Four-component coupling *via* a sequence of three Ad_E reactions involving arenesulfenyl chloride, two alkyl vinyl ether units, and silicon-containing π-donors as a method for the synthesis of polyfunctional compounds

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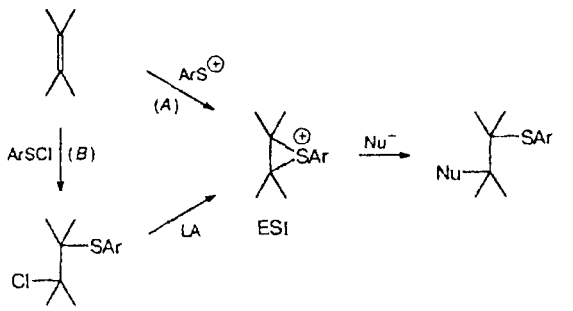
A protocol for the synthesis of polyfunctional compounds by a Lewis acid initiated tandem sequence of three Ad_E reactions of sulfur-containing electrophiles with two alkyl vinyl ether units and silicon containing π-donors is proposed.

Key words: arylenesulfenyl chloride, electrophilic addition reaction; episulfonium ion, thiophanium ion; alkyl vinyl ethers; silyl enol ethers, allylsilanes, allylstannanes.

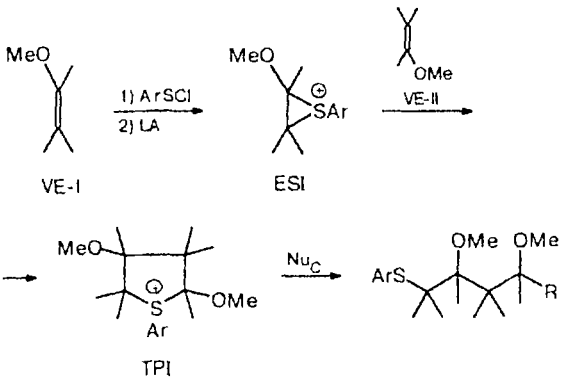
Electrophilic addition reaction (Ad_E reaction) of covalent arenesulfenyl halides with alkenes resulting in the formation of 1,2-adducts, β-haloalkyl aryl sulfides, as well as methods for the preparation of episulfonium ions (ESI) and further application of the latter as electrophiles for β-arylthioalkylation of various carbon nucleophiles (Nu_C) have been a subject of study in our research group for a number of years.[1] Episulfonium ions formed by interaction of alkyl- and aryl-substituted alkenes with the cationoid sulfur-containing electrophiles such as $ArS^+BF_4^-$ ($ArSCl + AgBF_4$ *in situ*; Scheme 1, path *A*) were used by us for the alkylation of aromatic and heteroaromatic π-donors.[2] Utilization of alkoxy-substituted olefins as unsaturated substrates in Ad_E reaction enabled us to develop a preparatively more convenient method for the preparation of ESI *in situ* (by the treatment of the prepared α-halo-β-arylthioalkyl ethers with the Lewis acids (LA); Scheme 1, path *B*)[3]. Due to the higher reactivity of these alkenes the synthetic potential of the reaction was substantially broadened with the involvement of silicon-containing C-nucleophiles such as trimethylsilyl enol ethers (TMSE)[4,5] and allyltrimethylsilanes as final nucleophiles.[6]

Further impulse to development of this work was provided by the finding that ESI, formed by interaction of ArSCl with an alkyl vinyl ether (VE-I), are able to react with the second molecule of vinyl ether (VE-II) (of the same or different structure) as a nucleophile giving rise to the formation of the next electrophilic intermediate, presumably the five-membered cyclic thiophanium ion (TPI) (Scheme 2).[7] Formation of TPI and its possible utilization as an electrophile in reactions with various carbon nucleophiles suggested an interesting synthetic development of the given reaction. In particular, it was found[8] that these intermediates are capable of reacting with organomagnesium compounds

Scheme 1



Scheme 2



Nu_C = RMgX

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as carbon nucleophiles. In this case it was possible to carry out the consecutive four-component one-pot coupling, resulting in the formation of two novel C—C bonds (see Scheme 2).

However, it is necessary to note that the use of Grignard reagents as final nucleophiles imposed certain limits on the nature of the substituents R in the product (R is allyl or aryl groups). In addition, it is evident that the generality of application of these nucleophiles is limited by the specific character of the conditions employed for the generation of TPI (presence of the Lewis acid, solvents such as CH_2Cl_2, $MeNO_2$).

In order to broaden the list of functional groups introduced into a molecule, the possibility of involving such well known π-donors was silyl enol ethers and allylsilanes as Nu_C in the final step of the reaction sequence described in the Scheme 2 was also investigated. The first attempts to carry out such a sequence of reactions turned out to be unsuccessful.[9] For example, the thiophanium intermediate formed, in accordance with the Scheme 2, from 4-TolSCl (Tol = MeC_6H_4), methyl vinyl ether (VE-I), and methyl isobutenyl ether (VE-II) in the presence of $TiCl_4$ in methylene chloride did not react with the allyltrimethylsilane and with the 2-methyl-1-trimethylsilyloxypropene at temperatures ranging from −78 to −20 °C, whereas an increase of the temperature up to +20 °C led to the rapid decomposition of the reaction components, resulting in a complex mixture of products, which, however, contained trace amount of the desired compound (MS data).

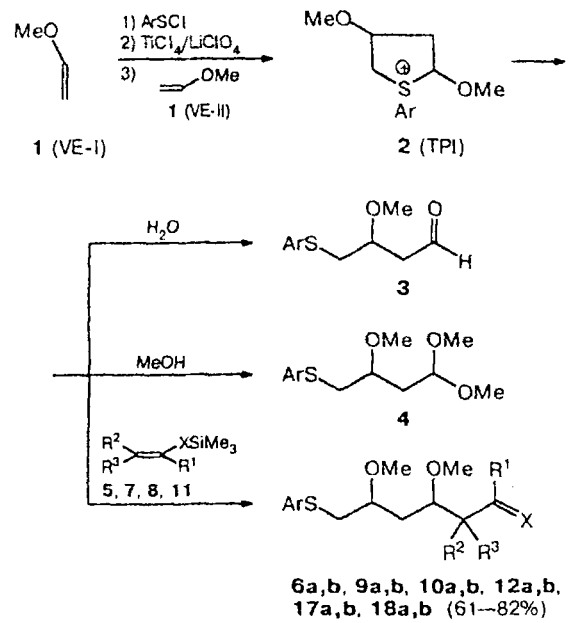
These data did not allow us to make any conclusion on the possibility for preparative realization of the requisite reaction. It was also clear that in order to find an answer to this question, a more profound study of the reaction course with wide variation in the nature of the components and reaction conditions is required. The present communication describes the results of these studies.[10]

As a model reaction a coupling of two methyl vinyl ether 1 units (VE-I and VE-II) was chosen which, as was assumed earlier, proceeds *via* formation of thiophanium intermediate **2** (Scheme 3).

We have found that this intermediate, formed at −78 °C in a solution of CH_2Cl_2 in the presence of $TiCl_4$ as a Lewis acid, is reasonably stable at 0 °C, at least for several hours with careful exclusion of traces of moisture. As a criterion to evaluate the stability of cation **2**, yields of the aldehyde **3** or of its dimethyl acetal **4**, the usual products of the TPI reaction with water and methanol, respectively, were used.[7] The yields of these products were invariably high (>80%), irrespective of whether the processing of cation **2** took place immediately after its generation or after keeping the reaction mixture at 0 °C for 5 h.

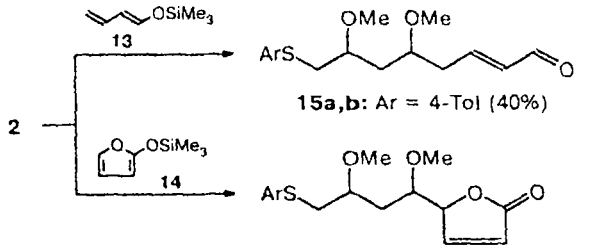
The stability of cation **2** under these conditions allowed us to study the possibility of its utilization as an electrophile in reactions with a number of silyl-containing Nu_C. It was found that the reaction of intermediate

Scheme 3



6a,b, 9a,b, 10a,b, 12a,b, 17a,b, 18a,b (61—82%)

5, 6, 17, 18: X = CH_2; $R^1 = R^2 = R^3$ = H
7, 9: X = O; R^1 = OMe, $R^2 = R^3$ = Me
8, 10: X = O; R^1 = H, $R^2 = R^3$ = Me
11, 12: X = O; R^1 = Me, $R^2 = R^3$ = H
Ar = 4-Tol (**6, 9, 10, 12**), 4-ClC_6H_4 (**17**), 2,4,6-$Me_3C_6H_2$ (**18**)



16a—d: Ar = 4-Tol (73%)

2 with allyltrimethylsilane **5** (2 equiv.) added as a nucleophile does not take place at −78 °C, but proceeds with a reasonable rate at 0 °C, and complete conversion of **2** (TLC data, practically complete absence of the aldehyde **3** after water processing of the test) is achieved within 5 h. The product, 4,6-dimethoxy-7-(4-tolylthio)hept-1-ene, was isolated in 66% yield as a mixture of two diastereomers (**6a,b**) in a ratio 1.0 : 1.2.

