DOI: 10.1002/adsc.201500721

Synthesis of Short-Chain Alkenyl Ethers from Primary and Bio-sourced Alcohols via the Nickel-Catalyzed Hydroalkoxylation Reaction of Butadiene and Derivatives

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Received: July 30, 2015; Revised: September 28, 2015; Published online: December 9, 2015

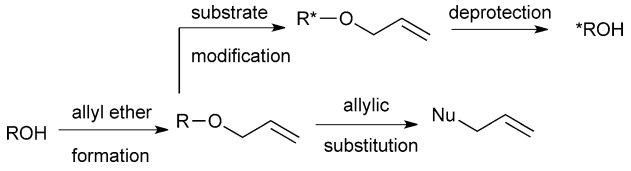
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500721.

Abstract: Hydroalkoxylation of butadiene has been performed in the presence of nickel precatalysts associated with chelating diphosphine ligands. High butadiene conversions and selectivities forming alkyl butenyl ethers were obtained with low catalyst loading. Reactions were performed with a wide scope of primary alcohols including benzylic alcohol derivatives and bio-sourced alcohols. In the same way, the scope of dienes that can be reacted according to this reaction has been also studied. Substituted butadiene derivatives have shown a lower reactivity compared to butadiene. Isoprene formed OC5 alkenyl ethers with a high regioselectivity for one branched isomeric form.

Keywords: butadiene; ether; hydroalkoxylation; nickel; polyol

Introduction

Allyl ethers or derivatives such as but-2-enyl ethers are found in many naturally occurring biologically active molecules, which are frequently involved in organic synthesis. For example, allyl ethers are classically used as protecting groups for alcohols,[1] especially in carbohydrates chemistry due to their stability under the conditions required for glycoside formation[2,3] or electrophiles in allylic alkylation reactions[4] (Scheme 1). Butenyl ethers can also be used as monomers in UV-induced cationic photopolymerization with commercial applications in the fields of coatings, inks and adhesives.[5] Allyl or butenyl ethers derived from polyols with a short C3 or C4 chain are also potent hydrotropes that can find applications as solvents. Several methods are described to obtain allyl or butenyl ethers. The oldest and undoubtedly most used is the Williamson reaction, which involves an alcohol and an alkyl halide in the presence of a base. Nevertheless, this synthetic pathway is not ideal for several reasons. Side reactions such as halide elimination are occurring and an excess of alkylating reagent is thus often needed. Besides this chemoselectivity issue, this transformation provides a stoichiometric amount of salts as waste that needs to be removed using costly processes.



Scheme 1. Applications of allyl ethers as protecting groups or reactants.

This reaction thus doesn't fill the criteria of the green chemistry concepts due to the lack of atom economy.[6] Consequently, new convenient methods oriented toward the synthesis of ethers with high atom economy and low salt formation are needed. With this objective in mind, the catalytic hydroalkoxylation reaction of unsaturated double or triple bonds by alcohols permits the formation of ethers without any waste.

Reactions between an alcohol and an alkene in the presence of Brønsted acids[7] or organometallic complexes[8] as catalysts have been reported for the intra- or intermolecular formation of alkyl ethers. Likewise, the use of alkynes[9] or allenes[10] gave enol ethers or

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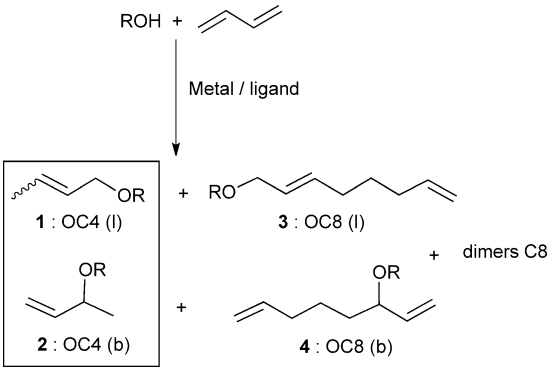
alkyl allyl ethers respectively, compounds known as useful intermediates in organic synthesis.[11] Regarding dienes, studies mainly focused on the telomerization reaction which corresponds to the metal catalyzed linear dimerization of butadiene with simultaneous addition of an alcohol to form octadienyl ethers.[12] Classical palladium precursors with phosphine[13] or carbene[14] ligands provided very efficient catalytic systems causing this reaction to now be included in an industrial process for the production of 1-octene.[15] Amphiphilic compounds were also obtained by grafting hydrocarbon C8 chains on agro-based polyol substrates thus yielding 100% agro-based molecules if considering the bio-ethanol to butadiene synthetic pathway.[16] The simple addition of an alcohol on one double bond of a butadiene unit (a hydroalkoxylation reaction) has received little attention, due to the lack of efficient catalytic process in terms of activity and selectivity. This approach would advantageously open an access to shorter amphiphiles and thus complement the scope of products already accessible from polyols and 1,3-butadiene according to the telomerization reaction. Indeed, the hydroalkoxylation reaction using butadiene and alcohols affords both linear **1** (*cis* and *trans*) and branched **2** butenyl ethers (OC4), but in many cases, octadienyl ethers **3**–**4** (OC8) and C8 dimers are also obtained as side products (Scheme 2). The first selective synthesis of OC4 ethers via metal-catalyzed hydroalkoxylation was reported with ethanol and 1,3-butadiene in the presence of a high loading of rhodium trichloride.[17] Smutny et al. showed that π-allyl palladium catalysts allowed the addition of phenol to butadiene, however with low yields and large amounts of by-products (*ortho*-, *para*-butenylphenol).[18] Interesting butadiene conversion and methylbutenyl ether selectivities were obtained with bis(π-allylpalladium) dichloride precursors in high methanol dilution conditions.[19] Due to the high cost of palladium, several groups have also been interested in the telomerization or hydroalkoxylation reactions catalyzed by more abundant transition metals.[20] In this context, nickel based catalysts have been evaluated, mainly in order to draw a comparison with palladium equivalents. Mixtures of butenyl or octadienyl ethers along with dimers were obtained with varying selectivities depending on the nature of the monophosphine used, but no satisfying selectivity for butenyl ethers was obtained.[21] In our group, we recently disclosed the nickel-catalyzed hydroalkoxylation of butadiene with primary alcohols to form selectively OC4 ethers (**1** and **2**) using specifically the bidentate diphenylphosphinobutane (dppb) ligand associated with a nickel precatalyst.[22] We wish now to report our progress on the optimization of this reaction as well as the extension of the scope to a wider variety of alcohols including biomass issued alcohols and substituted dienes.



Scheme 2. Hydroalkoxylation, telomerization and dimerization of butadiene.

