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Aromatic Allylsulfenylation with in Situ Generated Allylic Thiols under the Heck Conditions

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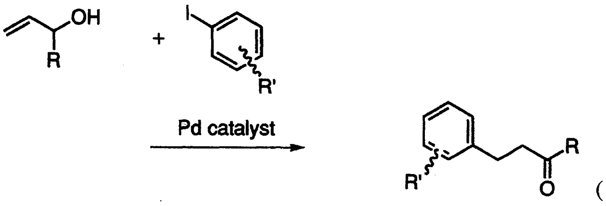
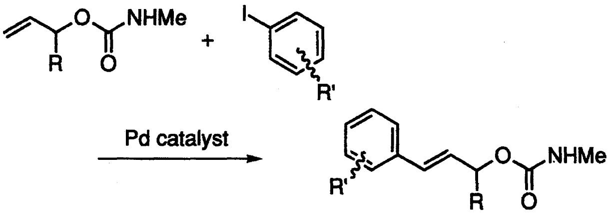
A wide structural variety of *S*-allylic thiocarbamates **2** can be prepared in good yields by the rearrangement of *O*-allylic thiocarbamates **1** under three different conditions: thermal activation (neat, 120—150 °C), palladium(0) (25—65 °C), and palladium(II) catalysis (25—65 °C). Of the two possible regioisomers of unsymmetrical *S*-allylic thiocarbamates **2**, those of higher thermodynamic stability can be prepared in high purity under either thermal activation or palladium(0) catalysis. Although the thermodynamically less stable regioisomers of **2** are, in general, hard to be prepared in high purity, some of them (e.g., **2d** and **2h′**) can be obtained with an exclusive or high selectivity by the catalysis of palladium(II). The stereoisomeric pair of **2j** and **2j′** can be prepared selectively by the palladium(0)-catalyzed rearrangement of **1j** and **1k**, respectively. These reactions proceed with retention of configuration at the allylic stereocenters. *S*-Allylic (**2**) and *S*-alkyl thiocarbamates (**7**) undergo fragmentation to generate thiolates in the presence of inorganic bases (e.g., K_2CO_3, $K_2CO_3 \cdot Et_4N^+I^-$) by heating in an aprotic solvent; the thus-formed thiolates react with aromatic iodides and vinyl bromides in the presence of palladium(0) complexes to furnish aryl and vinyl sulfides, respectively. A wide variety of aryl sulfides can be prepared in good yields irrespective of the kind of substituents and their substitution positions (*o*-, *m*-, *p*-) under conditions **B** [$Pd(OAc)_2$, PPh_3, $K_2CO_3 \cdot Et_4N^+I^-$, dioxane, 100 °C]. Under conditions **E** [$Pd(OAc)_2$, PPh_3, Cs_2CO_3, dioxane, 100 °C], better yields result specifically for the sulfenylation of aromatic iodides bearing substituents having large Hammett σ constants.

The Heck arylation of allylic alcohols with aromatic and heteroaromatic halides is an efficient entry to prepare β-aryl-substituted aliphatic aldehydes and ketones (Eq. 1).[1] In contrast, Heck arylations of *O*-allylic carbamates (Eq. 2) and *O*-allylic thiocarbamates **1** (Eq. 3) provide a completely different type of products. The former undergoes aryl group substitution at the double bond of *O*-allylic carbamates to furnish *O*-cinnamyl carbamates in good yields (Eq. 2).[2] The latter, on the other hand, gives rise to allylic aryl sulfides **3** selectively, though in rather low yields (Eq. 3): e.g., *O*-Allyl *N*-methylthiocarbamate (**1a**) and phenyl iodide (1.2 molar amounts) furnished allyl phenyl sulfide (**3a**) in 37% isolated yield [$Pd(PPh_3)_4$ (0.1 molar amounts), K_2CO_3 (1.3 molar amounts) in dioxane at 100 °C for 8 h].[3] In this reaction the phenyl substitution product at the double bond of **1a**, *O*-cinnamyl *N*-methylthiocarbamate, was not formed at all.



(1)



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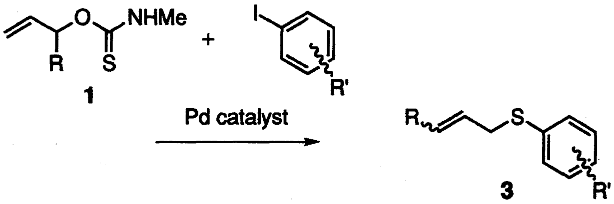
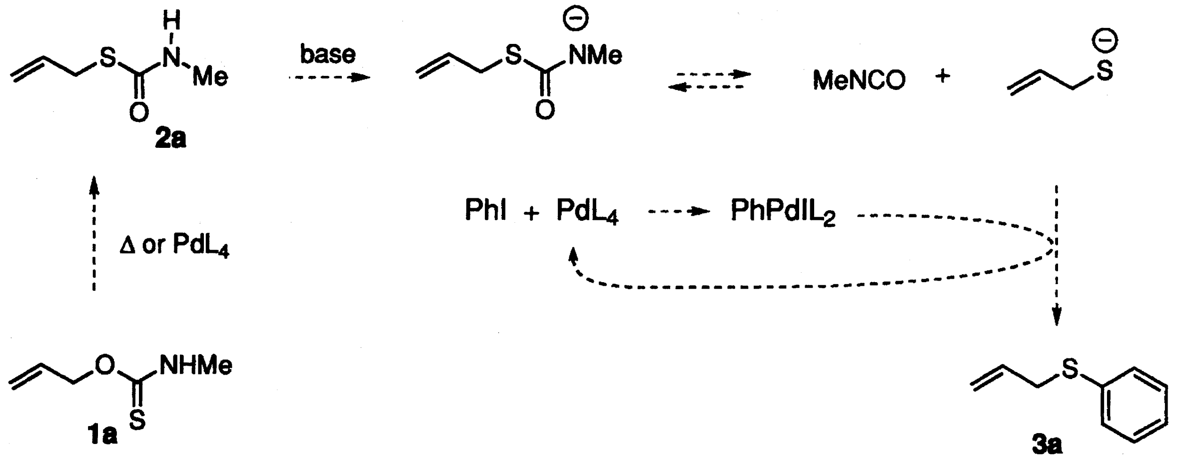


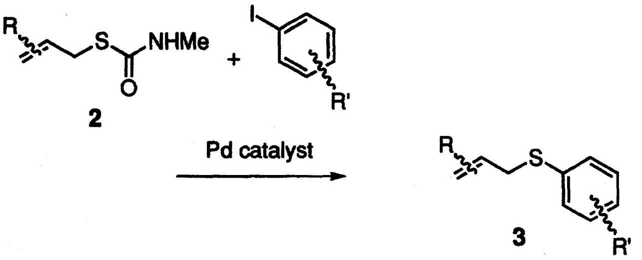
(3)

We reasoned the formation of **3a** as follows (Scheme 1): *O*-Allyl thiocarbamate **1a** would first undergo an allyl group rearrangement to provide *S*-allyl thiocarbamate **2a** by the catalysis of palladium(0) or by thermal activation. Then, **2a**, in the presence of a base, would fragment into methyl isocyanate and 2-propene-1-thiolate. The latter would further react with phenyl iodide by the catalysis of palladium(0) to furnish **3a** as a final product. Here, it was supposed that arylpalladium(II) iodide, a reactive intermediate of Heck arylation reaction, reacted selectively with 2-propene-1-thiolate at the sulfur atom rather than at the double bond.



Scheme 1. A rationale for aromatic allylsulfenylation with *O*-allyl thiocarbamate **1a** under the Heck reaction conditions.

Indeed, we found that (1) *O*-allylic thiocarbamates **1** underwent rearrangements to furnish *S*-allylic thiocarbamates **2** in good-to-excellent yields under either thermal activation or palladium catalysis, and that (2) **2** reacted under the Heck reaction conditions with aryl iodides bearing a variety of electron-donating and -attracting groups to give rise to allylic aryl sulfides **3** in good-to-excellent yields (Eq. 4). In this paper we describe the full details of the rearrangement of **1** into **2** and the palladium-catalyzed allylsulfenylation of aromatic iodides with **2**. This is a full account of our preliminary communication.[3)]

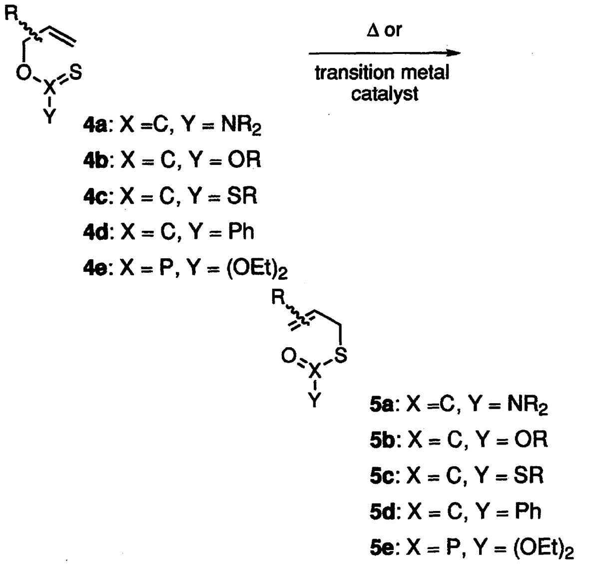


(4)

Results and Discussion

Thermal and Palladium-Catalyzed Rearrangements of *O*-Allylic Thiocarbamates 1 into *S*-Allylic Thiocarbamates 2. The allylic sulfide moiety is a structural component in a variety of synthetic and naturally occurring biologically active compounds. Accordingly, many preparation methods of allylic sulfides have been developed. Most of them rely on a thermal O→S allylic rearrangement of *O*-allylic thionoesters: *O*-allylic *N*,*N*-disubstituted thiocarbamates **4a**,[4)] *O*-allylic thiocarbonates **4b**,[5)] *O*-allylic dithiocarbonates **4c**,[6)] *O*-allylic thiobenzoates **4d**,[7)] and *O*-allylic thiophosphates **4e** (Eq. 5).[8)]

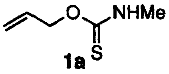
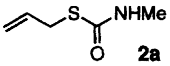
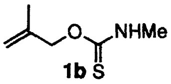
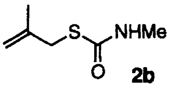
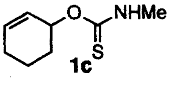
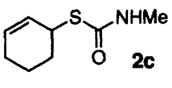
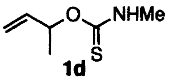
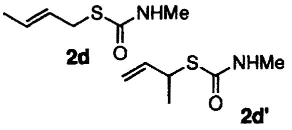
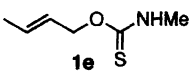
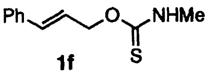
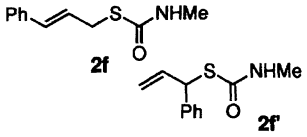
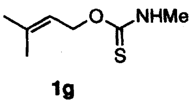
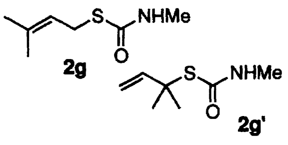
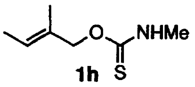
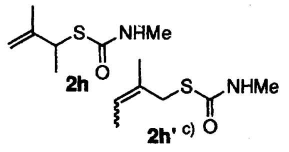
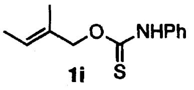
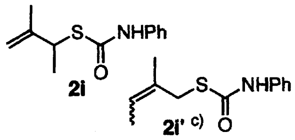
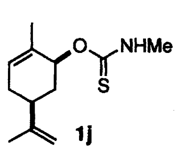
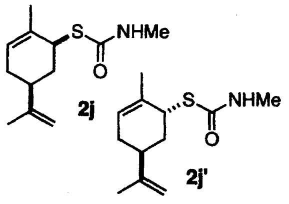
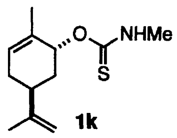
A wide structural variety of *O*-allylic thiocarbamates **1**, readily prepared in quantitative yields from the corresponding allylic alcohols and methyl isothiocyanate, were subjected to a thermal rearrangement in a neat state in the air (method A). The results are summarized in Table 1.



