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Quasi-Concerted Allylic Rearrangement in the Reaction of Allylic Chlorides with Methyltin Tris(methanethiolate)

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trans-6-Chloro-4-decene (4), 3-chloro-1-heptene (7), and *trans*-1-chloro-2-heptene (9) are converted quantitatively into allylic methyl sulfides upon treatment with a molar equivalent of methyltin tris(methanethiolate) at 70 °C in benzene–dichloromethane. Unlike the reactions of sodium thiolates with straight chain allylic chlorides, these nucleophilic displacements are accompanied by very significant amounts of allylic rearrangement, with the yields of rearranged sulfide being 78% and 100% for 4 and 7, respectively. In the case of 9, the yield of rearranged product drops from 33% to 25% when the extent of conversion increases from 40% to 100%. However, all of the product sulfides are stable under the reaction conditions, and the reactions seem to occur without concomitant dehydrochlorination or isomerization of the starting chlorides. Other salient features of these reactions are their autoaccelerating rates, a chloride reactivity order like that observed for S_N1 solvolysis, the production of internal double bonds that are exclusively trans, and the failure of methanethiol to react with 4 in a control experiment. An attractive reaction mechanism, not yet established conclusively, involves the discharge of unsymmetrical (allylic cation)$MeSn(SMe)_nCl^-_{4-n}$ ion pairs (n = 1–3) via MeS ligand transfer. The implications of this investigation for the thermal stabilization of poly(vinyl chloride) are considered briefly, and the ^{13}C NMR chemical shifts of several allylic chlorides and methyl sulfides are used to derive parameters that can be employed for shift predictions.

Organotin(IV) thiolates and carboxylates have been used commercially for many years as thermal stabilizers for poly(vinyl chloride) (PVC).[1] Thus it is not surprising that the mechanism by which they operate has attracted much attention.[1a,2] As a result of the numerous investigations that have been concerned with this problem, excellent evidence has become available to show that one of the principal functions of these additives is to deactivate PVC structural defects having relatively low thermal stabilities.[1a,2a] Defects containing allylic halogen are likely to be important in this regard,[2a,3] and a reasonable means for their eradication is depicted in eq 1. Initially proposed

$$\text{—CH=CH—CHCl} \xrightarrow{R_nSnY_{4-n}} \text{—CH=CH—CHY—} \qquad (1)$$

$$R = \text{alkyl};\ Y = \text{thiolate or carboxylate};\ n = 0\text{–}3$$

by Frye et al.[4] for R_2SnY_2 stabilizers, this simple displacement has now been observed in several studies where dialkyltin(IV) compounds and model allylic chlorides were allowed to react.[5]

Some investigators have been concerned with the possibility of allylic rearrangement in reaction 1.[4b,5a,c–f] Such a rearrangement was detected first by Ayrey et al.,[5c,d] who studied the reactions of 3-chloro-1-butene and 1-chloro-2-butene with some di-*n*-alkyltin dithiolates and with di-*n*-butyltin diacetate in sealed tubes at 180 °C. When the dithiolates were used, each of the chlorobutenes gave 1-butene-3-thiolate and 2-butene-1-thiolate in ratios that were about the same in every case (~10–20:80–90, respectively) and were said to be similar to those observed in earlier S_N1 solvolysis studies with the same chlorobutenes.[5c,d] These results were considered to be indicative of an allylic cation intermediate in all of the dithiolate reactions.[5c,d] In the experiments with the tin(IV) diacetate, each chlorobutene again yielded the expected products (3-acetoxy-1-butene and 1-acetoxy-2-butene) in ratios that were roughly comparable (ca. 1:1).[5c,d] However, because these ratios were quite different from those obtained with the tin(IV) dithiolates, the authors concluded that the carbocation pathway was not being traversed exclusively (if at all) in the diacetate displacements and that the mechanisms of these reactions were obscure.[5c,d] Interestingly, the findings of Ayrey et al.[5c,d] diverge remarkably from those of some other researchers,[5e] who detected no rearrangement whatsoever in the reaction of 3-chloro-1-pentene with di-*n*-butyltin dilaurate in a sealed ampule at 200 °C. Instead, these workers[5e] reported the formation of 3-(lauroyloxy)-1-pentene in almost quantitative yield. The most recent study of reaction 1 seems to be that of Michel et al.,[5f] who investigated the action of dimethyltin bis(methyl thioglycolate) upon mixtures containing different proportions of 4-chloro-2- and 2-chloro-3-hexene. At ca. 100 °C, equimolar amounts of the corresponding allylic thiolates were produced in every experiment, a result which led to the conclusion that these substances had been formed entirely from an allylic cation progenitor.[5f]

