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Journal of Molecular Catalysis A: Chemical 219 (2004) 29–40
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
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Isomerization of allyl aryl ethers to their 1-propenyl derivatives catalysed by ruthenium complexes

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Received 27 February 2004; received in revised form 27 April 2004; accepted 27 April 2004

Available online 15 June 2004

Abstract

The results of double-bond migration in allyl aryl ethers catalysed by ruthenium complexes, mainly by $[RuClH(CO)(PPh_3)_3]$ have been presented. The conversion of allyl to 1-propenyl ethers is quantitative. High *E*/*Z* selectivity of some 1-propenyl ethers has been achieved by the application of $[RuCl_2(COD)]_x + PR_3$ catalytic system (also with addition of inorganic hydrides). An explanation of *E*/*Z* selectivity control based on transition state of β-elimination has been proposed. The results are supplemented with elements of coordination effects of reactants, solvent influence and catalyst activity on chosen models. Separation of the 1-propenyl ethers might be achieved by simple techniques—distillation or crystallization. Moreover, it has been shown that less stable products, such as (4-aminophenyl) (1-propenyl) ether, might be separated from the reaction mixture using functionalized siliceous mesoporous cellular foams.

Keywords: Allyl ethers; Isomerization; Double bond migration; Ruthenium complexes; Siliceous mesoporous cellular foams; 1-propenyl ethers

1. Introduction

Double bond migration in allyl ether is catalysed by bases [1–3], metals on activated coal [4] and transition metal complexes: cobalt [5], nickel [6], palladium [7–9], rhodium [10,11]. There are many reports on isomerization on ruthenium complexes with carbene [12], aqua [13], Cp [14], carbonyl [15,16], hydride [17,18] ligands. Simple ruthenium hydride $[RuClH(CO)(PPh_3)_3]$ and dichloride $[RuCl_2(PPh_3)_3]$ complex were successfully applied to double-bond migration of functionalized alkenes [19], allyl alkyl ethers [20,21]. Also, our group has already reported successful isomerization of allyl ethers to their 1-propenyl derivatives on various ruthenium complexes [22–26].

Double bond migration is often conducted as the first step of tandem isomerization-metathesis or RCM, leading to many interesting heterocycles [27–29]. Isomerization might also be a competitive reaction for metathesis of some allyl systems [30]. Also, the double-bond migration products, i.e. 1-propenyl ethers are investigated as interesting monomers in cationic oligo- [16], photo- [20,21,31], and co-polymerisation [32]. *O*-Allyl systems serve often as protecting groups [33]. Deprotecting is carried out by double-bond migration of 1-propenyl derivative and its hydrolysis or reduction [34,35]. Here, we report our method of isomerization of substituted allyl aryl ethers with ruthenium complexes (Scheme 1). The advantages of our method are: convenience, tiny amount of catalyst used, moderate conditions and easy work-up.

2. Results and discussion

2.1. Isomerization of allyl aryl ethers

Isomerization of allyl aryl ethers in most cases is successful in moderate temperatures (60–80 °C), within 4 h (Table 1). The amount of the catalyst, $[RuClH(CO)(PPh_3)_3]$ is usually lower than 2%. Few exceptions from these

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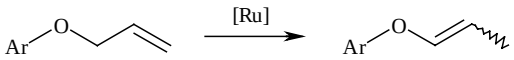
doi:10.1016/j.molcata.2004.04.039



Scheme 1. Isomerization of allyl aryl ethers with ruthenium complexes.

conditions are due to strong coordinating properties of substituents or their position as they exert steric hindrance on the reaction centre (for example: **14**, **22**).

Allyl (2-formylphenyl) ether **14** and its acetal **15** deserve some extra attention. While isomerization of aldehyde is difficult (also on Pd catalyst [9]) due to its strong coordination properties enhanced by *ortho* position of formyl group, which enables chelation, its acetal might be isomerized without any "special endeavour". The dominance of coordination and especially chelation effects (in comparison with the other isomer **16**) are undoubtedly proved.

We attempted the isomerization of 2,4,6-triallyloxy-1,3,5-triazine **29** and allyl pentachlorophenyl ether **30**, but, unfortunately, the conversion was unsatisfactory (**29**: $\varepsilon = 45\%$; 5% $[RuH_2(PPh_3)_4]$, 160 °C, 6 h in tetrachloroethene and **30**: $\varepsilon = 72\%$; 5% $[RuClH(CO)(PPh_3)_3]$, 160 °C, 6.5 h in tetrachloroethene, respectively). Many products of decomposition were observed for higher conversions, this is why we were not able to give full spectroscopic identification for these compounds. It is interesting to compare 2,4,6-triallyloxy-1,3,5-triazine **29** with allyl 2-pyridyl ether **24**. In triazine, each allyl group may coordinate with chelation, thus double-bond migration involving all the catalytic steps including dissociation of metal is more difficult, which might be observed from the results. We can also find similarities between allyl *o*-chlorophenyl ether **1** and allyl pentachlorophenyl ether **30**, where there are twice as much of Cl groups close to the reaction center. Additionally, pentachlorinated phenyl ring is a much better π-acceptor and thus it may coordinate to metal. We have proved strong coordination effects while attempting isomerizing allyl phenyl ether and allylbenzene with addition of **29**, **30** or perchlorocyclopentadiene (60 °C, 3 h, 1% $[RuClH(CO)(PPh_3)_3]$). No double-bond migration was observed, while allyl phenyl ether or allylbenzene isomerize very easily in these conditions.

In many cases the formation of new species from precatalyst $[RuClH(CO)(PPh_3)_3]$ and allyl ether is even visible: intensive bordeaux is observed during the isomerization of allyl (4-aminophenyl) ether, deep blue for 1,2-bisallyloxybenzene, blue-green for allyl (2-hydroxyphenyl) ether.

Table 1
Isomerization of allyl aryl ethers Q–O–CH_2–CH=CH_2 catalysed by $[RuClH(CO)(PPh_3)_3]$

No.	Q	Ru (%)	Solvent	t (°C); τ (h)	ε (%)	E/Z
1	*o*-Cl–C_6H_4–	1.00	C_6D_6; 0.32	50; 2	100	0.18
2	*m*-Cl–C_6H_4–	0.80	C_6D_6; 0.62	50; 2	100	0.25
3	*p*-Cl–C_6H_4–	0.88	C_6D_6; 0.67	50; 2	100	0.37
4	*o*-Br–C_6H_4–	0.55	THF; 0.43	80; 3	100	0.40
5	*m*-Br–C_6H_4–	0.50	THF; 2.13	60; 2	100	0.38
6	*o*-Me–C_6H_4–	1.00	CH_2Cl_2; 0.30	50; 2	100	0.52
7	*p*-Me–C_6H_4–	0.78	CH_2Cl_2; 0.30	50; 2	100	0.38
8	*o*-MeO–C_6H_4–	1.00	C_6H_6; 1.64	60; 3	100	0.45
9	*p*-MeO–C_6H_4–	1.00	C_6H_6; 0.64	50; 2	100	0.45
10	*o*-NO_2–C_6H_4–	1.00	CH_2Cl_2; 0.54	60; 3	100	0.45
11	*m*-NO_2–C_6H_4–	1.00	THF; 1.78	80; 2	100	0.44
12	*p*-NO_2–C_6H_4–	0.80	C_6D_6; 1.78	50; 2	100	0.33
13	*o*-HO–C_6H_4–	1.00	1,4-Dioxane; 0.32	130; 2	100	0.60
14	*o*-OHC-C_6H_4–	2.00	C_6H_6; 1.80	60; 4	70	Only *Z*
15	*o*-$(MeO)_2CH$–C_6H_4–	1.50	C_6H_6; 1.60	60; 3	100	0.31
16	*p*-OHC–C_6H_4–	0.80	CH_2Cl_2; 1.62	60; 3	100	0.38
17	*p*-Ac–C_6H_4–	1.00	THF; 1.75	60; 2	100	0.43
18	*p*-AcNH–C_6H_4–	1.00	THF; 1.92	60; 3	100	0.40
19	*p*-NH_2–C_6H_4–	2.00	C_6H_6; 1.85	80; 2	100	0.41
20	*p*-NC–C_6H_4–	2.00	C_6H_6; 1.59	60; 3	100	0.24
21	*p*-$HOCH_2$–C_6H_4–	1.50	CH_2Cl_2; 3.30	50; 2	100[a]	0.40
22	2,4,6-tribromophenyl–	5.00	Xylene; 3.70	140[b]; 4	100	Only *Z*
23	3-OH–4-PhC(O)–	1.33	–	120; 2	100	0.43
24	2-Pyridyl–	5.00	Xylene; 1.35	140[b]; 4	100	0.20
25	*o*-Allyl–O–C_6H_4–	1.00	C_6H_6; 0.57	60; 3	100	–[c]
26	*p*-Allyl–O–C_6H_4–	0.50	THF; 1.89	60; 2	100	–[c]
27	*o*-Allyl–C_6H_4–	0.50	THF; 2.17	60; 2	100	–[c]
28	*p*-(Allyl–O–CH_2)–C_6H_4–	0.80	THF; 2.04	80; 2	100	–[c]

No: entry number; %Ru: molar percentage of the catalyst in respect to allyl ether; Solvent (cm^3/mmol of substrate); t: temperature; τ: reaction time; ε: conversion of allyl to 1-propenyl ether; E/Z: ratio of *E* over *Z* products.

