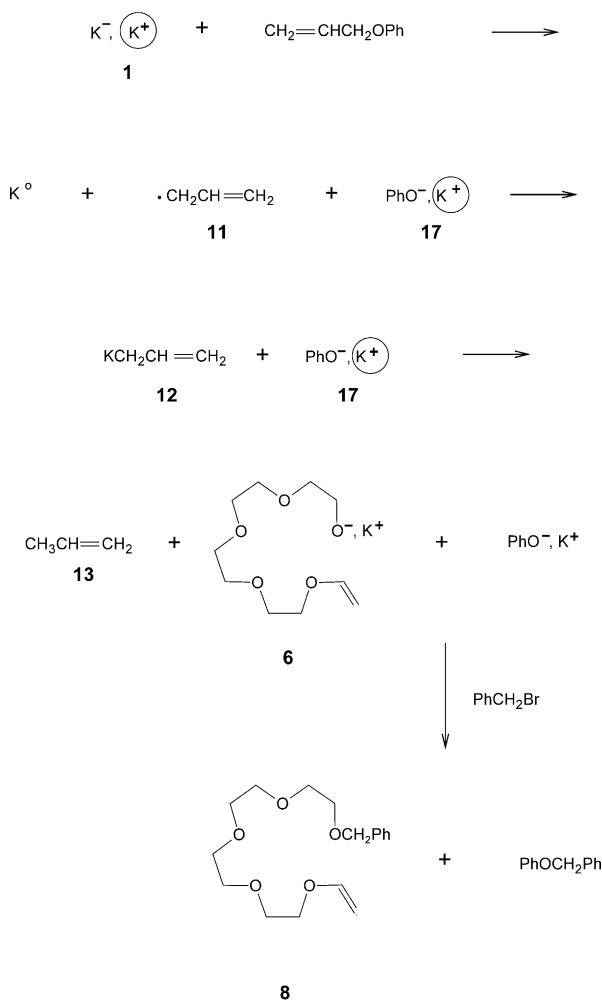


Scheme 4.

Various results of allyl ethers cleavage were presented till now in the literature. Angelo [7] found that the reaction of sodium naphthalenide, i.e. one-electron-transfer reagent, with allyl ethyl ether resulted in bialllyl (in 30% yield) as the main product. Ethanol was not isolated. Bialllyl (40%) and phenol (60%) were found in the case of allyl phenyl ether. It was suggested that the cleavage of the ether bond between the allyl carbon and the oxygen atom took place in the first step of the process and then allyl radicals formed underwent dimerization giving bialllyl. Bialllyl was also obtained by Weber [8] in the reaction of allyl methyl ether with sodium, being another one-electron-transfer reagent [9], in the presence of trimethylchlorosilane. The mechanism of this reaction was not proposed. On the other hand, Eisch [10] obtained allyllithium from allyl phenyl ether using the excess of lithium in tetrahydrofuran at $-10^\circ C$. However, Crandall [11] reported that allyl benzyl ether under the influence of lithium in tetrahydrofuran was cleaved to benzyllithium and lithium allyloxide. Allyllithium was not observed in the reaction mixture.

In such a situation we decided to check the reaction of **1** with allyl phenyl ether selected as a model compound and to confirm this way the reaction mechanism suggested for allyl glycidyl ether. Propylene, benzyl phenyl ether, and tetraethylene glycol benzyl vinyl ether were found in this case in the benzylated reaction mixture. Bialllyl was not observed. It indicated that allyl radicals formed initially did not dimerize but rather recombined with K^0 giving allylpotassium which then reacted with crown ether (Scheme 5). It seems that the rate of recombination is much faster than the rate of dimerization. Therefore, the latter can not occur in the presence of **1**.

The reactions of organometallic compounds were very fast, as it had been described already in our earlier works [2–4]. Their volatile derivatives were not observed



Scheme 5.

in benzylated or methylated samples in spite of the fact that the reaction mixture was treated with benzyl bromide or methyl iodide immediately after mixing of reagents.

It is necessary to emphasize that in all experiments the blue potassium alkali solution was dropped into the excess of glycidyl ethers. That resulted in low reaction yields, however, only under such conditions the original reaction products could be detected. In other cases, i.e. at the excess of **1** or even at the molar ratio of reagents close to 1:1, further reactions are expected to occur with the participation of potassium anions [12]. A mixture of various compounds can be finally formed and sometimes without the original reaction product or products. Therefore, one may draw misleading conclusions concerning the reaction mechanism.

