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Asymmetric oxyselenenylation–deselenenylation reactions of alkenes induced by camphor diselenide and ammonium persulfate. A convenient one-pot synthesis of enantiomerically enriched allylic alcohols and ethers

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Abstract

The reaction of β,γ-unsaturated esters and nitriles with camphor diselenide and ammonium persulfate in methanol, ethylene glycol or water affords enantiomerically enriched γ-alkoxy or γ-hydroxy α,β-unsaturated derivatives, respectively, in good chemical yields and with moderate to good enantioselectivity.

1. Introduction

Organoselenium reagents are largely used in organic synthesis to introduce new functional groups into organic substrates under very mild experimental conditions. In recent years, several research groups have described the synthesis of a number of chiral non-racemic diselenides which can be tranformed in situ into electrophilic selenenylating agents. The reactions of these intermediates with alkenes in the presence of an external or an internal nucleophile result in diastereoselective addition or cyclization reactions, respectively. By means of reduction, elimination or substitution reactions, the products so formed then lead to the enantioselective formation of the deselenenylated products.[1] Using different chiral diselenides good asymmetric inductions were obtained in the selenomethoxylation,[1–7] and selenohydroxylation[8] as well as in the selenium induced cyclofunctionalization of alkenes.[1–5,7b,9,10]

Our research group has recently reported that ammonium persulfate can be conveniently employed to oxidize the diphenyl diselenide to produce the strongly electrophilic phenylselenenyl sulfate which

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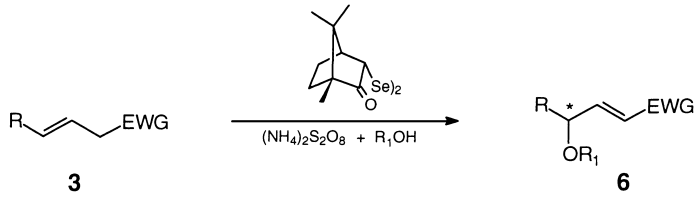
easily effects the selenenylation of alkenes.[11] Moreover, the so formed selenides further react with ammonium persulfate affording the deselenenylated products and, at the same time, regenerating the phenylselenenyl sulfate. On the basis of these observations a series of one-pot conversions, which are simply effected with catalytic amounts of diphenyl diselenide and an excess of ammonium persulfate, has been described. Depending on the solvent employed and on the structure of the starting unsaturated compounds, the deselenenylation step can evolve either towards the substitution[12] or towards the elimination products.[13,14]

By replacing the diphenyl diselenide with a chiral non-racemic diselenide, the above described catalytic oxyselenylation–elimination sequence has been very recently applied by our,[6] as well as by other, research groups,[1a,4a,15] to the one-pot conversion of alkenes into optically active allylic ethers. We now report that β,γ-unsaturated esters and nitriles **3** (Scheme 1), by reaction at room temperature with the easily available[16] camphor diselenide **1** and an excess of ammonium persulfate, in methanol, ethylene glycol or water, give rise to the one-pot oxyselenenylation–elimination reaction affording the enantiomerically enriched γ-alkoxy or γ-hydroxy α,β-unsaturated derivatives **6**, respectively, in good chemical yields and with moderate to good enantioselectivity.



3 **6**

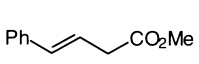
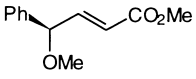
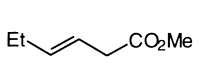
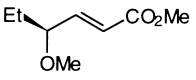
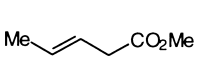
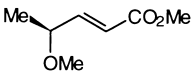
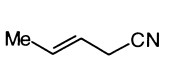
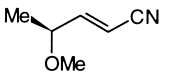
Scheme 1.

2. Results and discussion

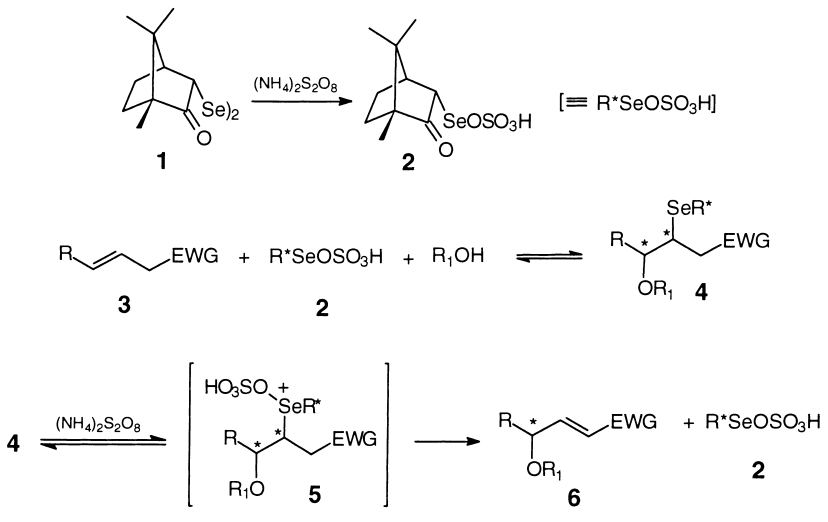
Preliminary experiments, carried out on the methyl styrylacetate **3a** in methanol with ammonium persulfate and catalytic amounts of the camphor diselenide **1**, indicated that the reaction was very slow and that the starting alkene was consumed to give other unidentified products. The reaction was therefore repeated using a stoichiometric amount of the diselenide **1**. Much better results were obtained under these conditions (Table 1, entry 1). Thus, after 36 h at room temperature, the expected product **6a** was obtained in 72% yield and with 65% *ee*.[6]

