Cohalogenation of Alkenes in Ethylene Oxide: Efficient Methodology for the Preparation of Allyl Vinyl Ether Precursors of γ,δ-Unsaturated Aldehydes

Jean-Pierre Dulcère, Jean Rodriguez

Laboratoire de Synthèse Organique, SM³B URA 1411, Université d' Aix-Marseille III, Faculté des Sciences de St Jérôme-D 12, Avenue Escadrille Normandie-Niemen, F-13397 Marseille Cedex 13, France

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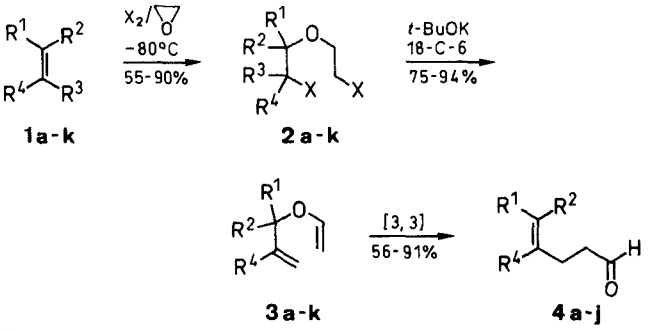
An investigation of the cohalogenation–dehydrohalogenation sequence as a method for the preparation of allyl vinyl ethers from simple olefins has been performed. Alkenes **1a–k** react with bromine or chlorine in the presence of ethylene oxide at −80°C to form β,β′-dihalo ethers **2a–k** regio- and stereoselectively in high yields. Two of these β,β′-dihalo ether intermediates were selectively monodehydrohalogenated by potassium *tert*-butoxide to give 2-haloalkyl vinyl ethers in almost quantitative yields. Use of an excess of base produces allyl vinyl ethers **3a–k** in good yields. Thermal rearrangement of the latter converts them into the corresponding γ,δ-unsaturated aldehydes **4a–j**.

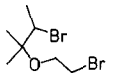
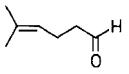
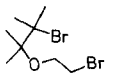
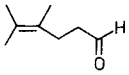
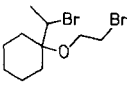
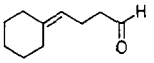
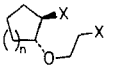
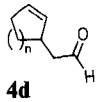
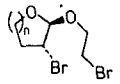
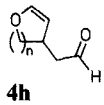
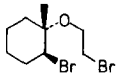
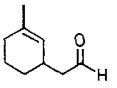
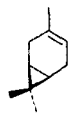
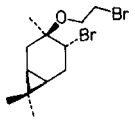
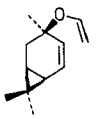
Since its discovery,[1] the aromatic Claisen rearrangement and particularly its aliphatic analog have stimulated much interest in mechanistic[2] and synthetic aspects of these transformations.[3] Investigations concerning the preparation of allyl vinyl ethers have been crucial to the widespread use of this important synthetic reaction for carbon–carbon bond formation. Indeed, since the early work of Bergmann and Corte,[4] and Lauer and Kilburn,[5] the preparation of allyl vinyl ethers has received much attention. Hurd and Pollack[6] described in 1938 a non-general three-step preparation of 1-vinyloxy-2-propene in low yield. This preparation was improved by Paul[7] and co-workers in 1950 using Reppe vinylation of allyl alcohol with pressurized acetylene. A more useful general method proposed in 1957 by Watanabe[8] is based on the mercuric acetate catalyzed exchange of alcohols with alkyl vinyl ethers. The acid-catalyzed ketalization of aldehydes[9] and ketones,[10] the condensation of vinyl Grignard reagents with α-chloro, β′-halo ethers followed by dehydrohalogenation,[11] and Wittig olefination[12] have also been used in the preparation of allyl vinyl ethers. In 1967 Saucy and Marbet[13] reported the acid-catalyzed exchange and rearrangement of allylic alcohols with low boiling vinyl ethers. More recently Coates[14] and co-workers proposed that the thermal condensation of acrolein diethyl acetal with β-dicarbonyl and related compounds takes place via an α-alkoxyallyl vinyl ether generated under mild conditions. Furthermore, the applicability of the Claisen allyl ester enolate rearrangement[15] and Johnson[16] and Eschenmoser[17] modifications has been demonstrated in recent years. However, these latter methods lead to carboxylic acid derivatives that must be further manipulated if aldehydes are required. Finally the synthetic usefulness of allyl vinyl ethers has been emphasized recently by the work of Grieco and co-workers[18] on unprecedented [1,3]-sigmatropic rearrangements at ambient temperature promoted by lithium perchlorate solutions in ether. In spite of its widespread use, the limitations of the Claisen rearrangement due to the lack of efficient general methods for the preparation of allyl vinyl ethers, have been emphasized by Büchi.[19] Although his modification based on the preparation and rearrangement of *trans*-3-(allyloxy)acrylic acids has the merit to be widely applicable and does not need catalysis by mercuric salts or mineral acids, it requires rather expensive and elaborated starting materials.

Our interest in the functionalization of alkenes by the cohalogenation–dehydrohalogenation sequence[20] prompted us to develop a general, high yield route to the synthetically valuable allyl vinyl ether precursors of aldehydes by a method which avoids the use of mercuric or mineral acid catalysis and starts from simple, inexpensive olefinic substrates. This goal has been reached by means of the double dehydrohalogenation of β,β′-dihalogenated ethers,[21] which are readily available by the cohalogenation of alkenes in ethylene oxide.[22] In this article we present results of an exploratory investigation of such transformations (cohalogenation–dehydrohalogenation) as a convenient new synthesis of allyl vinyl ethers that are then thermally converted into γ,δ-unsaturated aldehydes (Scheme 1).