3. Conclusions

The course of the reaction of **1** with selected alkyl glycidyl ethers depends on the kind of substituent. In the

case of saturated butyl substituent the oxirane ring is exclusively opened in the glycidyl ether molecule. The presence of the allyl group prefers the cleavage of the linear ether bond. It results in the formation of potassium alkoxide containing undisturbed oxirane ring, i.e. potassium glycidoxide. The selective linear ether bond scission in allyl glycidyl ether by **1** may be explained by a greater tendency to receive the electron by the unsaturated group rather than by the oxirane ring.

15-Crown-5 plays a dual role in the studied systems. It takes part in the occurring processes both as the complexing agent and as the reagent. Its oxacyclic ring is opened easily in the reactions with organometallic intermediates. Potassium tetraethylene glycolate vinyl ether is the product of this reaction.

A mixture of potassium alkoxides is formed in both series of experiments. It can be assumed that these alkoxides can be the real initiators in the polymerization of selected glycidyl ethers by potassium alkali.

4. Experimental

GC–MS analyses were run on a 30 m long DB 1701 fused silica capillary column, using a Varian 3300 gas chromatograph equipped with a Finnigan MAT 800 AT ion trap detector. Diethylene glycol dimethyl ether was used as the internal standard for the yield measurement. Gaseous products were searched for by gas chromatography (GC) with a 2.4 m long stainless steel column packed with Al_2O_3 , 0.2–0.3 mm, deactivated with 5% K_2CO_3 , in an INCO 505 gas chromatograph equipped with a flame ionization detector. ^1H - and ^{13}C -NMR spectra were recorded at 20 °C on a Varian VXR-300 multinuclear pulsed spectrometer operating at the ^1H resonance frequency of 300 MHz, and the ^{13}C resonance frequency of 75 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard for ^1H and ^{13}C measurements. Deuterated chloroform was used as the solvent. Proton signals assignment was done using a MestRe-C 2.3a spectrum simulator. Signals assignment in the ^{13}C spectra was done using a DEPT and HETCOR correlation technique.

Butyl glycidyl ether (Aldrich) and allyl glycidyl ether (Aldrich) were heated over CaH_2 for 6 h and then distilled under dry argon atmosphere; the fractions boiling at 165 and 154 °C were collected, respectively. Allyl phenyl ether (Aldrich) was distilled at 192 °C and used as a model compound. Tetrahydrofuran (POCH) was boiled over CuCl to decompose peroxides, then over CaH_2 for 10 h, and finally it was distilled at 66 °C. This fraction was dried over metallic potassium for 20 h and redistilled prior to use. 15-Crown-5 (Aldrich) was dried under vacuum at 50 °C for 8 h. Potassium (Fluka) was purified in boiling tetrahydrofuran and then distilled

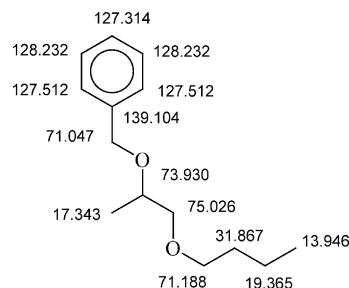
under high vacuum into a reactor described in [13]. Blue solution (0.1 M) of K^+ , K^+ (15-crown-5)₂ was obtained by dissolution of the potassium mirror in 0.2 M 15-crown-5 tetrahydrofuran solution at 25 °C as in [14]. The metal–solvent contact time was equal to 25 min. The reaction of glycidyl ether with potassium anions was conducted under dry argon atmosphere at 25 °C. Ten cubic centimeter of 0.1 M K^+ , K^+ (15-crown-5)₂ blue solution was dropped into 10 cm³ of 0.5 M butyl or allyl glycidyl ether in tetrahydrofuran solution while mixing, i.e. glycidyl ether was still at the excess. The reaction was very fast. Potassium anions vanished instantaneously in the system after mixing of reagents. It was easy to observe during experiments because the blue potassium solution becomes colorless at the same time [13]. Then, the reaction mixture was immediately treated with benzyl bromide or methyl iodide as the quenching agent. The obtained compounds were identified by matching their mass spectra, retention times, and NMR spectra with those of authentic compounds. The reaction of allyl phenyl ether with K^+ , K^+ (15-crown-5)₂ and the analysis of its products were conducted at the same conditions as for glycidyl ethers.

