

# Highly Chemo- and Regioselective Thiocarbonylation of Conjugated Enynes with Thiols and Carbon Monoxide Catalyzed by Palladium Complexes: An Efficient and Atom-Economical Access to 2-(Phenylthiocarbonyl)-1,3-dienes

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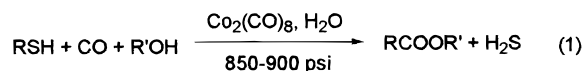
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The reaction of 1, 3-conjugated enynes bearing a terminal triple bond with thiols and carbon monoxide in the presence of catalytic quantities of Pd(OAc)<sub>2</sub> (3 mol %) and 1,3-bis(diphenylphosphino)propane (6 mol %) in THF at 110 °C gave 2-(phenylthiocarbonyl)-1,3-dienes in moderate to good yields. The thiocarbonylation takes place with high chemo- and regioselectivity, with the attack by the phenylthiocarbonyl group occurring exclusively at carbon-2 of the 1,3-conjugated enyne.

## Introduction

Carbonylation chemistry is widely used in organic synthesis in both academia and industry. Among numerous methods for the introduction of a carbonyl moiety into an organic molecule, the direct functionalization of a substrate using carbon monoxide has attracted a great deal of attention.<sup>1</sup> The development of transition-metal-catalyzed carbonylation involving the formation of a thiocarbonyl unit and employing chalcogen compounds as substrates represents a challenging goal in organic synthesis, because the strong thiophilicity of transition metals<sup>2</sup> may make catalytic reactions ineffective.<sup>3</sup> Transition-metal-catalyzed reactions with thiols and carbon monoxide have been investigated in our laboratories for some time.<sup>4</sup> For example, in 1985, we described the cobalt carbonyl catalyzed desulfurization and carbonylation of mercaptans to produce carboxylic esters (eq 1).<sup>4a</sup> The



latter process represented, to our knowledge, the first effective catalytic carbonylation of organosulfur compounds. Our group and others have subsequently discovered a series of reactions in which chalcogen compounds are used as substrates in transition-metal-catalyzed reactions. For example, thiols react with

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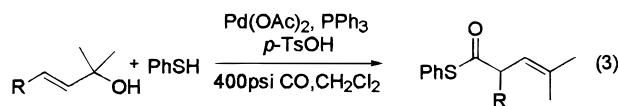
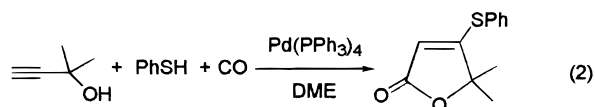
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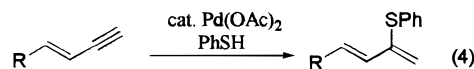
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propargyl or allylic alcohols in the presence of a palladium(0) catalyst to afford  $\beta$ -(arylthio)- $\alpha,\beta$ -unsaturated lactones or  $\beta,\gamma$ -unsaturated thioesters, depending on the reaction conditions (eq 2 and 3).<sup>5</sup> Highly regio-



selective carbonylation reactions of thiols with allenes<sup>6</sup> and acetylenes<sup>7</sup> have been the subject of recent publications. In 1994, an excellent publication on the palladium-catalyzed addition of thiophenol to conjugated enynes<sup>8</sup> appeared by Backvall and co-workers (eq 4). Stimulated



by these results, we reasoned that the thiocarbonylation of conjugated enynes with thiols should take place, producing the corresponding phenylthiocarbonyl-1,3-dienes.

Sulfur-substituted dienes have been widely used in Diels–Alder and other reactions.<sup>9</sup> The sulfur-containing group not only increases the reactivity of the diene but also acts as a handle for further functional group

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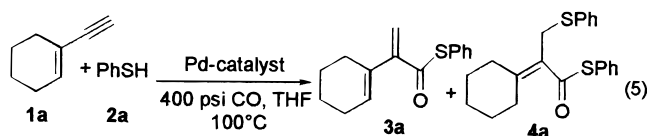
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transformations.<sup>10</sup> Thus, it is not surprising that considerable effort has been expended in the synthesis of such compounds.<sup>11</sup> From a synthetic point of view, controlling regioselectivity, as well as chemoselectivity, is always of great importance. Described here is a highly chemo- and regioselective thiocarbonylation reaction of conjugated enynes with thiols and CO catalyzed by a palladium complex, allowing a one-pot synthesis of 2-(phenylthio-carbonyl)-1,3-dienes.