The proposed course of this reaction, as well as that of all the other reactions which will be described below, is indicated in Scheme 2 and is similar to that suggested for the related conversions promoted by the diphenyl diselenide.[14] The camphorselenenyl sulfate **2**, produced from the reaction of the camphor diselenide **1** with ammonium persulfate, reacts with the alkenes **3** to give the alkoxy- or the hydroxyselenenylation products **4**. The reaction of these addition products with ammonium persulfate is suggested to generate the selenonium ions **5** which, by elimination, afford the observed reaction products **6** and regenerate the electrophilic reagent **2**. The elimination reaction occurs easily because it gives rise to an alkene which is conjugated with the electron withdrawing group. In the cases of the substrates, **3b**, **3c** and **3d**, the addition reaction was not completely regiospecific. GC–MS analysis at early reaction stages showed in fact that small amounts of the regioisomers of compounds **4** were also formed. No reaction products deriving from these compounds could be found in the final reaction mixtures. It is very likely that the selenonium ions deriving from these isomers cannot undergo the elimination reaction and therefore they revert to the starting alkenes.

Table 1
Alkoxyselenenylation–elimination reactions in dichloromethane and methanol

Entry	Alkenes	Time (h)	Products	Yield (%)[a]	ee	R/S
1	 **3a**	36	 **6a**	72	65[b]	R[c]
2	 **3b**	24	 **6b**	71	86[d]	S[c]
3	 **3c**	72	 **6c**	60	70[d]	S[c]
4	 **3d**	27	 **6d**	66	70[b]	S[c]

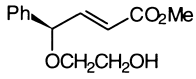
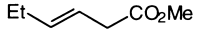
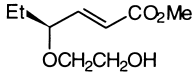
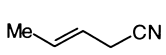
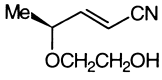
a) Based on isolated products after column chromatography. *b*) Determined by proton nmr in the presence of (*S*)-(+)-2,2,2-trifluoro-1-(9-antryl)ethanol. *c*) Absolute configuration assigned by analogy (see text). *d*) Determined by proton nmr in the presence of (+)-Eu(tfc)3.



Scheme 2.

On the basis of the results obtained in the preliminary experiments, all the other reactions were carried out with a stoichiometric amount of camphor diselenide. The alkoxyselenenylation–elimination reactions were effected in a mixture of dichloromethane and methanol or dichloromethane and ethylene glycol. Trifluoromethanesulfonic acid was also added in order to accelerate the formation of the camphorselenenyl sulfate.[17] The hydroxyselenenylation–elimination reactions were instead carried out in a mixture of acetonitrile and water. In order to avoid the formation of the selenoamidation products,[18] trifluoromethanesulfonic acid was not added in this case and the camphorselenenyl sulfate was prepared by the reaction of camphor diselenide with ammonium persulfate in acetonitrile at 70°C. The solution was cooled to 40°C and the alkene and water were then added. The progress of the reactions was monitored by TLC. After the usual work up, the enantiomerically enriched allylic ethers and alcohols were isolated

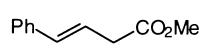
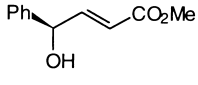
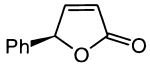
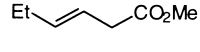
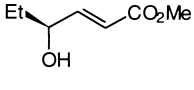
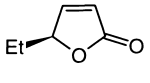
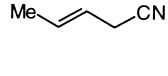
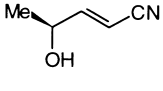
Table 2
Alkoxyselenenylation–elimination reactions in dichloromethane and ethylene glycol

Entry	Alkenes	Time (h)	Products	Yield (%)[a]	*ee*	*R/S*
1	**3a**	20	 **6e**	87	40[b]	*R*[c]
2	 **3b**	46	 **6f**	46	46[d]	*S*[c]
3	 **3d**	30	 **6g**	57[e]	64[f]	*S*[c]

a) Based on isolated products after column chromatography. *b*) Determined indirectly (see text). *c*) Absolute configuration assigned by analogy (see text). *d*) Determined by GC-MS. *e*) A 10% of the (*Z*) isomer was also present (44% *ee*). *f*) Determined by GC-MS and by proton nmr in the presence of (+)-Eu(tfc)$_3$.

by column chromatography on silica gel. The enantiomeric excesses were determined by proton NMR in the presence of (+)-Eu(tfc)$_3$ or (*S*)-(+)-2,2,2-trifluoro-1-(9-antryl)ethanol and/or by GC–MS using a Chirasil-dex column. The results of the experiments carried out using methanol, ethylene glycol or water as nucleophiles are collected in Tables 1–3, respectively.