O-Trimethylsilyl derivatives of methyl isobutyrate (**7**) and isobutanal (**8**) under these conditions also reacted with the intermediate **2** to yield diastereomers of methyl 3,5-dimethoxy-2,2-dimethyl-6-(4-tolylthio)hexanate (**9a,b**) and 3,5-dimethoxy-2,2-dimethyl-6-(4-tolylthio)hexanal (**10a,b**), respectively. These results attest to the possibility of introduction of ester and aldehyde

groups into the target molecule. In these cases predominant formation of one diastereomer (**a** : **b** = 9 : 1) was observed. Interaction of 2-trimethylsiloxypropene (**11**) with TPI **2** results in the formation of the expected product, 4,6-dimethoxy-7-(4-tolylthio)heptan-2-one (**12a,b**, ratio of isomers 1 : 1) in only 36% yield. The low yield in this reaction, probably, is due to the decomposition of acid-sensitive Si-derivative in the presence of such a strong Lewis acid as $TiCl_4$. Attempts to carry out this reaction in the presence of a number of other Lewis acids ($BF_3 \cdot OEt_2$, $ZnCl_2$, $ZnCl_2 \cdot OEt_2$, TMSOTf) utilized for the generation of intermediate **2** were unsuccessful.

It is known that for many reactions requiring Lewis acids catalysis, $LiClO_4$ can serve as an effective catalyst in diethyl ether,[11] methylene chloride,[12] or nitromethane[13] as solvents. We found that the $LiClO_4$—$MeNO_2$ system can also be used successfully for TPI **2** generation, and under these conditions interaction of the latter with **11** results in the formation of ketones **12a,b** in 77% yield in a ratio 1 : 2.

Interaction of the intermediate **2** with the trimethylsilyloxydienes **13** and **14** (Scheme 3) proceeds exclusively as 1,4-addition, giving the γ-alkylated products: *E*-5,7-dimethoxy-8-(4-tolylthio)oct-2-enals (**15a,b**) (40%, $LiClO_4$—$MeNO_2$) and 5,7-dimethoxy-8-(4-tolylthio)oct-2-en-4-olids (**16a—d**) (73%, $TiCl_4$—CH_2Cl_2). In both cases the products are obtained as mixtures of equal amounts of all possible diastereomers.

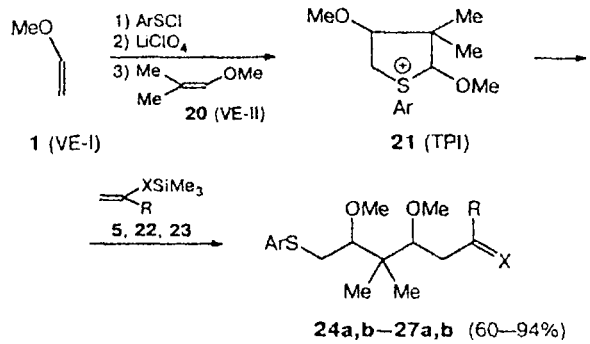
On the model reaction of the TPI intermediate **2** with allylsilane **5** we investigated the possible effects of various factors such as the nature of the Ar substituent, Lewis acid,[14] or C-nucleophile on the stereochemistry of the reaction. It was found that the variations of the Ar group (4-ClC_6H_4, 4-Tol, 2,4,6-$Me_3C_6H_2$) or of the nature of the Lewis acid ($TiCl_4$, $SnCl_4$, $ZnBr_2$, $LiClO_4$) caused only slight changes in the ratio of diastereomers for the products **6a,b**, **17a,b**, and **18a,b** (Table 1).

The replacement of allyltrimethylsilane **5** with the significantly more reactive allyltributylstannane[15] allowed us to carry out the reaction at lower temperature (−40 °C, $TiCl_4$—CH_2Cl_2) but did not influence the ratio of the isomers **6a,b** (1 : 1, 66%). The replacement of the methyl vinyl ether **1** with the sterically more hindered isopropyl vinyl ether, used as VE-I and VE-II, also did not produce noticeable effects on the stereochemistry of the reaction. In fact the corresponding thiophanium salt, formed in the presence of $TiCl_4$, reacted with **5** to give 4,6-di(isopropoxy)-7-(4-tolylthio)hept-1-ene (**19a,b**) as a 1 : 2 mixture of diastereomers (82%). Hence, only with the use, as final quenchers, of C-nucleophiles containing *gem*-dimethyl groups at the double bond as in **7** and **8** is it possible to observe predominant (9 : 1) formation of one diastereomer. To evaluate the generality of the reaction, the effects of variation of the structure of vinyl ethers, used for the generation of thiophanium intermediates, were also investigated. The results obtained for the reaction with the use of methyl vinyl ether **1** as VE-I and methyl isobutenyl ether (**20**) as VE-II are shown on Scheme 4.

Table 1. The ratio of isomers and yields of the products **6**, **17**, and **18** depending on the reaction conditions

Ar in ArSCl	Lewis acid	Product	Yield (%)	Ratio of diastereomers
4-Tol	$TiCl_4$	**6**	66	1.0 : 1.2
4-Tol	$SnCl_4$	**6**	63	1.0 : 1.6
4-Tol	$ZnBr_2$	**6**	65	1.0 : 1.1
4-Tol	$LiClO_4$	**6**	82	1.0 : 1.4
4-ClC_6H_4	$TiCl_4$	**17**	77	1.0 : 1.5
4-ClC_6H_4	$LiClO_4$	**17**	66	1.2 : 1.0
2,4,6-$Me_3C_6H_2$	$TiCl_4$	**18**	40	1.0 : 1.7

Scheme 4



24a,b—27a,b (60—94%)

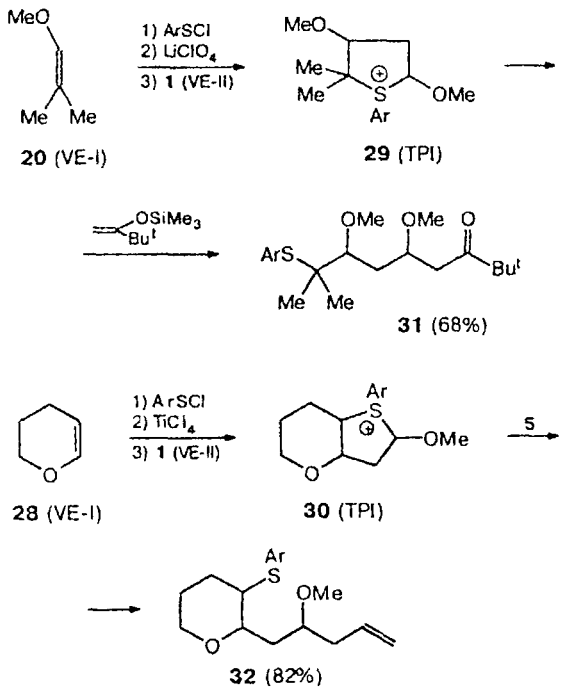
5, 21, 24, 25: X = CH_2; R = H
22, 26: X = O; R = *cyclo*-Pr
23, 27: X = O; R = Ph
Ar = 4-Tol (**21, 24, 26, 27**), 4-ClC_6H_4 (**25**)

It is noteworthy that thiophanium intermediate **21**, generated as chlorotitanate (see above and Ref. 9) and a rather unstable species, appeared to be stable in the $LiClO_4$—$MeNO_2$ system (*i.e.*, as a perchlorate) at room temperature over a few days. In these reactions TMSE derived from methyl cyclopropyl ketone (**22**) and acetophenone (**23**) were used. The expected products of the coupling (**24a,b—27a,b**) were obtained in preparatively acceptable yields (60—94%) as mixtures of diastereomers (ratio from 1 : 1 to 1.0 : 1.5).

Examples of the reactions in which methyl isobutenyl ether **20** or dihydropyran (**28**) were used as the first (VE-I) component are shown in Scheme 5. These two examples provide convincing demonstration of the complementarity of the two suggested alternative solvent—Lewis acid systems, which allowed us to involve fairly different components in the described four-component coupling. Thus, while TPI intermediate **2** (see Scheme 3) is easily generated in both systems (CH_2Cl_2—$TiCl_4$ and $LiClO_4$—$MeNO_2$), it was pos-

sible to prepare the intermediate **29** only in the $LiClO_4$—$MeNO_2$ system and the intermediate **30** only in the CH_2Cl_2—$TiCl_4$ system. Under alternative conditions a fast decomposition of the reaction mixture was observed in the first case, while in the second case ESI, formed from dihydropyran and 4-TolSCl, does not react with the ether **1** even at room temperature. Quenching of TPI **29** and **30** with the TMSE of pinacolone and allylsilane **5** correspondingly results in the products **31** and **32** as mixtures of diastereomers in the ratio 1.0 : 1.3 and 1.0 : 1.5.

Scheme 5



Thus, the above described coupling, which proceeds with the formation of two novel C—C bonds, allows one to assemble polyfunctional molecules from simple precursors with independent changes of all components involved. It is also important to note that the described synthetic scheme represents an unprecedented example of the controlled one-pot sequence of three Ad_E reactions proceeding *via* the formation of two stabilized cationoid intermediates, identified as three- and five-membered *S*-arylsulfonium salts.

