Reactions of alkenesulfenamides with olefins in the presence of $POHal_3$

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A new method for the synthesis of β,β′-dihaloalkyl vinyl sulfides was proposed. The method is based on reactions of alkenesulfenamides with olefins in the presence of $POCl_3$ or $POBr_3$. The reactions with cage olefins (norbornene, norbornadiene, camphene, and dimethyl 5,6-di-*endo*-norbornenedicarboxylate) afford stable products, while vinylsulfenylation of a conformationally labile olefin (cyclohexene) give products that decompose during their isolation.

Key words: alkenesulfenamides, vinylsulfenylation, alkyl vinyl sulfides, phosphorus oxohalides, electrophilic addition.

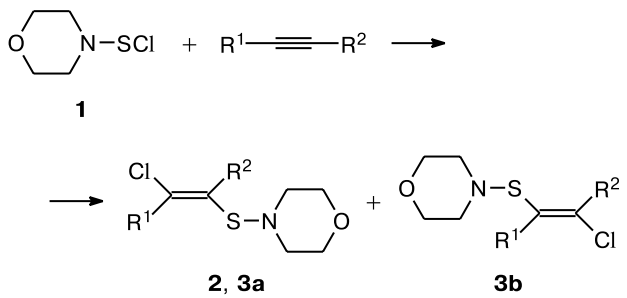
Vinyl sulfides play an important role in synthetic practice because they serve as synthetic equivalents of enolate ions[1] and acyl anions[2] and as important intermediates in the syntheses of oxetanes,[3] spirocyclic systems,[4] and many other organic substances,[5,6] including those exhibiting valuable biological activities.[7—10] Various methods for the synthesis of vinyl sulfides have been documented. Some of them involve radical intermediates,[11—13] S-nucleophiles,[14—16] and electrophilic sulfenylation of unsaturated compounds.[17—20] However, literature data on the possibility of electrophilic vinylsulfenylation of unsaturated compounds are very scarce.[21,22]

Earlier,[23] we have shown that arenesulfenamides activated with phosphorus oxohalides can add to the double bond of alkenes. With the aim of extending the synthetic potentialities of the method proposed for halosulfenylation of unsaturated compounds with a sulfenamide—phosphorus oxohalide system, we studied reactions of β-chloroalkenesulfenamides with some olefins in the presence of phosphorus oxohalides. Addition of 4-morpholinesulfenyl chloride (**1**) to hex-3-yne and hex-1-yne yielded alkenesulfenamides **2** and **3a**,**b** (Scheme 1).

In the case of hex-3-yne, a single alkenesulfenamide **2** is formed; the reaction with nonsymmetrical hex-1-yne affords a mixture of two regioisomers, which are Markownikoff (**3b**) and *anti*-Markownikoff adducts (**3a**) in the 1 : 4 ratio (^{1}H NMR). The resulting alkenesulfenamides were used without additional purification in subsequent reactions with olefins in the presence of phosphorus oxohalides.

Sulfenamides by themselves are weak electrophilic reagents, which cannot add to multiple bonds. However, their reactions with phosphorus oxohalides give reactive complexes, in which the positive charge on the S atom is

Scheme 1



$R^1 = R^2 = Et$ (**2**)
$R^1 = H$, $R^2 = Bu^n$ (**3**)

higher than that in the starting sulfenamide.[24] These complexes add to olefins according to the electrophilic mechanism. In the final reaction step, the halogen atom of phosphorus oxohalide acts as a nucleophile.[24]

Norbornene serves as a model unsaturated substrate for studying electrophilic addition reactions.[25] For example, the nature of the electrophilic species is unambiguously determined from the stereochemistry of the adduct, while the formation, or the absence, of Wagner—Meerwein rearrangement products enables one to estimate the degree of polarization of the intermediates. The reactions of alkenesulfenamides (**2**, **3a**,**b**) activated with $POHal_3$ (Hal = Cl, Br) with norbornene yielded *trans*-1,2-adducts **4**—**7** (Scheme 2).