Table 3
Hydroxyselenenylation–elimination reactions in acetonitrile and water

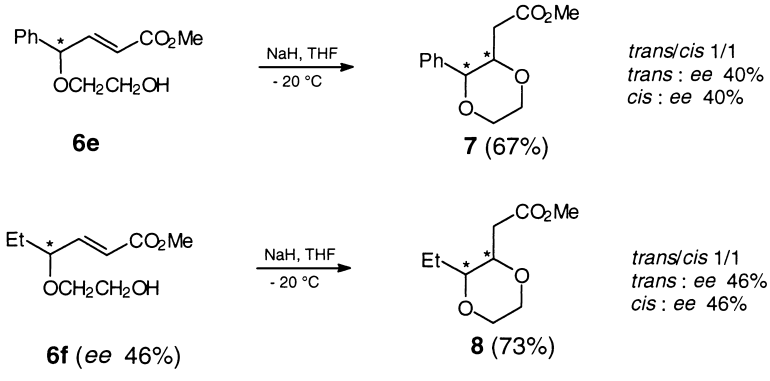
Entry	Alkenes	Time (h)	Products	Yield (%)[a]	*ee*	*R/S*
1	 **3a**	22	 **6h**	55	60[b]	*R*[c]
			 **10h**	33	40[b]	*R*[d]
2	 **3b**	26	 **6i**	33	60[b]	*S*[d]
			 **10i**	31	50[e]	*S*[d]
3	 **3d**	45	 **6j**	70	46[f]	*S*[d]

a) Based on isolated products after column chromatography. *b*) Determined by proton nmr in the presence of (+)-Eu(tfc)$_3$. *c*) Absolute configuration assigned by analogy (see text). *d*) Absolute configuration assigned by comparison of the specific rotation with that of the known compound. *e*) Determined by proton nmr in the presence of (*S*)-(+)-2,2,2-trifluoro-1-(9-antryl)ethanol. *f*) Determined by GC-MS.

Good chemical yields and good *ee*s were obtained in the case of methoxyselenenylation–elimination reactions (Table 1). The alkenes **3a**, **3b** and **3d** were also used in the methoxyselenenylation reactions

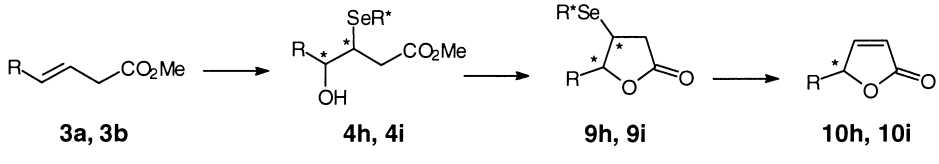
described in our previous work.[6] As expected on the basis of the proposed mechanism reported in Scheme 2, the diastereomeric excesses measured in those reactions (70, 80 and 76%, respectively) are in very good agreement with the enantiomeric excesses observed in the present case (Table 1, entries 1, 2 and 4).

Lower *ee*s were obtained from the reactions carried out in compounds **3a**, **3b** and **3d** in the presence of ethylene glycol as the nucleophile (Table 2). The *ee* of compound **6e** (entry 1) could not be determined either by proton NMR or by GC–MS. However, the determination of the enantiomeric excess could be achieved indirectly after transformation of **6e** into the corresponding dioxane derivative **7** by simple treatment with sodium hydride in THF at −20°C, according to the procedure previously reported[14] for the racemic compound (Scheme 3). Compound **7** was obtained as a 1:1 mixture of *trans* and *cis* derivatives which could not be separated by column chromatography. The mixture, however, could be easily analyzed both by GC–MS using a chiral column and by proton NMR in the presence of (+)-Eu(tfc)$_3$. Identical results were obtained from the two methods. Both the *trans* and the *cis* isomers presented an *ee* of 40%. Under the assumption that the cyclization reaction is not selective, the *ee* of **6e** should also be 40%. This assumption was verified by carrying out the same reaction on compound **6f** having an *ee* of 46%. In this case the dioxane derivative **8** was also a 1:1 mixture of two stereoisomers. These could be separated by column chromatography. Proton NMR analysis of **8** in the presence of (+)-Eu(tfc)$_3$ showed that both the *trans* and the *cis* isomers are formed with the same *ee* (46%) which is identical to that of the starting compound **6f**.



