Lewis Acid Activated Reactions of Mixed (O,Se) Acetals with Allyltrimethylsilane and Allyltributylstannane

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On the basis of preferential complexation of oxygen or selenium atoms by different Lewis acids, it was expected that, depending on the Lewis acid employed, the title reactions would lead to selective formation of homoallyl ethers or homoallyl selenides. This has not been confirmed by experiment: in almost all the reactions tried homoallyl ethers largely predominated, or were the exclusive allylation products, even when strongly oxygenophilic Lewis acids such as $TiCl_4$ were used. In the cases of the latter type of Lewis acids, the results observed with (O,Se) and a couple of (O,S) mixed acetals are interpreted in terms of two major factors operating in opposite directions. ^1H NMR data of a mixture of $TiCl_4$ and (O,Se) acetal indicate that preferential (but not exclusive) complexation of the oxygen moiety takes place indeed. However, because of the much stronger C–O bond as compared to the C–Se bond, this latter (also activated by the Lewis acid to some extent) undergoes cleavage by allyl metals to give homoallyl ethers as predominating products. In contrast with $BF_3{\cdot}OEt_2$, boron trichloride and boron tribromide were found to react with (O,Se) acetals to give the corresponding α-halo selenides, which in turn were cleanly transformed into homoallyl selenides on reaction with allyltrimethylsilane in the presence of tin tetrachloride.

Introduction

Because of their great synthetic value, the Lewis acid promoted coupling reactions of (O,O),[1] (S,S),[2] (Se,Se),[3] and mixed (O,S) acetals[4] with various carbon nucleophiles have been thoroughly studied during the past two decades. Recent investigations have shown that site selective complexation by Lewis acids of one of the two oxygen atoms of chiral cyclic (O,O) acetals plays a fundamental role in the highly asymmetric reactions of these acetals,[1def,5] site selective complexation being essentially due to steric factors.

It has also been reported[4b] that remarkable chemoselectivities could be achieved in the reactions of (O,S) mixed acetals with allyl- or allenyltributylstannanes by the use of an appropriate Lewis acid for the activation of the mixed acetals bearing methoxy and phenylthio groups. In all the cases tried, nearly exclusive formation of homoallylic (or homopropargylic) ethers was observed with $BF_3{\cdot}OEt_2$, whereas the use of titanium tetrachloride led to the corresponding homoallylic phenyl sulfides in excellent yields. These high selectivities have been rationalized in terms of the strong affinity of $TiCl_4$ for oxygen and of the greater stability of oxocarbenium ion intermediates formed in the cases of activation by $BF_3{\cdot}OEt_2$.

In the course of our continuing studies of the reactivity of selenium-stabilized carbocationic species[3a-m] and in light of the above findings, we reasoned that the two heteroatoms of (O,Se) acetals **1** possessing greater dissimilarities in their electronegativities and hard–soft properties should be even more differenciated by various Lewis acids. Therefore, on treatment with an appropriate Lewis acid, the mixed acetals **1** were expected to undergo selective complexation and to react differently in the presence of the title nucleophiles, leading to the formation of homoallyl ethers **2** or of homoallyl selenides **3**.

The results reported herein show that this expectation has not been borne out by experiment, presumably because the above considerations oversimplify and reduce the problem of product formation to the sole interaction between the Lewis acid and mixed acetals **1**. A some-

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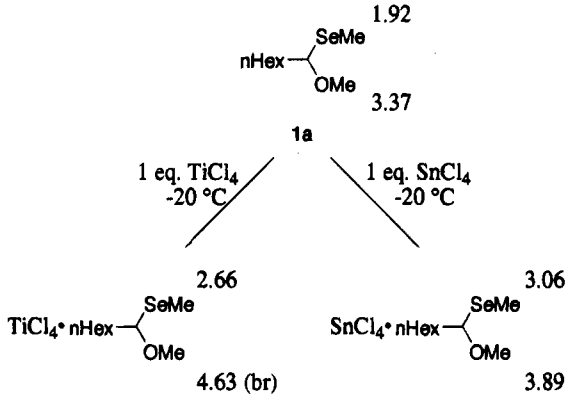
Chart 1. ^{1}H Chemical Shifts (δ, $CDCl_3$, TMS) of the $SeCH_3$ and OCH_3 of 1-Methoxy-1-(methylseleno)heptane (1a)



what more subtle reaction scheme is proposed wherein a combination of this interaction with the relative reactivity of the resulting complexes allows for a qualitative understanding of the observations.

Results and Discussion

To check the above ideas concerning the selective complexation by different Lewis acids of the methoxy or methylseleno moieties of mixed (O,Se) acetals, we have recorded ^{1}H NMR spectra of one of these acetals, 1-methoxy-1-(methylseleno)heptane (**1a**), in the presence of titanium tetrachloride, or in the presence of tin tetrachloride, but in the absence of any nucleophile. It appears quite instructive to consider the observed spectral changes displayed in Chart 1 for the heteroatom linked methyl groups.

Both methyl signals are found to be affected by complexation in either case, but judging from the relative values of $\Delta\delta = \delta_{complex} - \delta_{free}$, it seems legitimate to conclude that preferential complexation occurs indeed between $TiCl_4$ and the methoxy group on one hand and between $SnCl_4$ and the methylseleno group on the other. Interestingly, very similar chemical shifts have been observed for the $SeCH_3$ groups when complexation of the (Se,Se) acetal 1,1-bis(methylseleno)heptane (**4a**) with the same Lewis acids was examined.[3m]

In spite of these preliminary observations and their implications concerning the selective formation of homoallylic ethers **2** or selenides **3**, we found that the course of the reaction of mixed acetals **1** with the allylmetal (Si or Sn) nucleophiles was not significantly modified by the nature of the Lewis acids used to activate the acetals (Scheme 1).