Scheme 1

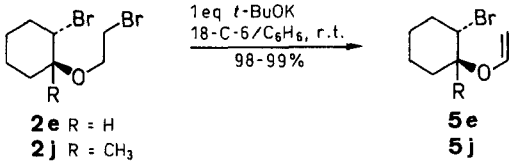
Table 1. Preparation of γ,δ-Unsaturated Aldehydes by Using the Cohalogenation–Dehydrohalogenation Sequence

Olefin	Dihalo Ether	Yield (%)	Allyl Vinyl Ether	Yield (%)	γ,δ-Unsaturated Aldehyde	Yield (%)
		87		75		65
1a	**2a**		**3a**[25]		**4a**[25]	
		86		76		60
1b	**2b**		**3b**[25]		**4b**[25]	
		90		77		78
1c	**2c**		**3c**[25]		**4c**[25]	
		85		86		82
n = 1, **1d**	**2d**		**3d**		**4d**	
n = 2, **1e**	**2e** (X=Br)	86	**3e**[26]	88	**4e**[26]	91
	2e' (X=Cl)	88		91		
n = 3, **1f**	**2f**	69	**3f**	90	**4f**	88
n = 4, **1g**	**2g**	55	**3g**	87	**4g**	64
						
n = 1, **1h**	**2h**	84	**3h**	94	**4h**	56
n = 2, **1i**	**2i**	86	**3i**	82	**4i**	78
		81		93		77
1j	**2j**		**3j**		**4j**	
		78		87	—	
1k	**2k**		**3k**			

Nonterminal alkenes **1a–k** reacted regio- and stereoselectively with bromine or chlorine in ethylene oxide to give good yields of β,β'-dihalogenated ethers **2a–k**. Low temperatures and high concentrations of ethylene oxide were required to decrease the formation of dihaloalkane as a byproduct (ca. 30% is formed at 0°C).[21,23] Therefore, the reactions were performed at −80°C using excess ethylene oxide as the solvent. Subsequent dehydrohalogenation with 2.5 equiv of potassium *tert*-butoxide in the presence of catalytic amounts of 18-crown-6[24] gave the corresponding allyl vinyl ethers **3a–k** in 75–94% isolated yield (Table 1).

The first step of the double dehydrohalogenation appears to be the chemoselective elimination of hydrogen bromide from the β'-bromoethyl side chain to give the corresponding vinyl β-halo ethers. Thus, vinyl ethers **5e** and **5j** were isolated from reactions using one equiv of potassium *tert*-butoxide on ethers **2e** and **2j**, respectively (Scheme 2).

In the presence of an excess of potassium *tert*-butoxide these intermediates were further dehydrohalogenated to the corresponding allyl vinyl ethers **3e** and **3j** (Table 1).



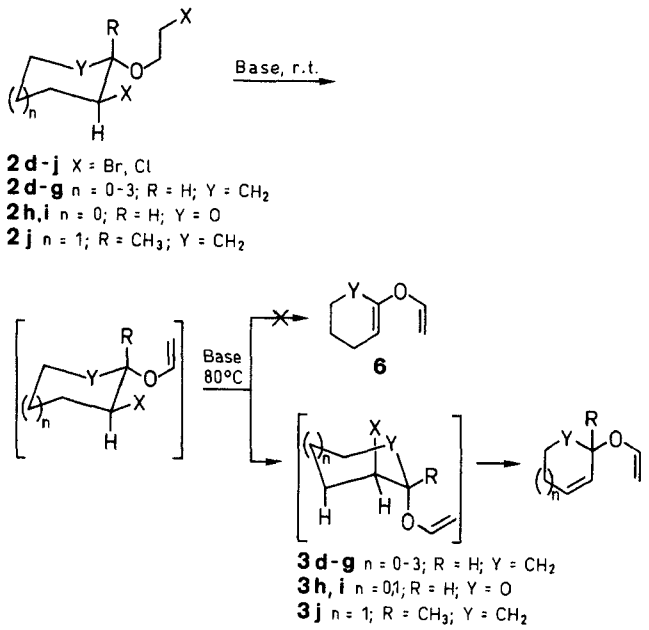
2e R = H
2j R = CH_3

5e
5j

Scheme 2

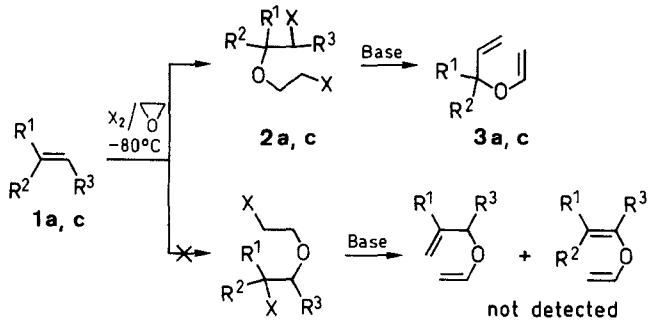
With cyclic olefins **1d–j** the *anti*-stereoselectivity of the dehydrohalogenation results in the regioselective formation of the double bond in the allylic position without a

trace of divinyl ethers **6**. This is consistant with the *trans*-stereochemistry of the starting β,β′-dihaloethers (Scheme 3).



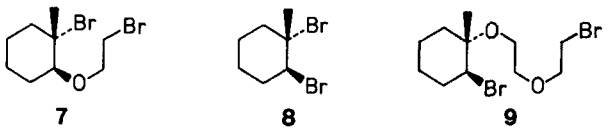
Scheme 3

Δ^3-Carene **1k** constitutes a particularly interesting case, since total diastereoselectivity is observed in the cohalogenation–dehydrohalogenation sequence which leads to the enantiomerically pure allyl vinyl ether **3k**. Cohalogenation of unsymmetrical olefins **1a,c,j,k** affords the β,β′-dihalo ethers regioselectively, in accord with Markovnikov's rule.[27] Formation of dibromo ketals **2h,i** is in accord with the expected reactivity of enol ethers **1h,i** towards electrophilic additions. Evidence for this regioselectivity is found in the ^{1}H NMR spectra of the derived allyl vinyl ethers **3a** and **3c** (see Experimental section) which show six ethylenic hydrogen atoms, but no methyl group bonded to a sp^2 carbon atom (Scheme 4).

