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Polyfunctional Compounds Containing the 4,6-Dialkoxy-7-arylthioheptene Moiety as Synthetically Useful Intermediates. The Course of Lewis Acid-Induced Transformations

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Data on the selectivity of the Lewis acids induced transformations of the title compounds are presented, and the routes leading to formation of products containing either cyclohexane or 1,3-diene units are described.

Introduction

Recently, we have described a novel methodology for the one-pot synthesis of polyfunctional compounds based upon the controlled sequence of three intermolecular arylthio-mediated Ad_E reactions.[1] In particular, this methodology was found to be useful for the ready preparation of a set of structurally diverse adducts, bearing the 4,6-dialkoxy-7-arylthioheptene fragment as a common moiety, from three variable alkene precursors as is shown in Scheme 1.[2a−d]

The presence of the aforementioned functionality pattern might have suggested quite a number of options for the utilization of these compounds as substrates for further transformations. However, it was also obvious that the practical usefulness of the various options depends primarily on the opportunity to exert efficient control over the selectivity of the reagent interaction with the polyfunctional substrates of the type shown. Below are presented the results of our investigation of the course of the Lewis acid-induced reactions of the title adducts.

It was reasonable to assume that an initial attack of Lewis acid could be primarily directed at either the β- or δ-alkoxy group present in the structure of the adducts (Scheme 2).

In both cases the subsequent elimination of the respective alkoxy group should be facilitated due to the nucleophilic assistance of the properly positioned arylthio substituent, and hence the formation of either the episulfonium ion (ESI) or thiophanium ion (TPI) intermediate is to be expected as an immediate result of the β- or δ-attack, respectively.

As was amply demonstrated earlier,[1,2a−d] the ESI salts, once formed as transient intermediates, exhibit a rather high reactivity as electrophiles, and in the structurally related systems these species are prone to react readily with the nucleophilic double bond present in the substrate to give cyclized products.[3a−d] Hence, the β-attack should lead eventually to the formation of the substituted cyclohexane derivatives as is shown in Scheme 2. At the same time, according to the literature data,[4] the TPI salts belong to the category of stable and comparatively unreactive compounds, and therefore the final outcome of δ-attack could not have been predicted with any certainty. It is also noteworthy that there were no literature data enabling one to predict whether the selectivity of the Lewis acid interaction with the polyfunctional adducts containing the aforementioned set of nucleophilic centers might be considered as an achievable goal.

Here we report that the title adducts can selectively undergo either type of these transformations, their course being dependent on the substrate structure and/or reaction conditions.[5]

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∥ Higher College of Chemistry.

(1) For a discussion of the principles of the suggested approach, see a review: Smit, W. A.; Lazareva, M. I.; Smolyakova, I. P.; Caple, R. *Russ. Chem. Bull.* **2001**, *50*, 1949.

(2) (a) Lazareva, M. I.; Kryschenko, Yu. K.; Hayford, A.; Lovdahl, M.; Caple, R.; Smit, W. A. *Tetrahedron Lett.* **1998**, *39*, 1083. (b) Lazareva, M. I.; Kryschenko, Yu. K.; Dilman, A. D.; Hayford, A.; Caple, R.; Smit, W. A. *Russ. Chem. Bull.* **1998**, *47*, 895. (c) Lazareva, M. I.; Kryschenko, Yu. K.; Caple, R.; Wakefield, D.; Hayford, A.; Smit, W. A.; Shashkov, A. S. *Tetrahedron Lett.* **1998**, *39*, 8787. (d) Lazareva, M. I.; Kryschenko, Yu. K.; Caple, R.; Smit, W. A.; Lyssenko, K. A.; Shashkov, A S. *Russ. Chem. Bull.* **2000**, *49*, 85.

(3) (a) Liu, C.; Kuda, K.; Hashimoto, Y.; Saigo, K. *J. Org. Chem.* **1996**, *61*, 494. (b) Harring, S, R.; Livinghouse, T. *Tetrahedron Lett.* **1989**, *30*, 1499. (c) Kamimura, A.; Sasatani, H.; Hashimoto, T.; Ono, N. *J. Org. Chem.* **1989**, *54*, 4998. (d) van Oeveren, A.; Feringa, B. L. *J. Org. Chem.* **1996**, *61*, 2920.

(4) See for a review, see: Knipe, A. C. Reactivity of Sulphonium Salts. In *The Chemistry of Sulfonium Group*; Stirling, C. J. M., Patai, S., Eds.; Wiley: New York, 1981; Chapter 14, pp 313−376.

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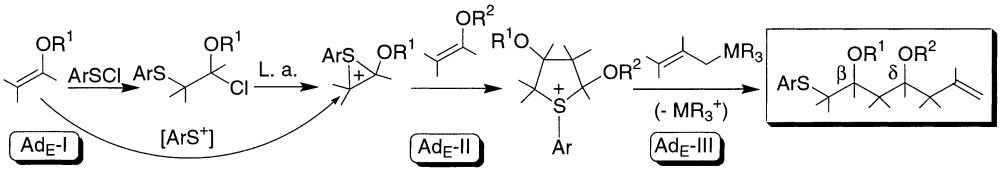
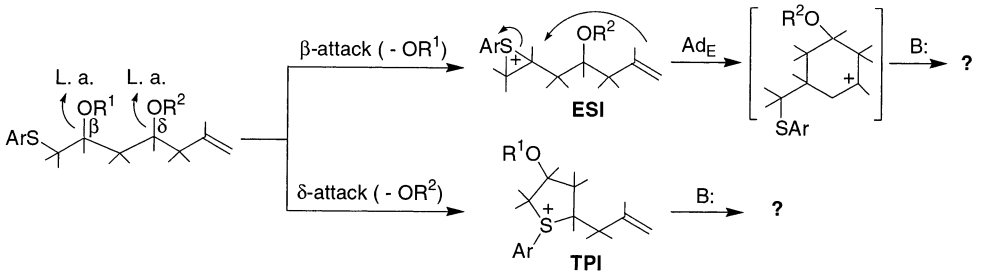
SCHEME 1[a]



[a] L.a. = Lewis acid.

SCHEME 2



Results and Discussion

The starting compounds used in the present study were prepared from three variable alkene precursors in accordance with the formal equation: ArSCl + vinyl ether-I + vinyl ether-II + allylsilane (or stannane) → adduct, following the unified protocol described earlier[2a,b] and outlined in Scheme 1. In all cases, *p*-TolSCl was used as the starting electrophile and the overall coupling was carried out as a one-pot procedure that involved a sequential addition of the reactants and Lewis acid. A list of the alkene precursors, reaction conditions, and prepared adducts **1**−**10** is given in Table 1.

Initial experiments were carried out with 4,6-dimethoxy-2-methyl-7-(*p*-tolylthio)hept-1-ene **1** taken as a model compound. It was found that the final outcome of the interaction of this adduct with Lewis acid depends crucially on the nature of the employed reagent. Thus, the treatment of either individual diastereomers (**1a** or **1b**) or their mixture (**1a**,**b**) with 2 equiv of trimethylsilyl triflate (TMSOTf) in CH_2Cl_2 at ambient temperature followed by the quenching of the reaction with 1,8-diazobicyclo[5.4.0]-undec-7-ene (DBU) resulted in the formation of mixture of the conjugated dienes (*E*)-6-methoxy-2-methyl-7-(*p*-tolylthio)hepta-2,4-diene **12a** and (*E*)-6-methoxy-2-methyl-7-(*p*-tolylthio)hepta-1,3-diene **12b** in 50% total yield[6] (**12a**:**12b** = 7:1, ^{1}H NMR data). TLC monitoring of this reaction revealed a gradual disappearance of the spot corresponding to the presence of the starting material **1a**,**b** (R_f = 0.5, 5:1 hexanes−ethyl acetate) substituted by the spot of a highly polar compound (R_f < 0.05) (total conversion time ca. 2 h), which was converted into the final product **12a**,**b** (R_f = 0.6) upon treatment with DBU. These observations suggested that under these conditions, the reaction of **1a**,**b** occurred as an initial attack of TMSOTf at the δ-methoxy group to give an intermediate that was presumably identified as the TPI salt **11**.[7] Base-induced proton elimination and thiophanium ring opening transformed the latter into a mixture of 1,3-dienes **12a**,**b** (Scheme 3). It is assumed that the predominant formation of the isomer **12a** could be explained as a result of the isomerization of the initially formed and thermodynamically less stable isomer **12b**.

On the other hand, treatment of adduct **1a** with the mixture Et_2AlCl (2 equiv)−TMSOTf (2 equiv)[8] followed by quenching with the DBU produced an entirely different product, namely, *cis*-5-methoxy-1-methyl-3-(*p*-tolylthiomethyl)cyclohexene **14a** in 59% yield.[6] Here again the TLC monitoring of the reaction revealed an initial formation of a highly polar material (R_f < 0.05, hexanes−ethyl acetate, 5:1). To isolate the latter, the reaction mixture formed upon the complete conversion of **1a** was poured into CCl_4 cooled to −25 °C. An oily precipitate was separated from the supernatant liquid, carefully washed with CCl_4, and dissolved in CD_2Cl_2. Due to the presence of the impurities, we were not able to carry out complete assignments of the proton signals in ^{1}H NMR spectrum of this sample, but its general pattern corresponded to that expected for the structure of the bicyclic TPI salt **13a**[9] as is presented in Scheme 3. This compound was shown to be a true intermediate in the described

(5) For a preliminary communication, see: Chekmarev, D. S.; Lazareva, M. I.; Zatonsky, G. V.; Caple, R.; Smit, W. A. *Tetrahedron Lett.* **2001**, *42*, 4289.

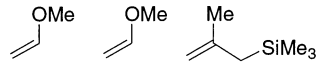
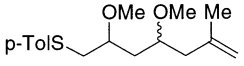
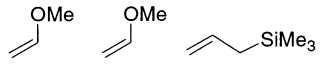
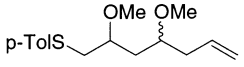
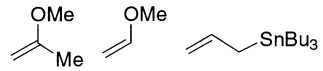
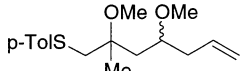
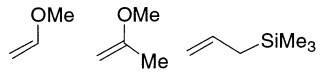
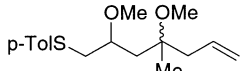
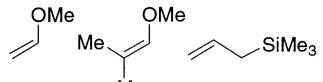
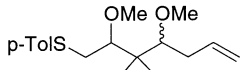
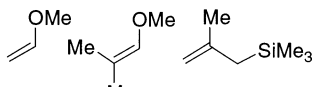
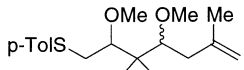
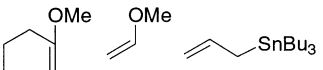
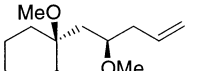
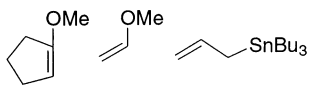
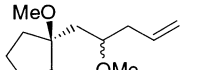
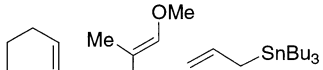
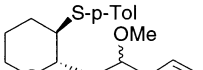
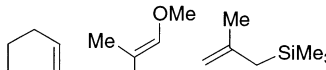
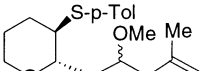
(6) Yields (nonoptimized) refer to the isolated products.