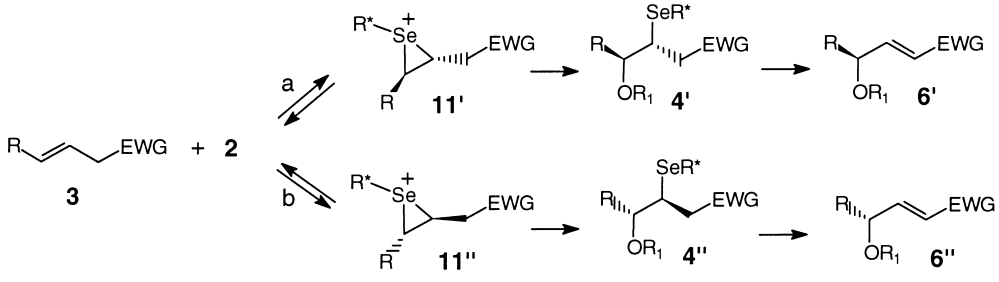
Scheme 3.

Finally, the results obtained from the hydroxyselenenylation–elimination sequence are reported in Table 3. In the cases of the reactions of the unsaturated esters **3a** and **3b** (entries 1 and 2), together with the expected allylic alcohols **6h** and **6i**, the butenolides **10h** and **10i** were also isolated in considerable amounts. It seems reasonable to assume that these compounds originate from the deselenenylation of the lactones **9h** and **9i** (Scheme 4).[19] These latter compounds can be formed from the hydroxyselenides **4h** and **4i** which are produced in the addition step as indicated in Scheme 2. The lower enantiomeric excesses observed for **10h** and **10i** in comparison to those measured for **6h** and **6i**, respectively, are not unexpected since it is known that the butenolides can suffer partial racemization during the work up.[22]



Scheme 4.

The absolute configurations of the major enantiomers are indicated in the last columns of Tables 1–3. In the cases of compounds **6i**,[20] **6j**,[21] **10h**[22] and **10i**[23] the configurations were assigned by comparison of their specific rotations with those reported for the known compounds. As expected on the basis of the reaction sequence proposed in Scheme 4, the allylic alcohol **6i** and the butenolide **10i** have the same configuration. It is thus reasonable to assume that the alcohol **6h** has the *R* configuration as the butenolide **10h**. These results indicate that the addition of the electrophilic selenenylating agent to the olefins **3a**, **3b** and **3d** occurs with the same facial selectivity and that path a (Scheme 5), which involves the formation of the seleniranium intermediates **11′**, the addition products **4′** and the elimination products **6′**, is preferred with respect to path b from which the diastereomers **11′′** and **4′′** and the enantiomers **6′′** are formed. It has been pointed out[4a,24] that in the case of (*E*)-olefins the stereochemistry of the addition products, and hence of the elimination products, is determined by the facial selective addition of the electrophilic reagent to the olefin leading to the two diastereomeric seleniranium intermediates. However, it can be expected that the final products can be formed with a different *ee* in the various cases because of the different experimental conditions employed to introduce the three nucleophiles and also the reversibility[25] of the addition step leading to **11′** and **11′′**. It is suggested, however, that these effects cannot be so important as to invert the stereoselectivity of the addition reactions. On the basis of these considerations the absolute configurations of the major isomers of **6a**, **6b**, **6c**, **6d** and of **6e**, **6f**, **6g**, deriving from the reactions carried out in methanol (Table 1) and in ethylene glycol (Table 2), respectively, can be assigned by analogy with those observed for the major isomers of **6h**, **6i** and **6j** (Table 3). This assumption has been verified by an independent experiment. Compound (*S*)-(+)-**6i** (*ee* 60%), by treatment with diazomethane in the presence of boron trifluoride diethyl etherate, afforded (−)-**6b** (*ee* 60%), demonstrating that the major enantiomer is the same as that obtained from the methoxyselenenylation of **3b** which therefore has the (*S*) configuration.



Scheme 5.

In a previous work[6] we have described the asymmetric methoxyselenenylation of compounds **3a**, **3b** and **3d** with camphorselenenyl sulfate. The two diastereomeric addition products were obtained in ratios of 85:15, 90:10 and 88:12, respectively. On the basis of the results described above it is now possible to assign structure **4′** (Scheme 5) to the major isomer and structure **4′′** to the minor isomer.

The results described above demonstrate that the reaction of camphor diselenide and ammonium persulfate with β,γ-unsaturated esters and nitriles in methanol, ethylene glycol or water represents a convenient procedure to effect the one-pot asymmetric synthesis of enantiomerically enriched γ-alkoxy or γ-hydroxy α,β-unsaturated derivatives, respectively. The allylic ethers are formed in good chemical yields. Lower yields are observed in the case of the allylic alcohols because of the competitive formation of butenolides.

Unfortunately, the catalytic process which can be effected with the diphenyl diselenide[14] cannot be applied in the present case, and the camphor diselenide must be employed in stoichiometric amounts. The enantioselectivity observed in the methoxyselenenylation–elimination process favourably compares with

those obtained with other chiral diselenides.[1a,4a,15] Moderate enantioselectivities were instead observed in the reactions with ethylene glycol and in the hydroxyselenenylation–elimination process.