The structures of products **4**—**7** were determined based on their ^{1}H NMR spectra. Thus the signals for the protons HCHal in compounds **4**—**7** appear at δ 3.98—3.90 as doublets of triplets ($^3J_{2,3} \approx {}^3J_{2,1} \approx 4.0$ Hz, $^4J_{2,6} \approx 2.0$ Hz), while signals for the protons HCS appear at δ 2.92—2.77

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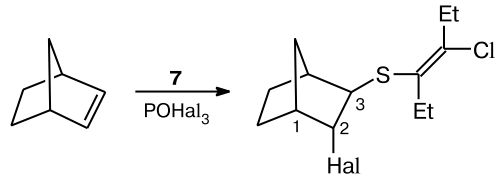
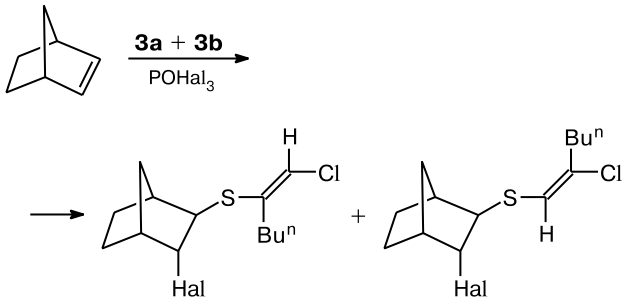
Scheme 2



4, **5**



6a, **7a** **6b**, **7b**

6a : **6b** = 4 : 1
7a : **7b** = 1 : 1

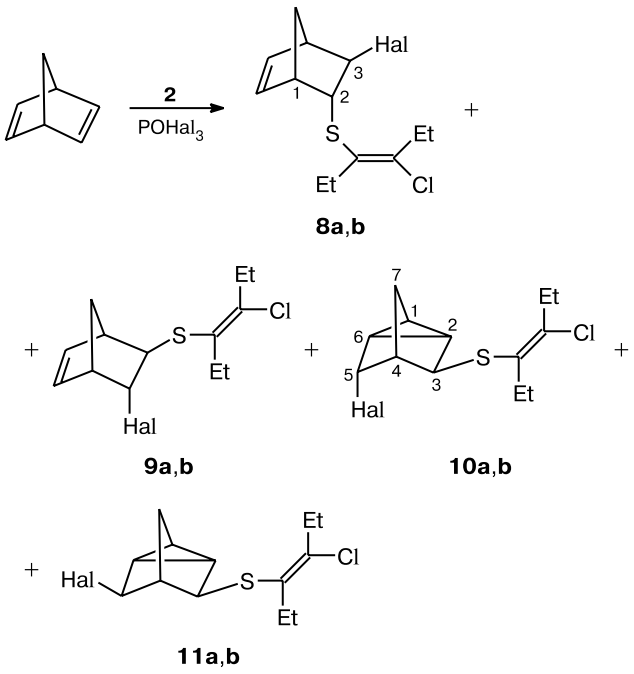
Hal = Br (**4**, **6**), Cl (**5**, **7**)

as doublets of doublets ($^3J_{3,2} \approx 4.0$ Hz, $^4J_{3,7} \approx 2.8$ Hz). The vicinal spin-spin coupling constant $^3J_{2,3}$ is close to 4.0 Hz, which is characteristic of *trans*-2,3-disubstituted norbornanes.[26] A rather high vicinal spin-spin coupling constant ($^3J_{2,1} \approx 4.0$ Hz) suggests the *exo*-position of the proton HCHal. The *endo*-protons of the HCS group show no coupling with the bridgehead protons, while the W coupling constant $^4J_{3,7} \approx 2.8$ Hz is observed.

A difference between the observed ratios of isomers **6a**/**6b** and **7a**/**7b** can probably be explained by isomerization of the *anti*-Markownikoff alkenesulfenamide **3a** into the Markownikoff isomer **3b**. Sulfenylation in the presence of $POCl_3$ as a reaction activator takes much longer time than in the activation by $POBr_3$ (10 and 4 h, respectively); therefore, partial transformation **3a** → **3b** is possible in the reaction mixture. The higher yield of the bromosulfenylation products (60%) can also be explained by the more rapid addition of the reagent and a lesser probability of side degradation processes.