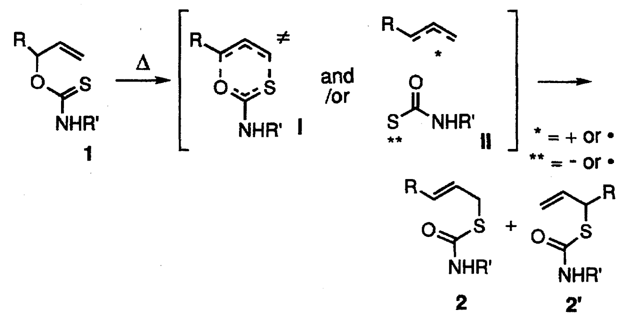
(5)

N-Monosubstituted thiocarbamates **1** showed a reactivity similar to that of *N*,*N*-disubstituted thiocarbamates **4a**, and attained completion of a rearrangement at around 120—150 °C within a few hours (Table 1); however, they displayed a regioselectivity apparently different from that of **4a**; **4a** was reported to rearrange with a complete allylic transposition, e.g., *O*-(1-methylallyl) and *O*-(*E*)-crotyl *N*,*N*-dimethylthiocarbamates yielded *S*-(*E*)-crotyl and *S*-(1-methylallyl) *N*,*N*-dimethylthiocarbamates, respectively, as single regioisomers. (No yields are reported.)[4c)] The regioselectivity of the rearrangement of **1** markedly depends on the substitution pattern of the allylic moiety. Although the allylic transposition is complete for **1d**, providing **2d** exclusively (Run 8, Table 1), it is incomplete for **1e**, furnishing the allylic transposition product **2d′** as the major product, together with a considerable amount of the positional retention product **2d** (Run 11, Table 1). A similar incomplete allylic transposition was observed for the thermal rearrangement of **1f** (Run 14) and **1g** (Run 16). To our surprise, the rearrangement of **1h** provided a positional retention product **2h′** exclusively (Run 19, Table 1).

Table 1. Thermal and Palladium-Catalyzed Rearrangement of *O*-Allylic Thiocarbamates **1** to *S*-Allylic Thiocarbamates **2**

Run	Strating material	Methods and conditions[a)] Temp (°C), [Time (h)][b)]	Product(s) 2	% Isolated yield of **2** [ratio]
1	 **1a**	**A** 100 [7]→120 [3]	 **2a**	66
2		**B** 25 [0.8]		86
3		**C** 25 [0.3]		76
4	 **1b**	**A** 120 [9]	 **2b**	84
5		**C** 25 [1]		86
6	 **1c**	**A** 150 [5]	 **2c**	86
7		**C** 25 [3]		84
8	 **1d**	**A** 100 [7]	 **2d** **2d'**	84 [**2d** : **2d′**=100 : 0]
9		**B** 25 [0.3]		82 [**2d** : **2d′**=100 : 0]
10		**C** 25 [3]		81 [**2d** : **2d′**=67 : 33]
11	 **1e**	**A** 100 [7]→120 [4]	2d+2d′	90 [**2d** : **2d′**=26 : 74]
12		**B** 25 [1.8]		86 [**2d** : **2d′**=0 : 100]
13		**C** 25 [3]		78 [**2d** : **2d′**=69 : 31]
14	 **1f**	**A** 120 [5]	 **2f** **2f'**	86 [**2f** : **2f′**=43 : 57]
15		**C** 25 [3]		74 [**2f** : **2f′**=100 : 0]
16	 **1g**	**A** 120 [5]	 **2g** **2g'**	81 [**2g** : **2g′**=62 : 38]
17		**B** 65 [20]		86 [**2g** : **2g′**=63 : 37]
18		**C** 25 [2]		78 [**2g** : **2g′**=100 : 0]
19	 **1h**	**A** 150 [6]	 **2h** **2h'** [c)]	54 [**2h** : **2h′**=0 : 100]
20		**B** 65 [30]		69 [**2h** : **2h′**=78 : 22]
21		**C** 65 [17]		86 [**2h** : **2h′**=0 : 100]
22	 **1i**	**A** 150 [2]	 **2i** **2i'** [c)]	86 [**2i** : **2i′**=33 : 67]
23		**C** 65 [3]		70 [**2i** : **2i′**=0 : 100]
24	 **1j**	**A** 130 [4]	 **2j** **2j'**	81 [**2j** : **2j′**=60 : 40]
25		**C** 65 [5]		25 [**2j** : **2j′**=76 : 24]
26		**C**[d)] 65 [15]		45 [**2j** : **2j′**=100 : 0]
27	 **1k**	**A** 130 [4]	2j+2j′	93 [**2j** : **2j′**=18 : 82]
28		**C** 65 [3]		75 [**2j** : **2j′**=16 : 84]
29		**C**[d)] 65 [3]		72 [**2j** : **2j′**=9 : 91]

a) **A**: **1** (3 mmol, neat) in a Kugel rohr oven, **B**: **1** (1 mmol), $PdCl_2(CH_3CN)_2$ (0.1 mmol) in THF (3 mL), **C**: **1** (1 mmol), $Pd(PPh_3)_4$ (0.1 mmol) in THF (3 mL). b) An approximate time required for complete conversion of **1**. c) A mixture of stereoisomers (ca. 2 : 1). d) In DMF (3 mL) in place of THF.



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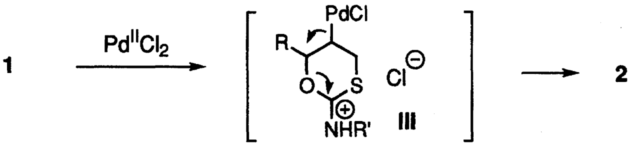

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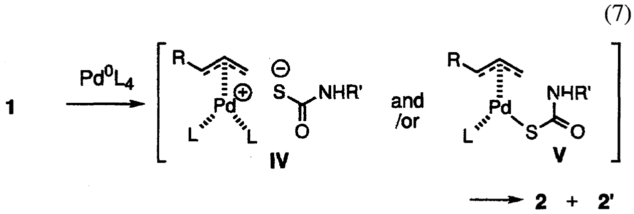


(8)

These contrasting regiochemical outcomes indicate that *t*-thiocarbamates **4a** undergo a rearrangement in a concerted fashion via a transition state like **I** (Eq. 6), while thiocarbamate **1** would follow two courses, a concerted route through **I** (as typified by **1d**) and a stepwise route involving an intermediate **II** (Eq. 6), that might be generated either by a homolytic or a heterolytic cleavage of the allylic C–O bond (as typified by **1h**). The rearrangement of **1e**—**g** is an intermediate case between these two. The formation of stereochemical inversion products, **2j′** (from **1j**, Run 24, Table 1) and **2j** (from **1k**, Run 27, Table 1), may be reconciled with a stepwise route involving **II** as an intermediate.

In order to improve the regio- and stereoselectivities, we examined the rearrangement of **1** by using palladium complexes as catalysts. Many precedents indicate that palladium(II) complexes are capable of accelerating [3.3] rearrangements and bringing about high regioselectivity. The acceleration and high regioselectivity have been attributed to an intermediacy of an intermediate **III** (Eq. 7).[7,9] Indeed, the rearrangement of **1d** and **1e** proceeded smoothly at room temperature by the catalysis of $PdCl_2(CH_3CN)_2$ (method **B**), and provided allylic transposition products **2d** (Run 9, Table 1) and **2d′** (Run 12), respectively, without contamination by each other. Unfortunately, however, method B could not be successfully applied to rearrangements of **1g** (Run 17) and **1h** (Run 20). In these reactions, allylic retention products **2g** and **2h′** were produced in significant amounts in addition to the expected allylic transposition products, **2g′** and **2h**, respectively. These reactions proceeded unacceptably slowly at room temperature. For the reaction to proceed at a reasonable rate, heating at around 65 °C was required. This was probably due to a steric inhibition of coordination of the Pd(II) species to the highly substituted double bonds. The formation of allylic retention products might be attributed to the catalysis of palladium(0) complexes that are partially generated under high-temperature conditions (vide infra).

The O→S allylic rearrangement of **1** turned out also to be promoted by the catalysis of $Pd(PPh_3)_4$ (method **C**). This rearrangement displayed the following characteristic regio- and stereoselectivities. As for the regioselectivity, the thermodynamically more stable regioisomers (with a higher number substituents on the double bonds) were produced either selectively (Runs 10,13, Table 1) or exclusively (Runs 15,18,21,23). These regioselectivities suggest that the rearrangement proceeds via a π-allylpalladium complex **IV** as an intermediate (Eq. 8). In this intermediate, the thiocarbamate anion would preferentially externally attack the allylic carbon bearing the least number of substituents.[10]

As for the stereoselectivity, to our surprise, the stereochemical inversion products, **2j′** from **1j** (Run 25, Table 1) and **2j** from **1k** (Run 28), were produced in considerable amounts when these reactions were undertaken in THF. We anticipated that a π-allylpalladium complex **IV**, formed by an oxidative addition of palladium(0) to the allylic C–O bond of **1** with an inversion of the configuration, would react with the thiocarbamate anion in an S_N2 fashion, accompanying an inversion of the configuration at the allylic stereocenter, to furnish net retention products.[10] The formation of inversion products may be rationalized by supposing a reductive elimination through an intermediate **V** formed by an attack of the thiocarbamate anion upon palladium(II) metal (Eq. 8). The supposition of the formation of **V** seems not to be very unreasonable, if one takes the high affinity of palladium(II) metal to a soft sulfur anion into consideration.