3. Experimental

New compounds were characterized by MS, ^{1}H and ^{13}C NMR spectroscopy. GLC analyses and MS spectra were carried out with an HP 5890 gas chromatograph (25 m dimethyl silicone capillary column and 25 m Chirasil-dex column) equipped with an HP 5971 mass selective detector. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.62 MHz, respectively, on a Bruker DRX 400 instrument; unless otherwise specified, $CDCl_3$ was used as the solvent and TMS as the standard. Optical rotations were measured with a Jasco DIP-1000 digital polarimeter. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyzer.

3.1. Conversion of β,γ-unsaturated esters and nitriles into allylic ethers. General procedure

The solution of camphorselenenyl sulfate was prepared at room temperature from camphor diselenide (0.5 mmol), ammonium persulfate (1 mmol) and trifluoromethanesulfonic acid (1 mmol) in dichloromethane (3 mL). After 15 minutes, ammonium persulfate (2 mmol) and a solution of the alkene **3** in methanol or in ethylene glycol (3 mL) were added. The mixture was stirred at room temperature for 20–72 h. The progress of the reaction was monitored by TLC and/or GC–MS. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated. Reaction products were obtained in a pure form after column chromatography of the residue on silica gel. The reaction of **3b** in ethylene glycol was carried out in the absence of trifluoromethanesulfonic acid. In this case the camphorselenenyl sulfate was prepared by stirring at 70°C a mixture of camphor diselenide (0.5 mmol) and ammonium persulfate (0.6 mmol) in ethylene glycol (5 mL) and THF (1 mL) for 40 minutes. The mixture was cooled at room temperature and the β,γ-unsaturated ester **3b** (1 mmol) and ammonium persulfate (2 mmol) were added. The reaction was stirred for 46 h and worked up in the usual way. Reaction yields and enantiomeric excesses are reported in Tables 1 and 2. Physical and spectral data of the reaction products **6a**–**g** are reported below.

*3.2. Methyl (*E*,4*R*)-4-methoxy-4-phenyl-2-butenoate **6a***

Oil; $[\alpha]_D^{23}$=+52.4 (c=5.00, $CHCl_3$). ^{1}H NMR δ 7.5–7.3 (m, 5H), 7.0 (dd, 1H, *J*=5.4, 15.8 Hz), 6.1 (dd, 1H, *J*=1.6, 15.8 Hz), 4.78 (dd, 1H, *J*=1.6, 5.4 Hz), 3.72 (s, 3H), 3.45 (s, 3H). ^{13}C NMR δ 166.6, 147.5, 138.9, 128.7, 128.2, 127.1, 120.5, 82.5, 56.7, 51.5. MS m/z (rel. int.) 206 (1), 191 (4), 174 (38), 147 (100), 115 (75), 91 (15), 77 (21), 51 (8). Anal. calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.81%. Found: C, 69.48; H, 7.00%.

*3.3. Methyl (*E*,4*S*)-4-methoxy-2-hexenoate **6b***

Oil; $[\alpha]_D^{25}$=−5.0 (c=1.50, $CHCl_3$). ^{1}H NMR δ 6.83 (dd, 1H, *J*=6.4, 15.8 Hz), 5.98 (dd, 1H, *J*=1.3, 15.8 Hz), 3.76 (s, 3H), 3.68 (ddt, 1H, *J*=1.3, 6.4, 6.4 Hz), 3.3 (s, 3H), 1.7–1.5 (m, 2H), 0.95 (t, 3H, *J*=7.4 Hz). ^{13}C NMR δ 164.8, 148.3, 121.7, 81.7, 57.0, 51.6, 27.5, 9.3. MS m/z (rel. int.) 158 (3), 129 (100), 101 (25), 99 (19), 69 (15), 45 (13), 41 (11). Anal. calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92%. Found: C, 60.48; H, 8.75%.

3.4. Methyl (E,4S)-4-methoxy-2-pentenoate **6c**

Oil; $[\alpha]_D^{20}$=−9.5 (c=1.50, $CHCl_3$). ^{1}H NMR δ 6.84 (dd, 1H, *J*=6.2, 15.8 Hz), 6.0 (dd, 1H, *J*=1.3, 15.8 Hz), 3.88 (ddq, 1H, *J*=1.3, 6.2, 6.5 Hz), 3.76 (s, 3H), 3.32 (s, 3H), 1.28 (d, 3H, *J*=6.5 Hz). ^{13}C NMR δ 166.0, 149.3, 120.8, 76.1, 56.7, 51.6, 20.4. MS m/z (rel. int.) 144 (2), 129 (100), 113 (32), 101 (26), 97 (51), 85 (62), 81 (25), 69 (24), 59 (34), 55 (41), 53 (28), 43 (24). Anal. calcd for $C_7H_{12}O_3$: C, 58.32; H, 8.39%. Found: C, 58.55; H, 8.15%.