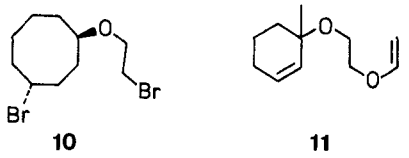


Scheme 4

Bromination of 1-methylcyclohexene **1j** in the presence of ethylene oxide has been previously reported[28] to give a mixture of the two regioisomers **2j** and **7** in ratios from 1:1 to 3:1 depending on the temperature. In our hands, this reaction proceeds with essentially total regioselectivity at −80 °C. The byproducts are dibromide **8** (8 % and diether **9** (5 %), which arises from double condensation of ethylene oxide. The structure of **9** was deduced from the spectroscopic data of the corresponding dehydrohalogenated ether **11** (see Experimental section).

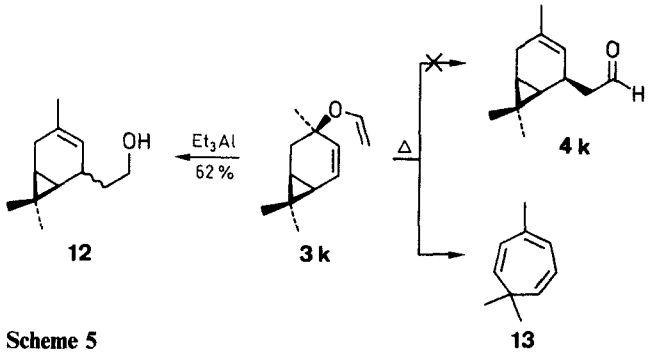


The moderate yield obtained with cyclooctene **1g** is a result of a competitive transannular 1,5-hydrogen shift[29] which leads to a mixture of **2g** (55 %) and 4-bromocyclooctyl 2-bromoethylether **(10)** (43 %).



The neat allyl vinyl ethers **3a–j** were heated at 190 °C in sealed pyrex tubes for 1.5 h to produce γ,δ-unsaturated aldehydes **4a–j**. Yields reported are not optimized, but are for pure isolated compounds (Table 1). The structures assigned to products **4a–j** are supported by detailed spectroscopic data (see Experimental section).

All attempts to prepare aldehyde **4k** by thermal rearrangement of allyl vinyl ether **3k** were unsuccessful and led instead to trimethylcycloheptatriene **13** by a cycloreversion reaction.[30] However, the use of trialkylaluminum as a catalyst for the Claisen rearrangement[31] promoted the conversion of **3k** into the corresponding rearranged alcohol **12** (Scheme 5). Interestingly, the rearrangement of **3k** into **12** occurred without stereochemical preference to generate a diastereomeric mixture of alcohols.



Scheme 5

In conclusion, the sequence of the cohalogenation of alkenes in ethylene oxide followed by dehydrohalogenation offers an efficient new and general synthesis of allyl vinyl ethers, which are valuable synthetic intermediates. The regio- and stereoselectivity of this process allow the selective functionalization of simple alkenes to γ,δ-unsaturated aldehydes in a manner which makes the latter easily accessible from nonterminal olefins.

Unless otherwise noted, all starting materials were obtained from commercial suppliers and used without purification. Reactions, whenever possible, were carried out under an atmosphere of

nitrogen. IR spectra of neat compounds (NaCl plates) were obtained on a Perkin-Elmer 298 spectrometer. ^{1}H NMR spectra were measured on a Bruker AC 200, Varian XL 200 or Varian EM 360 spectrometers and were recorded for $CDCl_3$ (or CCl_4) solutions containing Me_4Si as the internal standard. Unless otherwise noted, ^{13}C NMR spectra of $CDCl_3$ solutions were determined on a Bruker AC 200 or Varian XL 200 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in Hertz (Hz). Mass spectra were obtained on a Varian MAT 311 mass spectrometer.

β,β'-Dihalogenated Ethers 2a–k; General Procedure:
Ethylene oxide (80 mL) was condensed at −30 °C in a 250-mL three-necked round-bottomed flask. The olefins **1a–k** (0.1 mol) were added via syringe and the resulting solution was cooled to −80 °C. Br_2 (0.11 mol) or Cl_2[32] (0.2 mol) in CH_2Cl_2 (20 mL) was added slowly to the reaction mixture. Thirty minutes after addition was completed, the mixture was hydrolyzed with ice-cold water (200 mL) and extracted with pentane (3 × 60 mL). The combined organic fractions were washed with aq $Na_2S_2O_3$, water and saturated aq NaCl, and dried ($MgSO_4$). Solvent removal by rotatory evaporation and flash chromatography on silica gel using pentane–Et_2O (95:5) as eluant yielded pure β,β'-dihalogenated ethers **2a–k**. With cyclooctene **1g**, the β,β'-dibromo ether **2g** was obtained along with **10**. These isomers were separated by flash chromatography on silica gel using pentane–Et_2O (97:3) as eluant.

2-Bromoethyl 2-Bromo-1,1-dimethylpropyl Ether **(2a)** *(87%)*:
IR: ν = 2990, 2940, 2880, 1135 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.00 (1 H, q, J = 6), 3.58 (2 H, m), 3.32 (2 H, m), 1.65 (3 H, d, J = 6.8), 1.32 (3, s), 1.22 (3, s).
^{13}C NMR: δ = 77.5, 62.7, 56.8, 31.0, 23.7, 21.4, 21.1.
MS: m/z = 261, 259, 257 ($M^+ - CH_3$), 246, 244, 242, 195 (9), 193 (9), 167 (69), 165 (72), 109 (93), 107 (100).
Anal: Calc. for $C_7H_{14}Br_2O$: C, 30.66; H, 5.11. Found: C, 30.81; H, 5.10.

2-Bromoethyl 2-Bromo-1,1,2-trimethylpropyl Ether **(2b)** *(86%)*:
IR: ν = 2995, 2940, 2880, 1155 cm^{-1}.
^{1}H NMR (200 MHz): δ = 3.71 (2 H, t, J = 6.1), 3.40 (2 H, t, J = 6.1), 1.79 (6 H, s), 1.36 (6 H, s).
^{13}C NMR: δ = 79.6, 73.9, 63.0, 31.7, 29.7, 21.4.
MS: m/z = 275, 273, 271 ($M^+ - CH_3$), 211, 209, 207, 167 (40), 165 (48), 107 (100).
Anal: Calc. for $C_8H_{16}Br_2O$: C, 33.33; H, 5.56. Found: C, 33.28; H, 5.58.