[a] 90% selectivity: 10% of reagent was got oxidized to (4-formylphenyl) (1-propenyl) ether.

[b] Reflux of reaction mixture.

[c] Since both allyl groups isomerize to 1-propenyl, undetermined mixture of isomers.

It is important to add, that even if the isomerization of allyl aryl ethers is carried out at high temperatures (130–160 °C), it does not lead to Claisen rearrangements [36–38], neither to any other products of C–O bond cleavage, which requires at least additional irradiation [39].

2.2. Mechanism of double-bond migration

Our previous research [22] supported by general observations [40–42] that addition and consecutive β-elimination of hydride species is the dominant mechanism for double bond migration catalysed by hydride complexes. Grubbs and McGrath [43] have proved, that also non-hydride complexes, such as $[Ru(H_2O)(tos)_2]$ do isomerize alkenes and unsaturated alcohols via hydride mechanism. On the other hand, polycarbonyl ruthenium complexes are known for their hydride–π-allyl transient complex [40,44].

2.3. Selectivity of double bond migration towards Z or E isomer

In order to achieve high stereoselectivity modification of the catalytic system was considered. Our attempts at the synthesis of appropriate $[RuClH(CO)(PAr_3)_3]$ derivatives with other aryl phosphines P(1-naphthyl)$_3$, P(*o*-tollyl)$_3$ and tris(2,6-dimethoxyphenyl)phosphine applying similar method as for $[RuClH(CO)(PPh_3)_3]$ led to inactive complexes as double-bond migration catalysts.

An alternative way to control the bulkiness of ligands of the catalyst was to form the catalyst in situ $[RuCl_2(cod)]_x + PR_3$ (Table 2).

While plain $[RuCl_2(COD)]_x$ does not isomerize allyl ethers, external addition of phosphine not only enables its application as a double-bond migration catalyst, but also completely changes the isomeric product composition. The most characteristic feature of this catalytic system is that the ratio of *E*/*Z* is reversed. While *Z* isomer, as more stable [45], is dominant for regular catalysis with $[RuClH(CO)(PPh_3)_3]$, here *E* isomer is superior. In some cases, i.e. allyl *ortho*-bromophenyl ether, *Z* isomer amounts to 5% of the product. It is interesting that allyl *o*-nitrophenyl ether does not isomerize at all in these conditions.

The application of any other available phosphines (PR_3, R: 2,6-$(MeO)_2C_6H_3$; 1-pyrolidynyl; Bu; OPh; *o*-Tollyl), has not led to any higher *E*/*Z* selectivity accompanied with high conversion towards 1-propenyl ethers. Also, none of the tested catalytic precursors ($[RuCl_2(C_6H_6)]_2$, $[RuCl_2(NDB)]_x$, $[Rh_2Cl_2(COD)_2]$) were active in the reaction conditions. The results given in Table 2 are optimised in respect with the amount of the catalyst, time, temperature and phosphine over precursor ratio. Solvent was also optimised and slightly worse results were obtained using toluene, while very low conversion was achieved in THF and tetrachloroethene.

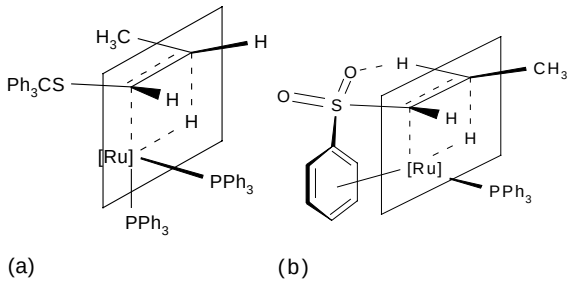


Fig. 1. Transition state of β-elimination for *S*-allyl systems.

How to explain such an *umpolung* in *E*/*Z* selectivity depending on the catalytic system used? We have already encountered other high selectivity dependence for *N*-allyl systems [46,47] and sulphones [48]. Selectivity among *N*-allyl-*N*-arylacetamides is most likely a result of the coordination effects of transient complex with aryl ring, which is in good agreement with quantum calculations. There, (*E*)-enamides were the only products of double-bond migration. We suspect that similar interactions of metal centre and aryl ring result in the isomerization of ally sulphones to (*E*)-1-propenyl isomers exclusively (Fig. 1b). In contrast, bulky allyl sulphides isomerize mainly to the products of *Z* geometry, most likely because of steric interactions in the transition state (Fig. 1a).

Controlling the bulkiness of externally added phosphines to the precursor $[RuCl_2(COD)]_x$ influences the number of phosphines, which are coordinated in the transition state of β-elimination. Such a superposition of relative electronic and steric properties [49] together with the possibility of coordination of aryl ring, might be a quantized response, which of the transient structures (2a or 2b) in β-elimination is dominant (Fig. 2).

Table 2
Isomerization of allyl-aryl ethers (Q-O-Allyl), with in situ catalytic system: $[RuCl_2(COD)]_x + PR_3$ (Ru:PR_3 = 1:1; solvent: 1,4-dioxane)

Q	Allyl/Ru	PR_3	H/Ru	Solvent	t (°C); τ (h)	ε; *E*/*Z*
o-Cl–C_6H_4–	50	{2,4,6-$(MeO)_3C_6H_2$}$_3$P	–	1.7	3; 120	90; 3.3
o-Br–C_6H_4–	39	{2,4,6-$(MeO)_3C_6H_2$}$_3$P	–	1.3	3; 120	100; 20.8
o-Me–C_6H_4–	25	{2,4,6-$(MeO)_3C_6H_2$}$_3$P	–	1.5	4; 120	100; 5.8
o-MeO–C_6H_4–	25	{2,4,6-$(MeO)_3C_6H_2$}$_3$P	–	1.6	4; 120	100; 8.4
Ph–	56	PPh_3	$NaBH_4$; 6	1.3	2; 100	100; 2.3

Allyl/Ru: molar ratio of allyl ether to ruthenium complex; H/Ru: inorganic hydride, molar ratio of the hydride over ruthenium complex; solvent (cm^3/mmol of substrate); t: temperature; τ: reaction time; ε: conversion of allyl to 1-propenyl ether; *E*/*Z*: ratio of *E* over *Z* products.

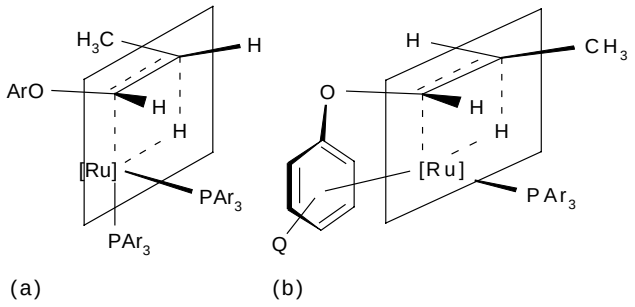


Fig. 2. Transition state of β-elimination for allyl aryl ethers.

Transition state is divided by Ru–C–C–H surface on two subspaces. If added phosphine has moderate bulkiness, like PPh_3 in $[RuClH(CO)(PPh_3)_3]$, two or even three such phosphines might be coordinated in the transition state resulting in **16** or even **18e** ruthenium species with highly crowded phosphines on one of the subspaces (Fig. 2a). This impedes Ru···Ar interactions. Formation of *Z* isomer is dominant. On the other hand, if bulky phosphine is coordinated in the transition state, we assume, that only one such phosphine might by coordinated at once, which enables Ru···Ar interactions. Surprisingly, there might be enough room for the methyl terminal group to fit in the "phosphine subspace". These factors might force the formation of *E* isomers. Such a coordination of only one of the bulky phosphines in the transition state of β-elimination is consistent with our observations that any increase of the ratio phosphine/precursor does not influence selectivity, but only decreases the conversion to 1-propenyl ethers. This decrease in the conversion is most likely due to shifting the equilibrium of coordination of alkene (allyl system) competing with the coordination of phosphine. Yanlong et al. [50] have proposed an interesting explanation of selective isomerization of alkenes using titanocene catalysts. They claim that auxiliary coordination of Cp substituents may diametrically change selectivity.

