Nickel-catalysed synthesis of tetrasubstituted vinyl sulfides from thiocarbamates and internal alkynes

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Nickel-catalysed synthesis of tetrasubstituted vinyl sulfides from thiocarbamates and internal alkynes

Tasuku Inami,[a] Takuya Kurahashi*,[a, b] and Seijiro Matsubara*,[a]

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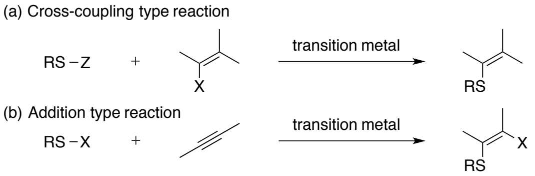
The thiocarbamoylation of internal alkynes to produce tetrasubstituted β-aminocarbonyl vinyl sulfides was demonstrated using a nickel catalyst. This reaction was successful with a wide variety of substituents, and gave the *syn*-adducts exclusively.

Vinyl sulfides are versatile and important synthetic intermediates in organic chemistry;[1] therefore, numerous synthetic methods have been reported.[2] Among these methods, the transition metal-catalysed synthesis of vinyl sulfides has attracted increased attention in the last few decades. The reported transition metal catalysed methods are classified into two groups. The first is the cross-coupling of vinyl halides with thiols[3] or metal thiolates (Scheme 1 (a)).[4] The second is the addition of an S–X bond (X = H,[5] B,[6] C,[7] P,[8] or S[9]) to alkynes (Scheme 1 (b)). The latter method is more attractive because it is more atom-economic and can give highly functionalized vinyl sulfides from readily available and simple compounds.

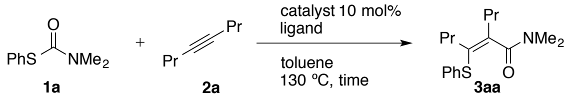


Scheme 1. Transition metal-catalysed synthesis of vinyl sulfides.

In 1991, the Sonoda group reported a pioneering study on the palladium-catalysed addition of disulfides to terminal alkynes.[9a] Since this report, many reactions that introduce sulfur simultaneously with various heteroatoms or hydrogen to alkynes have been reported.[5,6,8–10] In 2001, the Tanaka and Kurosawa groups independently reported carbothiolation reactions of terminal alkynes via the activation of a carbon–sulfur bond,[7a,b] and they and others have intensely developed various transition metal catalysed and mediated carbothiolation reactions.[7] Although these reactions are valuable methods for the synthesis of highly functionalized vinyl sulfides, it is still difficult to synthesize tetrasubstituted vinyl sulfides because internal alkynes have lower reactivity than terminal alkynes; the utilization of internal alkynes in this type of reaction remains a research topic to be developed.[7e,7f,7h,7i,7k,7l]

Recently, we reported the nickel-catalysed cycloaddition of thiophthalic anhydrides with alkynes to selectively produce thiochromones, benzothiophenes, or thioisocoumarins by changing the reaction conditions; internal alkynes could be applied in these reactions.[11] Based on this result, we hypothesized that it is possible to add S–C bonds to internal alkynes by using nickel catalysts and that tetrasubstituted vinyl sulfides could be obtained. Herein, we report the nickel-catalysed thiocarbamoylation of internal alkynes to produce tetrasubstituted vinyl sulfides. To the best of our knowledge, this is the first example of the direct intermolecular thiocarbamoylation of internal alkynes. Meyer and co-workers reported that this reaction did not proceed with palladium catalysts, even when a more reactive terminal alkyne was used,[12] whereas Kambe and co-workers showed a single example of palladium-catalysed intramolecular thiocarbamoylation of a terminal alkyne.[7d]

Table 1. Optimization of reaction conditions.[a]