2-Bromoethyl 1-(1-Bromoethyl)cyclohexyl Ether **(2c)** *(90%)*:
IR: ν = 2940, 2860, 1095 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.19 (1 H, q, J = 6.9), 3.76 (1 H, m), 3.54 (1 H, m), 3.43 (2 H, m), 1.80 (2 H, m), 1.67 (3 H, d, J = 6.9), 1.52 (8 H, m).
^{13}C NMR: δ = 77.2, 60.8, 56.0, 31.2, 29.6, 25.5, 21.4, 20.7.
Anal: Calc. for $C_{10}H_{18}Br_2O$: C, 38.22; H, 5.73. Found: C, 38.26; H, 5.68.

2-Bromoethyl 2-Bromocyclopentyl Ether **(2d)** *(85%)*:
IR: ν = 2970, 1345, 1100 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.21 (1 H, m), 4.09 (1 H, m), 3.76 (2 H, m), 3.41 (2 H, t, J = 6.1), 2.40–1.58 (6 H, m).
^{13}C NMR: δ = 88.3, 69.4, 53.9, 34.7 ($2CH_2$), 21.7 ($2CH_2$).
Anal: Calc. for $C_7H_{12}Br_2O$: C, 30.88; H, 4.41. Found: C, 30.78; H, 4.43.

2-Bromocyclohexyl 2-Bromoethyl Ether **(2e)** *(86%)*:
IR: ν = 2940, 2860, 1100 cm^{-1}.
^{1}H NMR (200MHz): δ = 3.90 (3 H, m), 3.42 (3 H, m), 2.31 (1 H, m), 2.12 (1 H, m), 1.75 (3 H, m), 1.29 (3 H, m).
^{13}C NMR: δ = 81.7, 69.5, 55.0, 35.1, 30.6, 30.5, 24.9, 22.8.
MS: m/z = 288, 286, 284, 165, 163 (8), 109, 107 (26), 95 (100), 55 (13).
Anal: Calc. for $C_8H_{14}Br_2O$; C, 33.57; H, 4.89. Found: C, 33.59; H, 4.83.

2-Chlorocyclohexyl 2-Chloroethyl Ether **(2e')** *(88%)*:
IR: ν = 2940, 2870, 1115 cm^{-1}.
^{1}H NMR (60 MHz, CCl_4): δ = 3.90–3.10 (6 H, m), 2.50–1.00 (8 H, m).
^{13}C NMR: δ = 82.7, 70.4, 62.7, 43.1, 34.7, 30.7, 24.2, 23.2.
Anal: Calc. for $C_8H_{14}Cl_2O$: C, 48.73; H, 7.11. Found: C, 48.81; H, 7.08.

2-Bromocycloheptyl 2-Bromoethyl Ether **(2f)** *(69%)*:
IR: ν = 2935, 2880, 1100 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.17 (1 H, td, J = 7.3, 3.7), 3.81 (2 H, t, J = 6.3), 3.65 (1 H, td, J = 7.3, 3.0), 3.45 (2 H, m), 2.25–1.43 (10 H, m).
^{13}C NMR: δ = 86.5, 69.5, 58.9, 34.5, 30.5, 29.9, 27.7, 24.4, 22.1.
Anal: Calc. for $C_9H_{16}Br_2O$: C, 36.00; H, 5.33. Found: C, 35.99; H, 5.34.

2-Bromocyclooctyl 2-Bromoethyl Ether **(2g)** *(55%)*:
IR: ν = 2930, 2860, 1110 cm^{-1}.
^{1}H NMR (60 MHz, CCl_4): δ = 4.24–3.85 (1 H, m), 3.85–3.10 (5 H, m), 2.40–1.10 (12 H, m).
^{13}C NMR: δ = 78.8, 68.3, 56.5, 34.6, 32.3, 31.1, 29.7, 29.6, 24.1, 21.9.
Anal: Calc. for $C_{10}H_{18}Br_2O$: C, 38.22; H, 5.73. Found: C, 38.31; H, 5.70.

4-Bromocyclooctyl 2-Bromoethyl Ether **(10)** *(43%)*:
^{13}C NMR: δ = 86.2, 70.0, 60.5, 31.9, 31.0, 30.5, 26.4, 25.5, 25.4, 25.2.
Anal. Calc. for $C_{10}H_{18}Br_2O$: C, 38.22; H, 5.73. Found: C, 38.28; H, 5.69.

2-Bromoethyl 3-Bromotetrahydrofuran-2-yl Ether **(2h)** *(84%)*:
IR: ν = 2950, 1130, 1040 cm^{-1}.
^{1}H NMR (200 MHz): δ = 5.23 (1 H, s), 4.27–3.70 (5 H, m), 3.41 (2 H, t, J = 6.1), 2.75–2.54 (1 H, m), 2.27–2.17 (1 H, m).
^{13}C NMR: δ = 108.3, 66.9, 66.8, 49.8, 33.7, 30.6.
MS: m/z = 195, 193, 151, 149 (33), 41 (100).

2-Bromoethyl 3-Bromotetrahydropyran-2-yl Ether **(2i)** *(86%)*:
IR: ν = 2960, 2870, 1130, 1070, 1030 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.43 (1 H, d, J = 3.9), 3.77 (1 H, m), 3.70–3.45 (2 H, m), 3.37–3.20 (1 H, m), 3.20–3.07 (1 H, m), 2.97 (2 H, t, J = 6.2), 2.05–1.88 (1 H, m), 1.67–1.45 (2 H, m), 1.02–0.82 (1 H, m).
^{13}C NMR (C_6D_6): δ = 100.9, 68.1, 62.2, 49.3, 30.7, 29.8, 23.2.
MS: m/z = 290, 288, 286, 181, 179 (5), 165, 163 (13), 136, 134 (42), 55 (100).
Anal: Calc. for $C_7H_{12}Br_2O_2$: C, 29.17; H, 4.17. Found: C, 29.19; H, 4.11.

