Novel Palladium(II)-Catalyzed Cyclization of Aziridines and Sulfur Diimides

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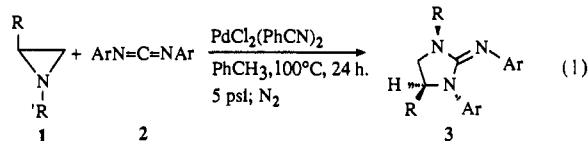
Abstract: Bis(benzonitrile)palladium dichloride is an effective catalyst for the cyclization reaction of aziridines and sulfur diimides, in toluene, affording imidazolidinethiones in 52–70% yield. Reaction of an aziridine, labeled with ^{13}C at one of the ring carbons, with a sulfur diimide resulted in incorporation of the label at the 2- and 5-positions of the imidazolidinethione. Thiazolidinimine formation results from the palladium(II)-catalyzed reaction of an aziridine with phenyl isothiocyanate.

The cycloaddition of three-membered-ring heterocycles with heterocumulenes is a useful method for the formation of five-membered-ring heterocycles. For example, succinimides were synthesized from aziridinones and diphenylketene,[1] and oxadi-azolidinones were obtained from oxaziridines and phenylisocy-anate.[2] Better yields and regioselectivities resulted using halides as catalysts. For instance, lithium bromide is capable of catalyzing the cycloaddition of oxiranes with isocyanates,[3] while organotin and organoantimony halides promote the cycloaddition of azidridines and oxiranes with heterocumulenes.[4–7] In recent years, significant improvement in regioselectivity and stereoselectivity was achieved by the use of transition metal complexes as catalysts (e.g., Pd(O),[8–10] Pd(II)[11]).

The synthesis and reactivity of sulfur diimides have been widely studied, particularly for Diels–Alder cycloaddition reactions.[12–14] Various electron-deficient sulfur diimides (employed as the heterodienophile) such as bis(arylsulfonyl)-,[15,16] bis(alkoxycar-bonyl)-,[17] or bis(p-nitrobenzoyl)sulfur diimide[18] readily react with dienes to form thiazines. Unlike other heterocumulenes, sulfur diimides have rarely been used in cycloaddition reactions with heterocycles.[19]

We recently found that bis(benzonitrile)palladium dichloride

catalyzes the cycloaddition of aziridines and carbodiimides to form imidazolidinimines **3** in fine yields (eq 1).[11]


$$\text{(1)}$$

We now wish to report the bis(benzonitrile)palladium dichloride catalyzed cycloaddition of aziridines with sulfur diimides affording imidazolidinethiones in good yields. In this novel reaction, both the thiocarbonyl carbon and the methylene group of the product arise from the methylene unit of the aziridine reactant.

Results and Discussion

It was anticipated that replacement of the heterocumulene carbon of **2** by a sulfur atom (i.e., sulfur diimide **4**) in the palladium-catalyzed reaction would result in the formation of a thiadiazolidenimine (**6**, Scheme 1). The latter compound was not obtained in the reaction. A unique cyclization process occurred instead. Specifically, treatment of 1-*tert*-butyl-2-phenylaziridine (**1**, R = Ph, R' = C(CH$_3$)$_3$) with di-*p*-tolylsulfur diimide (**4**, Ar = *p*-CH$_3$(C$_6$H$_4$)) in toluene at 130 °C, using bis(benzonitrile)-palladium dichloride as the catalyst, afforded the imidazoli-dinethione **5** (Ar = *p*-CH$_3$C$_6$H$_4$, R = Ph, R' = (CCH$_3$)$_3$) in 53% yield of pure material.

Scheme 1
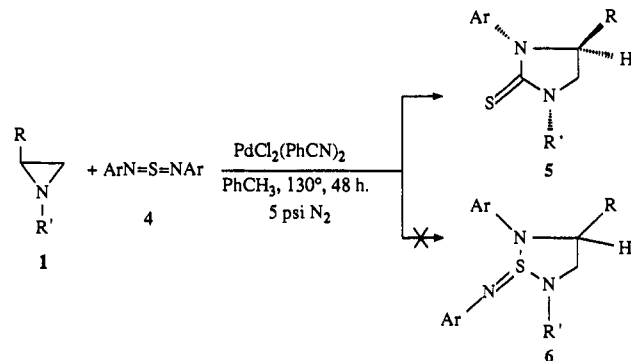
The ratio of aziridine to sulfur diimide to palladium catalyst used was 20:10:1.0. The reaction is sensitive to the ratio of aziridine **1** and sulfur diimide **4**. When the ratio of aziridine **1**

