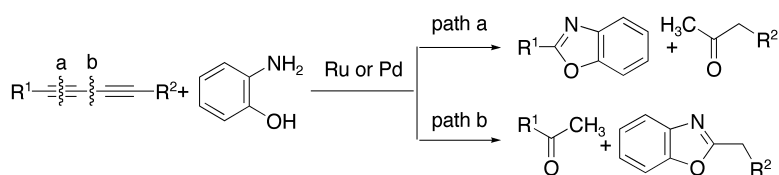


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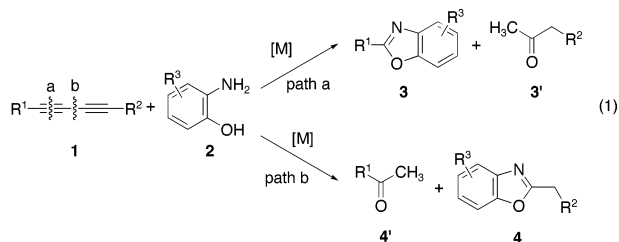
Carbon–Carbon Bond Cleavage of Diynes through the Hydroamination with Transition Metal Catalysts

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Although a number of researches on C–C bond cleavage have been carried out,¹ only a few examples on the cleavage of alkynes are known: C–C bond cleavage of alkynes ligated to metal complexes² and oxidative cleavage.³ Furthermore, most of these reactions do not proceed in a catalytic manner, and the use of a stoichiometric amount of reagents is needed.⁴ Recently, Jun et al. reported catalytic C–C triple bond cleavage through the rhodium-catalyzed hydroiminoacylation.⁵ During our investigation on palladium-catalyzed hydroamination of alkynes using *o*-aminophenol,⁶ we found that the C–C bond cleavage of diynes **1** with *o*-aminophenols **2** is catalyzed efficiently by Ru and Pd catalysts to give the corresponding 2-substituted benzoxazoles **3** and **4** (eq 1).



The results are summarized in Table 1. The reaction of 1,3-decadiyne **1a** (1.0 equiv) with *o*-aminophenol **2a** ($R^3 = \text{H}$, 1.5 equiv) in the presence of a catalytic amount of $\text{Ru}_3(\text{CO})_{12}$ and NH_4PF_6 , followed by hydrolysis of the products, gave the benzoxazoles **3a** and **4a**, almost quantitatively, in a ratio of 3:1 (entry 1). Apparently, **3a** was obtained through the C–C triple bond cleavage as shown in path a, and **4a** was obtained through path b. Since $R^2 = \text{H}$, acetone **3a'** must be produced in the same yield as **3a** and 2-octanone **4a'** in the same yield as **4a**. Although detection of acetone was not attempted due to its volatile characteristics, the formation of 2-octanone was detected (see also entry 2, *vide infra*). We examined a number of reaction conditions and finally found that the highest chemical yield and highest ratio of **3a/4a** were obtained under the conditions similar to those of Wakatsuki's hydroamination.⁷ We tested various kinds of d^8 and d^{10} transition metals that exhibit catalytic activities for hydroamination.⁸ When AuCl_3 and CuCl were used instead of $\text{Ru}_3(\text{CO})_{12}$, a 3:1 mixture of **3a** and **4a** was obtained almost quantitatively. However, the use of PdCl_2 , PtCl_2 , and CuI afforded the products in 45–64% yields although the product ratio was again 3:1. The reaction of 1,3-tetradecadiyne **1b** gave a 4:1 mixture of **3b** and **4b** in 74% yield along with 2-dodecanone **4b'** (11% yield) (entry 2). Cyclohexyl-substituted diyne **1c** also gave a mixture of benzoxazoles **3c** and **4c** in the ratio of 7:1 in 81% yield (entry 3). The sterically bulkier diyne **1c** gave higher ratio of **3:4**. Interestingly, sterically more hindered benzoxazoles **3a–c**, in comparison with **4a–c**, were obtained as the major product. The reaction of **1d** having *t*Bu group as R^1 substituent gave almost exclusively **3d** in 81% yield (entry