Thus, the two major products isolated from the great majority of the reactions tried were the homoallylic ethers **2** and the selenoacetals **4**, even when the most oxygenophilic (Lewis) acids, such as the proton, $TiCl_4$, or (trimethylsilyl)triflate (TMSOTf) (Scheme 1, entries 1–3), were used. In this series of experiments formation of homoallylic selenides **3** has been observed only in two cases (Scheme 1, entries 15 and 23). The behavior of titanium tetrachloride is particularly surprising when we recall that this Lewis acid did not induce reaction at all between selenoacetals and allylmetals.[3m] Predominant formation of homoallyl ethers **2** from (O,Se) acetals and the absence of reaction of (Se,Se) acetals in the presence of $TiCl_4$ might appear as a decisive argument in favor of the intermediacy of oxocarbenium ions in these reactions. The explanation would then be that even though preferential complexation by this Lewis acid occurs on the oxygen atom, one cannot exclude some interaction[6] with the methylseleno moiety (downfield by >0.7 ppm in the $TiCl_4$ complex of **1a** as compared to free **1a**, see Chart 1), which would be sufficient to allow the formation of the more stable oxocarbenium ion. In our opinion, this appealing argument is not satisfactory for two reasons. First, we have shown some time ago by a combination of *ab initio* calculations and experimental gas phase basicity measurements[7] that the difference in intrinsic stabilization between monochalcogen-substituted carbenium ions bearing OMe or SeMe groups is not greater than 1 kcal mol^{-1}, eventually in favor of the oxocarbenium ion. Consequently, both products **2** and **3** should be observed (as in entries 15 and 23, Scheme 1) through the competitive formation of seleno- and oxocarbenium ions. Second, if these ions were indeed implied in the reactions, they should form with increasing ease from (O,Se) acetals derived from aliphatic ketones and from aromatic carbonyls as compared to those derived from aliphatic aldehydes. Comparison of the results shown in Scheme 1, entries 1–8 with those of entries 13–14 and 15–18 does not support this: the homoallyl ethers **2** are seen to be formed even somewhat less efficiently from acetals **1b** and **1c** than from **1a**. On the contrary, entries 15 and 23 would suggest comparable stabilities for the OMe- and SeMe-substituted benzyl cations.

It is also remarkable in Scheme 1 that the nature of the nucleophilic allylmetal partner does not appear to play a significant role in these reactions, allyltrimethylsilane and the more nucleophilic allyltributylstannane[8] leading to essentially indistinguishable product distributions (compare entries 1–19 to 20–25). However, since we are not discussing rate data, one should not take this as an argument against an S_N2 type mechanism.

The results displayed in entries 9 and 10 of Scheme 1 ask for special comments since they show that the role of BCl_3 and BBr_3 in these experiments was not restricted to that of complexing Lewis acids; they participated in the reactions as reagents, the main products formed being 1-(methylseleno)-1-chloroheptane (**5a**) (50% yield) and 1-(methylseleno)-1-bromoheptane (**6a**) (80% yield) without any trace of the corresponding α-halo ethers or of the homoallylic ether **2a**. Obviously, exclusive coordination of the methoxy group of **1a** followed by nucleophilic substitution by halide (chloride or bromide) ions did take place. A closer look at these novel transformations led to the observations depicted in Scheme 2.

In sharp conrast to BF_3•OEt_2, boron trichloride and boron tribromide make it possible to transform the (O,Se) mixed acetal **1a** into α-halo selenides in very good yields.[9] Even though the latter are very labile compounds and their isolation in pure state is not easy, in the case of the crude bromide **6a** we succeeded in transforming it further into the homoallyl selenide **3a** in an acceptable 54% yield (Scheme 2, part c). Here again, the reaction proceeded with remarkable chemose-

(6) In fact, quite similar downfield ^{77}Se chemical shifts ($\Delta\delta(^{77}Se)$ = 120 ppm) have been observed upon complexation of selenoanisole with $TiCl_4$ and $SnCl_4$: Dieden, R.; Hevesi, L. *Bull. Magn. Reson.* **1989**, *11*, 193.

(7) Ösapay, K.; Delhalle, J.; Nsunda, K. M.; Rolli, E.; Houriet, R.; Hevesi, L. *J. Am. Chem. Soc.* **1989**, *111*, 5028.