An aspect of these earlier studies that, at least to us, has been surprising is that none of them has revealed a bias toward allylic rearrangement in reaction 1. The organotin reagents used undoubtedly have Lewis acid character,[6] and the reaction rate depends directly upon their concentrations.[5a] Thus it would not be unreasonable to suppose that the reaction might proceed to a significant extent by way of an intermediate complex (or transition state) such as 1 (later we discuss the involvement of analogous species in which some of the Y groups are replaced by Cl). Conversion of 1 into products could occur in a completely concerted fashion (eq 2) or via an ion pair intermediate (3) according to eq 3 and 4, and both routes might well be

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(1) For recent reviews, see: (a) Ayrey, G.; Poller, R. C. *Dev. Polym. Stab.* **1980**, *2*, 1. (b) Nass, L. I. *Encycl. PVC* **1976**, *1*, 295.

(2) (a) Starnes, W. H., Jr. *Dev. Polym. Degradation* **1981**, *3*, 135 and references cited therein. (b) Nass, L. I. *Encycl. PVC* **1976**, *1*, 271 and references cited therein.

(3) Braun, D. *Dev. Polym. Degradation* **1981**, *3*, 101. Starnes, W. H., Jr.; Schilling, F. C.; Plitz, I. M.; Cais, R. E.; Freed, D. J.; Hartless, R. L.; Bovey, F. A. *Macromolecules* **1983**, *16*, 790. Hjertberg, T.; Sörvik, E. M. *Polymer* **1983**, *24*, 685.

(4) (a) Frye, A. H.; Horst, R. W.; Paliobagis, M. A. *J. Polym. Sci., Part A* **1964**, *2*, 1765. (b) Frye, A. H.; Horst, R. W.; Paliobagis, M. A. *Ibid.* **1964**, *2*, 1801.

(5) (a) Klemchuk, P. P. *Adv. Chem. Ser.* **1968**, *No. 85*, 1. (b) Onozuka, M.; Asahina, M. *J. Macromol. Sci., Rev. Macromol. Chem.* **1969**, *3*, 235. (c) Ayrey, G.; Poller, R. C.; Siddiqui, I. H. *J. Polym. Sci., Part B* **1970**, *8*, 1. (d) *J. Polym. Sci., Part A-1* **1972**, *10*, 725. (e) Suzuki, T.; Takakura, I.; Yoda, M. *Eur. Polym. J.* **1971**, *7*, 1105. (f) Michel, A.; Guyot, A.; Nolle, D. *Polym. Degradation Stab.* **1980**, *2*, 277.

(6) Brecker, L. R. *Pure Appl. Chem.* **1981**, *53*, 577.