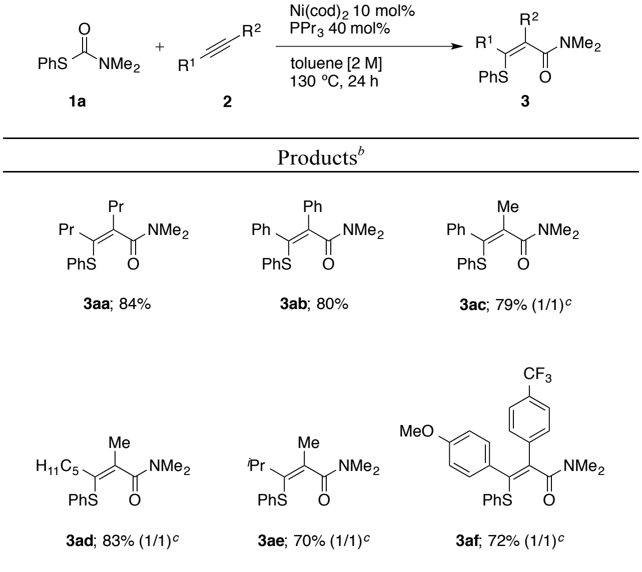


entry	cat.	ligand (mol%)	time [h]	conc. [M][b]	yield [%][c]
1	Ni(cod)$_2$	PMe$_3$ (20)	12	0.2	12
2	Ni(cod)$_2$	PPr$_3$ (20)	12	0.2	25
3	Ni(cod)$_2$	PCy$_3$ (20)	12	0.2	11
4	Ni(cod)$_2$	PPh$_3$ (20)	12	0.2	4
5	Ni(cod)$_2$	dcype (10)	12	0.2	2
6	Ni(cod)$_2$	IPr (10)	12	0.2	trace
7[d]	Ni(cod)$_2$	PPr$_3$ (20)	12	1.0	53
8[e]	Ni(cod)$_2$	PPr$_3$ (20)	12	2.0	63
9[e]	Ni(cod)$_2$	PPr$_3$ (40)	12	2.0	73
10[e]	Ni(cod)$_2$	PPr$_3$ (40)	24	2.0	86
11[e]	Pd(PPh$_3$)$_4$	— —	24	2.0	trace
12[e]	Pt(PPh$_3$)$_4$	— —	24	2.0	0

[a] Reactions were carried out using catalyst (10 mol%), ligand, *S*-phenyl-*N*,*N*-dimethyl thiocarbamate **1a** (0.2 mmol; 1 equiv.) and 4-octyne **2a** (0.4 mmol; 2 equiv.) in 1.0 mL of toluene at 130 ºC. [b] Concentration of thiocarbamate **1a**. [c] Determined by ^{1}H NMR. [d] 0.5 mmol of **1a** was used. [e] 1.0 mmol of **1a** was used. dcype = 1,2-bis(dicylohexylphosphino)ethane. IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazole-2-ylidene.

Initially, we chose *S*-phenyl-*N,N*-dimethylthiocarbamate (**1a**) and 4-octyne (**2a**) as model compounds for the optimization of reaction conditions. First, the reaction was performed in toluene at 130 ºC for 12 h in the presence of 10 mol% bis(1,5-cyclooctadiene)nickel and 20 mol% trimethylphosphine, and the desired product **3aa** was obtained in 12% yield (Table 1, entry 1). We then surveyed various ligands, such as PPr_3, PPh_3, PCy_3, 1,2-bis(dicyclohexylphosphino)ethane (dcype), and 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene (IPr) (entries 2–6), and found that PPr_3 gave the best result, albeit with a low yield (entry 2). In the course of our optimization studies, we realized that the concentration of the substrates was a significant factor in this reaction system. When the concentration of **1a** was 1 M, the yield increased to 53% (entry 7). Moreover, when the concentration **1a** was 2 M, the desired product was obtained in 63% yield (entry 8). Unfortunately, higher concentrations or neat conditions gave inferior results. Under conditions of 2 M **1a**, the yield was improved when 40 mol% PPr_3 was used (entry 9), and a prolonged reaction time gave the highest yield of 86% (entry 10). In accordance with previous reports, palladium or platinum catalysts did not give the desired product, even when the reactions were performed with 2 M **1a** (entries 11 and 12). Based on the ^{1}H NMR analyses of the crude mixtures and NOE analysis of isolated **3aa**, only the *syn*-adduct was produced under all reaction conditions.

Table 2. Scope of alkynes.[a]



3aa; 84%
3ab; 80%
3ac; 79% (1/1)[c]
3ad; 83% (1/1)[c]
3ae; 70% (1/1)[c]
3af; 72% (1/1)[c]

[a] Reactions were carried out using $Ni(cod)_2$ (10 mol%), PPr_3 (40 mol%), **1a** (1.0 mmol; 1 equiv.) and alkyne (2.0 mmol; 2 equiv.) in toluene (0.5 mL) at 130 ºC for 24 hours. [b] Isolated yields are given. [c] Ratio of regioisomers.

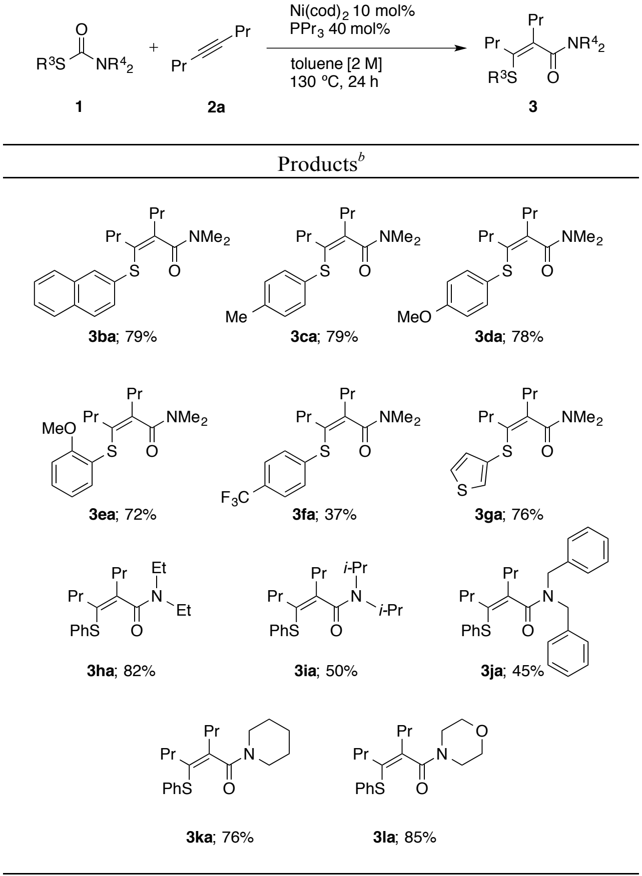
Using the optimized reaction conditions, we investigated the scope of the reaction using various alkynes and **1a** (Table 2). We found that not only dialkyl acetylenes but also diaryl acetylenes could be applied to this reaction to give the corresponding tetrasubstituted products in high yields (**3aa**: 84%, **3ab**: 80%). When 1-phenyl-1-propyne was used, the desired product **3ac** was obtained in 79% yield. Asymmetric dialkyl acetylenes also gave the corresponding products **3ad** and **3ae** in 83% and 70% yields, respectively. An electronically biased diarylalkyne reacted with **1a** smoothly (**3af**: 72%). Although various substituted alkynes gave the desired compounds in high yields, this reaction showed no regioselectivity and each product was obtained as a 1:1 ratio of the regioisomers.