Results and Discussion

In our preliminary work, the hydroalkoxylation of butadiene was performed in the presence of $Ni(acac)_2$ precursor and the dppb (diphenylphosphinobutane **L1**, Scheme 3) ligand with $NaBH_4$ as reducing agent for the in situ generation of the Ni(0) species. Although largely used in the literature, this method requires a fine control of the reaction conditions to avoid the possible formation of nickel nanoparticules.[23] $Ni(cod)_2$/dppb catalytic systems were therefore used in order to outline the best catalytic conditions for the ethoxylation reaction of butadiene (BD). In a typical experiment, the catalyst was prepared by stirring a solution of the nickel precursor and the ligand in ethanol for 5 min in a Schlenk tube under nitrogen. Liquid butadiene (BD/Ni = 125–2500) was then added at −15 °C and the mixture was heated to the desired temperature. The results are reported in Table 1. After 17 h, using 0.8 mol% catalyst, a 93% butadiene conversion was attained with 95% selectivity towards butenyl ethers (Entry 1).[22] The same reaction stopped after two hours showed a similar result. Nevertheless, the reaction mixture was cloudy in both experiments, probably due to the limited solubility of the ligand and catalyst in ethanol. We thus performed the reaction using toluene as a co-solvent (3 mL, entry 2) in order to obtain a clear solution. The butadiene/nickel ratio was increased up to 1250 with satisfactory conversions and selectivities (Entries 2–3). At higher BD/Ni ratios, the level of conversion was extremely limited (21% conv. after 2 h, Entry 4). EtOH/toluene (v/v) ratios were varied from 10:3 to 1:12. As the quantity of ethanol decreased, lower conversions of butadiene were obtained within the reaction time. In addition, the selectivity in butenyl ethers decreased, showing that the excess of ethanol favors the hydroalkoxylation process over the dimerization of 1,3-butadiene (Entries 3; 5–7). The in-

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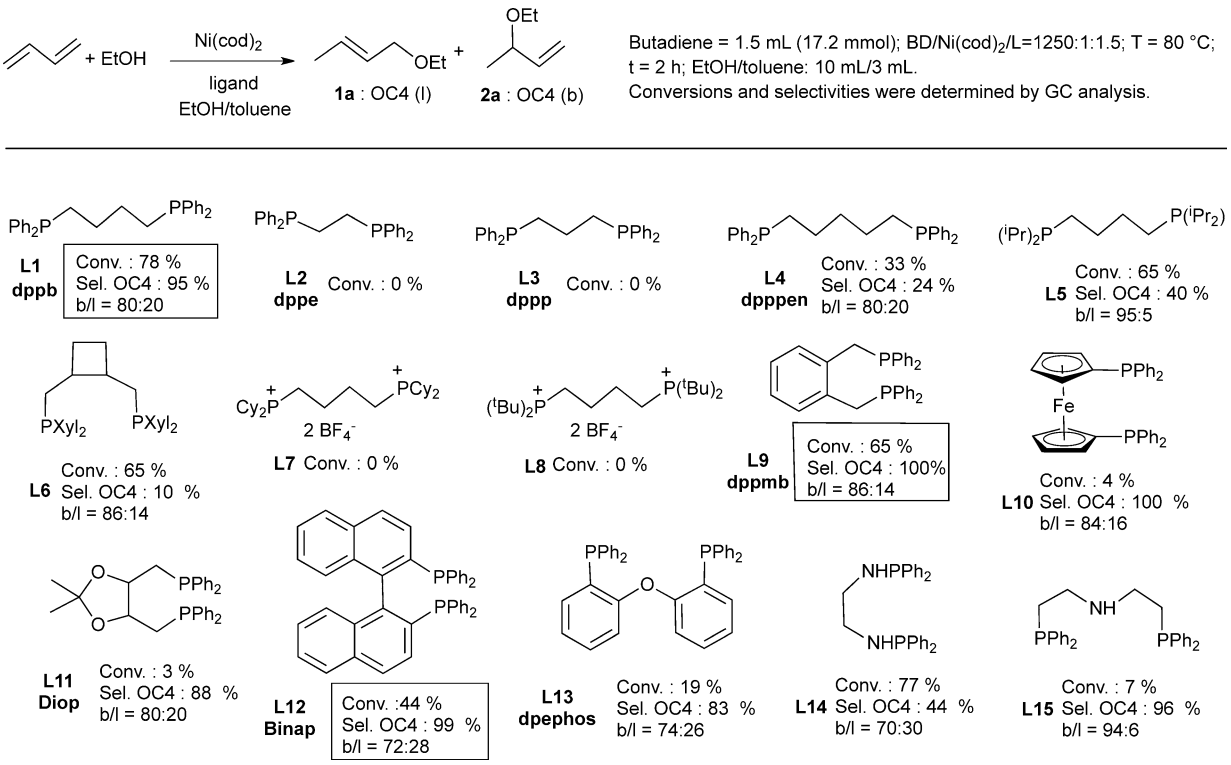

Scheme 3. Hydroethoxylation of butadiene: influence of the ligand.

fluence of the ligand/Ni ratio was also studied. At low ratios (0.5, 0.75 and 1), the conversion was rather low between 26 and 51% (Entries 8–10). The best results in terms of activity (78% conv.) and selectivities (95% and 84% respectively) were obtained with 1.5 and 2 L/Ni ratios (Entries 3 and 11 respectively). Using higher ratios was detrimental to the activity and selectivity. This limitation can be explained by the strongly favored formation of the less reactive nickel complex $Ni(dppb)_2$ in the presence of an excess of the diphosphine. As expected, upon decreasing the temperature, the reaction was much slower with only 13 and 18% conversions after 2 h at 60 and 70 °C respectively (Entries 13–14). Further increase of the temperature up to 90 °C did not lead to a notable improvement of the activity.

The catalytic activity and selectivity obtained during this reaction depend particularly on the nature of the ligand associated to the Ni(0) precursor. Monophosphines lead to the selective linear dimerization of 1,3-butadiene.[24] Diphosphines **L1**–**L15** were evaluated for the hydroethoxylation reaction of butadiene. Among those, linear diphosphines **L1**–**L8** with various substituents on the phosphorus atoms and **L15** possessing an amino group, aryl (**L9**, **L12**, **L13**) or ferrocenic **L10**, cyclic **L6**, **L11** and di(aminophosphine) **L14** ligands were tested (Scheme 3). Unexpected results were observed with dppe **L2** and dppp **L3** which did not give any conversion, whereas the dpppen **L4** allowed a 33% conversion with a 24% OC4 selectivity. The results indicate the importance of the chelation cycle size on this reaction. Other diphosphines that are able to form seven membered chelation cycles with the metal were tested. Among them, commercial diphosphines with the same skeleton as dppb, but with alkyl groups on the phosphorous atoms such as *i*Pr (**L5**), cyclohexyl (**L7**) and *t*Bu (**L8**) were evaluated. *i*Pr substituents led to moderate conversion and selectivities whereas more hindered Cy and *t*Bu substituents led to inactive catalysts. Concerning the importance of the diphosphine backbone, the di(aminophosphine) **L14** gave moderate results in terms of conversion (77%) and selectivity (44%) while the binap ligand **L12** affords the OC4 ethers with a 99% selectivity albeit with a lower butadiene conversion (44%).[25] The best results were obtained using the **L9** (dppmb) ligand leading to 65% conversion as well as total selectivity to the OC4 ethers. In comparison with the dppb ligand, the presence of a rigid aromatic skeleton appears to be favorable in terms of selectivity.