In order to facilitate the formation of hydridoruthenium complex in situ, additional source of hydride was inserted to the reaction mixture—stable inorganic hydrides: $NaBH_4$, $LiAlH_4$, CaH_2, NaH (in oil). Similar systems have been already successfully applied for double-bond migration of complex polyether antibiotics [51]. Unfortunately, although inorganic hydrides might serve as a source of hydrogen ligand, their influence on *E*/*Z* selectivity and conversion is hard to forecast (see Table 3).

The relative basicity of inorganic hydrides and very important factors like moisture of the hydride, solvent and other reagents used, might strongly influence the result. This field still needs further research.

2.4. Coordination effects

All the steps of the double-bond migration mechanism are reversible, no matter if it is: (a) hydride mechanism; or such with (b) transient hydride–π-allyl complex. For the mechanism (a), 1,2-insertion of coordinated alkene to Ru–H bond or β-elimination might be the rate-determining step. While for mechanism (b), the slowest step is oxidative addition leading to the formation of hydride–π-allyl complex. From the macroscopic point of view, such important factors as the rate of homogenisation of the precatalyst (see Section 2.6 for solvent effects), formation of the real catalyst (since the precatalyst—$[RuClH(CO)(PPh_3)_3]$ is **18e** species), which is involved in the catalytic cycle may strongly influence the overall rate. These two factors are certainly connected with homogenisation, which is in equilibrium with ligand dissociation and formation of the real catalyst. There is an additional set of equilibrium reactions, like coordination of the catalyst by substrate, products or products of decomposition. Such coordination effects might strongly retard the desired reaction or even kill the catalyst by its fast and permanent coordination, which was already reported by us for some allyl sulphides [48]. In order to estimate the coordination impact of some of the allyl ethers in the course of reaction, a set of experiments were prepared: isomerization of allyl phenyl ether together with equimolar amount of the researched ether in constant conditions. The results are presented in Table 4.

Allyl phenyl ether isomerizes in these conditions with 81% conversion to phenyl (1-propenyl) ether. Such a set of comparisons made it possible for us to evaluate coordination power of most of the allyl ethers described in this work. Comparing allyl ethers with *para* substituents, cyano-, and formyl- groups are of the highest coordination power, than acetyl or acetylamide. Methyl, metoxyl and halogens in *para* positions exert weak influence, just like *m*-Cl substituent. The steric hindrance of bulky groups (NO_2 observed for *N*-allyl(*o*-nitrophenyl)ethanamide [46]) in *ortho* positions are clearly observed, with one exception of *o*-Br derivative, which could not be explained on the grants of the mentioned theories. It is important to add that no simple Hammet's correlation [52] has been found for this set of allyl ethers derivatives. The ratio of relative conversion of allyl phenyl and the additional ether is close to 1 (±0.1), thus it proves the coordination impact on both ethers.

Table 3
Isomerization of allyl aryl ethers (Q–O–Allyl) catalysed by $[RuCl_2(cod)]_x + PR_3$ system with addition of inorganic hydrides

Q	Allyl/Ru	PR_3	H/Ru	Solvent	*t* (°C); *τ* (h)	*ε*; *E*/*Z*
Ph–	56	PPh_3	$NaBH_4$; 6	1,4-Dioxane; 1.3	2; 100	100; 2.30
Ph–	59	PPh_3	$LiAlH_4$; 3	1,4-Dioxane; 1.3	2; 100	100; 1.45
o-MeO–C_6H_4–	25	$\{2,4,6\text{-}(MeO)_3C_6H_2\}_3P$	$LiAlH_4$; 5	1,4-Dioxane; 1.6	4; 120	100; 6.90

Allyl/Ru: molar ratio of allyl ether to ruthenium complex; H/Ru: inorganic hydride, molar ratio of the hydride over ruthenium complex; solvent (cm^3/mmol of substrate); *t*: temperature; *τ*: reaction time; *ε*: conversion of allyl to 1-propenyl ether; *E*/*Z*: ratio of *E* over *Z* products.

Table 4
Comparative isomerization of allyl phenyl ether and researched ether in order to estimate the coordination effect of given ether (0.65% mol $[RuClH(CO)(PPh_3)_3]$, 40 °C, 2 h, benzene)

X–C_6H_4–O–Allyl; additional ether X:	$1_{AllylOPh}/\varepsilon_{AllylOPh}$
o-Me	1.5
p-Me	1.2
o-MeO	1.7
p-MeO	1.1
o-Cl	1.8
m-Cl	1.1
p-Cl	1.1
o-Br	1.0
p-Br	1.1
o-NO_2	4.4
p-NO_2	1.9
p-Ac	2.7
p-CN	16.2
p-CHO	13.5
p-AcNH	3.4

$\varepsilon^0{}_{AllylOPh}/\varepsilon_{AllylOPh}$: ratio of conversion of allyl phenyl ether without additional ether (conversion 81%) and with the ether added.

2.5. Catalyst

The most universal and also the most efficient catalyst for double-bond migration in allyl aryl ethers is $[RuClH(CO)(PPh_3)_3]$. Slightly worse results might be obtained using $[Ru(CO)_3(PPh_3)_2]$. $[RuCl_2(PPh_3)_3]$ is less active than the complex mentioned above, although it is frequently used for double-bond migration [20,21]. Rhodium catalysts, such as $[RhH(CO)(PPh_3)_3]$ show much lower activity in the isomerization of allyl ethers. It is interesting that the application of $[RuH_2(PPh_3)_4]$ was successful only in one case—isomerization of 2,4,6-triallyloxy-1,3,5-triazine **29** (Table 5). Although the isomerization was never complete and the product was not separated from the reaction mixture, the last mentioned complex worked for this reaction with the highest conversion (Table 5). Probably the other complexes were permanently coordinated by triazine, which disabled isomerization. On the other hand, the application of $[RuH_2(PPh_3)_4]$ to isomerization of allyl 2-pyridyl ether **24** did not lead to double-bond migration.

The catalytic system formed in situ non-phosphine ruthenium complex with external addition of phosphine is described in Section 2.3.

Table 5
Isomerization of 2,4,6-triallyloxy-1,3,5-triazine **29** (precatalyst: 5% mol, 160 °C, 6 h, solvent: tetrachloroethene)

Precatalyst	ε (%)
$[RuClH(CO)(PPh_3)_3]$	0
$[RuH_2(CO)(PPh_3)_3]$	0
$[RuCl_2(PPh_3)_3]$	40
$[RuH_2(PPh_3)_4]$	83

Table 6
Isomerization of allyl phenyl ether with 0.87% mol of $[RuCl_2(PPh_3)_3]$, 100 °C, 4 h

Solvent	Conversion (%)
THF	78
1,4-Dioxane	57
C_6H_6	40
CH_2Cl_2	40
$CHCl_3$	20
EtBr	20

2.6. Solvent

We have done series of double-bond isomerization with allyl phenyl ether, various solvents (EtBr, CH_2Cl_2, $CHCl_3$, C_6H_6, THF, CF_3CH_2OH, MeOH, tetrachloroethene) and various catalysts (0.87 mol.% of $[Ru(CO)_3(PPh_3)_2]$, $[RuClH(CO)(PPh_3)_3]$ in different reaction conditions 40; 80; 100 °C, 4 h. No solvent effect was observed—the conversion to phenyl (1-propenyl) ether was always above 98%. This is the most frequent case for the most active catalyst and allyl systems which isomerize quickly, i.e. which do not contain any strongly coordinating substituents and do not have bulky group in the neighbourhood of the reaction centre. The influence of solvent on the reaction is better observed for less active catalysts, such as $[RuCl_2(PPh_3)_3]$ (see Table 6).

THF is usually the most effective solvent probably due to its moderate polarity and coordinating properties. In these conditions, such active solvents, as EtBr, $CHCl_3$ or CH_2Cl_2, which may react with the Ru complexes by oxidative addition to C–X bond, most likely deactivate the catalyst resulting in a decreased conversion. Another solvent dependence is well seen for the isomerization of allyl (2-bromophenyl) ether, which contains quite bulky group near the reaction centre (Table 7).