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Scheme 1

1 2 3 4

1a: R^1 = nHex, R^2 = H
1b: R^1 = nHex, R^2 = Me
1c: R^1 = Ph, R^2 = H

M = $SiMe_3$, $SnBu_3$

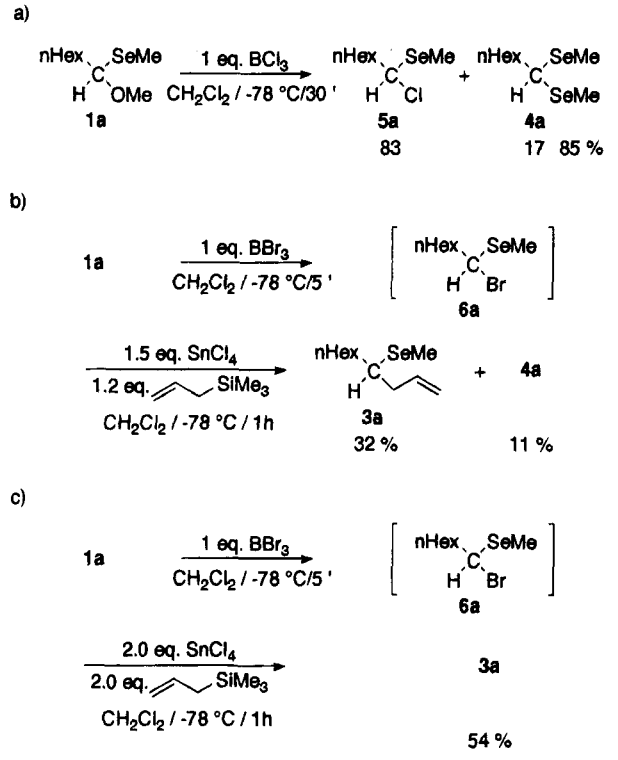
Entry	Acetal	M	Lewis Acid	Conditions	2	3	4
1	**1a**	$SiMe_3$	H_2SO_4	CH_2Cl_2/0 °C/2 h	29	0	37
2	**1a**	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/2 h	54	0	36
3	**1a**	$SiMe_3$	TMSOTf	CH_2Cl_2/-40 °C/4 h		no reaction	
4	**1a**	$SiMe_3$	TMSOTf	CH_3NO_2/0 °C/2 h		complex mixture [a]	
5	**1a**	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/2 h	55	0	18
6	**1a**	$SiMe_3$	$ZrCl_4$	CH_2Cl_2/-78 °C/2 h	26	0	30
7	**1a**	$SiMe_3$	2 eq. $AlCl_3$	CH_2Cl_2/-78 °C/3 h	24	0	24 [b]
8	**1a**	2 eq. $SiMe_3$	BF_3·OEt_2	CH_2Cl_2/-40 °C/2h->RT/15 h	40	0	38
9	**1a**	2 eq. $SiMe_3$	2 eq. BCl_3	CH_2Cl_2/-78 °C/ 4 h	0	0	20 [c]
10	**1a**	2 eq. $SiMe_3$	2 eq. BBr_3	CH_2Cl_2/-78 °C/4.5 h	0	traces	20 [d]
11	**1a**	$SiMe_3$	$AgClO_4$	CH_3NO_2/-40 °C/2 h	40	0	0
12	**1a**	$SiMe_3$	$AgClO_4$	CH_3NO_2/1 eq.$CaCO_3$/-40 °C/2 h	62	0	0
13	**1b**	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/2 h	33	0	18
14	**1b**	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/2 h	28	0	20
15	**1c**	$SiMe_3$	$TiCl_4$	CH_2Cl_2/-78 °C/2 h	20	23	22
16	**1c**	$SiMe_3$	$SnCl_4$	CH_2Cl_2/-78 °C/2 h	40	0	35
17	**1c**	$SiMe_3$	$ZrCl_4$	CH_2Cl_2/-78 °C/2 h	15	0	26
18	**1c**	$SiMe_3$	$AlCl_3$	CH_2Cl_2/-78 °C/2 h	52	0	45
19	**1c**	$SiMe_3$	$AgClO_4$	CH_3NO_2/1 eq.$CaCO_3$/-40 °C/2 h	42	0	0
20	**1a**	$SnBu_3$	$TiCl_4$	CH_2Cl_2/-78 °C/2 h	6	0	42
21	**1a**	$SnBu_3$	2 eq. $TiCl_4$	CH_2Cl_2/-78 °C/2 h	36	0	20
22	**1a**	$SnBu_3$	$SnCl_4$	CH_2Cl_2/-78 °C/2 h	20	0	7 [e]
23	**1c**	$SnBu_3$	$TiCl_4$	CH_2Cl_2/-78 °C/2h	20	10	30
24	**1c**	$SnBu_3$	BF_3·OEt_2	CH_2Cl_2/-40 °C/2 h	22	0	31
25	**1c**	$SnBu_3$	$SnCl_4$	CH_2Cl_2/-78 °C/2 h	36	0	30

a) Contains **4** but not **2** or **3**; b) Reaction mixture contains 22 % of unreacted **1a**; c) Reaction mixture also contains 10 % of unreacted **1a** and 50 % of **5a** (See also Scheme 2, entry a); d) Reaction mixture also contains 80 % of **6a** (See also Scheme 2b); e) About 10 % of **1a** remained unreacted.

lectivity; no trace of homoallylic bromide was formed. These observations suggest that the reactions of Scheme 2 may well represent a viable route from (O,Se) mixed acetals **1** to homoallyl selenides **3**, but at this stage it has not been explored further.

We have learned from our studies of the Lewis acid mediated reactions of (Se,Se) acetals with allyl metals that the best experimental procedure consisted of the addition of the allylmetal to a preformed cold mixture of the selenoacetal and the Lewis acid.[3m] In this way, precomplexation with the selenoacetal depressed the propensity of the Lewis acid to perform undesirable transmetalation side reactions with the allylmetal. Therefore, we have adopted the same procedure also for the present work; all the results of Scheme 1 have been obtained in this manner.

Scheme 2



It was, however, most intriguing that, in their study of the reactions of (OMe,SPh) acetals with allyl- and allenylstannanes, Otera and co-workers heavily insisted on the importance of the order of mixing the reagents. BF_3-OEt_2 or $TiCl_4$ added onto a mixture of (O,S) acetal and allyltributylstannane led with high selectivity to the corresponding homoallyl ether or homoallyl sulfide, respectively, whereas mixing the allylstannane with $TiCl_4$ first followed by the addition of the (O,S) acetal gave a mixture of products containing mainly homoallyl ether and (S,S) acetal and only a trace of homoallyl sulfide.[4b] The close similarity of this latter result with those of Scheme 1 prompted us to carry out the few control experiments gathered in Scheme 3.

First of all, it can be seen that in our hands too α-methoxy-α-(phenylthio)toluene (**7**) (compound **2d** in ref 4b), when mixed with allyltributylstannane followed by $TiCl_4$ at −78 °C, gave a 13:87 mixture of **2c** and **8** (Scheme 3, path a), a result quite comparable to what has been described.[4b] Surprisingly, the same experiment repeated using (O,S) acetal **9** led to a 70:30 mixture of **2c** and **10** in 40% yield accompanied by a large amount (40%) of (S,S) acetal (Scheme 3, path b). Assuming that the conclusion drawn from Chart 1 regarding the preferential complexation of the methoxy group of (O,Se) acetals by $TiCl_4$ can be extended to (O,S) acetals **7** and **9**, the results of Scheme 3, paths a and b argue against the intermediacy of sulfur-stabilized benzyl cations in these reactions. Indeed, taking into account the greater electron donating ability of the ethylthio group as compared to the phenylthio group,[10] the α-(ethylthio)benzyl cation would be expected to be more stable, hence to be formed faster than its phenylthio counterpart. Consequently, homoallylic sulfide **10** should be more favored in Scheme 3, path b than its analog **8** in Scheme 3, path a. Clearly, the reverse is observed.