We were then interested in the evolution of the product distribution during the reaction period. A glass reactor with a sampling release at the bottom of the Schlenk tube has been used to take the samples without any loss of butadiene. Using this procedure, aliquot samples of the reaction mixture were taken and analyzed by GC for 24 h. Figure 1 presents the

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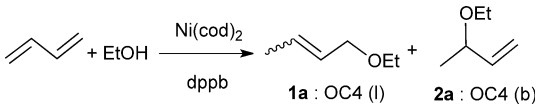
Table 1. Hydroethoxylation of butadiene: variation of experimental conditions.[a]



Entry	BD/Ni; L/Ni	Solvent (mL/mL)	Time (h)	Conv. (%)[b]	Sel. OC4 (**1a**/**2a**) (%)[b]
1	125; 1.5	EtOH (10)	17	93	95 (24/76)
2	125; 1.5	EtOH/toluene (10:3)	3	82	79 (27/73)
3	1250; 1.5	EtOH/toluene (10:3)	2	78	95 (20/80)
4	2500; 1.5	EtOH/toluene (10:3)	2	21	98 (47/53)
5	1250; 1.5	EtOH/toluene (6.5:6.5)	2	25	78 (16/84)
6	1250; 1.5	EtOH/toluene (1:3)	72	32	28 (24/76)
7	1250; 1.5	EtOH/toluene (1:12)	2	8	5 (43/57)
8	1250; 0.5	EtOH/toluene (10:3)	2	26	88 (16/84)
9	1250; 0.75	EtOH/toluene (10:3)	2	41	90 (16/84)
10	1250; 1	EtOH/toluene (10:3)	2	51	91 (18/82)
11	1250; 2	EtOH/toluene (10:3)	2	78	84 (18/82)
12	1250; 3	EtOH/toluene (10:3)	2	48	94 (17/83)
13[c]	1250; 1.5	EtOH/toluene (10:3)	2	13	85 (85/15)
14[d]	1250; 1.5	EtOH/toluene (10:3)	2	18	93 (85/15)

[a] BD = butadiene = 1.5 mL (17.2 mmol); $T = 80\,°C$.
[b] Conversions and selectivities were determined by GC analysis.
[c] 60 °C.
[d] 70 °C.

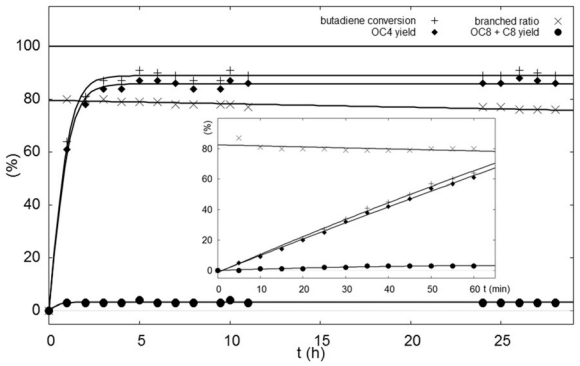


Figure 1. Time-dependent reaction progress of the hydroethoxylation of butadiene. Conditions: butadiene = 1.5 mL (17.2 mmol); BD/Ni(cod)$_2$/dppb = 1250:1:1.5; EtOH/toluene = 10/3 mL/mL; $T = 80\,°C$.

composition of the mixture as a function of time using **L1** (dppb) as ligand. As expected, the curves indicate that the reaction occurs very efficiently with 64% yield into OC4 products after 1 hour and 78% after 2 h. After 3 h, there is no more evolution of the products distribution and a maximum value of 85% OC4 is obtained with approximatively 5% of OC8 telomers and C8 dimers.

The linear/branched ratio remained almost stable during the reaction course at around 80:20; this indicates that no isomerization of the products takes place. As the curve depicting the conversion of butadiene as a function of time for the first hours is almost linear, the slope of the curve can be easily calculated. With these reaction conditions, the turn over frequency (TOF) of the nickel catalyst was found to be approximately 800 h^{-1}. The same calculation per-

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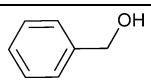
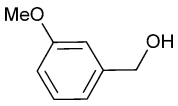
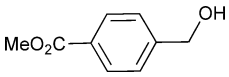
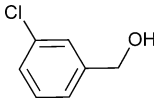
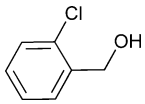
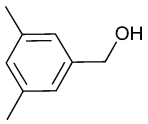
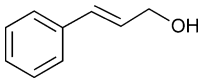
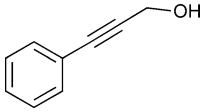
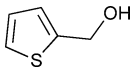
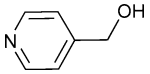
Table 2. Hydroalkoxylation of butadiene using various primary alcohols[a]

Entry	alcohol ROH	Ligand	Conv. (%)[b]	Sel.[b] OC4 (%)	**2**:**1** ratio	yield[c] (%)
1		**L1**	91	71	50:50	45
2		**L9**	99	96	50:50	67
3		**L1**	99	95	67:33	84
4		**L9**	76	100	80:20	58
5		**L1**	50	90	47:53	45
6		**L9**	70	95	68:32	67
7		**L1**	76	100	50:50	46
8		**L9**	99	100	84:16	62
9		**L1**	86	90	83:17	32
10		**L9**	99	100	79:21	36
11		**L1**	69	96	82:18	nd
12		**L1**	24	78	83:17	nd
13		**L9**	33	94	86:14	nd
14		**L1**	4	68	33:67	nd
15		**L9**	0	–	–	–
16		**L9**	99	100	80:20	80
17		**L9**	91	95	50:50	49

[a] Butadiene = 0.5 mL (5.7 mmol); BD/Ni(cod)$_2$/ligand: 125/1/1.5; ROH/BD = 3; toluene = 1 mL; T = 80 °C; t = 17 h.
[b] Determined by GC analysis.
[c] isolated yield.

formed from butadiene hydroethoxylation reaction at 60 °C gave a TOF of 112 h^{-1} (Entry 13, Table 1, OC4 = 18% after 2 h).

In our previous publication, we showed that primary alcohols such as methanol or benzyl alcohol could be used for this reaction whereas secondary or tertiary alcohols such as *i*PrOH or *t*BuOH failed to react. We next decided to extend our study to other primary alcohols, in particular benzyl alcohol derivatives and primary bio-sourced alcohols. The use of benzyl alcohol and its substituted derivatives allowed the isolation and the spectroscopic characterization of the corresponding ethers unambiguously.

Hydroalkoxylation of these alcohols was performed in the presence of nickel catalysts coordinated by the two most efficient phosphines, dppb **L1** and dppmb

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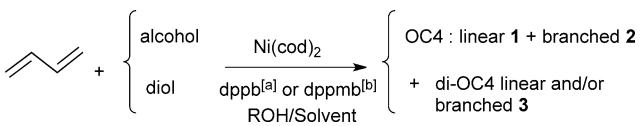
L9. The reaction conditions were beforehand optimized with benzyl alcohol and we found that a $PhCH_2OH$/BD ratio of 3 was the optimal value to obtain simultaneously satisfying conversions and OC4 selectivities. The reactions were performed for 17 h in order to attain maximum conversions and isolated yields. Results are reported in Table 2.