3.5. (E,4S)-4-Methoxy-2-pentenenitrile **6d**

Oil; $[\alpha]_D^{21}$=−2.1 (c=0.20, $CHCl_3$). ^{1}H NMR δ 6.65 (dd, 1H, *J*=5.2, 16.4 Hz), 5.55 (dd, 1H, *J*=1.6, 16.4 Hz), 3.92 (ddq, 1H, *J*=1.6, 5.2, 6.6 Hz), 3.3 (s, 3H), 1.25 (d, 3H, *J*=6.6 Hz). ^{13}C NMR δ 155.6, 116.9, 99.4, 76.0, 56.7, 19.7. MS m/z (rel. int.) 111 (10), 96 (100), 80 (24), 68 (24), 66 (18), 53 (38), 52 (20), 43 (43). Anal. calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60%. Found: C, 64.68; H, 8.40; N, 12.27%.

3.6. Methyl (E,4R)-4-(2-hydroxyethoxy)-4-phenyl-2-butenoate **6e**

Oil; $[\alpha]_D^{23}$=+16.8 (c=7.87, $CHCl_3$). ^{1}H NMR δ 7.4–7.2 (m, 5H), 7.0 (dd, 1H, *J*=5.4, 15.7 Hz), 6.10 (dd, 1H, *J*=1.5, 15.7 Hz), 4.95 (dd, 1H, *J*=1.5, 5.4 Hz), 3.8–3.65 (m, 2H), 3.73 (s, 3H), 3.6–3.5 (m, 2H), 2.2 (br s, 1H). ^{13}C NMR δ 166.5, 147.3, 138.8, 128.8, 122.4, 127.1, 120.6, 81.3, 70.2, 61.9, 51.5. MS m/z (rel. int.) 236 (5), 163 (38), 133 (28), 131 (23), 115 (100), 73 (31). Anal. calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%. Found: C, 66.42; H, 7.05%.

3.7. Methyl (E,4S)-4-(2-hydroxyethoxy)-2-hexenoate **6f**

Oil; $[\alpha]_D^{22}$=−1.5 (c=2.02, $CHCl_3$). ^{1}H NMR δ 6.82 (dd, 1H, *J*=6.3, 15.8 Hz), 6.0 (dd, 1H, *J*=1.2, 15.8 Hz), 3.84 (ddt, 1H, *J*=1.2, 6.3, 6.3 Hz), 3.8–3.71 (m, 2H), 3.76 (s, 3H), 3.6 (dt, 1H, *J*=4.5, 10.0 Hz), 3.46 (dt, 1H, *J*=4.8, 10.0 Hz), 2.2 (br s, 1H), 1.75–1.51 (m, 2H), 0.94 (t, 3H, *J*=7.4 Hz). ^{13}C NMR δ 166.5, 148.1, 121.6, 80.4, 70.8, 61.9, 51.6, 27.6, 9.4. MS m/z (rel. int.) 159 (37), 128 (19), 127 (18), 115 (100), 87 (15), 83 (22), 59 (21), 45 (29). Anal. calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57%. Found: C, 57.28; H, 8.75%.

3.8. (E,4S)-4-(2-Hydroxyethoxy)-2-pentenenitrile **6g**

(*E*) Isomer: oil. ^{1}H NMR (C_6D_6) δ 5.97 (dd, 1H, *J*=5.1, 16.3 Hz), 5.07 (dd, 1H, *J*=1.6, 16.3 Hz), 3.47–3.41 (m, 2H), 3.29 (ddq, 1H, *J*=1.6, 5.1. 6.6 Hz), 3.2–2.8 (m, 2H), 1.42 (br s, 1H), 0.98 (d, 3H, *J*=6.6 Hz). ^{13}C NMR δ 155.7, 116.9, 99.3, 74.8, 70.3, 61.5, 19.9. MS m/z (rel. int.) 141 (1), 126 (7), 97 (12), 96 (11), 81 (41), 80 (100), 68 (13), 54 (59), 53 (46), 45 (46). Anal. calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92%. Found: C, 59.50; H, 7.68; N, 9.75%.

(*Z*) Isomer: oil. ^{1}H NMR (C_6D_6) δ 5.65 (dd, 1H, *J*=8.1, 11.2 Hz), 4.61 (dd, 1H, *J*=1.0, 11.2 Hz), 4.16 (ddq, 1H, *J*=1.0, 6.6, 8.1 Hz), 3.6–3.5 (m, 2H), 3.23–4.14 (m, 2H), 1.6 (br s, 1H), 1.0 (d, 3H, *J*=6.6 Hz). ^{13}C NMR δ 155.5, 117.0, 100.0, 74.3, 70.3, 61.4, 20.1. MS m/z (rel. int.) 141 (1), 126 (4), 97 (6), 96 (8), 81 (39), 80 (100), 54 (22), 53 (31), 45 (18). Found: C, 59.32; H, 7.92; N, 10.05%.

