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Nickel-Catalyzed Thioallylation of Alkynes with Allyl Phenyl Sulfides

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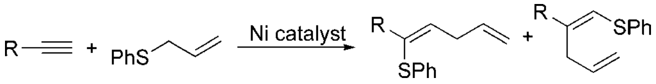
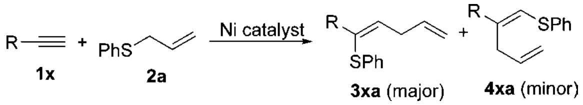
ABSTRACT



Allylic sulfides add to alkynes in the presence of nickel complexes efficiently to afford thio-1,4-dienes regio- and stereoselectively. Functional groups such as alkoxy, siloxy, hydroxy, carboalkoxy, chloro, and cyano groups are tolerated. A mechanism that involves a π-allyl nickel intermediate is proposed on the basis of isolation of π-allyl complexes and distribution of products in the reactions of α- or γ-methylated allyl sulfide.

The addition reactions of carbon−heteroatom bonds to unsaturated linkages are emerging as an important class of synthetic reactions.[1]Of particular synthetic importance in the category are addition reactions of S−C bonds. Although a number of papers have reported metal-catalyzed decarbonylative addition reactions of thio esters,[2] straightforward addition of S−C bonds has not been documented.[3] Because alkenyl sulfides are valuable and versatile intermediates in organic synthesis, we have focused our interest on an exploration of the addition of S−C bonds to alkynes.[4] In this paper, we report Ni(0)-catalyzed regio- and stereoselective additions of allylic sulfides to terminal and internal alkynes, which furnish thio-1,4-dienes in high yields (Scheme 1).

Scheme 1



1x **2a** **3xa** (major) **4xa** (minor)

Although palladium complexes catalyze addition reactions of *O*-methyl *S*-phenyl thiocarbonate to alkynes efficiently,[5] attempted reactions of 1-octyne (**1a**) with allyl phenyl sulfide (**2a**) using palladium complexes such as $Pd(PPh_3)_4$, $PdMe_2$-(dppb), and $Pd(PCy_3)_2$ did not proceed, and **2a** was recovered quantitatively. Other metal complexes such as $Pt(PPh_3)_4$, $RuH_2(CO)(PPh_3)_3$, and $RhCl(CO)$ $(PPh_3)_2$ were not active either.

Continued exploration for capable catalysts has uncovered that nickel complexes can catalyze the reaction smoothly. Screening of catalysts was carried out using a 3:1 ratio of **1a** and **2a** because **1a** tends to oligomerize in the presence

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(3) Carbonylation of allyl aryl sulfide is known. See: Crudden, C. M.; Alper, H. *J. Org. Chem.* **1995**, *60*, 5579.

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of nickel complexes. Plain Ni(cod)$_2$ and Ni(cod)$_2$ + ligand systems, where the ligand is dppb, (4*S*)-(−)-2-(2′-diphenylphosphinophenyl)-4-isopropyloxazoline, 1,2-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]ethane, 2,2-bis[(4*S*)-phenyloxazolin-2-yl]propane, or bis[(4*S*)-phenyloxazolin-2-yl]methane, have proven to be the best nickel catalysts (4 mol %), which afford 5-phenylthioundeca-1,4(*Z*)-diene (**3aa**) in a yield higher than 90% after 8 h at 60 °C in toluene. Ni(PPh$_3$)$_4$, Ni(CO)$_n$(PPh$_3$)$_{4-n}$ (n = 1 or 2), Ni[P(OPh)$_3$]$_4$, and the species generated by mixing of Ni(cod)$_2$ and a ligand such as dppf, 2,3-di(phenylimino)butane, (*S*)-(+)-2,2′-isopropylidenebis(4-*tert*-butyl-2-oxazoline), or 2,2′-methylenebis[(4*R*,5*S*)-4,5-diphenyl-2-oxazoline] are less active (yields ranging from 90 to 17% under the same conditions), and Ni(PEt$_3$)$_4$ is totally inactive.