The formation of episulfonium ions in the first stage of this sequence, as well as their reactivity toward heteroatomic and carbon nucleophiles, is well-documented in the earlier studies.[1] The structure of the second intermediate, TPI salt, required confirmation. An example of isolation of stable thiophanium salt by interaction of ArSCl with excess styrene was described earlier.[16] This salt turned out to be stable and rather inert toward further reactions with nucleophiles. In particular it was found that the reaction with AcO^- to give the respective δ-acetoxyalkylarylsulfide occurred only upon boiling this salt in mixture of glacial AcOH with AcONa for 5 h. The peculiarities in the structure of our thiophanium intermediate (cyclic mixed thioacetal) obviously predetermined the difficulties with its isolation. In fact, initial attempts to isolate this intermediate as chlorotitanate were not very successful, since the precipitated salt appeared to be unstable after filtration and decomposed quickly with the formation of a tar-like product.[9] However, the above-mentioned observations about the enhanced stability of the intermediate of structure **21** (see Scheme 4) in the $LiClO_4$—$MeNO_2$ system enabled us to isolate it as a perchlorate and characterize it by NMR spectroscopy (see Experimental).

In the proton spectrum the downfield shifts of the doublets of *ortho*- and *meta*-CH groups of the aryl substituent by 0.40 and 0.55 ppm as well as the downfield shift of Me group in Ar substituent by 0.15 ppm (as compared to those for uncharged *S*-aryl derivatives) were observed.

Data of the ^{13}C NMR spectrum turned to be more informative. The chemical shifts of C atoms of the aryl substituent in TPI significantly differ from the chemical shifts of the corresponding atoms in the reaction products (containing the uncharged S atom), for example, in **24a**:

Compound	δ			
	C(Me) arom.	C(S) arom.	CHS	CH_2S
TPI **21**	145.84	120.65	125.03	46.89
24a	137.08	133.46	85.81	37.31

Thus, the signal of quaternary C(S) atom in aryl substituent is shifted upfield by 13 ppm, while the signal of quaternary C(Me) atom is shifted downfield by 9 ppm. Slight downfield shifts are also observed for the signals of *ortho*- and *meta*-CH groups of the aryl substituent (see Experimental). As was shown in our earlier works,[17] which dealt specifically with the study and comparison of the ^{13}C NMR spectra of the aryl-substituted sulfonium salts of various structure and the corresponding compounds with uncharged S atom, the observed changes are typical and most likely are due to the influence of the cationic center which causes an electronic density decrease at the *para*-, *meta*- and *ortho*-C atoms of the aryl substituent (thus deshielding them) and an increase at the C atom bound to positive charged sulfur atom (thus shielding it). This is confirmed also by the data given in Ref. 16. It should also be noted that significant downfield shifts were observed for the signals of the CH_2S group (by about 10 ppm) and of the CHS group (by 40 ppm). Though the ^{13}C NMR spectra cannot be directly used for the evaluation of charge distribution at carbon atoms of the cycle, the observed difference in downfield shifts of the CH_2S and CHS signals justifies the suggestion that the positive charge is

largely located at the C atom of the CHS group, thus making it a preferred site for nucleophile attack and controlling the regiochemistry of opening of the thiophanium ring.

It was also shown that the isolated thiophanium perchlorate **21** reacts with allyltrimethylsilane **5** in a solution of $MeNO_2$ with the formation of the expected products **6a,b** in the ratio 1.0 : 1.4.

As a further development of this work we plan to continue the search for pathways to ensure the diastereoselective course of the described reaction due to either variation in the nature of the components used or modifications in coupling conditions.

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker WP-200-SY (200 MHz for ^1H and 50.3 MHz for ^{13}C), Bruker WM-250 (250 MHz for ^1H and 62.9 MHz for ^{13}C), Varian Nova 300 (300 MHz for ^1H and 75.4 MHz for ^{13}C) spectrometers. Assignments of the signals in the ^{13}C NMR spectra for the majority of the products were confirmed by application of the DEPT technique (with proton noise suppression and with an opposite phase for the signals of C atoms containing an even or odd number of protons). Mass spectra (EI, 70 eV) were recorded on Varian MAT CH-6 instrument with direct input of the sample into the ion source. Gas chromatography mass-spectrometric analyses were made on a Hewlett—Packard 5790 GS instrument with chromatographic input of the sample into the ion source (EI, 70 eV); the column was a 30 m × 0.25 mm ID J&W Scientific, Inc. DB5 coated capillary. High-resolution mass-spectra (HRMS) were performed by the Mass-Spectrometry Service Laboratory of the Chemistry Department, University of Minnesota on Finnigan MAT 95 instrument (EI, 70 eV). Elemental analyses were performed by the microanalysis laboratory of the N. D. Zelinsky Institute of Organic Chemistry of the RAS (Moscow) and Atlantic Microlab, Inc. (Norcross, Georgia).

All reactions were carried out under dry argon or nitrogen atmosphere in electrical oven-predried or flame-predried chemical glassware with use of the dried and freshly distilled solvents. Analytical TLC was performed on Merck precoated 0.2 mm aluminum plates of silica gel 60 F_{254}. Preparative isolation of the products was carried out by column chromatography with 200×20 mm Armsorb SI-10 (40—100 μm) silica gel layer.

4-Toluenesulfenyl chloride, 4-chlorobenzenesulfenyl chloride, and 2,4,6-trimethylbenzenesulfenyl chloride were obtained *via* chlorination of the corresponding disulfides or thiophenols with SO_2Cl_2 in CCl_4 at −10 °C.[18] Methyl vinyl ether **1** and isobutenyl vinyl ether were synthesized from butyl vinyl ether and MeOH or Pr^iOH, respectively, in the presence of $Hg(OAc)_2$.[19] 1-Methoxy-2-methylprop-1-ene **20** was obtained by pyrolysis of the dimethyl acetal of isobutyl aldehyde in the presence of TsOH.[20] Trimethylsilyl enol ethers were synthesized *via* treatment of the corresponding ketones and aldehydes with Me_3SiCl in the presence of NaI.[21,22]

4,6-Dimethoxy-7-(4-tolylthio)hept-1-enes (6a,b). *A. In the $TiCl_4$—CH_2Cl_2 system.* To a stirred solution of 4-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (20 ml) at −78 °C were added sequentially a solution of vinyl ether **1** (0.058 g, 1 mmol) in CH_2Cl_2 (1 mL), a solution of $TiCl_4$ (0.19 g, 1 mmol) in CH_2Cl_2 (1 mL) and once more a solution of the ether **1** (0.058 g, 1 mmol) in CH_2Cl_2 (1 mL). After 30 min $Me_3SiCH_2CH{=}CH_2$ (5, 0.229 g, 2 mmol) was added, and the temperature was allowed to rise to 0 °C. After stirring for 5 h under this temperature the reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (20 mL) and extracted with diethyl ether (2×20 mL). After separation by column chromatography on SiO_2 (hexane—AcOEt, 5 : 1) products **6a** (0.084 g, 30% yield) and **6b** (0.101 g, 36%) were obtained.

B. In the $LiClO_4$—$MeNO_2$ system. To a stirred solution of 4-TolSCl (0.159 g, 1 mmol) in $MeNO_2$ (20 mL) at −20 °C were added sequentially a solution of vinyl ether **1** (0.116 g, 2 mmol) in $MeNO_2$ (2 mL) and anhydrous $LiClO_4$ (0.426 g, 4 mmol). After 15 min $Me_3SiCH_2CH{=}CH_2$ (5, 0.229 g, 2 mmol) was added, the temperature was allowed to rise to ambient, and the reaction mixture was stirred for 24 h under this temperature. The usual workup and preparative isolation gave a mixture of products **6a,b** in the ratio 1.0 : 1.4 (82% yield).

Diastereomer 6a. R_f 0.40 (hexane—AcOEt, 5 : 1), oil. Found (%): C, 68.63; H, 8.69; S, 11.30. $C_{16}H_{24}O_2S$. Calculated (%): C, 68.53; H, 8.63; S, 11.43. ^1H NMR ($CDCl_3$), δ: 1.66 (m, 2 H, $CHC\underline{H}_2CH$); 2.25 (m, 2 H, $C\underline{H}_2CH{=}$); 2.28 (s, 3 H, $\underline{Me}Ph$); 2.99 (dd, 1 H, CH_AS, J_1 = 8.6 Hz, J_2 = 13.2 Hz), 3.02 (dd, 1 H, CH_BS, J_1 = 7.5 Hz, J_2 = 13.2 Hz); 3.32 and 3.34 (both s, 6 H, MeO); 3.38 (m, 1 H, $C\underline{H}OMe$); 3.54 (m, 1 H, $C\underline{H}OMe$); 5.04 (m, 2 H, $CH_2{=}$); 5.77 (m, 1 H, CH=); 7.06 and 7.27 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.81 ($\underline{Me}Ph$); 37.77, 38.65, and 39.07 (3 CH_2); 56.37 and 57.21 (2 MeO); 76.70 and 76.76 (2 $\underline{C}HOMe$); 117.10 ($CH_2{=}$); 129.47 (2 CH arom.); 129.98 (2 CH arom.); 132.95 and 135.86 (2 C arom.); 134.18 (CH=). HRMS: found, m/z 280.1500; calculated for $C_{16}H_{24}O_2S$ [M^+], m/z 280.1497.