Bearing this in mind, we repeated the palladium(0)-catalyzed rearrangement of **1j** (Run 26) and **1k** (Run 29) in DMF in the expectation of an increase in the selectivity of the retention products, which follows because in such a polar solvent an ionic intermediate **IV** might participate in the reaction preferably to a neutral intermediate **V**. Indeed, in DMF retention products were obtained with remarkably higher selectivities than in THF (cf. Runs 25 and 26 and Runs 28 and 29, Table 1).

In order to shed more light into the reaction mechanism of these rearrangements, we examined crossover experiments by using an equimolar mixture of **1h**-d_2 and **1i**. The results (summarized in Fig. 1) clearly indicate that in both reactions (methods **A** and **C**) **1h**-d_2 and **1i** exchange their allylic and thiocarbamate components almost completely. These results lend further support to an intermediacy of **II** (a solvent-separated ion pair or radical pair, method **A**) and **IV** (a solvent separated π-allylpalladium thiocarbamate, method **C**) in these rearrangements. The lower *D* distribution in **2i′** [**2i′**-d_2 : **2i′**-d_0=14 : 20 (method **A**), 22 : 29 (method **C**)] than in **2h′** [**2h′**-d_2 : **2h′**-d_0=33 : 20 (method **A**), 30 : 19 (method **C**)] may be attributed to the fact that **1i** undergoes a rearrangement more facilely than does **1h**-d_2 (cf. Runs 19 and 22 and Runs 21 and 23, Table 1).

In summary, in this session it is demonstrated that a wide structural variety of *S*-allylic thiocarbamates **2** can be pre-

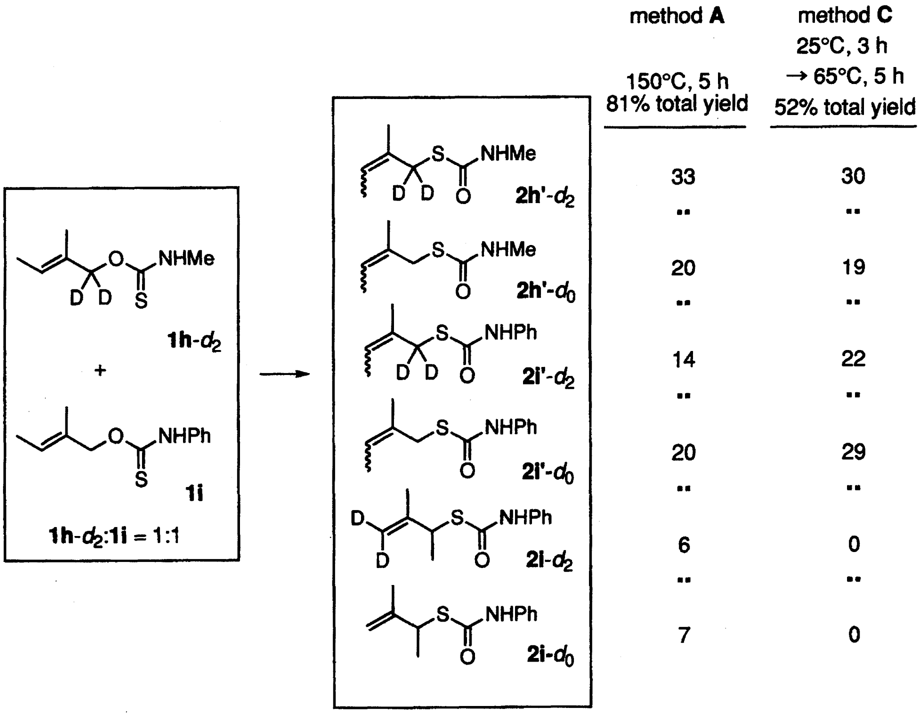


Fig. 1. Crossover experiments of an equimolar mixture of **1h**-d_2 and **1i**.

pared in good yields by the rearrangement of *O*-allylic thiocarbamates **1** under three different conditions: thermal activation (neat, 120—150 °C), palladium(0) (25—65 °C), and palladium(II) catalysis (25—65 °C). Of the two possible regioisomers of unsymmetrical *S*-allylic thiocarbamates **2**, those having a higher thermodynamic stability can be prepared in high purity under either thermal activation or palladium(0) catalysis. The thermodynamically less stable regioisomers of **2** are, in general, hard to be prepared in high purity; however, some of them can be obtained with an exclusive (e.g., **2d'**, Run 12, Table 1) or a high selectivity (e.g., **2h**, Run 20, Table 1) by the catalysis of palladium(II). As demonstrated by the stereoselective transformation of **1j** into **2j** (Run 26) and **1k** into **2j'** (Run 29), $Pd(PPh_3)_4$ effectively promotes a rearrangement while retaining the configuration at allylic stereocenters.

Palladium-Catalyzed Aromatic Allylsulfenylation with Allylic Thiols Generated from *S*-Allylic Thiocarbamates 2 under the Heck Conditions. Owing to the synthetic utilities of complex natural products as well as structurally simpler, industrially important intermediates, the palladium-catalyzed substitution of aromatic halides with carbon and heteroatom nucleophiles has been strongly desired by organic chemists.

As for aromatic sulfenylation,[11)] there have appeared two methods that utilize either alkali metal salts of aromatic and aliphatic thiols[12a)] or aromatic and aliphatic stannyl sulfides.[12b,12c)] The advantage of using allylic stannyl sulfides was demonstrated by the successful allylsulfenylation of phenyl iodide.[12c)]

Here, we report that *S*-allylic thiocarbamates **2**, prepared by the rearrangement of readily available *O*-allylic thiocarbamates (**1**) (as described in the previous section) serve as a convenient allylsulfenylation reagent of variously substituted aromatic iodides under the Heck arylation conditions (Eq. 4). This reaction provides the first practical method that enables one to prepare allylic aryl sulfides **3** in good yields, thus avoiding the use of allylic stannyl sulfides,[12c)] and, hence, allylic thiols as their precursor. Allylic thiols are notorious for their stink, instability (radical polymerization and autoxidation), and/or toxicity.

The reaction of *S*-(*E*)-crotyl thiocarbamate **2d** and phenyl iodide was first examined extensively under various conditions. The results are summarized in Table 2. The reactivity and yield greatly depended on the kind of ligands, bases, and additives. Conditions **A**, using $Pd(OAc)_2$ and PPh_3 in a molar ratio of 1 to 3 (Run 1, Table 2), were slightly more satisfactory than conditions **G**, using tetrakis(triphenylphosphine)palladium(0) as a catalyst (Run 7, Table 2). Phosphine ligands other than PPh_3 were ineffective. Examinations of Run 1 using either $P(o\text{-Tol})_3$ (0.3 molar amounts) or $P(OMe)_3$ (0.2—0.4 molar amounts) in place of PPh_3 resulted in the formation of **3d** in less than 8% yield.

In the absence of a base, the reaction was very slow; even after a prolonged reaction, the major part of the starting **2d** remained (Run 6, Table 2). Tetrabutylammonium iodide, in combination with K_2CO_3 or $KHCO_3$, remarkably accelerated the reaction and improved the yield (conditions **B** and **D**, Runs 2 and 4). A similar acceleration and an improvement in the yield were observed by using Cs_2CO_3 alone as a base (conditions **E**, Run 5). The rate acceleration by $Bu_4N^+I^-\cdot K_2CO_3$, $Bu_4N^+I^-\cdot KHCO_3$, and Cs_2CO_3 may be attributed to the high solubility of these inorganic bases in dioxane, which may facilitate the fragmentation of **2** into thiolates and methyl isocyanate. Throughout this study, reactions were uniformly undertaken with 0.1 molar amounts

Table 2. Palladium-Catalyzed Synthesis of (*E*)-Crotyl Phenyl Sulfide from Phenyl Iodide and *S*-(*E*)-Crotyl *N*-Methylthiocarbamate (**2d**)[a,b]

Run	Conditions	Pd complex	Ligand	Base	Additive	Time (h)	% Yield
1	**A**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	$\mathrm{K_2CO_3}$	None	24	60
2	**B**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	$\mathrm{K_2CO_3}$	$\mathrm{Bu_4N^+I^-}$	3	77[c]
3	**C**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	$\mathrm{KHCO_3}$	None	18	77
4	**D**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	$\mathrm{KHCO_3}$	$\mathrm{Bu_4N^+I^-}$	7	81
5	**E**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	$\mathrm{Cs_2CO_3}$	None	4	62
6	**F**	$\mathrm{Pd(OAc)_2}$	$\mathrm{PPh_3}$	None	None	46	—[d]
7	**G**	$\mathrm{Pd(PPh_3)_4}$	None	$\mathrm{K_2CO_3}$	None	8	55

a) Equation 4 (R=*trans*-3-methyl, R′=H). b) **2d** (1.0 mmol), phenyl iodide (1.3 mmol), palladium catalyst (0.1 mmol), ligand (0.3 mmol), base (1.3 mmol), and additive (1.0 mmol) in dioxane (5 mL) at 100 °C under $\mathrm{N_2}$. c) 73% isolated yield of (*E*)-crotyl phenyl sulfide under conditions **B** with reduced amount of palladium and ligand [**2d** (1.0 mmol), phenyl iodide (1.3 mmol), $\mathrm{Pd(OAc)_2}$(0.05 mmol), $\mathrm{PPh_3}$ (0.15 mmol), $\mathrm{K_2CO_3}$ (1.3 mmol), $\mathrm{Bu_4N^+I^-}$ (1.0 mmol) at 100 °C for 22 h]. d) Isolation of (*E*)-crotyl phenyl sulfide in less than 5% with 67% recovery of **2d**.

of palladium catalyst; however, the amount may be reduced to 0.05 molar amounts without any serious deterioration in the yields (see footnote c, Table 2). Judging from the reaction time and yields, we applied conditions **B**, **D**, and **E** to most cases.

The present allylsulfenylation may proceed through the following sequence of reactions (Scheme 1): In the presence of a base, **2** fragments into methyl isocyanate and a thiolate. Arylpalladium iodide, generated by an oxidative addition of aryl iodide to palladium(0), reacts with the thus-formed 2-propene-1-thiolate at the sulfur atom to give an (allylthio)-arylpalladium(II) intermediate, which undergoes reductive elimination to provide **3** and regenerate palladium(0) species. The generation of the thiolate anion was confirmed by the isolation of benzyl crotyl sulfide in 76% yield for the reaction of **2d** and benzyl bromide (1.1 molar amounts) in dioxane at 100 °C for 26 h in the presence of $\mathrm{K_2CO_3}$ (1.1 molar amounts). The selective reaction of an allylic thiolate at the sulfur atom is in contrast to the selective reaction of allylic alcohols at their double bonds to furnish β-aryl-substituted aliphatic aldehydes and ketones (Eq. 1).[1]

Next, we examined the reaction of **2d** with aryl iodides bearing electron-donating and -attracting substituents at the *o*-, *m*-, and *p*-positions under conditions **B**, **D**, and **E**. The results (summarized in Table 3) clearly indicate that conditions **B** and **D** are satisfactory for allylsulfenylation of all of the aryl iodides examined, irrespective of the electronic nature of the substituents and their substitution positions (Runs 1—24, Table 3). On the other hand, conditions **E** are generally superior to conditions **B** and **D** for the sulfenylation of aryl iodides with electron-attracting substituents (Runs 35—39), while they are inferior for the sulfenylation of aryl iodides with electron-donating groups (Runs 25—34).