2-Bromoethyl 2-Bromo-1-methylcyclohexyl Ether **(2j)** *(81%)*:
IR: ν = 2950, 2890, 1110 cm^{-1}.
^{1}H NMR (200 MHz): δ = 4.16 (1 H, dd, J = 7.6, 3.8), 3.67 (2 H, t, J = 6.3), 3.40 (2 H, t, J = 6.3), 2.35–2.19 (1 H, m), 1.93–1.72 (2 H, m), 1.72–1.45 (3 H, m), 1.45–1.30 (2 H, m), 1.29 (3 H, s).
^{13}C NMR: δ = 76.9, 61.9, 59.7, 33.2, 33.1, 31.6, 23.4, 22.0, 21.9.
Anal: Calc. for $C_9H_{16}Br_2O$: C, 36.00; H, 5.33. Found: C, 36.05; H, 5.28.

2-Bromoethyl 4-Bromo-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yl Ether **(2k)** *(78%)*:
IR: ν = 2940, 2870, 1380, 1145, 1110, 1070 cm^{-1}.
^{1}H NMR (200 MHz): δ = 3.98 (1 H, t, J = 8.9), 3.68 (2 H, t, J = 6.3), 3.38 (2 H, t, J = 6.3), 2.38 (2 H, m), 2.12 (1 H, m), 1.40 (1 H

m), 1.32 (3 H, s), 0.98 (3 H, s), 0.95 (3 H, s), 0.77 (1 H, td, J = 8.7, 4.2), 0.65 (1 H, m).

^{13}C NMR: δ = 75.9, 61.6, 59.3, 31.8, 30.9, 30.0, 28.4, 21.5, 19.4, 18.4, 17.7, 15.5.

Anal: Calc. for $C_{12}H_{20}Br_2O$: C, 42.35; H, 5.88. Found: C, 42.31; H, 5.84.

Allyl Vinyl Ethers 3a–k; General Procedure for Dehydrohalogenation of β,β'-Dihaloethers:

(a) t-BuOK (28.06 g, 0.25 mol) was added to a well stirred solution of the β,β'-halo ethers **2d–i** (0.1 mol) and 18-crown-6 (0.320 g, 1.2 mmol) in anhydrous benzene (150 mL) and the reaction mixture was brought to reflux under a nitrogen atmosphere. Light petroleum (bp 40–65 °C) was used for the dehydrohalogenation of **2j**. The progress of the reaction was monitored by TLC using a mixture of pentane–Et_2O (70:30) as eluent. After completion (2.5–5 h) the mixture was filtered through a short path of silica gel (70–230 mesh, 25 g), the column was rinsed with pentane (3 × 50 mL) and pentane–Et_2O (90:10, 50 mL). Evaporation of the filtrate gave allyl vinyl ethers **3d–j** with purity higher than 90% (NMR). Further purification was performed by flash chromatography on silica gel using a mixture of pentane–Et_2O (95:5) as eluent or by distillation under reduced pressure. Xylene was used as the solvent in the dehydrohalogenation of **2k** into **3k**, which was purified by distillation under reduced pressure.

(b) For the preparation of compounds **3a–c** the reaction was performed in dimethyl sulfoxide as solvent (100 mL) at room temperature without the crown ether. After completion, the brown mixture was quenched with ice-cold water (100 mL) and extracted with pentane (3 × 60 mL). The combined extracts were washed with water (3 × 60 mL) and dried ($MgSO_4$). Filtration and evaporation of the solvent gave crude allyl vinyl ethers **3a–c**. **3a, b** were purified by distillation under reduced pressure and compound **3c** by flash chromatography on silica gel using a mixture of pentane–Et_2O (98:2) as eluent.

(c) Procedure (a) using 1.1 equiv. of t-BuOK at room temperature gave the corresponding β-bromovinyl ethers **5e** and **5j** in almost quantitative yields.

1,1-Dimethylallyl Vinyl Ether **(3a)**:[25]

Yield: 75%; bp 50–54 °C (48 Torr).

IR: ν = 3120, 3090, 1630, 1200 cm^{-1}.

^{1}H NMR (60 MHz, CCl_4): δ = 6.02 (1 H, dd, J = 14.0, 6.0), 6.01–5.50 (1 H, m), 5.32–4.92 (2 H, m), 4.20 (1 H, d, J = 14.0), 3.80 (1 H, d, J = 6.0), 1.20 (6 H, br s).

^{13}C NMR: δ = 143.9, 113.7, 90.3, 73.2, 27.7.

Anal: Calc. for $C_7H_{12}O$: C, 75.00; H, 10.71. Found: C, 75.03; H, 10.76.

1,1,2-Trimethylallyl Vinyl Ether **(3b)**:[25]

Yield: 76%; bp 80–82 °C (19 Torr).

IR: ν = 3100, 2995, 1630, 1135, 910 cm^{-1}.

^{1}H NMR (60 MHz, CCl_4): δ = 5.97 (1 H, dd, J = 14.0, 6.0), 4.80 (2 H, br s), 4.20 (1 H, d, J = 14.0), 3.80 (1 H, d, J = 6.0), 1.70 (3 H, br s), 1.32 (6 H, br s).

Anal: Calc. for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.23; H, 11.18.

Vinyl 1-Vinylcyclohexanyl Ether **(3c)**[25] *(77%)*:

IR: ν = 3120, 3080, 1625, 1175 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.28 (1 H, dd, J = 13.8, 6.3), 5.77 (1 H, dd, J = 17.2, 11.3), 5.15 (2 H, m), 4.41 (1 H, d, J = 13.8), 3.98 (1 H, d, J = 6.3), 1.82–1.38 (10 H, m).

^{13}C NMR: δ = 146.7, 142.6, 115.2, 90.2, 78.3, 34.8, 25.4, 21.4.