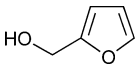
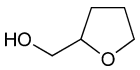
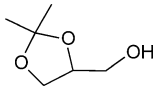
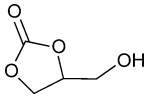
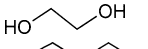
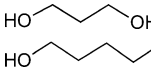
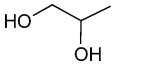
The reactions were successful with benzylic alcohol and its derivatives regardless of the nature and position of the substituents on the aromatic cycle. Conversions of 69–99% and high to total selectivity to the OC4 ethers were obtained in all cases (Entries 1–11, Table 2). As previously observed with ethanol, the branched isomer was the major product.

We then examined the possibility to perform this reaction with cinnamyl and 3-phenylpropargyl alcohols (Entries 12–15) but in these two cases, the conversion dropped drastically with no conversion in the case of propargylic alcohol using **L9** (dppmb, Entry 15). Finally two heteroaromatic primary alcohols were evaluated in the presence of **L9** ligand with interesting results in terms of conversions and OC4 selectivities (Entries 16 and 17, Table 2). We then focused our attention particularly on bio-sourced alcohols. Furfuryl and tetrahydrofurfuryl alcohols are obtained from the reduction of furfural. The furfural itself is produced from the hydrolysis and dehydration of agricultural wastes. Hydrogenolysis of sorbitol or xylitol, originating respectively from glucose, affords the production of ethane-1,2-diol or propane-1,3-diol. On the other hand, butane-1,4-diol can be obtained by fermentation of biomass sugars. Glycerol carbonate and solketal were synthesized according to described procedures from glycerol which is available in large amounts as a by-product of biodiesel production.[26] We performed catalytic reactions in the presence of dppb **L1** or dppmb **L9** based nickel catalysts. Only the best results for each alcohol in terms of activity and chemoselectivity into OC4 ethers are reported in Table 3. In the first set of experiments, we used the initial catalytic conditions: $Ni(cod)_2$/ligand in toluene as the solvent. It appeared that furfuryl alcohol, tetrahydrofurfuryl alcohol and solketal could be converted into the corresponding OC4 ethers with satisfying selectivities (79 to 100% conversions, Entries 1–3, Table 3) whereas in the case of glycerol carbonate, no reaction occurred (Entry 4). In the case of the diols that are more hydrophilic, conversions were always very limited regardless of the ligand (48% conversion for butane-1,3-diol and <10% for ethane-1,2-diol and 1,2- or 1,3-propanediol).

While performing these catalytic reactions, we observed that these diols were not entirely soluble in toluene. We then used THF as the solvent in which the diols were much more soluble. With these conditions, the alcohols could be converted into OC4 ethers with moderate to high conversions and selectivities (conversions = 54–93%, OC4 selectivities = 52–83%, Entries 5–8). As two hydroxyl functions are present, diethers were also found in the reaction mixture. In the case of propane-1,2-diol, the secondary hydroxyl moiety was almost unreactive as we already observed in the case of 2-propanol or *tert*-butanol hydroalkoxylation.[22] The monoether produced from the etherification of the primary hydroxyl group was the sole reaction product.

Table 3. Hydroalkoxylation of butadiene with bio-sourced alcohols



Entry	alcohol	Conv. (%)[c]	Sel. **1**+**2** (%) (**2**/**1** ratio)[c]	Sel. **3**[c] (%)
1[a]		100	98 (67:33)	–
2[a]		92	46 (50:50)	–
3		79[a] 100[b]	51 (50:50) 98 (71:29)	– –
4		0[a,b]	– –	–
5[b]		81	83 (55:45)	13
6[b]		90	83 (52:48)	13
7[b]		93	85 (63:37)	11
8[b]		54	52 (nd)	12

[a] Butadiene = 1.5 mL (17.2 mmol); BD/$Ni(cod)_2$/dppb = 125:1:1.5; ROH/BD = 3; toluene = 3 mL; T = 80 °C; t = 17 h.

[b] Butadiene = 1.5 mL (17.2 mmol); BD/$Ni(cod)_2$/dppmb = 125:1:1.5; ROH/BD = 1.7; THF = 2.5 mL; T = 80 °C; t = 17 h.

[c] Determined by GC analysis.

The scope of the reaction was then further studied with butadiene derivatives such as isoprene, piperylene, 1-phenylbuta-1,3-diene and hexa-2,4-diene as well as myrcene (Table 4). In comparison to butadiene, a larger number of possible isomeric alkenyl ethers can be obtained due to the substituents on the dienes. In the case of the ethoxylation of isoprene, five isomers are potentially accessible depending on the regioselectivity of the reaction (Scheme 4).

The reaction of isoprene with ethanol and methanol, at 65 °C, afforded the corresponding OC5 ethers with 86% and 80% of isoprene conversion respectively after 17 h (Entries 1 and 2, Table 4). Among the

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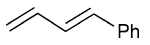
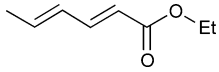
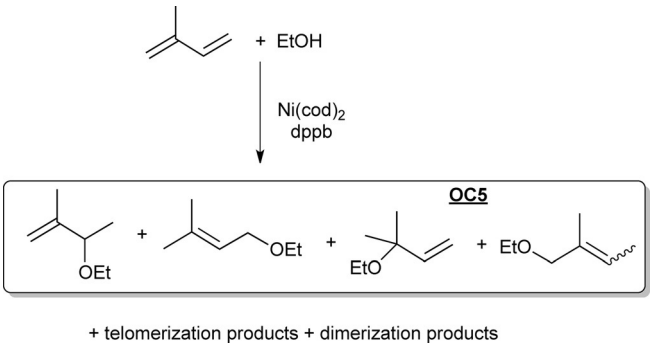
Table 4. Hydroalkoxylation of substituted dienes with various alcohols.[a]

Entry	Diene	ROH	T (°C)	Conv. (%)	Yield **OC5** (%)[b]
1		MeOH	65	86	86 (nd)[c]
2		EtOH	65	80	80 (nd)
3		EtOH	80	86	82 (nd)
4		BzOH	65	80	80 (73)
5		EtOH	80	43	0 (0)
6		BzOH	65	55	37 (19)
7		BzOH	65	81	16 (16)
8		BzOH	80	0	–
9		BzOH	80	0	–
10	Myrcene	EtOH	80	24	13 (nd)
11		BzOH	65	0	–
12		BzOH	80	29	29 (10)

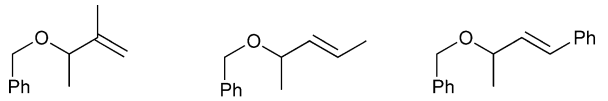
[a] Diene = 17.2 mmol; diene/Ni(cod)$_2$/dppmb = 125:1:1.5; ROH/diene = 3; toluene = 3 mL; t = 17 h.
[b] Determined by GC analysis, isolated yield of major isomer in parentheses; please see Scheme 5 for the structures.
[c] not determined.