(7) ^{1}H NMR-monitored experiment (CD_2Cl_2, 20 °C) revealed a gradual disappearance of one MeO signal. The formation of sulfonium salt-like intermediate tentatively identified as TPI **11** is substantiated by the observed downfield shifts of the newly emerged ^{1}H signals of MeC_6H_4 fragment (ca. 0.5 ppm, as compared to those of **1a**,**b**), which is typical for various arylsulfonium salt (e.g., data in ref. 2c,d; see also ref 9).

(8) Adducts **1a** and **1b** turned out to be rather inert toward the action of Et_2AlCl (20 °C, several hours) alone. For the literature data attesting to the increased strength of the mixed Et_2AlCl−TMSOTf system as a Lewis acid, see: Oishi, M.; Aratake, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1998**, *120*, 8271.

(9) ^{1}H NMR spectrum revealed a nearly complete absence of the proton signals of the $=CH_2$ fragment present in the starting material **1a** and appearance of a new signal of Me protons as a singlet shifted upfield to 1.3 ppm instead of the Me singlet at 1.79 ppm of **1a**. The observed downfield shift of the signals of aromatic protons (2d at 7.5 and 7.7 ppm as compared to values of 7.1 and 7.3 ppm for the respective signals of the H_{aryl} fragment in the covalent precursors or products, e.g., **1a** and **14a**) corresponds to that expected for the *S*-arylthiophanium salts (e.g., data in ref 3a,c). Unfortunately, attempts to purify the intermediate **13a** by dissolving the latter in CH_2Cl_2 and precipitating with either precooled ether or hexane failed, obviously due to the extreme lability of this salt.

TABLE 1. Preparation of Adducts Containing the 4,6-Dialkoxy-7-arylthiohept-1-ene Moiety

Entry	Starting alkene components	Conditions L.a./solvent, t°C, time	Product	Yield (ratio of diastereomers)
1		$LiClO_4/MeNO_2$ - 25°, 3 h	 **1a**,**b**	98% (1.5 : 1)
2		$LiClO_4/MeNO_2$ - 25° -> 20°, 10 h	 **2a**,**b**	82% (1.4 : 1)
3		$TiCl_4/CH_2Cl_2$ - 78° -> 0°, 6h	 **3a**,**b**	98% (1.6 : 1)
4		$SnCl_4/CH_2Cl_2$ - 50°, 4 h	 **4a**,**b**	49% (1 : 1)
5		$LiClO_4/MeNO_2$ - 25° -> 20°, 12 h	 **5a**,**b**	94% (1.2 : 1)
6		$LiClO_4/MeNO_2$ - 25°C -> 20°, 12 h	 **6a**,**b**	93% (1.1 : 1)
7		$TiCl_4/CH_2Cl_2$ - 78° -> -10°, 12 h	 **7**	65%
8		$TiCl_4/CH_2Cl_2$ - 78° -> -10°, 1 h	 **8a**,**b**	61% (1.4 : 1)
9		$LiClO_4/MeNO_2$ - 25° -> 20°, 24 h	 **9a**,**b**	90% (4 : 1)
10		$LiClO_4/MeNO_2$ - 25° -> 20°, 12 h	 **10a**,**b**	78% (1.4 : 1)

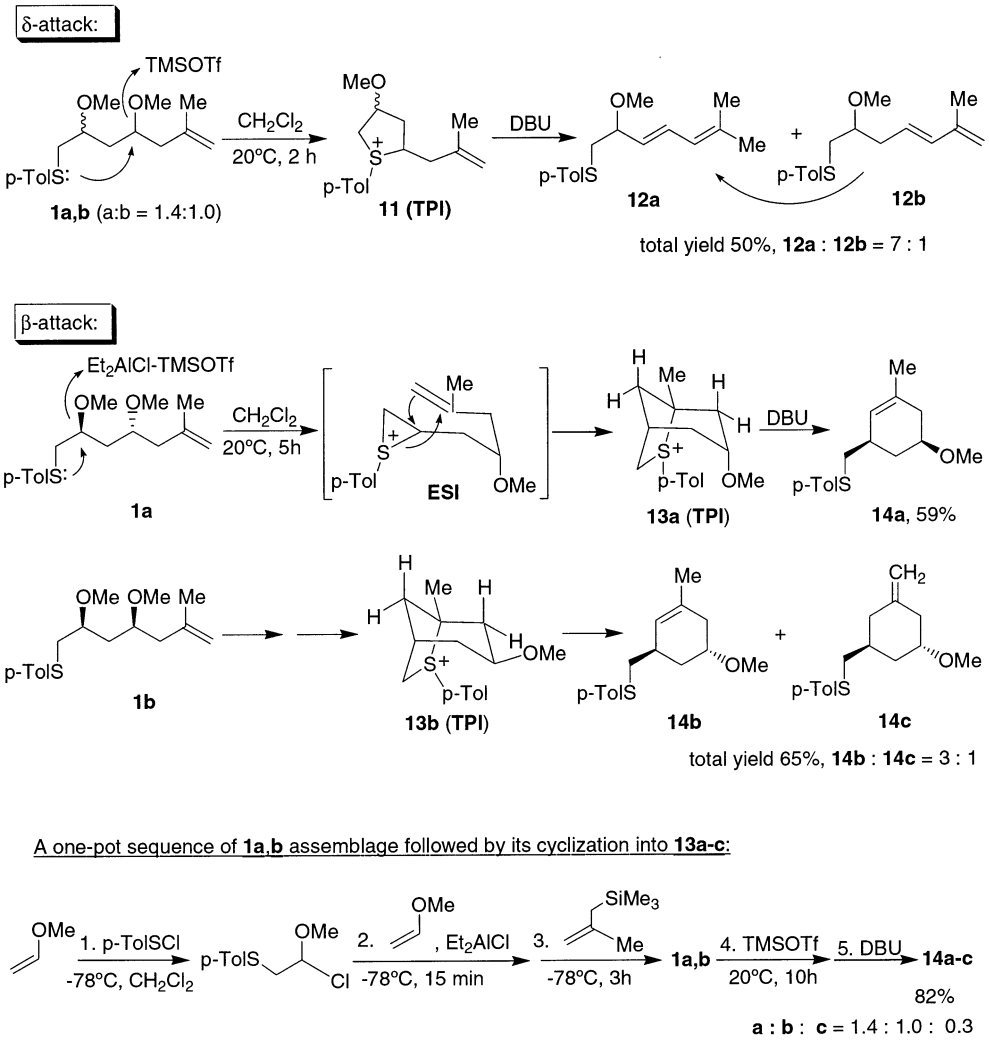
transformation of **1a** since the treatment of the isolated salt **13a** with DBU furnished the same product **14a**. These data taken together implied that the cyclohexane derivative **14a** was formed as a result of the multistep sequence starting with an initial attack of Lewis acid (Et_2-AlCl−TMSOTf) at the β-methoxy group followed by a nearly-concerted intramolecular cyclization of the transient ESI-like intermediate to give the stabilized bicyclic TPI salt **13a** (cf. data in ref 3a,d,e), which is further converted into the final adduct via the ring opening and proton elimination triggered by the action of the strong base as is shown in Scheme 3.

Interaction of the diastereomer **1b** with TMSOTf−Et_2-AlCl followed the pattern established for **1a** (TLC monitoring data) except that, in this case, the respective TPI intermediate **13b** turned out to be noticeably less stable and more reactive than **13a**. Conversion of this intermediate into a mixture of the cyclized products **14b**,**c** (yield 65%)[10] did not require the presence of DBU and proceeded easily upon the treatment of the reaction mixture with aqueous $NaHCO_3$. Adduct **14b** was shown to differ from product **14a** only by the configuration of the methoxy substituent that was justified with the help of two-dimensional gradient-enhanced NMR experiments. Hence, one may conclude that conversions **1a** to **14a** and **1b** to **14b** proceed as highly diastereoselective reactions.

Finally, it was also observed that both the preparation of adducts **1a**,**b** (via a four component coupling, cf. Scheme 1) and their cyclization to give products **14a**−**c** (82%, **a**:**b**:**c** = 1.4:1.0:0.3) can be carried out as *a one-pot sequence of three intermolecular and one intramolecular* Ad_E *reactions* as is represented in Scheme 3. The net

(10) No attempts were made to isolate the individual adducts **14b** and **14c**, and the presence of up to 20% exo-methylene isomer **14c** was ascertained from the analysis of ^1H NMR data for the mixture **14b**,**c**.

SCHEME 3



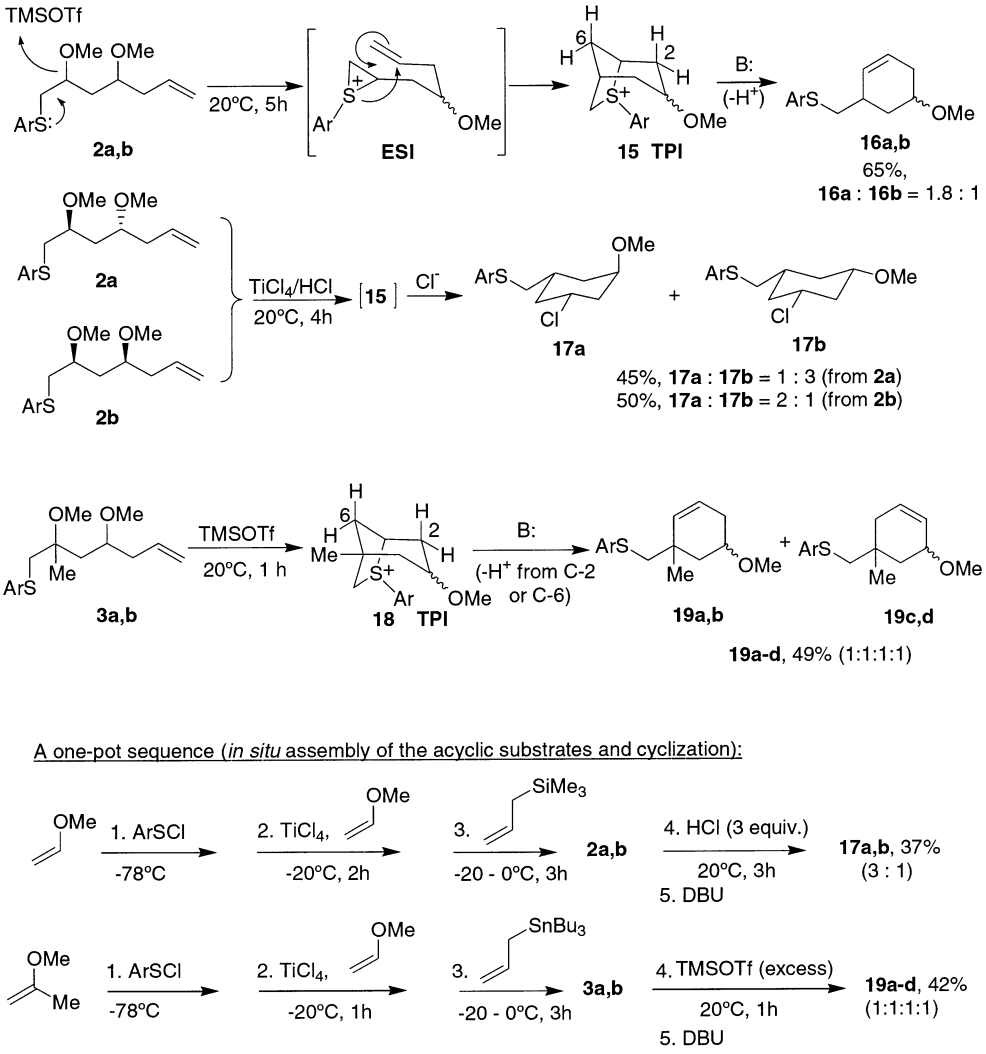
outcome of this unprecedented sequence[11] is the ready *assembly of the cyclohexane framework from simple precursors with the formation of three novel C−C bonds*.