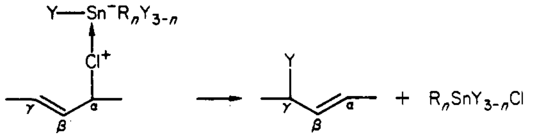
0022-3263/84/1949-2758$01.50/0

Table I. ^{13}C Chemical Shifts of Allylic Chlorides and Allylic Methyl Sulfides

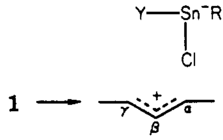
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3S
	δ,[a] ppm (±0.05) vs. Me_4Si										
4	13.62	22.23[b]	34.06	133.18	131.44	63.61	38.73	28.87	22.23[b]	13.96	
11[c]	13.51	19.91	41.06	63.34	131.21	133.44	31.72	31.20	22.23	13.91	
7	116.23	138.87	63.16	38.05	28.60	22.15	13.92				
9	45.52	125.90	136.22	31.79	31.03	22.23	13.92				
6	13.96 (13.81)[d]	22.87	34.33[b]	131.74	131.40	49.69	34.33[b]	29.66	22.53	13.96 (13.81)[d]	13.96 (13.81)[d]
5	13.81 (13.96)[d]	20.64	36.76	49.43	131.14	131.93	31.94[b]	31.94[b]	22.27	13.81 (13.96)[d]	13.81 (13.96)[d]
10	114.90	139.10	50.41	33.72	29.55	22.50	13.92 (13.73)[d]				13.73 (13.92)[d]
8	36.08	125.60	133.87	31.94	31.67	22.23	13.92				14.23

[a] In $CDCl_3$ solution at ca. 30 °C. [b] Not resolved. [c] *trans*-4-Chloro-5-decene. [d] Possible alternative assignment.

expected to lead to the preferred formation of the rearranged product, **2**.[7]



1 **2** (2)



3 (3)

$$\mathbf{3} \longrightarrow \mathbf{2} + R_nSnY_{3-n}Cl \qquad (4)$$

This prediction follows by analogy with the observations that have been made, for example, on the "S_Ni'" process by which allylic chlorosulfites decompose.[7b,d–g] This decomposition may be truly concerted (an authentic S_Ni' pathway), or it may proceed by an S_N1' mechanism involving an unsymmetrical (and rigidly oriented) carbocation/$ClSO_2^-$ ion pair.[7b,d–g] Whatever its mechanism actually is in any specific instance, the decomposition does have a propensity for producing a preponderant amount of rearranged allylic chloride,[7b,d–g] and cases have, in fact, been reported wherein the rearrangement is essentially complete (e.g., eq 5 and 6).[7g]

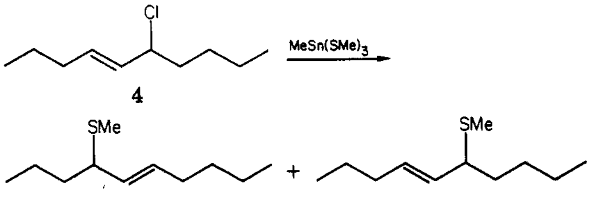
$$CH_3CH{=}CHCH_2OSOCl \xrightarrow[-SO_2]{\text{ether}} CH_3CClHCH{=}CH_2\ (99\%) \qquad (5)$$

$$CH_3C(OSOCl)HCH{=}CH_2 \xrightarrow[-SO_2]{\text{ether}} CH_3CH{=}CHCH_2Cl\ (100\%) \qquad (6)$$

In connection with other studies of the chemistry of monoalkyl organotins,[8] we have had occasion to examine the regiospecificities of the reactions of some simple allylic chlorides with methyltin tris(methanethiolate). Reported here are the results of this brief investigation, which have shown that rearrangement is, indeed, a predominant feature of reaction 1 in certain cases.