Scheme 4. Hydroalkoxylation of isoprene with ethanol.

OC5 ethers formed, a major product was always observed (ca 80% selectivity), but as seen previously in the case of butadiene, the isoprenyl methyl and ethyl ethers could not be isolated due to their high volatility. The products obtained from the reaction with benzyl alcohol allowed isolation of the main isomer via silica gel column chromatography, and the product was further fully characterized by NMR (Scheme 5). As in the case of butadiene, the major product is the branched isomer at the less substituted position.

Piperylene was also evaluated but this diene appears to be less reactive than isoprene with only 43% conversion for the ethoxylation reaction at 80°C



Scheme 5. Major products obtained from the reaction between benzylic alcohol and substituted butadiene derivatives.

(Table 4, Entry 5) whereas the benzyl alcohol led to 65% conversion at 65°C (Entry 6). Selectivities to OC5 ethers were also disappointing with no OC5 ethyl ethers and only 37% of OC5 in the case of benzyl alcohol. Even then, a major product was observed and isolated from the reaction mixture with 19% yield (see experimental part). A similar result was obtained with 1-phenyl-buta-1,3-diene which led to a poor product yield in the hydroalkoxylation reaction (16% selectivity, entry 7). Hexa-2,4-diene and ethyl sorbate also proved to be unsuitable for hydroalkoxylation with no diene conversion: the substitution of the two double bonds led to bulky substrates, which are much less reactive. Finally, we used myrcene which can be extracted from plants. Although the reactivity of this natural diene was very limited, ethyl and benzyl ethers could be formed.

Conclusions

We have developed an efficient and selective synthesis of alkyl butenyl ethers from butadiene and primary alcohols using simple and readily accessible nickel catalysts. To access high selectivities, the choice of ligand associated to the nickel precursor is crucial and diphosphines with two phosphorous atoms bridged with four carbons led to superior catalytic efficiency. From this observation, the use of the dppmb ligand is a good alternative to the dppb ligand for the synthesis of OC4 ethers, giving rise to better selectivities. With this optimized catalytic system, OC4 ethers were synthesized from a large range of primary alcohols under mild conditions. Agro-based alcohols and diols were efficiently converted according to this reaction thus showing the interest of the synthetic methodology in the context of the valorization of polyols. The reaction was then extended to substituted dienes, but they were less reactive. Further studies are in progress to investigate the mechanistic details of this reaction by NMR spectroscopic analyses, together with X-Ray characterizations of some nickel intermediates, and results will be reported in due time.

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Experimental Section

General methods: Hydroalkoxylation reactions were carried out under nitrogen. Furthermore, the glass reactor closed with a Rotaflo® stopcock was filled in a glove box under argon with catalyst and solvents. Other reactants were added out of the gloves box with Schlenk tube techniques. Chemicals were purchased from Aldrich, Alfa Aesar, Acros, Linde Gas France and Strem. Benzyl alcohol was distilled over CaH_2 before use. Benzyl alcohol derivatives, 4-pyridinemethanol, 2-thiophenemethanol, cinnamyl alcohol, 3-phenylpropargyl alcohol, butadiene and its derivatives were used without further purification. Ethanol and methanol were distilled over magnesium turnings. Toluene and tetrahydrofuran were obtained from a solvent purification system MBraun SPS-800. Furfuryl alcohol, tetrahydrofurfuryl alcohol and diols were distilled over $CaSO_4$ and $NaHCO_3$. Analytical thin layer chromatography (TLC) was carried out using commercial silica gel plates (Merck 60 F254), spots were determined with UV light. Conversions were determined by gas chromatography on a Shimadzu 2010 apparatus equipped with an Equity-5 column (30 m, i.d.= 0.32 mm). The isolated yields were determined after flash chromatography on Reveleris® Flash Chromatography equipped with ELSD and UV (254 nm, 280 nm) detectors. The compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using a Bruker AC 300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported to the center of the solvent resonance [$CDCl_3$: 7.27 (^{1}H), 77.0 (^{13}C) ppm].

General procedures

General procedure for the catalytic hydroalkoxylation of 1,3-butadiene with ethanol: The catalytic solution is prepared in a glove box by mixing $Ni(cod)_2$ (3.8 mg, 0.014 mmol) and the ligand (0.021 mmol) in 3 mL toluene in a glass reactor closed by a Rotaflo® stopcock. Under nitrogen atmosphere, the tube was cooled at −15 °C and dry and degassed EtOH was added (10 mL). A precise amount of butadiene (1.5 mL, 17.2 mmol) was then condensed at low temperature and transferred into the reaction mixture via a cannula. The glass reactor was closed and heated to 80 °C for 2 h. After reaction, the mixture was cooled and vented before GC analyses with heptane as internal standard.

General procedure for the catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives: The catalytic solution is prepared in a glove box by mixing $Ni(cod)_2$ (12.6 mg, 0.046 mmol) and the ligand (0.069 mmol) in 1 mL toluene or a glass reactor closed by a Rotaflo® stopcock. Under nitrogen atmosphere, the tube was cooled at −15 °C and the degassed benzyl alcohol derivative was added (51.6 mmol, 3 equiv). A precise amount of butadiene (1.5 mL, 17.2 mmol) was then condensed at low temperature and transferred into the reaction mixture via a cannula. The glass reactor was closed and heated to 80 °C for 17 h. After reaction, the mixture was cooled and vented before GC analyses with heptane as internal standard. The compounds were isolated by flash chromatography column.

General procedure for the catalytic hydroalkoxylation of 1,3-butadiene with bio-sourced alcohols: The catalytic solution is prepared in a glove box by mixing $Ni(cod)_2$ (26.3 mg, 0.096 mmol) and the ligand (0.143 mmol) in 3 mL toluene or 2.5 mL THF in a glass reactor closed by a Rotaflo® stopcock. Under nitrogen atmosphere, the tube was cooled at −15 °C and degassed polyol derivative was added (29.1 mmol, 1.5 equiv). A precise amount of butadiene (1.5 mL, 17.2 mmol) was then condensed at low temperature and transferred in the reaction mixture via a cannula. The glass reactor was closed and heated to 80 °C for 17 h. After reaction, the mixture was cooled and vented before GC analyses with heptane as internal standard. The compounds were isolated by flash chromatography column.

General procedure for the catalytic hydroalkoxylation of 1,3-dienes with alcohols: The catalytic solution is prepared in a glove box by mixing $Ni(cod)_2$ (38.2 mg, 0.14 mmol) and the ligand (0.21 mmol) in 3 mL toluene or 2.5 mL THF in a glass reactor closed by a Rotaflo® stopcock. Under nitrogen atmosphere, purified and degassed alcohol was added (51.9 mmol, 3 equiv). A precise amount of 1,3-diene (17.2 mmol) was then added to the mixture. The glass reactor was closed and heated to 80 °C for 17 h. After reaction, the mixture was cooled and vented before GC analyses with heptane as internal standard. The compounds were isolated by flash chromatography column.