Instead of going along the observations of Otera *et al.*, the results obtained under the same conditions for (O,Se) acetals **1c** and **11** (Scheme 3, paths c and d) confirm those shown in Scheme 1. In fact, homoallyl ether **2c** is now even more predominant in the product mixture than in Scheme 1, entry 23, and homoallyl selenide **12** is not detected in the reaction of (O,Se) acetal **11** (Scheme 3, path d).

For a correct appreciation of these results, it was important to establish the origin of homoallyl chloride **5c**. The experiments of Scheme 4 have been performed with this aim in mind.

While homoallyl ether **2c** was completely transformed (1 equiv of $TiCl_4/CH_2Cl_2$/−78 °C/1 h) into a mixture of the chloride **5c** and some polymeric material, homoallyl selenides **3c** and **12** were recovered unchanged after being exposed to the same reaction conditions. Thus, we can admit with reasonable confidence that homoallyl chloride **5c** formed in the reactions of **1c** and **11** (Scheme 3, paths c and d) arises from further transformation of the homoallyl ether **2c**, increasing thereby the actual chemoselectivity of these reactions in favor of the latter product.

Although we have not checked the origin of allylphenyl selenide **13** (Scheme 3, path d), it seems reasonable to attribute the formation of this compound to the reaction of excess allyltributyltin with some electrophilic phenylselenium species formed for example from diphenyl diselenide and $TiCl_4$.

In light of the recent detailed studies related to the mechanism and origin of stereoselectivity of substitution reactions of chiral (O,O) acetals,[1f,g,5] as well as on the basis of our own observations disclosed above, these apparently divergent results can be accommodated by the following considerations.

Starting with the cases of $TiCl_4$-promoted reactions of (O,Se) acetals **1** (Scheme 5), we expect complex **1A** to be thermodynamically more stable than complex **1B** (Chart 1). Therefore, **1A** should be present in the reaction mixtures at higher concentrations than **1B**. Each of these complexes undergoes dissociative activation into mixtures **1A′** and **1B′** of intimate ion pairs and seleno-/oxocarbenium ions upon reaction with the allylmetal nucleophile.

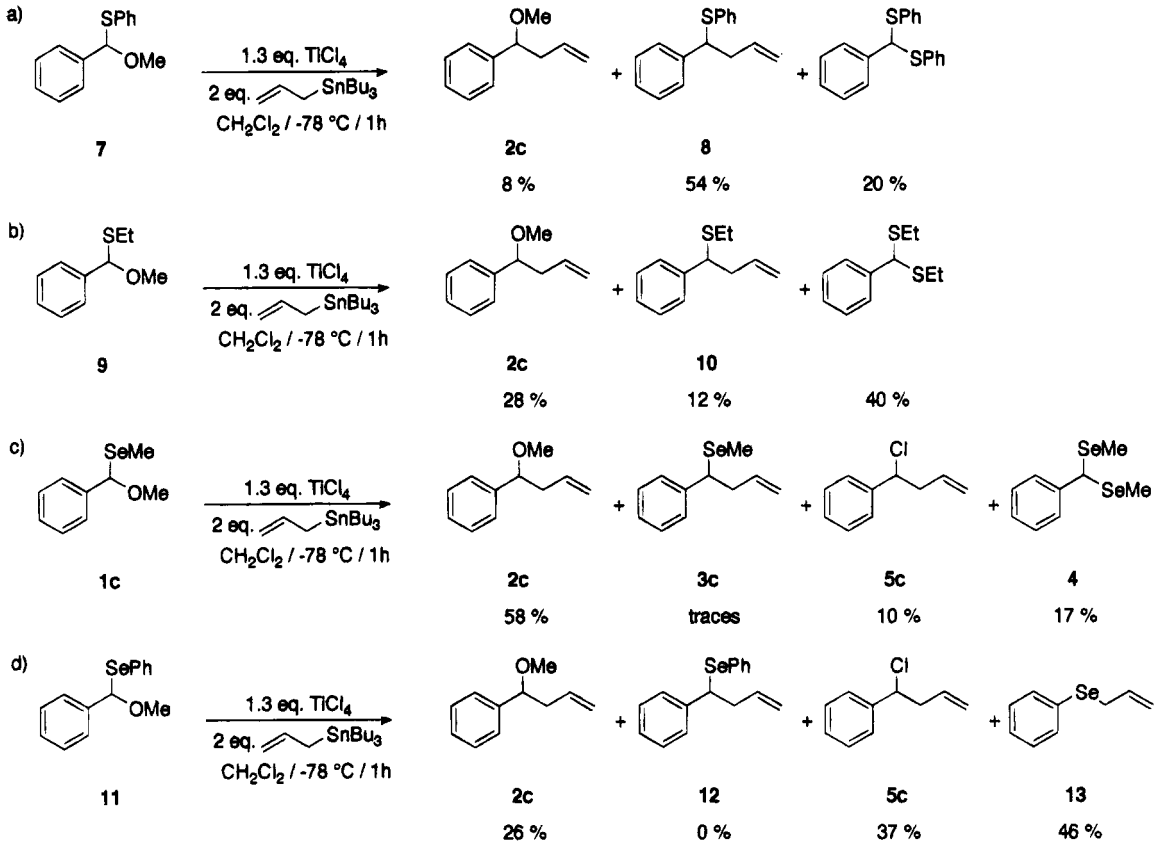
Our interpretation is that the product (**2** or **3**) forming selectivity is determined at this stage. As mentioned earlier, oxo- and selenocarbenium ions are not likely intermediates, so the products **2** and/or **3** should arise from S_N2 type attack of the allylmetal on **1B′**/**1B** or **1A′**/**1A**, respectively.