Results and Discussion

All of the organotin reactions were carried out in sealed NMR tubes at 70 °C by using equimolar amounts of reactants and with benzene-d_6–dichloromethane-d_2 as solvent, and the progress of these experiments was monitored periodically (though not continuously) by ^1H NMR measurements (see Experimental Section for details). After 0.2_5 h, $MeSn(SMe)_3$ and *trans*-6-chloro-4-decene (**4**) had reacted to only a minor extent (ca. 5%), but their reaction was 80–90% complete at 0.5 h and quantitative at 1.0 h. The ^{13}C NMR spectrum (see Table I) of the final product mixture showed that the trans allylic sulfides **5** and **6** had been formed (eq 7) in a ratio of about 3.5 to 1, respectively, and the same ratio was observed after 3.0 h in another run.[9] These results show that the sulfides were stable under the reaction conditions, for if they had been equilibrating, their ratio should have tended toward a value of ca. 1:1 with increasing reaction time.



(7)

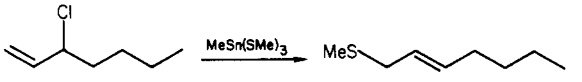
In order to investigate the possibility that **5** and **6** had been formed indirectly via the mechanism of eq 8 and 9

$$HCl + MeSn(SMe)_3 \rightarrow MeSn(SMe)_2Cl + MeSH \qquad (8)$$

$$\mathbf{4} + MeSH \rightarrow \mathbf{5} + \mathbf{6} + HCl \qquad (9)$$

(which would require only a catalytic amount of HCl),[5f] **4** and 2.6 equiv of methanethiol were subjected to the usual reaction conditions for 3.0 h in the absence of the organotin. This experiment afforded no detectable sulfide products.

The tendency to react with rearrangement was even greater in the case of 3-chloro-1-heptene (**7**), which was



7 **8** (10)

converted quantitatively into sulfide **8** (eq 10) under our standard conditions. This reaction was much slower than that of **4**, but in accord with that reaction, it exhibited autocatalysis, with conversions of about 0%, 50%, and 100% being observed, for example, after 3 h, 1 day, and 2 days, respectively.

Lastly, we examined the reaction of the organotin with a primary allylic chloride, *trans*-1-chloro-2-heptene (**9**), which proved to be less reactive than its secondary isomer, **7**. With **9** the extents of conversion were ca. 0%, 40%, and 100% after 2, 3, and 4 days, respectively, a trend which,

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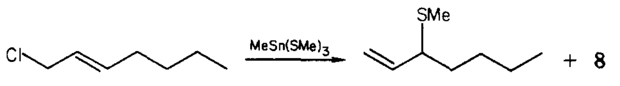
(7) For reviews of nucleophilic substitution and rearrangement in allylic systems, see: (a) Magid, R. M. *Tetrahedron* **1980**, *36*, 1901, 3326. (b) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; pp 303–307. (c) DeWolfe, R. H. *Compr. Chem. Kinet.* **1973**, *9*, 417. (d) Mackenzie, K. *Chem. Alkenes* **1964**, 387. (e) DeWolfe, R. H.; Young, W. G. *Ibid.* **1964**, 681. (f) de la Mare, P. B. D. *Mol. Rearrangements* **1963**, *1*, 27. (g) DeWolfe, R. H.; Young, W. G. *Chem. Rev.* **1956**, *56*, 753.

(8) Katz, H. E.; Starnes, W. H., Jr. *Macromolecules*, in press.

(9) The mixtures of **5** and **6** successfully resisted all attempts to analyze them by VPC or ^1H NMR.

as before, is indicative of significant autocatalysis. At 40% conversion, the product sulfides, **10** and **8** (eq 11), were



9 **10**

(11)

present in a ratio of 1:2, respectively (as determined by integration of the vinyl proton NMR signals), but this ratio was observed to be 1:3 when the reaction was complete, a change that appears to be greater than the possible range of experimental error. Such a change is unlikely to have resulted from the isomerization of **10** into **8**, since the 1:3 mixture remained intact when it was treated for 90 h, under our usual conditions, with 0.3 mol equiv of $MeSnCl_3$, which is the strongest Lewis acid that one could reasonably expect to be present in the $MeSn(SMe)_3$ reaction mixture.[6,10] It might be argued that $MeSnCl_3$ caused no detectable isomerization because it was simply catalyzing the interconversion of an equilibrium (1:3) mixture of **8** and **10**. However, this possibility was excluded by another control experiment, which showed that sulfide **8** was stable when it was exposed to the action of $MeSnCl_3$ (1.3 mol equiv) for 90 h.