## Results and Discussion

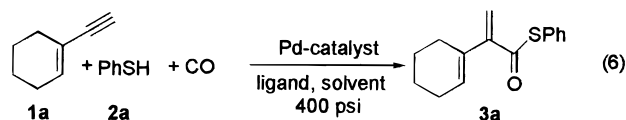
**Reaction of 1-Ethynylcyclohexene with Thiophenol. Demonstration of Process and Yield Optimization.** The palladium-catalyzed reaction of 1-ethynylcyclohexene (**1a**) with thiophenol (**2a**) and carbon monoxide was chosen as a model reaction to determine the viability of the process and the optimum reaction conditions (eq 5). The reaction conditions previously used for the



thiocarbonylation of allenes<sup>6</sup> were initially applied to the reaction of **1a**, **2a**, and carbon monoxide (CO) [1 equiv of enyne, 1 equiv of thiophenol, 3 mol % Pd(OAc)<sub>2</sub>, 12 mol % PPh<sub>3</sub>, 400 psi of CO, THF (3.5 mL per 1 mmol of thiophenol), and 100 °C]. Two products, **3a** and **4a**, were obtained in 18% and 7% yield, respectively. Byproduct **4a** may arise by the 1,4-addition of **3a** with thiophenol and, in that event, it should be possible to control the consecutive reaction by increasing the mole ratio of **1a** to **2a** and decreasing the concentrations of the reactants. Indeed, treatment of **1a** (3 mmol) with **2a** (1 mmol) in the presence of Pd(OAc)<sub>2</sub> (0.03 mmol) and PPh<sub>3</sub> (0.12 mmol) in THF (15 mL) at 100 °C under 400 psi of carbon monoxide gave exclusively **3a** in 38% yield (no **4a** was formed). The effect of varying the catalyst, ligand, solvent, reaction temperature, and reaction time on the yield of **3a** was examined, and the results are summarized in Table 1.

A series of reactions between **1a** and **2a** were carried out under various conditions to optimize the reaction yield. It was shown that Pd(OAc)<sub>2</sub> with 1,3-bis(diphenylphosphino)propane (dppp) was the best catalyst system among those examined and the reaction proceeded efficiently in THF as the solvent (Table 1, entry 8). Increasing the reaction temperature to 110 °C and decreasing the reaction time to 6 h further improved the yield to 76% (Table 1, entry 9). Pd(OAc)<sub>2</sub> with 1,4-bis(diphenylphosphino)butane (dppb) is also a good catalytic system for this reaction (Table 1, entry 6); however, Pd(OAc)<sub>2</sub> with 1,2-bis(diphenylphosphino)ethane (dppe) was ineffective here (Table 1, entry 7). Other palladium catalysts, such as Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub>, with-

**Table 1. Optimization of Reaction Conditions (eq 6)<sup>a</sup>**



entry	catalyst	ligand	solvent	temp (°C)	time (h)	yield of <b>3a</b> (%) <sup>b</sup>
1	Pd(OAc) <sub>2</sub>	none	THF	100	24	0 <sup>c</sup>
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	none	THF	100	24	20
3	Pt(PPh <sub>3</sub> ) <sub>4</sub>	none	THF	100	24	47
4	Pd <sub>2</sub> (dba) <sub>3</sub> ·CHCl <sub>3</sub> <sup>d</sup>	none	THF	100	24	12
5	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	THF	100	24	38
6	Pd(OAc) <sub>2</sub>	dppb	THF	100	12	62
7	Pd(OAc) <sub>2</sub>	dppe	THF	100	24	0
8	Pd(OAc) <sub>2</sub>	dppp	THF	100	8	70
9	Pd(OAc) <sub>2</sub>	dppp	THF	110	6	76
10	Pd(OAc) <sub>2</sub>	dppp	CH <sub>2</sub> Cl <sub>2</sub>	110	6	43
11	Pd(OAc) <sub>2</sub>	dppp	DME	110	6	8 <sup>e</sup>
12	Pd(OAc) <sub>2</sub>	dppp	C <sub>6</sub> H <sub>6</sub>	110	6	62
13	Pd(OAc) <sub>2</sub>	dppp	CH <sub>3</sub> CN	110	6	37
14	Pd(OAc) <sub>2</sub>	dppp	THF	130	6	36
15	Pd(OAc) <sub>2</sub>	dppp	THF	140	24	7
16	Pd(OAc) <sub>2</sub>	dppp	THF	110	60	tr