Diastereomer 6b. R_f 0.33 (hexane—AcOEt, 5 : 1), oil. Found (%): C, 68.43; H, 8.64; S, 11.51. $C_{16}H_{24}O_2S$. Calculated (%): C, 68.53; H, 8.63; S, 11.43. ^1H NMR ($CDCl_3$), δ: 1.80 (m, 2 H, $CHC\underline{H}_2CH$); 2.25 (m, 2 H, $C\underline{H}_2CH{=}$); 2.29 (s, 3 H, $\underline{Me}Ph$); 3.01 (dd, 1 H, CH_AS, J_1 = 4.1 Hz, J_2 = 13.4 Hz); 3.04 (dd, 1 H, CH_BS, J_1 = 3.6 Hz, J_2 = 13.4 Hz); 3.29 and 3.31 (both s, 6 H, MeO); 3.32 (m, 1 H, $C\underline{H}OMe$); 3.43 (m, 1 H, $C\underline{H}OMe$); 5.05 (m, 2 H, $CH_2{=}$); 5.78 (m, 1 H, CH=); 7.07 and 7.27 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.95 ($\underline{Me}Ph$); 37.01, 37.71, and 38.57 (3 CH_2); 56.30 and 56.86 (2 MeO); 77.27 and 77.64 (2 $\underline{C}HOMe$); 117.15 ($CH_2{=}$); 129.60 (2 CH arom.); 130.16 (2 CH arom.); 132.98 and 136.13 (2 C arom.); 134.40 (CH=). HRMS: found, m/z 280.1498, calculated for $C_{16}H_{24}O_2S$ [M^+], m/z 280.1497.

The compounds **9a,b, 10a,b, 12a,b, 15a,b, 16a—d, 17a,b, 18a,b, 19a,b, 24a,b, 25a,b, 26a,b, 27a,b, 31a,b,** and **32a,b** were synthesized similarly (all isolated products are colorless or pale-yellow oils).

Methyl 3,5-dimethoxy-2,2-dimethyl-6-(4-tolylthio)hexanates (9a,b). Diastereomer 9a. R_f 0.43 (hexane—AcOEt, 15 : 1), 0.235 g (69%). Found (%): C, 63.37; H, 8.43; S, 9.32. $C_{18}H_{28}O_4S$. Calculated (%): C, 63.50; H, 8.29; S, 9.42. ^1H NMR ($CDCl_3$), δ: 1.09 and 1.19 (both s, 6 H, Me); 1.72 (t, 2 H, CH_2, J = 5.8 Hz), 2.32 (s, 3 H, $\underline{Me}Ph$); 3.04 (dd, 1 H, CH_AS, J_1 = 3.5 Hz, J_2 = 13.4 Hz); 3.07 (dd, 1 H, CH_BS, J_1 = 3.0 Hz, J_2 = 13.4 Hz); 3.31 and 3.36 (both s, 6 H, MeO); 3.43 (m, 2 H, $2C\underline{H}OMe$); 3.66 (s, 3 H, MeOC=O); 7.10 and 7.31 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.62, 20.76, and 20.95 (3 Me); 35.46 (CH_2); 38.65 (CH_2S); 47.78 ($\underline{Me}OC{=}O$); 51.71 (C); 56.92 and 59.70 (2 MeO); 78.39 and 83.22 (2 $\underline{C}HOMe$); 129.65 (2 CH arom.); 130.43 (2 CH arom.); 132.68 and 136.33 (2 C arom.); 177.16 (C=O). MS,

m/z (I_{rel} (%)): 340 [M^+] (6), 276 (5), 239 (4), 181 (8), 171 (100), 149 (52), 145 (26), 139 (27), 123 (13), 107 (15). HRMS: found, *m/z* 340.1709; calculated for $C_{18}H_{28}O_4S$ [M^+], *m/z* 340.1708.

Diastereomer 9b. R_f 0.37 (hexane—AcOEt, 15 : 1), 0.027 g (8%). ^1H ($CDCl_3$), δ: 1.10 and 1.16 (both s, 6 H, Me); 1.62 (m, 2 H, CH_2); 2.32 (s, 3 H, MePh); 2.94 (dd, 1 H, CH_AS, J_1 = 6.8 Hz, J_2 = 13.1 Hz); 3.13 (dd, 1 H, CH_BS, J_1 = 4.2 Hz, J_2 = 13.1 Hz); 3.35 and 3.39 (both s, 6 H, MeO); 3.55 (m, 2 H, 2 CHOMe); 3.68 (s, 3 H, MeOC=O); 7.09 and 7.30 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.47, 20.91, and 21.35 (3 Me); 35.92 (CH_2); 38.28 (CH_2S); 47.28 (MeOC=O); 51.63 (C); 56.25 and 60.79 (2 MeO); 76.70 and 82.67 (2 CHOMe); 129.60 (2 CH arom.); 130.45 (2 CH arom.); 132.66 and 136.30 (2 C arom.); 177.21 (C=O). MS, *m/z* (I_{rel} (%)): 340 [M^+] (7), 276 (4), 239 (5), 207 (6), 171 (100), 149 (80), 145 (37), 139 (38), 123 (30), 108 (25). HRMS: found, *m/z* 340.1711; calculated for $C_{18}H_{28}O_4S$ [M^+], *m/z* 340.1708.

3,5-Dimethoxy-2,2-dimethyl-6-(4-tolylthio)hexanals (10a,b). Diastereomer 10a. R_f 0.33 (hexane—AcOEt, 20 : 1), 0.020 g (6%). ^1H NMR ($CDCl_3$), δ: 0.99 and 1.07 (both s, 6 H, Me); 1.75 (m, 2 H, CH_2); 2.31 (s, 3 H, MePh); 2.96 (dd, 1 H, CH_AS, J_1 = 6.2 Hz, J_2 = 13.4 Hz); 3.12 (dd, 1 H, CH_BS, J_1 = 5.0 Hz, J_2 = 13.4 Hz); 3.18—3.28 (m, 1 H, CHOMe); 3.29 and 3.33 (both s, 6 H, MeO); 3.41 (m, 1 H, CHOMe); 7.10 and 7.30 (both d, 4 H arom., J = 8.0 Hz); 9.55 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$), δ: 17.38 and 19.05 (2 Me); 20.95 (MePh); 34.84 (CH_2); 38.41 (CH_2S); 51.10 (C); 56.86 and 59.21 (2 MeO); 78.10 and 82.33 (2 CHOMe); 129.76 (2 CH arom.); 130.49 (2 CH arom.); 132.52 and 136.54 (2 C arom.); 205.74 (C=O). MS, *m/z* (I_{rel} (%)): 310 [M^+] (20), 218 (4), 181 (8), 173 (17), 149 (50), 141 (55), 123 (25), 115 (45), 102 (19), 87 (100).

Diastereomer 10b. R_f 0.27 (hexane—AcOEt, 20 : 1), 0.170 g (55%). ^1H NMR ($CDCl_3$), δ: 1.00 and 1.05 (both s, 6 H, Me); 1.65 (m, 2 H, CH_2); 2.31 (s, 3 H, MePh); 2.93 (dd, 1 H, CH_AS, J_1 = 7.2 Hz, J_2 = 13.2 Hz), 3.14 (dd, 1 H, CH_BS, J_1 = 3.8 Hz, J_2 = 13.2 Hz); 3.30—3.42 (m, 1 H, CHOMe); 3.34 and 3.38 (both s, 6 H, MeO); 3.54 (m, 1 H, CHOMe); 7.10 and 7.30 (both d, 4 H arom., J = 8.0 Hz); 9.59 (s, 1 H, CHO). ^{13}C NMR ($CDCl_3$), δ: 17.25 and 19.01 (2 Me); 20.87 (MePh); 35.86 (CH_2); 38.12 (CH_2S); 50.84 (C); 56.40 and 60.77 (2 MeO); 76.60 and 81.68 (2 CHOMe); 129.65 (2 CH arom.); 130.53 (2 CH arom.); 132.54 and 136.45 (2 C arom.); 205.77 (C=O). MS, *m/z* (I_{rel} (%)): 310 [M^+] (30), 281 (10), 221 (11), 207 (12), 173 (22), 149 (72), 141 (70), 123 (29), 115 (50), 87 (100). HRMS: found, *m/z* 310.1601; calculated for $C_{17}H_{26}O_3S$ [M^+], *m/z* 310.1603.