Table 1. Ru-Catalyzed Carbon–Carbon Bond Cleavage of Terminal Diynes **1** with 2-Aminophenol **2a**^a

entry	R ¹	R ²	1	reaction time, h	yield, % ^b	3:4
1	ⁿ Hex	H	1a	20	98	3:1
2	ⁿ Dec	H	1b	36	74 ^c	4:1
3	Cyclohexyl	H	1c	20	81	7:1
4	^t Bu	H	1d	20	81	>30:1
5	Ph(CH ₂) ₂	H	1e	20	77	3:1
6	TIPSO(CH ₂) ₄	H	1f	20	70	3:1
7	Cl(CH ₂) ₃	H	1g	20	58	1:1

^a Reaction conditions: 0.75 mmol 2-aminophenol **2a**, 0.50 mmol diyne, 1 mol % $\text{Ru}_3(\text{CO})_{12}$, 3 mol % NH_4PF_6 , methanol (10 M), 80 °C. ^b Combined isolated yields based on 2-aminophenol. ^c 2-Dodecanone was obtained in 11% yield. TIPS = tris(triisopropyl)silyl

Table 2. Ru-Catalyzed Carbon–Carbon Bond Cleavage of 1,3-Decadiyne **1a** with Substituted Aminophenols **2a**

entry	R ³	2	reaction time, h	yield, % ^b	3:4
1	4-NO ₂	2b	20	81	3:1
2	4-Cl	2c	20	97	3:1
3	4-Me	2d	20	95	3:1
4	4-OMe	2e	48	70	3:1
5	5-NO ₂	2f	20	68	3:1
6 ^c	5-Me	2g	20	87	3:1
7	3-Me	2h	20	79	4:1

^a Reaction conditions: 0.75 mmol 2-aminophenol **2**, 0.50 mmol diyne, 1 mol % $\text{Ru}_3(\text{CO})_{12}$, 3 mol % NH_4PF_6 , methanol (10 M), 80 °C. ^b Combined isolated yields based on 2-aminophenols. ^c Concentration 5 M, due to the insolubility of **2g**.

4). When the phenyl- and siloxy-substituted diynes **1e** and **1f** were employed, the cleavage reaction also proceeded in good yields (entries 5 and 6). Even the chlorine-substituted diyne **1g** gave the C–C bond cleavage products **3g** and **4g** in 58% yield (entry 7).

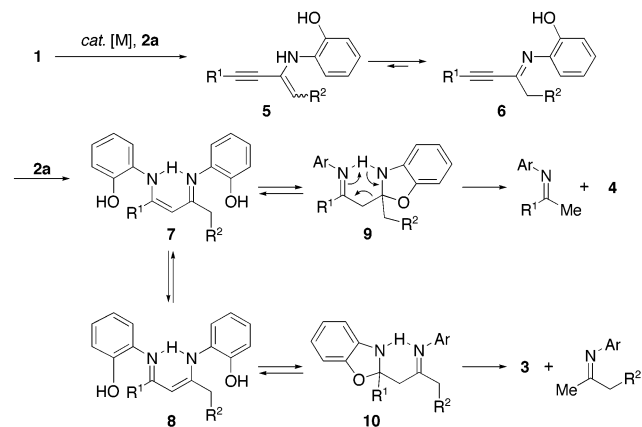
Next, we investigated the C–C bond cleavage with substituted aminophenols (Table 2). When a proton at the C-4 position was substituted with an electron-withdrawing NO₂ group (**2b**), the yield of the products became lower than that of **2a** (entry 1 of Table 2 vs entry 1 of Table 1). The chloro- and methyl-substituted aminophenols **2c** and **2d** gave results similar to those for **2a**. The reaction of 4-methoxy-aminophenol **2e**, having a strong electron-donating group, was very sluggish (entry 4). Thus, both a strong EWG and EDG at the C-4 position retarded the C–C bond cleavage. This trend was also observed when the 5-substituted aminophenols **2f** and **2g** were employed (entries 5 and 6).⁹ The sterically hindered aminophenol, 3-methyl-aminophenol **2h**, gave the products in lower yield, but the selectivity for **3** was slightly higher than for the others (entry 7).