These results are consistent with our previous findings for allyl trisubstituted silanes [53]. Relatively strong coordination properties of CH_3CN, the presence of acidic hydrogen in CH_3OH and $CHCl_3$ are the most important factors causing such a low conversion. The elimination or substitution

Table 7
Isomerization of allyl (2-bromophenyl) ether with 1.12% mol of $[RuClH(CO)(PPh_3)_3]$, 50 °C, 2 h

Solvent	Conversion (%)
C_6H_6	100
THF	100
1,4-Dioxane	100
CH_2Cl_2	95
$CHCl_3$	68
CH_3COCH_3	67
CCl_4	63
CH_3OH	18
t-BuOH	18
CH_3CN	8

of hydride ligand in reaction with such solvents, such as *t*-BuOH or MeOH should also be taken into account.

Another important factor influencing the conversion of allyl to 1-propenyl ether is the rate of the dissolution of the precatalyst. General observations for ruthenium complexes presented in this work, reveal that they dissolve faster in polar solvents, while in benzene they may even stay partially undissolved till the end of the reaction period if the amount of the complex is bigger. Therefore, the precatalyst concentration is higher from the very beginning of the reaction in such solvents like THF, dioxane, CH_2Cl_2 in comparison with the benzene solution.

For ethers which require the most drastic conditions for isomerization [i.e. allyl (2,4,6-tribromophenyl) **22**, allyl pentachlorophenyl **30** and allyl (4-benzoil-2-hydroxyphenyl) **23** ethers], the best solvents are refluxing toluene, xylene, or even the reaction without any solvent.

2.7. Separation of (1-propenyl)ethers on siliceous mesoporous cellular foams

Most of the aryl (1-propenyl) ethers might be successfully separated by crystallization or distillation. For the less stable ethers, such as (4-aminophenyl) (1-propenyl) ether separation of the catalyst and phosphines might be applied using siliceous mesoporous cellular foams. Successful adsorption of catalyst and released phosphines (with oxide) was achieved on functionalized foams. The best results were achieved on siliceous foams with groups: $–CH_2CH_2CH_2SH$ (R1), $–CH_2CH_2CH_2NH_2$ (R2), $–CH_2CH_2CH_2NHCH_2CH_2NH_2$ (R3). Nor the non-functionalized foam neither the foam with $–CH_2CH_2CH_2SO_3H$, did adsorb the components selectively. Similar lack of selectivity of separation of the post-reaction mixture was observed for regular silica gel.

3. Conclusions

Isomerization of allyl aryl ethers catalysed by ruthenium complexes is a convenient method of syntheses of 1-propenyl ethers. In most cases the conversion to 1-propenyl derivatives is quantitative. The most effective and universal catalyst for these reactions is simple $[RuClH(CO)(PPh_3)_3]$. The reaction may be carried out in THF, 1,4-dioxane, or benzene. Other solvents may retard the reaction rate. The coordination effects of allyl aryl ethers with coordinating substituents might be well observed in a competitive reaction method. The highest coordinating power express: cyano-, and formyl groups, next acetyl and acetylamide. Methyl, metoxyl and halogens in *para* positions exert weak influence, just like *m*-Cl substituent.

Higher selectivity towards one of the isomers (*E* or *Z*) might be achieved by applying a catalytic system formed in situ: $\{[RuCl_2(cod)]_x\} + PR_3$. The best results were obtained with tris(2,4,6-trimetoxyphenyl)phosphine. Addition of inorganic hydrides, such as $LiAlH_4$ or $NaBH_4$ may increase reaction rate, although the results are difficult to forecast. We assume that the crucial step for selectivity is a planar transition state of β-elimination, where the presence of one bulky or two phosphines of moderate bulkiness might determine about $Ru\cdots Ar$ interactions and the position of terminal methyl group.

Most of the aryl (1-propenyl) ethers might be successfully separated by crystallization or distillation. For less stable ethers separation of the catalyst and phosphines might be achieved using functionalized siliceous mesoporous cellular foams.

4. Experimental

4.1. General experimental details

All reactions were performed under dry argon atmosphere. Solvents were dried with appropriate drying agents (molecular sieves, CaH_2 or Na) and distilled prior to use. NMR spectra were taken on a Varian Unity Inova 300 MHz spectrometer at room temperature. GC–MS analysis conditions: GC–MS system: GC Trace with MS Trace (Thermo Finnigan); injector: split/splitless injector with 4 mm deactivated glass liner, injector temperature: 280 °C; autosampler: CombiPAL (CTC), sample volume: 0.5 μl; GC column: MDN 5S (Supelco) 30 m × 0.25 mm × 0.25 μm; flow: constant pressure 100 kPa; temperature program: 40 °C for 1 min, 40–220 °C, 12 °C/min, 220 °C–8 min; transfer line: direct coupling to MS ion source, 250 °C constant; mass spectrometer: EI mode 70 eV ion source at 200 °C.

Ruthenium complexes were synthesized according to literature procedures: $[RuClH(CO)(PPh_3)_3]$ [54,55], $[RuCl_2(PPh_3)_3]$ [56], $\{[RuCl_2(NBD)_x]\}$ [57], $[RuH_2(PPh_3)_4]$ [58], $\{[RuCl_2(COD)]_x\}$ [59], $[Rh_2Cl_2(COD)_2]$ [60].

The general procedure of the synthesis of allyl aryl ethers: PTC catalysis—is a modification of the described procedures [61], Method A: allyl (2-chlorophenyl) ether **1**, allyl (3-chlorophenyl) ether **2**, allyl (4-chlorophenyl) ether **3**, allyl (2-tollyl) ether **6**, allyl (4-tollyl) ether **7**, allyl (2-methoxyphenyl) ether **8**, allyl (4-methoxyphenyl) ether **9**, ally (2-hydroxyphenyl) ether **13**, allyl (4-cyanophenyl) ether **20**, allyl (2-pyridyl) ether **24**. Classic Williamson synthesis [36,62–64], Method B: allyl (2-bromophenyl) ether **4**, allyl (3-bromophenyl) ether **5**, allyl (2-nitrophenyl) ether **10**, allyl (3-nitrophenyl) ether **11**, allyl (4-nitrophenyl) ether **12**, allyl (2-formylphenyl) ether **14**, allyl (4-formylphenyl) ether **16**, 1,2-bisallyloxybenzene **25**, 1,4-bisallyloxybenzene **26**.

Allyl 2,4,6-tribromophenyl ether, allyl (4-benzoyl-2-hydroxyphenyl) ether were purchased from Aldrich.

4.1.1. Method A

In a round-bottomed flask equipped with a mechanic stirrer and condenser phenol (0.15 mol), aqueous solution of

NaOH (50 cm^3 of 50% (m/m)), triethylbenzylammonium chloride (0.01 mol) in benzene (50 cm^3) were placed. While stirring, allyl bromide (0.1 mol) was added through a condenser. After 3 h of refluxing, the layers were separated. The organic layer was washed three times (each 50 cm^3) with 5% aqueous NaOH solution, with water and then dried with anhydrous Na_2SO_4. After evaporation of benzene on rotatory evaporator, the residue was vacuum distilled or recrystallized. Yield: 80% and higher.

4.1.2. Method B

In a round-bottomed flask equipped with a mechanic stirrer and condenser phenol (0.1 mol), allyl bromide (0.12 mol), anhydrous potassium carbonate (0.12 mol) and anhydrous acetone (50 cm^3) were placed. The mixture was refluxed for 6 h and than left overnight without heating. Volatile substances were evaporated from the reaction mixture, followed by dissolving the residue in water (0.5 dm^3). The product was extracted two times with dichloromethane (50 cm^3 each). The organic layer was washed three times with 5% NaOH, once with water and dried with anhydrous $MgSO_4$. After evaporation of solvents, the product was purified by vacuum distillation or recrystallized. Yield: 75% and higher.

4.2. Allyl [2-(dimethoxymethyl)phenyl] ether, **15**

Allyl (2-formylphenyl) ether (3 cm^3; 18.5 mmol), methanol (20 cm^3; 0.625 mol), *p*-toluenesulfonic acid (20 mg; 0.12 mmol), anhydrous $MgSO_4$ (5 g, 41.5 mmol) placed in an Erlenmeyer flask was left for 5 days. After that time, 80% conversion to acetal was observed. The solution was decanted, methanol (50 cm^3, 1.56 mol), *p*-toluenesulfonic acid (10 mg; 0.06 mmol), and molecular sieves 4 Å and left for 4 days. This led to complete conversion of aldehyde to acetal. After the filtration and decantation of solvent, the crude product was used without any further purification.