4,6-Dimethoxy-7-(4-tolylthio)heptan-2-ones (12a,b). Diastereomer 12a. R_f 0.38 (hexane—AcOEt, 8 : 1), 0.151 g (51%). Found (%): C, 64.90; H, 8.32; S, 10.72. $C_{16}H_{24}O_3S$. Calculated (%): C, 64.83; H, 8.16; S, 10.82. ^1H NMR ($CDCl_3$), δ: 1.60 and 1.83 (both m, 2 H, CH_2); 2.15 (s, 3 H, MeC=O); 2.31 (s, 3 H, MePh); 2.51 (dd, 1 H, CH_AC=O, J_1 = 5.3 Hz, J_2 = 16.3 Hz); 2.68 (dd, 1 H, CH_BC=O, J_1 = 7.2 Hz, J_2 = 16.3 Hz); 2.94 (dd, 1 H, CH_AS, J_1 = 6.6 Hz, J_2 = 13.3 Hz); 3.11 (dd, 1 H, CH_BS, J_1 = 4.9 Hz, J_2 = 13.3 Hz); 3.28 and 3.30 (both s, 6 H, MeO); 3.38 (m, 1 H, CHOMe); 3.81 (dd, 1 H, CHOMe, J_1 = 5.3 Hz, J_2 = 7.2 Hz); 7.09 and 7.28 (both d, 4 H arom., J = 8.0 Hz). MS, *m/z* (I_{rel} (%)): 296 [M^+] (16), 281 (15), 232 (40), 219 (13), 207 (38), 189 (18), 159 (90), 149 (100), 137 (62), 123 (18). HRMS (for the mixture): found, *m/z* 296.1447; calculated for $C_{16}H_{24}O_3S$ [M^+], *m/z* 296.1446.

Diastereomer 12b. R_f 0.34 (hexane—AcOEt, 8 : 1), 0.077 g (26%). Found (%): C, 64.90; H, 8.32; S, 10.72. $C_{16}H_{24}O_3S$. Calculated (%): C, 64.83; H, 8.16; S, 10.82. ^1H NMR ($CDCl_3$), δ: 1.60 and 1.83 (both m, 2 H, CH_2); 2.16 (s, 3 H, MeC=O); 2.31 (s, 3 H, MePh); 2.50 (dd, 1 H, CH_AC=O, J_1 = 5.3 Hz, J_2 = 16.1 Hz); 2.69 (dd, 1 H, CH_BC=O, J_1 = 6.6 Hz, J_2 = 16.1 Hz); 2.91 (dd, 1 H, CH_AS, J_1 = 7.0 Hz, J_2 = 13.2 Hz); 3.10 (dd, 1 H, CH_BS, J_1 = 4.7 Hz, J_2 = 13.2 Hz); 3.31 and 3.32 (both s, 6 H, MeO); 3.49 (m, 1 H, CHOMe); 3.85 (m, 1 H, CHOMe); 7.09 and 7.28 (both d, 4 H arom., J = 8.0 Hz). MS, *m/z* (I_{rel} (%)): 296 [M^+] (15), 281 (9), 264 (2), 232 (11), 207 (5), 159 (10), 149 (12), 127 (100), 123 (10), 101 (38). HRMS (for the mixture): found, *m/z* 296.1447; calculated for $C_{16}H_{24}O_3S$ [M^+], *m/z* 296.1446.

***E*-5,7-Dimethoxy-8-(4-tolylthio)oct-2-enals (15a,b).** R_f 0.33 (hexane—AcOEt, 20 : 1), 0.125 g (40%, the mixture of isomers, 1 : 1). Found (%): C, 66.27; H, 7.79; S, 9.90. $C_{17}H_{24}O_3S$. Calculated (%): C, 66.20; H, 7.84; S, 10.40. ^1H NMR ($CDCl_3$), δ: 1.49—1.64 and 1.72—1.89 (both m, 4 H, 2 CH_2); 2.31 (s, 6 H, 2 MePh); 2.37—2.69 (m, 4 H, 2 CH_2CH=); 2.94 (dd, 2 H, 2 CH_AS, J_1 = 6.8 Hz, J_2 = 13 Hz); [3.09]* (dd, 1 H, CH_BS, J_1 = 6.8 Hz, J_2 = 13.4 Hz); {3.13}* (dd, 1 H, CH_BS, J_1 = 4.8 Hz, J_2 = 13.4 Hz); 3.31, 3.32, and 3.35 (all s, 12 H, 4 MeO); 3.33—3.62 (m, 4 H, 4 CHOMe); 6.14 (ddt, 2 H, 2 CHCHO, J_1 = 1.2 Hz, J_2 = 8.0 Hz, J_3 = 16.0 Hz), [6.83] and {6.85} (both dt, 2 H, 2 CH=, [J_1] = {J_1} = 7.0 Hz, [J_2] = {J_2} = 16.0 Hz); 7.10 and 7.28 (both d, 8 H arom., J = 8.0 Hz), 9.50 (d, 2 H, 2 CH=O, [J] = {J} = 8.0 Hz). MS, *m/z*: 308 [M^+].

5,7-Dimethoxy-8-(4-tolylthio)oct-2-en-4-olides (16a—d). Diastereomers 16a,b. R_f 0.37 (hexane—AcOEt, 10 : 1), 0.119 g (37%, the mixture of isomers, 1 : 1). ^1H NMR ($CDCl_3$), δ: [1.66—1.80] (m, 2 H, CH_2); {1.87—2.01} (m, 2 H, CH_2); 2.32 (s, 6 H, 2MePh); [2.94] (dd, 1 H, CH_AS, J_1 = 7.0 Hz, J_2 = 13.5 Hz); {2.95} (dd, 1 H, CH_AS, J_1 = 6.7 Hz, J_2 = 13.4 Hz); [3.11] (dd, 1 H, CH_BS, J_1 = 4.6 Hz, J_2 = 13.5 Hz); {3.16} (dd, 1 H, CH_BS, J_1 = 4.8 Hz, J_2 = 13.4 Hz); 3.30, 3.33, 3.34, and 3.41 (all s, 12 H, 4 MeO); 3.50 (m, 4 H, 4 CHOMe); [5.03] (ddd, 1 H, CHO, J_1 = 1.6 Hz, J_2 = 2.0 Hz, J_3 = 5.0 Hz); {5.11} (ddd, 1 H, CHO, J_1 = 1.6 Hz, J_2 = 2.0 Hz, J_3 = 5.8 Hz); [6.15] (dd, 1 H, CH=, J_1 = 2.0 Hz, J_2 = 5.6 Hz); {6.18} (dd, 1 H, CH=, J_1 = 2.0 Hz, J_2 = 5.8 Hz); 7.11 and 7.29 (both d, 8 H arom., J = 8.0 Hz); [7.49] (dd, 1 H, CHC=O, J_1 = 1.6 Hz, J_2 = 5.8 Hz); {7.50} (dd, 1 H, CHC=O, J_1 = 1.6 Hz, J_2 = 5.6 Hz). HRMS: found, *m/z* 322.1239; calculated for $C_{17}H_{22}O_4S$ [M^+], *m/z* 322.1239.

Diastereomers 16c,d. R_f 0.30 (hexane—AcOEt, 10 : 1), 0.116 g (36%, the mixture of isomers, 1 : 1). ^1H NMR ($CDCl_3$), δ: 1.50—1.92 (m, 4 H, 2 CH_2); 2.32 (s, 6 H, 2 MePh); 2.94 (dd, 2 H, 2 CH_AS, J_1 = 7.0 Hz, J_2 = 13.3 Hz); [3.11] (dd, 1 H, CH_BS, J_1 = 8.6 Hz, J_2 = 13.3 Hz); {3.12} (d, 1 H, CH_BS, J = 13.3 Hz); 3.33, 3.34, 3.41, and 3.45 (all s, 12 H, 4 MeO); 3.35—3.80 (m, 4 H, 4 CHOMe); [4.91] (dd, 1 H, CHO, J_1 = 1.8 Hz, J_2 = 2.2 Hz); {5.06} (dt, 1 H, CHO, J_1 = 2.0 Hz, J_2 = 3.4 Hz); 6.17 (m, 2 H, 2CH=); 7.10 and 7.29 (both d, 8 H arom., J = 8.0 Hz); [7.44] and {7.45} (both dd, 1 H, CHC=O, J_1 = J'_1 = 1.8 Hz, J_2 = J'_2 = 6.0 Hz); {7.58} (dt, 1 H, CHC=O, J_1 = 2.0 Hz, J_2 = 6.0 Hz). HRMS: found, *m/z* 322.1239; calculated for $C_{17}H_{22}O_4S$ [M^+], *m/z* 322.1239.

4,6-Dimethoxy-7-(4-chlorophenylthio)hept-1-enes (17a,b). Diastereomer 17a. R_f 0.38 (hexane—AcOEt, 10 : 1), 0.093 g

* Here and further in the spectra of mixtures of diastereomers the chemical shifts and values of J for different isomers are given in brackets and braces, respectively.

(31%). Found (%): C, 60.16; H, 7.15; S, 10.44. $C_{15}H_{21}ClO_2S$. Calculated (%): C, 59.88; H, 7.04; S, 10.66. ^{1}H NMR ($CDCl_3$), δ: 1.66 (m, 2 H, $CHCH_2CH$); 2.28 (m, 2 H, CH_2CH=); 3.02 (dd, 1 H, CH_AS, J_1 = 2.4 Hz, J_2 = 13.2 Hz); 3.05 (dd, 1 H, CH_BS, J_1 = 1.7 Hz, J_2 = 13.2 Hz); 3.34 and 3.36 (both s, 6 H, MeO); 3.42 (m, 1 H, CHOMe); 3.56 (m, 1 H, CHOMe); 5.07 (m, 2 H, CH_2=); 5.77 (m, 1 H, CH=); 7.23 and 7.29 (both d, 4 H arom., J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 37.82, 38.51, and 39.27 (3 CH_2); 56.59 and 57.42 (2 MeO); 76.87 (2 CHOMe); 117.36 (CH_2=); 128.93 (2 CH arom.); 130.70 (2 CH arom.); 131.95 and 135.45 (2 C arom.); 134.19 (CH=). MS, m/z (I_{rel} (%)): 300 [M^+] (7), 259 (3), 236 (8), 227 (10), 201 (22), 169 (60), 143 (20), 111 (12), 108 (16), 85 (100). HRMS (for the mixture): found, m/z 300.0962; calculated for $C_{15}H_{21}ClO_2S$ [M^+], m/z 300.0950.