<sup>a</sup> Reaction conditions: 1-ethynylcyclohexene (3 mmol), thiophenol (1 mmol), catalyst (0.03 mmol), PPh<sub>3</sub> (0.12 mmol, if used), bidentate phosphine (0.06 mmol, if used), 400 psi CO, solvent (15 mL). <sup>b</sup> Isolated yield based on the amount of thiophenol employed. <sup>c</sup> The decarbonylation product, phenyl 2-(1'-cyclohexenyl)-ethenyl sulfide, was isolated in 53% yield. <sup>d</sup> 0.015 mmol of the catalyst was used. <sup>e</sup> 27% of thiophenol was recovered, and polymerization of the enyne was observed.

out an added phosphine ligand, were not useful for this transformation (Table 1, entries 2 and 4). Although Pd(OAc)<sub>2</sub>/4 PPh<sub>3</sub> was found to be an excellent catalyst system for the thiocarbonylation of allenes,<sup>6</sup> it was not of genuine value for this carbonylative coupling reaction. The reaction of **1a** and **2a** catalyzed by Pd(OAc)<sub>2</sub> with PPh<sub>3</sub> afforded **3a** in 38% yield (Table 1, entry 5), whereas using Pd(OAc)<sub>2</sub> without any ligand only gave the decarbonylation product (Table 1, entry 1). Tetrakis(triphenylphosphine)platinum(0), which was very effective for the regioselective hydrothiocarbonylation of acetylenes with thiols,<sup>7b</sup> does catalyze this thiocarbonylation, but in appreciably lower yield of **3a** when compared with Pd(OAc)<sub>2</sub> and dppp (Table 1, entry 3).

The nature of the solvent, and the reaction time, greatly affected the yield of **3a** in the model reaction. With the Pd(OAc)<sub>2</sub>-dppp catalyst system, THF was found to be the best solvent for the reaction, whereas **3a** was obtained in only 8% yield when 1,2-dimethoxyethane (DME) was the reaction solvent (compare entries 9 to 13 in Table 1). The reaction works well at 110 °C in THF and is complete in 6 h. Raising the reaction temperature to 140 °C resulted in decomposition of the catalyst, and prolonged heating proved detrimental for the reaction (Table 1, entries 14–16), probably because of the facile polymerization of the product.<sup>12</sup>

**Scope of the Thiocarbonylation of Enynes.** The thiocarbonylation reactions of a series of enynes (**1a–h**) with thiols (**2a–c**) were performed using 3 mol % of Pd(OAc)<sub>2</sub> and 6 mol % of dppp in THF (15 mL per 1 mmol of thiol) at 400 psi of carbon monoxide for 8–15 h at 110 °C, and the results are summarized in Table 2.

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**Table 2. Palladium-Catalyzed Thiocarbonylation of Enynes with Thiols and CO<sup>a</sup>**

entry	enyne (E/Z) <sup>b</sup>	thiol	time (h)	product (E/Z) <sup>b</sup>	yield (%) <sup>c</sup>
1		PhSH <b>2a</b>	10		76
2	<b>1a</b>	<i>p</i> -BrC <sub>6</sub> H <sub>4</sub> SH <b>2b</b>	8		70
3	<b>1a</b>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SH <b>2c</b>	12		73
4	<b>1a</b>	C <sub>8</sub> H <sub>17</sub> SH <b>2d</b>	15		73
5		<b>2a</b>	8		54
6		<b>2a</b>	8		52
7	<b>1c</b>	<b>2c</b>	12		72
8		<b>2a</b>	8		33
9		<b>2a</b>	8		56
10		<b>2a</b>	8		51
11		<b>2a</b>	12		67
12		<b>2a</b>	12		74

<sup>a</sup>Reaction conditions: enyne ( 3.0-5.0 mmol ), thiol ( 1.0 mmol ), CO ( 400 psi ), Pd(OAc)<sub>2</sub> ( 0.03 mmol ), dppp ( 0.06 mmol ), THF ( 15 mL ), 110°C. <sup>b</sup>The E/Z ratio was determined by <sup>1</sup>H NMR. <sup>c</sup>Isolated yield based on the reactant thiol. <sup>d</sup>**1b** ( 6.0 mmol ) was used. <sup>e</sup>**1d** ( 5.0 mmol ) was used. <sup>f</sup>**1f** ( 6.0 mmol ) was used.

