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Platinum(II)-Catalyzed Reaction of 2-Alkynylbenzoates or Benzothioates with Vinyl Ethers: A Concise Method for Synthesis of 1-Acyl-4-alkoxy- or 1-Acyl-4-alkylsulfanylnaphthalene Derivatives

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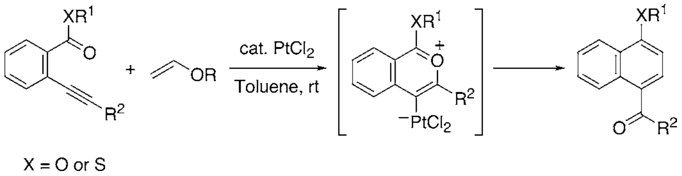
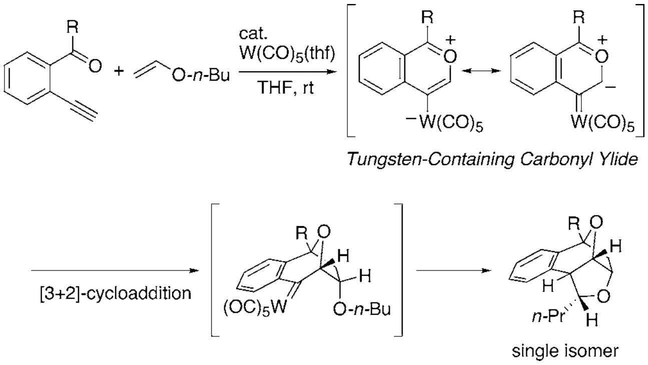
ABSTRACT



A concise method for the preparation of 1-acyl-4-alkoxy- or 1-acyl-4-alkylsulfanylnaphthalenes has been developed by the reaction of *o*-ethynylbenzoates or benzothioates with vinyl ethers, in the presence of a catalytic amount of PtCl$_2$. It is proposed that the reaction proceeds through [3 + 2]-cycloaddition of the platinum-containing carbonyl ylides followed by 1,2-alkyl migration.

In a previous paper,[1] we reported a novel method for the generation of tungsten-containing carbonyl ylides[2] by the reaction of *o*-(1-alkynyl)phenyl ketones with pentacarbonyltungsten and their [3 + 2]-cycloaddition reaction with electron-rich alkenes to give polycyclic compounds through the insertion of the unstabilized tungsten carbene intermediates into the neighboring C−H bond (Scheme 1). As formation of metal-containing ylides[3] is rarely known and synthetic utility of such species still remains relatively unexplored, we have continued our efforts to examine the

Scheme 1



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[1] (a) Iwasawa, N.; Shido, M.; Kusama, H. *J. Am. Chem. Soc.* **2001**, *123*, 5814. For generation of tungsten-containing azomethine ylides, see: (b) Kusama, H.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 11592. (c) Takaya, J.; Kusama, H.; Iwasawa, N. *Chem. Lett.* **2004**, *33*, 16.

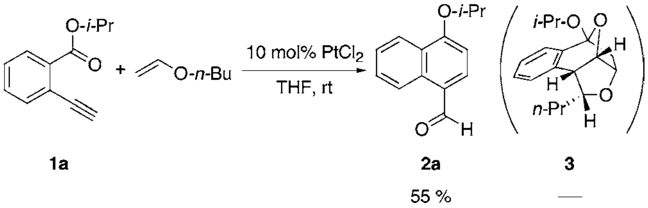
[2] For reviews on the carbonyl ylides, see: (a) Padwa, A.; Weingarten, M. D. *Chem. Rev.* **1996**, *96*, 223. (b) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, 1999; p 206. (c) Padwa, A.; Pearson, W. H. *Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry Toward Heterocycles and Natural Products*; Wiley-Interscience: Hoboken, 2003; p 253. For some recent examples, see: (d) Hodgson, D. M.; Labande, A. H.; Pierard, F. Y. T. M.; Exposito Castro, M. A. *J. Org. Chem.* **2003**, *68*, 6153. (e) Nakamura, S.; Hirata, Y.; Kurosaki, T.; Anada, M.; Kataoka, O.; Kitagaki, S.; Hashimoto, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 5351.