A noticeably different reactivity pattern was observed for the closely related compound **2**. In fact, the *β*-attack route was shown to be a highly preferred pathway for this substrate regardless of the nature of Lewis acid employed. Thus treatment of the individual diastereomers **2a** or **2b** (or a mixture of diastereomers **2a**,**b**) in CH_2Cl_2 with 2−3 equiv of TMSOTf at ambient temperature for 5 h followed by the quenching of the reaction by DBU (20 °C, 2 h) and usual workup furnished products **16a**,**b** in 65% yield[6] as an inseparable mixture of two diastereomers in a ratio of 1.8:1 (Scheme 4). Formation of the same mixture of diastereomers **16a**,**b** suggests that in a contrast to the related transformation of **1a** or **1b**, the cyclization of **2a** or **2b** is accompanied by an equilibration at the CHOMe center. The same results were obtained for the reactions of **2a** or **2b** with the mixed Lewis acid Et_2AlCl−TMSOTf.

Most likely the described transformation also involves the intermediate formation of the stabilized bicyclic cationoid intermediate TPI **15**. To check this suggestion, the reaction of **2a** with TMSOTf was carried out in an NMR tube (CD_2Cl_2, 20 °C). Comparison of the ^{1}H NMR spectral pattern taken immediately upon mixing and after 10, 70, and 150 min of reaction time clearly indicated that to the end of this period almost half of the starting material underwent a conversion into a novel compound. Unfortunately, the complexity of the observed ^{1}H NMR spectra did not allow the unambiguous assignment of all signals. Nevertheless, the appearance of downfield-shifted signals of aromatic protons (ca. 0.4 ppm) and Me_{arom} (ca. 0.2 ppm) at the expense of the reduced intensity of the respective signals of the starting material coupled together with the reduction of the intensity of MeO and CH═CH_2 proton signals could be taken as strong evidence supporting the validity of the above suggestion about the structure of the cationoid intermediate represented by formula **15** (cf. the above discussion of the structure of **13a**). Further treatment of this sample with DBU resulted in the formation of the expected cyclized product **16a**,**b**. Similar changes of the proton signals pattern have been observed for the ^{1}H NMR-monitored reaction of **2b** with TMSOTf.

(11) Numerous examples of cationic reactions employed as basic steps in sequential transformations are described in the literature (for pertinent data, see the reviews: Tietze, L. F. *Chem. Rev.* **1996**, *96*, 115. Hudlicky, T. *Chem. Rev.* **1996**, *96*, 3). However, practically all of them belong to the type of intramolecular electrophilic cyclizations.

SCHEME 4



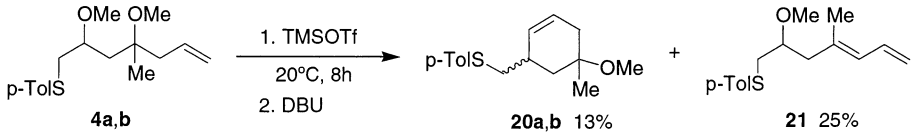
Cyclization of either diastereomer **2a** or **2b** could be also triggered by a $TiCl_4$/HCl system to give the chloro-adduct **17a**,**b** in 45−50% yield,[6] presumably due to the reaction of the intermediate **15** with Cl^- present in the reaction media. It is noteworthy that this transformation exhibited a noticeable diastereoselectivity. In fact, the reaction of **2a** furnished the product with a 3:1 ratio of diastereomers **17a**:**17b**, while the conversion of **2b** gave a 1:2 ratio of the same isomers. We have also found that preparation of the substrate **2a**,**b** and its cyclization to give **17a**,**b** can be carried out via a nonstop protocol involving a *tandem sequence of three intermolecular and one intramolecular Ad_E reactions* as is shown in Scheme 4.

Reaction of adduct **3a**,**b** with TMSOTf also followed the β-attack route and produced the inseparable 1:1:1:1 mixture of the isomers **19a**−**d**.[6] One may speculate that the observed formation of a mixture of the positional isomers **19a**,**b** and **19c**,**d** is due to the presence of the angular Me-group in the intermediate TPI **18**, which hinders the otherwise preferable proton removal from C-6. The same mixture of products was also prepared with the help of a one-pot assembly of **3a**,**b** from the starting alkene components followed by its cyclization upon the treatment with an additional amount of the Lewis acid (Scheme 4).

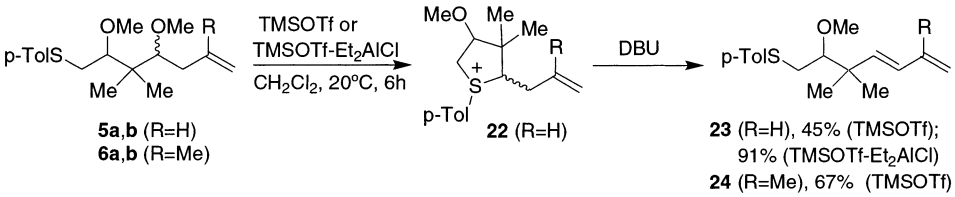
The presence of the Me-group at C-4 in adduct **4a**,**b** facilitated the preferential removal of the MeO-group from this center, and under all conditions checked, the interaction of this compound with Lewis acid was shown to proceed nonselectively producing both 1,3-dienes and the cyclized product. Thus, reaction of adduct **4a**,**b** with TMSOTf led to the formation of a mixture of the cyclized derivatives **20a**,**b** and conjugated diene **21**, formed as a result β- or δ-attack, respectively (Scheme 5).

At the same time, δ-attack turned out to be a highly preferable pathway for the reactions of the adducts bearing a gem-dimethyl group at C-5. Thus, interaction of the substrates **5a**,**b** or **6a**,**b** with Lewis acid followed by the quenching of the reaction with DBU yielded the respective 1,3-dienes **23**[6] or **24**[6] as the sole products regardless of the conditions used (TMSOTf or Et_2AlCl−TMSOTf for **5a**,**b**; Et_2AlCl−TMSOTf for **6a**,**b**, Scheme 6). The initial formation of TPI-like intermediates (e.g., **22**) in these transformations was ascertained by the data of TLC monitoring, which indicated the conversion of the starting material into a highly polar compound (R_f < 0.05, 10:1 ether−hexane, the conversion was complete within

SCHEME 5

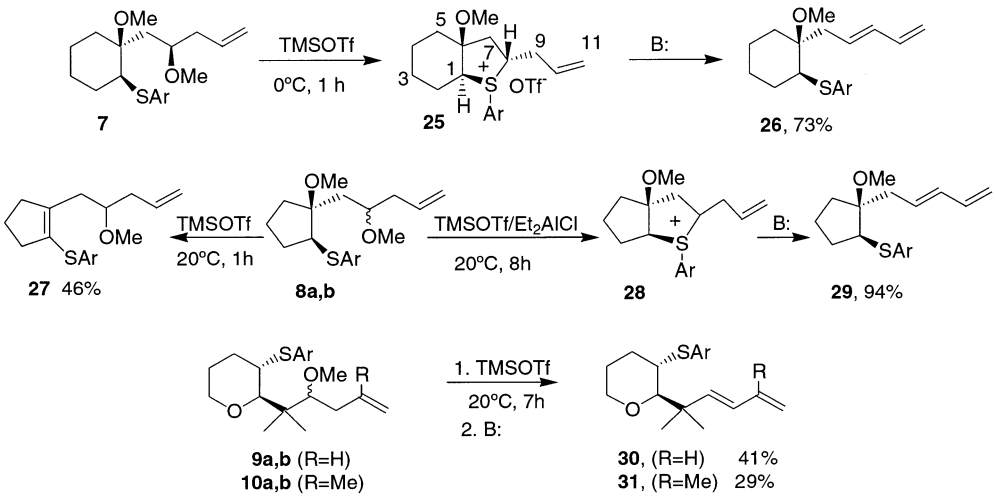


SCHEME 6



One-pot assembly of the adduct 5a,b and its conversion into diene 22:

SCHEME 7



5 h at 20 °C). The treatment of the latter with DBU produced 1,3-diene **23**. Product **23** was also assembled from three alkene precursors via a one-pot sequence as is shown in Scheme 6.

Adduct **7** prepared from 1-methoxycyclohexene contains the axial MeO-group at the tertiary center, and one might have thought that this group would be the preferential target for the attack of electrophile. However, it turned out that this group is rather inert toward the action of Lewis acid and an exclusive elimination of MeO group from the secondary position takes place upon the interaction of **7** with TMSOTf. A subsequent treatment of the reaction mixture with DBU gave the respective 1,3-diene **26** as the only isolable product (Scheme 7). For this conversion the intermediacy of the bicyclic thiophanium salt **25** was firmly established from the results of the NMR monitored experiment. In fact, the ^{1}H NMR spectrum of the sample prepared by the mixing of **7** with TMSOTf in CD_2Cl_2 at 0 °C revealed that after 1 h, the reaction mixture does not contain signals of the starting material. Instead, the signals of a nearly individual compound were observed. The structure of the latter as TPI salt **25** fully correlated with the results of the detailed analysis of its ^{1}H and ^{13}C NMR spectral parameters (see Experimental Section). The appearance of downfield-shifted proton signals at 4.06 (1H, dd) and 4.23 (1H, m) identified as protons at C-1 and C-8, respectively, taken together with the observation of the substantial downfield shift of the signals of MeC_6H_4 group (2.51, s, 3H; 7.55 and 7.71, 2d, 4H; cf. data for the respective proton signals for adduct **7** and see also data in ref 2c,d) could be taken as diagnostic features substantiating the suggested structure.

Rather surprisingly, an interaction of the five-membered analogues **8a**,**b** with the same reagent under closely similar conditions proceeded with attack at the tertiary methoxy group resulting in the elimination of an MeOH fragment and formation of 1,6-diene **27**. This conversion did not involve the intermediate formation of the stabilized cationoid complexes, and hence no quenching of the reaction with a strong base was required. At the same time, an exclusive attack at the secondary methoxy group resulting in the formation of stabilized intermediate, presumably TPI **28**, occurred upon the

treatment of **8a**,**b** with the mixed Lewis acid, Et_2AlCl−TMSOTf. Quenching of this intermediate with DBU led to the formation of 1,3-diene **29** in a nearly quantitative yield (Scheme 7).