4.1. 1-Butoxy-2-propanol

A mixture of 0.5 mol 1,2-propanediol, 0.1 mol 1-bromobutane, 150 cm³ 50% aqueous (aq.) NaOH, and 0.01 mol tetrabutylammonium hydrogensulfate has been stirred and heated on a water bath for 3 h at 80–90 °C. After cooling 100 cm³ hexane and 500 cm³ water has been added. The layers have been separated, the organic layer has been washed three times with 20 cm³ water and dried with anhydrous MgSO₄. The product has been distilled and 1-butoxy-2-propanol was obtained in 80% yield (purity 93%; contained 7% of 2-butoxy-1-propanol). Boiling point (b.p.) = 169–172 °C per 760 mmHg.

4.2. 1-Butoxy-2-benzyloxypropane (7)

A mixture of 0.1 mol 1-butoxy-2-propanol, 0.11 mol benzyl chloride, 0.4 mol powdered NaOH, 0.01 mol tetrabutylammonium hydrogensulfate, and 60 cm³ toluene has been intensively stirred in 50–60 °C on a water bath for 3 h. After cooling 100 cm³ water and 100 cm³ hexane has been added. The layers have been separated, the organic layer has been washed three times with 20 cm³ water and dried with anhydrous MgSO₄. Having removed hexane and toluene on a rotatory evaporator the residue has been distilled under reduced pressure. 1-Butoxy-2-benzyloxypropane has been finally obtained in 75% yield (purity 95%; contained 5% 2-butoxy-1-benzyloxypropane). B.p. = 106–107 °C per 1 mmHg. ¹³C-NMR CDCl₃ δ:



¹H-NMR CDCl₃ δ 7.38–7.17 (m, 5H, Ph–); 4.572 (s, 2H, Ph–CH₂–); 3.669 (ddd, 1H, CH₃–CH–, *J* = 6.2 Hz, *J* = 6.2 Hz, *J* = 4.8 Hz); 3.466 (dd, 1H, CH₃–CH–CH₂–O–, *J*_{gem} = –9.9 Hz, *J* = 6.2 Hz); 3.406 (t, 2H, –O–CH₂–CH₂–CH₂–CH₃, *J* = 6.6 Hz); 3.337 (dd, 1H, CH₃–CH–CH₂–O–, *J*_{gem} = 9.9 Hz, *J* = 4.8 Hz); 1.544 (tt, 2H, –O–CH₂–CH₂–CH₂–CH₃, *J* = 7.0 Hz, *J* = 6.6 Hz); 1.367 (qt, 2H, –O–CH₂–CH₂–CH₂–CH₃, *J* = 7.3 Hz, *J* = 7.0 Hz); 1.160 (d, 3H, CH₃–CH–CH₂–O–, *J* = 6.2 Hz); 0.906 (t, 3H, –O–CH₂–CH₂–CH₂–CH₃, *J* = 7.3 Hz). MS *m/z* (%) 222 [*M*⁺, 6], 148 (40), 135 (12), 107 (30), 91 (100), 87 (10), 65 (15), 57 (78), 41 (17).

4.3. Tetraethylene glycol benzyl vinyl ether (8)

The method of its preparation as well as its ¹H-, ¹³C-NMR and mass spectra were described in [3].

4.4. Benzyl glycidyl ether (12)

Its ¹H- and ¹³C-NMR spectra were described in [15]. MS *m/z* (%) 164 [*M*⁺, 25], 107 (86), 91 (100), 79 (64), 65 (43), 57 (18), 51 (18), 39 (18).

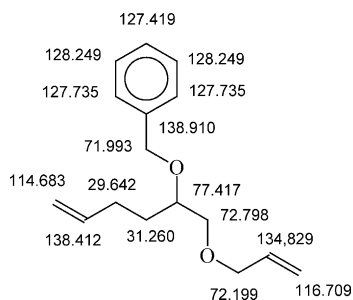
4.5. 1-Allyloxy-5-hexen-2-ol

A mixture of 0.1 mol 1,2-epoxy-5-hexene, 0.6 mol allyl alcohol, 0.3 mol powdered NaOH and 0.01 mol tetrabutylammonium hydrogensulfate has been intensively stirred in 50–60 °C on a water bath for 3 h. After cooling, 200 cm³ water and 100 cm³ hexane have been added. The layers have been separated, the organic layer has been washed three times with 20 cm³ of water and dried with anhydrous MgSO₄. Volatile constituents (mostly hexane) have been removed by distillation on a rotatory evaporator. The residue has been distilled under reduced pressure. 1-Allyloxy-5-hexen-2-ol has been obtained in 60% yield. B.p. = 59–60 °C per 1 mmHg.

