Au-Catalyzed Reaction of Propargylic Sulfides and Dithioacetals

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Received September 9, 2006

Propargylic sulfides and dithioacetals are found to undergo similar transformations as propargylic carboxylates when catalyzed by AuCl or AuCl3, affording indene derivatives through pentannulation of aromatic rings. The reaction presumably involves Au carbene as the reactive intermediate.

Introduction

The chemistry of transition-metal-complex-activated alkynes has witnessed increasing development in recent years.1 Among the various catalytic systems, Au(I) and Pt(II) complexes have attracted particular attention due to their high affinity to the π system of the alkyne substrates. A number of novel transformations have emerged based on the Au(I)- or Pt(II)-catalyzed reactions of alkynes.2 One of the general processes that is involved in those transformations is the transition-metal-catalyzed reaction of propargyl esters that generates a metal carbene intermediate, as shown by eq 1.3 The activation of the triple bond by a transition metal triggers an intramolecular nucleophilic attack by the ester carbonyl oxygen, generating a cyclic five-centered ionic species. Subsequent 1,2-acyl group migration leads to the formation of a metal carbene.

Given the high affinity of gold to alkynes as well as the high reactivity of metal-activated alkynes toward nucleophiles, we have envisioned that other nucleophiles, such as a thio group and a halogen group, may also trigger a similar reaction through a three-centered ionic intermediate, which is generated by intramolecular 1,3-nucleophilic attack (eqs 2 and 3). Although sulfur-containing functional groups are known to have a strong coordination ability toward transition metals, recent reports demonstrate that the reaction of allenyl compounds bearing sulfur groups can also be catalyzed with transition-metal complexes. Gevorgyan and co-workers have reported 1,2-thio migration in Cu-catalyzed reactions of allenyl sulfides.4 A recent


10.1021/jo0618674 CCC: $37.00 © 2007 American Chemical Society Published on Web 01/19/2007

1192 J. Org. Chem. 2007, 72, 1192−1197
Results and Discussion

The propargylic sulfide 1a was subjected to the reaction with transition-metal catalysts (Table 1). The reaction of 1a with 5 mol % of AuCl in toluene at room temperature for 5 h afforded a 5:1 mixture of isomeric products in 63% yield (Table 1, entry 1). The structures of the products are characterized as indene derivatives 2a and 3a by spectral data. The reaction time could be significantly shortened when the reaction was conducted at 80 °C, with some improvements in both yield and the selectivity for 2a (Table 1, entry 2). The addition of AgSbF4 or AgOTf to the gold catalyst led to a complex mixture, and addition of PPh3 to AuCl markedly slowed down the reaction (entries 3–5). The reaction of 1a with 5 mol % of AuCl gave similar yields of the indene products under the same conditions.

PtCl2 was next examined. It was found that this catalyst had higher reactivity toward sulfide 1a, as compared with the gold catalysts. The reaction of 1a with 5 mol % of PtCl2 gave a better yield but with essentially no selectivity for 2a and 3a (Table 1, entries 8 and 9). Other metal catalysts were also examined. RuCl2 (p-cymene) gave a 5:1 mixture of isomeric products in 63% yield (Table 1, entry 1). The reaction time could be significantly shortened when the reaction was conducted at 80 °C, with some improvements in both yield and the selectivity for 2a (Table 1, entry 2). The addition of AgSbF4 or AgOTf to the gold catalyst led to a complex mixture, and addition of PPh3 to AuCl markedly slowed down the reaction (entries 3–5). The reaction of 1a with 5 mol % of AuCl gave similar yields of the indene products under the same conditions.