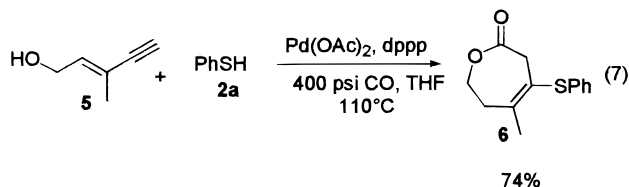
The thiocarbonylation of enynes was highly chemoselective, and only the triple bond was attacked by the sulfur nucleophile (Table 2). Such behavior was observed for the palladium-catalyzed chloropalladation<sup>13a</sup> and hydro-palladation of nonconjugated enynes.<sup>13b</sup> Importantly, only one regioisomer was formed in these reactions, by selective attack of the phenylthiocarbonyl group at carbon-2 of the 1,3-conjugated enyne (Table 2). Both cyclic

and acyclic conjugated enynes can be smoothly and regioselectively transformed into the corresponding 2-(phenylthiocarbonyl)-1,3-dienes in moderate to good yields of isolated pure products via the palladium-catalyzed carbonylative coupling reactions with thiols (Table 2). This regiochemical outcome is in excellent accord with the related transition-metal-catalyzed addition reactions of alkynes<sup>14</sup> and enynes.<sup>8</sup> Note that the stereochemical characteristics of the products were the same as those of the substrates when 1,2-disubstituted enynes were em-

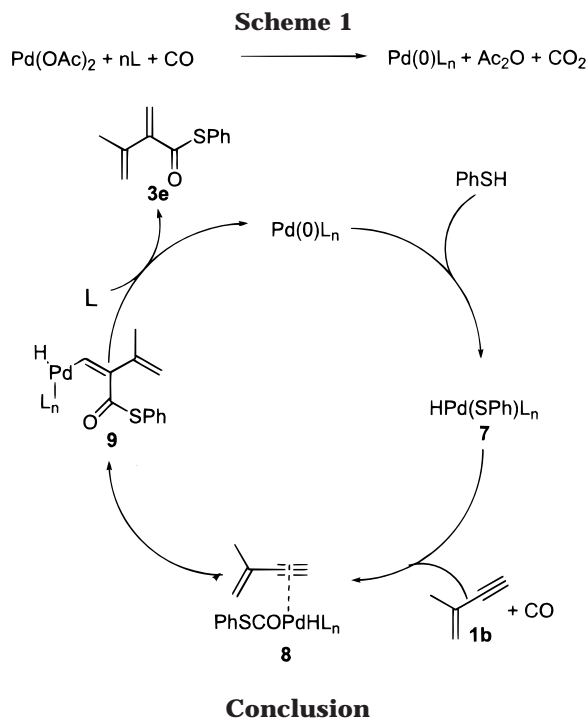
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ployed as the starting materials (Table 2, entries 6–9 and 12). It further demonstrates that the double bond of the enyne is not affected by the reaction.

The yields and selectivities using arenethiols or alkanethiols as reactants are similar, although the reaction time for arenethiols is less than that for alkanethiols in these carbonylative coupling reactions (Table 2, entries 1–4). The higher acidity of aromatic thiols may contribute to this difference in reactivity. Unlike the palladium-catalyzed addition of thiols to acetylenes,<sup>14b</sup> attempts to thiocarbonylate enynes with internal triple bonds were unsuccessful (e.g., 2-methyl-1-hepten-3-yne and 3-octen-5-yne were recovered using the standard reaction conditions for 48 h). An enyne bearing a hydroxyl group (**5**) in the allylic position afforded a sulfur-substituted lactone (**6**) in 74% yield instead of an  $\alpha,\beta$ -unsaturated thioester on reaction with thiophenol and CO (eq 7).