A close examination of the results in runs 25—35 (Table 3) reveals the presence of a rough correlation between the yields and the Hammett σ constants. The larger are the σ values, the higher are the yields. For example, *m*-iodoanisole (σ=0.115 of *m*-OMe) and *m*-fluorophenyl iodide (σ=0.337 of *m*-F)

Table 3. Palladium-Catalyzed Synthesis of Aryl (*E*)-Crotyl Sulfides **3** from *S*-(*E*)-Crotyl *N*-Methylthiocarbamate (**2d**) and Aryl Iodides[a]

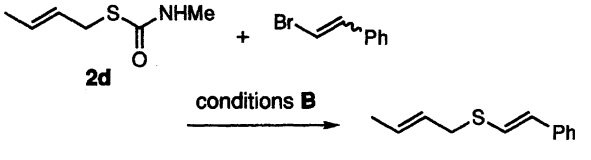
Aryl iodide	σ value[b]	Conditions **B**[c]			Conditions **D**[c]			Conditions **E**[c]		
R′		Run	Time (h)	Yield[d]	Run	Time (h)	Yield[d]	Run	Time (h)	Yield[d]
o-OMe		1	18	69				25	4	25
m-OMe	0.115	2	3	72	16	5	68	26	3	80
p-OMe	−0.268	3	22	65	17	6	60	27	5	14
o-Me		4	4	83				28	3	71
m-Me	−0.069	5	5	71				29	3	35
p-Me	−0.170	6	4	71	18	7	70	30	3	37
H		7	3	77	19	7	81	31	4	63
o-F		8	19	76	20	20	64	32	4	11
m-F	0.337	9	6	69	21	7	66	33	4	69
p-F	0.062	10	7	65	22	11	62	34	5	19
o-$\mathrm{CO_2Me}$		11	3	82				35	3	85
m-$\mathrm{CO_2Me}$	0.32	12	5	82				36	3	94
p-$\mathrm{CO_2Me}$	0.39	13	3	78	23	5	79	37	3	96
m-$\mathrm{NO_2}$	0.710	14	3	77				38	2	59
p-$\mathrm{NO_2}$	0.778	15	3	76	24	5	85	39	1	80

a) Equation 4 (R=*trans*-3-methyl). b) Hammett σ constant. c) Table 2, for the details of reaction conditions **B**, **D**, and **E**. d) Isolated yield for spectroscopically homogeneous **3**.

provided sulfenylation products in remarkably good yields, while *p*-iodoanisole ($\sigma=-0.268$ of *p*-OMe) and *p*-fluorophenyl iodide ($\sigma=0.062$ of *p*-F) did so in miserably poor yields. Notably, the yields of crotyl *m*-methoxyphenyl sulfide (Run 26) and crotyl *m*-fluorophenyl sulfide (Run 33) under conditions **E** were better than or comparable to those under conditions **B** and **D**.

The low-yield formation of **3** generally observed for aryl iodides with substituents of small or negative Hammett σ values under conditions **E** may be partly attributed to a certain imbalance of the concentrations of the reactive intermediates, arylpalladium(II) iodide and 2-butene-1-thiolate. The former may be generated slowly, due to a slow oxidative addition of such aryl iodides to palladium(0); also, the latter may be formed facilely, especially by the reaction with soluble Cs_2CO_3 (conditions **E**), as compared with by a reaction with less soluble bases, K_2CO_3 (conditions **B**) and $KHCO_3 \cdot Et_4N^+I^-$ (conditions **D**). Under the circumstances, the excess 2-butene-1-thiolate may decompose in many ways, most likely via radical polymerization.

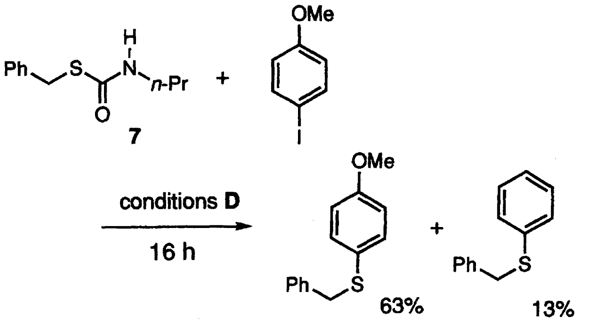
The aromatic sulfenylation with other *S*-allylic thiocarbamates (**2a**—**c**, **2f**, and **2g**) was examined under conditions **B**. The results (summarized in Fig. 2) indicate that the present aromatic allylsulfenylation is generally applicable to a wide structural variety of **2**. The reason for the apparently lower yield of **3a**, as compared with those of the other **3**, is not clear. A deterioration in the yield due to a further arylation of **3a** at the double bond is unlikely, since in the reaction mixture was not detected the expected arylation product, **3f** (^{1}H NMR and GLC).



(9)

The present reaction is not confined to aromatic sulfenylation, but is applicable to vinyl sulfenylation (Eq. 9).[13] (*E*)-Crotyl (*E*)-β-styryl sulfide **6** was obtained selectively in 53% isolated yield by the reaction of a mixture of (*E*)- and (*Z*)-β-bromostyrene (1.3 molar amounts, 5.3 : 1) and **2d** under conditions **B** (100 °C, 3 h). Product **6** was rather stable, and no products derived from the thia-Claisen rearrangement[14] were detected.

In order to test the generality of the present aromatic sulfenylation with thiocarbamates **2**, we next examined the reaction of *S*-benzyl *N*-propylthiocarbamate **7** with various aryl iodides under conditions **D**. The results obtained with *p*-methoxyphenyl iodide and other aromatic iodides are summarized in Eq. 10 and Fig. 3, respectively.



(10)

The reaction of **7** with *p*-methoxyphenyl iodide provided benzyl *p*-methoxyphenyl sulfide in 63% yield together with an unexpected benzyl phenyl sulfide in 13% yield (Eq. 10). The formation of benzyl phenyl sulfide was only observed for the reaction with *p*-methoxyphenyl iodide. With other aromatic iodides, only the corresponding aromatic benzyl sulfides were obtained in reasonable yields (Fig. 3).

The unusual formation of benzyl phenyl sulfide (Eq. 10) may be rationalized by supposing an equilibrium between **VI** and **VIII** via an intermediacy of phosphonium iodide **VII** (Scheme 2).[15] A reductive elimination of the methoxyphenyl and triphenylphosphine groups from **VI** might provide **VII** and the palladium(0) complex. The oxidative addition of

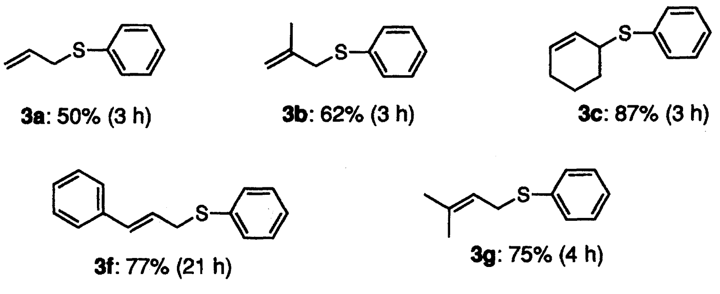


Fig. 2. Yields of allyl phenyl sulfides **3a**—**c**, **3f**, and **3g** obtained by the reaction of **2a**—**c**, **2f**, and **2g** with phenyl iodide under conditions **B**. Reaction time is shown in parentheses.

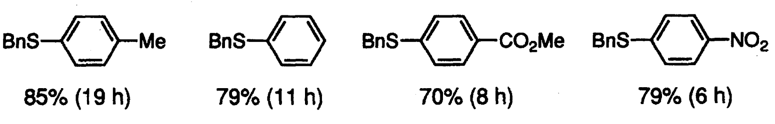
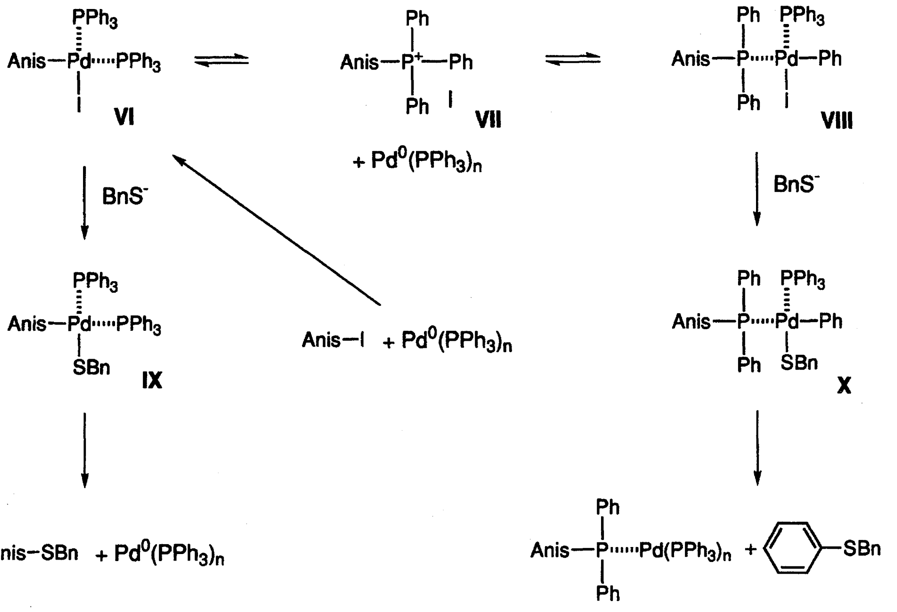
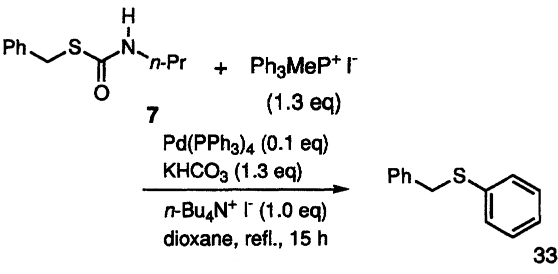


Fig. 3. Yields of aryl benzyl sulfides obtained by the reaction of *S*-benzyl *N*-propylthiocarbamate **7** and aryl iodides under conditions **D**. Reaction time is shown in parentheses.



Scheme 2. A mechanistic rationale for the formation of benzyl phenyl sulfide as a by-product for the benzylsulfenylation of *p*-methoxyphenyl iodide (Anis=*p*-methoxyphenyl, Bn=benzyl).

the palladium(0) complex into the methoxyphenyl–P^+ bond of **VII** regenerates **VI**, while the oxidative addition of the palladium(0) complex into the phenyl–P^+ bond of **VII** furnishes **VIII**. Both **VI** and **VIII** are responsible for the formation of benzyl methoxyphenyl sulfide and benzyl phenyl sulfide via **IX** and **X**, respectively.