Table 1. Reaction of Propargyl Sulfide 1a under Various Conditions

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>ratio 2a:3a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AuCl</td>
<td>PhCH3</td>
<td>25</td>
<td>5</td>
<td>63</td>
<td>5:1</td>
</tr>
<tr>
<td>2</td>
<td>AuCl</td>
<td>PhCH3</td>
<td>80</td>
<td>1</td>
<td>75</td>
<td>10:1</td>
</tr>
<tr>
<td>3</td>
<td>AuCl + AgSbF4</td>
<td>PhCH3</td>
<td>80</td>
<td>1</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>4</td>
<td>AuCl + AgOTf</td>
<td>PhCH3</td>
<td>80</td>
<td>1</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>5</td>
<td>AuCl + PPh3</td>
<td>PhCH3</td>
<td>80</td>
<td>26</td>
<td>30</td>
<td>1:1</td>
</tr>
<tr>
<td>6</td>
<td>AuCl</td>
<td>PhCH3</td>
<td>25</td>
<td>3</td>
<td>78</td>
<td>3:1</td>
</tr>
<tr>
<td>7</td>
<td>AuCl</td>
<td>PhCH3</td>
<td>80</td>
<td>1</td>
<td>85</td>
<td>5:1</td>
</tr>
<tr>
<td>8</td>
<td>PtCl2</td>
<td>PhCH3</td>
<td>25</td>
<td>30</td>
<td>80</td>
<td>1:1</td>
</tr>
<tr>
<td>9</td>
<td>PtCl2</td>
<td>PhCH3</td>
<td>80</td>
<td>1</td>
<td>97</td>
<td>1:1</td>
</tr>
<tr>
<td>10</td>
<td>[RuCl2(p-cymene)]</td>
<td>PhCH3</td>
<td>80</td>
<td>19</td>
<td>30</td>
<td>2:1</td>
</tr>
<tr>
<td>11</td>
<td>Rh2(OOCOCF3)3</td>
<td>PhCH3</td>
<td>80</td>
<td>8</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>AuCl</td>
<td>DCE</td>
<td>70</td>
<td>1</td>
<td>76</td>
<td>6:1</td>
</tr>
<tr>
<td>13</td>
<td>AuCl</td>
<td>MeCN</td>
<td>60</td>
<td>1</td>
<td>40</td>
<td>1:1</td>
</tr>
<tr>
<td>14</td>
<td>AuCl</td>
<td>DCE</td>
<td>70</td>
<td>1</td>
<td>82</td>
<td>5:1</td>
</tr>
<tr>
<td>15</td>
<td>AuCl</td>
<td>MeCN</td>
<td>60</td>
<td>1</td>
<td>50</td>
<td>1:1</td>
</tr>
<tr>
<td>16</td>
<td>PtCl2</td>
<td>DCE</td>
<td>70</td>
<td>6</td>
<td>80</td>
<td>1:1</td>
</tr>
</tbody>
</table>

* All reactions were carried out with 5 mol % of catalyst. † Isolated yield after silica gel column chromatography. ‡ Ratio determined by 1H NMR of the crude product. § The reaction gave a complex mixture.

Rh2(OOCOCF3)3 gave only a trace amount of indene products (entries 10 and 11).

Finally, the effect of solvent was investigated. Switching the solvent to 1,2-dichloroethane (DCE) afforded comparable results (entries 12, 14, and 16). However, employing MeCN as the solvent resulted in diminished yields (entries 13 and 15).

Indene formations have been previously reported in the transition-metal-catalyzed reaction of propargylic esters. Metal carbene has been suggested to be the likely intermediate. Here, we propose a reaction pathway for the formation of 2a and 3a (Scheme 1). As expected, the lone pair of sulfur attack the adjacent metal-activated triple bond, resulting in the formation of a three-centered thiirenium intermediate B. Subsequent 1,2-migration of the thio group through B generates the metal carbene species C or D, which are considered to be in resonance with E. E might be viewed as a metal-stabilized allylic cation. As a result, C and D are in rapid equilibrium. From C, aromatic substitution by the metal carbene leads to the formal C−H insertion product 2a. The formation of 3a suggests that a different pathway for the formal C−H insertion may also operate. One possibility might be a Friedel–Crafts-type reaction of a phenyl ring with the metal-stabilized cation-like species, which leads to intermediate F, from which the release of the metal and the proton transfer to the a or b position generate 2a and 3a, respectively. Another possible pathway for the formation of 2a and 3a is intramolecular nucleophilic attack of the phenyl group on the vinyl metal moiety to generate intermediate F directly. Intramolecular nucleophilic attack of the C=C bond does not occur under the reaction conditions.
reaction with secondary propargyl sulfides. However, the PtCl\(_2\)–
insertion into an aliphatic C–H bond, which has been suggested as a
concerted process in most cases.\(^{7,9,10}\) Consequently, the small
kinetic isotope effect seen in the present work does not provide
evidence to differentiate the possible pathways hypothesized
in Scheme 2. More rigorous studies will be necessary to
assuredly clarify this complicated mechanistic issue.