3.9. Conversion of β,γ-unsaturated esters and nitriles into allylic alcohols. General procedure

A mixture of camphor diselenide (0.5 mmol) and ammonium persulfate (1 mmol) in acetonitrile (5 mL) was heated at 70°C for 40 minutes. The reaction mixture was cooled to 40°C and the alkenes **3a**,**b**,**d** (1 mmol), water (1 mL) and ammonium persulfate (2 mmol) were added. The progress of the reaction was monitored by TLC and GC–MS. After 22–45 h the reaction mixture was worked up in the usual way. The allylic alcohols and the butenolides were isolated in pure form by column chromatography. Reaction yields and enantiomeric excesses are reported in Table 3. Physical and spectral data of the reaction products **6h**–**j** and **10h**,**i** are reported below.

3.10. Methyl (E,4R)-4-hydroxy-4-phenyl-2-butenoate **6h**

Oil; $[\alpha]_D^{25}$=+30.1 (c=8.39, $CHCl_3$). ^{1}H NMR δ 7.4–7.2 (m, 5H), 7.03 (dd, 1H, *J*=4.8, 15.6 Hz), 6.18 (dd, 1H, *J*=1.8, 15.6 Hz), 5.3 (dd, 1H, *J*=1.8, 4.8 Hz), 3.7 (s, 3H), 3.0 (br s, 1H). ^{13}C NMR δ 166.9, 148.9, 140.9, 128.7, 128.2, 126.5, 119.7, 73.4, 51.5. MS m/z (rel. int.) 192 (1), 174 (31), 163 (90), 133 (43), 132 (24), 131 (100), 115 (27), 1.05 (59), 103 (27), 87 (75), 79 (24), 77 (51), 55 (39). Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29%. Found: C, 68.55; H, 6.03%.

3.11. (5R)-5-Phenyl-2,5-dihydro-2-furanone **10h**

Oil; $[\alpha]_D^{21}$=+103.6 (c=0.71, $CHCl_3$) (lit.[22] oil; $[\alpha]_D^{15}$=+304 (c=1.0, $CHCl_3$)). ^{1}H NMR δ 7.58 (dd, 1H, *J*=1.7, 5.6 Hz), 7.49–7.39 (m, 3H), 7.34–7.27 (m, 2H), 6.28 (dd, 1H, *J*=2.0, 5.6 Hz), 6.07 (dd, 1H, *J*=1.7, 2.0 Hz). ^{13}C NMR δ 173.0, 155.9, 138.7, 128.8, 128.6, 126.2, 120.3, 84.0. MS m/z (rel. int.) 140 (90), 131 (70), 115 (15), 105 (100), 82 (33), 77 (46), 51 (20).

3.12. Methyl (E,4S)-4-hydroxy-2-hexenoate **6i**

Oil; $[\alpha]_D^{25}$=+16.4 (c=4.08, $CHCl_3$) (lit.[20] oil; $[\alpha]_D^{25}$=+24 (c=3.1, $CHCl_3$)). ^{1}H NMR δ 6.95 (dd, 1H, *J*=4.9, 15.6 Hz), 6.05 (dd, 1H, *J*=1.6, 15.6 Hz), 4.25 (ddt, 1H, *J*=1.6, 6.6, 6.6 Hz), 3.75 (s, 3H), 1.75–1.55 (m, 2H), 0.95 (t, 3H, *J*=7.0 Hz). ^{13}C NMR δ 158.0, 150.2, 120.0, 72.3, 51.6, 29.6, 9.4. MS m/z (rel. int.) 144 (1), 115 (100), 87 (82), 83 (45), 57 (22), 55 (37).

3.13. (5S)-5-Ethyl-2,5-dihydro-2-furanone **10i**

Oil; $[\alpha]_D^{21}$=+64.1 (c=1.82, CH_2Cl_2) (lit.[23] oil; *R* form, $[\alpha]_D^{20}$=−97.6 (c=2.08, CH_2Cl_2). ^{1}H NMR δ 7.49 (dd, 1H, *J*=1.4, 5.7 Hz), 6.13 (dd, 1H, *J*=1.9, 5.7 Hz), 5.1–4.9 (m, 1H), 1.98–1.65 (m, 2H), 1.02 (t, 3H, *J*=7.4 Hz).

3.14. (E,4S)-4-Hydroxy-2-pentenenitrile **6j**

Oil; $[\alpha]_D^{23}$=+25.2 (c=0.74, $CHCl_3$) (lit.[21] oil; *R* form, $[\alpha]_D^{20}$=−28 (c=1.0, $CHCl_3$). ^{1}H NMR δ 6.75 (dd, 1H, *J*=3.9, 16.2 Hz), 5.65 (dd, 1H, *J*=1.9, 16.2 Hz), 4.52 (ddq, 1H, *J*=0.9, 3.9, 7.0 Hz), 2.8 (br s, 1H), 1.3 (d, 3H, *J*=7.0 Hz). ^{13}C NMR δ 157.8, 117.3, 97.9, 66.8, 22.3. MS m/z (rel. int.) 97 (1), 96 (6), 82 (39), 55 (26), 54 (100), 52 (13), 43 (17).