(11)

Scheme 2 indicates that an aromatic phosphonium salt **VII** serves as an arylation reagent under the Heck reaction conditions. Indeed, this was proved by the reaction of **7** and methyltriphenylphosphonium iodide, which furnished benzyl phenyl sulfide in 33% isolated yield (Eq. 11).

In summary, in this section it is demonstrated that *S*-allylic (**2**) and *S*-alkyl thiocarbamates (**7**) undergo fragmentation to generate thiolates in the presence of inorganic bases (e.g., K_2CO_3, $K_2CO_3{\cdot}Et_4N^+I^-$) by heating in aprotic solvents (e.g., dioxane, 100 °C); the thus-formed thiolates react with aromatic iodides and vinyl bromides in the presence of palladium(0) complexes to furnish aryl and vinyl sulfide, respectively. A wide variety of aryl sulfides can be prepared in good yields irrespective of the kind of substituents and the substitution positions (*o*-, *m*-, *p*-) under conditions **B** [$Pd(OAc)_2$, PPh_3, $K_2CO_3{\cdot}Et_4N^+I^-$, dioxane, 100 °C]. Under conditions **E** [$Pd(OAc)_2$, PPh_3, Cs_2CO_3, dioxane, 100 °C], the better yields result specifically for the sulfenylation of aromatic iodides bearing substituents having large Hammett σ constants.

Allylic thiols are notorious for their stink and instability (polymerization, autoxidation) and sometimes for high volatility. *S*-Allylic thiocarbamates are generally stable and can withstand storage for a long period of time; also, some of them readily form fine crystalline solids. All of these properties associated with *S*-allylic thiocarbamates may augment the synthetic utility of the present method.

Experimental

Melting Points: Uncorrected values. Unless stated otherwise, short-path (bulb-to-bulb) distillations were carried out in a Kugel rohr apparatus. In these cases, the boiling points refer to the oven temperature, ^1H NMR: 60, 90, or 400 MHz, internal standard TMS. ^{13}C NMR: 22.5 or 100 MHz, internal standard TMS. The chemical shifts are relative to an internal standard. TLC: Kieselgel $60F_{254}$ (Merck). Column chromatography: Kieselgel 60, mesh size 0.2—0.5 mm (Merck). Elemental analyses: Microanalysis Center of Nagasaki University. High-resolution MS: Microanalysis Center of Nagasaki University.

Solvents and Reagents: THF and diethyl ether were dried and distilled under nitrogen from benzophenone sodium ketyl immediately before use. Dioxane was dried over Na and distilled prior to use. DMF and benzene were dried and distilled from CaH_2. (*E*)-2,3-Dimethyl-2-propen-1-ol-1,1-d_2 was prepared by a reduction of (*E*)-2,3-dimethyl-2-propenoic acid with $LiAlD_4$ (0 °C, ether, 54% isolated yield). All other organic solvents and organic and inorganic reagents used were of reagent grade and were employed without further purification.

General Procedure for the Preparation of *O*-Allylic Thiocarbamates (1). Into a nitrogen-purged suspension of NaH (760 mg, 18.2 mmol, 60% assay) over THF (8 ml) was slowly added a solution of an allylic alcohol (15.2 mmol) in THF (3 ml) with stirring in an ice bath. After stirring for 1 h at 0 °C, a solution of MeNCS (1.12 g, 15.3 mmol) in THF (3 ml) was introduced to the reaction mixture via a syringe. The mixture was stirred at the same temperature for 1 h and then quenched with sat. $NaHCO_3$ (10 ml). The mixture was extracted with ethyl acetate (3×10 ml). The combined organic layers were dried over anhydrous magnesium sulfate and concentrated. The residue was purified by column chromatography over silica gel (hexane-benzene gradient) to give **1** in quantitative yields (90—96%).

General Procedure for Thermal Rearrangement of 1 (Method A). A distillation flask containing **1** (3 mmol) was heated under air in a thermostated glass kugelrohl oven at the temperature and for the period of time indicated in Table 1. The mixture was then cooled to room temperature and directly subjected to column chromatography over silica gel (benzene–ethyl acetate) to give **2** in the yields summarized in Table 1.

General Procedure for Palladium-Catalyzed Rearrangement of 1 (Method B). Into a nitrogen-purged flask containing $PdCl_2(MeCN)_2$ (26 mg, 0.10 mmol) was added a solution of **1** (1 mmol) in THF (3 ml) via a syringe. The mixture was stirred at the temperature and for the period of time indicated in Table 1. The reaction mixture was diluted with ethyl acetate and filtered with suction through a celite pad on a funnel. After evaporation of the solvents, the residue was chromatographed over silica gel (benzene–ethyl acetate gradient) to give **2** in the yields summarized in Table 1.

General Procedure for Palladium-Catalyzed Rearrangement of 1 (Method C). Into a nitrogen-purged flask containing $Pd(PPh_3)_4$ (158 mg, 0.10 mmol) was added a solution of **1** (1 mmol) in THF (3 ml) via a syringe. The mixture was stirred at the temperature and for the period of time indicated in Table 1. The reaction mixture was diluted with ethyl acetate and filtered with suction through a celite pad on a funnel. After evaporation of the solvents, the residue was chromatographed over silica gel (benzene–ethyl acetate gradient) to give **2** in the yields summarized in Table 1.

***S*-Allyl *N*-Methylthiocarbamate (2a):** Oil; IR (neat film) 3310 (br s), 2940 (m), 1660 (s), 1530 (s), 1420 (s), 1220 (s), 1160 (m), 1010 (m), 990 (m), 920 (s), 810 (s), 740 cm^{-1} (m); ^{1}H NMR (60 MHz, CCl_4) δ=2.85 (d, J=4.8 Hz, 3 H), 3.50 (d, J=6.2 Hz, 2 H), 5.00 (dd, J=1.6, 9.4 Hz, 1 H), 5.15 (dd, J=1.6, 16.0 Hz, 1 H), 5.85 (ddt, J=9.4, 16.0, 6.2 Hz, 1 H), 6.15 (br s, 1 H). HRMS, Calcd for C_5H_9NOS: M, 131.0405. Found: *m*/*z* (rel intensity) 131.0380 (M$^+$; 7.6), 75.1 (6.0), 74.1 (100), 57.6 (43.7).

***S*-(2-Methylallyl) *N*-Methylthiocarbamate (2b):** Oil; IR (neat film) 3300 (br s), 2950 (m), 2920 (m), 1660 (s), 1530 (s), 1420 (m), 1220 (s), 1020 (s), 900 (s), 820 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=1.85 (d, J=1.5 Hz, 3 H), 2.85 (d, J=5.0 Hz, 3 H), 3.55 (s, 2 H), 4.80 (quint, J=1.5 Hz, 1 H), 4.95 (d, J=1.5 Hz, 1 H), 6.15 (br s, 1 H). HRMS, Calcd for $C_6H_{11}NOS$: M, 145.0561. Found: *m*/*z* (rel intensity) 145.0552 (M$^+$; 6.8), 89.0 (10.3), 88.0 (100.0).

***S*-(2-Cyclohexenyl) *N*-Methylthiocarbamate (2c):** Mp 56.2—57.2 °C (hexane); IR (KBr disk) 3320 (s), 3030 (m), 2920 (m), 1650 (s), 1520 (m), 1410 (w), 1230 (s), 1200 (m), 1160 (w), 1040 (w), 1010 (w), 920 (w), 870 (w), 820 (m), 750 (m), 720 cm^{-1} (w); ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.40—2.40 (m, 6 H), 2.85 (d, J=5.6 Hz, 3 H), 4.20 (br m, 1 H), 5.35 (br s, 1 H), 5.65 (br s, 1 H), 5.70 (br s, 1 H). HRMS, Calcd for $C_8H_{13}NOS$: 171.0718. Found: *m*/*z* (rel intensity) 171.0732 (M$^+$; 51.7), 162.0 (11.7), 81.1 (14.7). Anal. Calcd for $C_8H_{13}NOS$: C, 56.11; H, 7.65; N, 8.18; S, 18.72%. Found: C, 56.23; H, 7.45; N, 8.18; S, 18.89%.

***S*-(*E*)-Crotyl *N*-Methylthiocarbamate (2d):** Oil; IR (neat film) 3210 (br s), 3030 (w), 2910 (m), 1660 (s), 1520 (s), 1410 (m), 1220 (s), 1200 (m), 960 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.67 (dd, J=1.5, 6.6 Hz, 3 H), 2.88 (d, J=4.8 Hz, 3 H), 3.53 (d, J=7.0 Hz, 2 H), 5.29 (br s, 1 H), 5.50 (dtq, J=15.0, 7.0, 1.5 Hz, 1 H), 5.66 (dt, J=15.0, 6.6 Hz, 1 H). HRMS, Calcd for $C_6H_{11}NOS$: M, 145.0561. Found: *m*/*z* (rel intensity) 145.0559 (M$^+$; 70.9), 112.0 (5.9), 89.0 (5.3), 88.0 (100).

***S*-(1-Methylallyl) *N*-Methylthiocarbamate (2d′):** Oil; IR (neat film) 3300 (s), 2950 (w), 2920 (w), 1660 (s), 1530 (m), 1420 (m), 1230 (s), 1020 (m), 920 (m), 820 cm^{-1} (m); ^{1}H NMR (60 MHz, CCl_4) δ=1.45 (d, J=7.2 Hz, 3 H), 2.85 (d, J=5.0 Hz, 3 H), 4.15 (dt, J=6.8, 7.2 Hz, 1 H), 5.00 (dd, J=1.5, 10.4 Hz, 1 H), 5.10 (dd, J=1.5, 16.0 Hz, 1 H), 5.80 (br s, 1 H), 5.90 (ddd, J=6.8, 10.4, 16.0 Hz, 1 H). HRMS, Calcd for $C_6H_{11}NOS$: M, 145.0561. Found: *m*/*z* (rel intensity) 145.0571 (M$^+$; 50.0), 92.0 (18.0), 91.0 (11.2), 88.0 (100.0).

***S*-(*E*)-Cinnamyl *N*-Methylthiocarbamate (2f):** Mp 95.2—96.2 °C (benzene–hexane); IR (KBr disk) 3330 (s), 1670 (m), 1650 (s), 1550 (m), 1450 (w), 1400 (w), 1250 (m), 1220 (m), 1160 (w), 1020 (w), 970 (m), 740 (m), 690 cm^{-1} (m); ^{1}H NMR (60 MHz, CCl_4) δ=2.90 (d, J=5.4 Hz, 3 H), 3.65 (d, J=6.6 Hz, 2 H), 5.55 (br s, 1 H), 6.10 (dt, J=15.0, 6.6 Hz, 1 H), 6.55 (d, J=15.0 Hz, 1 H), 7.00—7.50 (m, 5 H). Anal. Calcd for $C_{11}H_{13}NOS$: C, 63.73; H, 6.32; N, 6.76; S, 15.47%. Found: C, 63.55; H, 6.28; N, 6.65; S, 15.54%.