4.6. 6-Allyloxy-5-benzyloxy-1-hexene (16)

A mixture of 0.05 mol 1-allyloxy-5-hexen-2-ol, 0.55 mol benzyl chloride, 0.17 mol powdered NaOH, 0.005 mol tetrabutylammonium hydrogensulfate and 40 cm³ toluene has been stirred intensively in 50–60 °C on a

water bath for 3 h. After cooling 100 cm³ water and 100 cm³ hexane have been added. The layers have been separated, the organic layer has been washed three times with 20 cm³ water and dried with anhydrous MgSO₄. Volatile constituents (mostly hexane and toluene) have been removed by distillation on a rotatory evaporator. The residue has been distilled under reduced pressure. Finally, 6-allyloxy-5-benzyloxy-1-hexene has been obtained in 70% yield. B.p. = 118 °C per 1 mmHg. ¹³C-NMR CDCl₃ δ:



¹H-NMR CDCl₃ δ 7.38–7.18 (m, 5H, Ph–); 5.873 (ddt, 1H, –O–CH₂–CH=CH₂, *J* = 17.2 Hz, *J* = 10.6 Hz, *J* = 5.5 Hz); 5.771 (ddt, 1H, CH₂=CH–CH₂–CH₂–, *J* = 16.8 Hz, *J* = 10.2 Hz, *J* = 6.6 Hz); 5.254 (dtd, 1H, –O–CH₂–CH=CH₂–*cis*, *J* = 17.2 Hz, *J* = 1.4 Hz, *J* = 1.3 Hz); 5.142 (dtd, 1H, –O–CH₂–CH=CH₂–*trans*, *J* = 10.6 Hz, *J* = 1.8 Hz, *J* = 1.3 Hz); 4.983 (dtd, 1H, *cis*–CH₂=CH–CH₂–CH₂–, *J* = 16.8 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz); 4.931 (dtd, 1H, *trans*–CH₂=CH–CH₂–CH₂–, *J* = 10.2 Hz, *J* = 1.8 Hz, *J* = 1.3 Hz); 4.664, 4.521 (qAB, 2H, Ph–CH₂–, *J*_{AB} = 11.7 Hz); 3.956 (ddd, 2H, –O–CH₂–CH=CH₂, *J* = 5.5 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz); 3.557 (dddd, 1H, CH₂=CH–CH₂–CH₂–CH–, *J* = 7.6 Hz, *J* = 5.8 Hz, *J* = 4.5 Hz, *J* = 4.3 Hz); 3.493 (dd, 1H, –CH–CH₂–O–, *J*_{gem} = –10.1 Hz, *J* = 5.8 Hz); 3.438 (dd, 1H, –CH–CH₂–O–, *J*_{gem} = –10.1 Hz, *J* = 4.3 Hz); 2.183 (dddd, 1H, CH₂=CH–CH₂–CH₂–, *J*_{gem} = –14.7 Hz, *J* = 6.8 Hz, *J* = 6.6 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz); 2.100 (dddd, 1H, CH₂=CH–CH₂–CH₂–, *J*_{gem} = –14.7 Hz, *J* = 7.3 Hz, *J* = 6.6 Hz, *J* = 1.8 Hz, *J* = 1.4 Hz); 1.634 (ddd, 1H, CH₂=CH–CH₂–CH₂–, *J*_{gem} = –13.6 Hz, *J* = 7.6 Hz, *J* = 7.3 Hz); 1.611 (ddd, 1H, CH₂=CH–CH₂–CH₂–, *J*_{gem} = –13.6 Hz, *J* = 6.8 Hz, *J* = 4.5 Hz). MS *m/z* (%) 246 [M⁺, 2], 188 (2), 175 (21), 157 (15), 131 (4), 107 (28), 91 (100), 71 (20), 64 (20), 41 (40).

4.7. Benzyl phenyl ether (19)

Its ¹H-, ¹³C-NMR and mass spectra were described in [2].

Tri- and tetraethylene glycol dimethyl ethers. Their ¹H-, ¹³C-NMR and mass spectra were described in [3].

To the best of our knowledge two of these compounds, i.e. 1-butoxy-2-benzyloxypropane (7) and 6-allyloxy-5-benzyloxy-1-hexene (16) were till now not described in the literature.

Acknowledgements

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