^{1}H NMR ($CDCl_3$) $\delta = 4.57$ (ddd, 2H, $J = 5.1, 1.5, 1.5$, O–CH_2), 5.26; (ddt, 1H, $J = 10.5, 1.5, 1.5$, *cis*-HC=C*H*), 5.42 (ddt, 1H, $J = 17.4, 1.5, 1.5$, *trans*-HC=C*H*), 6.05 (ddt, 1H, $J = 17.4, 10.5, 5.1$, C–C*H*=C), 3.37 (s, 6H, $C(OMe)_2$), 5.70 (s, 1H, C*H*$(OMe)_2$), 6.86 (d, 1H, $J = 7.8$, C_{Ar}2–H), 6.96 (dd, 1H, $J = 7.8, 7.8$, C_{Ar}3–H), 7.26 (ddd, 1H, $J = 7.8, 7.8, 1.7$, C_{Ar}4–H), 7.52 (dd, 1H, $J = 7.8, 1.7$, C_{Ar}5–*H*).

^{13}C NMR ($CDCl_3$) $\delta = 53.8$ (C(O<u>Me</u>)$_2$), 69.0 (O–CH_2), 99.4 (*C*H$(OMe)_2$), 117.2 (=CH_2), 133.3 (CH=), 112.1, 120.5, 126.7, 127.3, 129.6, 156.1 (C_{Ar}).

MS (70 eV) *m/e* (int[%]): 208 (4) M^+; 177 (25); 121 (14); 107 (19); 77 (10); 75 (15); 71 (100); 65 (12); 51 (10).

4.3. Allyl (4-aminophenyl) ether, **19**

Allyl [4-(*N*-acetylamino)phenyl] ether (1.5 g; 7.8 mmol), conc. hydrochloric acid (2.5 cm^3) and ethanol (7.5 cm^3) were placed into a round-bottomed flask and refluxed for 4 h. The next day volatile fractions were removed on a rotatory evaporator. Aqueous solution of NaOH (8 cm^3, 5%) was added to the residue. The mixture was extracted with hexane (3 × 15 cm^3). After removal of the solvent, 1 g (78% yield) of product was collected. It was pure enough for further research.

^{1}H NMR ($CDCl_3$) $\delta = 3.36$ (s, 2H, NH_2), 4.43 (ddd, 2H, $J = 5.4, 1.5, 1.5$, O–CH_2), 5.23 (ddt, 1H, $J = 10.5, 1.5, 1.5$, *cis*-HC=C*H*), 5.37 (ddt, 1H, $J = 17.3, 1.5, 1.5$, *trans*-HC=C*H*CH, 6.02 (ddt, 1H, $J = 17.3, 10.5, 5.4$, C–C*H*CH=C), 6.60 (d, 2H, $J = 8.8$, C_{Ar}–H), 6.74 (d, 2H, $J = 8.8$, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 69.6$ (O–CH_2), 115.9, 116.3, 117.3, 133.8, 140.2, 151.7 (C_{Ar} and CH=CH_2).

MS (70 eV) *m/e* (int[%]): 149 (16) M^+; 108 (100); 86 (21); 84 (34); 80 (37); 54 (14); 49 (10); 43 (10).

4.4. Allyl (4-allyloxybenzyl) ether, **28**

^{1}H NMR ($CDCl_3$) $\delta = 3.99$ (2H, ddd, $J = 4.2, 1.5, 1.5$, longer chain: O–CH_2), 5.18 (ddt, 1H, $J = 9.8, 1.5, 1.5$, longer chain: *cis*-HC=C*H*), 5.28 (ddt, 1H, $J = 17.8, 1.5, 1.5$, longer chain: *trans*-C=C*H*), 5.58 (ddt, 1H, $J = 17.8, 9.8, 4.2$, longer chain: C–C*H*=C), 4.44 (s, 2H, longer chain: O–CH_2–Ar), 4.52 (ddd, 2H, $J = 5.4, 1.5, 1.5$, shorter chain: O-CH_2), 5.26 (ddt, 1H, $J = 9.8, 1.5, 1.5$, shorter chain: *cis*-HC=C*H*), 5.40 (ddt, 1H, $J = 17.8, 1.5, 1.5$, shorter chain: *trans*-HC=C*H*), 6.10 (ddt, 1H, $J = 17.8, 9.8, 5.4$, shorter chain: C–C*H*=C), 6.88 (d, 2H, $J = 8.7$, C_{Ar}–H), 7.26 (d, 2H, $J = 8.7$, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 68.8, 70.9, 71.8$ (CH_2), 114.6, 115.0, 117.0, 117.6, 129.3, 130.6, 133.3, 134.8, 158.2 (CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]): (*Z*) + (*E*): 204 (45) M^+; 162 (78); 147 (100); 133 (23); 107 (42); 78 (22); 55(13).

4.5. Standard procedure of isomerization

Isomerization has been carried out in screw-capped ampoules in scale 0.5–50 mmol. Substrate—allyl aryl ether has been placed into the ampoule together with given amount of precatalyst and solvent, if necessary. The reaction mixture was purged with dry argon by bubbling through the solution for 1 min. After tight screwing, the ampoule was placed into a thermostated (±0.5 °C) oil bath, where it was kept for given period of time. Next, the ampoule was cooled down, solvent evaporated if necessary, and the residue was taken for NMR analysis. In order to remove ruthenium complexes, the organic product was extracted with hexane or petroleum ether, while ruthenium complexes stayed undissolved. The mixture was filtered, and the solvent removed.

4.6. (2-Nitrophenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) $\delta = 1.68$ (dd, 3H, $J = 5.4, 1.2$, (*E*) CH_3), 1.72 (dd, 3H, $J = 5.4, 1.2$, (*Z*) CH_3), 5.10 (dq, 1H,

J = 6.9, 5.4, (*Z*) =C*H*–CH_3), 5.52 (dq, 1H, J = 12.2, 5.4, (*E*) =C*H*–CH_3), 6.39 (dq, 1H, J = 6.9, 1.2, (*Z*) –O–C*H*=), 6.39 (dq, 1H, J = 12.2, 1.2, (*E*) –O–C*H*=), 7.00–7.90 (m, 4H, (*Z*) + (*E*) C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.5 ((*Z*) *C*H_3), 12.2 ((*E*) *C*H_3), 111.0, 112.2, 115.7, 116.8, 120.4, 121.9, 125.6, 125.8, 128.3, 133.9, 139.2, 139.3, 140.1, 142.5, 150.6, 162.1 (CH=CH_2 and C_{Ar}).

MS (70 eV) *m*/*e* (int[%]):

(*Z*): 179 (100) M^+; 162 (31); 131 (11); 63 (13).

(*E*): 179 (100) M^+; 162 (36); 103 (10); 63 (17).

4.7. (3-Nitrophenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.72 (dd, 3H, J = 6.8, 1.5, (*E*) CH_3), 1.73 (dd, 3H, J = 6.8, 1.5, (*Z*) CH_3), 5.07 (dq, 1H, J = 6.8, 6.8, (*Z*) =C*H*–CH_3), 5.51 (dq, 1H, J = 12.2, 6.8, (*E*) =C*H*–CH_3), 6.41 (dq, 1H, J = 6.8, 1.5, (*Z*) –O–C*H*=), 6.43 (dq, 1H, J = 12.2, 1.5, (*E*) –O–C*H*=), 7.30–7.51 (m, 4H, (*Z*) + (*E*) C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.3 ((*Z*) CH_3), 12.1 ((*E*) CH_3), 110.4 ((*E*) C_{Ar}2), 110.7 ((*Z*) =*C*H–CH_3), 111.4 ((*E*) =*C*H–CH_3), 117.1 ((*Z*) C_{Ar}2), 122.5 ((*Z*) –O–CH=), 112.6 ((*E*) –O–CH=), 130.2 ((*Z*) C_{Ar}3), 132.0 ((*E*) C_{Ar}3), 139.6 ((*Z*) C_{Ar}4), 140.6 ((*E*) C_{Ar}4), 149.2 ((*E*) C_{Ar}1), 158.0 ((*Z*) C_{Ar}1).

MS (70 eV) *m*/*e* (int[%]): (*Z*) + (*E*): 179 (100) M^+; 162 (10); 138 (9); 93 (7); 77 (7); 76 (6); 63 (6); 46 (8); 41 (10); 39 (16).

4.8. (4-Nitrophenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.70 (dd, 3H, J = 6.8, 1.8, (*E*) CH_3), 1.72 (dd, 3H, J = 6.0, 1.8, (*Z*) CH_3), 5.12 (dq, 1H, J = 6.8, 6.0, (*Z*) =C*H*–CH_3), 5.56 (dq, 1H, J = 12.0, 6.8, (*E*) =C*H*–CH_3), 6.38 (dq, 1H, J = 6.8, 1.8, (*Z*) –O–C*H*=), 6.41 (dq, 1H, J = 12.0, 1.8, (*E*) –O–C*H*=), 7.04 (d, 2H, J = 9.3, (*E*) C_{Ar}3–H), 7.08 (d, 2H, J = 9.3, (*Z*) C_{Ar}3–H), 8.21 (d, 2H, J = 9.3, (*Z*) C_{Ar}2–H), 8.21 (d, 2H, J = 9.3, (*E*) C_{Ar}2–H).