Characterization of butenyl ethers

(Butenyloxymethyl)benzene: The products were synthesized according to the general procedure for the catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 67% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 92:8 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.28–7.43 (m, 5H), 5.86 (ddd, J=17.3, 10.2, 7.2 Hz, 1H), 5.62–5.82 (m, 2H), 5.20–5.31 (m, 2H), 4.63 (d, J=12.1 Hz, 1H), 4.57 (s, 1H), 4.55 (s, 1H), 4.45 (d, J=11.7 Hz, 1H), 4.02 (dq, J=5.8, 1.3 Hz, 1H), 3.95–3.99 (m, 2H), 3.93–3.97 (m, 2H), 1.78 (dd, J=6.0, 1.1 Hz, 3H), 1.70 (dd, J=5.8, 0.8 Hz, 3H), 1.35 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 13.0, 17.6, 21.2, 65.3, 69.8, 70.7, 71.8, 71.9, 76.1, 115.9, 127.2, 127.47, 127.6, 127.6, 128.2, 129.3, 138.4, 138.7, 140.1. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{11}H_{15}O$: 163.1118; found: 163.1109.

1-(Butenyloxy)methyl-3-methoxybenzene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 84% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 92:8 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.28 (t, J=8.0 Hz, 1H), 6.92–6.99 (m, 2H), 6.81–6.89 (m, 1H), 5.83 (ddd, J= 17.3, 10.2, 7.3 Hz, 1H), 5.60–5.77 (m, 2H), 5.15–5.32 (m, 2H), 4.59 (d, J=12.1 Hz, 1H), 4.53 (s, 1H), 4.51 (s, 1H), 4.41 (d, J=12.2 Hz, 1H), 4.13 (d, J=6.0 Hz, 1H), 3.96 (qd, J=6.0, 0.8 Hz, 1H), 3.83 (s, 3H), 1.76 (dq, J=6.0, 1.1 Hz, 3H), 1.69 (d, J=6.0 Hz, 3H), 1.33 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 17.65, 21.26, 55.01, 69.69, 71.65, 76.08, 112.86, 13.10, 115.94, 119.73, 119.84, 127.50, 129.21, 129.44, 127.50, 129.21, 129.44, 140.12, 140.39, 159.65. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{12}H_{17}O_2$: 193.1223; found: 193.1223.

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Methyl 4-(Butenyloxy)methylbenzoate: The products were synthesized according to the general procedure for the catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 67% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 92:8 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), branched isomer: δ 7.99 (d, J=8.3 Hz, 2H), 7.40 (d, J=8.5 Hz, 2H), 5.78 (ddd, J=17.3, 10.2, 7.3 Hz, 1H), 5.21 (dq, J=12.1, 0.9 Hz, 1H), 5.17 (dq, J=5.1, 0.9 Hz, 1H), 4.61 (d, J=12.8 Hz, 1H), 4.43 (d, J=12.8 Hz, 1H), 3.92 (dq, J=6.4, 0.8 Hz, 1H), 3.90 (s, 3H), 1.30 (d, J=6.4 Hz, 3H). Linear isomer: δ 8.00 (d, J=8.3 Hz, 2H), 7.39 (d, J=8.1 Hz, 2H), 5.55–5.85 (m, 2H), 5.20 (m, J=12.2, 1.2 Hz, 2H), 5.16 (m, J=5.8, 2.1 Hz, 2H), 4.54 (s, 2H), 4.52 (s, 2H), 3.89 (s, 3H), 1.71 (dd, J=6.1, 1.2 Hz, 3H), 1.63 (dd, J=6.0, 0.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), branched isomer: δ 144.14, 139.85, 129.07, 127.02, 116.22, 76.61, 69.25, 51.88, 21.22. Linear isomer: δ 166.78, 143.77, 129.75, 129.14, 127.08, 126.99, 116.19, 71.06, 51.85, 17.62. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{13}H_{17}O_3$: 221.1172; found: 221.1173.

1-(Butenyloxy)methyl-3-chlorobenzene: The products were synthesized according to the general procedure for catalytic hydroakoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 62% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate 95:5 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.22–7.33 (m, 3H), 5.85 (ddd, J=17.5, 10.4, 7.3 Hz, 1H), 5.62–5.78 (m, 2H), 5.20–5.33 (m, 2H), 4.59 (d, J=12.2 Hz, 1H), 4.53 (s, 2H), 4.51 (s, 2H), 4.41 (d, J=12.2 Hz, 1H), 4.16 (d, J=6.0 Hz, 2H), 3.90–4.06 (m, 3H), 1.80 (dq, J=6.0, 1.1 Hz, 3H), 1.72 (dd, J=6.0, 0.8 Hz, 3H), 1.37 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 120.08, 17.56, 21.14, 65.43, 68.93, 70.91, 76.41, 16.07, 125.26, 125.37, 127.23, 127.31, 127.35, 127.42, 129.36, 129.51, 134.04, 139.80, 140.57, 140.89.

1-(Butenyloxy)methyl-2-chlorobenzene: The products were synthesized according to the general procedure for the catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 36% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 95:5 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.50–7.63 (m, 1H), 7.17–7.41 (m, 3H), 5.86 (ddd, J=17.3, 10.2, 7.2 Hz, 1H), 5.63–5.80 (m, 2H), 5.17–5.35 (m, 2H), 4.77 (s, 2H), 4.67 (d, J=13.2 Hz, 1H), 4.63 (s, 2H), 4.57 (d, J=13.2 Hz, 1H), 4.20 (d, J=5.7 Hz, 1H), 4.02 (s, 3H), 1.77 (d, J=6.2 Hz, 3H), 1.70 (s, 3H), 1.37 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 17.67, 21.22, 65.91, 67.05, 68.72, 69.67, 71.32, 76.88, 116.01, 126.57, 128.24, 128.79, 129.02, 129.05, 129.14, 132.62, 136.54, 139.94. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{11}H_{14}OCl$: 197.0728; found: 197.0729.

1-(Butenyloxymethyl)-3,5-dimethylbenzene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol derivatives. The crude mixture gave 10% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 80:20 eluent (R_f=0.9). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.00 (br. s, 2H), 6.95 (s, 1H), 5.60–5.90 (m, 2H), 5.18–5.30 (m, 2H), 4.56 (d, J=13.4 Hz, 1H), 4.48 (s, 2H), 4.46 (s, 2H), 4.34 (d, J=11.7 Hz, 1H), 4.12 (ddt, J=6.0, 1.9, 0.9 Hz, 2H), 3.99 (ddt, J=6.0, 2.3, 1.1 Hz, 2H), 2.34 (s, 6H), 1.76 (dtd, J=6.0, 1.2, 1.2, 1.1 Hz, 3H), 1.69 (dtd, J=6.0, 1.1, 1.1, 0.8 Hz, 3H), 1.33 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 13.18, 17.76, 21.02, 21.20, 21.32, 21.37, 65.39, 67.10, 70.01, 70.92, 71.99, 72.12, 76.21, 100.50, 116.00, 124.61, 125.52, 125.61, 125.63, 125.78, 126.93, 127.51, 127.59, 127.89, 129.01, 129.10, 129.14, 129.58, 130.00, 136.15, 137.83, 138.20, 138.23, 140.28. HRMS (EI) m/z $[M+Na]^+$: calcd for $C_{13}H_{17}ONa$: 212.1172; found: 212.1184.