The scope of this catalytic reaction is demonstrated by a series
of propargylic sulfides 1b–j, as shown in Table 2. Both AuCl
and AuCl\(_3\) were tested for all of the sulfide substrates. The
substrate on the sulfur seems to have only a marginal effect
on the reaction (entries 1–5). The slow conversion in the case
of the naphthyl-substituted substrate 1c should be due to steric
effects. The substrate with the alkyl substituent on the sulfur
gave similar results (entry 4). On the other hand, the substituent
in the alkyl moiety seems to have a significant effect on the
outcome of the reaction (entries 6 and 8). In the case of 1g,
the reaction with AuCl or AuCl\(_3\) proceeded slowly. In this case,
the corresponding Au carbene intermediate has a methyl
substitute attached to carbene carbon. The reactivity of the Au
 carbene is thus diminished due to the stabilizing effect of the
methyl group. In the case of 1i, the reaction with both AuCl
and AuCl\(_3\) gave only one product, 2i. This may be due to the
attachment of an electron-withdrawing ester group to the metal
carbene, which may lead to a more carbene-like intermediate
(rather than a cation-like intermediate). Formal C–H insertion
should be more likely to occur from a carbene-like intermediate.
The secondary sulfide was found to be less reactive under the
same reaction conditions (entry 9). This is similar to the catalytic
reaction of propargylic acetate.\(^3c\)

This catalytic reaction can be extended to the sulfide with a
vinyl substituent 11 (Scheme 4). In this case, the reaction
effect has been reported in the range of 1.2–3.3.\(^9\) However,
the formal aromatic C–H insertion by a metal carbene has been
known to proceed by initial cyclopropanation, followed by the
hydride shift and the opening of the cyclopropyl ring.\(^7\) This is
obviously different from the direct metal carbene insertion
into the aliphatic C–H bond, which has been suggested as a
concerted process in most cases.\(^7,9,10\) Consequently, the small
kinetic isotope effect seen in the present work does not provide
evidence to differentiate the possible pathways hypothesized
in Scheme 2. More rigorous studies will be necessary to
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methyl group. In the case of 1i, the reaction with both AuCl
and AuCl\(_3\) gave only one product, 2i. This may be due to the
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carbene, which may lead to a more carbene-like intermediate
(rather than a cation-like intermediate). Formal C–H insertion
should be more likely to occur from a carbene-like intermediate.
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reaction of propargylic acetate.\(^3c\)

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**Scheme 1. Mechanistic Hypothesis**

**Scheme 2. Experiment on Reaction Mechanism**

**Scheme 3. Kinetic Isotopic Effects**
TABLE 2. AuCl- or AuCl3-Catalyzed Reaction of 1b-j

<table>
<thead>
<tr>
<th>entry</th>
<th>sulfide</th>
<th>catalyst</th>
<th>time (h)</th>
<th>yield (%)</th>
<th>ratio a (2:3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b, X = R′ = H; R = CH3</td>
<td>AuCl3</td>
<td>1</td>
<td>56</td>
<td>15:1</td>
</tr>
<tr>
<td>2</td>
<td>1e, X = R′ = H; R = CH3</td>
<td>AuCl3</td>
<td>1</td>
<td>24</td>
<td>60:1</td>
</tr>
<tr>
<td>3</td>
<td>1d, X = R′ = H; R = CH3</td>
<td>AuCl3</td>
<td>1</td>
<td>75</td>
<td>6:1</td>
</tr>
<tr>
<td>4</td>
<td>1e, X = R′ = H; R = CH3</td>
<td>AuCl3</td>
<td>1</td>
<td>68</td>
<td>6:1</td>
</tr>
<tr>
<td>5</td>
<td>1f, X = R′ = H; R = CH3</td>
<td>AuCl3</td>
<td>1</td>
<td>65</td>
<td>4:1</td>
</tr>
<tr>
<td>6</td>
<td>1g, X = H; R′ = R = CH3</td>
<td>CH3AuCl</td>
<td>1</td>
<td>25</td>
<td>70:1</td>
</tr>
<tr>
<td>7</td>
<td>1h, X = Br; R′ = H</td>
<td>CH3AuCl</td>
<td>1</td>
<td>53</td>
<td>15:1</td>
</tr>
<tr>
<td>8</td>
<td>1l, H = X; R′ = CH3</td>
<td>CH3AuCl</td>
<td>1</td>
<td>67</td>
<td>11:1 &gt; 20:1</td>
</tr>
<tr>
<td>9</td>
<td>1j, X = R′ = R = H</td>
<td>CH3AuCl</td>
<td>1</td>
<td>24</td>
<td>9:32</td>
</tr>
</tbody>
</table>