Diaastereomer 17b. R_f 0.33 (hexane—AcOEt, 10 : 1), 0.138 g (46%). Found (%): C, 60.16; H, 7.15; S, 10.44. $C_{15}H_{21}ClO_2S$. Calculated (%): C, 59.88; H, 7.04; S, 10.66. ^{1}H NMR ($CDCl_3$), δ: 1.79 (m, 2 H, $CHCH_2CH$); 2.28 (m, 2 H, CH_2CH=); 3.06 (d, 2 H, CH_2S, J = 5.7 Hz); 3.31 and 3.32 (both s, 6 H, MeO); 3.34 (m, 1 H, CHOMe); 3.49 (quint, 1 H, CHOMe, J = 5.7 Hz); 5.06 (m, 2 H, CH_2=); 5.78 (m, 1 H, CH=); 7.24 and 7.29 (both d, 4 H arom., J = 9.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.86, 37.61, and 38.20 (3 CH_2); 56.21 and 56.86 (2 MeO); 77.06 and 77.14 (2 CHOMe); 117.33 (CH_2=); 128.95 (2 CH arom.); 130.63 (2 CH arom.); 131.96 and 135.44 (2 C arom.); 134.21 (CH=). HRMS (for the mixture): found, m/z 300.0962; calculated for $C_{15}H_{21}ClO_2S$ [M^+], m/z 300.0950.

4,6-Dimethoxy-7-(2,4,6-trimethylphenylthio)hept-1-enes (18a,b). Diastereomer 18a. R_f 0.4 (hexane—AcOEt, 8 : 1), 0.046 g (15%). ^{1}H NMR ($CDCl_3$), δ: 1.66 (m, 2 H, $CHCH_2CH$); 2.24 (s, 3 H, 4-MePh); 2.26 (m, 2 H, CH_2CH=); 2.50 (s, 6 H, 2,6-Me_2Ph); 2.74 (d, 2 H, CH_2S, J = 6.4 Hz); 3.29 and 3.33 (both s, 6 H, MeO); 3.35—3.55 (m, 2 H, 2 CHOMe); 5.05 (m, 2 H, CH_2=); 5.77 (m, 1 H, CH=); 6.90 (s, 2 H arom.). MS, m/z: 308 [M^+].

Diastereomer 18b. R_f 0.3 (hexane—AcOEt, 8 : 1), 0.077 g (25%). ^{1}H NMR ($CDCl_3$), δ: 1.76 (m, 2 H, $CHCH_2CH$); 2.24 (s, 3 H, 4-MePh); 2.28 (m, 2 H, CH_2CH=); 2.50 (s, 6 H, 2,6-Me_2Ph); 2.77 (d, 2 H, CH_2S, J = 6.0 Hz); 3.26 and 3.27 (both s, 6 H, MeO); 3.25—3.45 (m, 2 H, 2 CHOMe); 5.05 (m, 2 H, CH_2=); 5.78 (m, 1 H, CH=); 6.90 (s, 2 H arom.). MS, m/z: 308 [M^+].

4,6-Diisopropoxy-7-(4-tolylthio)hept-1-enes (19a,b). R_f 0.37 (hexane—AcOEt, 10 : 1), 0.276 g (82%, the mixture of isomers, 1 : 2). Found (%): C, 71.34; H, 9.48; S, 9.69. $C_{20}H_{32}O_2S$. Calculated (%): C, 71.38; H, 9.58; S, 9.53. ^{1}H NMR ($CDCl_3$), δ: 1.06—1.15 (m, 24 H, 8 Me); 1.61—1.82 (m, 4 H, 2 CH_2); 2.19—2.30 (m, 4 H, 2 CH_2CH=); 2.31 (s, 6 H, 2 MePh); [2.97] (dd, 1 H, CH_AS, J_1 = 6.4 Hz, J_2 = 13.0 Hz); {2.98} (dd, 1 H, CH_AS, J_1 = 5.8 Hz, J_2 = 13.1 Hz); [3.03] (dd, 1 H, CH_BS, J_1 = 4.6 Hz, J_2 = 13.0 Hz); {3.04} (dd, 1 H, CH_BS, J_1 = 5.8 Hz, J_2 = 13.1 Hz); 3.45, 3.58, and 3.66 (quint and 2m, 8 H, 8 CHO); 5.02 (m, 4 H, 2 CH_2=); 5.80 (ddt, 2 H, 2 CH=, J_1 = 7.2 Hz, J_2 = 10.5 Hz, J_3 = 16.8 Hz); 7.07, [7.28], and {7.29} (all d, 8 H arom., J = 7.3 Hz). ^{13}C NMR ($CDCl_3$), δ: (**19a**) 20.99 (MePh); 22.41, 22.46, 23.37, and 23.51 (4 Me); 39.36, 40.03, and 40.56 (3 CH_2); 69.05 and 69.79 (2 $CHMe_2$); 72.87 and 72.92 (2 $CHCH_2$); 117.00 (CH_2=); 129.56 (2 CH arom.); 130.47 (2 CH arom.); 133.18 and 136.08 (2 C arom.); 134.74 (CH=); (**19b**) 20.99 (MePh); 22.59, 22.62, 22.89, and 22.95 (4 Me); 39.28 and 39.83 (3 CH_2); 69.38 and 70.04 (2 $CHMe_2$); 73.00 and 73.30 (2 $CHCH_2$); 116.91 (CH_2=); 129.62 (2 CH arom.); 130.09 (2 CH arom.); 133.23 and 136.02 (2 C arom.); 134.99 (CH=). HRMS: found, m/z 336.2121; calculated for $C_{20}H_{32}O_2S$ [M^+], m/z 336.2123.

4,6-Dimethoxy-5,5-dimethyl-7-(4-tolylthio)hept-1-enes (24,b). Diastereomer 24a. R_f 0.32 (hexane—AcOEt, 30 : 1), 0.173 g (56%). ^{1}H NMR ($CDCl_3$), δ: 0.83 and 0.94 (both s, 6 H, Me); 2.03—2.38 (m, 2 H, CH_2CH=); 2.30 (s, 3 H, MePh); 2.89 (dd, 1 H, CH_AS, J_1 = 9.1 Hz, J_2 = 13.7 Hz); 3.07 (dd, 1 H, CHOMe, J_1 = 3.4 Hz, J_2 = 7.8 Hz); 3.21 (dd, 1 H, CH_BS, J_1 = 3.6 Hz, J_2 = 13.7 Hz); 3.32 and 3.50 (both s, 6 H, MeO); 3.36 (m, 1 H, CHOMe); 5.05 (m, 2 H, CH_2=); 5.90 (ddt, 1 H, CH=, J_1 = 7.0 Hz, J_2 = 10.2 Hz, J_3 = 17.0 Hz); 7.09 and 7.29 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.71 and 19.85 (2 Me); 20.95 (MePh); 35.44 (CH_2); 37.31 (CH_2S); 44.17 (C); 59.76 and 61.15 (2 MeO); 85.49 and 85.81 (2 CHOMe); 116.00 (CH_2=); 129.58 (2 CH arom.); 130.02 (2 CH arom.); 133.46 and 137.08 (2 C arom.); 135.97 (CH=). MS, m/z (I_{rel} (%)): 308 [M^+] (6), 267 (3), 244 (1), 212 (2), 191 (4), 181 (24), 149 (70), 137 (8), 123 (20), 85 (100). HRMS: found, m/z 308.1812; calculated for $C_{18}H_{28}O_2S$ [M^+], m/z 308.1810.

Diastereomer 24b. R_f 0.28 (hexane—AcOEt, 30 : 1), 0.117 g (38%). ^{1}H NMR ($CDCl_3$), δ: 0.84 and 0.85 (both s, 6 H, Me); 2.08—2.35 (m, 2 H, CH_2CH=); 2.30 (s, 3 H, MePh); 2.91 (dd, 1 H, CH_AS, J_1 = 7.7 Hz, J_2 = 13.4 Hz); 3.11 (dd, 1 H, CH_BS, J_1 = 3.1 Hz, J_2 = 13.4 Hz); 3.17 (dd, 1 H, CHOMe, J_1 = 3.9 Hz, J_2 = 7.8 Hz); 3.35 (dd, 1 H, CHOMe, J_1 = 3.1 Hz, J_2 = 7.7 Hz); 3.36 and 3.48 (both s, 6 H, MeO); 5.05 (m, 2 H, CH_2=); 5.90 (ddt, 1 H, CH=, J_1 = 7.0 Hz, J_2 = 10.2 Hz, J_3 = 17.0 Hz); 7.08 and 7.28 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 18.67 and 18.80 (2 Me); 20.89 (MePh); 35.14 (CH_2); 36.93 (CH_2S); 43.84 (C); 59.41 and 60.37 (2 MeO); 84.31 and 84.88 (2 CHOMe); 116.02 (CH_2=); 129.80 (2 CH arom.); 130.19 (2 CH arom.); 133.50 and 137.27 (2 C arom.); 136.10 (CH=). MS, m/z (I_{rel} (%)): 308 [M^+] (2), 276 (5), 267 (4), 244 (1), 212 (3), 191 (8), 181 (36), 149 (100), 137 (12), 123 (40).