The addition of alkenesulfenamide **2** to norbornadiene in the presence of phosphorus oxohalides affords the expected set of products **8**—**11** (Scheme 3) in yields 67% (**a**) and 65% (**b**) (*cf.* Ref. 25); 3,5-disubstituted nortricyclanes **10** are dominant (the ratio of the reaction products is 1.78 : 3.67 : 4.67 : 1 (**a**) and 1.78 : 2 : 6.33 : 1 (**b**)). The preferential formation of isomers **10** in these reactions can be explained in terms of the concept of the ion pair mechanism.[27] In the case of norbornadiene, an electrophile can attack the double bond from both the *exo*- and *endo*-sides. The intermediate resulting from the *endo*-attack gives a single product **8a** (**8b**) and seems to be a tight ion pair. A tight ion pair formed upon the *exo*-attack affords product **9a** (**9b**) and, through homoallylic participation of the second double bond, product **10a**,**b**. In addition, the tight ion pair can be transformed into a solvent-separated ion pair to give compounds **10** and **11**.

Scheme 3



8a,**b** **9a**,**b** **10a**,**b** **11a**,**b**

Hal = Br (**a**), Cl (**b**)

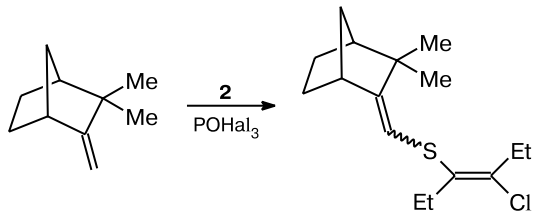
The reactions in solvents differing in polarity yield *exo*- and *endo*-adducts in different ratios.[24] In more polar solvents, an electrophilic species is solvated to a higher extent, it is bulkier, and the percentage of the *exo*-adduct is higher than in less polar solvents.[24]

The structures of the adducts were determined based on their ^{1}H NMR spectra by analogy with the products obtained in the reactions of arenesulfenamides activated with phosphorus oxohalides with norbornadiene.[24]

Reactions of electrophilic reagents with camphene can result in both skeletal rearrangement and addition—elimination products. It is known[28] that the rearrangement of the camphene skeleton requires a highly electrophilic reagent. We found that the reactions of camphene with alkenesulfenamide **2** in the presence of phosphorus oxohalides afford mixtures of *E*- and *Z*-isomers **12**, which represent the addition—elimination products (Scheme 4).

The *E*-/*Z*- ratio of vinyl sulfides **12** was determined from the integral intensities for the olefinic protons (^{1}H NMR). Signals for these protons were assigned with consideration of the NOE data[29] for related compounds,

Scheme 4



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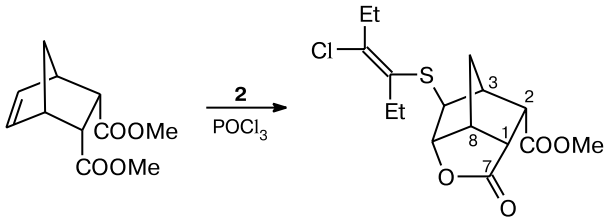
Hal = Br ($E:Z$ = 1 : 2), Cl ($E:Z$ = 1 : 1)

in which the proton at the double bond in the *E*-isomer was found to be shifted upfield.

In vinylsulfenylation of dimethyl norbornenedicarboxylate with arenesulfenylamides **2** in the presence of $POCl_3$ (Scheme 5), the methoxycarbonyl group acts as a nucleophile in the final step to give γ-lactone **13** in 50% yield as a single product. Its structure was determined using the criteria developed previously[28] for such molecules. The IR spectrum[17] contains an absorption band at 1790 cm^{-1} for a γ-lactone ring and a band at 1730 cm^{-1} for an ester group. The ^1H NMR spectrum of lactone **13** shows resonance signals at δ 3.73 and 4.54 for the protons HCS and HCO, respectively. The vicinal coupling constant $^3J_{4,5}$ is low, which suggests a nearly right dihedral angle H(4)—C—C—H(5).