^{13}C NMR ($CDCl_3$) δ = 9.4 ((*Z*) CH_3), 12.2 ((*E*) CH_3), 110.4, 110.7, 111.4, 117.1, 122.5, 122.5, 128.4, 130.2, 139.6, 140.6, 149.3, 157.9 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m*/*e* (int[%]):

(*Z*): 179 (100) M^+; 162 (45); 131 (20); 105 (18); 63 (22); 39 (31).

(*E*): 179 (100) M^+; 162 (23); 131 (16); 63 (20); 39 (37).

4.9. (2-Hydroxyphenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.63 (dd, 3H, J = 6.9, 1.6, (*E*) CH_3), 1.71 (dd, 3H, J = 6.9, 1.6, (*Z*) CH_3), 4.90 (qd, 1H, J = 6.9, 6.1, (*Z*) =C*H*–CH_3), 5.33 (dq, 1H, J = 12.1, 6.9, (*E*) =C*H*–CH_3), 6.29 (dq, 1H, J = 6.1, 1.6, (*Z*) –O–C*H*=), 6.36 (dq, 1H, J = 12.1, 1.6, (*E*) –O–C*H*=), 6.42 (br, 1H, (*Z*) and (*E*) OH), 6.68–6.98 (m, 4H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.4 ((*Z*)CH_3), 12.1 ((*E*) CH_3), 108.3, 108.5, 115.1, 115.3, 115.6, 115.8, 120.2, 120.6, 123.4, 123.5, 141.0, 142.1, 144.4, 144.7, 146.1, 146.2 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m*/*e* (int[%]):

(*Z*): 150 (46) M^+; 121 (100); 110 (38); 81 (16); 63 (10); 53 (10).

(*E*): 150 (35) M^+; 121 (100); 110 (39); 81 (10); 63 (9); 53 (10).

4.10. [2-(Dimethoxymethyl)phenyl] (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.66 (dd, 3H, J = 6.8, 1.6, (*E*) CH_3), 1.74 (dd, 3H, J = 6.8, 1.5, (*Z*) CH_3), 3.38 (s, 6H, (*E*) C(OMe)$_2$), 3.40 (s, 6H, (*Z*) C(OMe)$_2$), 4.91 (dq, 1H, J = 6.9, 6.8, (*Z*) =C*H*–CH_3), 5.36 (dq, 1H, J = 15.0, 6.8, (*E*) =C*H*–CH_3), 5.65 (s, 1H, (*E*) C*H*(OMe)$_2$) 5.69 (s, 1H, (Z) C*H*(OMe)$_2$), 6.37 (dq, 1H, J = 6.9, 1.5, (*Z*) –O–CH=), 6.39 (dq, 1H, J = 15.0, 1.6, (*E*) –O–CH=), 6.93–7.58 (m, 4H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.4 ((*Z*) *C*H_3), 12.2 ((*E*) *C*H_3), 50.8 ((*E*) C(OMe)$_2$), 54.1 ((*Z*) C(OMe)$_2$), 99.2 ((*E*) *C*H(OMe)$_2$), 99.5 ((*Z*) *C*H(OMe)$_2$), 107.7 ((*E*) =*C*H–CH_3), 109.9 ((*Z*) =*C*H–CH_3), 114.4, 115.2, 122.2, 122.4, 127.4, 128.4, 129.4, 135.8, 139.8, 141.0, 141.2, 142.4, 155.1, 159.8 ((*Z*) and (*E*) O–CH= and C_{Ar}).

MS (70 eV) *m*/*e* (int[%]):

(*Z*) + (*E*): 208 (2); 177 (12); 162 (12); 161 (13); 145 (39); 137 (19); 136 (59); 134 (10); 122 (13); 121 (68); 120 (74); 115 (16); 107 (54); 105 (16); 93 (13); 92 (43); 91 (23); 86 (64); 84 (100); 77 (26); 76 (17); 75 (37); 65 (27).

4.11. (4-Formylphenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.71 (dd, 3H, J = 6.8, 1.7, (*E*) CH_3), 1.72 (dd, 3H, J = 6.8, 1.7, (*Z*) CH_3), 5.06 (dq, 1H, J = 6.8, 6.8, (*Z*) =C*H*–CH_3), 5.53 (dq, 1H, J = 12.0, 6.8, (*E*) =C*H*–CH_3), 6.45 (dq, 1H, J = 6.8, 1.7, (*Z*) –O–C*H*=), 6.48 (dq, 1H, J = 12.0, 1.7, (*E*) –O–C*H*=), 7.11 (d, 2H, J = 8.8, (*E*) and (*Z*) C_{Ar}–H), 7.86 (d, 2H, J = 8.8, (*E*) and (*Z*) C_{Ar}–H), 9.92 (s, 1H, (*E*) and (*Z*) CHO).

^{13}C NMR ($CDCl_3$) δ = 9.3 ((*Z*) CH_3), 12.2 ((*E*) CH_3), 110.1, 112.2, 115.9, 130.9, 131.8, 132.1, 139.2, 140.2, 162 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}), 190.6 ((*Z*) and (*E*) C=O).

MS (70 eV) *m*/*e* (int[%]):

(Z): 162 (100) M^+; 133 (15); 121 (88); 105 (18); 65 (23); 51 (28).

(E): 162 (81) M^+, 133 (15); 121 (100); 105 (28); 65 (18); 51 (26).

4.12. [4-(N-acetylamino)phenyl] (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.63 (dd, 3H, J = 6.9, 1.5, (*E*) CH_3), 1.69 (dd, 3H, J = 7.2, 1.8, (*Z*) CH_3), 2.07 (s, 3H, (*Z*) and (*E*) NCOC*H*$_3$), 4.85 (dq, 1H, J = 7.2, 7.2, (*Z*)

=C*H*–CH_3), 5.34 (dq, 1H, $J = 12.0$, 6.9, (*E*) =C*H*–CH_3), 6.32 (dq, 1H, $J = 7.2$, 1.8, (*Z*) –O–C*H*=), 6.36 (dq, 1H, $J = 12.0$, 1.5, (*E*) –O–C*H*=), 6.66 (d, 2H, $J = 8.7$, C_{Ar}–H), 6.74 (d, 2H, $J = 8.7$, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 9.4$ ((*Z*) CH_3), 12.2 ((*E*) CH_3), 24.3 ((*Z*) and (*E*) CO*C*H_3), 107.3, 108.1, 116.5, 116.7, 121.8, 128.4, 132.6, 141.1, 142.2, 154.3, 154.1 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}), 168.5 ((*Z*) and (*E*) C=O).

MS (70 eV) *m/e* (int[%]): (*Z*) + (*E*): 191 (71) M^+; 149 (67); 120 (32); 109 (100); 93 (29); 80 (35); 63 (22); 53 (30).

4.13. (4-Aminophenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) $\delta = 1.62$ (dd, 3H, $J = 6.8$, 1.7, (*E*) CH_3), 1.70 (dd, 3H, $J = 6.8$, 1.7, (*Z*) CH_3), 3.31 (br, 2H, (*Z*) + (*E*) NH_2), 4.74 (dq, 1H, $J = 6.8$, 6.8, (*Z*) =C*H*–CH_3), 5.22 (dq, 1H, $J = 12.0$, 6.8, (*E*) =C*H*–CH_3), 6.27 (dq, 1H, $J = 6.8$, 1.7, (*Z*) –O–C*H*=), 6.32 (dq, 1H, $J = 12.0$, 1.7, (*E*) –O–CH=), 6.60–6.88 (m, 4H, (*Z*) + (*E*) C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 9.3$ ((*Z*) CH_3), 12.2 ((*Z*) CH_3), 105.6, 106.1, 116.2, 117.5, 117.9, 142.3, 141.5, 150.7, 150.2 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]): 149 (95) M^+; 120 (15); 109 (100); 108 (66); 93 (10); 81 (11); 80 (41); 65 (18); 54 (19); 53 (13).