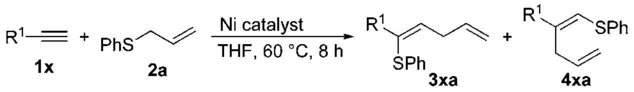
Ni(cod)$_2$, one of the most active catalysts, promotes the reaction even at room temperature (67% yield after 5 days). On the other hand, a Ni(cod)$_2$-catalyzed reaction run at 110 °C promotes oligomerization of 1-octyne more extensively, although it affords **3aa** in a high yield. Use of coordinative solvents such as THF and 1,4-dioxane has proven to suppress the oligomerization of 1-octyne.

Applicability of the new addition reaction to various alkynes is summarized in Table 1. Most of the reactions were carried out in THF using either plain Ni(cod)$_2$ (catalyst **A**) or Ni(cod)$_2$−dppb (1:1 molar ratio; catalyst **B**).

The following reaction (entry 1) exemplifies the procedure. A mixture of **1a** (1.5 mmol), **2a** (0.5 mmol), and Ni(cod)$_2$ (4 mol %) in toluene (0.5 mL) was heated at 60 °C for 8 h. Analysis of the resulting mixture by GC revealed that **3aa** and 2-hexyl-1-phenylthiopenta-1(*Z*),4-diene (**4aa**) were formed in 98% total yield with 89% selectivity for **3aa**. Removal of volatiles, silica gel column chromatography (hexane), and preparative TLC (silica gel, hexane/diethyl ether = 10:1) gave an analytically pure product. ^{1}H NMR, ^{13}C NMR, and mass spectroscopies agreed with the structure. An NOE experiment suggested a (*Z*)-configuration (cis addition of PhS and allyl moieties), which was unequivocally confirmed by X-ray diffraction in the case of product **3qa**, formed in the reaction of diphenylacetylene (**1q**) (vide infra).

As Table 1 shows, various alkynes undergo the addition reaction in the presence of catalyst **A** or **B**. Although exceptions are found, catalyst **B** works better for most aliphatic alkynes. For instance, an attempted reaction of propyne (**1b**, balloon) using catalyst **A** did not work at all; introduction of propyne to the reaction system at room temperature resulted in very rapid catalyst decomposition, as visualized by immediate black precipitate formation. Catalyst **B**, on the other hand, did form the desired product **3ba** in 27% yield with 90% regioselectivity (entry 3). The addition reaction of sterically congested 3,3-dimethylbutyne **1c** did not proceed with catalyst **A**; both **1c** and **2a** were recovered unchanged. However, catalyst **B** promoted the reaction to give **3ca** in 62% yield as the sole product after

Table 1. Ni-Catalyzed Addition of Allyl Phenyl Sulfide to Alkynes[a]



x = a: R^1 = n-C$_6$H$_{13}$
x = b: R^1 = CH$_3$
x = c: R^1 = t-C$_4$H$_9$
x = d: R^1 = Cl(CH$_2$)$_3$
x = e: R^1 = CN(CH$_2$)$_3$
x = f: R^1 = TBDMSO(CH$_2$)$_4$
x = g: R^1 = (HO)(CH$_3$)$_2$C
x = h: R^1 = CH$_3$OCH$_2$
x = i: R^1 = C$_2$H$_5$OOC(CH$_2$)$_2$
x = j: R^1 = CH$_2$=C(CH$_3$)
x = k: R^1 = C$_6$H$_5$CH$_2$
x = l: R^1 = C$_6$H$_5$
x = m: R^1 = p-FC$_6$H$_4$
x = n: R^1 = p-CH$_3$C$_6$H$_4$
x = o: R^1 = p-CH$_3$OC$_6$H$_4$

