Reaction of Alkyne Having Hydroxyphenyl Group with Mo(CO)$_6$

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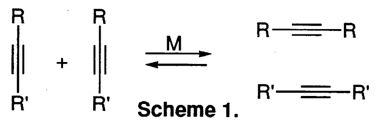
(Received April 26, 1995)

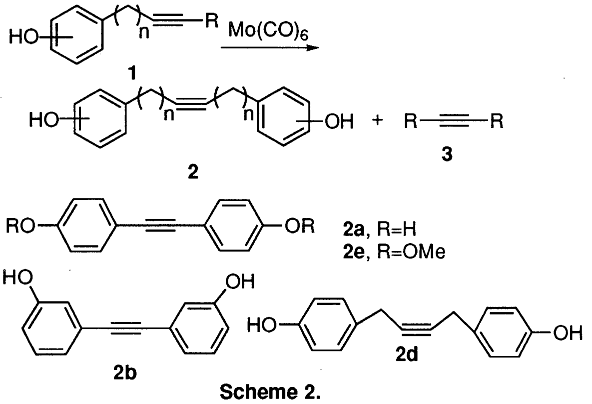
The reaction of *m*-and *p*-hydroxyphenylpropyne, **1a** and **1b**, with Mo(CO)$_6$ (5 mol%) affords metathesis products, **2a** and **2b**, in 78% and 14% (conversion yield, 78%) yields, respectively. However, *o*-hydroxyphenylpropyne **1f** gave trimerization product **4** in 65% yield.

Carbon-carbon bond formation or bond fission is the most important reaction in organic synthesis. Especially bond fission of the unsaturated bonds, such as an alkene or an alkyne, is quite interesting. Alkyne metathesis has been attracted much attention as a new process of acetylene reformation. Since the discovery of this remarkable alkyne metathesis, intensive studies of this process using transition metal carbyne complex have been reported.[1] Mortreux reported[2a] that a catalytic amount of Mo(CO)$_6$-PhOH was quite effective for the alkyne metathesis, but the reaction mechanism was not yet clear. Now we wish to report the reaction of alkyne **1** having *o*-, *m*-, and *p*-hydroxyphenyl group with Mo(CO)$_6$.



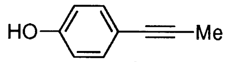
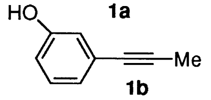
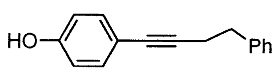
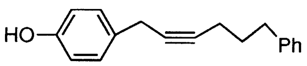
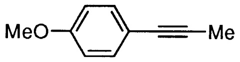
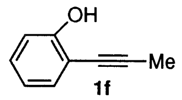
Scheme 1.

It is generally accepted that phenol was required for the molybdenum catalyzed alkyne metathesis,[2] but the role of phenol was not clear.[1a-c,3] In order to investigate the role of phenol, we prepared alkynes **1** having *o*-, *m*-, and *p*-hydroxypheny group. The metathesis reaction of these compounds **1** was carried out using 5 mol% of Mo(CO)$_6$ in toluene upon heating in the absence of phenol and the results were shown in Table 1. The reaction of *p*-hydroxyphenylpropyne (**1a**) with Mo(CO)$_6$ smoothly proceeded to give **2a** in high yield (78%, Table1, run 1) and *m*-substituted phenol **1b** also afforded metathesis product **2b** in 14% yield (conversion yield, 78%, run 2). Moreover, the reaction of alkynes, **1c** or **1d**, with Mo(CO)$_6$ gave the metathesis products, **2a** and **3c** or **2d** and **3d**, in moderate yields, respectively (runs 3 and 4). However, metathesis product was not obtained from *p*-methoxyphenylpropyne **1e**. In the presence of phenol, the reaction of **1e** with Mo(CO)$_6$ gave desired product **2e**. (Table 1, runs 5 and 6). On the other hand, it was very surprised to find that when a toluene solution of *o*-hydroxyphenylpropyne (**1f**) and Mo(CO)$_6$ (5 mol%) was refluxed for 5 h, trimerisation product **4** was obtained in 65% yield as a single isomer. None of the metathesis product was obtained. The structure of trimerization product **4** was determined by the spectral data and the X-ray crystal structure analysis. In a similar manner, reaction of **1g** with Mo(CO)$_6$ (5 mol%) in toluene at 110 °C for 5 h followed by treatment with MeI afforded **5** and/or **5'** in 24% yield (**1g** was recovered in 62% yield).[4] However, none of the metathesis product nor the trimerization product was obtained in the reaction of **1h** with Mo(CO)$_6$ without phenol.