Scheme 5



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Note that the reaction products are stable only in vinylsulfenylation of the cage olefins. In the case of conformationally labile alkene (cyclohexene), vinylsulfenylation products are unstable and resinify in the course of the reaction. Similar results were obtained[22] in the study of sulfamatosulfenylation of olefins using alkenesulfenamides activated with SO_3.

Thus, we developed a method for the vinylsulfenylation of cage olefins using vinylsulfenamides activated with phosphorus oxohalides.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Varian VXR-400 instrument (400 and 100 MHz, respectively) in $CDCl_3$. IR spectra were recorded on a UR-20 instrument (Carl Zeiss, Jena). The course of the reaction was monitored and the purity of products was checked by TLC on Silufol plates. Preparative separation of reaction mixtures was carried out by column chromatography on silica gel (SiO_2 5/40).

Synthesis of the starting β-haloalkenesulfenamides (general procedure). A solution of 4-morpholinesulfenyl chloride (**1**) (20 mmol) in CH_2Cl_2 was added to a vigorously stirred solution of an alkyne (20 mmol) in CH_2Cl_2. After the reaction was completed, the excess of the alkyne and the solvent were removed *in vacuo* to give a nonviscous light yellow oil. The products were used without additional purification in subsequent reactions.

***N*-[(*E*)-4-Chlorohex-3-en-3-ylthio]morpholine (2).** ^1H NMR ($CDCl_3$), δ: 3.65 (t, 4 H, OCH_2, J = 4.7 Hz); 2.97 (t, 4 H, NCH_2, J = 4.7 Hz); 2.67 (q, 2 H, =C(Cl)CH_2, J = 7.5 Hz); 2.56 (t, 2 H, =C(S)CH_2, J = 7.5 Hz); 1.09, 1.06 (both t, 3 H each, CH_3, J = 7.5 Hz).

***N*-[(*E*)-1-Chlorohex-1-en-2-ylthio]morpholine (3a) and *N*-[(*E*)-2-chlorohex-1-en-1-ylthio]morpholine (3b).** ^1H NMR ($CDCl_3$), δ: 6.61 (s, HC=, **3b**); 6.19 (s, HC=, **3a**); 3.64 (t, OCH_2, **3a**, J = 4.7 Hz); 3.36 (t, OCH_2, **3b**, J = 4.7 Hz); 2.95 (t, NCH_2, **3a**, J = 4.7 Hz); 2.93 (t, NCH_2, **3b**, J = 4.7 Hz); 2.49 (t, =C(Cl)CH_2, **3b**, J = 7.5 Hz); 2.35 (t, =C(S)CH_2, **3a**, J = 7.5 Hz); 1.56—1.45 (m, CH_3, **3a** and **3b**). The ratio between **3a** and **3b** was 1 : 4.

Vinylsulfenylation (general procedure). A solution of phosphorus oxohalide (20 mmol) was slowly added at −40 °C to a vigorously stirred solution of freshly prepared alkenesulfenamide (20 mmol) in CH_2Cl_2. The reaction mixture was stirred for

Table 1. Chromatographic characteristics and elemental analysis data for compounds **4**—**13**

Compound	R_f [a]	Found / Calculated (%)		Molecular formula
		C	H	
4	0.60	48.39 / 48.23	6.26 / 6.18	$C_{13}H_{20}BrClS$
5	0.61	56.33 / 55.91	6.67 / 7.17	$C_{13}H_{20}Cl_2S$
6a + **6b**	0.64	48.39 / 48.23	6.04 / 6.18	$C_{13}H_{20}BrClS$
7a + **7b**	0.63	55.74 / 55.91	7.16 / 7.17	$C_{13}H_{20}Cl_2S$
8a + **9a**	0.53	48.45 / 48.52 [b]	5.60 / 5.99 [b]	$C_{13}H_{18}BrClS$
10a + **11a**	0.43			
8b + **9b**	0.53	56.02 / 56.32 [c]	6.71 / 6.50 [c]	$C_{13}H_{18}Cl_2S$
10b + **11b**	0.40			
12	0.62	67.78 / 67.72	8.69 / 8.46	$C_{16}H_{24}ClS$
13	0.41 [d]	52.25 / 55.73	6.10 / 6.14	$C_{16}H_{21}ClO_4S$

[a] Light petroleum.
[b] For a mixture of compounds **8a**, **9a**, **10a**, and **11a**.
[c] For a mixture of compounds **8b**, **9b**, **10b**, and **11b**.
[d] EtOAc—light petroleum (1 : 3).