Many allylic substitution reactions have several possible mechanisms that are difficult to disentangle.[7a,b,d-g] Our reactions with $MeSn(SMe)_3$ are no exception, and more work obviously will be needed if their mechanisms are to be well understood. Nevertheless, some important features of these mechanisms can be deduced from the results already in hand.

As was noted above, methanethiol is unlikely to have been involved in the reaction with chloride **4**. Its involvement in our other reactions seems improbable as well, in view of its unreactivity toward **4**, and because its characteristic odor was not detected in the experiments with the other chlorides. Moreover, its formation (eq 8) must be preceded by dehydrochlorination, whereas our final and interim NMR spectra contained no evidence for the presence of the dienes that would have resulted from such a process. These spectra also failed to reveal any intermediate or final products resulting from allylic rearrangement of the starting chlorides or from the trans-to-cis isomerization of double bonds. In fact, the product sulfides appear to be wholly unreactive under the conditions that were used. Since the reaction mixtures were examined only intermittently and our estimated detection level for byproducts is only ca. 5%, it is possible that such products would be revealed by studies that were more intensive. However, all of the information available thus far suggests that reactions other than 1 are unimportant in these systems.

In the reaction with chloride **4**, the product ratio clearly is inconsistent with the exclusive operation of a mechanism involving a kinetically free allylic cation. Such a mechanism should lead to the formation of equal amounts of **5** and **6**, by analogy with the results of Michel et al.[5f] The observed preponderance of **5** can only be explained by the incursion of a mechanism that is *quasi-concerted*, in that its resultant regiospecificity would be consistent with concurrent C–Cl cleavage, C–SMe creation, and migration of the double bond. With **7** this mechanism seems to be unaccompanied by any others, since here a free cation should have produced at least a minor amount of **10**. On the other hand, if solvolysis results for similar substrates[7e,g] were the only mechanistic criteria, one might conclude that the product ratios found with **9** do not require quasi-concertedness. For **9**, any mechanism leading to allylic rearrangement would, of course, be rendered less likely by the contrathermodynamic emplacement of the incipient double bond and by steric factors favoring nucleophilic attack upon the terminal carbon.

A complicating feature of all of our organotin reactions is that the tin reagent is changing as the reactions proceed. The initial product containing tin should be $MeSn(SMe)_2Cl$ in all cases, but other studies[10b,c] very strongly suggest that this species would exist in equilibrium with $MeSn(SMe)Cl_2$ and $MeSnCl_3$. The Lewis acidities of the tin compounds are expected to increase in the following order: $MeSn(SMe)_3 < MeSn(SMe)_2Cl < MeSn(SMe)Cl_2 < MeSnCl_3$.[10a] Hence, the net acidity of the tin reagent should increase continuously with increasing conversion. This increase can account for the autoacceleration of all of our reactions with $MeSn(SMe)_3$, since enhanced reactivity (in reaction 1) with increasing Lewis acidity can be inferred from the analogous behavior of dialkyltin(IV) compounds.[5a,f] On the other hand, one might expect to observe a lowered tendency for quasi-concerted MeS transfer when fewer MeS ligands are present. This effect could have contributed to the suppression of the quasi-concerted mechanism for **9**, since **9** was less reactive than the other chlorides studied, and a relatively large proportion of its reaction may thus have involved the more reactive tin species containing fewer MeS groups. Similarly, the decrease in the **10**:**8** ratio found for **9** with increasing conversion can be explained by a decreasing degree of quasi-concertedness as the tin reagent is changed.