Anal: Calc. for $C_{10}H_{16}O$: C, 78.95; H, 10.53. Found: C, 79.01; H, 10.48.

2-Cyclopentenyl Vinyl Ether **(3d)** *(86%)*:

IR: ν = 3120, 3060, 1630, 1610, 1190 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.19 (1 H, dd, J = 14.2, 6.7), 5.87 (1 H, m), 5.66 (1 H, m), 4.78 (1 H, m), 4.04 (1 H, dd, J = 14.2, 1.6), 3.80 (1 H, dd, J = 6.7, 1.6), 2.26 (1 H, m), 2.04 (2 H, m), 1.63 (1 H, m).

^{13}C NMR: δ = 151.0, 136.2, 128.5, 87.5, 83.5, 31.2, 30.0.

MS: m/z = 110 (3), 83 (25), 67 (100), 57 (83), 41 (18).

HRMS calc. for $C_7H_{10}O$: 110.0731. Found: 110.0728.

2-Cyclohexenyl Vinyl Ether **(3e)**:[26] Yield 88%; bp 48–49 °C (11 Torr).

IR: ν = 3125, 3040, 1640, 1610, 1200, 1140 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.34 (1 H, dd, J = 14.1, 6.6), 5.91 (1 H, m), 5.73 (1 H, m), 4.30 (1 H, m), 4.29 (1 H, dd, J = 14.1, 1.5), 3.99 (1 H, dd, J = 6.6, 1.5), 2.01 (2 H, m), 1.90–1.45 (4 H, m).

^{13}C NMR: δ = 150.5, 131.7, 126.5, 83.1, 72.4, 28.5, 25.1, 19.1.

Anal: Calc. for $C_8H_{12}O$: C, 74.42; H, 9.68. Found C, 77.39; H, 9.60.

2-Cycloheptenyl Vinyl Ether **(3f)**:

Yield: 90%; bp 68–70 °C (15 Torr);

IR: ν = 3125, 3040, 1635, 1615, 1210, 1185 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.34 (1 H, dd, J = 14.3, 6.8), 5.77 (2 H, m), 4.47 (1 H, d, J = 9.0), 4.23 (1 H, dd, J = 14.3, 1.5), 4.02 (1 H, dd, J = 6.8, 1.5), 2.32–1.87 (3 H, m), 1.80–1.19 (5 H, m).

^{13}C NMR: δ = 150.7, 136.1, 130.4, 88.2, 78.5, 33.3, 28.7, 27.5, 26.8.

Anal: Calc. for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.31; H, 10.07.

2-Cyclooctenyl Vinyl Ether **(3g)** *(87%)*:

IR: ν = 3120, 3020, 1630, 1610, 1200, 1180 cm^{-1}.

^{1}H NMR (60 MHz, CCl_4): δ = 6.16 (1 H, dd, J = 14.0. 6.0), 5.81–5.23 (2 H, m), 4.10 (1, br s), 3.91–3.63 (2 H, m), 2.35–1.15 (10 H, m).

^{13}C NMR: δ = 150.6, 132.4, 129.6, 88.2, 79.7, 35.5, 31.4, 30.8, 25.8, 21.5.

Anal: Calc. for $C_{10}H_{16}O$: C, 78.95; H, 10.53. Found: C, 79.03; H, 10.57.

2,5-Dihydrofuran-2-yl Vinyl Ether **(3h)** *(94%)*:

IR: ν = 3040, 2925, 1680, 1090 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.29, (1 H, dd, J = 14.0, 6.5), 5.88–5.60 (2 H, m), 5.53 (1 H, m), 4.43 (1 H, dd, J = 14.0, 1.0), 4.42 (1 H, dm, J = 14.2), 4.24 (1 H, dm, J = 14.2), 4.01 (1 H, dd, J = 6.5, 1.0).

^{13}C NMR: δ = 148.5, 132.0, 124.6, 107.2, 90.0, 74.1.

MS: m/z = 113 (M + 1), 84 (27), 78 (30), 69 (100), 68 (42), 57 (20), 41 (27), 39 (34), 28 (53).

5,6-Dihydro-2H-pyran-2-yl Vinyl Ether **(3i)** *(82%)*:

IR: ν = 3110, 3060, 1625, 1175 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.48 (1 H, dd, J = 14.0, 6.5), 5.60 (2 H, m), 5.08 (1 H, s), 4.70 (1 H, dd, J = 14.0, 1.0), 4.12 (1 H, dd, J = 6.5, 1.0), 3.77 (1 H, dt, J = 11.0, 3.5), 3.47 (1 H, dt, J = 11.0, 6.1), 1.91 (1 H, m), 1.25 (1 H, dt, J = 11.0, 4.9).

^{13}C NMR: δ = 150.0, 129.7, 125.2, 93.6, 90.7, 57.7, 24.5.

MS: m/z = 83 (100), 55 (39), 39 (18).

Anal. Calc. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.64; H, 7.89.

1-Methyl-2-cyclohexenyl Vinyl Ether **(3j)** *(93%)*:

IR: ν = 3125, 2950, 1630, 1180 cm^{-1}.

^{1}H NMR (200 MHz): δ = 6.24 (1 H, dd, J = 14.0, 6.8), 5.63 (1 H, dm, J = 10.3), 5.49 (1 H, d, J = 10.3), 4.66 (1 H, d, J = 14.0), 4.08 (1 H, d, J = 6.8), 1.82–1.23 (6 H, m), 1.20 (3 H, s).

^{13}C NMR (C_6D_6): δ = 147.4, 131.6, 131.1, 90.1, 75.6, 35.3, 23.7, 25.1, 19.9.

Anal: Calc. for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.33; H, 10.01.

3,7,7-Trimethylbicyclo[4.1.0]hept-4-en-3-yl Vinyl Ether **(3k)** *(87%):*

bp 62–60 °C (0.5 Torr).

IR: ν = 3110, 2940, 1625, 1390, 1375, 1370, 1100 cm^{-1}.