a Isolated yields after silica gel column chromatography. Numbers in parentheses refer to the starting material recovered. b Determined by 1H NMR of the crude product. c The reaction can only give one isomer when R = R′. d No 3l could be identified by crude 1H NMR.

SCHEME 4. Catalytic Reaction with 11

Afforded a cyclopentadiene derivative 12, which was formed through vinyl C–H insertion of the metal carbene.

After establishing that the metal carbene could be generated through the metal-catalyzed reaction of propargyl sulfide, we proceeded to investigate the reaction with propargyl dithioacetals. As shown by eq 3, it can be anticipated that propargyl dithioacetals may work in the same way as propargyl sulfide upon catalysis with transition metals. In this case, the five-membered dithioacetal ring is expanded to a six-membered ring with the generation of vinylcarbenoids.

The investigation started with dithioacetal 13a, as summarized in Table 3. The PtCl2-catalyzed reaction gave a complicated mixture. From the crude 1H NMR spectra, 15a was identified as the major product (entry 1). To our delight, the reaction with both AuCl and AuCl3 afforded 14a as the only isomer with high isolated yields (entries 2–5). Ru(II) and Rh(II) catalysts were also tested. In both cases, most of the starting material 13a was recovered after prolonged reaction time (entries 6 and 7).

The generality of the AuCl-catalyzed reaction of propargyl dithioacetals is demonstrated by a variety of substrates, as shown in Scheme 5. Indene derivatives were isolated in good to excellent yields, except in the case of 2-furyl substrate 16, in which case the reaction proceeded slowly to afford 17. Compared to the reaction with propargyl sulfide, the Au-catalyzed reaction with propargyl dithioacetals is generally more efficient, presumably due to the rigidity of the substrate in the latter case. Moreover, since dithioacetals are easily available from the corresponding ketones, this catalytic reaction provides an unique and efficient entry to the indene derivatives.

In conclusion, we have demonstrated that a neighboring sulfur group can participate in the transition-metal-catalyzed reactions of alkynes to generate a vinylcarbenoid as the reactive intermediate through 1,2-sulfur migration. This result provides a new entry to these important intermediates and thus significantly expands the scope of the chemistry of alkylene-generated metal carbenes. Further studies on the detailed reaction mechanism and the application of this process in organic synthesis are underway in our laboratory.

Experimental Section

The Synthesis of Propargylic Sulfides 1a—f, h—j. The propargylic sulfides were synthesized through a catalyzed propargylic substitution reaction of propargylic alcohols with thiols. We mainly used two methods, catalysis with ZnI2 (Method A) or catalysis with PTS (p-toluene sulfonic acid monohydrate) (Method B). The sulfides can also be synthesized by catalysis with a thiolate-bridged diruthenium complex or NaAuCl2⋅H2O. Recently, some other methods for preparing propargylic sulfides have appeared in literature.

Phenyl-1-methyl-1-phenyl-2-propynyl Sulfide 1a. Yield 49%. Method A: white solid; mp 45–46 °C; IR (film) 3291, 1438, 1027, 749, 692 cm−1; 1H NMR (CDCl3, 300 MHz) δ 1.94 (s, 3H), 2.70 (s, 1H), 7.20–7.36 (3m, 8H), 7.57–7.61 (2m, 2H); 13C NMR (CDCl3, 75 MHz) δ 29.9, 49.2, 74.7, 86.1, 126.7, 127.4, 128.0, 128.2, 132.8, 137.9; EI−MS (m/z, relative intensity) 238 (M+, 8), 225 (26), 129 (100). Anal. Calcd for C16H14S: C, 80.63; H, 5.92.