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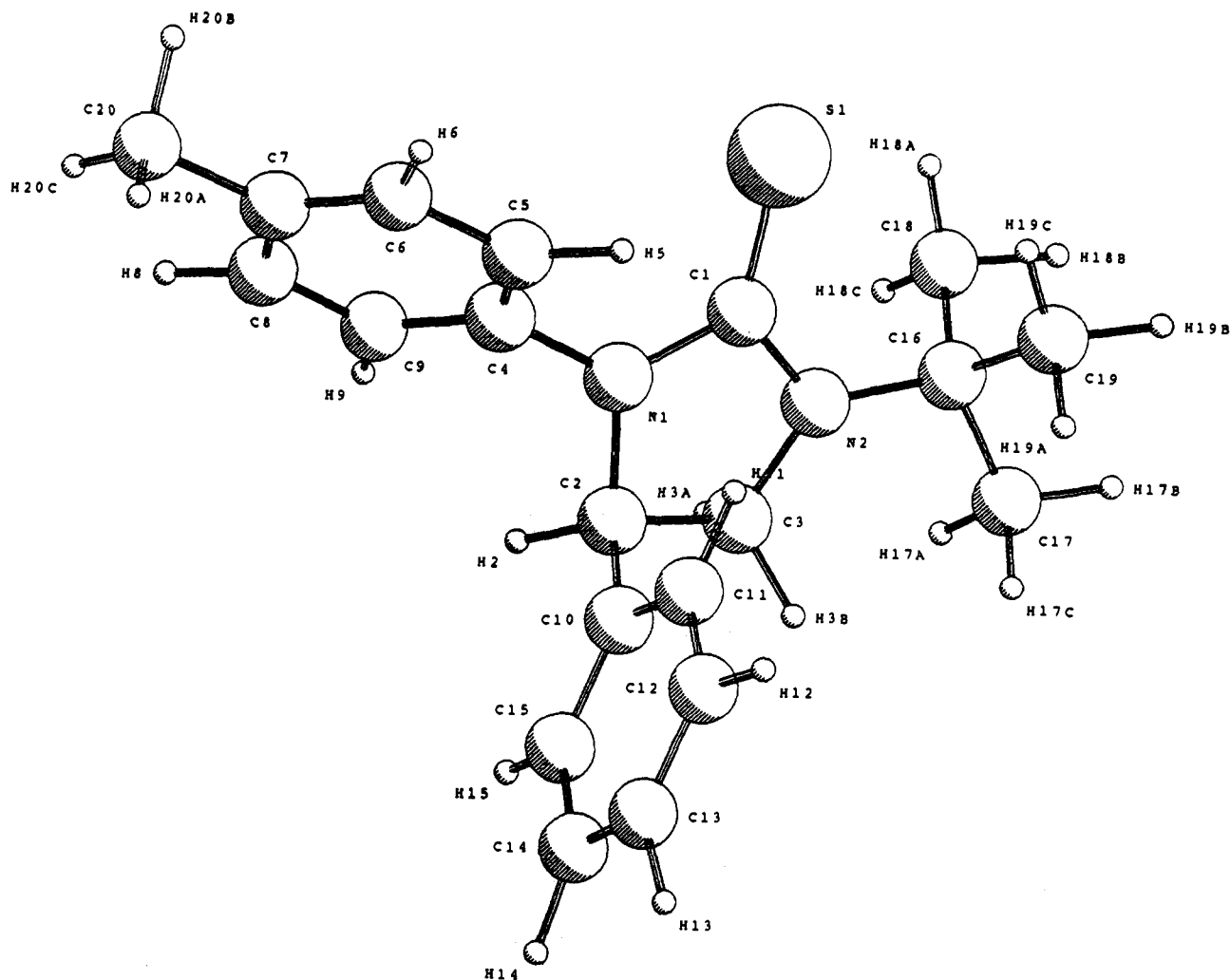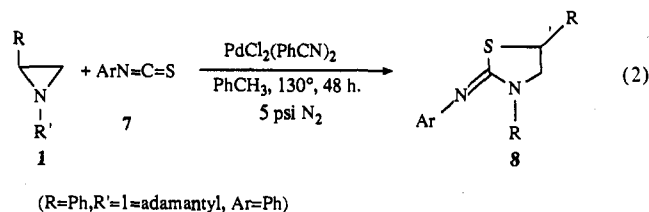(19) Hänssgen, D.; Odenhausen, E. *J. Organomet. Chem.* **1977,** *124,* 143.

Figure 1. View of **5** (R = Ph, R' = C(CH₃)₃, Ar = p-CH₃C₆H₄) showing the atom-numbering scheme.

(R = Ph, R' = C(CH₃)₃) and sulfur diimide **4** (Ar = p-tolyl) was 1:1, the yield decreased to 36%.

The bis(benzonitrile)palladium dichloride analyzed cycloaddition reaction was effected using different aziridines and either diphenyl or di-p-tolylsulfur diimide, affording imidazolidinethiones **5** in 52–70% yields. In all of these reactions the aziridine experiences cleavage of the more substituted ring carbon–nitrogen bond. The imidazolidinethione **5** was identified by means of spectral data (see Experimental Section) as well as an X-ray analysis of **5** (R = Ph, R' = C(CH₃)₃, Ar = p-CH₃C₆H₄). The thiocarbonyl stretching frequency of **5** occurred in the infrared spectrum at 1241–1251 cm⁻¹,[20] and the thiocarbonyl carbon occurred at δ 182.00–183.16 in the ¹³C-NMR spectrum.[21] Two doublets of doublets and a triplet (i.e., two overlapping doublets) were normally observed for the ring protons of **5** in the ¹H NMR. The mass spectra displayed molecular ion peaks in all cases. An X-ray structure determination revealed that the phenyl substituent of **5** (R = Ph, R' = C(CH₃)₃, Ar = p-CH₃C₆H₄) was trans to both of the substituents (p-CH₃C₆H₄, C(CH₃)₃) attached to the nitrogen atoms. An ORTEP drawing is presented in Figure 1.