4.14. (4-Cyanophenyl) (1-propenyl) ether

^{1}H NMR (C_6D_6) $\delta = 1.37$ (dd, 3H, $J = 6.9$, 1.5, (*E*) CH_3), 1.54 (dd, 3H, $J = 6.9$, 1.8, (*Z*) CH_3), 4.70 (qd, 1H, $J = 6.9$, 6.0, (*Z*) =C*H*–CH_3), 5.27 (dq, 1H, $J = 12.0$, 6.9, (*E*) =C*H*–CH_3), 5.93 (dq, 1H, $J = 6.0$, 1.8, (*Z*) –O–C*H*=), 5.96 (dq, 1H, $J = 12.0$, 1.5, (*E*) –O–C*H*=), 6.47 (d, 2H, $J = 8.7$, C_{Ar}–H), 7.00 (d, 2H, $J = 8.7$, C_{Ar}–H).

^{13}C NMR (C_6D_6) $\delta = 9.4$ ((*Z*) CH_3), 12.1 ((*E*) CH_3), 106.2, 110.0, 111.3, 114.0, 115.4, 116.4, 118.8, 139.5, 140.4, 160.3, 160.5 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]): (*Z*) + (*E*): 159 (100) M^+; 144 (5); 130 (19); 119 (85); 91 (11); 75 (10); 64 (13).

4.15. (4-Hydroxymethylphenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) $\delta = 1.66$ (dd, 3H, $J = 6.8$, 1.8, (*E*) CH_3), 1.71 (dd, 3H, $J = 6.6$, 1.5, (*E*) CH_3), 4.50 (s, 2H, (*E*) CH_2OH), 4.50 (s, 2H, (*Z*) CH_2OH), 4.88 (dq, 1H, $J = 6.9$, 6.6, (*Z*) =C*H*–CH_3), 5.38 (dq, 1H, $J = 12.0$, 6.8, (*E*) =C*H*–CH_3), 6.38 (dq, 1H, $J = 6.9$, 1.5, (*Z*) –O–C*H*=), 6.44 (dq, 1H, $J = 12.0$, 1.8, (*E*) –O–C*H*=), 6.97 (d, 2H, $J = 8.5$, C_{Ar}–H), 7.29 (d, 2H, $J = 8.5$, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 9.4$ ((*Z*) CH_3), 12.2 ((*E*) CH_3), 64.9 ((*Z*) + (*E*) CH_2OH), 107.7, 108.4, 116.2, 116.3, 128.4, 128.6, 134.9, 140.8 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]):

(*Z*): 164 (100) M^+; 123 (18); 107 (45); 105 (19); 79 (37); 51 (20).

(*E*): 164 (100) M^+; 123 (25); 107 (63); 105 (27); 79 (43); 51 (28).

4.16. 2,4,6-Tribromophenyl (1-propenyl) ether

^{1}H NMR ($CDCl_3$) $\delta = 1.58$ (dd, 3H, $J = 6.8$, 1.5, (*E*) CH_3), 1.80 (dd, 3H, $J = 6.8$, 1.8, (*Z*) CH_3), 4.81 (qd, 1H, $J = 6.8$, 6.0, (*Z*) =C*H*–CH_3), 4.88 (dq, 1H, $J = 12.0$, 6.8, (*E*) =C*H*–CH_3), 5.95 (dq, 1H, $J = 6.0$, 1.8, (*Z*) –O–C*H*=), 6.29 (dq, 1H, $J = 12.0$, 1.5, (*E*) –O–C*H*=), 7.67 (s, 2H, (*Z*) + (*E*) C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 8.4$ ((*Z*) CH_3), 13.1 ((*E*) CH_3), 104.8, 117.2, 117.5, 134.0, 141.6, 150.3 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]): (*Z*) + (*E*): 370 (48) M^+; 341 (23); 330 (100); 210 (15); 153 (8); 141 (16).

4.17. (4-Benzoyl-2-hydroxyphenyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) $\delta = 1.70$ (dd, 3H, $J = 6.3$, 1.5, (*E*) CH_3), 1.71 (dd, 3H, $J = 6.3$, 1.5, (*Z*) CH_3), 5.06 (dq, 1H, $J = 6.6$, 6.3, (*Z*) =C*H*–CH_3), 5.52 (dq, 1H, $J = 12.0$, 6.3, (*E*) =C*H*–CH_3), 6.43 (dq, 1H, $J = 12.0$, 1.5, (*E*) –O–C*H*=), 6.50 (dq, 1H, $J = 6.6$, 1.5, (*Z*) –O–C*H*=), 6.50 (dd, 1H, $J = 9.0$, 2.6, (*Z*) + (*E*) C_{Ar}–H), 6.60 (d, 1H, $J = 2.6$, (*E*) C_{Ar}–H), 6.61 (d, 1H, $J = 2.6$, (*Z*) C_{Ar}–H), 7.48–7.68 (m, 6H).

^{13}C NMR ($CDCl_3$) $\delta = 9.5$ ((*Z*) CH_3), 12.2 ((*E*) CH_3), 103.5, 103.6, 107.8, 110.6, 111.7, 114.3, 128.1, 128.4, 128.7, 128.9, 129.6, 131.6, 134.6, 135.5, 138.2, 139.1, 139.9, 163.6, 163.8, 165.9, ((*Z*) and (*E*) CH=CH_2 and C_{Ar}), 200.2 ((*Z*) and (*E*) C=O).

MS (70 eV) *m/e* (int[%]): 254 (45) M^+; 253 (100); 177 (33); 137 (18); 105 (16); 77 (13).

4.18. 1,2-Bis(1-propenyloxy)benzene

bp: 92–95 °C/5mmHg.

From spectroscopic point of view 1-propenyloxy groups do not influence each other, thus, not isomers, but separate 1-propenyloxy groups are observed.

^{1}H NMR ($CDCl_3$) $\delta = 1.64$ (dd, 3H, $J = 6.9$, 1.8, (*E*) CH_3), 1.73 (dd, 3H, $J = 6.9$, 1.8, (*Z*) CH_3), 4.82 (dq, 1H, $J = 6.9$, 6.2, (*Z*) =C*H*–CH_3), 5.30 (dq, 1H, $J = 12.1$, 6.9, (*E*) =C*H*–CH_3), 6.32 (dq, 1H, $J = 6.2$, 1.8 (*Z*) –O–C*H*=), 6.56 dq, 1H, $J = 12.1$, 1.8 (*E*) –O–C*H*=), 6.92–7.02 (m, 4H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) $\delta = 9.3$ ((*Z*) CH_3), 12.1 ((*E*) CH_3), 106.6, 141.8, 117.3. 122.9, 147.6 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]): 190 (27) M^+; 161 (21); 148 (45); 121 (100); 109 (33); 107 (10); 105 (10); 81 (19).

4.19. 1,4-Bis(1-propenyloxy)benzene

From spectroscopic point of view 1-propenyloxy groups do not influence each other, thus, not isomers, but separate 1-propenyloxy groups are observed.

^{1}H NMR ($CDCl_3$) $\delta = 1.67$ (dd, 6H, $J = 6.6$, 1.5, (*E*) –CH_3), 1.74 (dd, 6H, $J = 6.6$, 1.5, (*Z*) –CH_3), 4.85 (dq, 2H,

J = 6.6, 6.6, (*Z*) =C*H*–CH_3), 5.33 (dq, 2H, J = 12.3, 6.6, (*E*) =C*H*–CH_3), 6.33 (dq, 2H, J = 6.6, 1.5, (*Z*) –O–C*H*=), 6.38 (dq, 2H, J = 12.3, 1.5, (*E*) –O–CH=), 6.94, 6.95, 6.96 (s, 4H, isomers C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.3 ((*Z*) CH_3), 12.2 ((*E*) CH_3), 106.8, 107.4, 115.9, 117.2, 117.3, 117.5, 128.3, 141.5, 141.6, 142.8, 152.7, 152.9, 153.0 (all isomers CH=CH_2 and C_{Ar}).

MS (70 eV) *m/e* (int[%]) mixture of isomers: 190 (100) M^+; 161 (10); 150 (14); 121 (26); 110 (40); 105 (9); 81 (8).

4.20. [2-(1-Propenyl)phenyl] (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.65, 1.75, 1.89, 1.90 (dd, 6H, J = 6.9, 1.7, isomers –CH_3), 4.32 (dq, 2H, J = 6.8, 6.8, isomers =C*H*–CH_3), 4.58 (dq, 2H, J = 6.8, 6.8, isomers =C*H*–CH_3), 4.87 (dq, 2H, J = 6.8, 6.8, isomers =C*H*–CH_3), 5.32 (dq, 2H, J = 12.1, 6.8, isomers =C*H*–CH_3), 5.85 (dq, 2H, J = 12.1, 6.8, isomers =C*H*–CH_3), 6.16–6.80 (m, 2H, isomers –O–C*H*= and –C_{Ar}–C*H*=), 6.88–7.45 (m, 4H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.4, 12.3, 14.7, 18.4 (isomers CH_3), 107.1, 107.6, 115.4, 116.1, 121.8, 122.5, 122.7, 124.6, 125.1, 126.4, 126.9, 127.0, 127.3, 127.4, 127.6, 127.8, 127.9, 130.3, 141.4, 142.7, 154.1 (all isomers CH=CH_2 and C_{Ar}).