In addition to the mechanism of eq 2 and that of eq 3 and 4, one can conceive of a completely concerted process that bypasses complexes such as **1** and gives **2** in a single step. Other possible mechanisms that would yield **2** preferentially are those involving the reaction of **1** and/or **3** with a second molecule of organotin. However, analogous S_N2' reactions of the allylic chlorides themselves are unlikely to be important, because if they were, then the overall rates should have been autoretarded, owing to the decreasing basicity (or nucleophilicity) of the tin reagent with time. It is important to note that the relative reactivities of the allylic chlorides (**4** >> **7** > **9**) are like those found for similar compounds during S_N1 solvolysis,[7e-g] a result that implies a large amount of transition state charge separation during the tin-induced C–Cl scission. This feature and our other findings can be explained most economically by the mechanism of eq 3 and 4, accompanied by another collapse mode of **3** which gives the product that is not rearranged [as discussed already, some of the Y (i.e., MeS) ligands in **1** and **3** would be replaced eventually by Cl]. Kinetic and stereochemical studies should help to confirm or disprove this attractive scheme.

The exploratory results presented here suggest that the reaction of allylic chlorides with organotin trithiolates may have some synthetic utility for the preparation of rearranged allylic sulfides. Thus far, the reaction has proved to be stereospecific, insofar as the configuration of the double bond is concerned, and it is regiochemically quite different from the reaction of allylic chlorides with sodium thiolates, which gives little, if any, rearranged product when linear chlorides are used.[7e,g]

At present, it is difficult to rationalize mechanistically the divergent regioselectivities found with $MeSn(SMe)_3$

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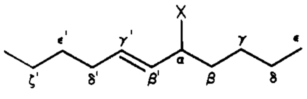
(10) (a) Rockett, B. W.; Hadlington, M.; Poyner, W. R. *J. Appl. Polym. Sci.* **1974**, *18*, 745. (b) Van den Berghe, E. V.; Van der Kelen, G. P. *J. Organomet. Chem.* **1974**, *72*, 65. (c) Hutton, R. E.; Burley, J. W. *Ibid.* **1976**, *105*, 61. (d) Van Hoang, T.; Michel, A.; Guyot, A. *Polym. Degradation Stab.* **1980–81**, *3*, 137. (e) Van Hoang, T.; Michel, A.; Guyot, A. *Ibid.* **1982**, *4*, 213.

and with dialkyltin dithiolates in experiments similar to ours.[5c,d,f] This interpretational problem arises, in part, from differences in reaction conditions. However, there is another complication which is even harder for one to address, viz., that all of the reported dithiolate reactions were accompanied by extensive isomerization of the starting chlorides[5c,d,f] and, at least in certain cases, by the loss of HCl.[5c] As is noted above, the latter process was not detected in our experiments with $MeSn(SMe)_3$, a finding which suggests that monoalkyltin trithiolates may be unusually good suppressors of dehydrochlorination during their reaction with PVC. This property could contribute to the relatively high initial effectiveness found for stabilizers of this type.[6,10a,11]

Table I contains the ^{13}C chemical shifts of all of the allylic chlorides and sulfides that were examined in this study, as well as the shifts of the trans allylic isomer (**11**) of chloride **4**. The assignments given here are based on the shifts of the analogous hydrocarbons[12] and on those of some other chlorides[13] and sulfides,[13d,14] including a few simple substances containing the MeS group.[14b,15] From the values in the table and the shifts of the parent alkenes (measured under conditions very similar to ours[12]), it is possible to derive sets of parameters that can be used to estimate the shift variations for structure **12** when X in this structure is changed from H to Cl or MeS. These parameters and their mean deviations are as follows: (a) Cl for H: α, +29.6 ± 1.2; β, +9.1 ± 0.1; γ, −2.8 ± 0.2; δ, $-0.5_5 \pm 0.0_5$; ϵ, −0.1 ± 0.0; β', +0.6 ± 0.5; γ', +3.1 ± 0.7; δ', −0.8 ± 0.1; ϵ', −0.9 ± 0.1; ζ', −0.1 ± 0.1 ppm. (b) MeS for H: α, +17.1 ± 0.5; β, +4.7 ± 0.0; γ, −2.0 ± 0.1_5; δ, −0.2 ± 0.0; ϵ, −0.1 ± 0.0; β', +0.5 ± 0.3; γ', +1.4 ± 0.4; δ', −0.6 ± 0.0; ϵ', −0.2 ± 0.1; ζ', 0.0 ± 0.2 ppm. It is instructive to note that most of the parameters have the same sign for the carbons at a given position, but that the Cl values generally are greater than the corresponding ones for MeS. The very small ϵ and ζ' values are the only exceptions to this rule.