One can consider the formation of **5** by a formal [3 + 2] cycloaddition of an aryl isothiocyanate **7** and aziridine **1**. However, treatment of 1-(1-adamantyl)-2-phenylaziridine (**1**, R = Ph, R' = 1-adamantyl) with phenyl isothiocyanate (**7**, Ar = Ph) under the same reaction conditions as in Scheme 1 gave the

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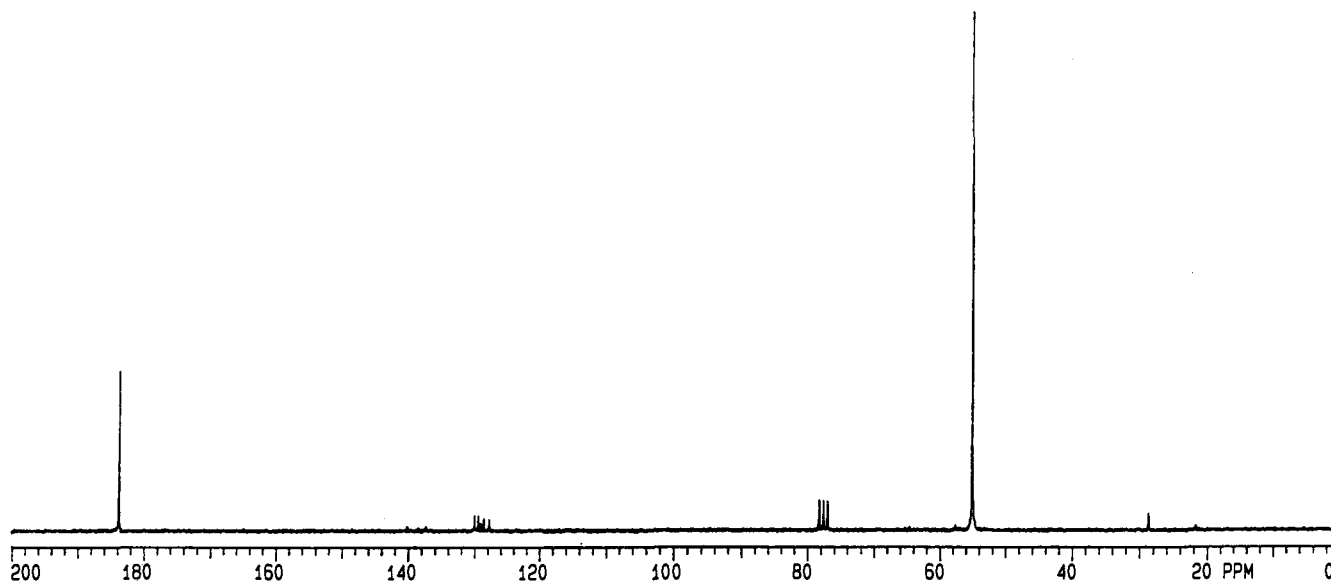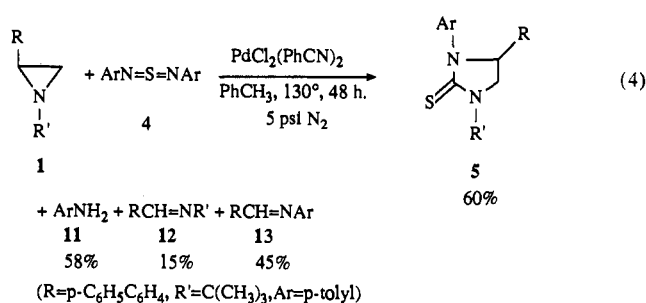
thiazolidinimine **8** in 85% isolated yield, and no imidazolidinethione **5** was detected in the reaction (eq 2).

$$R \diagdown_{\substack{N \\ | \\ R'}} \diagup \; + \; ArN{=}C{=}S \xrightarrow[\substack{PhCH_3,\ 130°,\ 48\ h. \\ 5\ psi\ N_2}]{PdCl_2(PhCN)_2} \; Ar{-}N{=}\diagup_{\substack{S \\ \diagdown N \\ | \\ R}}^{R} \tag{2}$$

(R=Ph,R'=1=adamantyl, Ar=Ph)

This result is analogous to the organoantimony halide catalyzed cycloaddition of aziridines with phenyl isothiocyanate.[7] Therefore, the imidazolidinethiones **5** do *not* originate from the cycloaddition reaction of aziridines and *in situ* generated aryl isothiocyanates.

Several experiments were then undertaken to probe the source of the carbon in the thiocarbonyl group of **5**. The benzonitrile ligand is an unlikely source of the thiocarbonyl carbon, since use of excess benzonitrile (equimolar with respect to **1**) in the reaction of **1** and **4** resulted in a lower yield of **5** [e.g., **1**, R = Ph, R' = C(CH₃)₃, reacted with **4**, Ar = p-CH₃C₆H₄, to give **5** in 5% yield]. The methyl group of the solvent, toluene, is not incorporated in the product, since similar product yields were obtained in benzene or toluene, using the conditions described above. It seemed conceivable that the thiocarbonyl carbon of **5** derived from a second molecule of the reactant aziridine **1**, with the ring carbons (i.e., at the 2- or 3-position) being the likely candidates. In order to address this possibility, 1-*tert*-butyl-2-

Figure 2. ^{13}C-NMR spectrum of 10.