10.1021/ol0364024 CCC: $27.50

possibility of generating these carbonyl ylide species using other transition metal complexes. In this paper is described the result of such examination, that is, generation of platinum-containing carbonyl ylide species by the reaction of *o*-alkynylbenzoates or benzothioates with a catalytic amount of $PtCl_2$[4] and their use for the concise synthesis of 1-acyl-4-alkoxy- or 1-acyl-4-alkylsulfanylnaphthalenes by the reaction with vinyl ethers.

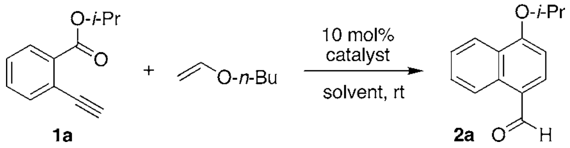
In the first place, we examined the above reactions employing $PtCl_2$ as a catalyst instead of the tungsten complex. The reaction of *o*-ethynylbenzaldehyde or *o*-ethynylacetophenone with butyl vinyl ether in the presence of a catalytic amount of $PtCl_2$ resulted in a complex mixture, and none of the addition product was obtained. On the other hand, when a mixture of isopropyl *o*-ethynylbenzoate **1a** and butyl vinyl ether was treated with $PtCl_2$ (10 mol %) in THF, the starting material was consumed within several hours at room temperature,[5] and purification of the crude products revealed that 4-isopropoxynaphthalene-1-carbaldehyde **2a** was obtained in moderate yield instead of the polycyclic compound **3** (Scheme 2). As formation of the naphthalene derivative **2a** was rather unexpected, we decided to examine this platinum(II)-catalyzed naphthalene synthesis in more detail.

Scheme 2



To improve efficiency of this reaction, we first investigated the above reaction in various solvents (Table 1). Although the use of acetonitrile did not improve the yield of **2a** (entry 1), the reaction in dichloromethane, ether, and toluene smoothly proceeded to afford **2a** in 71, 84, and 86% yield, respectively (entries 2−4). In addition, when the reaction was carried out in toluene in the presence of molecular sieves 4A, the yield of **2a** was further improved to 91% (entry 5). Some other transition-metal compounds such as $PtBr_2$ and $AuCl_3$ were also examined under the conditions of entry 4; however, the naphthalene **2a** was obtained in low yield and $PtCl_2$ was found to be the most suitable catalyst for this reaction.

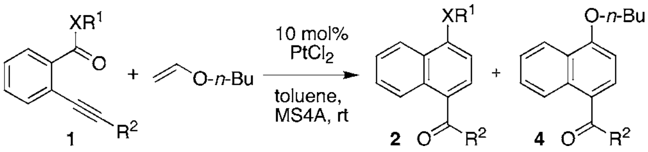
Table 1. Screening of the Reaction Conditions



entry	catalyst	solvent	time	yield/%
1	$PtCl_2$	CH_3CN	2 days	47
2	$PtCl_2$	CH_2Cl_2	16 h	71
3	$PtCl_2$	Et_2O	9 h	84
4	$PtCl_2$	toluene	6 h	86
5[a]	$PtCl_2$	toluene	10 h	91
6	$PtBr_2$	toluene	2 days	47
7	$AuCl_3$	toluene	2 days	10

[a] MS4A was added.

Table 2. Reaction of Various *o*-Alkynylbenzoates and *o*-Alkynylbenzothioate



entry	XR^1	R^2		time	yield/%	ratio **2**/**4**
1	O-*i*-Pr	H	**1a**	10 h	91	100:0
2	OMe	H	**1b**	12 h	84	61:39
3	OPh	H	**1c**	10 h	90	51:49
4	O-*p*-ClPh	H	**1d**	11 h	86	50:50
5	OCH_2Ph	H	**1e**	8 h	77	56:44
6	SC_8H_{17}	H	**1f**	9 h	60	65:35
7	NEt_2	H	**1g**	9 h	–	
8	O-*i*-Pr	*n*-Pr	**1h**	3 days	89	100:0
9[a]	O-*i*-Pr	Ph	**1i**	5 days	64	100:0

[a] The reaction was performed in the presence of 30 mol % of $PtCl_2$.