For adducts **9a**,**b** and **10a**,**b** prepared with the use of dihydropyran as the first alkene component, β-attack seems to be an unlikely option due to the well-known stability of this ring system toward the action of Lewis acid. Therefore, it was not surprising to find that interaction of these substrates with TMSOTf or TMSOTf−Et_2AlCl led to the formation of the respective dienes **30** and **31** as the only isolable products. In both cases, the formation of 3−4 unidentified minor products was also observed.

Conclusion

Results presented in this paper clearly demonstrate the possibility of controlling the selectivity of the Lewis acid-induced transformations of multifunctional adducts that could be easily assembled with the help of consecutive intermolecular Ad_E reactions.[1a−d] Even more important is the finding that both the preparation of adducts and their subsequent conversion into the cyclohexane derivatives or the products bearing 1,3-diene moiety can be achieved as a result of a one-pot sequence of four cationic reactions (three intermolecular plus one intramolecular). Our current studies are aimed at the evaluation of the potential of the newly elaborated mode of consecutive transformations as a promising protocol for the synthesis of polycyclic compounds.

Experimental Section

General. All reactions were carried out under argon in oven-dried glassware. ^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded in $CDCl_3$ solution unless stated otherwise. Chemical shifts (δ) are reported in parts per million with tetramethylsilane as an internal standard. *J* values are given in hertz. Signal assignments were ascertained using standard protocols with the help of two-dimensional gradient-enhanced experiments geCOSY, geHNQC, and geHMBC. Results of geNOESY and geROESY experiments were employed to establish the stereochemistry of the products. Organic solvents used were dried by standard methods. Flash chromatography was performed on silica gel (230−400 mesh) and TLC on silica gel.

4,6-Dimethoxy-2-methyl-7-(*p*-tolylthio)hept-1-ene (1a,b). To a stirred solution of *p*-TolSCl (0.159 g, 1 mmol) in $MeNO_2$ (20 mL) at −25 °C was added a solution of methyl vinyl ether (0.116 g, 2 mmol) in CH_2Cl_2 followed by a solution of anhydrous $LiClO_4$ (0.426 g, 4 mmol) in $MeNO_2$ (4 mL). Almost immediately, the formation of white precipitate (LiCl) was observed. TLC monitoring revealed the gradual disappearance of the spot with R_f = 0.35 (5:1 hexanes−ethyl acetate) corresponding to the initial adduct *p*-TolSCH$_2$CH(Cl)OMe substituted by a more polar compound with R_f = 0.25. After completion of this conversion (30 min), trimethylmethallyl silane (0.257 g, 2 mmol) was added, and the mixture was kept at −25 °C for 3 h and the reaction quenched with an $NaHCO_3$−ether mixture. Extraction with ether, washing with water, drying over $MgSO_4$, and solvent removal furnished **1a**,**b** (0.290 g, yield 98%) as a mixture of diastereomers in ratio of **a**:**b** = 1:1.5 (^{1}H NMR data) uncontaminated by other products. Individual diastereomers were isolated by flash chromatography over SiO_2 (17:1 hexanes−ethyl acetate).

1a. 0.110 g, R_f = 0.46 (5:1 hexanes−ethyl acetate). ^{1}H NMR ($CDCl_3$) δ: 1.76 (s, 3H, Me), 1.82 (m, 2H, CHCH_2CH), 2.13 and 2.33 (m, 2H, AB-part ABX system, J_{AB} = 14.5, $J_{AX} = J_{BX}$ = 7.3, CH_2C=), 2.32 (s, 3H, *Me*Ph), 3.06 (m, 2H, AB-part ABX system, J_{AB} = 13.5, $J_{AX} = J_{BX}$ = 5.5, CH_2S), 3.31 (s, 3H, MeO), 3.33 (s, 3H, MeO), 3.46 (m, 2H, 2*CH*OMe), 4.78 and 4.83 (2 s, broadened, CH_2=), 7.10 and 7.29 (dd, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.9 (*Me*Ph), 23.8 (Me), 38.2 (CH*CH*$_2$CH), 39.6 (CH_2S), 43.2 (*CH*$_2$C=), 57.2 and 57.8 (2 MeO), 77.3 and 78.2 (2*CH*OMe), 113.8 (CH_2=), 130.6 and 131.1 (CH_{arom}), 134.1 and 137.2 (C_{arom}).

1b. 0.160 g, R_f = 0.51 (hexanes−ethyl acetate, 5:1). ^{1}H NMR ($CDCl_3$) δ: 1.68 (m, 2H, CH*CH*$_2$CH), 1.76 (s, 3H, Me), 2.05 and 2.37 (m, 2H, AB-part ABX system, J_{AB} = 16.5, $J_{AX} = J_{BX}$ = 7.5, CH_2C=), 2.32 (s, 3H, *Me*Ph), 2.97 and 3.1 (m, 2H, AB-part ABX system, J_{AB} = 15, $J_{AX} = J_{BX}$ = 8.0, CH_2S), 3.35 (s, 3H, MeO), 3.39 (s, 3H, MeO), 3.58 (m, 2H, 2*CH*OMe), 4.72 and 4.78 (2 s, broadened, CH_2=), 7.10 and 7.29 (dd, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.9 (*Me*Ph), 23.8 (Me), 39.8 (CH_2S), 40.3 (CH*CH*$_2$CH), 43.2 (*CH*$_2$C=), 57.4 and 58.3 (2 MeO), 77.0 and 78.0 (2*CH*OMe), 113.9 (CH_2=), 130.6 and 131.1 (CH_{arom}), 134.1 and 137.2 (C_{arom}). Anal. Calcd for $C_{17}H_{26}0_2S$: C, 69.34; H, 8.75; S, 10.64. Found: C, 69.37; H, 8.90; S, 10.89.

4,6-Dimethoxy-7-(*p*-tolylthio)hept-1-ene (2a,b) was prepared using the same procedure described for **1a**,**b**, the only difference being that the final step (the reaction with less active Nu_C, trimethylallylsilane) was carried out at 20 °C for 10 h. Adduct **2a**,**b** was prepared in 82% yield (ratio **a**:**b** = 1.4:1). Individual diastereomers were isolated with the help of flash chromatography on SiO_2. The identity of **2a** and **2b** was established by comparison (^{1}H NMR) with the samples prepared earlier.[1b]

4,6-Dimethoxy-6-methyl-7-(*p*-tolylthio)hept-1-ene (3a,b). To a stirred solution of *p*-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (10 mL) at −70 °C were added sequentially a solution of 2-methoxypropene (0.072 g, 1 mmol), $TiCl_4$ (0.228 g, 1.2 mmol), and methyl vinyl ether (0.116 g, 2 mmol). The mixture was kept for 1 h at this temperature; then, tributylallyl stannane (0.99 g, 3 mmol) was added, and the temperature was raised to 0 °C. After the reaction was complete (6 h, TLC control), the reaction was quenched with $NaHCO_3$−ether followed by the usual workup. The residue after solvent removal was additionally washed with aqueous NaOH (20%) to remove tin-containing impurities. Product **3a**,**b** was isolated after column chromatography on SiO_2 as a colorless oil (R_f = 0.66, 30:1 hexanes−ethyl acetate, 290 mg, 98% yield) as a mixture of two diastereomers in ratio of 1.6:1.0. ^{1}H NMR (for the major isomer **3a**) ($CDCl_3$) δ: 1.31 (s, 3H, Me), 1.75−1.81 (m, 2H, CH_2), 2.27−2.31 (m, 2H, $CH_{2,all}$), 2.31 (s, 3H, *Me*Ar), 3.12 (m, 2H, CH_2S), 3.18 and 3.32 (2s, 3H, MeO), 3.44 (m, 1H, *CH*OMe), 5.09 (m, 2H, CH_2=), 5.80 (m, 1H, CH=), 7.09 and 7.28 (dd, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 20.9 (*Me*Ph), 22.6 (Me), 38.3 (*CH*$_2$-CH=), 41.6 (C*CH*$_2$CH), 43.9 (CH_2S), 49.3 (*Me*OC), 55.9 (*Me*OCH), 77.0 (*C*HOMe), 117.4 (CH_2=), 129.5 (2CH-arom), 139.8 (2CH-arom), 133.8 and 135.7 (2C-arom), 134.3 (CH=). Nonoverlapping signals of the isomer **3b**. ^{1}H NMR ($CDCl_3$) δ: 1.27 (s, 3H, Me), 3.16 and 3.34 (2s, 3H, MeO)-group. ^{13}C NMR ($CDCl_3$) δ: 20.9 (*Me*Ph), 23.1 (Me), 38.3 (*CH*$_2$CH=), 40.9 (C*CH*$_2$CH), 43.6 (CH_2S), 49.3 (*Me*OC), 55.9 (*Me*OCH), 77.0 (*C*HOMe), 117.4 (CH_2=), 129.5 (2CH-arom), 139.8 (2CH-arom), 133.8 and 135.7 (2C-arom), 134.3 (CH=). Anal. Calcd for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90; S, 10.89. Found (for the mixture **3a**,**b**): C, 69.37; H, 9.02; S, 11.16.

4,6-Dimethoxy-4-methyl-7-(*p*-tolylthio)hept-1-ene (4a,b). To a stirred solution of *p*-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (20 mL) at −70 °C were added sequentially a solution of methyl vinyl ether (0.058 g, 1 mmol), $SnCl_4$ (0.52 g, 2 mmol), and 2-methoxypropene (0.144 g, 2 mmol). After 30 min, trimethylallyl silane (0.23 g, 2 mmol) was added, and the temperature was raised to −50 °C; the mixture was kept at this temperature for 4 h. After the usual quenching and standard workup, product **4a**,**b** was isolated after column chromatography on SiO_2 as a colorless oil (R_f = 0.6, 30:1 hexanes−ethyl acetate, 140 mg, 49% yield) as a mixture of two diastereomers in a 1:1

ratio (GC-MS). ^{1}H NMR (for the mixture **4a**,**b**) ($CDCl_3$) δ: 1.13 and 1.16 (2s, 3H), 1.68−1.93 (m, 2H), 2.26 (m, 2H), 2.32 (s, 3H), 2.9−3.14 (m, 2H), 3.20 and 3.31 (2s, 6H), 3.51 (m, 2H), 5.04 (m, 2H), 5.82 (m, 1H), 7.08 and 7.26 (dd, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.0, 22.9, 23.2, 38.7, 38.8, 40.9, 41.6, 42.9, 49.0, 56.5, 56.6, 75.6, 75.7, 76.5, 76.6, 117.5, 117.6, 129.6, 129.9, 132.7, 136.0, 134.0, 134.5. Anal. Calcd for $C_{17}H_{26}O_2S$: C, 69.34; H, 8.90; S, 10.89. Found (for the mixture **4a**,**b**): C, 69.44; H, 8.83; S, 10.89.