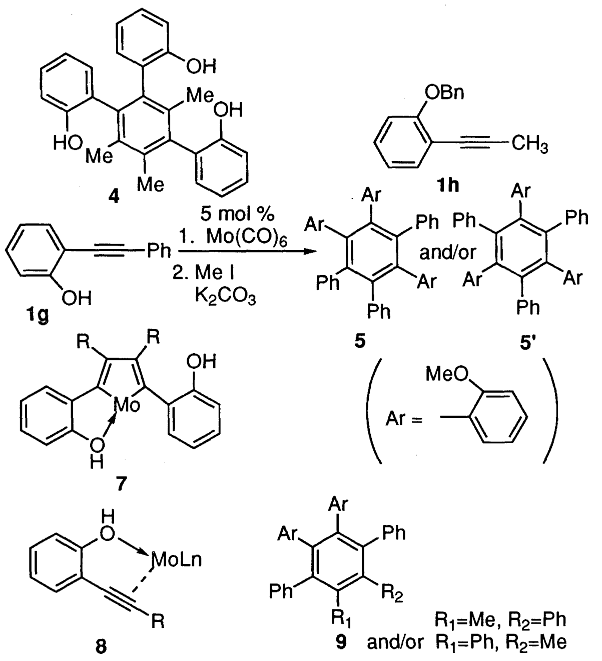
Scheme 2.

Table 1. Reaction of alkyne 1 with Mo(Co)$_6$

Run	Substrate	Yield of 2 (%)	3 (%)	1 (%)
1	 **1a**	78	—	15
2	 **1b**	14	—	82
3	 **1c**	35	39	42
4	 **1d**	16	20	61
5	 **1e**	—	—	72
6	**1e**	23 [a]	—	21
7	 **1f**	— [b]	—	7

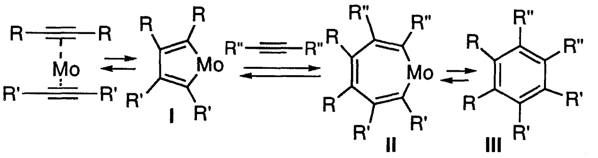
All reactions were carried out in toluene in the presence of Mo(CO)$_6$ (5 mol %) upon heating. [a] p-Cl-C_6H_5OH(100 mol %) was added.
[b] Metathesis product was not obtained and the trimerization product was obtained.

These trimers would be formed from **7** *via* **8**. That is, molybdenacyclopentadiene **I** was generated from two alkynes. The insertion of other alkyne into Mo-carbon bond of **I** results in the formation of molybdenacycloheptatriene **II**. The reductive elimination occurs to give trimer **III**.[6] The reaction of **1g** with Mo(CO)$_6$ in the presence of phenylpropyne (2 equiv.) followed by treatment with MeI afforded **5** and/or **5'** in 41% yield along with **9** [<14%, m/z 438 (M^+)]. The fact that



Scheme 3.

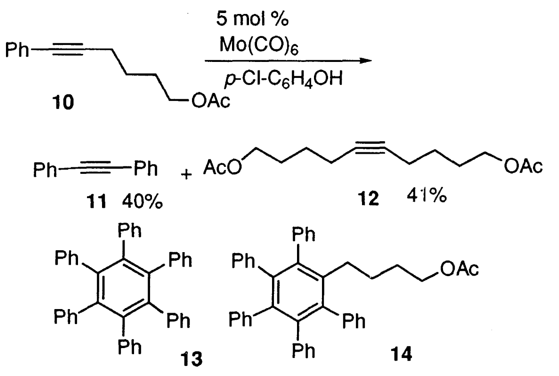
trimer **9** was obtained in this reaction supports the formation of **7**. On the other hand, when a toluene solution of **10**, $Mo(CO)_6$ (5 mol%), and p-Cl-C_6H_4OH (1 equiv.) was refluxed for 5 h to give metathesis products **11** and **12** in 40% and 41% yields, respectively, along with a small amount of trimerization products, **13** and **14**. The latter products would be formed from molybdenacyclopentadiene **I** as shown in Scheme 4.



Scheme 4. Possible Reaction Mechanism.

These results indicates that the $Mo(CO)_6$-PhOH system can catalyze both the metathesis reaction and the trimerization reactions and may provide an important clue of the mechanism for the metathesis reaction.[5]

In these reaction phenol would not form π-molybdenum-phenol complex[6] and phenol oxygen would coordinate to molybdenum complex. Further studies for the alkyne synthesis and for the role of the phenol are in progress.