2-(Butenyloxymethyl)thiophene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 80% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 95:5 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.24–7.34 (m, 1H), 6.94–7.07 (m, 2H), 5.81 (ddd, J=17.4, 10.1, 7.3 Hz, 1H), 5.73 (s, 2H), 5.17–5.32 (m, 2H), 4.72 (td, J=12.2, 0.7 Hz, 1H), 4.56–4.71 (m, 2H), 4.10–4.15 (m, 2H), 3.91–4.06 (m, 1H), 1.75 (dq, J=6.2, 1.1 Hz, 3H), 1.66–1.71 (m, 3H), 1.31 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 12.92, 17.69, 21.27, 64.38, 66.08, 66.28, 70.41, 75.76, 116.31, 125.37, 125.85, 126.47, 127.26, 129.85, 139.84, 141.66.

4-(Butenyloxymethyl)pyridine: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 49% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 20:80 eluent (R_f=0.4). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 8.50 (dt, J=4.3, 1.7 Hz, 2H), 7.20 (d, J=6.0 Hz, 2H), 5.63–5.79 (m, 2H), 5.50–5.63 (m, 1H), 5.09–5.21 (m, 1H), 4.43 (dd, J=50.9, 13.6 Hz, 2H), 4.45 (s, 2H), 4.45 (s, 2H), 4.07 (d, J=6.6 Hz, 1H), 3.94 (dt, J=6.2, 0.8 Hz, 2H), 3.86 (dquin, J=0.6, 6.4 Hz, 1H), 1.68 (dd, J=6.1, 1.0 Hz, 3H), 1.61 (dd, J=6.1, 0.7 Hz, 3H), 1.27 (d, J=6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 13.04, 17.61, 21.11, 30.14, 65.78, 68.03, 69.81, 71.28, 16.88, 116.46, 121.58, 121.63, 121.91, 126.05, 126.82, 128.44, 130.03, 139.44, 147.53, 147.88, 149.55, 151.08.

2-(Butenyloxy)methylfuran: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 75% yield of the branched/linear (*Z*/*E*) isomers as yellow oil after flash column chromatography on silica gel with petroleum ether/diethyl ether: 60:40 eluent (R_f=0.8). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 7.31–7.5 (m, 2H), 6.20–6.28 (m, 4H), 5.45–5.75 (m, 3H), 5.09–5.19 (m, 2H), 4.39–4.44 (m, 1H), 4.38 (s, 1H), 4.36 (s, 1H), 4.23–4.29 (m, 1H), 4.01 (d, J=6.0 Hz 1H), 3.80–3.92 (m, 2H), 1.56–1.68 (m, 3H), 1.19 (d, J=6.0, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 17.6, 21.17, 25.41, 25.51, 28.09, 28.21, 66.54, 68.17, 70.82, 70.92, 77.37, 78.03, 115.58, 115.61, 140.30.

2-(Butenyloxy)methyltetrahydrofuran: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with benzyl alcohol and derivatives. The crude mixture gave 13% yield of the

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branched/linear (*Z*/*E*) isomers as yellow oil after flash column chromatography on silica gel with petroleum ether/diethyl ether: 60:40 eluent (R_f = 0.64). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.78–5.65 (m, 1H), 5.58–5.53 (m, 1H), 5.17–5.07 (m, 2H), 4.06–3.94 (m, 1H), 3.88–3.79 (m, 2H), 3.76–3.69 (m, 1H), 3.48–3.36 (m, 1H), 3.32–3.26 (m, 1H), 2.05–1.97 (m, 1H), 1.95–1.79 (m, 3H), 1.69–1.52 (m, 2H), 1.23 (dt, J = 6.4, 1.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 17.6, 21.17, 25.41, 25.51, 28.09, 28.21, 66.54, 68.17, 70.82, 70.92, 77.37, 78.03, 115.58, 115.61, 140.30.

4-(Butenoxymethyl)-2,2-dimethyl-1,3-dioxolane: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with bio-sourced derivatives. The crude mixture gave 61% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 1:1 eluent (R_f = 0.3). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.56–5.73 (m, 1H), 5.41–5.56 (m, 1H), 5.02–5.16 (m, 2H), 4.12–4.25 (m, 1H), 4.03 (d, J = 7.0 Hz, 1H), 3.98 (dd, J = 8.3, 6.4 Hz, 1H), 3.86–3.92 (m, 2H), 3.73–3.84 (m, 2H), 3.60–3.72 (m, 2H), 3.20–3.54 (m, 2H), 1.62–1.69 (m, 3H), 1.57–1.62 (m, 3H), 1.33–1.38 (m, 6H), 1.29 (s, 6H), 1.18 (d, J = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 12.9, 17.5, 21.0, 21.0, 25.2, 25.2, 66.6, 67.0, 69.1, 69.2, 70.7, 70.9, 72.0, 74.6, 74.7, 74.7, 77.6, 109.1, 109.1, 109.0, 115.8, 115.8, 126.5, 127.2, 127.8, 129.5, 139.9. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{11}H_{19}O_3$: 187.1329; found: 187.1328.

2-(Butenyloxy)ethanol: The products were synthesized according to general procedure for catalytic hydroalkoxylation of 1,3-butadiene with bio-sourced derivatives. The crude mixture gave 38% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 1:1 eluent (R_f = 0.3). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.58–5.78 (m, 1H), 5.43–5.58 (m, 1H), 5.01–5.18 (m, 1H), 3.97–4.07 (m, 1H), 3.88 (ddd, J = 3.8, 2.4, 1.1 Hz, 1H), 3.74–3.85 (m, 1H), 3.64 (br. s., 2H), 3.42–3.55 (m, 2H), 3.31–3.40 (m, 2H), 2.89 (br. s., 1H), 1.61–1.68 (m, 3H), 1.57–1.61 (m, 3H), 1.19 (dd, J = 6.4, 3.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 12.91, 17.47, 20.95, 61.46, 61.60, 66.16, 69.27, 70.93, 71.62, 77.17, 115.75, 126.46, 127.28, 127.79, 129.56, 138.88. HRMS (EI) m/z $[M+H]^+$: calcd for $C_6H_{13}O_2$: 117.0910; found: 117.0919.