Scheme 1 outlines a possible pathway for the palladium-catalyzed thiocarbonylation of **1** (**1b** as the example) with thiophenol (**2a**). The reaction may proceed by initial palladium acetate reduction to palladium(0),<sup>15</sup> followed by oxidative addition of **2a** to the palladium(0) complex to form the PhSPdH species **7**, which undergoes coordination to the triple bond of the enyne and then insertion of carbon monoxide to form **8**. Regioselective intramolecular acylpalladation of the latter would give complex **9**,<sup>16</sup> and subsequent reductive elimination would produce the observed 2-(phenylthiocarbonyl) 1, 3-diene and regenerate the palladium(0) catalyst.



In summary, this research has resulted in the first chemo- and regioselective thiocarbonylation of enynes

bearing a terminal triple bond with thiols and carbon monoxide catalyzed by Pd(OAc)<sub>2</sub> and dppp to form  $\alpha,\beta$ -unsaturated thioesters in moderate to good yields. This methodology is particularly impressive as a one-pot, atom-economical synthesis of 2-(phenylthiocarbonyl)-1,3-dienes, which are versatile and useful reagents in organic synthesis. For example, they are of genuine value in cycloaddition and Michael addition reactions.

## Experimental Section

**Materials.** The following enynes were prepared. 3-Nonen-1-yne (**1h**) was obtained by Wittig reaction of propargyltriphenylphosphonium bromide with hexanal following a literature method.<sup>17</sup> 1-Ethynylcyclopentene (**1g**), 3,5-dimethyl-3-hexen-1-yne (**1c**), 3-methyl-3-penten-1-yne (**1d**), and 3-ethyl-3-penten-1-yne (**1e**) were prepared by treating the corresponding propargylic alcohols with POCl<sub>3</sub> in pyridine following the literature procedure.<sup>18</sup> 2-Phenyl-1-buten-3-yne (**1f**) was prepared by the Pd-catalyzed reaction of lithium acetylide with alkenyl halide.<sup>19</sup> Other enynes and thiols were commercially available and were used as received. Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> was prepared according to the reported procedure.<sup>20</sup> Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and benzene were dried and deoxygenated by continuous refluxing over sodium/benzophenone ketyl under nitrogen, followed by distillation. CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub> under N<sub>2</sub> prior to use, and CH<sub>3</sub>CN was dried with molecular sieves (4A, 1.6 mm pellets).

**General Procedure for the Palladium-Catalyzed Thiocarbonylation of Enynes with Thiols and Carbon Monoxide.** To a 45 mL Parr autoclave fitted with a glass liner and stirring bar was added Pd(OAc)<sub>2</sub> (0.03 mmol), dppp (0.06 mmol), enyne (3.0–6.0 mmol), thiol (1.0 mmol), and THF (15 mL). The carbon monoxide line was flushed three times with CO, the autoclave was filled and vented at least three times with CO to displace the air, and subsequently the pressure was increased to 400 psi. The mixture was stirred in the autoclave at 110 °C (the temperature of the oil bath) for 8–15 h. After cooling, excess carbon monoxide was released, the reaction mixture was filtered through Florisil, and the solvent was removed by rotary evaporation. The residue was separated by preparative silica gel TLC (eluants: *n*-hexane/ethyl acetate 95:5). Preparative HPLC was used to further purify the products.

**S-Phenyl 2-(1'-Cyclohexenyl)-3-propenethioate (3a):** oil; IR (neat) 1689 cm<sup>-1</sup> (C=O); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  1.58–1.72 (m, 4H), 2.14–2.17 (m, 4H), 5.49 (s, 1H), 5.72 (s, 1H), 6.06 (t, 1H, *J* = 7.4 Hz), 7.44–7.45 (m, 5H); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  21.71, 22.45, 25.71, 26.00, 116.22, 128.21, 129.10, 129.30, 130.06, 132.01, 134.49, 149.76, 193.20; MS (EI) *m/z* 244.1 (M<sup>+</sup>); HRMS calcd for C<sub>15</sub>H<sub>16</sub>OS 244.0938, found

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244.0934. Anal. Calcd for  $C_{15}H_{16}OS$ : C, 73.73; H, 6.60.  
Found: C, 73.65; H, 6.58.

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**Supporting Information Available:** Characterization data for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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