Undoubtedly, bond dissociation energies are important factors in determining the overall activation enthalpies of this kind of processes. Aliphatic C−Se bonds are approximately 25 kcal/mol weaker than aliphatic C−O bonds and weaker than aromatic C−Se bonds by about 10 kcal/mol.[11] Even if one assumes that formation of complexes **1A** and **1B** or of the intimate ion pairs **1A′** and **1B′** considerably reduces the difference in C−O and C−Se bond energies in these species, the still remaining differences may well be sufficient to translate into preferential C−Se bond cleavages and hence into the

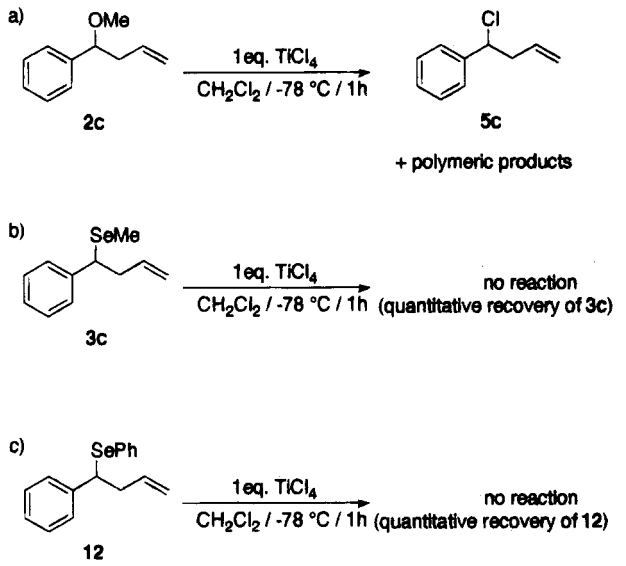
(10) This can be inferred from σ_p and σ_p^+ values of SMe and SPh groups, see for example: Exner, O. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 10.

(11) Batt, L. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, U.K., 1986; Vol. 1, p 157.

Scheme 3



Scheme 4



observed product distributions. Obviously, in view of such significant differences in activation energies, the greater thermodynamic stability of complex **1A** and its higher concentration do not influence the issue of the reactions very much.

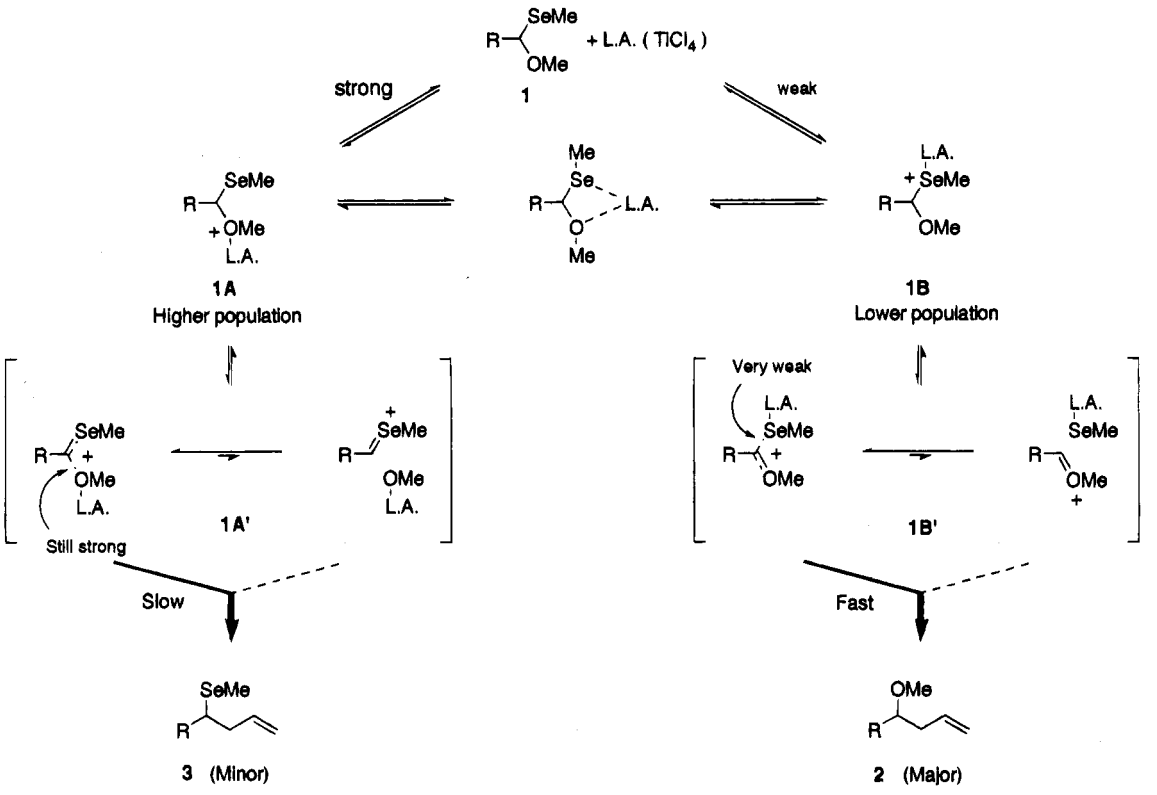
Product distributions obtained in the reactions of (O,S) acetals **7** and **9** can be rationalized similarly. Although the difference in the C–OMe and C–SPh bond energies is still close to 15–20 kcal/mol,[12] the reduced electron donating ability of the phenylthio group[10] gives rise to very weak complexation of this group by $TiCl_4$, so that the latter factor compensates the former one, and in the case of acetal **7** the homoallyl phenyl sulfide **8** largely predominates over the ether **2c** (Scheme 3, path a). The two factors appear more convergent in the case of acetal **9**, since the difference in bond dissociation energies of the C–OMe and C–SEt bonds is diminished to 7–10 kcal/mol and the ethylthio group is more strongly complexed. As a result, both homoallylic products **2c** and **10** are obtained in almost comparable quantities (Scheme 3, path b).