3.15. Conversion of allylic ethers **6e** and **6f** into dioxane derivatives **7** and **8**

The allylic ethers **6e** or **6f** (1 mmol) were treated with sodium hydride (1.1 mmol) in THF at −20°C. After 3 h the mixtures were worked up in the usual way. GC–MS and ^{1}H NMR analyses of the crude reaction mixtures showed that both **7** and **8** were a 1:1 mixture of two stereoisomers. Purification was effected by column chromatography on silica gel. Only in the case of **8** could the two isomers be separated. Physical and spectral data of the obtained products are reported below.

3.16. Methyl 2-(3-phenyl-1,4-dioxan-2-yl)acetate **7**

This was a 1:1 mixture of the *cis* and *trans* isomers. ^{1}H NMR δ 7.4–7.1 (m, 10H, *cis*+*trans*), 4.82 (d, 1H, *J*=3.3 Hz, *cis*), 4.36 (ddd, 1H, *J*=3.3, 4.3, 10.3 Hz, *cis*), 4.2 (d, 1H, *J*=9.0 Hz, *trans*), 4.05–3.7 (m, 9H, *cis*+*trans*), 3.5 (s, 3H), 3.49 (s, 3H), 2.85 (ddq, 1H, *J*=10.3, 15.2 Hz, *cis*), 2.29 (dd, 1H, *J*=8.6, 15.2 Hz, *trans*), 2.12 (dd, 1H, *J*=3.8, 15.2 Hz, *trans*), 2.0 (dd, 1H, *J*=4.3, 15.2 Hz, *cis*). ^{13}C NMR δ 171.9 (two carbons), 138.8, 138.1, 129.3, 129.2, 129.0, 128.4, 128.1, 126.7, 83.0, 80.7, 78.1, 77.6, 68.4, 68.2, 67.8, 67.4, 52.7, 52.3, 37.7, 35.9. MS m/z (rel. int.) *cis* isomer, 236 (1), 193 (13), 106 (50), 1.05 (100), 91 (14), 77 (19); *trans* isomer, 236 (1), 193 (13), 106 (50), 105 (100), 91 (14), 77 (19). Anal. calcd for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83%. Found: C, 65.82; H, 6.85%.

3.17. Methyl 2-(3-ethyl-1,4-dioxan-2-yl)acetate **8**

cis Isomer: ^{1}H NMR δ 4.17 (ddd, 1H, *J*=3.3, 4.2, 10.0 Hz), 3.9 (ddd, 1H, *J*=3.2, 8.4, 11.7 Hz), 3.8 (ddd, 1H, *J*=3.2, 3.8, 11.7 Hz), 3.74 (s, 3H), 3.65 (ddd, 1H, *J*=3.1, 8.4, 11.6 Hz), 3.36–3.58 (m, 1H), 2.86 (dd, 1H, *J*=10.0, 14.9 Hz), 2.4 (dd, 1H, *J*=4.2, 14.9 Hz), 1.65–1.5 (m, 1H), 1.38–1.28 (m, 1H), 0.98 (t, 3H, *J*=7.2 Hz). ^{13}C NMR δ 171.7, 96.0, 72.6, 64.6, 61.8, 51.8, 32.7, 22.1, 9.8. MS m/z (rel. int.) 188 (2), 157 (9), 145 (15), 129 (20), 115 (44), 114 (43), 113 (100), 99 (31), 87 (17), 85 (18), 74 (27), 71 (31), 59 (26), 58 (35), 57 (68). Anal. calcd for $C_9H_{16}O_4$: C, 54.43; H, 8.57%. Found: C, 54.65; H, 8.73%.

trans Isomer: ^{1}H NMR (C_6D_6) δ 3.88 (dt, 1H, *J*=3.9, 8.8 Hz), 3.49–3.40 (m, 4H), 3.47 (s, 3H), 3.1 (ddd, 1H, *J*=5.1. 6.7, 8.8 Hz), 2.39 (dd, 1H, *J*=8.6, 15.0 Hz), 2.5 (dd, 1H, *J*=3.9, 15.0 Hz), 1.52–1.45 (m, 2H), 1.05 (t, 3H, *J*=7.4 Hz). ^{13}C NMR δ 171.3, 79.9, 76.2, 66.8, 66.7, 51.8, 37.2, 24.2, 9.3. MS m/z (rel. int.) 188 (2), 157 (17), 145 (11), 129 (20), 115 (26), 114 (43), 113 (100), 99 (17), 85 (19), 74 (21), 71 (26), 59 (21), 58 (29), 57 (59), 43 (36). Found: C, 54.38; H, 8.45%.

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