4,6-Dimethoxy-5,5-dimethyl-7-(4-chlorophenylthio)hept-1-enes (25a,b). Diastereomer 25a. R_f 0.30 (hexane—AcOEt, 30 : 1), 0.168 g (51%). Found (%): C, 62.13; H, 7.70; S, 9.65. $C_{17}H_{25}ClO_2S$. Calculated (%): C, 62.08; H, 7.66; S, 9.75. ^{1}H NMR ($CDCl_3$), δ: 0.85 and 0.95 (both s, 6 H, Me); 2.05—2.41 (m, 2 H, CH_2CH=); 2.92 (dd, 1 H, CH_AS, J_1 = 9.3 Hz, J_2 = 13.8 Hz); 3.07 (dd, 1 H, CHOMe, J_1 = 3.4 Hz, J_2 = 8.2 Hz); 3.24 (dd, 1 H, CH_BS, J_1 = 2.3 Hz, J_2 = 13.8 Hz); 3.34 and 3.49 (both s, 6 H, MeO); 3.38 (m, 1 H, CHOMe); 5.05 (m, 2 H, CH_2=); 5.91 (m, 1 H, CH=); 7.24 and 7.31 (both d, 4 H arom., J = 9.0 Hz). MS, m/z (I_{rel} (%)): 328 [M^+] (3), 287 (2), 232 (1), 212 (5), 201 (45), 169 (70), 157 (8), 143 (18), 108 (10), 85 (100).

Diastereomer 25b. R_f 0.27 (hexane—AcOEt, 30 : 1), 0.131 g (40%). Found (%): C, 62.13; H, 7.70; S, 9.65. $C_{17}H_{25}ClO_2S$. Calculated (%): C, 62.08; H, 7.66; S, 9.75. ^{1}H NMR ($CDCl_3$), δ: 0.84 (s, 6 H, 2 Me); 2.05—2.43 (m, 2 H, CH_2CH=); 2.95 (dd, 1 H, CH_AS, J_1 = 8.1 Hz, J_2 = 13.4 Hz); 3.14 (dd, 1 H, CH_BS, J_1 = 3.0 Hz, J_2 = 13.4 Hz); 3.21 (m, 1 H, CHOMe); 3.36 (m, 1 H, CHOMe); 3.38 and 3.48 (both s, 6 H, MeO); 5.05 (m, 2 H, CH_2=); 5.91 (m, 1 H, CH=); 7.24 and 7.30 (both d, 4 H arom., J = 9.0 Hz). MS, m/z (I_{rel} (%)): 328 [M^+] (1), 296 (4), 287 (3), 264 (2), 201 (77), 169 (95), 157 (10), 143 (30), 121 (17), 85 (100).

2,4-Dimethoxy-3,3-dimethyl-5-(4-tolylthio)pentyl cyclopropyl ketones (26a,b). Diastereomer 26a. R_f 0.38 (hexane—AcOEt, 10 : 1), 0.163 g (47%). Found (%): C, 68.53; H, 8.75; S, 9.04. $C_{20}H_{30}O_3S$. Calculated (%): C, 68.53; H, 8.63; S, 9.15. ^{1}H NMR ($CDCl_3$), δ: 0.83 and 0.94 (both s, 6 H, Me); 0.85—0.96 and 1.01—1.09 (both m, 4 H, 2 CH_2 ring);

1.96 (m, 1 H, CH ring); 2.31 (s, 3 H, MePh); 2.63 (dd, 1 H, $CH_AC{=}O$, J_1 = 7.2 Hz, J_2 = 16.6 Hz); 2.74 (dd, 1 H, $CH_BC{=}O$, J_1 = 3.4 Hz, J_2 = 16.6 Hz); 2.89 (dd, 1 H, CH_AS, J_1 = 9.2 Hz, J_2 = 13.5 Hz); 3.23 (s, 3 H, MeO); 3.19—3.40 (m, 2 H, CHOMe, CH_BS); 3.51 (s, 3 H, MeO); 3.70 (dd, 1 H, CHOMe, J_1 = 3.4 Hz, J_2 = 7.2 Hz); 7.09 and 7.30 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 10.92 (2 CH_2 ring); 19.80, 20.08, and 20.95 (3 Me); 21.24 (CH ring); 37.28 (CH_2S); 43.73 (C); 44.89 ($CH_2C{=}O$); 59.01 and 61.30 (2 MeO); 81.50 and 85.38 (2 CHOMe); 129.58 (2 CH arom.); 130.11 (2 CH arom.); 133.45 and 136.00 (2 C arom.); 209.88 (C=O). MS, *m/z* (I_{rel} (%)): 350 [M^+] (2), 213 (30), 195 (25), 191 (20), 181 (15), 163 (6), 149 (57), 137 (14), 127 (100), 123 (16).

Diastereomer 26b. R_f 0.32 (hexane—AcOEt, 10 : 1), 0.162 g (46%). Found (%): C, 68.55; H, 8.70; S, 9.04. $C_{20}H_{30}O_3S$. Calculated (%): C, 68.53; H, 8.63; S, 9.15. ^1H NMR ($CDCl_3$), δ: 0.81 and 0.84 (both s, 6 H, Me); 0.82—0.94 and 0.99—1.09 (both m, 4 H, 2 CH_2 ring); 1.96 (m, 1 H, CH ring); 2.30 (s, 3 H, MePh); 2.64 (m, 2 H, $CH_2C{=}O$); 2.92 (dd, 1 H, CH_AS, J_1 = 8.1 Hz, J_2 = 13.4 Hz); 3.15 (dd, 1 H, CH_BS, J_1 = 2.9 Hz, J_2 = 13.4 Hz); 3.27 and 3.48 (both s, 6 H, MeO); 3.31 (dd, 1 H, CHOMe, J_1 = 2.9 Hz, J_2 = 8.1 Hz); 3.80 (dd, 1 H, CHOMe, J_1 = 4.6 Hz, J_2 = 6.2 Hz), 7.08 and 7.27 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 11.03 (2 CH_2 ring); 19.15 and 21.00 (3 Me); 21.26 (CH ring); 37.12 (CH_2S); 43.50 (C); 44.78 ($CH_2C{=}O$); 58.84 and 60.61 (2 MeO); 81.07 and 84.66 (2 CHOMe); 129.68 (2 CH arom.); 130.21 (2 CH arom.); 133.49 and 136.13 (2 C arom.); 209.92 (C=O). MS, *m/z* (I_{rel} (%)): 350 [M^+] (5), 312 (20), 217 (17), 189 (8), 163 (19), 150 (30), 147 (27), 137 (100), 125 (57), 111 (60).

2,4-Dimethoxy-3,3-dimethyl-5-(4-tolylthio)pentyl phenyl ketones (27a,b). Diastereomer 27a. R_f 0.35 (hexane—AcOEt, 8 : 1), 0.116 g (30%). ^1H NMR ($CDCl_3$), δ: 0.87 and 0.93 (both s, 6 H, Me); 2.24 (s, 3 H, MePh); 2.83—3.36 (m, 5 H, $CH_2C{=}O$, CH_2S, CHOMe); 3.25 and 3.50 (both s, 6 H, MeO); 4.00 (dd, 1 H, CHOMe, J_1 = 3.2 Hz, J_2 = 7.5 Hz); 7.00—8.00 (m, 9 H arom.). MS, *m/z*: 286 [M^+].

Diastereomer 27b. R_f 0.29 (hexane—AcOEt, 8 : 1), 0.116 g (30%). ^1H NMR ($CDCl_3$), δ: 0.90 and 0.99 (both s, 6 H, Me); 2.29 (s, 3 H, MePh); 2.82—3.45 (m, 5 H, $CH_2C{=}O$, CH_2S, CHOMe); 3.20 and 3.52 (both s, 6 H, MeO); 3.90 (dd, 1 H, CHOMe, J_1 = 3.2 Hz, J_2 = 6.8 Hz); 7.00—8.00 (m, 9 H arom.). MS, *m/z*: 286 [M^+].