phenyl[3-^{13}C]aziridine (9) was prepared from [^{13}C]iodomethane. Treatment of [^{13}C]iodomethane with triphenylphosphine afforded labeled methyltriphenylphosphonium iodide in 96% yield.[22] Reaction of the latter with 5 N aqueous sodium hydroxide in benzene gave the labeled styrene (PhCH=^{13}CH$_2$) in 42% GC yield.[23] The benzene solution, containing Ph$_3$PO as a byproduct, was reacted *in situ* with *m*-chloroperbenzoic acid to give 2-phenyl-[3-^{13}C]oxirane in 52% isolated yield.[24] Subsequent reaction of the labeled oxirane with *tert*-butylamine, followed by treatment with bromine/PPh$_3$ and Et$_3$N in acetonitrile, gave 9 in 66% yield.[25] When 9 was treated with di-*p*-tolylsulfur diimide (4, Ar = *p*-CH$_3$C$_6$H$_4$) using conditions identical to those for the unlabeled reaction [PdCl$_2$(PhCN)$_2$, PhCH$_3$, 130 °C, 48 h], the ^{13}C-labeled imidazolidinethione 10 was obtained in 52% yield (eq 3).

(3)
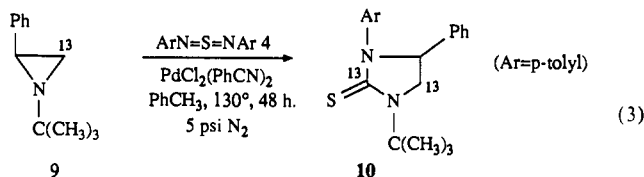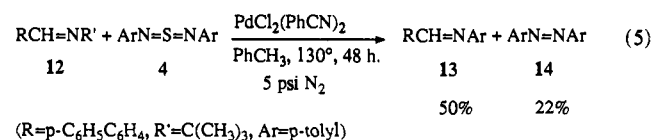
The ^{13}C-NMR spectrum of 10 clearly shows that the product contains ^{13}C at the 2- and 5-positions (δ 183.17 (^{13}C=S) and δ 54.46 (^{13}CH$_2$), respectively) (Figure 2). The mass spectrum gave an intense molecular ion peak at *m/e* 326. Therefore, the ^{13}C-labeling experiment demonstrated that the source of the new carbon atom in 5 is the CH$_2$ group of the reactant aziridine 1.

Some additional information relevant to the reaction was obtained by analysis of the products accompanying the cycloaddition of 1 and 4 (eq 4). The primary arylamine 11 and two imines 12 and 13 were also isolated when 1 (R = *p*-C$_6$H$_5$C$_6$H$_4$, R' = C(CH$_3$)$_3$) was treated with 4 (Ar = *p*-tolyl) to give 5 under the standard conditions. The yield of amine 11 (originally part of the sulfur diimide 4) was almost the same as that of the imidazolidinethione 5. The yield of the imine 12, which results from formal loss of methylene from the aziridine 1, was 15%. Imine 13, isolated in 45% yield, may arise from an exchange reaction between 12 and 4. Some evidence for the latter reaction

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(4)

5
60%

+ ArNH$_2$ + RCH=NR' + RCH=NAr
   11   12   13
   58%   15%   45%

(R=p-C$_6$H$_5$C$_6$H$_4$, R'=C(CH$_3$)$_3$,Ar=p-tolyl)

was obtained by treating the amine 12 with the sulfur diimide 4 in the presence of PdCl$_2$(PhCN)$_2$, which afforded a mixture of imine 13 (50%) and azoarene 14 (22% yield) (eq 5). Any azoarene

RCH=NR' + ArN=S=NAr $\xrightarrow[\substack{\text{PhCH}_3, 130°, 48 \text{ h.} \\ 5 \text{ psi N}_2}]{\text{PdCl}_2(\text{PhCN})_2}$ RCH=NAr + ArN=NAr   (5)

12   4   13   14

                                                                50%   22%

(R=p-C$_6$H$_5$C$_6$H$_4$, R'=C(CH$_3$)$_3$, Ar=p-tolyl)

14, formed by treatment of 1 with 4 (eq 4), could react with an palladoazacyclobutane, to give 11 and 13. This would explain the generation of only traces of 14 in the reaction leading to 5 (eq 4). This rationale assumes occurrence of a metathesis pathway for the production of the imidazolidinethione.

In conclusion, (PhCN)$_2$PdCl$_2$ is an effective catalyst for the reaction of aziridines with sulfur diimides to form imidazolidinethiones.

Experimental Section

General Methods. A Fisher-Johns apparatus was used for melting point determinations. The following spectrometers were used to obtain spectral data: Bomem MB 100-C15 (FT-IR); Bruker AMX 500, Varian XL-300, and Gemini 200 (NMR); VG 7070 E (MS). The aziridines, sulfur diimides, and palladium catalyst were prepared according to literature procedures.[25-28] The organic solvents were dried and distilled prior to use. Elemental analyses were carried out by MHW Laboratories, Phoenix, AZ. All reactions were conducted under a dry nitrogen atmosphere.

General Procedure for the Palladium-Catalyzed Cycloaddition Reaction of Aziridines and Sulfur Diimides. A mixture of aziridine (2.0 mmol), sulfur diimide (1.0 mmol), and bis(benzonitrile)palladium dichloride

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(0.038 g, 0.10 mmol) in toluene (3.0 mL) was heated with stirring in a glass autoclave for 48 h at 130 °C (oil bath temperature) under a slight pressure of nitrogen (5 psi). After being cooled to room temperature, the autoclave was opened and the red-brown homogeneous solution was filtered through Celite. The filtrate was concentrated by rotary evaporation, and the crude product was purified by silica gel thin-layer chromatography using 10:1 toluene/acetonitrile as the developer.