3-(Butenoxy)propanol: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-butadiene with bio-sourced derivatives. The crude mixture gave 89% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 1:1 eluent (R_f = 0.3). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.54–5.71 (m, 1H), 5.38–5.53 (m, 1H), 4.97–5.14 (m, 2H), 3.96 (d, J = 6.4 Hz, 1H), 3.78–3.86 (m, 2H), 3.63 (br. s, 2H), 3.48 (t, J = 6.0 Hz, 1H), 3.16 (br. s., 1H), 1.66–1.79 (m, 2H), 1.62 (dd, J = 6.2, 0.9 Hz, 3H), 1.58 (dd, J = 7.5, 0.8 Hz, 3H), 1.15 (dd, J = 6.4, 2.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 12.87, 17.45, 20.99, 31.96, 32.02, 60.70, 61.03, 66.05, 68.16, 71.48, 77.02, 115.59, 126.47, 127.18, 127.65, 129.23, 139.85. HRMS (EI) m/z $[M+H]^+$: calcd for $C_7H_{15}O_2$: 131.1067; found: 131.1075.

1,3-Di(butenoxy)propane: The products were synthesized according to the general procedure for catalytic hydroakoxylation of 1,3-butadiene with bio-sourced derivatives. The crude mixture gave 10% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid by flash column chromatography on silica gel with petroleum ether/diethyl ether: 1:1 eluent (R_f = 0.9). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.61–5.77 (m, 2H), 5.47–5.60 (m, 1H), 5.02–5.19 (m, 2H), 3.97–4.03 (m, 1H), 3.86 (dd, J = 6.0, 0.8 Hz, 2H), 3.78 (quin, J = 6.5 Hz, 1H), 3.42–3.56 (m, 3H), 3.31–3.42 (m, 1H), 1.75–1.88 (m, 2H), 1.68 (dd, J = 6.2, 1.1 Hz, 3H), 1.61–1.66 (m, 1H), 1.20 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 13.03, 17.64, 21.13, 30.11, 30.24, 30.35, 65.15, 67.04, 67.20, 71.49, 76.76, 115.26, 127.03, 127.42, 127.66, 129.03, 140.44, 140.48. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{11}H_{21}O_2$: 185.1536; found: 185.1531.

4-(Butenoxy)butanol: The products were synthesized according to the general procedure for catalytic hydroakoxylation of 1,3-butadiene with bio-sourced derivatives. The crude mixture gave 53% yield of the branched/linear (*Z*/*E*) isomers as colorless liquid after flash column chromatography on silica gel with petroleum ether/diethyl ether: 1:1 eluent (R_f = 0.3). ^{1}H NMR (300 MHz, $CDCl_3$), mixture isomers: δ 5.60–5.76 (m, 1H), 5.45–5.60 (m, 1H), 5.01–5.19 (m, 2H), 4.00 (d, J = 6.4 Hz, 2H), 3.86 (d, J = 6.2 Hz, 2H), 3.79 (quin, J = 6.6 Hz, H), 3.58 (d, J = 4.3 Hz, 2H), 3.37–3.51 (m, 2H), 3.22–3.35 (m, 2H), 2.94 (br. s., 1H), 2.86 (br. s, 1H), 1.66 (dd, J = 6.2, 0.9 Hz, 3H), 1.54–1.64 (m, 4H), 1.20 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$), mixture isomers: δ 13.40, 17.99, 21.45, 27.03, 27.21, 30.41, 30.52, 62.81, 62.84, 66.41, 68.51, 70.32, 71.87, 77.39, 116.03, 127.01 127.73, 128.18, 129.77, 140.50. HRMS (EI) m/z $[M+H]^+$: calcd for $C_8H_{17}O_2$: 145.1223; found: 145.1222.

Characterization of alkenyl ethers

(((3-Methylbut-3-en-2-yl)oxy)methyl)benzene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-dienes with alcohols at 65 °C. The crude mixture gave 73% yield of the branched major isomer as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 98:2 eluent (R_f = 0.9). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.36 (m, 5H), 4.94–4.96 (m, 2H), 4.48 (d, J = 11.8 Hz, 1H), 4.27 (d, J = 11.8 Hz, 1H), 3.91–3.97 (q, J = 6.4 Hz, 1H), 1.72 (s, 3H), 1.30 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.6, 20.2, 69.8, 78.7, 112.6, 127.4, 127.7, 128.4, 138.8, 146.0. HRMS (EI) m/z $[M+H]^+$: calcd for $C_{12}H_{17}O$: 177.1274; found: 177.1274.

((Pent-3-en-2-yloxy)methyl)benzene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-dienes with alcohols at 65 °C. The crude mixture gave 19% yield of the linear isomers with *Z*/*E* configuration as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 95:5 eluent (R_f = 0.76). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.20 (m, 5H), 5.62–5.55 (m, 1H), 5.41–5.38 (m, 1H), 4.50 (d, J = 12.0 Hz, 1H), 4.31 (d, J = 12.0 Hz, 1H), 3.82 (q, J = 6.2 Hz, 1H), 1.67 (dd, J = 1.6, 6.4 Hz 3H), 1.58 (dd, J = 2.0, 6.8 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.20 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.0, 22.0, 70.0, 76.1, 127.6, 127.9, 128.0, 128.6, 133.3, 133.6, 139.4.

(3-(Benzyloxy)but-1-en-1-yl)benzene: The products were synthesized according to the general procedure for catalytic

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hydroalkoxylation of 1,3-dienes with alcohols at 65 °C. The crude mixture gave 16% yield of the branched isomer as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 95:5 eluent (R_f = 0.44). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–7.13 (m, 10H), 6.46 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 7.5, 15.9 Hz, 1H), 4.54 (d, J = 12.0, 1H), 4.36 (d, J = 12.0, 1H), 4.07–3.98 (m, 1H, 1.30 (d, J = 6.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 70.1, 75.9, 126.6, 127.5, 127.8, 128.4, 128.7, 128.7, 131.5, 131.8.

(((7-Methyl-3-methyleneoct-6-en-2-yl)oxy)methyl)benzene: The products were synthesized according to the general procedure for catalytic hydroalkoxylation of 1,3-dienes with alcohols at 80 °C. The crude mixture gave 10% yield of the branched isomer as colorless liquid after flash column chromatography on silica gel with petroleum ether/ethyl acetate: 95:5 eluent (R_f = 0.47). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.38 (m, 5H), 5.49–5.59 (m, 1H), 5.43 (td, J = 1.2, 6.7 Hz, 1H), 5.10–5.19 (m, 3H), 4.47–4.54 (m, 2H), 4.34 (s, 2H), 4.30 (s, 2H), 4.01–4.07 (m,1H), 3.92–3.98 (m,2H), 2.03–2.24 (m, 4H), 1.56–1.78 (m, 9H), 1.31 (d, J = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.1, 20.6, 25.7, 26.5, 30.3, 39.66, 66.6, 69.9, 71.4, 74.6, 76.6, 110.8, 124.2, 127.3, 127.5, 127.6, 127.7, 127.8, 128.3, 150.1. HRMS (EI) m/z [M + H]$^+$: calcd for $C_{17}H_{25}O$: 245.1900; found: 245.1899.

Acknowledgements

We are grateful to the Region Nord-Pas de Calais for A. Mifleur's fellowship. Chevreul institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Institut Universitaire de France, Région Nord – Pas de Calais and FEDER are acknowledged for supporting and funding this work.

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