5,7-Dimethoxy-2,2,8,8-tetramethyl-8-(4-tolylthio)octan-3-ones (31a,b). Diastereomer 31a. R_f 0.33 (hexane—AcOEt, 10 : 1), 0.110 g (30%). Found (%): C, 68.91; H, 9.44; S, 8.74. $C_{21}H_{34}O_3S$. Calculated (%): C, 68.81; H, 9.35; S, 8.75. ^1H NMR ($CDCl_3$), δ: 1.15 and 1.22 (both s, 6 H, Me); 1.16 (s, 9 H, 3 Me); 1.53 (ddd, 1 H, CH_A, J_1 = 3.1 Hz, J_2 = 10.1 Hz, J_3 = 14.2 Hz); 2.16 (ddd, 1 H, CH_B, J_1 = 1.6 Hz, J_2 = 9.6 Hz, J_3 = 14.2 Hz); 2.35 (s, 3 H, MePh); 2.55 (dd, 1 H, $CH_AC{=}O$, J_1 = 5.7 Hz, J_2 = 17.2 Hz); 2.92 (dd, 1 H, $CH_BC{=}O$, J_1 = 6.1 Hz, J_2 = 17.2 Hz); 3.29 (m, 1 H, CHOMe); 3.37 and 3.46 (both s, 6 H, MeO); 3.97 (m, 1 H, CHOMe); 7.12 and 7.44 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.16 (MePh); 23.76 and 26.52 (2 Me); 26.20 (3 Me from Bu^t); 37.58 (CH_2); 42.00 ($CH_2C{=}O$); 44.35 and 52.93 (2 C); 57.08 and 61.31 (2 MeO); 74.81 and 84.55 (2 CHOMe); 128.20 (C arom.); 129.17 (2 CH arom.); 137.68 (2 CH arom.); 138.71 (C arom.); 213.96 (C=O). MS, *m/z*: 366 [M^+].

Diastereomer 31b. R_f 0.28 (hexane—AcOEt, 10 : 1), 0.139 g (38%). Found (%): C, 68.75; H, 9.29; S, 8.88. $C_{21}H_{34}O_3S$. Calculated (%): C, 68.81; H, 9.35; S, 8.75. ^1H NMR ($CDCl_3$), δ: 1.16 (s, 9 H, 3 Me); 1.18 and 1.25 (both s, 6 H, Me); 1.74 (ddd, 1 H, CH_A, J_1 = 4.8 Hz, J_2 = 8.7 Hz, J_3 = 14.4 Hz); 2.12 (ddd, 1 H, CH_B, J_1 = 2.4 Hz, J_2 = 7.4 Hz, J_3 = 14.4 Hz); 2.35 (s, 3 H, MePh); 2.50 (dd, 1 H, $CH_AC{=}O$, J_1 = 4.5 Hz, J_2 = 17.2 Hz); 2.90 (dd, 1 H, $CH_BC{=}O$, J_1 = 7.6 Hz, J_2 = 17.2 Hz); 3.05 (dd, 1 H, CHOMe, J_1 = 2.4 Hz, J_2 = 8.7 Hz); 3.34 and 3.44 (both s, 6 H, MeO); 3.90 (m, 1 H, CHOMe); 7.12 and 7.42 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.21 (MePh); 24.18 (Me); 26.24 (4 Me); 35.95 (CH_2); 41.73 ($CH_2C{=}O$); 44.33 and 53.51 (2 C); 57.08 and 60.51 (2 MeO); 75.66 and 85.20 (2 CHOMe); 128.26 (C arom.); 129.31 (2 CH arom.); 137.53 (2 CH arom.); 138.84 (C arom.); 214.28 (C=O). MS, *m/z*: 366 [M^+].

***trans*-2-(2-Methoxypent-4-enyl)-3-(4-tolylthio)tetrahydropyrans (32a,b). Diastereomer 32a.** R_f 0.37 (hexane—AcOEt, 10 : 1), 0.101 g (33%). Found (%): C, 70.63; H, 8.49; S, 10.35. $C_{18}H_{26}O_2S$. Calculated (%): C, 70.54; H, 8.55; S, 10.46. ^1H NMR ($CDCl_3$), δ: 1.31—1.70 (m, 4 H, 2 CH_2 ring); 2.31 (s, 3 H, MePh); 2.00—2.42 (m, 4 H, 2 CH_2 chain); 2.71 (dt, 1 H, CHS, J_1 = 3.9, J_2 = 10.6); 3.35 (s, 3 H, MeO); 3.23—3.55 (m, 3 H, CH_aOCH ring, CHOMe); 3.89 (m, 1 H, CH_eO ring); 5.01 (m, 2 H, CH_2=); 5.78 (ddt, 1 H, CH=, J_1 = 7.0, J_2 = 10.0, J_3 = 17.0); 7.07 and 7.32 (both d, 4 H arom., J = 8.0). ^{13}C NMR ($CDCl_3$), δ: 20.92 (MePh); 27.07 and 31.65 (2 CH_2 ring); 38.43 and 38.76 (2 CH_2 chain); 49.49 (CHS); 56.83 (MeO); 67.58 (CH_2O); 76.50 and 78.02 (CHOMe, CHO ring); 116.83 (CH_2=); 129.39 (2 CH arom.); 129.66 (C arom.); 133.65 (2 CH arom.); 134.68 (CH=); 137.32 (C arom.). MS, *m/z* (I_{rel} (%)): 306 [M^+] (8), 274 (7), 265 (12), 233 (3), 215 (4), 207 (100), 189 (57), 161 (37), 123 (22), 85(50). HRMS: found, *m/z* 306.1651; calculated for $C_{18}H_{26}O_2S$ [M^+], *m/z* 306.1654.

Diastereomer 32b. R_f 0.27 (hexane—AcOEt, 10 : 1), 0.150 g (49%). Found (%): C, 70.55; H, 8.63; S, 10.37. $C_{18}H_{26}O_2S$. Calculated (%): C, 70.54; H, 8.55; S, 10.46. ^1H NMR ($CDCl_3$), δ: 1.43—1.83 (m, 4 H, 2 CH_2 ring); 2.32 (s, 3 H, MePh); 2.03—2.47 (m, 4 H, 2 CH_2 chain); 2.81 (dt, 1 H, CHS, J_1 = 4.0 Hz, J_2 = 10.6 Hz); 3.34 (s, 3 H, MeO); 3.19—3.55 (m, 3 H, CH_aOCH ring, CHOMe); 3.90 (m, 1 H, CH_eO ring); 5.10 (m, 2 H, CH_2=); 5.88 (ddt, 1 H, CH=, J_1 = 7.0 Hz, J_2 = 10.0 Hz, J_3 = 17.0 Hz); 7.09 and 7.31 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.06 (MePh); 27.02 and 31.92 (2 CH_2 ring); 36.98 and 37.55 (2 CH_2 chain); 49.82 (CHS); 56.32 (MeO); 67.71 (CH_2O); 77.64 and 78.63 (CHOMe, CHO ring); 116.75 (CH_2=); 129.60 (2 CH arom.); 129.87 (C arom.); 133.49 (2 CH arom.); 135.01 (CH=); 137.47 (C arom.). MS, *m/z* (I_{rel} (%)): 306 [M^+] (12), 274 (5), 265 (15), 233 (4), 215 (10), 207 (100), 189 (67), 161 (17), 123 (32), 85 (97). HRMS: found, *m/z* 306.1657; calculated for $C_{18}H_{26}O_2S$ [M^+], *m/z* 306.1654.

2,4-Dimethoxy-3,3-dimethyl-1-(4-tolyl)thiophanium perchlorate (21). To a stirred solution of 4-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (10 mL) at −20 °C were added sequentially a solution of vinyl ether **1** (0.058 g, 1 mmol) in CH_2Cl_2 (2 mL), an anhydrous $LiClO_4$ suspension (0.426 g, 4 mmol) in CH_2Cl_2 (5 mL), and methyl isobutenyl ether **20** (0.103 g, 1.2 mmol) in CH_2Cl_2 (5 mL). During addition of the ether **20** a white precipitate of LiCl was observed. After stirring at room temperature for 30 min the reaction mixture was filtered and poured into a mixture of absolute diethyl ether and hexane (1 : 1, 40 mL), precooled to −20 °C and left in the refrigerator overnight. Then the oil-like precipitate that formed on the walls and bottom of the flask was decanted from the solution, and the residue was washed with cold absolute ether (2×20 mL) and evaporated in vacuum without heating. The thus isolated

salt **21** (0.275 g, yield 75%) in the form of a pale-yellow viscous oil was characterized by spectral methods. ^{1}H NMR ($CDCl_3$), δ: 1.18 and 1.33 (both s, 6 H, Me); 2.46 (s, 3 H, MePh); 3.52 and 3.57 (both s, 6 H, MeO); 4.05 and 4.32 (both m, 3 H, SCH_2CH); 5.90 (s, 1 H, CHOMe); 7.49 and 7.85 (both d, 4 H arom., J = 8.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.21 and 19.33 (2 Me); 21.34 (MePh); 46.89 (CH_2); 50.78 (C); 58.38 and 62.83 (2 MeO); 87.65 (CHOMe); 120.65 (CS arom.); 125.03 (SCHOMe); 131.30 (2 CH arom.); 132.29 (2 CH arom.); 145.84 (CMe arom.).

Interaction of 2,4-dimethoxy-3,3-dimethyl-1-(4-tolyl)thiophanium perchlorate (21) with trimethylallylsilane (5). To a stirred solution of the salt **21** (0.183 g, 0.5 mmol) in $MeNO_2$ (10 mL) at −20 °C allylsilane **5** (0.115 g, 1 mmol) was added, the temperature was allowed to rise to ambient, and the reaction mixture was stirred overnight. The usual workup and preparative isolation carried out after 24 h gave a mixture of products **6a,b** in a ratio 1.0 : 1.4 (0.091 g, yield 65%).

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