Yields (based on sulfur diimide), melting points, IR, NMR, MS, and either high-resolution mass spectra (HRMS) determinations or analytical data for 5 are as follows:

(a) R = Ph, R' = C(CH)₃, Ar = *p*-tolyl: 53% yield; mp 203–204 °C; IR ν(C=S) 1242 cm⁻¹; ¹H NMR (CDCl₃) δ 1.52 (s, 9H, C(CH₃)₃), 2.22 (s, 3H, CH₃), 3.66 (dd, 1H, *J* = 8.4 and 9.9 Hz), 4.17 (t, 1H, *J* = 9.9 Hz), 4.95 (dd, 1H, *J* = 8.4 and 9.9 Hz), 7.01–7.26 (m, 9H, aromatic protons); ¹³C NMR (CDCl₃) δ 21.26 (*p*-CH₃C₆H₄), 28.05 (CH₃), 54.48 (CH₂), 57.07 (C(CH₃)₃), 64.36 (CHAr), 127.23, 128.03, 128.48, 128.85, 129.40 (CH-aromatic), 136.70, 137.79, 139.52 (quaternary aromatic carbons), 183 (C=S); MS (*m/e*) 324 [M]⁺; HRMS (*m/e*) 324.1643 (calcd for C₂₀H₂₄N₂S, 324.1660).

(b) R = Ph, R' = *n*-C₄H₉, Ar = *p*-tolyl: 52% yield; mp 109–110 °C; IR ν (C=S) 1251 cm⁻¹; ¹H NMR (CDCl₃) δ 0.95 (t, 3H, CH₃), 1.38 (q, 2H, CH₂CH₃), 1.63 (m, 2H, CH₂CH₂CH₃), 2.22 (s, 3H, CH₃), 3.71 (m, 3H, NCH₂ and 1H of CH₂ ring), 4.08 (t, 1H, CH₂ ring, *J* = 10.0 Hz), 5.11 (dd, 1H, CHPh, *J* = 7.6 and 10.0 Hz), 6.99–7.30 (m, 9H, aromatic); ¹³C NMR (CDCl₃) δ 14.03 (CH₃), 20.10, 29.25 (CH₃CH₂-CH₂), 21.12 (CH₃), 47.62 (NCH₂), 55.58 (CH₂ ring), 64.61 (CHPh), 127.17, 128.54, 128.59, 129.01, 129.40 (CH-aromatic), 136.57, 137.46, 139.66 (quaternary carbons of aromatic group), 182.60 (C=S); MS (*m/e*) 324 [M]⁺. Anal. Calcd for C₂₀H₂₄N₂S: C, 73.03; H, 7.45; N, 8.63. Found: C, 73.86; H, 7.36; N, 8.58.

(c) R = Ph, R' = 1-adamantyl, Ar = Ph: 52% yield; mp 215–216 °C; IR ν (C=S) 1244 cm⁻¹; ¹H NMR (CDCl₃) δ 1.61–2.60 (m, 15H, adamantyl protons), 3.68 (dd, 1H, *J* = 8.2 and 10.0 Hz), 4.18 (t, 1H, *J* = 10.0 Hz), 4.60 (dd, 1H, *J* = 8.2 and 10.0 Hz), 7.10–7.25 (m, 10H, aromatic ring protons); ¹³C NMR (CDCl₃) δ 29.93, 36.27, 39.34 (secondary and tertiary adamantyl carbons), 53.52 (CH₂), 58.34 (quaternary carbon of adamantyl group), 64.27 (CHPh), 126.80, 127.14, 128.21, 128.43, 128.53, 128.83 (CH-aromatic), 139.50, 140.26 (quaternary carbons of Ph), 182.01 (C=S); MS (*m/e*) 388 [M]⁺. Anal. Calcd for C₂₅H₂₈N₂S: C, 77.28; H, 7.26; N, 7.21. Found: C, 77.08; H, 7.19; N, 7.14.

(d) R = Ph, R' = 1-adamantyl, Ar = *p*-tolyl: 56% yield; mp 217–218 °C; IR ν(C=S) 1246 cm⁻¹; ¹H NMR (CDCl₃) δ 1.59–2.52 (m, 15H, adamantyl protons), 2.21 (s, 3H, CH₃), 3.67 (dd, 1H, *J* = 8.2 and 10.0 Hz), 4.16 (t, 1H, *J* = 10.0 Hz), 4.92 (dd, 1H, *J* = 8.2 and 10.0 Hz), 6.96–7.25 (m, 9H, aromatic ring protons); ¹³C NMR (CDCl₃) δ 21.14 (*p*-CH₃C₆H₄), 29.94, 36.30, 39.36 (secondary and tertiary adamantyl carbons), 53.51 (CH₂), 58.27 (quaternary carbon of adamantyl group), 64.37 (CHPh), 127.20, 128.08, 128.40, 128.80, 129.33 (CH-aromatic), 136.58, 137.69, 139.65 (quaternary carbons of Ph), 182.22 (C=S); MS (*m/e*) 402 [M]⁺. Anal. Calcd for C₂₆H₃₀N₂S: C, 77.57; H, 7.51; N, 6.96. Found: C, 77.73; H, 7.46; N, 6.90.