4,6-Dimethoxy-5,5-dimethyl-7-(*p*-tolylthio)hept-1-ene (5a,**b**). To a stirred solution of TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (20 mL) at −25°C were added sequentially a solution of methyl vinyl ether (0.058 g, 1 mmol), a solution of $LiClO_4$ (0.426 g, 4 mmol) in $MeNO_2$ (4 mL), and after 10 min of stirring, 1-methoxy-2-methylpropene (0.172 g, 2 mmol). The mixture was kept at this temperature for 3 h. Then trimethylallyl silane (0.229 g, 2 mmol) was added, the temperature was raised to 20 °C and the reaction mixture left overnight. Standard quenching and workup, followed by the column chromatography at SiO_2, furnished product **5a**,**b** as a mixture of diastereomers **5a** and **5b** (0.303 g, yield 94%, **5a**:**5b** = 1.2:1.0, GC-MS, R_f = 0.48, 5:1 hexanes−ethyl acetate). ^{1}H NMR (for the mixture **5a**,**b**) ($CDCl_3$) δ: 0.86 and 0.97 (2s, 6H), 2.05−2.25 (m, 2H), 2.33 (s, 3H), 2.95 and 3.20 (2m, 2H), 3.20−3.45 (m, 2H), 3.43, 3.45, 3.51, and 3.53 (4s, 3H), 5.0−5.15 (m, 2H), 5.83−6.05 (m, 1H), 7.10 and 7.32 (2d, 4H). ^{13}C NMR ($CDCl_3$) δ: 18.7, 18.8, 19.7, 19.9, 20.9, 21.0, 35.1, 35.4, 36.9, 37.3, 43.8, 44.2, 59.4, 59.8, 60.4, 61.2, 84.3, 84.9, 85.5, 85.8, 116.0, 116.0, 129.68, 129.8, 130.0, 130.2, 133.5, 133.5, 137.1, 137.3, 136.0, 136.1. Anal. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15; S, 10.39. Found (for the mixture **5a**,**b**): C, 70.30; H, 9.28; S, 10.05.

4,6-Dimethoxy-2,5,5-trimethyl-7-(*p*-tolylthio)hept-1-ene (6a,**b)** was prepared by the coupling of methyl vinyl ether, 1-methoxy-2-methylpropene, and trimethylmethallyl silane following the procedure described for the preparation of **5a**,**b**. This produced an inseparable mixture of diastereomers **6a** and **6b** (yield 93%, **6a**:**6b** = 1.1:1.0, R_f = 0.55, 5:1 hexanes−ethyl acetate). ^{1}H NMR (for the mixture **6a**,**b**) ($CDCl_3$) δ: 0.86 and 0.97 (2s, 6H, Me_2), 1.82 (s, 3H, *Me*C=), 2.05−2.25 (m, 2H, CH_2C=), 2.33 (s, 3H, *Me*Ar), 2.95 and 3.20 (2m, 2H, CH_2S), 3.20−3.45 (2m, 2H, *CH*OMe), 3.32, 3.36, 3.51 and 3.52 (4s, 3H, MeO), 4.75−4.85 (m, 2H, CH_2=), 7.1 and 7.42 (2d, 4H, H_{ar}). ^{13}C NMR ($CDCl_3$) δ: 18.5, 18.7, 19.7 and 19.8 (4Me), 21.0 (*Me*Ph), 22.8 (CH_3-allyl), 37.0 and 37.3 ($2CH_2$S), 39.2 and 39.4 ($2CH_2$-allyl), 43.8 and 44.2 (2C), 59.6, 60.0, 60.3, and 61.1 (4MeO), 83.1, 84.2, 84.3, and 85.4 (4*C*HOMe), 112.5 and 112.6 ($2CH_2$=), 129.6 (2CH-arom), 130.1 (2CH-arom), 133.4 and 136.1 (2C-arom), 144.0 and 144.2 (2C=). Anal. Calcd for $C_{19}H_{30}O_2S$: C, 70.76; H, 9.38; S, 9.94. Found (for the mixture **6a**,**b**): C, 70.57; H, 9.35; S, 9.65.

***cis*-1-Methoxy-1-(2′-methoxypent-4′-enyl)-2-(*p*-tolylthio)cyclohexane (7).** To a stirred solution of *p*-TolSCl (0.238 g, 1.5 mmol) in CH_2Cl_2 (20 mL) at −70 °C were added sequentially 1-methoxycyclohexene (0.168 g, 1.5 mmol), $TiCl_4$ (0.342 g, 1.8 mmol), and the solution of methyl vinyl ether (0.116 g, 2 mmol). After 30 min, tributylallyl stannane (0.99 g, 3 mmol) was added, and the temperature was raised to −0 °C and the mixture kept at this temperature overnight. After quenching of the reaction with NaOH (20%, 40 mL) and ether (30 mL), followed by the standard workup, product **7** was obtained as an individual isomer after column chromatography on SiO_2 (colorless oil, R_f = 0.54, 20:1 hexanes−ethyl acetate, 325 mg, 65% yield). ^{1}H NMR ($CDCl_3$) δ: 1.3−2.0 (m, 8H), 1.8 and 2.2 (dd, J_1 = 15.1, J_2 = 9.0) (AB-part of ABX system, 2H at C-5′), 2.33 (s, 3H, *Me*Ar), 2.36 (m, 2H, CH_2C=), 3.24 and 3.34 (2s, 3H, MeO-groups), 3.35 (dd, 1H, CHS, J_1 = 9.3, J_2 = 3.5), 3.47 (m, 1H, *CH*OMe), 5.12 (m, 2H, CH_2=), 5.85 (m, 1H, CH=), 7.05 and 7.35 (2d, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 20.8 (*Me*Ar), 21.7, 24.4, 29.4 and 31.5 (4 $CH_{2,ring}$), 37.6 and 38.2 ($2CH_{2,chain}$), 48.5 (CHS), 55.8 and 56.1 (2MeO), 76.7 (*C*OMe), 77.1 (*C*HOMe), 117.4 (CH_2=), 129.4 (2CH $_{arom}$), 132.1 ($2CH_{arom}$), 132.9 and 136.3 ($2C_{arom}$), 134.5 (CH=). Anal. Calcd for $C_{20}H_{30}O_2S$: C, 71.81; H, 9.04; S, 9.59. Found: C, 71.60; H, 9.28; S, 9.65.

***cis*-1-Methoxy-1-(2′-methoxypent-2′-enyl)-2-(*p*-tolylthio)cyclopentane (8a,b**) was prepared following the procedure described for adduct **7**, the only difference being the milder reaction conditions (1 h at −10 °C). Product **8** was obtained in 61% yield as a mixture of diastereomers **8a** and **8b** (**a**:**b** = 1.4:1, GC-MS). ^{1}H NMR (for **8a**,**b**) ($CDCl_3$) δ: 1.55−2.1 (m, 8H, $3CH_{2,ring}$ and $CH_{2,chain}$), 2.10 and 2.20 (2m, 2H, $CH_{2,all}$), 2.30 (s, 3H, Me_{Ar}), 3.22, 3.29. 3.30 and 3.35 (4s, 3H, MeO), 3.49 and 3.55 (2m, 1H, *CH*OMe), 3.41 and 3.59 (2m, 1H, CHS), 5.10 (m, 2H, CH_2=), 5.82 (m, 1H, CH=), 7.05 and 7.35 (2d, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 20.4 (CH_2-ring), 20.9 (*Me*Ph), 32.2 and 32.7 (CH_2-ring), 32.9 and 33.0 (CH_2-ring), 37.7 and 38.2 (C*CH*$_2$-CH), 38.2 and 38.6 (C*H*$_2$CH=), 49.9, 50.8, 55.9 and 56.0 (MeO), 55.3 and 57.5 (CHS), 76.8 and 77.2 (*CH*OMe), 86.2 (*C*OMe), 117.6 and 117.7 (CH_2=), 129.6 (2CH-arom), 130.9 and 131.04 (2CH-arom), 133.6, 133.6, 136.0 and 136.1 (2C-arom), 134.5 (CH=). Anal. Calcd for $C_{19}H_{28}O_2S$: C, 71.20; H, 8.81; S, 10.01. Found (for the mixture **8a**,**b**): C, 71.06; H, 8.67; S, 10.10.

***trans*-2-(3′-Methoxy-2′-methylhex-5′-en-2′-yl)-3-(*p*-tolylthio)tetrahydropyran (9a,b)** was prepared as described in ref 2d: yield 90%, **9a**:**9b** = 4:1.

***trans*-2-(3′-Methoxy-2′,5′-dimethylhex-5′-en-2′-yl)-3-(*p*-tolylthio)tetrahydropyran (10a,b)** was prepared under the conditions described in ref 2d for the preparation of **9a**,**b** with the use of trimethylmethallyl silane as a final Nu_C: yield 78%, **10a**:**10b** = 1.4:1 (GC-MS). ^{1}H NMR ($CDCl_3$) δ: 0.93, 1.09, 1.11 and 1.15 (4s, 3H, Me), 1.54−1.66 and 1.90−1.98 (m, 4H, $2CH_{2,ring}$), 1.83 and 1.85 (2s, 3H, Me), 2.12−2.20 (m, 2H, CH_{2all}), 2.35 (s, 3H, *Me*Ar), 3.12 (d, 1H, CHO_{ring}), 3.19−3.29 (m, 1H, CHS), 3.33 and 3.45 (2m, 2H, CH_2O_{ring}), 3.40 and 3.41 (2s, 3H, MeO), 3.94 (m, 1H, *CH*OMe), 4.84 (m, 2H, C=CH_2), 7.12 and 7.33 (2d, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 19.9 and 19.9 (2Me), 20.0 (*Me*Ph), 22.8 and 22.9 (CH_3-allyl), 25.2 and 31.0 ($2CH_2$-ring), 39.5 and 39.6 (CH_2-allyl), 46.8 and 47.0 (CHS), 60.8 and 61.1 (MeO), 67.3 and 68.3 (CH_2O), 82.2 and 82.3 (*C*HOMe), 85.6 (CHO-ring), 112.9 and 113.0 (CH_2=), 129.9 (2CH-arom), 131.7 and 131.8 (C-arom), 133.6 and 133.7 (2CH-arom), 137.3 (C-arom), 138.6 (C=). Anal. Calcd for $C_{21}H_{32}O_2S$: C, 72.37; H, 9.29; S, 8.70. Found (for the mixture **10a**,**b**): C, 72.35; H, 9.25; S, 9.20.