***S*-(1-Phenylallyl) *N*-Methylthiocarbamate (2f′):** As a mixture with **2f**: ^{1}H NMR (60 MHz, CCl_4) δ=2.80 (d, J=5.4 Hz, 3 H), 5.10 (dd, J=1.5, 11.0 Hz, 1 H), 5.15 (dd, J=1.5, 16.5 Hz, 1 H), 5.20 (d, J=6.0 Hz, 1 H), 5.70 (br s, 1 H), 6.05 (ddd, J=6.0, 11.0, 16.5 Hz, 1 H), 7.10—7.45 (m, 5 H).

***S*-(3,3-Dimethylallyl) *N*-Methylthiocarbamate (2g):** Oil; IR (neat film) 3310 (br s), 2970 (m), 2940 (m), 1660 (s), 1520 (s), 1450 (m), 1420 (m), 1380 (m), 1220 (s), 1060 (m), 1020 (m), 820 cm^{-1} (m), ^{1}H NMR (60 MHz, CCl_4) δ=1.70 (s, 6 H), 2.80 (d, J=5.2 Hz, 3 H), 3.50 (d, J=7.6 Hz, 2 H), 5.25 (br t, J=7.6 Hz, 1 H), 5.90 (br s, 1 H). HRMS, Calcd for $C_7H_{13}NOS$: M, 159.0718. Found: *m*/*z* (rel intensity) 159.0673 (M$^+$; 100.0), 102.1 (70.3), 69.1 (84.7).

***S*-(1,1-Dimethylallyl) *N*-Methylthiocarbamate (2g′):** As a mixture with **2g**: ^{1}H NMR (60 MHz, CCl_4) δ=1.60 (s, 6 H), 2.70 (d, J=5.2 Hz, 3 H), 5.00 (dd, J=1.5, 10.0 Hz, 1 H), 5.05 (dd, J=1.5, 16.5 Hz, 1 H), 5.80 (br s, 1 H), 6.20 (dd, J=10.0, 16.5 Hz, 1 H).

***S*-(1,2-Dimethylallyl) *N*-Methylthiocarbamate (2h):** As a mixture with **2h′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.46 (d, J=7.0 Hz, 3 H), 1.82 (s, 3 H), 2.87 (d, J=5.9 Hz, 3 H), 4.14 (q, J=7.0 Hz, 1 H), 4.85 (s, 1 H), 5.00 (s, 1 H), 5.30 (br s, 1 H).

***S*-(2,3-Dimethylallyl) *N*-Methylthiocarbamate (2h′):** As a mixture of stereoisomers (2 : 1): Oil; IR (neat film) 3290 (br s), 3030 (m), 2970 (s), 2930 (s), 1660 (s), 1520 (s), 1450 (m), 1420 (s), 1380 (m), 1230 (s), 1160 (m), 1070 (w), 1010 (m), 960 (w), 900 (w), 870 (w), 810 (s), 780 (w), 700 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ=1.60 (dq, J=6.8, 1.1 Hz, 3 H), 1.67 (d, J=1.1 Hz, 3 H), 2.89 (d, J=5.2 Hz, 3 H), 3.59 (d, J=1.1 Hz, 2 H), 5.33 (br s, 1 H), 5.50 (qq, J=1.1, 6.8 Hz, 1 H); ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer) δ=1.46 (d, J=7.0 Hz, 3 H), 1.75 (d, J=1.5 Hz, 3 H), 2.88 (d, J=5.1 Hz, 3 H), 3.65 (s, 2 H), 5.33 (br s, 1 H), 5.36 (br q, J=7.0 Hz, 1 H). HRMS, Calcd for $C_7H_{13}NOS$: M, 159.0718. Found: *m*/*z* (rel intensity) 159.0720 (M$^+$; 63.5), 102.0 (100), 69.1 (55.7).

***S*-(1,2-Dimethylallyl) *N*-Phenylthiocarbamate (2i):** As a mixture with **2i′**: ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.50 (d, J=7.0 Hz, 3 H), 1.84 (s, 3 H), 4.20 (q, J=7.0 Hz, 1 H), 4.87 (t, J=1.0 Hz, 1 H), 5.03 (d, J=1.0 Hz, 1 H), 7.10 (t, J=7.5 Hz, 1 H), 7.25 (br s, 1 H), 7.29 (t, J=7.5 Hz, 2 H), 7.40 (d, J=7.5 Hz, 2 H).

***S*-(2,3-Dimethylallyl) *N*-Phenylthiocarbamate (2i′):** As a mixture of stereoisomers (2 : 1): Oil; IR (neat film) 3300 (br m), 3130 (w), 3060 (w), 3040 (w), 2980 (m), 2920 (m), 2860 (w), 1660 (s), 1600 (s), 1540 (s), 1500 (s), 1440 (s), 1380 (m), 1310 (s), 1240 (s), 1150 (s), 1110 (w), 1080 (m), 1030 (w), 880 (m), 820 (m), 810 (m), 750 (s), 690 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ=1.61 (dd, J=1.1, 6.8 Hz, 3 H), 1.70 (d, J=1.1 Hz, 3 H), 3.66 (s, 2 H), 5.55 (dq, J=1.1, 6.8 Hz, 1 H), 7.05 (br s, 1 H), 7.10 (tt, J=1.5, 7.5 Hz, 1 H), 7.30 (dt, J=7.5, 1.5 Hz, 2 H), 7.41 (dd, J=1.5, 7.5 Hz, 2 H); ^{1}H NMR (400 MHz, $CDCl_3$, minor isomer) δ=1.51 (d, J=7.0 Hz, 3 H), 1.78 (d, J=1.1 Hz, 3 H), 3.72 (s, 2 H), 5.40 (dq, J=1.1, 7.0 Hz, 1 H), 7.05 (br s, 1 H), 7.10 (tt, J=1.5, 7.5 Hz, 1 H), 7.30 (dt, J=7.5, 1.5 Hz, 2 H), 7.41 (dd, J=1.5, 7.5 Hz, 2 H). HRMS, Calcd for $C_{12}H_{15}NOS$: M, 221.0874. Found: m/z (rel intensity) 221.0859 (M^+; 79.3), 153.0 (21.4), 153.0 (21.4), 152.0 (5.2), 103.0 (3.4), 102.0 (100).

***S-cis*-6-Carvyl *N*-Methylthiocarbamate (2j):** Mp 96.1—96.9 °C (ether–hexane); IR (KBr disk) 3320 (s), 2940 (m), 2910 (m), 1660 (s), 1530 (m), 1460 (w), 1440 (w), 1410 (w), 1380 (w), 1230 (s), 1020 (w), 930 (w), 900 (w), 810 (m), 780 (w), 710 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.69 (dt, J=11.1, 12.4 Hz, 1 H; coalescing to t, J=12.4 Hz, by irradiation at 4.2), 1.73 (s, 3 H), 1.77 (q, J=1.1 Hz, 3 H; coalescing to t, J=1.1 Hz, by irradiation at 5.6), 1.96 (m, 1 H), 2.08 (m, 1 H), 2.26 (tt, J=2.2, 12.4 Hz, 1 H), 2.33 (ddt, J=6.2, 12.4, 2.2 Hz, 1 H; coalescing to dt, J=12.4, 2.2 Hz, by irradiation at 4.2), 2.89 (d, J=5.1 Hz, 3 H), 4.20 (br s, 1 H), 4.70 (d, J=1.1 Hz, 1 H), 4.72 (t, J=1.1 Hz, 1 H), 5.31 (br s, 1 H), 5.61 (m, 1 H); NOEs for one of the C_6 methylene protons (5.7%) and C_5H (3.8%) by irradiation at C_1H. Anal. Calcd for $C_{12}H_{19}NOS$: C, 63.96; H, 8.50; N, 6.22; S, 14.23%. Found: C, 63.97; H, 8.42; N, 6.23; S, 14.25%.

***S-trans*-6-Carvyl *N*-Methylthiocarbamate (2j′):** Mp 79.7—80.3 °C (ether–hexane); IR (KBr disk) 3330 (s), 2970 (m), 2940 (m), 2910 (m), 2880 (m), 2840 (w), 1660 (s), 1530 (m), 1440 (w), 1410 (w), 1380 (w), 1230 (s), 1200 (m), 1150 (w), 1010 (w), 920 (w), 900 (m), 810 (w), 800 cm^{-1} (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.73 (s, 3 H), 1.78 (t, J=1.0 Hz, 3 H), 1.88 (ddd, J=2.4, 4.9, 17.6 Hz, 1 H; coalescing to dd, J=2.4, 17.6 Hz, by irradiation at 5.60), 1.93 (ddd, J=4.4, 12.2, 13.7 Hz, 1 H; coalescing to dd, J=12.2, 13.7 Hz, by irradiation at 4.15), 2.03 (dq, J=13.7, 2.0 Hz, 1 H; coalescing to dt, J=13.7, 2.0 Hz, by irradiation at 4.15), 2.15 (br d, J=17.6 Hz, 1 H; coalescing to dd, J=4.9, 17.6 Hz, by irradiation at 5.60), 2.33 (br t, 1 H), 2.88 (d, J=4.9 Hz, 3 H), 4.15 (br s, 1 H), 4.72 (d, J=1.1 Hz, 1 H), 4.74 (t, J=1.1 Hz, 1 H), 5.25 (br s, 1 H), 5.58 (br s, 1 H); NOEs for one of the C_6 methylene protons (3.7%) and C_5H (0%) by irradiation at C_1H. Anal. Calcd for $C_{12}H_{19}NOS$: C, 63.96; H, 8.50; N, 6.22; S, 14.23%. Found: C, 63.92; H, 8.41; N, 6.23; S, 14.50%.

General Procedure for Aromatic Allylsulfenylation with *S*-Allylic Thiocarbamates (2). Into a flask, equipped with a reflux condenser, were added K_2CO_3 (180 mg, 1.3 mmol), $Pd(OAc)_2$ (23 mg, 0.1 mmol), PPh_3 (79 mg, 0.3 mmol), and n-$Bu_4N^+I^-$ (369 mg, 1.0 mmol). The flask was purged with N_2. Into this flask was introduced a solution of an aromatic iodide (1.3 mmol) and **2** (1.0 mmol) in dioxane (5 ml) via a syringe. The mixture was stirred and heated at the temperature for the period of time indicated in Table 3. The mixture was diluted with hexane (30 ml) and filtered with suction through a celite pad on a funnel. The filtrate was washed with water (2×10 ml) and the organic layer was dried over anhydrous magnesium sulfate. Evaporation of the solvents and subsequent purification by column chromatography over silica gel (hexane–chloroform gradient) provided **3** in the yields summarized in Table 3. Reactions under other conditions **A**, **C**—**G** were performed similarly.