Observations pertinent to the present chemoselectivity problem have also been made recently by Kataoka and co-workers in their study of Lewis acid induced cyclization reactions of (O,Se) olefinic acetals in which the alkenyl chains are attached to the selenium atom.[13] In the presence of titanium tetrachloride[13a] no cyclized products could be isolated from the reactions of (OMe,-Se-alkenyl) acetals; instead, these acatals decomposed into dialkenyl diselenides. The desired cyclizations did take place when the methoxy group was replaced by the OCH_2CH_2OMe group in the (O,Se) acetals and using $TiCl_4$ or Et_2AlCl as Lewis acid.[13b] These results agree completely with our views (also expressed in ref 13b): in the former case both methoxy and Se-alkenyl groups are complexed, but because of the great difference in bond energies only the C–Se bond is broken, leading to exclusive formation (after air oxidation) of dialkenyl diselenides. However, in the case of MEM selenides, the presence of two oxygen atoms chelating $TiCl_4$ prevents any activation of the selenium moieties, so that C–O bond cleavage gives cyclized products.[13b]

(12) Takagi, W. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum Press: New York, 1978; p 231.

(13) (a) Yoshimatsu, M.; Fujimoto, M.; Shimizu, H.; Hori, M.; Kataoka, T. *Chem. Pharm. Bull.* **1993**, *41*, 1160. (b) Yoshimatsu, M.; Sato, T.; Shimizu, H.; Hori, M.; Kataoka, T. *J. Org. Chem.* **1994**, *59*, 1011.

Scheme 5



In conclusion, it appears that the concept of preferential complexation by Lewis acids of mixed chalcogen acetals based on the difference in hardness (softness) of the chalcogen atoms can lead to selective reactions with nucleophiles only in exceptional situations resulting either from a delicate balance between electronic effects influencing complexation and relative carbon–chalcogen bond energies or from structural effects allowing for tight binding of particular Lewis acids to one of the complexation sites exclusively.

Experimental Section

All reactions were carried out under argon, in septum-fitted glassware. Dry dicloromethane and nitromethane were obtained by distillation from P_2O_5; $SnCl_4$, $TiCl_4$, and $BF_3{\cdot}OEt_2$ were distilled prior to use. Lewis acids were purchased from Aldrich, Merck, or Acros Chimica and, except otherwise stated, were used without further purification. BCl_3 and BBr_3 were purchased as solutions in hexane or dichloromethane, respectively.

Synthesis of Mixed (O,Se) Acetals 1. The convenient method of Krief and co-workers[14a] has been used to prepare the starting mixed acetals **1a-c**.

General Procedure for the Synthesis of Mixed (O,Se) Acetals 1. Into a solution of 20 mmol of the (O,O) acetal in 20 mL of dry CH_2Cl_2 at −78 °C were successively introduced 20 mmol of MeSeH and 2 mmol of $BF_3{\cdot}OEt_2$. After reaction completion (1.5 → 2h, monitored by TLC), the reaction mixture was poured into a 30 mL 2 N KOH solution and extracted with ether. The organic phase was washed with brine, dried over $MgSO_4$, and evaporated. The crude products have been purified by distillation under vacuum.[15]

(14) (a) Krief, A.; Hobe, M.; Badaoui, E.; Dumont, W.; Nazih, A. *Synlett.* **1993**, 707. This paper provides a brief review of the most frequently used other methods. For additional examples, see: (b) Hevesi, L.; Piquard, J.-L.; Wauthier, H. *J. Am. Chem. Soc.* **1981**, *103*, 870. (c) Nishiyama, Y.; Aoyama, S.; Hamanaka, S. *Phosphorus, Sulfur Silicon* **1992**, *67*, 267. (d) Reference 13a.

(15) Mixed (O,Se) acetals can also be purified by column or PLC (preparative layer chromatography).

1-(Methylseleno)-1-methoxyheptane (1a): bp (0.5 Torr) 64–66 °C, 72% yield. ^{1}H NMR (90 MHz, $CDCl_3$, ppm): 0.88 (3H, t, J = 7 Hz), 1.1–1.5 (8H, m), 1.75–2.15 (2H, m), 1.93 (3H, s), 3.35 (3H, s), 4.61 (1H, t, J = 7 Hz). ^{13}C NMR (22.5 MHz, $CDCl_3$, ppm): 0.19, 13.94, 22.49, 26.62, 28.74, 31.65, 36.90, 56.22, 84.71. ^{77}Se NMR (17.5 MHz, $CDCl_3$): 145.6 ppm. MS (EI, 70 eV, m/z, rel intensity): 129 (20, M − SeMe), 97 (30, 129 − CH_3OH), 71 (96), 55 (100). Anal. Calcd for $C_9H_{20}OSe$: C, 48.43; H, 9.03. Found: C, 49.12; H, 9.07.

2-(Methylseleno)-2-methoxyoctane (1b): SiO_2 column, pentane, 68% yield. ^{1}H NMR (90 MHz, $CDCl_3$, ppm): 0.87 (3H, t, J = 7 Hz), 1.1–1.6 (8H, m), 1.53 (3H, s), 1.65–2.0 (2H, m), 1.82 (3H,s), 3.21 (3H, s). ^{13}C NMR (22.5 MHz, $CDCl_3$, ppm): 1.3, 14.0, 22.6, 24.3, 25.6, 29.4, 31.7, 41.0, 51.3, 87.9. ^{77}Se (17.5 MHz, $CDCl_3$): 199.4 ppm.

α-(Methylseleno)-α-methoxytoluene[14a] (1c): bp (0.1 Torr) 68–70 °C, 56% yield. ^{1}H NMR (90 MHz, $CDCl_3$, ppm): 1.77 (3H, s), 3.48 (3H, s), 5.79 (1H, s), 7.1–7.5 (5H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$, ppm): 1.46, 57.15, 83.52, 125.57, 127.20, 127.91, 140.65. ^{77}Se NMR (17.5 MHz, $CDCl_3$): 249.9 ppm. MS (EI, 70 eV, m/z, rel intensity): 185 (85, M − OMe), 169 (35, 185 − CH_4), 170 (53, 185 − CH_3), 121 (13, M − SeMe), 104 (100), 89 (62), 77 (53). Anal. Calcd for $C_8H_{11}OSe$: C, 50.00; H, 5.55. Found: C, 50.12; H, 5.53.