Phenyl-1,3-dimethyl-1-phenyl-2-propynyl Sulfide 1g. For this sulfide, the following procedure is followed. Under a nitrogen atmosphere, BuLi was added dropwise to a solution of phenyl-1,3-dimethyl-1-phenyl-2-propynyl sulfide (0.2 mmol) in dry anhydrous THF (10 mL) at −78 °C. After 1 h, CH2Cl2 (0.13 mL, 2.0 M) was added, and the temperature was allowed to increase up to room temperature. After 5 h, saturated NH4Cl was added, and the mixture was extracted with CH2Cl2. The combined organic layers were dried over Na2SO4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether to afford 1g (91%): oil; IR (film) 2917, 1438, 1027, 749, 692 cm−1; 1H NMR (CDCl3, 300 MHz) δ 1.89 (s, 3H), 3.11 (d, 1J H–C = 3.8 Hz, 1H), 3.51 (m, 4H), 7.37 (m, 8H), 7.54 (78), 128 (100); 13C NMR (CDCl3, 75 MHz) δ 14.2, 45.5, 124.9, 126.8, 128.3, 128.4, 131.6, 138.7, 145.7; EI−MS (m/z, relative intensity) 282 (M+, 4), 237 (7), 143 (100), 128 (27). Anal. Calcd for C17H16S: C, 81.77; H, 6.10. Found: C, 81.53; H, 5.91.

Typical Procedure for AuCl-Catalyzed Rearrangement Reactions of 1a–j and 11. Under a nitrogen atmosphere, metal catalyst (AuCl, AuCl3) (0.01mmol) and propargylic sulfide (0.2 mmol) were mixed in dry toluene, and the system was heated at 80 °C. Upon completion of the reaction as judged by TLC, solvent was removed in vacuo to give a crude residue, which was purified by a silica gel column eluted with petroleum ether. Isomeric products 2 and 3 were found to be inseparable on a silica gel column.

3-Methyl-2-phenylthiophosphate 2a: oil; IR (film) 3067, 1476, 1461, 1439, 1024, 757, 739, 691 cm−1; 1H NMR (CDCl3, 300 MHz) δ 2.27 (t, J = 2.1 Hz, 3H), 3.44 (d, J = 2.1 Hz, 2H); 7.16–7.37 (m, 9H); 13C NMR (CDCl3, 75 MHz) δ 11.7, 42.1, 119.1, 123.3, 125.3, 126.2, 126.5, 129.0, 129.3, 132.0, 136.4, 143.2, 144.0, 145.5; EI−MS (m/z, relative intensity) 238 (M+, 44), 129 (100). Anal. Calcd for C19H14S: C, 80.63; H, 5.92. Found: C, 80.55; H, 5.95.

Phenyl-1-methyl-1-phenyl-1,3-dithiolane 13a: white solid; mp 62–63 °C; IR (film) 3053, 1476, 1440, 1373, 752, 739, 690 cm−1; 1H NMR (CDCl3, 300 MHz) δ 2.12 (t, J = 2.1 Hz, 3H), 3.51–3.52 (m, 2H), 6.83 (s, 1H), 7.10–7.32 (m, 8H), 7.40–7.46 (m, 2H); 13C NMR (CDCl3, 75 MHz) δ 14.2, 45.5, 124.9, 125.5, 127.2, 127.7, 128.6, 128.9, 130.6, 135.3, 138.3, 147.9, 149.7; EI−MS (m/z, relative intensity) 264 (M+, 43), 249 (9), 171 (13), 155 (100). Anal. Calcd for C18H10S3: C, 81.77; H, 6.10. Found: C, 81.53; H, 5.91.