***(E)*-6-Methoxy-2-methyl-7-(*p*-tolylthio)hepta-2,4-diene (12a) and (*E*)-6-Methoxy-2-methyl-7-(*p*-tolylthio)-hepta-1,3-diene (12b).** TMSOTf (0.556 g, 2.5 mmol) was added at 20 °C to the stirred solution of **1a**,**b** (0.263 g, 1 mmol) in CH_2Cl_2. After 2 h, TLC data revealed a complete disappearance of the spot corresponding to the starting material substituted by the spot of the highly polar compound (R_f < 0.05). The reaction mixture was treated with DBU (0.60 g, 4 mmol) and left overnight. Subsequent treatment with $NaHCO_3$/KH_2PO_4 and ether followed by the standard workup and column chromatography furnished a mixture of isomers **12a** and **12b** (0.120 g, 50%, ratio of **a**:**b** = 7:1, GC-MS). ^{1}H NMR (for the mixture **12a**,**b**) ($CDCl_3$) δ: for **12a**, 1.78 (s, 3H, Me), 1.80 (s, 3H, Me), 2.33 (s, 3H, *Me*Ph), 2.98 and 3.10 (pair of dd, AB part ABX system, 2H, CH_2S, J_{AB} = 13.0, J_{AX} = 5.4, J_{BX} = 6.9), 3.29 (s, 3H, MeO), 3.77 (m, 1H, *CH*OMe), 5.40 (dd, J_1 = 7.9, J_2 = 15.2, 1H, at C-5), 5.84 (d, J = 11.1, 1H, at C-3), 6.43 (dd, J_1 = 11.1, J_2 = 15.2, 1H, at C-4), 7.10 and 7.28 (2d, $4H_{arom}$). ^{1}H NMR for **12b** (only nonoverlapping signals are given) δ: 1.83 (s, 3H, Me), 3.37 (s, 3H, MeO), 3.41 (m, 1H, *CH*OMe), 4.88, 5.6 and 6.2 (d, dd and dd, ratio 2:1:1, conjugated diene system). ^{13}C NMR for **12a** ($CDCl_3$) δ: 18.5 (Me), 21.1 (*Me*Ph), 26.1 (Me), 40.1 (CH_2S), 56.5 (MeO), 81.2 (*CH*OMe), 124.2 (C-3), 128.9 (C-5), 129.7, 130.2, 132.9 and 136.1 (C_{arom}), 130.5 (C-4), 136.9 (C-2). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45; S, 12.22. Found (for the mixture **12a**,**b**): C, 73.13; H, 8.45; S, 11.82.

***cis*-5-Methoxy-1-methyl-3-(*p*-tolylthiomethyl)cyclohexene (14a).** To a stirred solution of **1a** (0.140 g, 0.45 mmol) in

CH_2Cl_2 (9 mL) at 20 °C were added sequentially solutions of $EtAlCl_2$ (0.121 g, 1 mmol) in toluene (0.56 mL) and TMSOTf (0.220 g, 0.18 mL). After 5 h, TLC revealed a complete conversion of the starting compound into a highly polar material (R_f < 0.05, 5:1 hexanes−ethyl acetate). DBU (0.38 g, 2.5 mmol) was added to the reaction mixture, and the reaction was left overnight and then quenched with $NaHCO_3/KH_2PO_4$ (20 mL) and ether (10 mL). After extraction with ether, drying with $MgSO_4$, solvent removal, and flash chromatography (SiO_2, 15:1 hexanes−ethyl acetate) adduct **14a** was obtained as a colorless oil (R_f = 0.44, 5:1 hexanes−ethyl acetate, 0.078 mg, 59%). ^{1}H NMR ($CDCl_3$) δ: 1.19 (q, $1H_a$ at C-4, J = 12.0), 1.70 (s, 3H, Me), 1.94 and 2.22 (2 m, 2H at C-6), 2.33 (s, 3H, *Me*Ph), 2.38 (m, 1H at C-3), 2.88 (m, AB part ABX system, 2H, CH_2S), 3.37 (s, 3H, MeO), 3.42 (m, 1H, *CH*OMe), 5.38 (s, 1H, CH═), 7.10 and 7.28 (dd, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.1 (*Me*Ph), 23.6 (Me at C-1), 34.3 (CH_2, C-4), 35.7 (CH_{all}), 36.8 ($CH_{2,all}$), 41.1 (CH_2S), 55.9 (MeO), 76.7 (*CH*OMe), 124.0 (CH═), 129.8 and 130.2 ($4CH_{arom}$), 132.0 and 136.1 ($2C_{arom}$), 133.1 (C═). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45; S, 12.22. Found: C, 73.44; H, 8.58; S, 11.97.

***trans*-5-Methoxy-1-methyl-3-(*p*-tolylthiomethyl)cyclohexene (14b)** was prepared under similar conditions by the interaction of **1b** with $EtAlCl_2$ and TMSOTf. **14b**: yield 65%, a colorless oil, R_f 0.40, 5:1 hexanes−ethyl acetate. ^{1}H NMR ($CDCl_3$) δ: 1.30 (m, 2H, CH_2), 1.68 (s, 3H, Me), 1.98 and 2.08 (2m, 2H at C-6), 2.33 (s, 3H, *Me*Ph), 2.48 (m, 1H at C-3), 2.86 (m, AB part ABX system, 2H, CH_2S), 3.34 (s, 3H, MeO), 3.61 (m, 1H, *CH*OMe), 5.42 (s, 1H, CH═), 7.10 and 7.28 (dd, $4H_{arom}$). The presence of the exo-methylene isomer **14c** (ca. 25%, GC-MS) was ascertained from the appearance of the following nonoverlapping signals: 3.3 (s, 3H, MeO), 3.55 (m, 1H, *CH*OMe), and 4.78 (C═CH_2).

One-Pot Synthesis of 14a−c via Preparation of 1a,b in Situ. 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 methyl vinyl ether (0.174 g, 3 mmol) in CH_2Cl_2 (2 mL) and Et_2AlCl (0.363 g, 3 mmol) in toluene (1.08 mL). After additional stirring for 15 min at this temperature, methallyltrimethylsilane (0.257 g, 2 mmol) was added and the mixture was kept for 3 h at −78 °C until TLC data revealed complete conversion of the intermediate compound into adduct **1a**,**b**. Then, the temperature was raised to 20 °C and TMSOTf (0.66 g, 3 mmol) was added. The mixture was kept at this temperature for 10 h. Toward the end of this period, TLC data indicated a nearly complete transformation of **1a**,**b** into a highly polar material (R_f < 0.05). The reaction was next quenched with DBU as described above. Usual workup and chromatography separation furnished product **14a−c** (0.215 g, yield 82%). ^{1}H NMR spectrum of this product revealed the presence of all three isomers, their ratio (**a**:**b**:**c** = 1.4:1.0:0.3) having been evaluated by the integration of the nonoverlapping signals.

5-Methoxy-3-(*p*-tolylthiomethyl)cyclohexene (16a,b) was prepared as an inseparable mixture of diastereomers from either of the individual diastereomers **2a** or **2b** with the use of TMSOTf as a Lewis acid under the conditions described above for the synthesis of **14a**,**b** (yield 65%, **16a**:**16b** = 1.8:1). ^{1}H NMR (for the mixture **16a**,**b**) ($CDCl_3$) δ: 1.24, 1.70, 1.94 and 2.07 (4m, 2H), 2.21−2.56 (m, 3H, allyl), 2.31 (s, 3H, *Me*Ph), 2.89 (m, 2H, CH_2S), 3.32 and 3.36 (2s, 3H, MeO), 3.41 and 3.56 (2m, 1H, *CH*OMe), 5.65 (m, 2H, CH═CH), 7.09 and 7.26 (2d, 4H). ^{13}C NMR ($CDCl_3$) δ: 21.0 (*Me*Ph), 31.0, 31.4, 31.7, 34.4, 40.4 and 40.6 (6 CH_2), 32.4 and 35.9 (2CH), 55.7 and 55.8 (2 MeO), 73.2 and 76.1 (2 *CH*OMe), 124.9 and 125.1 (2 CH═CH), 129.6 and 130.1 (CH_{arom}), 132.7, 13.8 and 136.1 (C_{arom}). GC-MS: M^+ 248 for both **16a** and **16b**. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12; S, 12.91. Found (for the mixture **16a**,**b**): C, 72.40; H, 8.25; S, 12.70.

1-Chloro-3-methoxy-5-(*p*-tolylthiomethyl)cyclohexane (17a,b). To a solution of **2a** (0.04 g, 0.014 mmol) in CH_2Cl_2 (5 mL) at 20 °C was introduced a flow of dry HCl for 15 min (ca. 3 equiv); then, $TiCl_4$ (0.040 g, 0.020 mmol) was added, and the mixture was kept for 4 h at this temperature. After the quenching with $NaHCO_3$−ether and the usual workup, the mixture of **17a** and **17b** was obtained (0. 018 g, yield 45%, **17a**:**17b** = 3:1). These diastereomers were separated by flash chromatography on SiO_2. **17a**, 1,5-cis, 1,3-trans: R_f = 0.5 (15:1 hexanes−ethyl acetate). ^{1}H NMR ($CDCl_3$) δ: 1.06 (m, 1H, H_a at C-4, 1.34 (q, $1H_a$ at C-6, J = 13.0), 1.59 (m, $1H_a$ at C-2), 2.00 (m, $1H_a$, at C-5), 2.15 (m, $1H_e$ at C-4), 2.32 (s, 3H, *Me*Ar), 2.36 (m, 1H, H_e at C-6), 2.41 (m, $1H_e$ at C-2), 2.81 (dd, 2H, CH_2S, J_1 = 6.8, J_2 = 1.2), 3.25 (s, 3H, MeO), 3.62 (quint, *CH*OMe, J = 2.8), 4.12 (tt, 1H, CHCl, J_1 = 1.5, J_2 = 3.8), 7.09 and 7.25 (2d, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.0 (*Me*Ar), 32.1 (C-5), 34.0 (C-4), 40.3 (C-2), 41.2 (CH_2S), 42.7 (C-6), 55.1 (CHCl), 55.9 (MeO), 75.8 (*CH*OMe), 129.7 and 130.0 (CH_{arom}), 132.9 and 136.2 (C_{arom}). MS: *m*/*z* 284 and 282 (M^+). **17b**, 1,3,5-cis: (R_f = 0.43, 15:1 hexanes−ethyl acetate). ^{1}H NMR ($CDCl_3$) δ: 0.93 (q, 1H, H_a at C-4, J = 12.5), 1.30 (q, $1H_a$ at C-6, J = 12.5.), 1.47 (q, $1H_a$ at C-2, J = 12.5), 1.60 (m, $1H_a$, at C-5), 2.32 (s, 3H, *Me*Ar), 2.41 (m, $1H_e$ at C-4), 2.52−2.62 (m, 2H, H_e at C-2 and C-6), 2.84 (d, 2H, CH_2S, J = 7.5), 3.12 (tt, *CH*OMe, J_1 = 3.8, J_2 = 12.5), 3.35 (s, 3H, MeO), 3.75 (tt, 1H, CHCl, J_1 = 12.5, J_2 = 3.8), 7.09 and 7.25 (2d, $4H_{arom}$). MS: *m*/*z* 284 and 282 (M^+).

Under essentially the same conditions, the diastereomer **2b** was converted into a mixture of the same products **17a**,**b** in 50% yield (**17a**:**17b** = 1:2).

One-Pot Synthesis of 17a,b via Preparation of 2a,b in Situ. To a stirred solution of 4-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (20 mL) at −78°C was added a solution of methyl vinyl ether (0.058 g, 1 mmol) in CH_2Cl_2 (1 mL) followed by $TiCl_4$ (0.190 g, 1 mmol) and an additional 1 equiv of methyl vinyl ether. The mixture was kept for 2 h at −20 °C; then, the temperature was raised to 0 °C, and trimethylallylsilane (0.229 g, 3 mmol) was added, and mixture was kept at this temperature for 3 h. Toward the end of this period, the TLC control indicated the complete formation of **2a**,**b**. After that, the temperature was raised to 20 °C and the mixture saturated with dry HCl (ca. 3 equiv); an additional amount of $TiCl_4$ (2 equiv) was added, and stirring was continued for 3 h. Quenching of the reaction with $NaHCO_3$−ether, followed by the standard workup and chromatography on SiO_2, gave **17a**,**b**: 0.12 g, yield 37%, **17a**:**17b** = 3:1 (^{1}H NMR).