		alkyne	conversion (%)[c]		yield	selectivity
entry	catalyst[b]	**1x**	1x	2a	(%)[d]	(%)[e]
1[f]	**A**	**1a**	88	100	98 (**3aa** 87)	89
2[f]	**B**	**1a**	72	100	91	88
3[g]	**B**	**1b**	nd[h]	27	27 (**3ba** 17)	90
4[i]	**B**	**1c**	nd[h]	68	62 (**3ca** 58)	100
5	**A**	**1d**	80	100	99 (**3da** 87)	92
6	**A**	**1e**	44	40	33	94
7	**B**	**1e**	93	94	92 (**3ea** 77)	93
8	**A**	**1f**[i]	81	63	65	94
9	**B**	**1f**[i]	87	99	95 (**3fa** 72)	89
10	**A**	**1g**	86	37	24	99
11	**B**	**1g**	99	86	81 (**3ga** 74)	99
12	**A**	**1h**	100	69	68 (**3ha** 58)	80
13	**B**	**1h**	100	37	28	80
14	**A**	**1i**	99	99	99 (**3ia** 89)	90
15	**B**	**1i**	90	98	97	89
16	**A**	**1j**	100	27	14	94
17	**B**	**1j**	100	24	18 (**3ja** 10)	94
18	**A**	**1k**	92	97	95 (**3ka** 90)	89
19	**B**	**1k**	96	81	68	88
20	**A**	**1l**	88	91	87 (**3la** 78)	99
21	**B**	**1l**	99	46	8	nd
22	**A**	**1m**	94	84	84 (**3ma** 76)	99
23	**B**	**1m**	99	38	21	99
24	**A**	**1n**	76	43	40 (**3na** 35)	99
25	**B**	**1n**	93	40	37	99
26	**A**	**1o**	93	57	55 (**3oa** 42)	99
27	**B**	**1o**	99	39	31	99

[a] Unless otherwise noted, the reactions were carried out using 4.0 mmol of **1x**, 2.0 mmol of **2a**, 0.08 mmol of catalyst, and THF (2.0 mL) at 60 °C for 8 h. [b] Catalyst **A** = Ni(cod)$_2$. Catalyst **B** = Ni(cod)$_2$ + 1dppb. [c] Conversion of **1x**, based on **1x** used (4 mmol), and conversion of **2a**, based on **2a** used (2 mmol), were determined by GC. [d] Total yield of **3xa** and **4xa** determined by GC. The figures in parentheses are isolated yields of **3xa**. [e] 100 [**3xa**]/([**3xa**] + [**4xa**]) determined by GC. [f] The reaction was run in toluene (0.5 mL) using **1a** (1.5 mmol), **2a** (0.5 mmol), and catalyst **A** or **B** (0.02 mmol). [g] Run under an atmospheric pressure of propyne. [h] Not determined. [i] Reaction time = 24 h.

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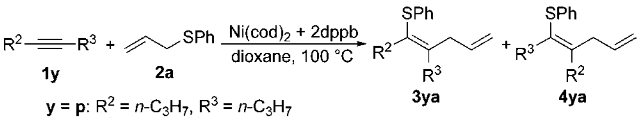
24 h (entry 4). Although the present reaction tolerates various functional groups in alkynes, the activity of catalysts **A** and **B** is significantly affected by functional groups bound even at a remote location. Thus, when catalyst **A** was used, 5-chloro-1-pentyne (**1d**) formed adduct **3da** near quantitatively with 92% selectivity (entry 5), whereas alkynes substituted by cyano (**1e**), siloxy (**1f**), and hydroxy (**1g**) groups displayed rather low reactivity (entries 6, 8, and 10). For the latter cases, catalyst **B** worked well to give satisfactory yields (entries 7, 9, and 11). In sharp contrast, catalyst **A** showed higher catalytic activity for methyl propargyl ether (**1h**) than catalyst **B** (entries 12 and 13). On the other hand, ethyl 4-pentynoate (**1i**) displayed high reactivity with both catalysts **A** and **B** (entries 14 and 15). The reaction of 2-methyl-1-buten-3-yne (**1j**), a conjugated enyne, also displayed high reactivity with both catalysts (entries 16 and 17). However, as the large gap between conversions of **2a** and **1j** suggests, extensive oligomerization of **1j** took place, and the yield of **3ja** was less than 20%. Benzylic and aromatic alkynes also conform to the addition reaction, with catalyst **A** being higher yielding (entries 18−27). Note that aromatic alkynes displayed near 100% regioselectivity. The electronic influence of the *p*-substituent is clearly seen; phenylacetylene and *p*-fluorophenylacetylene gave very high yields of the adducts when catalyst **A** was used, and the use of catalyst **B** resulted in very low yields (entries 20−23). For *p*-methyl- and *p*-methoxyphenylacetylenes, both catalysts showed moderate catalytic activity.