Next, we surveyed the effect of the substituent on the sulfur of the thiocarbamates (Table 3). The compounds with 2-naphthyl or *p*-tolyl substituents gave the corresponding products **3ba** or **3ca** in high yields. Although the thiocarbamate with a *p*-anisyl group on sulfur gave the desired product **3da** in 78% yield, the substrate with a 4-trifluoromethylphenyl group gave product **3fa** in low yield. Product **3ea** was obtained in 72% yield, indicating that compounds with sterically demanding substituents can also participate in this reaction. *S*-(3-thienyl)-*N,N*-dimethylthiocarbamate also gave the desired product **3ga** in 76% yield.

Finally, we investigated the scope of the substituents on the nitrogen of the thiocarbamates (Table 3). The thiocarbamate with a diethylamino group gave the corresponding vinyl sulfide **3ha** in high yield. Even when the substrate had sterically demanding substituents on nitrogen, the desired product was obtained in acceptable yield (**3ia**: 50%). Benzyl groups on nitrogen survived under the reaction conditions (**3ja**). Thiocarbamates obtained from cyclic amines did not suppress the reaction and gave the corresponding products in high yields (**3ka**: 76%, **3la**: 85%).

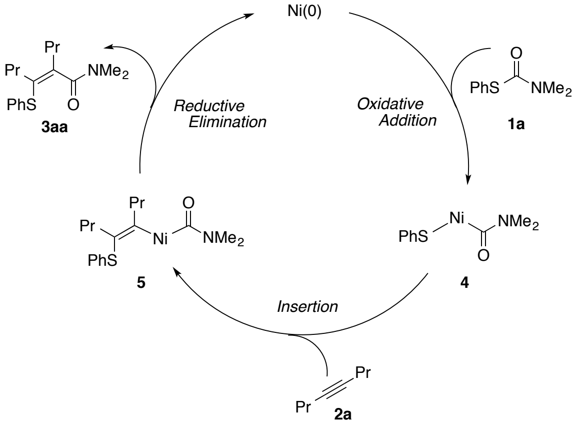
Although the exact reaction mechanism remains unknown at this point, a possible mechanism is shown in Scheme 2 that is based on the previously proposed mechanisms for similar reactions.[7a,7e,7f,7h,7i] First, thiocarbamate **1** oxidatively adds to nickel centre to give complex **4**. Then, the migratory insertion of the alkyne into this complex occurs, followed by reductive elimination to give the product and the regenerated nickel catalyst to close the catalytic cycle.

Table 3. Scope of substituents of thiocarbamates.[a]



3ba; 79%
3ca; 79%
3da; 78%
3ea; 72%
3fa; 37%
3ga; 76%
3ha; 82%
3ia; 50%
3ja; 45%
3ka; 76%
3la; 85%

[a] Reactions were carried out using $Ni(cod)_2$ (10 mol%), PPr_3 (40 mol%), **1** (1.0 mmol; 1 equiv.) and 4-octyne **2a** (2.0 mmol; 2 equiv.) in toluene (0.5 mL) at 130 ºC for 24 hours. [b] Isolated yields are given.



Scheme 2. Plausible reaction mechanism.

In summary, we developed the nickel-catalysed thiocarbamoylation of internal alkynes. In this reaction, tetrasubstituted vinyl sulfides could be obtained in a single step from a diverse selection of thiocarbamates and alkynes. Only the *syn*-adducts were obtained, and their stereoisomers were not detected. Further efforts to expand the scope of the chemistry and studies on the detailed reaction mechanism are currently underway in our laboratories.

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Notes and references

[a] Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: kurahashi.taskuya.2c@kyoto-u.ac.jp, matsubara.seijiro.2e @kyoto-u.ac.jp; Fax: +81 75 383 2438; Tel: +81 75 383 2440
[b] JST, ACT-C, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012 (Japan).

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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