Table 2. ^{1}H NMR data for compounds **4**—**11**

Compound	δ (*J*/Hz)						
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
4 [a,b]	2.47 (m)	3.94 (dt, $J_{2,1}$ = $J_{2,3}$ = 3.9, $J_{2,6_{exo}}$ = 2.0)	2.90 (t, $J_{3,2}$ = 3.9, $J_{3,7_{anti}}$ = 2.7)	2.14 (d, $J_{4,5_{exo}}$ = 4.3)	*exo* 1.66 (tt, $J_{5_{exo},5_{endo}}$ = $J_{5_{exo},6_{exo}}$ = 12.4, $J_{5_{exo},6_{endo}}$ = $J_{5_{exo},4}$ = 4.3	*exo* 1.52 (dtt, $J_{6_{exo},6_{endo}}$ = $J_{6_{exo},5_{exo}}$ = 12.4, $J_{6_{exo},5_{endo}}$ = $J_{6_{exo},1}$ = 4.3, $J_{6_{exo},2}$ = 2.0	*syn* 1.80 (dtt, $J_{7_{syn},7_{anti}}$ = 10.5, $J_{7_{syn},5_{endo}}$ = $J_{7_{syn},6_{endo}}$ = 2.2, $J_{7_{syn},1}$ = $J_{7_{syn},4}$ = 1.6
					endo 1.30 (ddt, $J_{5_{endo},5_{exo}}$ = 12.4, $J_{5_{endo},6_{endo}}$ = 9.0, $J_{5_{endo},6_{exo}}$ = 4.3, $J_{5_{endo},7_{syn}}$ = 2.2)	*endo* 1.96 (ddt, $J_{6_{endo},6_{exo}}$ = 12.4, $J_{6_{endo},5_{endo}}$ = 9.0, $J_{6_{endo},5_{exo}}$ = 4.3, $J_{6_{endo},7_{syn}}$ = 2.2)	*anti* 1.39 (ddt, $J_{7_{anti},7_{syn}}$ = 10.5, $J_{7_{anti},3}$ = 2.7, $J_{7_{anti},1}$ = $J_{7_{anti},4}$ = 1.6)
5 [a,c]	2.45 (dt, $J_{1,2}$ = $J_{1,6_{exo}}$ = 4.0)	3.90 (dt, $J_{2,1}$ = $J_{2,3}$ = 4.0, $J_{2,6_{exo}}$ = 1.9)	2.78 (t, $J_{3,2}$ = 4.0, $J_{3,7_{anti}}$ = 2.8)	2.14 (d, $J_{4,5_{exo}}$ = 4.6)	*exo* 1.67 (dtt, $J_{5_{exo},5_{endo}}$ = $J_{5_{exo},6_{exo}}$ = 12.7, $J_{5_{exo},6_{endo}}$ = $J_{5_{exo},4}$ = 4.6)	*exo* 1.45 (dtt, $J_{6_{exo},6_{endo}}$ = $J_{6_{exo},5_{exo}}$ = 12.7, $J_{6_{exo},5_{endo}}$ = $J_{6_{exo},1}$ = 4.0, $J_{6_{exo},2}$ = 1.9)	*syn* 1.79 (dtt, $J_{7_{syn},7_{anti}}$ = 10.5, $J_{7_{syn},5_{endo}}$ = $J_{7_{syn},6_{endo}}$ = 2.4, $J_{7_{syn},1}$ = $J_{7_{syn},4}$ = 1.4)