Finally, ethyl propiolate, ethyl 3-butynoate, and ethynyl *p*-tolyl sulfone gave only traces of the desired adducts (<5%), due to extensive oligomerization of these alkynes.

Internal alkynes are much less reactive than terminal ones, but heating at 100 °C using dioxane as solvent for longer periods affords the desired products in acceptable yields (Table 2), as exemplified by the reaction of 4-octyne (**1p**; entry 1). Because $Ni(cod)_2$ decomposes within 5 min under the reaction conditions, $Ni(cod)_2$−phosphine ligand systems with a relatively large quantity of the ligand (relative to Ni) are desirable (entries 1 and 2). Quick screening of ligands for the reaction of **1p** has suggested that $Ni(cod)_2$−2dppb (catalyst **C**) is higher yielding than $Ni(cod)_2$−4PPh_3 (48 h, 65%), −4$P(OPh)_3$ (24 h, 38%), and −(4*S*)-(−)-2-(2′-diphenylphosphinophenyl)-4-isopropyloxazoline (48 h, 55%). Diphenylacetylene (**1q**) displayed a very low reactivity compared with 4-octyne even in the presence of catalyst **C**; the corresponding adduct **3qa** was obtained in 54% yield after 96 h (entry 3). The structure of **3qa** was confirmed by X-ray crystallography (Figure 1).[6] Unsymmetrical internal alkynes such as 1-phenyl-1-propyne (**1r**), 2,7-dimethyl-1-octen-3-yne (**1s**), and 1-phenyl-1-propyn-3-ol (**1t**) reacted with **2a** to give two regioisomers in moderate to good yields (entries 4−6). Only **1t** displayed a high regioselectivity.

Table 2. Ni-Catalyzed Addition Reaction of **2a** to Internal Alkynes **1y**[a]



y = p: $R^2 = n\text{-}C_3H_7$, $R^3 = n\text{-}C_3H_7$
y = q: $R^2 = C_6H_5$, $R^3 = C_6H_5$
y = r: $R^2 = C_6H_5$, $R^3 = CH_3$
y = s: $R^2 = (CH_3)_2CH(CH_2)_2$, $R^3 = H_2C{=}C(CH_3)$
y = t: $R^2 = C_6H_5$, $R^3 = CH_2OH$

entry	1y	time (h)	conversion (%)[b] 1y	2a	yield (%)[c]	selectivity (%)[d]
1	**1p**	48	86	85	85 (75)	–
2[f]	**1p**	48	70	68	68	–
3	**1q**	96	57	59	54 (41)	–
4	**1r**	48	85	90	76 (67)	78
5	**1s**	48	51	60	48	69
6	**1t**	48	85	90	83 (79)	92

[a] Reaction conditions: **1y** (2.0 mmol), **2a** (2.0 mmol), 1,4-dioxane (2.0 mL), $Ni(cod)_2$ + 2dppb (catalyst **C**; Ni, 4.0 mol %), 100 °C. [b] Determined by GC. [c] Total yield of **3ya** and **4ya** determined by GC. The figures in parentheses are isolated yields. [d] 100 [**3ya**]/([**3ya**] + [**4ya**]) determined by GC. [f] Catalyst **B** ($Ni(cod)_2$ + 1dppb) was used.