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When the mean deviations are expressed as percentages of the listed parameters, the β' deviations are unusually large. The principal reason for this is that the data for the terminal alkenes, **7** and **10**, lead to β' values of −0.4 and −0.1, respectively, whereas the other data give β' values that are positive and significantly greater. If the results for **7** and **10** are simply omitted from the calculations, the β' parameters then have the following values and mean deviations: Cl for H, +0.9 ± 0.2; MeS for H, +0.8 ± 0.1.

Experimental Section

trans-1-Chloro-2-heptene[16] (**9**) was obtained from the reaction of *trans*-2-hepten-1-ol (10 g) with 32 g of triphenylphosphine in 47 mL of CCl_4 over 3 days at room temperature.[17] The preparations of 3-chloro-1-heptene[18] (**7**) and *trans*-6-chloro-4-decene[19] (**4**) are described elsewhere. After distillation at reduced pressure, all three chlorides had a purity of ≥95% according to ^{13}C NMR analysis. The ^{13}C shifts of *trans*-4-chloro-5-decene (**11**) were obtained from a mixture of **4** and **11** that had been prepared by allowing pure **4** to remain in a closed vessel at room temperature for several months. Methyltin tris(methanethiolate) was synthesized from methyltin trichloride according to the method of Van den Berghe et al.[20] and purified by Kugelrohr distillation, bp 130 °C (0.3 torr). Deuterated solvents (Aldrich "Gold Label"), methanethiol (Eastman), methyltin trichloride (Alfa), and all of the other chemicals were commercial products of high purity and were used as received. Nuclear magnetic resonance spectra of pure compounds and binary mixtures were recorded for $CDCl_3$ solutions on a JEOL FX90Q FT spectrometer, whereas those of crude reaction mixtures were obtained with a Varian T-60A instrument. Tetramethylsilane was used as an internal standard in all of the NMR work.

The allylic chlorides were converted into allylic methyl sulfides as follows. A 2-mL volumetric flask containing 550 mg (2.0 mmol) of $MeSn(SMe)_3$ and 0.60 mL of CD_2Cl_2 was brought to volume with C_6D_6. Aliquots of 0.60 mL [each containing 0.60 mmol of $MeSn(SMe)_3$] were added to each of three 5-mm NMR tubes that had been charged with 0.60 mmol of **4**, **7**, or **9**. The tubes were held at 70 ± 2 °C in an oil bath until complete reaction was noted by ^1H NMR analysis (all reactions were monitored conveniently by observing the intensities of the resonances at 3.8–4.4 and 2.8–3.1 ppm, which are produced by the protons geminal to Cl and MeS, respectively). The mixtures were then diluted with 3 mL of petroleum ether (nominal bp 35–60 °C), washed with dilute aqueous NaOH in order to remove tin compounds, dried with anhydrous $MgSO_4$, filtered, and carefully stripped of solvents under vacuum. The resulting liquids consisted entirely of allylic methyl sulfides, as was shown by ^1H NMR, ^{13}C NMR, and elemental analysis[21] (C, H, and S values were within 0.24% of theory). Isolated yields of the sulfides were ca. 90%. The following data were obtained for methyl *trans*-2-heptenyl sulfide (**8**), which apparently is a new substance: ^1H NMR ($CDCl_3$) δ 5.2–5.7 (m, 2, $CH{=}CH$), 3.05 (d, 2, $J = 6$ Hz, CH_2SCH_3), 1.9–2.1 (m with sharp s at 2.00, 5, CH_3S and $CH_2CH_2CH{=}CH$), 1.2–1.5 (m, 4, $CH_2CH_2CH_3$), and 0.89 (t, 3, $J = 6$ Hz, CH_3CH_2) ppm vs. Me_4Si. Anal. Calcd for $C_8H_{16}S$: C, 66.60; H, 11.18; S, 22.22. Found: C, 66.40; H, 10.98; S, 21.98.