					endo 1.32 (dddd, $J_{5_{endo},5_{exo}}$ = 12.7, $J_{5_{endo},6_{endo}}$ = 9.2, $J_{5_{endo},6_{exo}}$ = 4.0, $J_{5_{endo},7_{syn}}$ = 2.4)	*endo* 1.96 (dddd, $J_{6_{endo},6_{exo}}$ = 12.7, $J_{6_{endo},5_{endo}}$ = 9.2, $J_{6_{endo},5_{exo}}$ = 4.6, $J_{6_{endo},7_{syn}}$ = 2.4)	*anti* 1.40 (dddd, $J_{7_{anti},7_{syn}}$ = 10.5, $J_{7_{anti},3}$ = 2.8, $J_{7_{anti},1}$ = $J_{7_{anti},4}$ = 1.9)
6a [d]	2.48 (t, $J_{1,2}$ = $J_{1,6_{exo}}$ = 4.0)	3.96 (dt, $J_{2,1}$ = $J_{2,3}$ = 4.0, $J_{2,6_{exo}}$ = 1.9)	2.92 (t, $J_{3,2}$ = 4.0, $J_{3,7_{anti}}$ = 2.8)	2.17 (d, $J_{4,5_{exo}}$ = 4.5)		2.01—1.29 (m)	
6b [e]	2.48 (t, $J_{1,2}$ = $J_{1,6_{exo}}$ = 4.0)	3.98 (dt, $J_{2,1}$ = $J_{2,3}$ = 4.0, $J_{2,6_{exo}}$ = 2.0)	2.91 (t, $J_{3,2}$ = 4.0, $J_{3,7_{anti}}$ = 2.9)	2.19 (d, $J_{4,5_{exo}}$ = 4.5)		2.01—1.29 (m)	
7a [f]	2.46 (br.s)	3.93 (dt, $J_{2,1}$ = $J_{2,3}$ = 4.1, $J_{2,6_{exo}}$ = 1.9)	2.80 (t, $J_{3,2}$ = 4.1, $J_{3,7_{anti}}$ = 2.7)	2.20 (d, $J_{4,5_{exo}}$ = 4.5)		2.02—1.27 (m)	
7b [g]	2.46 (br.s)	3.95 (dt, $J_{2,1}$ = $J_{2,3}$ = 4.1, $J_{2,6_{exo}}$ = 2.0)	2.77 (t, $J_{3,2}$ = 4.1, $J_{3,7_{anti}}$ = 2.8)	2.20 (d, $J_{4,5_{exo}}$ = 4.5)		2.02—1.27 (m)	
8a [h]	3.33 (br.s)	3.51 (t, $J_{2,3}$ ≅ $J_{2,7'}$ = 3.0)	3.48 (t, $J_{3,2}$ ≅ $J_{3,4}$ = 3.0)	2.96 (br.s)	6.17 (t, $J_{5,6}$ = 5.2, $J_{5,4}$ = 2.4)	6.26 (t, $J_{6,5}$ = 5.2, $J_{6,1}$ = 2.7	2.02 (d, $J_{7,7'}$ = 9.0); 1.79 (ddt, $J_{7,7'}$ = 9.0, $J_{7',2}$ = 2.5, $J_{7',1}$ = $J_{7',4}$ = 1.8)
8b [h]	3.20 (br.s)	3.56 (t, $J_{2,3}$ ≅ $J_{2,7'}$ = 2.8)	3.35 (t, $J_{3,2}$ ≅ $J_{3,4}$ = 2.8)	2.99 (br.s)	6.21 (t, $J_{5,6}$ = 5.8, $J_{5,4}$ = 2.6)	6.24 (t, $J_{6,5}$ = 5.8, $J_{6,1}$ = 2.7)	1.98 (d, $J_{7,7'}$ = 9.2); 1.79 (dq, $J_{7,7'}$ = 9.0, $J_{7',3}$ = $J_{7'1}$ = $J_{7',4}$ = 2.0)