The reactivity of other allylic sulfides is highly dependent on the substituent (Scheme 2). Thus, allyl methyl sulfide (**2b**) is much less reactive than **2a**, indicative of the necessity of an aromatic group bound to sulfur for the reaction to smoothly proceed. *β*-Methylated allylic sulfide **2c** is somewhat less reactive than **2a**. The reaction of **2d** that has a methyl at the α-position proceeds smoothly to give products **5**−**7**. The structure and distribution of **5**−**7** are diagnostic of a mechanism that involves *π*-allylnickel species as intermediates (vide infra). The reactivity of **2d′** that has a methyl group at the *γ*-position, on the other hand, is much lower than that of **2d**, but the same products **5**−**7** are formed with nearly the same distribution, which suggests the involvement of the same *π*-allylnickel intermediate as that generated from **2d**.[7] Cinnamyl phenyl sulfide (**2e**), more congested at the *γ*-position, did not react at all.

The addition reaction is envisioned to proceed via the sequence of events shown in Scheme 3, which accommodates the following experimental results.

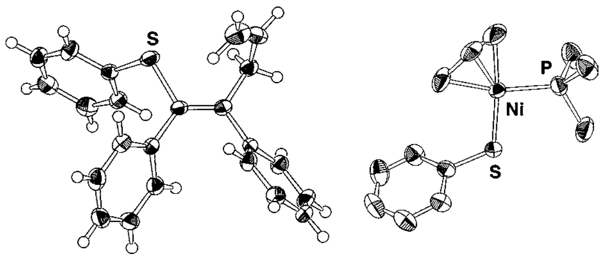


Figure 1. ORTEP drawings of (a) **3qa** (left) and (b) $Ni(\pi\text{-}C_3H_5)(SPh)(PMe_3)$ **8a** (right).

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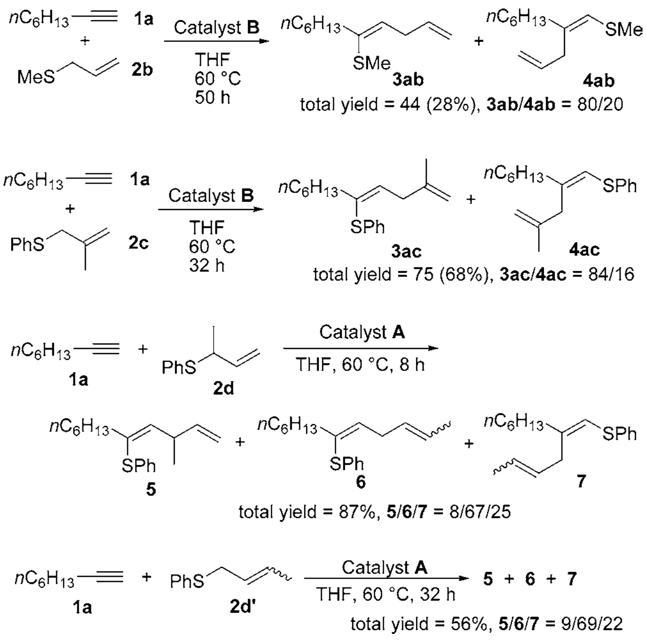
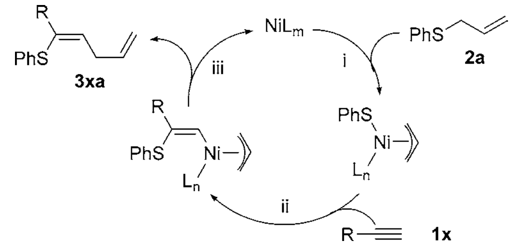
(6) Crystals for X-ray diffraction analysis were obtained by recrystallization from hexane at 0 °C. Crystal data for **6b**: colorless needles, orthorhombic, space group $P2_12_12_1$, $a = 16.382(2)$ Å, $b = 17.248(2)$ Å, $c = 6.272(3)$ Å, $V = 1772.2(8)$ Å^3, $Z = 4$, $D_c = 1.231$ g/cm^3, fw = 328.47, μ(Mo Kα) = 1.82 cm^{-1}, R1 = 0.041, wR2 = 0.103, GOF = 1.08. See Supporting Information for details.