(e) R = *p*-BrC₆H₄, R' = C(CH₃)₃, Ar = Ph: 60% yield; mp 153–154 °C; IR ν (C=S) 1246 cm⁻¹; ¹H NMR (CDCl₃) δ 1.67 (s, 9H, C(CH₃)₃), 3.60 (dd, 1H, *J* = 8.4 and 9.9 Hz), 4.17 (t, *J* = 9.9 Hz), 4.97 (dd, 1H, *J* = 8.4 and 9.9 Hz), 7.09–7.43 (m, 10H, aromatic protons); ¹³C NMR (CDCl₃) δ 28.02 (CH₃), 54.27 (CH₂), 57.21 (C(CH₃)₃), 63.58 (CHAr), 127.01, 128.03, 128.72, 128.85, 132.06 (aromatic carbons), 122.45, 138.45, 140.16 (quaternary aromatic carbons), 182.86 (C=S); MS (*m/e*) 389 [M]⁺ and 391 [M + 2]⁺. Anal. Calcd for C₁₉H₂₁BrN₂S: C, 58.61; H, 5.44; N, 7.20. Found: C, 58.86; H, 6.01; N, 6.65.

(f) R = *p*-BrC₆H₄, R' = C(CH₃)₃, Ar = *p*-tolyl: 58% yield; mp 175–176 °C; IR ν (C=S) 1241 cm⁻¹; ¹H NMR (CDCl₃) δ 1.66 (s, 9H, C(CH₃)₃), 2.22 (s, 3H, CH₃), 3.58 (dd, 1H, *J* = 8.2 and 10.0 Hz), 4.15 (t, 1H, *J* = 10.0 Hz), 4.92 (dd, 1H, *J* = 8.2 and 10.0 Hz), 7.01–7.41 (m, 8H, aromatic protons); ¹³C NMR (CDCl₃) δ 21.15 (*p*-CH₃C₆H₄), 28.03 (CH₃), 54.23 (CH₂), 57.13 (C(CH₃)₃), 63.67 (CHAr), 127.88, 128.90, 129.47, 132.01 (aromatic carbons), 122.39, 136.79, 137.59, 138.59 (quaternary aromatic carbons), 183.07 (C=S); MS (*m/e*) 403 [M]⁺ and 405 [M + 2]⁺. Anal. Calcd for C₂₀H₂₃BrN₂S: C, 59.55; H, 5.75; N, 6.94. Found: C, 59.21; H, 5.82; N, 6.81.

(g) r = *p*-PhC₆H₄, R' = 1-adamantyl, Ar = Ph; 70% yield; mp 211–212 °C; IR ν (C=S) 1245 cm⁻¹; ¹H NMR (CDCl₃) δ 1.69–2.55 (m, 15H, adamantyl protons), 3.71 (dd, 1H, *J* = 8.4 and 10.0 Hz), 4.20 (t, 1H, *J* = 10.0 Hz), 5.02 (dd, 1H, *J* = 8.4 and 10.0 Hz), 7.14–7.71 (m, 14H, aromatic ring protons); ¹³C NMR (CDCl₃) δ 30.04, 36.37, 39.41

(secondary and tertiary adamantyl carbons), 53.59 (CH₂), 58.41 (quaternary carbon of adamantyl group), 63.96 (CHPh), 127.03, 127.40, 127.55, 127.64, 128.26, 128.63, 128.89, 129.09 (CH-aromatic), 138.59, 140.28, 140.43, 141.24 (quaternary carbons of aromatic group), 182.02 (C=S); MS (*m/e*) 464 [M]⁺. Anal. Calcd for C₃₁H₃₂N₂S: C, 80.13; H, 6.94; N, 6.03. Found: C, 80.06; H, 7.03; N, 5.82.

(h) R = *p*-PhC₆H₄, R' = 1-adamantyl, Ar = *p*-tolyl: 68% yield; mp 142–143 °C; IR ν (C=S) 1245 cm⁻¹; ¹H NMR (CDCl₃) ν 1.69–2.62 (m, 15H, adamantyl protons), 2.23 (s, 3H, CH₃), 3.70 (dd, 1H, *J* = 8.4 and 9.8 Hz), 4.19 (t, 1H, *J* = 9.8 Hz), 4.98 (dd, 1H, *J* = 8.4 and 9.8 Hz), 7.04–7.97 (m, 13H, aromatic ring protons); ¹³C NMR (CDCl₃) δ 21.21 (*p*-CH₃C₆H₄), 30.03, 36.37, 39.43 (secondary and tertiary adamantyl carbons), 53.57 (CH₂), 58.34 (quaternary carbon of adamantyl group), 64.10 (CHPh), 127.02, 127.52, 127.69, 128.14, 128.87, 129.09, 129.43 (CH-aromatic), 136.63, 137.81, 138.68, 140.30, 141.22 (quaternary carbons of aromatic group), 182.28 (C=S); MS (*m/e*) 478 [M]⁺. Anal. Calcd for C₃₂H₃₄N₂S: C, 80.29; H, 7.16; N, 5.85. Found: C, 80.50; H, 7.85; N, 5.35.