Since the optimal reaction conditions had become clear, we then investigated generality of the reaction using various *o*-alkynylbenzoic acid derivatives, and the results were summarized in Table 2. As for the ester functionality, alkoxy, aryloxy, and alkylsulfanyl groups were applicable and the corresponding naphthalenes were obtained in high yield (entries 1−6). In particular, formation of *n*-octylsulfanyl-substituted naphthalene **2f** is noteworthy as it is not necessarily easy to introduce alkylsulfanyl group onto naphthalene. On the contrary, the reaction of an amide derivative **1g** did not proceed and the starting material was recovered. Except

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(3) For formation of metal-containing ylides, see: (a) Padwa, A.; Gasdaska, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 1104. For a recent related example, see: (b) Miki, K.; Nishino, F.; Ohe, K.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 5260.

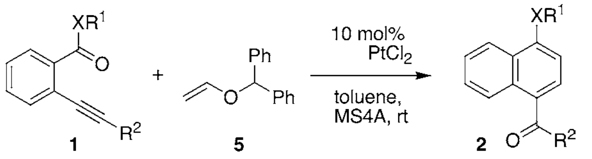
(4) (a) Mendez, M.; Mamame, V.; Fürstner, A. *Chemtracts − Org. Chem.* **2003**, *16*, 397. (b) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. (c) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. (d) Chatani, N.; Inoue, H.; Ikeda, T.; Murai, S. *J. Org. Chem.* **2000**, *65*, 4913. (e) Fernández-Rivas, C.; Méndez, M.; Echavarren, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 1221. (f) Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Chem. Eur. J.* **2003**, *9*, 2627. (g) Mainetti, E.; Mouriès, V.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2132. (h) Fürstner, A.; Stelzer, F.; Szillat, H. *J. Am. Chem. Soc.* **2001**, *123*, 11863. (i) Oi, S.; Tsukamoto, I.; Miyano, S.; Inoue, Y. *Organometallics* **2001**, *20*, 3704. For recent examples of the use of $PtCl_4$, see: (j) Pastine, S. J.; Youn, S. O.; Sames, D. *Tetrahedron* **2003**, *59*, 8859. (k) Baidossi, W.; Schumann, H.; Blum, J. *Tetrahedron* **1996**, *52*, 8349.

(5) In marked contrast with the platinum catalyzed reaction, treatment of isopropyl *o*-ethynylbenzoate **1a** and butyl vinyl ether with a catalytic amount of preformed $W(CO)_5(thf)$ did not produce the expected adduct **3** at all, and the starting material **1a** remained intact.

for the reaction of the isopropyl ester **1a**, the products **2b**−**f** contained considerable amounts of butoxy-substituted naphthaldehyde **4**. This compound was presumably produced during the reaction by alkoxy exchange with butanol, which eliminated from intermediates of the final step of the reaction (see Scheme 3).

To avoid this alkoxy exchange reaction, we further examined several vinyl ethers and found that formation of this byproduct could be suppressed by using diphenylmethyl vinyl ether **5**, a very sterically demanding substrate, and the desired naphthalenes were obtained without the formation of the alkoxy-exchanged naphthalenes in good yield (Table 3). Substituent effect on the alkyne carbon was also investigated; not only the terminal alkyne, but also alkyl- or aryl-substituted internal alkynes **1h**−**k** gave the corresponding naphthyl ketone derivatives in good to high yield (entries 8, 9 in Table 2 and entries 7, 8 in Table 3).