^1H NMR (60 MHz, CCl_4): δ = 6.23 (1 H, dd, J = 14.0, 6.5), 5.68 (2 H, m), 4.23 (1 H, d, J = 14.0), 3.82 (1 H, d, J = 6.5), 1.72 (2 H, m), 1.30 (3 H, s), 1.10 (3 H, s), 0.95 (3 H, s), 0.88 (2 H, m).

^{13}C NMR: δ = 147.9, 136.9, 128.1, 91.9, 79.0, 33.7, 29.0, 28.4, 27.6, 23.4, 21.4, 16.6.

Anal: Calc. for $C_{12}H_{18}O$: C, 80.90; H, 10.11. Found: C, 80.96; H, 10.08.

2-Bromocyclohexyl Vinyl Ether **(5e)** *(98%):*

IR: ν = 3115, 2975, 2875, 1640, 1190 cm^{-1}.

^1H NMR (200 MHz): δ = 6.32 (1 H, dd, J = 14.0, 6.5), 4.31 (1 H, dd, J = 14.0, 1.7), 4.03 (1 H, dd, J = 6.5, 1.7), 3.97 (1 H, m), 3.80 (1 H, m), 2.29 (1 H, m), 2.12 (1 H, m), 1.73 (3 H, m), 1.37 (3 H, m).

^{13}C NMR (C_6D_6): δ = 151.0, 88.7, 81.0, 53.5, 35.0, 30.4, 24.5, 23.0.

Anal: Calc. for $C_8H_{13}BrO$: C, 46.83; H, 6.34. Found: C, 46.87; H, 6.32.

2-Bromo-1-methylcyclohexyl Vinyl Ether **(5j)** *(99%):*

IR: ν = 3125, 3040, 2955, 1635, 1180, 1020, 840 cm^{-1}.

^1H NMR (200 MHz): δ = 6.12 (1 H, dd, J = 13.6, 6.1), 4.60 (1 H, dd, J = 13.6, 2.3), 4.06 (1 H, dd, J = 6.1, 2.3), 3.98 (1 H, dd, J = 6.5, 3.7), 2.02 (1 H, m), 1.80–1.26 (7 H, m), 1.18 (3 H, s).

^{13}C NMR (C_6D_6): δ = 145.1, 92.3, 78.4, 58.8, 33.5, 32.3, 23.0, 22.4, 21.4.

Anal: Calc. for $C_9H_{15}BrO$: C, 49.32; H, 6.85. Found: C, 49.41; H, 6.79.

1,2-Dibromo-1-methylcyclohexane **(8)** *(8%):*

^1H NMR (200 MHz): δ = 4.62 (1 H, t, J = 3.6), 2.60–2.41 (1 H, m), 2.10–1.83 (3 H, m), 1.94 (3 H, s), 1.83–1.51 (4 H, m).

3-Methyl-3-(2-vinyloxyethoxy)cyclohexene **(11)**.

Dehydrohalogenation of crude **2j** according to procedure (a) allows the isolation of diether **11** in 5% yield:

IR: ν = 3120, 3020, 2950, 1620, 1200, 1100 cm^{-1}.

^1H NMR (200 MHz): δ = 6.48 (1 H, dd, J = 14.3, 6.8), 5.82 (1 H, dt, J = 10.3, 3.6), 5.55 (1 H, dt, J = 10.3, 2.3), 4.16 (1 H, dd, J = 14.3, 2.0), 3.96 (1 H, dd, J = 6.8, 2.0), 3.78 (2 H, m), 3.59 (2 H, m), 2.29–1.42 (6 H, m), 1.24 (3 H, s).

^{13}C NMR: δ = 151.6, 131.9, 130.2, 86.1, 73.0, 67.5, 60.4, 33.5, 26.4, 24.9, 19.7.

Anal: Calc. for $C_{11}H_{18}O_2$: C, 72.52; H, 9.89. Found: C, 72.56; H, 9.92.

γ,δ-Unsaturated Aldehydes 4a–j; General Procedure:

The starting allyl vinyl ether (1 g) was vacuum sealed in a Pyrex tube. The tubes were heated in an oil bath at 190 °C for 1.5 h (0.5 h for **3j**; times are unoptimized), cooled to room temperature, and carefully opened. The crude aldehydes were purified by flash chromatography on silica gel using a mixture of pentane–Et_2O (85:15) as eluent.

5-Methyl-4-hexenal **(4a)**[25] *(65%):*

IR: ν = 2980, 2930, 2730, 1725, 1450, 1060 cm^{-1}.

^1H NMR (200 MHz): δ = 9.73 (1 H, t, J = 1.5), 5.05 (1 H, t, J = 6.0), 2.42 (2 H, m), 2.29 (2 H, m), 1.64 (3 H, s), 1.58 (3 H, s).

^{13}C NMR: δ = 202.5, 133.2, 122.2, 44.0, 25.6, 20.9, 17.7.

Anal. Calc. for $C_7H_{12}O$: C, 75.00; H, 10.71. Found: C, 75.10; H, 10.75.

4,5-Dimethyl-4-hexenal **(4b)**[25] *(60%):*

IR: ν = 2980, 2710, 1720 cm^{-1}.

^1H NMR (200 MHz): δ = 9.74 (1 H, t, J = 1.7), 2.42 (2 H, m), 2.32 (2 H, m), 1.62 (3 H, s), 1.61 (6 H, s).

^{13}C NMR: δ = 202.4, 125.2, 124.8, 42.4, 26.7, 20.4, 19.9, 17.9.

Anal: Calc. for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 76.23; H, 11.06.

4-Cyclohexylidenebutanal **(4c)**[25] *(78%):*

IR: ν = 2920, 2850, 2750, 1725, 1015 cm^{-1}.

^1H NMR (200 MHz): δ = 9.73 (1 H, s), 5.01 (1 H, t, J = 6.0), 2.38 (4 H, m), 2.05 (4 H, m), 1.49 (6 H, br s).

^{13}C NMR: δ = 202.3, 141.1, 118.7, 44.2, 37.0, 28.6, 28.5, 27.6, 27.4, 19.9.

