Rhenium-catalyzed [2 + 2] Cycloadditions of Norbornenes with Internal and Terminal Acetylenes

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Treatment of norbornenes with internal and terminal acetylenes in the presence of a catalytic amount of [ReBr(CO)$_3$(thf)]$_2$ gave cyclobutene derivatives in good to excellent yields.

[2 + 2] Cycloadditions of olefins with acetylenes is one of the most powerful tools to synthesize cyclobutene derivatives. Following Woodward–Hoffman rules, [2 + 2] cycloaddition reactions usually proceed under UV-irradiation conditions. However, using transition-metal complexes sometimes enables the reaction to be promoted without UV-irradiation. There have been many reports on metal-mediated[1] or catalyzed [2 + 2] cycloadditions of norbornenes with acetylenes; the following metal complexes have been used: ruthenium,[2] iron,[3] cobalt,[4] rhodium,[5] nickel,[6] palladium,[7] and copper.[8] Recently, we have been investigating the catalytic abilities of rhenium complexes.[9,10] In the process, we found that a rhenium complex also has the ability to catalyze [2 + 2] cycloadditions between norbornenes and acetylenes.

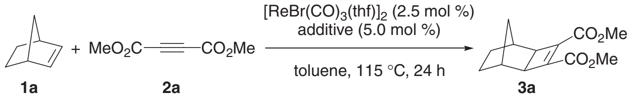
By treatment of norbornene (**1a**) with dimethyl but-2-ynedioate (**2a**) in the presence of a rhenium complex, [ReBr(CO)$_3$(thf)]$_2$, as a catalyst, [2 + 2] cycloaddition reaction proceeded and cyclobutene derivative **3a** was formed in 30% yield (Table 1, Entry 1). Another rhenium complex, ReBr(CO)$_5$, also provided **3a** in the same yield.[11] To the best of our knowledge, this is the first example of rhenium-catalyzed [2 + 2] cycloaddition between a norbornene derivative and an acetylene.

To improve the yield of **3a**, several additives were examined (Table 1). The yield of **3a** did not increase by addition of various Lewis acids and bases (Table 1, Entries 2–10). However, when *tert*-butyl isocyanide was added, the yield of **3a** was increased (Table 1, Entry 11). Benzyl isocyanide and 2,6-dimethylphenyl isocyanide also provided **3a** in moderate yields, respectively (Table 1, Entries 12 and 13). By using a bulky isocyanide, 2,6-diisopropylphenyl isocyanide, cyclobutene derivative **3a** was obtained in 71% yield (Table 1, Entry 14).[12]

By increasing the amounts of the rhenium catalyst, [ReBr(CO)$_3$(thf)]$_2$, and 2,6-diisopropylphenyl isocyanide, the yield of cyclobutene derivative **3a** was increased slightly (Table 2, Entry 1). Norbornadiene (**1b**) also gave the corresponding cyclobutene **3b**; however, the yield of **3b** was low (Table 2, Entry 2). In this reaction, a 1:2-adduct was not formed. Treatment of benzonorbornadiene (**1c**) with acetylene **2a** provided cyclobutene **3c** in 68% yield (Table 2, Entry 3). When the reaction was conducted at higher temperature (150 °C), the yield of **3c** increased to 92% yield (Table 2, Entry 4).

Next, we investigated the reactivities of several acetylenes (Table 3). Diethyl but-2-ynedioate (**2b**) also afforded **3d**; however, the yield of **3d** was low (Table 3, Entry 1). By using acetylenes having a phenyl or an alkyl group, **2c** and **2d**, also produced the corresponding cyclobutene derivatives **3e** and **3f** in 57 and 77% yields, respectively (Table 3, Entries 2 and 3). It is usually difficult to obtain cyclobutene derivatives from terminal acetylenes.[13,14] By using a rhenium catalyst, cyclobutene derivatives **3g**–**3j** were also obtained from terminal acetylenes **2e**–**2h** (Table 3, Entries 4–7). In these reactions, trimerization products of acetylenes were not detected.