MS (70 eV) m/e (int[%]) mixture of isomers: 204 (5) M^+; 148 (10); 147 (100); 119 (7); 107 (77); 89 (16); 77 (19); 51 (7).

4.21. (1-Propenyl) {4-(1-propenyloxy)benzyl} ether (mixture of isomers)

^{1}H NMR ($CDCl_3$) δ = 1.56, 1.61, 1.66, 1.71 (dd, 6H, J = 6.8, 1.7, all isomers –CH_3), 4.43, 4.89, 5.06, 5.37 (dq, 2H, J = 6.8, 6.8, all isomers =C*H*–CH_3), 6.02 (dq, 2H, J = 6.8, 1.1, all isomers -O–C*H*=), 6.30 (dq, 2H, J = 12.0, 1.7, all isomers –O–C*H*=), 6.37 (dq, 2H, J = 6.8, 1.7, all isomers –O–C*H*=), 6.45 (dq, 2H, J = 6.8, 1.7, all isomers –O–C*H*=), 6.47 (dq, 2H, J = 12.0, 1.7, all isomers –O–C*H*=), 4.64, 4.74 (s, 2H, all isomers O–C*H*–Ar), 6.88–7.40 (m, 4H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 9.3, 9.4, 12.6 (isomers CH_3), 68.0, 70.7, 73.1 (isomers C_{Ar}–CH_2O–), 99.4, 101.8, 107.6, 116.1, 116.2, 129.0, 129.1, 140.8, 145.1, 146.3, 157.8 (all isomers CH=CH_2 and C_{Ar}).

MS (70 eV) m/e (int[%]) mixture of isomers: 174 (29) M^+; 159 (100); 145 (95); 131 (64); 118 (41); 115 (55); 104 (13); 91 (18); 77 (20); 65 (14); 51 (10).

4.22. (2-Pyridyl) (1-propenyl) ether

^{1}H NMR ($CDCl_3$) δ = 1.70 (dd, 3H, J = 6.9, 1.5, (*Z*) –CH_3), 1.85 (dd, 3H, J = 6.9, 1.8, (*E*) –CH_3), 5.81 (dq, 1H, J = 6.9, 6.9, (*Z*) =C*H*–CH_3), 5.94 (dq, 1H, J = 12.0, 6.9, (*E*) =C*H*–CH_3), 6.12–6.22 (m, 1H, (*Z*) and (*E*) C_{Ar}–H), 6.18 (dq, 1H, J = 6.9, 1.5, (*Z*) –O–C*H*=), 6.55 (d, 1H, J = 9.3, (*Z*) C_{Ar}–H), 6.60 (d, 1H, J = 9.0, (*E*) C_{Ar}–H),6.70 (dq, 1H, J = 12.0, 1.8, (*Z*) –O–C*H*=), 7.00–7.80 (m, 2H, C_{Ar}–H).

^{13}C NMR ($CDCl_3$) δ = 12.1 ((*Z*) CH_3), 13.4 ((*E*) CH_3), 105.5, 106.4, 118.6, 121.2, 121.4, 123.1, 127.7, 128.3, 128.5, 134.0, 134.3, 137.3, 139.5 ((*Z*) and (*E*) CH=CH_2 and C_{Ar}).

MS (70 eV) m/e (int[%]):

(*Z*): 135 (16) M^+; 134 (14); 120 (100); 106 (18); 79 (8); 51 (8).

(*E*): 135 (24) M^+, 134 (18); 120 (100); 106 (14); 67 (8); 51 (10).

4.23. Comparative isomerization of ally phenyl ether and other allyl aryl ethers

In a screw-capped ampoule allyl phenyl ether (174.5 mg; 1.3 mmol), allyl aryl ether (1.3 mmol) together with [$RuClH(CO)(PPh_3)_3$] (8 mg; 8.4×10^{-3} mmol) were placed in deuterated benzene (0.8 cm^3). The reaction mixture was purged with argon for 1 min. The screwed-capped ampoule was submerged in an oil bath (40 °C) for 2 h. Next, ^{1}H NMR spectrum was taken from the reaction mixture.

4.24. Solvent influence on double-bond migration

Isomerization has been carried out in sealed ampoules in scale 1 mmol. Substrates—allyl phenyl ether and allyl (2-bromophenyl) ether have been placed into the ampoule together with given amount of precatalyst and the investigated solvent. The reaction mixture was purged with dry argon flow by bubbling through the solution for 1 min. After sealing, the ampoule was placed into a thermostated (±0.5 °C) oil bath, where it was kept for given period of time (2 or 4 h, see Section 2.6). Next, the ampoule was cooled down, solvent evaporated and the residue was taken for NMR analysis.

4.25. Siliceous mesoporous cellular foams

The siliceous mesoporous cellular foams (MCFs) structure is templated by oil in water microemulsions. The preparation procedure was the same as those proposed in literature [65,66]. The texture parameters (specific surface area, S_{BET}; pore volume, V_p; diameter of cells, d_s and diameter of interconnected windows, d_w) of calcined materials were obtained using nitrogen adsorption method. Nitrogen isotherms were measured by Micromeritics ASAP 2000 instrument at 77 K.

Preparation of MCFs: In a typical procedure, surfactant Pluronic PE 9600 (0.4 mmol) was dissolved in 1.6 M HCl (75 ml) at room temperature. 1,3,5-Trimethylbenzene (17 mmol) and NH_4F (0.6 mmol) were added under vigorous stirring and the mixture was heated to 333 K. Following 1 h of stirring TEOS was added (4.4 g). The mixture was stirred for 2 h and, subsequently, stored at 333 K for 20 h and at 373 K for 24 h. After cooling to room temperature, the precipitate was isolated by filtration, dried at room temperature for 4 days and calcined at 773 K for 8 h. Texture

Table 8
Characteristic parameters of the texture of MCFs samples

Sample	Molar ratio of $SiO_2/R_xSi(OR)_3$	S_{BET} (m^2/g)	V_p (cm^3/g)	d_s (nm)	d_w (nm)
MCF	–	650	2.5	30	15
MCF(R1)	0.8–0.2	283	1.30	25	10
MCF(R2)	0.95–0.05	535	2.10	25	13
MCF(R3)	0.95–0.05	530	2.20	29	13

Thermogravimetric analysis showed that MCF(R1) is thermally stable up to 573 K and samples with R2 and R3 groups are stable up to 533 K.

parameters of calcined MCFs were: S_{BET}, 650 m^2/g; V_p, 2.5 cm^3/g; d_s, 30 nm and d_w, 15 nm.

Three samples with organic groups were prepared: MCF(R1), MCF(R2), MCF(R3), where R1–$(CH_2)_3SH$, R2–$(CH_2)_3NH_2$, R3–$(CH_2)_3NHCH_2CH_2NH_2$, respectively.

Organic groups were introduced to MCFs by post-synthesis procedure via direct grafting, i.e. reacting under reflux conditions, suitable organosilane ($R_xSi(OR)_3$ with silanols present on silica surface using hexane as a solvent. Before grafting MCFs were contacted with water vapour during 5 h and subsequently dried at 473 K for 3 h. The silanols concentration, determined by thermogravimetric method, was ca. 2.9 OH/nm^2. Texture parameters of samples are given in Table 8.

4.26. Separation of 1-propenyl ethers using siliceous mesoporous cellular foams

From the reaction mixture after successful isomerization of allyl (4-aminophenyl) ether (3.36 mmol of allyl (4-aminophenyl) ether, 80 °C, 2 h, 2% [$RuClH(CO)(PPh_3)_3$], benzene) the solvent was removed and 10 cm^3 of mixture hexane + benzene (4:1) was added. One tenth of the resulting solution was put on the column prepared from 200 mg of foam and 2 cm^3 of hexane. Clean organic product was eluted with hexane:benzene mixture (3 cm^3; 5:1).

Acknowledgements

This work was supported by the State Committee for Scientific Research as a research grant for the years 2003–2005 (4T09A 132 25). Dr. J. Mrowiec-Białoń also gratefully acknowledges State Committee for Scientific Research for funding (4T09C 023 23).

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