(*to be continued*)

Table 2 (*continued*)

Compound	δ (*J*/Hz)						
	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)
9a [h]	3.18 (br.s)	2.88 (t, $J_{2,3} \cong J_{2,1} = 3.1$)	4.01 (t, $J_{3,2} \cong J_{3,7'} = 3.1$)	3.10 (br.s)	6.15 (t, $J_{5,6} = 5.6$, $J_{5,4} = 2.4$)	6.31 (t, $J_{6,5} = 5.6$, $J_{6,1} = 3.1$)	1.84 (d, $J_{7,7'} = 9.2$); 1.67 (ddt, $J_{7,7'} = 9.2$, $J_{7',3} = 2.7$, $J_{7',1} = J_{7',4} = 1.6$)
9b [h]	3.15 (br.s)	2.80 (t, $J_{2,3} \cong J_{2,1} = 3.2$)	4.08 (t, $J_{3,2} \cong J_{3,7'} = 3.2$)	3.02 (br.s)	6.19 (t, $J_{5,6} = 5.6$, $J_{5,4} = 3.4$)	6.34 (t, $J_{6,5} = 5.6$, $J_{6,1} = 3.3$)	1.86 (d, $J_{7,7'} = 9.5$); 1.70 (ddt, $J_{7,7'} = 9.5$, $J_{7',3} = 2.8$ $J_{7',1} = J_{7',4} = 1.8$)
10a [h]	1.38 (t, $J_{1,2} = J_{1,6} = 5.1$)	1.62 (t, $J_{2,1} = J_{2,6} = 5.1$)	4.02 (t, $J_{3,2} = J_{3,4} = 1.5$)	2.06 (br.s)	3.69 (br.s)	1.42 (t, $J_{6,1} = J_{6,2} = 5.1$)	1.93 (dt, $J_{7,7'} = 11.1$, $J_{7,1} = J_{7,4} = 1.4$); 1.43 (dt, $J_{7,7'} = 11.1$, $J_{7',1} = J_{7',4} = 1.4$)
10b [h]	1.45 (t, $J_{1,2} = J_{1,6} = 5.1$)	1.56 (t, $J_{2,1} = J_{2,6} = 5.1$)	4.03 (t, $J_{3,2} = J_{3,4} = 1.6$)	2.05 (br.s)	3.68 (br.s)	1.47 (t, $J_{6,1} = J_{6,2} = 5.1$	2.00 (dt, $J_{7,7'} = 11.3$, $J_{7,1} = J_{7,4} = 1.7$); 1.43 (d, $J_{7,7'} = 11.3$)
11a [h]	1.52 (m)	1.62 (t, $J_{2,1} = J_{2,6} = 5.1$)	3.90 (t, $J_{3,2} = J_{3,4} = 1.3$)	2.06 (br.s)	2.95 (br.s)	1.52 (m)	2.02 (m, 2 H)
11b [h]	1.45 (m)	1.58 (t, $J_{2,1} = J_{2,6} = 5.0$)	3.89 (t, $J_{3,2} = J_{3,4} = 1.7$)	2.09 (br.s)	2.98 (t, $J_{5,6} = J_{5,4} = 1.3$)	1.50 (t, $J_{6,1} = J_{6,2} = 5.0$)	2.02 (m, 2 H)

[a] Other signals in the ^{1}H NMR spectra of compounds **4** and **5** are identical; δ: 2.74, 2.48 (both q, 2 H each, =C(Cl)CH_2, =C(S)CH_2, J = 7.4 Hz); 1.09 (t, 6 H, CH_3, J = 7.4 Hz).
[b] ^{13}C NMR ($CDCl_3$), δ: 137.3, 116.0, 58.8, 57.0, 44.6, 43.2, 35.5, 31.3, 29.5, 28.7, 23.9, 22.2, 13.9.
[c] ^{13}C NMR ($CDCl_3$), δ: 135.3, 119.3, 59.1, 57.0, 44.7, 43.5, 35.4, 34.6, 29.1, 28.8, 23.8, 21.7, 13.8.
[d] Other signals in the ^{1}H NMR spectrum, δ: 6.14 (s, HC=); 2.40 (t, 2 H, =C(S)CH_2, J = 7.7 Hz); 1.57—1.29 (m, CH_2CH_2); 0.92 (t, 3 H, Me, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 137.3, 116.0, 58.8, 57.0, 44.6, 43.2, 35.5, 31.3, 29.5, 28.7, 23.9, 22.2, 13.9.
[e] Other signals in the ^{1}H NMR spectrum, δ: 6.17 (s, HC=); 2.45 (t, 2 H, =C(Cl)CH_2, J = 7.3 Hz); 1.57—1.29 (m, CH_2CH_2); 0.91 (t, 3 H, Me, J = 7.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 135.3, 119.3, 59.1, 57.0, 44.7, 43.5, 35.4, 34.6, 29.1, 28.8, 23.8, 21.7, 13.8.
[f] Other signals in the ^{1}H NMR spectrum, δ: 6.11 (s, HC=); 2.40 (t, 2 H, =C(S)CH_2, J = 7.8 Hz); 1.57—1.27 (m, CH_2CH_2); 0.92 (t, 3 H, Me, J = 7.7 Hz).
[g] Other signals in the ^{1}H NMR spectrum, δ: 6.15 (s, HC=); 2.45 (t, 2 H, =C(Cl)CH_2, J = 7.5 Hz); 1.57—1.27 (m, CH_2CH_2); 0.91 (t, 3 H, Me, J = 7.7 Hz).
[h] Other signals in the ^{1}H NMR spectra of compounds **8**—**11a**,**b** are identical; δ: 2.76, 2.30 (both q, 2 H each, =C(Cl)CH_2, =C(S)CH_2, J = 7.4 Hz); 1.14—1.10 (m, 6 H, Me).