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Registry No. **4**, 90147-08-3; **5**, 90370-32-4; **6**, 90370-33-5; **7**, 55682-98-9; **8**, 89965-89-9; **9**, 68703-33-3; **10**, 90370-34-6; **11**, 90370-35-7; $MeSn(SMe)_3$, 4848-74-2; *trans*-2-hepten-1-ol, 33467-76-4.

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(11) Andreas, H. In "Taschenbuch der Kunststoff-Additive"; Gächter, R., Müller, H., Eds.; Carl Hanser: Munich, 1979; Chapter 4. Abeler, G.; Büssing, J. *Kunststoffe* **1981**, *71*, 315.

(12) Couperus, P. A.; Clague, A. D. H.; van Dongen, J. P. C. M. *Org. Magn. Reson.* **1976**, *8*, 426.

(13) (a) Abbàs, K. B.; Bovey, F. A.; Schilling, F. C. *Makromol. Chem., Suppl.* **1975**, *1*, 227. (b) Starnes, W. H., Jr.; Hartless, R. L.; Schilling, F. C.; Bovey, F. A. *Adv. Chem. Ser.* **1978**, *No. 169*, 324. (c) Starnes, W. H., Jr.; Villacorta, G. M.; Schilling, F. C.; Plitz, I. M. "Proceedings, 28th Macromolecular Symposium of the International Union of Pure and Applied Chemistry", Amherst, Mass., July 1982; p 226. (d) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 5. (e) Caraculacu, A.; Buruiană, E. C.; Robilă, G.; Hjertberg, T.; Sörvik, E. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 323. In this reference the olefinic carbons of *trans*-2-chloro-3-hexene are given shift assignments that should be interchanged, as can be seen from comparisons based on published shift data for propene and allyl chloride.[13d] The revised assignments are also supported very strongly by the shift parameters discussed below.

(14) (a) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: Philadelphia, 1980; p 37. (b) Villacorta, G. M.; unpublished observations.

(15) Of particular use for comparison were the shifts of allyl methyl sulfide, which have the following values under our conditions ($CDCl_3$ solution ca. 30 °C): 134.09 ($CH{=}CH_2$), 116.82 ($CH{=}CH_2$), 36.88 (CH_2SCH_3), and 14.26 (CH_3) ppm (±0.05) vs. Me_4Si.[14b]

(16) Hatch, L. F.; Weiss, H. D.; Li, T. P. *J. Org. Chem.* **1961**, *26*, 61.

(17) Cf. Snyder, E. I. *J. Org. Chem.* **1972**, *37*, 1466.

(18) Macdonald, T. L.; Narayanan, B. A.; O'Dell, D. E. *J. Org. Chem.* **1981**, *46*, 1504.

(19) Haynie, S. L.; Villacorta, G. M.; Plitz, I. M.; Starnes, W. H., Jr. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1983**, *24* (2), 3.

(20) Van den Berghe, E. V.; Van de Vondel, D. F.; Van der Kelen, G. P. *Inorg. Chim. Acta* **1967**, *1*, 97.

(21) Performed by Galbraith Laboratories, Inc., Knoxville, TN.