Table 3. Reaction with Diphenylmethyl Vinyl Ether



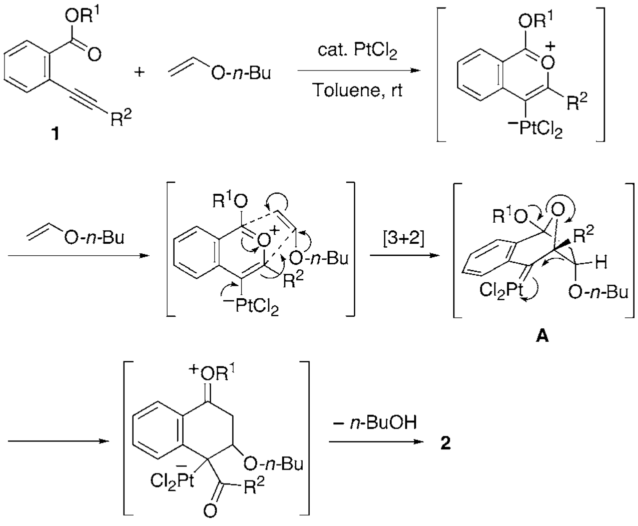
entry	XR^1	R^2		time	yield/%
1	O-*i*-Pr	H	**1a**	8 h	86
2	OMe	H	**1b**	8 h	83
3	OPh	H	**1c**	10 h	87
4	O-*p*-ClPh	H	**1d**	8 h	60
5	OCH$_2$Ph	H	**1e**	8 h	83
6^a	SC$_8$H$_{17}$	H	**1f**	10 h	60
7	OCH$_2$Ph	*n*-Pr	**1j**	2 days	83
8^a	SC$_8$H$_{17}$	*n*-Pr	**1k**	2 days	79

[a] The reaction was performed in the presence of 30 mol % of PtCl$_2$.

Yamamoto and co-workers recently reported related AuCl$_3$- and Cu(OTf)$_2$-catalyzed reactions of *o*-(1-alkynyl)phenylcarbonyl compounds and alkynes or alkenes to give naphthylcarbonyl or dihydronaphthylcarbonyl derivatives.[6] They proposed that the reactions proceed through the similar gold(III)- or copper(II)-containing zwitterionic intermediates, which undergo [4 + 2]-cycloaddition with alkynes or alkenes followed by demetalation to give the products. However, there seem to be several differences between their reactions and ours. The most important difference is the platinum-catalyzed reactions proceed well with *o*-(1-alkynyl)benzoates or benzothioates to give 4-alkoxy- or 4-alkylsulfanyl-1-acylnaphthalenes, while gold(III)- or copper(II)-catalyzed reactions proceed with *o*-(1-alkynyl)phenyl ketone or aldehyde to give 4-alkyl-1-acylnaphthalene derivatives. Additionally, the platinum(II)-catalyzed reactions proceed at lower temperature (room temperature) compared to the other two reactions (∼80 °C).

Concerning the mechanism of the reaction, we at present believe that the reaction proceeded through [3 + 2]-cycloaddition of the platinum(II)-containing carbonyl ylides, followed by 1,2-alkyl-migration[1b,7,8] of the produced carbene intermediates as shown in Scheme 3 based on the following experimental results.[9]

Scheme 3



When 2,4-dimethoxyphenylmethyl vinyl ether is employed as an electron-rich alkene,[10] the C−H insertion product **6** of the carbene intermediate A[4d,f,g] is obtained albeit in low yield along with alkoxy naphthalene **2d** and **2l** in 29% and 55% yield, respectively. Furthermore, the platinum(II)-catalyzed

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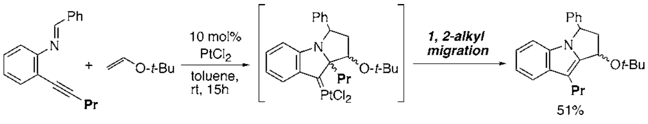
[6] (a) Asao, N.; Takahashi, K.; Lee, S.; Kasahara, T.; Yamamoto, Y. *J. Am. Chem. Soc.* **2002**, *124*, 12650. (b) Asao, N.; Kasahara, T.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 3504. (c) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921. See also: (d) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *Org. Lett.* **2003**, *5*, 4121.