Allyl Phenyl Sulfide (3a): Oil; IR (neat film) 3080 (w), 2930 (w), 1620 (m), 1580 (m), 1480 (s), 1440 (m), 1230 (m), 1090 (m), 1030 (m), 950 (m), 920 (s), 730 (s), 690 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=3.45 (dd, J=1.0, 6.0 Hz, 2 H), 5.00 (dd, J=1.0, 11.0 Hz, 1 H), 5.10 (dd, J=1.0, 15.0 Hz, 1 H), 5.90 (ddd, J=6.0, 11.0, 15.0 Hz, 1 H), 7.00—7.40 (m, 5 H). HRMS, Calcd for $C_9H_{10}S$: M, 150.0503. Found: m/z (rel intensity) 150.0497 (M^+; 100), 135.0 (32.1), 110.0 (7.8).

2-Methylallyl Phenyl Sulfide (3b): Oil; IR (neat film) 3090 (m), 2970 (m), 1580 (s), 1480 (s), 1430 (s), 1030 (s), 900 (s), 740 (s), 690 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=1.90 (d, J=1.0 Hz, 3 H), 3.40 (s, 2 H), 4.85 (d, J=1.0 Hz, 1 H), 4.90 (d, J=1.0 Hz, 1 H), 7.00—7.50 (m, 5 H). HRMS, Calcd for $C_{10}H_{12}S$: M, 164.0660. Found: m/z (rel intensity) 164.0658 (M^+; 100), 149.0 (25.3), 122.0 (5.4), 110.0 (15.6).

2-Cyclohexenyl Phenyl Sulfide (3c): Oil; IR (neat film) 3030 (m), 2940 (s), 1580 (s), 1480 (s), 1440 (s), 1200 (m), 1090 (m), 1030 (m), 870 (m), 730 (m), 690 cm^{-1} (m); ^{1}H NMR (60 MHz, CCl_4) δ=1.40—2.30 (m, 6 H), 3.90 (br m, 1 H), 5.70 (d, J=10.0 Hz, 1 H), 5.80 (d, J=10.0 Hz, 1 H), 7.00—7.50 (m, 5 H). HRMS, Calcd for $C_{12}H_{14}S$: M, 190.0816. Found: m/z (rel intensity) 190.0821 (M^+; 79.3), 111.0 (2.4), 110.0 (16.4), 109.0 (11.3), 81.1 (100.0).

Crotyl Phenyl Sulfide (3d): Oil; IR (neat film) 3020 (m), 2920 (m), 1670 (w), 1585 (s), 1485 (s), 1440 (s), 1230 (m), 1090 (m), 1030 (m), 970 (s), 740 (s), 690 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.65 (dq, J=4.8, 1.1 Hz, 1 H; coalescing to d, J=4.8 Hz, by irradiation at 3.51), 3.51 (dd, J=1.1, 6.6 Hz, 2 H; coalescing to d, J=6.6 Hz, by irradiation at 1.65), 5.51 (m, 1 H; coalescing to dt, J=15.0, 6.6 Hz, by irradiation at 1.65), 5.58 (m, 1 H; coalescing to d, J=15.0 Hz, by irradiation at 1.65), 7.17 (tt, J=1.1, 7.3 Hz, 1 H), 7.27 (tt, J=1.1, 7.3 Hz, 2 H), 7.33 (dd, J=1.1, 7.3 Hz, 2 H). HRMS, Calcd for $C_{10}H_{12}S$: M, 164.0660. Found: m/z (rel intensity) 164.0678 (M^+; 64.1), 110.0 (63.1).

Cinnamyl Phenyl Sulfide (3f): Mp 77.5—78.1 °C (ethanol); IR (KBr disk) 3040 (m), 3020 (m), 1580 (s), 1480 (s), 1430 (s), 1260 (m), 1090 (s), 1070 (m), 1020 (s), 960 (s), 750 (s), 730 (s), 690 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=3.65 (d, J=6.0 Hz, 2 H), 6.10 (dd, J=6.0, 10.0 Hz, 1 H), 6.40 (d, J=16.0 Hz, 1 H), 7.05—7.70 (m, 5 H). Anal. Calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.17%. Found: C, 79.39; H, 6.29; S, 14.19%.

3,3-Dimethylallyl Phenyl Sulfide (3g): Oil; IR (neat film) 3030 (m), 2950 (s), 2890 (s), 1580 (s), 1480 (s), 1440 (s), 1370 (m), 1090 (m), 1030 (m), 840 (m), 730 (s), 690 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=1.60 (s, 3 H), 1.80 (s, 3 H), 3.40 (d, J=7.4 Hz, 2 H), 5.20 (m, 1 H), 7.00—7.45 (m, 5 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 178.0816. Found: m/z (rel intensity) 178.0817 (M^+; 71.2), 110.0 (69.5), 69.1 (53.8).

Crotyl *o*-Methoxyphenyl Sulfide: Oil; IR (neat film) 3040 (m), 3000 (m), 2920 (s), 2810 (m), 1665 (w), 1580 (s), 1480 (s), 1435 (s), 1380 (m), 1310 (m), 1280 (s), 1250 (s), 1185 (m), 1140 (m), 1075 (s), 1030 (s), 960 (s), 930 (m), 790 (m), 750 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=1.65 (d, J=4.0 Hz, 3 H), 3.40 (d, J=4.0 Hz, 2 H), 3.85 (s, 3 H), 5.35—5.70 (m, 2 H), 6.65—7.35 (m, 4 H). HRMS, Calcd for $C_{11}H_{14}OS$: M, 194.0766. Found: m/z (rel intensity) 194.0782 (M^+; 100.0), 140.0 (98.7), 125.0 (20.7).

Crotyl *m*-Methoxyphenyl Sulfide: Oil; IR (neat film) 3020 (m), 2950 (m), 2820 (m), 1590 (s), 1480 (s), 1420 (m), 1280 (s), 1250 (s), 1180 (w), 1100 (m), 1040 (s), 960 (s), 880 (m), 770 (s), 680 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=1.75 (d, J=4.0 Hz, 3 H), 3.50 (d, J=5.0 Hz, 2 H), 3.75 (s, 3 H), 5.40—5.75 (m, 2 H), 6.50—7.30 (m, 4 H). HRMS, Calcd for $C_{11}H_{14}OS$: M, 194.0766. Found: m/z (rel intensity) 194.0760 (M^+; 100.0), 179.0 (9.9), 165.0 (16.9), 140.0 (87.1), 125.0 (12.2), 96.0 (6.6).

Crotyl *p*-Methoxyphenyl Sulfide: Oil; IR (neat film) 3020 (w), 2910 (m), 2820 (w), 1590 (s), 1490 (s), 1280 (s), 1240 (s), 1170 (m), 1030 (s), 950 (m), 820 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=5.0 Hz, 3 H), 3.20 (d, J=5.0 Hz, 2 H), 3.85 (s, 3 H), 5.20—5.90 (m, 2 H), 6.80 (d, J=9.0 Hz, 2 H), 7.20 (d, J=9.0 Hz 2 H). HRMS, Calcd for $C_{11}H_{14}OS$: M, 194.0766. Found: m/z (rel intensity) 194.0768 (M^+; 100.0), 97.0 (2.2), 96.0 (3.9), 95.1 (3.9).

Crotyl *o*-Methylphenyl Sulfide: Oil; IR (neat film) 3020 (w), 2900 (m), 1600 (m), 1470 (s), 1220 (w), 1060 (m), 960 (s), 730 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.75$ (d, J=4.0 Hz, 3 H), 2.30 (s, 3 H), 3.45 (d, J=5.0 Hz, 2 H), 5.40—5.75 (m, 2 H), 6.90—7.40 (m, 4 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 178.0816. Found: m/z (rel intensity) 178.0808 (M^+; 30.8), 124.0 (19.7), 123.0 (0.6), 91.0 (1.1).

Crotyl *m*-Methylphenyl Sulfide: Oil; IR (neat film) 3020 (w), 2900 (m), 1600 (m), 1465 (m), 1440 (m), 1210 (w), 1085 (w), 950 (s), 750 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=4.0 Hz, 3 H), 2.30 (s, 3 H), 3.40 (d, J=5.0 Hz, 2 H), 5.30—5.70 (m, 2 H), 6.70—7.40 (m, 4 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 178.0816. Found: m/z (rel intensity) 178.0834 (M^+; 100.0), 124.0 (80.1), 91.0 (14.5).

Crotyl *p*-Methylphenyl Sulfide: Oil; IR (neat film) 3030 (w), 2925 (w), 1500 (m), 1100 (w), 960 (m), 800 $\mathrm{cm^{-1}}$ (m); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.65$ (d, J=4.0 Hz, 3 H), 2.30 (s, 3 H), 3.25 (m, 2 H), 5.25—5.65 (m, 2 H), 6.95 (d, J=8.0 Hz, 2 H), 7.20 (d, J=8.0 Hz, 2 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 178.0816. Found: m/z (rel intensity) 178.0817 (M^+; 62.8), 124.0 (62.5), 91.0 (23.6), 55.0 (19.2).

Crotyl *o*-Fluorophenyl Sulfide: Oil; IR (neat film) 3030 (m), 2920 (m), 1570 (m), 1475 (s), 1445 (s), 1260 (s), 1220 (s), 1120 (m), 1075 (s), 1030 (s), 960 (s), 820 (s), 750 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.65$ (d, J=4.0 Hz, 3 H), 3.45 (d, J=5.0 Hz, 2 H), 5.35—5.65 (m, 2 H), 6.75—7.65 (m, 4 H). HRMS, Calcd for $C_{10}H_{11}FS$: M, 182.0565. Found: m/z (rel intensity) 182.0569 (M^+; 7.4), 128.0 (12.1), 105.0 (2.4), 96.0 (2.4), 91.0 (4.8).

Crotyl *m*-Fluorophenyl Sulfide: Oil; IR (neat film) 3020 (m), 2900 (m), 1600 (s), 1580 (s), 1480 (s), 1430 (s), 1265 (s), 1220 (s), 1160 (m), 1090 (m), 1065 (m), 965 (s), 880 (s), 770 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=4.0 Hz, 3 H), 3.50 (d, J=4.0 Hz, 2 H), 5.40—5.75 (m, 2 H), 6.55—7.50 (m, 4 H). HRMS, Calcd for $C_{10}H_{11}FS$: M, 182.0565. Found: m/z (rel intensity) 182.0566 (M^+; 47.3), 153.0 (2.0), 149.9 (3.2), 129.0 (2.4), 83.0 (5.7), 55.0 (26.5).

Crotyl *p*-Fluorophenyl Sulfide: Oil; IR (neat film) 3020 (m), 2900 (m), 1590 (s), 1490 (s), 1450 (m), 1220 (s), 1160 (s), 1090 (s), 1010 (m), 960 (s), 830 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=4.5 Hz, 3 H), 3.40 (d, J=4.5 Hz, 2 H), 5.30—5.65 (m, 2 H), 7.00 (d, J=8.0 Hz, 2 H), 7.20—7.60 (m, 2 H). HRMS, Calcd for $C_{10}H_{11}FS$: M, 182.0565. Found: m/z (rel intensity) 182.0563 (M^+; 69.1), 129.0 (4.5), 110.0 (5.0), 83.0 (7.1).