Scheme 2



Oxidative addition of allyl sulfides with Pd, Rh, and Ru has been documented.[8] To substantiate the oxidative addition with Ni(0), we treated a THF solution of Ni(cod)$_2$ with **2a** (1 equiv) in the presence of PMe$_3$ (2 equiv) at −60 °C ~ room temperature overnight. Routine workup and recrystallization from octane afforded (π-allyl)Ni(SPh)(PMe$_3$) (**8a**, 46%), the structure of which was verified by X-ray diffraction analysis (Figure 1).[9] A similar reaction using PPh$_3$ in place of PMe$_3$ also afforded the corresponding π-allyl complex (**8b**, 61%), which appeared less stable than **8a**.[10] Upon treatment of complex **8a** or **8b** with **1a** (5 equiv) in THF at 60 °C for 1 h, a mixture of **3aa** and **4aa** was obtained in 26 or 28% yield, respectively (**3aa** selectivity = 83%, irrespective of the starting complex). In addition to these observations, the structure and essentially the same distribution of the products **5**−**7** formed in the reactions of **2d** and **2d′** strongly support that these two reactions proceed through the same π-allylnickel intermediate. The formation of **6** and **7** in preference to **5** is envisaged to have come from the C−C reductive elimination that took place at the sterically less congested allylic carbon. It is well-established that oxidative addition of an alkyl halide proceeds via an S$_N$2-type mechanism.[11] In the present reaction, we envision that the oxidative addition of allylic sulfides proceeds through precoordination of the olefinic linkage to the transition metal[11c,12] and/or S$_N$2′-type mechanism,[8e] either of which agrees with the low reactivity of **2d′** as compared with that of **2d** (and also **2c**).

Scheme 3



In summary, nickel-catalyzed addition of allylic sulfides to alkynes proceeds to furnish alkenes having organothio and allylic moieties, which can be elaborated in many ways. Thus the products will find useful synthetic applications.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 18065008, “Chemistry of Concerto Catalysis”) from the Ministry of Education, Culture, Sports, Science and Technology, Japan

Supporting Information Available: Experimental procedures, spectral data for new compounds, and crystallographic data for **3qa** and **8a** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Heating a 54:46 mixture of **2d** and **2d′** under the catalytic conditions (THF, 60 °C) over 8 h in the presence of Ni(cod)$_2$ (4.0 mol %) did not change the ratio, suggesting that the very similar distribution of products is not due to possible isomerization between **2d** and **2d′** under the reaction conditions.

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(9) Crystal data for **8a**: red needles, monoclinic, space group $P2_1/c$, $a = 9.153(2)$ Å, $b = 15.111(1)$ Å, $c = 10.390(1)$ Å, $V = 1391.3(4)$ Å^3, $Z = 4$, $D_c = 1.361$ g/cm^3, fw = 285.02, μ(Mo Kα) = 16.28 cm^{-1}, R1 = 0.032, wR2 = 0.113, GOF = 1.24. See Supporting Information for details.

(10) Reactions of Ni(cod)$_2$ or Ni(cod)$_2$−dppb (dppb/Ni = 2 or 4) with **2a**−**c** failed to give possible allyl−nickel complexes because of instability.

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