General Procedure for the Reactions of Scheme 1. Into a solution of 1.1 mmol of Lewis acid in 2 mL of dry CH_2Cl_2 cooled under argon to the desired temperature were successively introduced 1.0 mmol of (O,Se) acetal **1** dissolved in 2 mL of CH_2Cl_2 and 1.2 mmol of the allylmetal dissolved in the same solvent, in that order. After appropriate reaction time (monitored by TLC), the cooling bath was removed, the reaction was rapidly quenched by addition of 10 mL of saturated aqueous $NaHCO_3$, and the mixture was extracted with ether. The organic phase was washed with brine, dried over $MgSO_4$, and evaporated. The so-obtained crude product was resolved into its components by preparative layer chromatography (PLC, SiO_2, eluent pentane/ether, 96/4, v/v).

4-Methoxy-1-decene (2a). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 0.88 (3H, t, J = 7 Hz), 1.20–1.50 (10H, m), 2.23 (2H, m), 3.20 (1H, m), 3.33 (3H, s), 5.0–5.1 (2H, m), 5.7–5.9 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 14.1, 22.6, 25.3, 29.5, 31.8, 33.3, 38.7, 56.5, 80.5, 116.7, 135.0. MS (EI, 70 eV, m/z,

rel intensity): 129 (22, M − C_3H_5), 97 (40, 129 − CH_3OH), 85 (13), 69 (13), 55 (100).

4-Methoxy-4-methyl-1-decene (2b). ^1H NMR (90 MHz, $CDCl_3$, ppm): 0.97 (3H, t, J = 7 Hz), 1.18 (3H, s), 1.20−1.60 (10H, m), 2.31 (2H, d, J = 7 Hz), 3.26 (3H, s), 4.95−5.25 (2H, m), 5.60−6.15 (1H, m). ^{13}C NMR (22.5 MHz, $CDCl_3$, ppm): 14.1, 22.6, 22.7, 23.3, 29.9, 31.9, 37.4, 42.3, 48.8, 76.3, 117.2, 134.5.

1-Methoxy-1-phenyl-3-butene[16] **(2c).** ^1H NMR (90 MHz, $CDCl_3$, ppm): 2.25−2.70 (2H, m), 3.21 (3H, s), 4.16 (1H, t, J = 6.9 Hz), 7.40 (5H, br s). ^{13}C NMR (22.5 MHz, $CDCl_3$, ppm): 42.5, 56.5, 83.6, 116.8, 126.6, 127.5, 128.3, 134.7, 141.6.

4-(Methylseleno)-1-decene[17] **3a.** ^1H NMR (60 MHz, $CDCl_3$, ppm): 0.88 (3H, t, J = 6 Hz), 1.08−1.75 (10H, m), 1.93 (3H, s), 2.42 (2H, m), 2.8 (1H, m), 4.90−5.20 (2H, m), 5.8−6.0 (1H, m). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 2.3, 14.0, 22.6, 27.6, 29.1, 31.8, 34.7, 39.7, 41.1, 116.4, 136.4.

4-(Methylseleno)-4-methyl-1-decene[17] **(3b).** ^1H NMR (60 MHz, $CDCl_3$, ppm): 0.88 (3H, t, J = 6 Hz), 1.08−1.68 (10H, m), 1.88 (3H, s), 2.33 (2H, dd, J_1 = 6 Hz, J_2 = 0.5 Hz), 4.82−5.28 (2H, m), 5.53−6.23 (1H, m).

1-(Methylseleno)-1-phenyl-3-butene (3c). ^1H NMR (60 MHz, $CDCl_3$, ppm): 1.58 (3H, s), 2.51−2.84 (2H, m), 3.86 (1H, t, J = 8 Hz), 4.83−5.05 (2H, m), 5.35−6.33 (1H, m), 7.21 (5H, m). MS (EI, 70 eV, m/z): 226 ($M^{+\cdot}$), 185 (M − C_3H_5), 131 (M − CH_3Se). Anal. Calcd for $C_{11}H_{14}Se$: C, 58.67; H, 6.27. Found: C, 58.14; H, 6.30.

Synthesis of 1-Chloro-1-(methylseleno)heptane (5a). To a cooled (−78 °C) solution of boron trichloride (1 mmol, 1 M in hexane) in 2 mL of dry dichloromethane was added another solution of 1-methoxy-1-(methylseleno)heptane (**1a**, 226 mg, 1 mmol) in 2 mL of the same solvent dropwise by means of a syringe. After 15 min of reaction at this temperature, TLC (SiO_2, eluent pentane/ether, 95/5, v/v) monitoring indicated complete consumption of **1a** and the appearence of two new spots (R_f = 0.5 and 1.0). The reaction mixture was then poured on a mixture of 30 mL of ether and 20 mL of 1 M aqueous KOH. Extraction, separation, and drying over $MgSO_4$ of the organic phase followed by evaporation of the solvents led to 204 mg (85%) of an 83/17 mixture of products **5a** and **4a**.

^1H NMR (90 MHz, $CDCl_3$, ppm) of **4a**: 0.88 (3H, t, J = 6 Hz), 1.1−1.8 (8H, m), 1.9−2.3 (2H, m), 2.02 (3H, s), 3.91 (1H, t, J = 6 Hz).

^1H NMR (90 MHz, $CDCl_3$, ppm) of **5a**: 0.88 (3H, t, J = 6 Hz), 1.1−1.8 (8H, m), 1.9−2.3 (2H, m), 2.24 (3H, s), 5.12 (1H, t, J = 6 Hz).

Synthesis of 1-Bromo-1-(methylseleno)heptane (6a). Following the same procedure as above for **5a**, the essentially pure bromo analog **6a** was isolated similarly (220 mg, 84% yield) after 3 h of reaction at −78 °C.