5-Methoxy-3-methyl-3-(*p*-tolylthiomethyl)cyclohexene (19a,b) and 3-Methoxy-5-methyl-5-(*p*-tolylthiomethyl)cyclohexene (19c,d) were prepared as an inseparable mixture of diastereomers from the mixture of diastereomers **3a**,**b** using TMSOTf as a Lewis acid under the conditions described above for the synthesis of **14a**,**b** (yield 49%, **19a**:**19b**:**19c**:**19d** = 1:1:1:1). ^{1}H NMR ($CDCl_3$) δ: 1.08, 1.14, 1.17 and 1.19 (4s, 3H), 1.35, 1.5, 1.6 and 1.7 (4dd, 2H), 1.9−2.35 (m, 2H), 2.32 (s, 3H), 2.9−3.1 (4dd, 2H), 3.26, 3.35, 3.39 and 3.40 (4s, 3H), 3.45−3.6 (2m, 1H), 3.78 and 3.88 (2m, 1H), 5.5, 5.6, 5.75 and 5.80 (4m, 1H), 7.09 and 7.28 (dd, $4H_{arom}$). The ratio of isomers was estimated by the integration of nonoverlapping signals. Similarly, four sets of closely related signals were observed in ^{13}C NMR. ^{13}C NMR ($CDCl_3$) δ: 21.2, 24.5, 27.7, 28.0, 28.3, 32.0, 37.0, 38.0, 38.9, 39.1, 39.5, 40.1, 45.7, 74.80, 49.1, 49.2, 56.0, 56.1, 74.6, 74.1, 123.7, 123.9, 127.3, 127.5, 128.1, 128.1, 129.7, 129.9, 130.5, 130.6, 134.8 and 135.3. Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45; S, 12.22. Found (for the mixture **19a−d)**: C, 73.48; H, 8.52; S, 11.66.

One-Pot Synthesis of 19a−c via Preparation of 3a,b in Situ. To a stirred solution of 4-TolSCl (0.159 g, 1 mmol) in CH_2Cl_2 (10 mL) at −78 °C were added sequentially a solution of 2-methoxypropene (0.072 g, 1 mmol) in CH_2Cl_2 (2 mL), $TiCl_4$ (0.230 g, 1.2 mmol), and methyl vinyl ether (0.094 g, 1.8 mmol). After additional stirring for 1 h at −20 °C, allyltributyl stannane (0.663 g, 2 mmol) was added, the temperature raised to 0 °C, and the mixture kept at this temperature for 3 h until TLC data revealed complete conversion of the intermediate compound into adduct **3a**,**b**. At this moment, the temperature was raised to 20 °C and TMSOTf (0.44 g, 2 mmol) was added.

The mixture was kept at this temperature for 1 h. Toward the end of this period, TLC data indicated a nearly complete transformation of **3a**,**b** into a highly polar material (R_f < 0.05). Quenching of the reaction mixture with DBU, followed by the standard workup, furnished product **19** as a mixture **19a**−**d** (0.06 g, yield 42%), its ^{1}H NMR spectrum being identical to that described in the previous experiment.

5-Methoxy-5-methyl-3-(*p*-tolylthiomethyl)cyclohexene (20a,b) and (*E*)-6-methoxy-4-methyl-7-(*p*-tolylthio)-hepta-1,3-diene (21). A mixture of these products was prepared by the initial treatment of **4a**,**b** with TMSOTf following the procedure described above for the preparation of **14a**,**b**. Products **20a**,**b** and **21** were isolated by flash chromatography on SiO_2. **20a**,**b**: yield 13%, R_f = 0.6, 15:1 hexanes−ether, **20a**:**20b** = 1.5:1, GC-MS. ^{1}H NMR ($CDCl_3$) δ: 1.15 and 1.20 (2s, 3H), 1.25 (m, 2H), 1.90−2.25 (m, 2H), 2.31 (s, 3H), 2.90 (m, 2H), 3.15 and 3.25 (2s, 3H), 5.60−5.60 (CH=CH), 7.09 and 7.27 (dd, $4H_{arom}$). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45; S, 12.22. Found (for the mixture of **20a**,**b**): C, 73.35; H, 8.62; S, 11.58. **21**: yield 25%, R_f = 0.7, 15:1 hexanes−ether. ^{1}H NMR ($CDCl_3$) δ: 1.77 (s, 3H), 2.33 (s, *3H*), 2.36 (m, 2H), 3.00 (m, 2H), 3.35 (s, 3H), 3.48 (m, 1H), 5.06 (m, 2H), 5.88 (dd, 1H, J = 10.5), 6.55 (m, 1H), 7.10 and 7.27 (dd, $4H_{arom}$). Anal. Calcd for $C_{16}H_{22}OS$: C, 73.23; H, 8.45; S, 12.22. Found: C, 73.45; H, 8.38; S, 12.40.

(*E*)-6-Methoxy-5,5-dimethyl-7-(*p*-tolylthio)hepta-1,3-diene (23). To a stirred solution of adduct **5a**,**b** (0.140 g, 0.45 mmol) in CH_2Cl_2 (15 mL) at 20 °C were added sequentially Et_2AlCl (0.121 g, 1 mmol in toluene solution, 0.56 mL) and TMSOTf (0.022 g, 1 mmol). After 5 h, TLC data indicated a complete conversion of the starting material (R_f = 0.48, 5:1 hexanes−ethyl acetate) into a highly polar compound, presumably TPI salt **22** (R_f < 0.05, the same system). Treatment of the mixture with DBU (0.45 g, 3 mmol) overnight followed by the quenching with aqueous $NaHCO_3/KH_2PO_4$ (20 mL)−ether (20 mL) and standard workup yielded after purification on SiO_2 adduct **23** (R_f = 0.45, 17:1 hexane−ethyl acetate, 0.110 g, yield 91%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.07 (s, 6H, 2Me), 2.33 (s, 3H, *Me*Ar), 2.83 (dd, 1H, CH_AS, J_1 = 9.0, J_2 = 13.5), 3.04 (dd, 1H, *CH*OMe, J_1 = 2.2, J_2 = 9.0), 3.11 (dd, 1H, CH_BS, J_1 = 2.2, J_2 = 13.5), 3.53 (s, 3H, MeO), 5.04 and 5.16 (2d, 2H, CH_2=, J_1 = 10.2, J_2 = 17.0), 5.72 (d, 1H, C−*CH*=, J = 15.7), 6.04 (dd, 1H, C−CH=*CH*, J_1 = 10.2, J_2 = 15.7), 6.33 (dt, *CH*=CH2, J_1 = 10.2, J_2 = 17.0), 7.11 and 7.27 (dd, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.0 (*Me*Ar), 2.6 and 24.5 (2Me), 37.2 (CH_2S), 45.0 (C), 61.7 (MeO), 87.9 (*CH*OMe), 115.7 (CH_2=), 128.8 (CH=*CH*CH=), 129.6 ($2CH_{arom}$), 129.8 ($2CH_{arom}$), 133.5 and 137.1 ($2C_{arom}$), 137.4 (*CH*=CH2), 141.1 (C*CH*=). Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75; S, 11.60. Found: C, 74.05, H, 8.98, S, 11.20.

One-Pot Synthesis of 23 via the Preparation of 5a,b in Situ. 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 methyl vinyl ether (0.058 g, 1 mmol) in CH_2Cl_2 (1 mL), TMSOTf (0.022 g, 1.0 mmol), and 1-methoxy-2-methylpropene (0.172 g, 2.0 mmol). After additional stirring overnight, allyltrimethylsilane (0.229 g, 2 mmol) was added, the temperature raised to 20 °C, and the mixture kept for 3 h at this temperature until TLC data revealed complete conversion of the intermediate compound into adduct **5a**,**b**. At this moment, the temperature was raised to 20 °C, and TMSOTf (0.088 g, 4 mmol) was added. The mixture was kept at this temperature for 100 h. Toward the end of this period, TLC data indicated a complete transformation of **5a**,**b** into a highly polar material (R_f < 0.05). Quenching of the reaction mixture with DBU followed by the standard workup furnished product **23** (0.180 g, yield 65%), its ^{1}H NMR spectrum being identical to that described in the previous experiment.

(*E*)-6-Methoxy-2,5,5-trimethyl-7-(*p*-tolylthio)hepta-1,3-diene (24). To a stirred solution of adduct **6a**,**b** (0.140 g, 0.42 mmol) in CH_2Cl_2 (15 mL) at 20 °C was added TMSOTf (0.033 g, 1.5 mmol). After 7 h, TLC data indicated a complete conversion of the starting material (R_f = 0.45, 5:1 hexanes−ethyl acetate) into a highly polar compound (R_f < 0.05, the same system). Treatment of the mixture with DBU (0.60 g, 4 mmol) overnight followed by quenching with aqueous $NaHCO_3/KH_2PO_4$ (20 mL)−ether (20 mL) and standard workup yielded after purification on SiO_2 adduct **24** (R_f = 0.45, 17:1 hexane−ethyl acetate, 0.194 g, yield 67%) as a colorless oil. ^{1}H NMR ($CDCl_3$) δ: 1.09 (s, 6H, 2Me), 1.86 (s, 3H, Me), 2.33 (s, 3H, *Me*Ar), 2.82 (dd, 1H, CH_AS, J_1 = 8.8, J_2 = 13.2), 3.04 (dd, 1H, *CH*OMe, J_1 = 2.2, J_2 = 8.8), 3.11 (dd, 1H, CH_BS, J_1 = 2.2, J_2 = 13.2), 3.53 (s, 3H, MeO), 4.94 (s, broad, 2H, CH_2=), 5.17 (d, 1H, C−*CH*=, J = 16.2), 6.12 (d, 1H, C−CH=*CH*, J_1 = 16.2), 7.11 and 7.27 (dd, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 18.7 (Me_{all}), 20.9 (*Me*Ar), 22.4 and 24.8 (2Me), 37.2 (CH_2S), 45.3 (C), 61.8 (MeO), 88.0 (*CH*OMe), 115.3 (CH_2=), 129.6 ($2CH_{arom}$), 129.7 ($2CH_{arom}$), 130.5 (CH_2=), 133.2 and 135.9 ($2C_{arom}$). Anal. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02; S, 11.04. Found: C, 74.22; H, 8.81; S, 11.40.