(i) R = *p*-PhC₆H₄, R' = C(CH₃)₃, Ar = *p*-tolyl: 60% yield; mp 183–184 °C; IR ν (C=S) 1243 cm⁻¹; ¹H NMR (CDCl₃) δ 1.69 (s, 9H, C(CH₃)₃), 2.23 (s, 3H, CH₃), 3.68 (dd, 1H, *J* = 8.4 and 9.9 Hz), 4.19 (t, 1H, *J* = 9.9 Hz), 4.95 (dd, 1H, *J* = 8.4 and 9.9 Hz), 7.04–7.58 (m, 13H, aromatic protons); ¹³C NMR (CDCl₃) δ 21.18 (*p*-CH₃C₆H₄), 28.09 (CH₃), 54.49 (CH₂), 57.13 (C(CH₃)₃), 64.08 (CHAr), 127.00, 127.53, 127.67, 128.05, 128.84, 129.46, 129.74 (CH-aromatic), 136.74, 137.87, 138.51, 140.26, 141.28 (quaternary aromatic carbons), 183.16 (C=S); MS (*m/e*) 400 [M]⁺; HRMS (*m/e*) 400.19876 (calcd for C₂₆H₂₈N₂S, 400.19721).

Procedure for the Palladium-Catalyzed Cycloaddition Reaction of 1-Adamantyl-2-phenylaziridine and Phenyl Isothiocyanate. A mixture of aziridine (1, 1 mmol), phenyl isothiocyanate (7, 1 mmol), and bis-(benzonitrile)palladium dichloride (0.038 g, 0.10 mmol) in toluene (3.0 mL) was heated with stirring in a glass autoclave, for 48 h at 130 °C (oil bath temperature) under a slight pressure of nitrogen (5 psi). The workup procedure was the same as that described in the general procedure for the palladium-catalyzed cycloaddition reaction of aziridines and sulfur diimides. The isolated yield of 8 was 0.33 g: 85% yield; mp 133–134 °C; IR ν (C=N) 1619 cm⁻¹; ¹H NMR (CDCl₃) δ 1.66–2.50 (m, 15H, adamantyl protons), 3.67 (dd, 1H, *J* = 8.2 and 9.7 Hz, CH₂), 4.01 (dd, 1H, *J* = 6.6 and 9.7 Hz, CH₂), 4.55 (m, 1H, CHPh), 6.95–7.46 (m, 10H, aromatic ring protons); ¹³C NMR (CDCl₃) δ 30.73, 37.27, 40.29 (secondary and tertiary adamantyl carbons), 46.51 (CHPh), 56.57 (CH₂), 58.94 (quaternary carbon of adamantyl group), 122.53, 123.27, 128.17, 128.62, 129.37, 129.43 (CH-aromatic), 140.13, 153.26 (quaternary carbons of Ph), 156.75 (C=N); MS (*m/e*) 388 [M]⁺. Anal. Calcd for C₂₅H₂₈N₂S: C, 77.23; H, 7.26; N, 7.21. Found: C, 77.08; H, 7.15; N, 7.50.

Synthesis of 1-*tert*-Butyl-2-phenyl[3-¹³C]aziridine (9). (i) Methyl-[¹³C]triphenylphosphonium Iodide. A solution containing 9.4 g (36.0 mmol) of triphenylphosphine dissolved in dry benzene (6.0 mL) was placed in a pressure bottle, the bottle was cooled in an ice bath, and 5.0 g (36.0 mmol) of [¹³C]methyl iodide was added. The bottle was sealed, allowed to stand at room temperature for 2 days, and then reopened. The white solid was collected by filtration with the aid of about 100 mL of hot benzene and was dried in a vacuum at 100 °C over phosphorus pentoxide. The yield was 13.9 g (96%), mp 183–184 °C.

(ii) 2-Phenyl[3-¹³C]oxirane. A heterogeneous mixture of benzaldehyde (1.83 g, 17.2 mmol), methyl[¹³C]triphenylphosphonium iodide (13.9 g, 34.3 mmol), benzene (34 mL), and 5 N aqueous sodium hydroxide (102 mL) was stirred for 24 h at 40 °C. The reaction mixture was extracted with benzene (3 × 25 mL), the alkali was removed by washing with water, and the benzene solution was dried (MgSO₄) and filtered. The yield of 1-phenyl[2-¹³C]ethene was 42% (GC yield, using *n*-undecane as internal standard). The benzene solution (also containing Ph₃PO as a byproduct) was used for the subsequent epoxidation.

To the benzene solution was added 7.6 g (22.0 mmol) of *m*-chloroperbenzoic acid (50%). The mixture was kept at 0 °C for 40 h and was shaken frequently during the first hour. The formed *m*-chloroperbenzoic acid was removed from the benzene solution by shaking with an excess of 10% aqueous sodium hydroxide, and the alkali was removed by washing with water. The benzene layer was dried (MgSO₄) and evaporated, and the residue was distilled *in vacuo* to give 0.91 g (52%) of oxirane: bp 38–40 °C/1 mmHg; ¹H NMR (CDCl₃) δ 2.78 (ddd, 1H, *J* = 2.5, 5.8, and 176.0 Hz, ¹³CH₂), 3.12 (ddd, 1H, *J* = 4.1, 5.8, and 178.0 Hz, ¹³CH₂), 3.83 (m, 1H, CHPh), 7.26–7.43 (m, 5H, Ph); MS (*m/e*) 121 [M⁺].