[7] For other examples of the 1,2-alkyl migration of transition metal carbene intermediates, see: (a) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim. 1999; p 193. (b) Zora, M.; Herndon, J. W.; Li, Y.; Rossi, J. *Tetrahedron* **2001**, *57*, 5097 and references therein. (c) Nagao, K.; Chiba, M.; Kim, S.-W. *Synthesis* **1983**, 197. (d) Bly, R. S.; Bly, R. K.; Hossain, M. M.; Lebioda, L.; Raja, M. *J. Am. Chem. Soc.* **1988**, *110*, 7723. (e) Jiang, N.; Ma, Z.; Qu, Z.; Xie, L.; Wang, J. *J. Org. Chem.* **2003**, *68*, 893 and references therein.

[8] As we previously reported,[1b] 1,2-alkyl migration of the tungsten carbene complex generated by [3 + 2]-cycloaddition of a tungsten-containing azomethine ylide with a vinyl ether occurred smoothly. This reaction also proceeded using a catalytic amount of PtCl$_2$ to give the same product in moderate yield. This result suggests that 1,2-alkyl migration of the platinum carbene complex is a possible reaction pathway. Unpublished results.

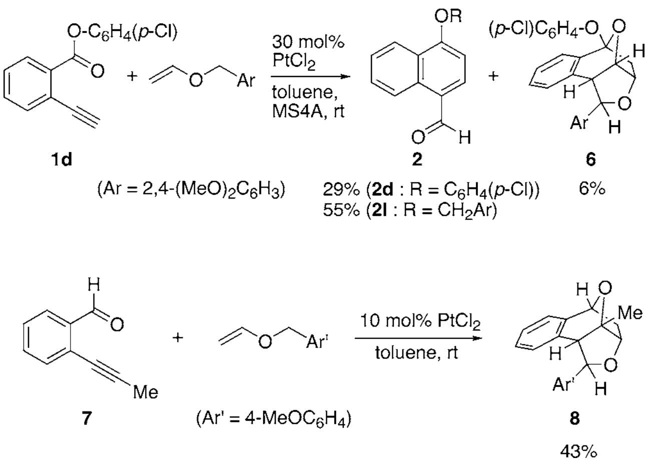


[9] It is not necessarily easy to completely rule out the possibility of [4 + 2]-cycloaddition pathway proposed by Yamamoto.[6] We are currently analyzing the possible reaction pathways by calculations.

[10] It is expected that C−H insertion is facilitated by the strong electron-donation from the electron-rich aryl group. For the electronic factor of carbene insertion into C−H bonds, see: (a) Seyferth, D.; Mai, V. A.; Gordon, M. E. *J. Org. Chem.* **1970**, *35*, 1993. (b) Adams, J.; Poupart, M.-A.; Grenier, L.; Schaller, C.; Ouimet, N.; Frenette, R. *Tetrahedron Lett.* **1989,** *30*, 1749.

reaction of *o*-(1-propynyl)benzaldehyde with 4-methoxyphenylmethyl vinyl ether also gave the [3 + 2]-cycloaddition-carbene insertion product **8** in reasonable yield (Scheme 4).

Scheme 4



Although further detailed mechanistic studies are required, these results suggest that the naphthalene would be produced through [3 + 2]-cycloaddition followed by 1,2-alkyl-migration. Probably the alkoxy group of the ester moiety promotes 1,2-alkyl-migration by electron-donation as shown in Scheme 3 to afford 4-alkoxy-1-naphthylcarbonyl compounds as the product.

In conclusion, we have developed a PtCl$_2$-catalyzed preparation of 1-acyl-4-alkoxy- or 1-acyl-4-alkylsulfanyl-naphthalenes from *o*-alkynylbenzoates or benzothioates and vinyl ethers through the novel platinum(II)-containing carbonyl ylides. Further study on the chemistry of the metal-containing ylides is in progress in our laboratory.

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Supporting Information Available: Preparative methods and spectral and analytical data of compounds **1**, **2**, **5**, **6**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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