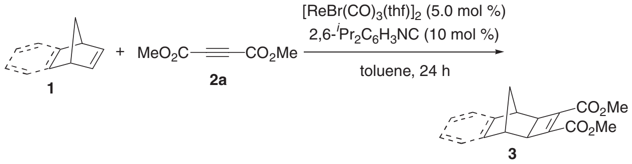
Table 1. Investigation of various additives[a]

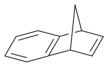


Entry	Additive	Yield/%[b]	Entry	Additive	Yield/%[b]
1	none	30	8	benzonitrile	5
2	Sc(OTf)$_3$	30	9	*N*,*N*-dimethylimidazolidinone	10
3	Y(OTf)$_3$	28	10	tetrahydrothiophene	1
4	In(OTf)$_3$	36	11	*t*-BuNC	43
5	PPh$_3$	5	12	PhCH$_2$NC	52
6	*N*,*N*-dimethylaniline	5	13	2,6-Me$_2$C$_6$H$_3$NC	58
7	pyridine	1	14	2,6-*i*-Pr$_2$C$_6$H$_3$NC	71

[a]**2a** (2.0 equiv.). [b]^{1}H NMR yield.

Table 2. Reactions between norbornene **1** and dimethyl but-2-ynedioate (**2a**)[a]

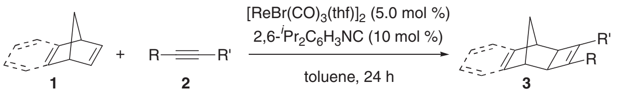


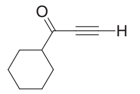
Entry	Norbornene	Temp/°C	Yield/%[b]
1	 **1a**	115	**3a** 79 (86)
2	 **1b**	115	**3b** 37 (41)
3	 **1c**	115	**3c** 68 (70)
4	**1c**	150	**3c** 92 (95)

[a]**2a** (2.0 equiv.) [b]Isolated yield. The yield determined by ^{1}H NMR is reported in parentheses.

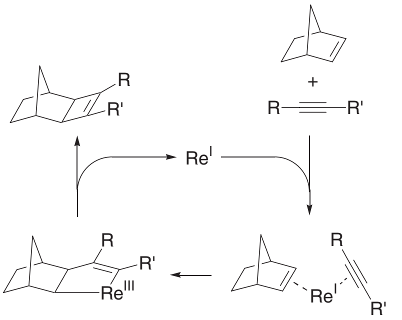
The proposed reaction mechanism is as follows (Scheme 1):

Table 3. Reactions between norbornadienes **1** and acetylenes **2**[a]



Entry	Norbornene	Acetylene		Temp/°C		Yield/%[b]
1	**1c**	$EtO_2C{\equiv}CO_2Et$	**2b**	150	**3d**	40 (45)
2[c]	**1c**	$MeO_2C{\equiv}Ph$	**2c**	180	**3e**	57 (60)
3	**1c**	$MeO_2C{\equiv}Me$	**2d**	150	**3f**	77 (82)
4	**1c**	$MeO_2C{\equiv}H$	**2e**	150	**3g**	76 (77)
5	**1c**	$EtO_2C{\equiv}H$	**2f**	150	**3h**	72 (73)
6	**1c**		**2g**	150	**3i**	22 (41)
7	**1b**	$Ph{\equiv}H$	**2h**	115	**3j**	17 (20)

[a] **2a** (2.0 equiv.) [b] Isolated yield. The yield determined by ^{1}H NMR is reported in parentheses. [c] Benzonorbornadiene (2.0 equiv.), acetylene (1.0 equiv.), ReBr(CO)$_5$ was used as a catalyst.



Scheme 1. Proposed mechanism of the formation of cyclobutene derivatives.

(1) coordination of a norbornene and an acetylene to a rhenium center; (2) formation of a rhenacyclopentene intermediate;[9f,15,16] (3) reductive elimination.

In summary, we have succeeded in the [2 + 2] cycloaddition of norbornenes with both internal and terminal acetylenes using a rhenium complex, [ReBr(CO)$_3$(thf)]$_2$, as a catalyst and an isocyanide, 2,6-diisopropylphenyl isocyanide, as an additive. Recently, we have reported rhenium-catalyzed insertion of acetylenes into a carbon–carbon single bond of non-strained cyclic compounds under mild conditions.[9f] In the first step of the ring-enlargement, we have postulated the formation of a rhenacyclopentene intermediate by the reaction of the rhenium catalyst, a β-keto ester and a terminal acetylene. To the best of our knowledge, this is the first example of rhenium-catalyzed [2 + 2] cycloaddition, and this result supports the mechanism for the ring-enlargement.

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12 The role of isocyanides is not clear. However, addition of the isocyanide inhibited the polymerization of acetylenes.

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16 In this step, the orientation of the acetylene is not clear.

17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) August 18, 2007; doi:10.1246/cl.2007.1162