(iii) **1-Phenyl-2-(*tert*-butylamino)[2-^{13}C]1-ethanol.** A mixture of 0.91 g (7.5 mmol) of 2-phenyl[3-^{13}C]oxirane and 2.74 g (37.5 mmol) of *tert*-butylamine was stirred in an autoclave for 60 h at 95 °C. After evaporation of excess *tert*-butylamine, the residual solid was crystallized from hexane to give 1.03 g (71%) of the white amino alcohol: mp 85–86 °C; IR (CHCl$_3$) $\nu_{OH,NH}$ 3600, 3400–3300 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.12 (s, 9H, C(CH$_3$)$_3$), 2.26–3.15 (m, 4H, ^{13}CH$_2$, NH, OH), 4.55 (m, 1H, CHOH), 7.28 (m, 5H, Ph); MS (*m/e*) 194 [M$^+$].

(iv) **1-*tert*-Butyl-2-phenyl[3-^{13}C]aziridine (9).** To an ice-cold solution of 1.40 g (5.3 mmol) of triphenylphosphine in 12 mL of acetonitrile (N$_2$ atmosphere) was added, drop-by-drop, an ice-cold solution of 0.85 g (5.3 mmol) of bromine in 3.5 mL of acetonitrile. To the resulting red solution was slowly added 1.03 g (5.3 mmol) of the β-amino alcohol, followed by drop-by-drop addition of 1.62 g (16.0 mmol) of distilled triethylamine in 3.5 mL of acetonitrile (all done at 0 °C). The reaction mixture was then stirred at ambient temperature for 20 min, triethylamine hydrobromide (2.24 g, 77%) was filtered, and the filtrate was concentrated by rotary evaporation. The residue was treated with hexane (6 × 15 mL), concentrated to 7 mL, and then filtered to remove triphenylphosphine oxide, and the filtrate was evaporated. The aziridine **9** was obtained in 66% yield by distillation at 40 °C (0.5 mmHg): ^{1}H NMR (CDCl$_3$) δ 1.06 (s, 9H, C(CH$_3$)$_3$), 1.66 (ddd, 1H, J = 0.8, 3.0, and $J_{^{13}C-^1H}$ = 176.0 Hz, ^{13}CH$_2$), 1.91 (ddd, 1H, J = 0.8, 6.4, and $J_{^{13}C-^1H}$ = 162.0 Hz, ^{13}CH$_2$), 2.64 (m, 1H, CHPh), 7.20–7.37 (m, 5H, Ph); ^{13}C NMR (CDCl$_3$) δ 27.20 (CH$_3$), 30.95 (^{13}CH$_2$, intense signal), 34.30 (C(CH$_3$)$_3$), 51.83 (CHPh), 127.20, 128.78 (CH-aromatic), 128.95 (quaternary aromatic (carbon); MS (*m/e*) 176 [M$^+$].

Procedure for the Palladium-Catalyzed Cycloaddition Reaction of 1-*tert*-Butyl-2-phenyl[3-^{13}C]aziridine and 1,3-Di-*p*-tolylsulfur Diimide. The reaction procedure was the same as that described in the general procedure for the palladium-catalyzed cycloaddition reaction of aziridines and sulfur diimides. The isolated yield of the pure product **10** was 52%: mp 203–204 °C; IR ν (^{13}C=S) 1214 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.69 (s, 9H, C(CH$_3$)$_3$), 2.23 (s, 3H, CH$_3$), 3.66 (doublet of multiplets, 1H, $J_{^{13}C-^1H}$ = 144.0 Hz, ^{13}CH$_2$), 4.19 (doublet of multiplets, 1H, $J_{^{13}C-^1H}$ = 146.0 Hz, ^{13}CH$_2$), 4.96 (m, 1H, CHPh), 7.02–7.35 (m, 9H, aromatic protons); ^{13}C NMR (CDCl$_3$) δ 21.16 (*p*-CH$_3$C$_6$H$_4$), 28.06 (CH$_3$), 54.46 (^{13}CH$_2$, intense signal), 57.07 (C(CH$_3$)$_3$), 64.23 (CHAr), 127.25, 128.04, 128.49, 128.87,

129.40 (CH-aromatic), 136.69, 137.85, 139.60 (quaternary aromatic carbons), 183.17 (^{13}C=S, intense signal); MS *m/e* 326 [M$^+$].

X-ray Analysis. A plate crystal of C$_{20}$H$_{24}$N$_2$S was mounted on a glass capillary, and all measurements were made on a Rigaku diffractometer with Mo Kα radiation. Cell dimensions and the orientation matrix were obtained from least-squares refinement using the setting angles of 25 reflections in the range 40° < 2θ < 47°, corresponding to an orthorhombic cell with dimensions given in the supplementary material. For Z = 4 and FW = 324.48, the calculated density is 1.147 g/cm^3. The space group was determined to be $P2/2/2$. The data were collected at 21 °C using the ω – 2θ scan technique to a maximum 2θ value of 47, and the data were corrected for Lorentz and polarization effects.[29]

The structure was solved by direct methods. All of the atoms with the exception of hydrogen were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 789 observed reflections ($I > 2.5\sigma(I)$) and 185 variable parameters. All calculations were performed using the NRC VAX crystallographiic software package.[30]

Supplementary Material Available: Experimental details and tables of atomic parameters (x, y, z, and B_{iso}) and bond distances and angles for **5**, R = Ph, R′ = C(CH$_3$)$_3$, Ar = *p*-CH$_3$C$_6$H$_4$ (13 pages); tables of structure factors for **5** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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