***cis*-1-Methoxy-1-((*E*)-penta-2′,4′-dienyl)-2-(*p*-tolylthio)-cyclohexane (26).** To a stirred solution of **7** (0.1 g, 0.3 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added TMSOTf (0.133 g, 0.6 mmol). After 1 h, TLC data indicated the complete conversion of the starting material into a highly polar compound **25** (see below). The reaction mixture was then treated with DBU followed by the quenching with $NaHCO_3/KH_2PO_4$−ether and standard workup. Column chromatography on SiO_2 gave adduct **26** as a colorless liquid (0.060 g, 73%, R_f = 0.71, 5:1 hexanes−ether). ^{1}H NMR ($CDCl_3$) δ: 1.1−2.0 (m, 8H, $4CH_{2ring}$), 2.3 (s, 3H, *Me*Ar), 2.43 and 2.82 (2H, $CH_{2,all}$, AB-part of ABX system, J_1 = 13.3, J_2 = 8.2, J_3 = 7.3), 3.0 (dd, 1H, CHS, J_1 = 11.2, J_2 = 4.1), 3.27 (s, 3H, MeO), 5.02 and 5.1 (2d, 2H, CH_2=, J_1 = 16.9, J_2 = 10.1), 5.7 (m, 1H, CH_2CH=), 6.2 (dd, 1H, CH_2-CH=*CH*, J_1 = 15.0, J_2 = 10.1), 6.34 (dt, 1H, CH=CH_2, J_1 = 16.9, J_2 = 10.1), 7.1 and 7.32 (2d, $4H_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.0 (*Me*Ar), 21.1, 25.6, 29.7 and 31.0 ($CH_{2,\ ring}$), 38.7 ($CH_{2,all}$), 48.5 (MeO), 55.3 (CHS), 78.0 (*C*OMe), 115.6 (CH_2=), 129.5 ($2CH_{arom}$), 129.6 (C−*CH*=CH), 132.2 ($2CH_{arom}$), 132.5 and 136.5 ($2C_{arom}$), 134.7 (C=*CH*CH=), 137.0 (*CH*=CH_2). Anal. Calcd for $C_{19}H_{20}OS$: C, 75.45; H, 8.66; S, 10.60. Found: C, 75.60; H, 8.91; S, 9.87.

Identification of the Structure of Intermediate 25. Interaction of adduct **7** dissolved in CD_2Cl_2 with TMSOTf (0 °C, 30 min, cf. previous experiment) produced a solution of the salt **25**, which was transferred into a NMR tube, and its ^{1}H and ^{13}C NMR spectra were immediately recorded at this temperature. ^{1}H NMR did not reveal the presence of **7** in a noticeable amount. ^{1}H NMR (CD_2Cl_2) δ: 1.41 (m, 1H, H_a at C-3), 1.51 (m, 1H, H_a at C-4), 1.63 (m, 1H, H_a at C-5), 1.69 (m, 1H, H_e at C-4), 1.91 (m, 1H, H_e at C-2), 1.98 (m, 1H, H_e at C-3), 2.11 (dd, $1H_A$ at C-7, J_1 = 12.3, J_2 = 14.0), 2.19 (m, 1H, H_a at C-2), 2.25 and 2.43 (2 m, 2H at C-9); 2.40 (m, 1H, H_e at C-5), 2.51(s, 3H, MeAr), 2.92 (dd, $1H_B$ at C-7, J_1 = 6.0, J_2 = 14.0); 3.29 (3H, s, MeO); 4.06 (dd, 1H at C-1, J_1 = 4.2, J_2 = 12.3); 4.23 (m, 1H at C-8); 4.82 (d, 1H at C-11, J = 17.2); 5.24 (d, 1H at C-11, J = 10.3); 5.52 (m, 1H at C-10); 7.55 and 7.71 (2d, 4H, Ar). ^{13}C −NMR (CD_2Cl_2) δ: 19.0 (C-4), 21.3 (MeAr), 23.0 (C-2), 24.8 (C-3), 28.3 (C-5), 33.5 (C-9), 40.5 (C-7), 49.0 (MeO), 58.0 (C-8), 70.9 (C-1), 82.0 (C-6), 119.2 (C-11), 131.5 (C-10), 131.8, 133.0, 132.2, 147.4 (C−Ar). Assignment of all ^{1}H and ^{13}C signals was made with the help DEPT, HETCOR, COSY, and NOESY protocols. The attempt to isolate the salt in the free state by precipitation with the cooled hexane or carbon tetrachloride led to the formation of the oily residue, which decomposed almost instantaneously at room temperature.

1-(2′-Methoxypent-4′-enyl)-2-(*p*-tolylthio)cyclopentene (27). To a stirred solution of **8a**,**b** (0.10 g, 0.33 mmol) in CH_2Cl_2 (5 mL) at 20 °C was added TMSOTf (0.1 g, 0.45 mmol). After 1 h, TLC data indicated the complete conversion of the starting material into a product **27**. The reaction mixture was then treated with $NaHCO_3$/ether. Standard workup and column chromatography on SiO_2 gave adduct **27** as a colorless

liquid (0.045 g, 46%, R_f = 0.75, 5:1 hexanes−ether). ^{1}H NMR ($CDCl_3$) δ: 1.88 (m, 2H, $CH_{2,ring}$), 2.32 (m, 2H$_{all,yl\ chain}$), 2.42 and 2.58 (m, 4H, $CH_{2,\ allyl,\ ring}$), 2.61(m, 2H, $CH_{2,allyl,\ chain}$), 3.41 (s, 3H, MeO), 3.48 (m, 1H, *CH*OMe), 5.10 (m, 2H, CH_2=), 5.90 (m, 1H, CH=), 7.05 and 7.31 (2d, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 20.7 (*Me*Ar), 22.0, 33.7, 36.5, 36.9, 38.3 (5CH_2), 56.5 (MeO), 79.7 (*CH*OMe), 116.9 (CH_2=), 118.3 (SC=*C*), 129.5 and 129.8 (4CH$_{arom}$), 133.9 and 135.9 (2C$_{arom}$), 134.9 (CH=), 144.5 (S*C*=C). Anal. Calcd for $C_{18}H_{24}OS$: C, 74.95; H, 8.39; S, 11.11. Found: C, 74.78; H, 8.19; S, 11.06.

***cis*-1-Methoxy-1-((*E*)-penta-2′,4′-dienyl)-2-(*p*-tolylthio)-cyclopentane (29).** To a stirred solution of **8a**,**b** (0.32 g, 1.0 mmol) in CH_2Cl_2 (5 mL) at 20 °C were added sequentially Et_2-AlCl (0.445 g, 2 mmol, toluene solution) and TMSOTf (0.55 g, 2.0 mmol). After 8 h, TLC data indicated the complete conversion of the starting material into a highly polar compound (R_f < 0.05, 10:1 hexanes−ethyl acetate). The reaction mixture was then treated with DBU followed by the quenching with $NaHCO_3$/KH_2PO_4−ether and standard workup. Column chromatography on SiO_2 afforded adduct **29** as a colorless liquid (0.27 g, 94%, R_f = 0.7, 5:1 hexanes−ether). ^{1}H NMR ($CDCl_3$) δ: 1.75−2.2 (m, 6H, 3CH_{2ring}), 2.33 (s, 3H, *Me*Ar), 2.56 (d, 2H, $CH_{2,all}$, J = 7.6), 3.26 (d, 1H, CHS, J = 5.6), 3.30 (s, 3H, MeO), 5.01 and 5.07 (dd, 2H, CH_2=, J_1 = 16.9, J_2 = 10.0), 5.68 (dt, 1H, CH_2*CH*=, J_1 = 14.9, J_2 = 7.6), 6.07 (dd, 1H, CH_2-CH=*CH*, J_1 = 14.9, J_2 = 10.4), 6.30 (dt, 1H, CH=CH_2, J_1 = 16.9, J_2 = 10.3), 7.08 and 7.33 (2d, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.0 (*Me*Ar), 20.7, 30.8, and 32.6 ($CH_{2,\ ring}$), 36.4 ($CH_{2,all}$), 50.3 (CHS), 56.0 (MeO), 86.9 (*C*OMe), 115.8 (CH_2=), 129.6 (2CH$_{arom}$), 129.7 (C−*CH*=CH), 131.7 (2CH$_{arom}$), 133.2 and 136.3 (2C$_{arom}$), 134.5 (C=*CH*CH=), 136.9 (*CH*=CH_2). Due to instability, it was not possible to obtain reproducible elemental analysis data for **29**. The homogeneity of the compound was substantiated by GC-MS data: M^+ 288.

***trans*-2-((*E*)-2′-Methylhexa-3′,5′-dien-2′-yl)-3-(*p*-tolylthio)tetrahydropyran (30)** was prepared upon the treatment of **9a**,**b** with TMSOTf under conditions described in the previous experiment. **30**: colorless oil, yield 41%, R_f = 0.93 (30:1 hexanes−ethyl acetate). ^{1}H NMR ($CDCl_3$) δ: 1.23 (s, 6H, Me_2), 1.61 (m, 1H, CH_aCHS), 1.67 (m, 2H, CH_2CH_2O), 1.94 (m, 1H, CH_bCHS), 2.38 (s, 3H, Me$_{arom}$), 3.12 (m, 2H, CHS, CHO), 3.46 and 4.01 (2m, 2H, CH_2O), 5.05 and 5.18 (2d, 2H, J_1 = 10.1, J_2 = 16.9, C=CH_2), 5.97 (d, 1H, C−*CH*=CH, J = 15.6), 6.12 (dd, 1H, C−CH=*CH*, J_1 = 15.6, J_2 = 10.2), 6.39 (dt,1H, *CH*=CH_2, J_1 = 15.6, J_2 = 10.1), 7.1 and 7.32 (2d, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 21.1 (*Me*Ar), 23.1 and 26.0 (2Me), 24.4 (CH_2CH_2O), 29.9 (CH_2CHS), 41.2 (C_{quat}), 46.8 (CHS), 67.2 (CH_2O), 87.2 (CHO), 115.1 (CH_2=), 128.0 (C−CH=*CH*), 129.6 and 133.2 (4CH$_{arom}$), 131.0 and 137.2 (2C$_{arom}$), 137.8 (*CH*=CH_2), 142.6 (C−*CH*=CH). Anal. Calcd for $C_{19}H_{26}OS$: C, 75.45; H, 8.66; S, 10.60. Found: C, 75.19; H, 8.84; S, 9.82.

***trans*-2-((*E*)-2′,5′-Dimethylhexa-3′,5′-dien-2′-yl)-3-(*p*-tolylthio)tetrahydropyran (31)** was prepared upon the treatment of **10a**,**b** with TMSOTf under conditions described in the previous experiment. **31**: colorless oil, yield 29%, R_f = 0.90 (30:1 hexanes−ethyl acetate). ^{1}H NMR ($CDCl_3$) δ: 1.19 (s, 6H), 1.61 and 1.89 (2m, 4H), 1.89 (s, 3H), 2.34 (s, 3H), 3.09 (m, 2H), 3.42 and 3.98 (2m, 2H), 4.92 (s, 2H), 5.93 (d, 1H, J = 17.0), 6.17 (d, 1H, J = 17.0), 7.1 and 7.32 (2d, 4H$_{arom}$). ^{13}C NMR ($CDCl_3$) δ: 18.8, 21.0, 22.7, 26.4, 24.4, 29.8, 41.0, 46.8, 67.2, 87.4, 114.5, 129.6, 131.0, 137.1, 138.1, 142.5. Anal. Calcd for $C_{20}H_{28}OS$: C, 75.90; H, 8.92; S, 10.13. Found: C, 75.68; H, 8.74; S, 9.70.

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Supporting Information Available: Assignment of signals for compounds **4a**,**b**, **5a**,**b**, **19a**−**d**, **20a**,**b**, **21**, and **31**; ^{1}H NMR spectra for compounds **17a**,**b** and **29**; and copies of ^{1}H and ^{13}C NMR, DEPT, HETCOR, COSY, and NOESY spectra for **25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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