The Synthesis of Propargylic Dithiocacetals 13a–h and 16. The propargylic dithiocacetals were prepared from the corresponding propargylic ketones and 1,2-ethanedithiol in the presence of BF3⋅Et2O. There are two ways to prepare the propargylic ketones. Method A by a direct coupling reaction (for the synthesis of 13a, 1f, h) and Method B by two-step reaction that involves first a nucleophilic addition and then oxidation (for the synthesis of 13b–e, g, and 16).

Method B. A flame-dried, three-necked flask was charged with dry THF (20 mL) and phenylacetylene (12.0 mmol). The solution was cooled to −78 °C, and n-BuLi (12.0 mmol, 2.0 M in hexane) was added slowly. The solution was allowed to stir for 1 h at −78 °C; then, aldehyde (10.0 mmol) in 20 mL of THF was added slowly over 20 min. The mixture was stirred for an additional 1 h at −78 °C; then, the dry ice/acetone bath was removed, and the mixture was allowed to warm to room temperature. After about 5 h, saturated NH4Cl was added, and most of the organic solvent was then removed in vacuum. The mixture was extracted with CH2Cl2. The combined organic layers were dried over Na2SO4 and evaporated, and the residue was purified by a silica gel column eluted with petroleum ether/EtOAc (20:1) to afford the corresponding propargylic alcohol.

A solution of propargylic alcohol (10.0 mmol) in CH2Cl2 (50 mL) was cooled to 0 °C, and MnO2 (50.0 mmol) was added by portion. This was kept in the ice bath for another 2 h. Then, the solid was removed by filtration. The filtrate was evaporated, and the crude residue was purified by a silica gel column eluted with petroleum ether/EtOAc (100:1) to afford the propargylic ketone.

2-Phenyl-2-(2-phenylethynyl)-1,3-dithiolane 13a,[18] yield 72%; IR (film) 1597, 1489, 1446, 756, 718, 690 cm−1; 1H NMR (CDCl3, 300 MHz) δ 3.67–3.81 (m, 4H), 7.30–7.42 (m, 6H), 7.50–7.54 (m, 2H), 8.03–8.06 (m, 2H); 13C NMR (CDCl3, 75 MHz) δ 41.3, 62.2, 86.8, 91.0, 122.7, 127.6, 128.2, 128.4, 131.6, 138.7; EI−MS (m/z, relative intensity) 282 (M+, 72), 254 (65), 221 (100), 189 (54), 145 (57), 77 (20).

Typical Procedure for AuCl-Catalyzed Rearrangement Reactions of 13a–h and 16. Under a nitrogen atmosphere, AuCl (0.01 mol) was added to a mixture of 13a–h and 16 in dry toluene, and the solution was heated at 80 °C. Upon completion of the reaction as judged by TLC, solvent was removed in vacuo to give a crude residue, which was purified by a silica gel column eluted with petroleum ether/EtOAc (20:1) to afford the corresponding propargylic alcohols.
mmol) and propargylic dithioacetal (0.2 mmol) were mixed in dry toluene, and the system was heated at 80 °C by a boil bath. The temperature was kept until the reaction was completed as judged by TLC. Removal of the solvent in vacuo gave a crude residue, which was purified by a silica gel column eluted with petroleum ether.

9-Phenyl-2,3-dihydro-1,4-dithiofluorene 14a:19 white solid; mp 122–123 °C; IR (film) 1600, 1536, 1463, 1265, 754, 734, 701 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 3.20–3.25 (m, 4H), 4.53 (s, 1H), 7.04–7.31 (m, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 26.1, 27.3, 59.3, 116.7, 123.0, 123.7, 124.8, 127.0, 127.2, 128.2, 128.7, 132.5, 138.9, 143.0, 145.0; EI–MS (m/z, relative intensity) 282 (M⁺, 100), 254 (53), 221 (64), 189 (6), 177 (18), 165 (8), 111 (15).

Acknowledgment. The project is generously supported by the Natural Science Foundation of China (Grant Nos. 20572002, 20521202, 20225205, 20390050) and the Ministry of Education of China.

Supporting Information Available: Synthesis of propargylic sulfides and dithioacetals, spectra data for all new compounds, X-ray structure of sulfone, cyclopropanation and kinetic isotope effect experiments, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.