10 min and then cooled to −70 °C. A solution of an alkene (20 mmol) in CH_2Cl_2 was added, and the mixture was gradually warmed to ~20 °C and stirred until the reaction was completed. The solvent was removed *in vacuo*, and the residue was chromatographed on SiO_2 in light petroleum; R_f and elemental analysis data for compounds **4**—**13** are given in Table 1. The ^{1}H and ^{13}C NMR spectra of compounds **4**—**11** are present in Table 2.

2*E*- and 2*Z*-(4-Chlorohex-3-en-3-yl)thiomethylidene-3,3-dimethylbicyclo[2.2.1]heptanes (12). ^{1}H NMR ($CDCl_3$), δ: 5.48 (s, HC=, (*Z*)-**12**); 5.43 (s, HC=, (*E*)-**12**); 3.20 (br.s, HC(1), (*E*)-**12**); 3.01 (br.s, HC(1), (*Z*)-**12**); 2.70, 2.30 (both q, =C(Cl)CH_2, =C(S)CH_2, (*Z*)-**12** and (*E*)-**12**, J = 7.4 Hz); 1.96 (br.s, HC(4), (*E*)-**12**); 1.94 (br.s, HC(4), (*Z*)-**12**); 1.80—0.70 (m, skeleton protons, (*Z*)-**12** and (*E*)-**12**).

Methyl (1*R,2*R**,3*S**,4*S**,5*S**,8*R**)-4-[4(*E*)-4-chlorohex-3-en-3-yl]thio-7-oxo-6-oxatricyclo[3.2.3.3^{3,8}]nonane-2-carboxylate (13)**, m.p. 119—120 °C (from heptane). ^{1}H NMR ($CDCl_3$), δ: 4.54 (d, 1 H, OCH, $J_{5,8}$ = 5.0 Hz); 3.73 (d, 1 H, SCH, $J_{4,9}$ = 2.2 Hz); 3.71 (s, 3 H, OMe); 3.31 (dd, 1 H, H(8), $J_{8,1} = J_{8,5}$ = 5.0 Hz); 3.11 (dd, 1 H, H(2), $J_{2,3}$ = 10.8 Hz, $J_{2,1}$ = 3.0 Hz); 2.83 (dd, 1 H, H(1), $J_{1,2}$ = 10.8 Hz, $J_{1,8}$ = 5.0 Hz); 2.72 (q, 2 H, =C(Cl)CH_2, J = 7.4 Hz); 2.58 (d, 1 H, H(3), $J_{3,2}$ = 3.0 Hz); 2.52 (q, 2 H, =C(S)CH_2, J = 7.4 Hz); 2.26 (d, 1 H, *syn*-H(9), $J_{9_{syn},9_{anti}}$ = 11.5 Hz); 1.65 (d, 1 H, *anti*-H(9), $J_{9_{anti},9_{syn}}$ = 11.5 Hz); 1.12 (t, 3 H, Me, J = 7.4 Hz); 1.11 (t, 3 H, Me, J = 7.4 Hz). IR (thin film), ν/cm^{-1}: 1790 (C=O, γ-lactone); 1730 (COOMe); 1610 (C=C).

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