Crotyl *o*-Methoxycarbonylphenyl Sulfide: Oil; IR (neat film) 3030 (m), 2948 (s), 1720 (s), 1590 (s), 1565 (m), 1470 (s), 1425 (s), 1380 (w), 1280 (s), 1250 (s), 1195 (s), 1150 (s), 1110 (s), 1065 (s), 985 (s), 820 (m), 710 (s), 690 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=5.0 Hz, 3 H), 3.50 (d, J=5.0 Hz, 2 H), 3.90 (s, 3 H), 5.05—6.00 (m, 2 H), 6.90—7.55 (m, 3 H), 7.85 (d, J=7.0 Hz, 1 H). HRMS, Calcd for $C_{12}H_{14}O_2S$: M, 222.0715. Found: m/z (rel intensity) 222.0732 (M^+; 100.0), 190.0 (30.9), 168.0 (19.0), 167.0 (48.5), 152.0 (11.6), 136.0 (79.3).

Crotyl *m*-Methoxycarbonylphenyl Sulfide: Oil; IR (neat film) 3400 (br m), 3030 (w), 2870 (m), 1730 (s), 1590 (w), 1580 (m), 1440 (s), 1290 (s), 1270 (s), 1230 (m), 1200 (m), 1135 (s), 1100 (m), 1090 (m), 970 (s), 930 (w), 845 (m), 755 (s), 730 $\mathrm{cm^{-1}}$ (w); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.65$ (d, J=5.0 Hz, 3 H), 3.55 (d, J=5.0 Hz, 2 H), 3.90 (s, 3 H), 5.45—5.75 (m, 2 H), 7.30 (t, J=8.0 Hz, 1 H), 7.35 (d, J=8.0 Hz, 1 H), 7.70—8.00 (m, 2 H). HRMS, Calcd for $C_{12}H_{14}O_2S$: M, 222.0715. Found: m/z (rel intensity) 222.0722 (M^+; 86.1), 191.0 (12.1), 168.0 (100.0), 137.0 (23.5), 55.0 (34.9).

Crotyl *p*-Methoxycarbonylphenyl Sulfide: Oil; IR (neat film) 2930 (w), 1720 (s), 1590 (s), 1430 (m), 1280 (s), 1270 (s), 1100 (s), 750 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.70$ (d, J=5.0 Hz, 3 H), 3.50 (d, J=5.0 Hz, 2 H), 3.85 (s, 3 H), 5.20—6.10 (m, 2 H), 7.20 (d, J=8.4 Hz, 2 H), 7.90 (d, J=8.4 Hz, 2 H). HRMS, Calcd for $C_{12}H_{14}O_2S$: M, 222.0715. Found: m/z (rel intensity) 222.0707 (M^+; 100.0), 191.0 (8.9), 137.0 (34.4).

Crotyl *m*-Nitrophenyl Sulfide: Oil; IR (neat film) 3020 (w), 2900 (m), 1530 (s), 1350 (s), 1270 (m), 1230 (m), 1130 (s), 970 (s), 880 (m), 800 (m), 730 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.75$ (d, J=5.0 Hz, 3 H), 3.60 (d, J=6.0 Hz, 2 H), 5.40—5.80 (m, 2 H), 7.45—7.55 (d, J=8.0 Hz, 2 H), 7.85—8.15 (m, 2 H). HRMS, Calcd for $C_{10}H_{11}NO_2S$: M, 209.0511. Found: m/z (rel intensity) 209.0498 (M^+; 73.1), 155.0 (34.4), 154.0 (2.8), 108.0 (10.1), 55.0 (100.0).

Crotyl *p*-Nitrophenyl Sulfide: Oil; IR (neat film) 2900 (w), 1590 (m), 1570 (s), 1510 (s), 1330 (s), 1090 (s), 960 (m), 850 (s), 830 (m), 740 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.80$ (d, J=5.8 Hz, 3 H), 3.60 (d, J=5.8 Hz, 2 H), 5.20—6.00 (m, 2 H), 7.30 (d, J=9.0 Hz, 2 H), 8.10 (d, J=9.0 Hz, 2 H). HRMS, Calcd for $C_{10}H_{11}NO_2S$: M, 209.0511. Found: m/z (rel intensity) 209.0509 (M^+; 56.8), 200.0 (0.6), 109.0 (0.8), 110.0 (0.6).

Cinnamyl Crotyl Sulfide (6): Oil; IR (neat film) 3020 (m), 2900 (w), 1600 (s), 1570 (m), 1500 (s), 1440 (s), 1220 (m), 960 (s), 940 (s), 735 (s), 690 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta=1.72$ (dq, J=6.6, 1.1 Hz, 3 H), 3.38 (dt, J=7.0, 1.1 Hz, 2 H), 5.54 (dtq, J=15.0, 7.0, 1.1 Hz, 1 H), 5.68 (dtq, J=15.0, 6.6, 1.1 Hz, 1 H), 6.51 (d, J=15.8 Hz, 1 H), 6.70 (d, J=15.8 Hz, 1 H), 7.16—7.48 (m, 5 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 190.0816. Found: m/z (rel intensity) 190.0805 (M^+; 100.0), 164.1 (7.7), 135.0 (85.1), 91.1 (37.0), 77.0 (10.9).

Benzyl Crotyl Sulfide: Oil; IR (neat film) 3400 (br s), 3020 (w), 2900 (w), 1495 (m), 1450 (m), 1220 (w), 1070 (w), 1030 (w), 960 (s), 690 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, CCl_4) $\delta=1.75$ (d, J=3.6 Hz, 3 H), 2.95 (d, J=5.2 Hz, 2 H), 3.70 (s, 2 H), 5.30—5.75 (m, 2 H), 7.20—7.30 (m, 5 H). HRMS, Calcd for $C_{11}H_{14}S$: M, 178.0816. Found: m/z (rel intensity) 178.0814 (M^+; 100.0), 125.0 (1.9), 123.0 (6.7), 91.1 (44.3), 87.0 (9.4).

Preparation of *S*-Benzyl *N*-Propylthiocarbamate (7). Into a solution of phenylmethanethiol (1.47 ml, 10 mmol) in THF (15 ml) was slowly added propyl isocyanate (11 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h and then diluted with ethyl acetate (20 ml). The mixture was washed with 2 M NaOH (3×3 ml) (1 M=1 $\mathrm{mol\,dm^{-3}}$) and the organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was recrystallized from benzene-hexane to give **7** in 52% yield. Mp 42.0—43.0 °C (benzene–hexane); IR (KBr disk) 3250 (s), 2040 (m), 2950 (s), 2870 (s), 1640 (s), 1530 (s), 1480 (m), 1455 (s), 1410 (s), 1220 (s), 1070 (m), 910 (m), 820 (s), 750 $\mathrm{cm^{-1}}$ (s); ^{1}H NMR (60 MHz, $CDCl_3$) $\delta=0.90$ (t, J=6.5 Hz, 3 H), 1.50 (sextet, J=6.5 Hz, 2 H), 3.25 (q, J=6.5 Hz, 2 H), 4.15 (s, 2 H), 5.40 (br m, 1 H), 7.25—7.35 (m, 5 H). Anal. Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69; S, 15.32%. Found: C, 63.11; H, 7.32; N, 6.91; S, 15.40%.

Benzyl *p*-Methoxyphenyl Sulfide: Mp 48.0—49.0 °C (hexane); IR (KBr disk) 3000 (m), 2950 (m), 1595 (s), 1565 (s), 1490 (s), 1450 (s), 1280 (s), 1240 (s), 1175 (s), 1100 (m), 1060 (s), 1020 (s), 910 (s), 810 (s), 700 cm^{-1} (s); ^{1}H NMR (60 MHz, $CDCl_3$) δ=3.75 (s, 3 H), 4.00 (s, 2 H), 6.80 (d, J=8.0 Hz, 2 H), 7.10 (d, J=8.0 Hz, 2 H), 7.15—7.30 (m, 5 H). Anal. Calcd for $C_{14}H_{14}OS$: C, 73.00; H, 6.13; S, 13.92%. Found: C, 72.79; H, 6.18; S, 13.81%.

Benzyl *p*-Methylphenyl Sulfide: Mp 42.0—43.0 °C (hexane); IR (KBr disk) 3040 (m), 2920 (m), 1600 (w), 1490 (s), 1450 (s), 1235 (m), 1090 (m), 1020 (m), 790 cm^{-1} (s); ^{1}H NMR (60 MHz, CCl_4) δ=2.25 (s, 3 H), 3.95 (s, 2 H), 7.00 (d, J=8.0 Hz, 2 H), 7.05 (d, J=8.0 Hz, 2 H), 7.05—7.20 (m, 5 H). Anal. Calcd for $C_{14}H_{14}S$: C, 78.46; H, 6.58; S, 14.96%. Found: C, 78.23; H, 6.60; S, 14.80%.

Benzyl Phenyl Sulfide: Mp 42.0—43.0 °C (hexane); IR (KBr disk) 3050 (m), 2920 (w), 1590 (s), 1480 (s), 1460 (s), 1440 (s), 1240 (m), 1190 (m), 1170 (m), 1095 (s), 1075 (s), 1030 (s), 920 (m), 890 (m), 730 cm^{-1} (s); ^{1}H NMR (60 MHz, $CDCl_3$) δ=4.15 (s, 2 H), 7.05—7.25 (m, 10 H). Anal. Calcd for $C_{13}H_{12}S$: C, 77.95; H, 6.04; S, 16.01%. Found: C, 77.73; H, 6.07; S, 15.99%.

Benzyl *p*-Methoxycarbonylphenyl Sulfide: Mp 93.5—94.5 °C (benzene–hexane); IR (KBr disk) 3025 (w), 2945 (m), 2925 (w), 1710 (s), 1490 (s), 1430 (s), 1400 (s), 1285 (s), 1180 (s), 1110 (s), 1010 (s), 970 (m), 840 (s), 770 (s), 750 (s), 710 cm^{-1} (s); ^{1}H NMR (60 MHz, $CDCl_3$) δ=3.95 (s, 3 H), 4.25 (s, 2 H), 7.20 (d, J=7.0 Hz, 2 H), 7.20—7.35 (m, 5 H), 7.95 (d, J=7.0 Hz, 2 H). Anal. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46; S, 12.41%. Found: C, 69.47; H, 5.54; S, 12.37%.

Benzyl *p*-Nitrophenyl Sulfide: Mp 128.0—129.0 °C (benzene–hexane); IR (KBr disk) 3060 (w), 1570 (s), 1510 (s), 1340 (s), 1180 (m), 1090 (s), 850 (s), 830 (s), 740 (s), 710 cm^{-1} (s); ^{1}H NMR (60 MHz, $CDCl_3$) δ=4.25 (s, 2 H), 7.25 (d, J=8.0 Hz, 2 H), 7.10—7.60 (m, 7 H), 8.10 (d, J=8.0 Hz, 2 H). Anal. Calcd for $C_{13}H_{11}NO_2S$: C, 63.65; H, 4.52; N, 5.71; S, 13.07%. Found: C, 63.41; H, 4.60; N, 5.62; S, 13.19%.

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