^1H NMR (90 MHz, $CDCl_3$, ppm) of **6a**: 0.88 (3H, t, J = 6 Hz), 1.1−1.7 (8H, m), 2.0−2.3 (2H, m), 2.23 (3H,s), 5.18 (1H, t, J = 6 Hz).

Synthesis of 3a from 6a. To a solution of 520 mg (2 mmol) of tin tetrachloride in 2 mL of dry dichloromethane under argon and cooled to −78 °C were added slowly and successively 275 mg (1 mmol) of crude **6a** diluted in 2 mL of CH_2Cl_2 and 230 mg (2 mmol) of allyltrimethylsilane dissolved in 1 mL of CH_2Cl_2. After 1 h the reaction was quenched with 20 mL of 5% aqueous HCl and the solution was extracted with ether. The organic phase was dried over $MgSO_4$, and the solvents were evaporated to give 480 mg of crude product. Purification (PLC, SiO_2, eluent pentane/ether, 97/3, v/v) led to 126 mg of **3a**, 54% yield.

Allylation of α-Methoxy-α-(phenylthio)toluene (7). In accordance with the literature procedure,[4b] a dichloromethane (2 mL) solution of 246 mg (1.3 mmol) of titanium tetrachloride was slowly injected into a solution containing 230 mg (1 mmol) of mixed acetal **7** and 670 mg (2 mmol) of allyltributylstannane in 5 mL of dry dichloromethane under argon and cooled to −78 °C. After 1 h the reaction was quenched with 30 mL of 2 N KOH and the solution was extracted with ether. The organic layer was washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum to give 717 mg of crude product. Chromatographic purification (PLC, SiO_2, eluent pentane/ether, 95/5, v/v) led to 127 mg (53% yield) of 1-(phenylthio)-1-phenyl-3-butene (**8**), as well as to 75 mg of a 1/2.5 mixture of homoallylic ether **2c** (8% yield) and α,α-bis-(phenylthio)toluene (20% yield).

^1H NMR (90 MHz, $CDCl_3$, ppm) of **8**: 2.7 (2H, d, J = 6.8 Hz), 4.19 (1H, t, J = 7.5 Hz), 4.9−5.2 (2H, m), 5.45−5.95 (1H, m), 7.16 (10H, br s).

^{13}C NMR (22.5 MHz, $CDCl_3$, ppm) of **8**: 40.4, 53.1, 117.1, 127.0, 127.1, 127.8, 128.2, 128.5, 128.6, 132.4, 135.1, 141.4.

Allylation of α-methoxy-α-(ethylthio)toluene (9). Following the above procedure, 182 mg (1 mmol) of α-methoxy-α-(ethylthio)toluene (**9**) and 668 mg (2 mmol) of allyltributylstannane were reacted in the presence of 246 mg (1.3 mmol) of titanium tetrachloride at −78 °C for 1 h. Aqueous 2 N KOH workup led to 760 mg of crude product which gave upon chromatographic purification (PLC, SiO_2, eluent pentane/ether, 95/5, v/v) 24 mg (12%) of 1-(ethylthio)-1-phenyl-3-butene (**10**), 46 mg (28%) of 1-methoxy-1-phenyl-3-butene (**2c**), and 84 mg (40%) of α,α-bis(ethylthio)toluene.

^1H NMR (400 MHz, $CDCl_3$, ppm) of **10**:[18] 1.17 (3H, t, J = 7.3 Hz), 2.2−2.4 (2H, m), 2.64 (2H, q, J = 7.3 Hz), 3.88 (1H, t, J = 7.6 Hz), 5.01 (1H, d, J = 10.2 Hz), 5.06 (1H, d, J = 17.1 Hz), 5.74 (1H, tdd, J_1 = 7.6 Hz, J_2 = 10.2 Hz, J_3 = 17.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, ppm) of **10**: 14.4, 24.9, 40.9, 49.2, 116.8, 127.0, 127.8 128.3 135.4, 142.2.

Allylation of α-methoxy-α-(phenylseleno)toluene (11). Following the above procedure, 254 mg (1 mmol) of α-methoxy-α-(phenylseleno)toluene (**11**) and 668 mg (2 mmol) of allyltributylstannane were reacted in the presence of 246 mg (1.3 mmol) of titanium tetrachloride at −78 °C for 1 h. Aqueous 2 N KOH workup led to 930 mg of crude product which gave upon chromatographic purification (PLC, SiO_2, eluent pentane/ether, 96/4, v/v) 42 mg (26%) of 1-methoxy-1-phenyl-3-butene (**2c**), 60 mg (37%) of 1-chloro-1-phenyl-3-butene (**5c**), and 91 mg (46%) of allyl phenyl selenide (**13**).

^1H NMR (90 MHz, $CDCl_3$, ppm) of **5c**:[19] 2.81 (2H, t, J = 7 Hz), 5.84 (1H, t, J = 7 Hz), 4.9−5.2 (2H, m), 5.5−6.0 (1H, m), 7.1−7.7 (5H, m).

^1H NMR (90 MHz, $CDCl_3$, ppm) of **13**: 3.45 (2H, d, J = 8 Hz), 4.6−5.1 (2H, m), 5.5−6.3 (1H, m), 7.0−7.6 (5H, m).

Reaction of 1-Methoxy-1-phenyl-3-butene (2c) with $TiCl_4$. A dichloromethane (2 mL) solution of 380 mg (2 mmol) of $TiCl_4$ was slowly injected into a solution of 324 mg (2 mmol) of 1-methoxy-1-phenyl-3-butene (**2c**) in 3 mL of the same solvent cooled to −78 °C. TLC monitoring of the reaction showed the disappearence of **2c** in favor of a new, less polar compound. After 1 h of reaction, the mixture was poured on 20 mL of 2 N KOH and worked up in the usual manner to give 247 mg of crude, polymer containing product, from which 38 mg (12%) of 1-chloro-1-phenyl-3-butene (**5c**) could be isolated by PLC (SiO_2, eluent pentane/ether, 95/5, v/v) purification.

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