Anal: Calc. for $C_{10}H_{16}O$: C, 78.95; H, 10.53. Found: C, 79.03; H, 10.59.

2-Cyclopentenylethanal **(4d)** *(82%):*

IR: ν = 3080, 2725, 1725, 1620 cm^{-1}.

^1H NMR (200 MHz, C_6D_6): δ = 9.29 (1 H, t, J = 1.7), 5.54 (1 H, m), 5.47 (1 H, m), 2.83 (1 H, m), 2.07 (2 H, m), 1.85 (4 H, m).

^{13}C NMR (C_6D_6): δ = 200.2, 133.7, 131.3, 49.8, 39.8, 32.0, 29.8.

MS: m/z = 110 (1), 84 (100), 82 (10), 56 (16), 54 (14), 28 (72).

HRMS: Calc. for $C_7H_{10}O$: 110.0732. Found: 110.0733.

2-Cyclohexenylethanal **(4e)**[26] *(91%):*

IR: ν = 3020, 2720, 1720, 1650 cm^{-1}

^1H NMR (200 MHz): δ = 9.75 (1 H, t, J = 2.1), 5.73 (1 H, m), 5.49 (1 H, dd, J = 10.1, 2.0), 2.67 (1 H, m), 2.41 (2 H, m), 1.96 (2 H, m), 1.93–1.41 (3 H, m), 1.38–1.17 (1 H, m).

^{13}C NMR (C_6D_6): δ = 200.6, 130.6, 128.2, 50.2, 30.3, 29.3, 25.3, 21.4.

Anal: Calc. for $C_8H_{12}O$: C, 77.42, H, 9.68. Found: C, 77.40; H, 9.56.

2-Cycloheptenylethanal **(4f)** *(88%):*

IR: δ = 3020, 1725, 1650 cm^{-1}.

^1H NMR (200 MHz, C_6D_6): δ = 9.30 (1 H, t, J = 1.9), 5.70 (1 H, dtd, J = 10.0, 7.1, 2.4), 5.32 (1 H, dd, J = 10.0, 3.8), 2.51 (1 H, m), 1.91 (4 H, m), 1.88–1.02 (6 H, m).

^{13}C NMR (C_6D_6): δ = 200.7, 136.3, 132.1, 50.8, 34.5, 33.7, 30.4, 28.9, 27.0.

Anal: Calc. for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.22; H, 10.17.

2-Cyclooctenylethanal **(4g)** *(64%):*

IR: ν = 3020, 2720, 1725, 1655 cm^{-1}.

^1H NMR (60 MHz, CCl_4): δ = 9.50 (1 H, t, J = 1.0), 5.65–5.35 (2 H, m), 2.50–1.20 (13 H, m).

Anal: Calc. for $C_{10}H_{16}O$: C, 78.95; H, 10.53. Found: C, 78.96; H, 10.58.

2,3-Dihydrofuran-3-ylethanal **(4h)** *(56%):*

IR: ν = 3100, 2725, 1710, 1610, 1050 cm^{-1}.

^1H NMR (200 MHz): δ = 9.74 (1 H, s), 6.31 (1 H, dd, J = 2.7, 1.9), 4.92 (1 H, t, J = 2.6), 4.42 (1 H, t, J = 9.3), 3.90 (1 H, dd, J = 9.3, 6.0), 3.30 (1 H, m), 2.68 (1 H, ddd, J = 16.1, 6.0, 1.0), 2.56 (1 H, ddd, J = 16.1, 6.0, 1.0).

^{13}C NMR: δ = 200.3, 146.5, 102.9, 74.6, 49.7, 36.1.

Anal: Calc. for $C_6H_8O_2$: C, 64.29, H, 7.14. Found: C, 64.33; H, 7.08.

3,4-Dihydro-2H-pyran-4-ylethanal **(4i)** *(78%):*

IR: ν = 3035, 2725, 1720, 1650, 1070 cm^{-1}.

^1H NMR (200 MHz, C_6D_6): δ = 9.20 (1 H, s), 6.35 (1 H, dd, J = 6.2, 1.8), 4.35 (1 H, dd, J = 6.2, 2.9), 3.56 (2 H, m), 2.32 (1 H, m), 1.71 (2 H, m), 1.47 (1 H, m), 1.03 (1 H, m).

^{13}C NMR (C_6D_6): δ = 200.0, 144.7, 103.9, 63.9, 50.2, 28.9, 25.0.

Anal: Calc. for $C_7H_{10}O_2$: C, 66.67; H, 7.94. Found: C, 66.72; H, 7.90.

3-Methyl-2-cyclohexenylethanal **(4j)** *(77%):*

IR: ν = 3040, 2940, 2870, 2840, 2730, 1730, 1450 cm^{-1}.

^1H NMR (200 MHz): δ = 9.76 (1 H, t, J = 2.2), 5.22 (1 H, s), 2.63 (1 H, m), 2.38–2.33 (2 H, m), 1.98–1.52 (5 H, m), 1.62 (3 H, s), 1.18 (1 H, m).

^{13}C NMR: δ = 202.3, 135.3, 123.9, 50.2, 30.2, 29.6, 28.6, 23.6, 21.3.

Anal: Calc. for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.2, H, 10.18.

5-(2-Hydroxyethyl)-3,7,7-trimethylbicyclo[4.1.0]hept-3-ene (12): Obtained following the literature procedure.[31] Mixture of diastereomers (1:1); Yield: 62%.

IR: ν = 3350, 2920, 1630, 1050 cm^{-1}.

^1H NMR (60 MHz, CCl_4): δ = 5.06 (1H, m), 3.63 (2H, m), 2.70–1.70 (3H, m), 1.53 (3H, br s), 1.70–1.10 (2H, m), 1.01–0.62 (8H, m).

^{13}C NMR: δ = 132.4, 131.9, 124.1, 123.8, 61.6, 61.2, 40.0, 37.5, 30.1, 29.5, 28.6, 28.4, 25.9, 25.4, 23.6, 23.5, 23.4, 22.8, 20.1, 18.9, 18.1, 16.7, 15.6, 13.4.

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