Scheme 5.

References and Notes

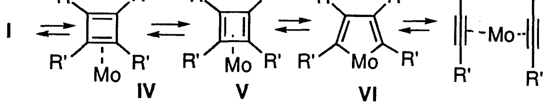
1 For examples, a) J. H. Wengrovius, J. Sancho, and R. R. Schrock, *J. Am. Chem. Soc.*, **103**, 3932 (1981); b) L. G. McCullough and R. R. Schrock, *J. Am. Chem. Soc.*, **106**, 4067 (1984); c) H. Strutz, J. C. Dewan, and R. R. Schrock, *J. Am. Chem. Soc.*, **107**, 5987 (1985); d) S. A. Krouse and R. R. Schrock, *Macromolecules*, **22**, 2569 (1989). e) R. R. Schrock, *Acc. Chem. Res.*, **19**, 342 (1986); f) M. Petit, A. Mortreux, and F. Petit, *J. Chem. Soc., Chem. Commun.*, **1982**, 1385; g) L. M. Atagi, S. C. Chritchlow, and J. M. Mayer, *J. Am. Chem. Soc.*, **114**, 9223 (1992); h) A. Bray, A. Mortreux, F. Petit, and M. Petit, and T. Szymanska-Buzar, *J. Chem. Soc., Chem. Commun.*, **1993**, 197; i) T. M. Sivarec and T. J. Katz, *Tetrahedron Lett.*, **26**, 2159 (1985); j) G. J. Leigh, M. T. Rahman, and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, **1982**, 541; Carbonyl-Carbyne coupling: k) R. N. Vtris, C. P. Rao, S. Warner, and S. J. Lippard, *J. Am. Chem. Soc.*, **110**, 2669 (1988); l) J. D. Protasiewicz, A. Masschelein, and S. J. Lippard, *J. Am. Chem. Soc.*, **115**, 808 (1993); m) N. Chatani, Y. Fukumoto, T. Ida, and S. Murai, *J. Am. Chem. Soc.*, **115**, 11614 (1993).

2 a) A. Mortreux and M. Blanchard, *J. Chem. Soc., Chem. Commun.*, **1974**, 786; b) A. Mortreux, N. Dy, and M. Blanchard, *J. Mol. Catal.*, **1**, 101 (1975/76); c) A. Mortreux, J. C. Delgrange, M. Blanchard, and B. Lubochinsky, *J. Mol. Catal.*, **2**, 73 (1977); d) A. Mortreux, F. Petit, annd M. Blanchard, *Tetrahedron Lett.*, **1978**, 4967 (1978); e) D. Villemin and P. Cadiot, *Tetrahedron Lett.*, **23**, 5139 (1982)

3 S. Devarajan and D. R. M. Walton, *J. Organomet. Chem.*, **181**, 99 (1979).

4 The structure of **5** was determined by spectral data.

5 We can consider that metathesis product is obtained from the same molybdenacyclopentadiene **I**. That is, from complex **I**, if reductive elimination occurs, molybdenum complex **IV** coordinated by cyclobutadiene should be formed. Isomerization of cyclobutadiene of **IV** followed by the oxidative addition gives the molybdenum complex **VI**, which is a regio isomer of molybdenacyclobutadiene **I**. From this complex **VI**, metathesis products would be formed.



Scheme 6.

6 a) J. A. Potenza, R. Johnson, R. Chirico, and A. Efraty, *Inorg. Chem.*, **16**, 2354 (1977); b) W. -Y. Yeh and L. -K. Liu, *J. Am. Chem. Soc.*, **114**, 2267 (1992); c) W. -Y. Yeh, S. -M. Peng, and G. -H. Lee, *J. Chem. Soc., Chem. Commun.*, **1993**, 1056; d) J. L. Keschner, P. E. Fanwick, and I. P. Rothwell, *J. Am. Chem. Soc.*, **109**, 5840 (1987); e) J. L. Keschner, P. E. Fanwick, and I. P. Rothwell, *J. Am. Chem. Soc.*, **110**, 8235 (1988); f) C. E. Kriley, J. L. Kerschner, P. E. Fanwick, and I. P. Rothwell, *Organometallics*, **12**, 2051 (1993); g) W. Hirpo and M. D. Curtis, *J. Am. Chem. Soc.*, **110**, 5218 (1988).