The C–C cleavage reaction of internal diynes proceeded smoothly with palladium(II) catalysts. The catalyst $\text{Pd}(\text{NO}_3)_2$ gave the best result among palladium catalysts.¹⁰ Other catalysts such as Ru and Au did not work at all in the case of internal diynes. Among various solvents, ⁿBuOH was the most efficient.¹¹ The

Table 3. Pd-Catalyzed Carbon–Carbon Bond Cleavage of Internal Diynes **1** with 2-Aminophenol **2a**^a

entry	R ¹	R ²	1	reaction time, h	yield, % ^b	3:4
1	ⁿ Bu	ⁿ Bu	1o	4	97	1:1
2	Ph	Ph	1p	24	89	1:3

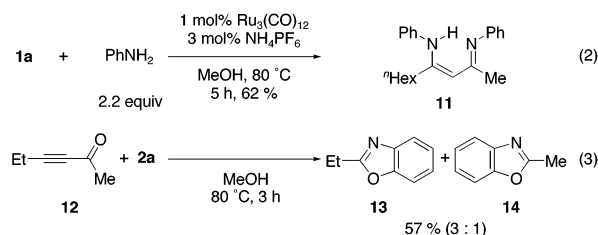
^a Reaction conditions: 0.75 mmol 2-aminophenol **2a**, 0.50 mmol diyne, 6 mol % Pd(NO₃)₂, *n*-butanol (10 M), 120 °C. ^b Combined isolated yields based on 2-aminophenol.

Scheme 1. A Proposed Mechanism for the C–C Bond Cleavage of Diynes

reaction of 5,7-dodecadiyne **1o** (0.50 mmol) with **2a** (0.75 mmol) in the presence of Pd(NO₃)₂ gave a 1:1 mixture of **3o** and **4o** in 97% yield (entry 1, Table 3). Here again, 2-heptanone **3o'** and 2-hexanone **4o'** were obtained along with **3o** and **4o**. Very similarly, the reaction of diphenylbutadiyne **1p** produced a 1:3 mixture of **3p** and **4p** in 89% yield together with 1-phenyl-2-pentanone **3p'** and acetophenone **4p'** (entry 2, Table 3).

The catalytic hydroamination of one of the alkyne groups of the diynes **1** to give the enamines **5** is the key step of the C–C bond cleavage (Scheme 1).^{6–8} Tautomerization of **5** gives the corresponding α,β -unsaturated imines **6**. The conjugate addition of aminophenol **2a** to **6** provides the β -aminoiminines **7** and their tautomers **8**. The intramolecular cyclization of the iminophenol groups of **7** and **8** gives the ketals **9** and **10**, respectively. The C–C bond cleavage through the retro-Mannich-type reaction produces the benzoxazoles **4** and **3**. The selectivity of products is determined by the relative size of R¹ and R²CH₂. When sterically hindered terminal diynes are used, the relative size of R¹ is larger than that of R²CH₂. Then, formation of **10** becomes more favorable than that of **9**; with the bulkier R¹, steric repulsion between R¹ and Ar of the sp² plane of **9** becomes stronger than that between R²CH₂ and Ar of **10**.¹² In the case of internal diyne **1p**, the size of R¹ is smaller than that of R²CH₂, and **4p** is selectively obtained.

To obtain supportive data for this mechanism, 2.2 equiv of aniline were treated with **1a** under the reaction conditions of the C–C bond cleavage. As expected, the β -aminoimine **11** was obtained in 62% yield (eq 2). Next, the ketone **12** and aminophenol **2a** were reacted in MeOH at 80 °C, giving the expected oxazole products **13** and **14** in 57% yield in a ratio of 3:1 (eq 3). These results strongly support the proposed mechanism shown in Scheme 1.



Catalytic C–C bond cleavage procedures are not popular in organic chemistry, and no method employing diynes is known. The present method supplies a new pair of scissors for C–C bond cleavage.

Supporting Information Available: Spectroscopic and analytical data of synthesized compounds and information on procedures (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (10) The yields of the reaction of 5,7-dodecadiyne **1o** with **2a** in the presence of palladium catalysts (6 mol %) and NH₄PF₆ (12 mol %) are as follows; Pd(NO₃)₂ (97%), PdCl₂(PPh₃)₂ (76%), Na₂PdCl₄ (69%) and PdCl₂ (65%).
- (11) Higher reaction temperature was needed (120 °C); therefore, ⁿBuOH was used instead of MeOH.
- (12) The steric congestion at the quaternary carbon center of the oxazole ring is not so influential on the relative stability of **9** and **10** since the substituent R²CH₂ or R¹ takes an orthogonal direction to the oxazole plane.

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