

Novel 1,3-Diene Synthesis from Alkyne and Ethylene by Ruthenium-Catalyzed Enyne Metathesis

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1,3-Diene is useful in synthetic organic chemistry, and many synthetic procedures are known:^{1,2} elimination from allyl bromide, allyl alcohol, 1,4- or 2,3-dihalogenated compound by a base or Zn, or ring opening of cyclobutene, and symmetrical or unsymmetrical coupling reactions of vinylic compounds using organometallic complexes. Here we report a novel 1,3-diene synthesis from alkyne and ethylene using a ruthenium-catalyzed metathesis reaction. Our plan is shown in Scheme 1. Namely, the double bond of ethylene is cleaved by the ruthenium catalyst, and each methylene part is introduced onto the alkyne carbon.

Metathesis reaction is a powerful strategy in synthetic organic chemistry,³ and it is generally accepted that this reaction is catalyzed by highly efficient transition metal alkylidenes.⁴ Intermolecular-diene metathesis produces many olefins,⁵ and it has usually been used as intramolecular-diene metathesis.⁶

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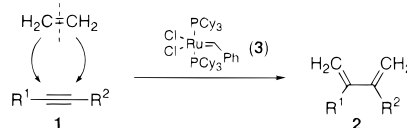
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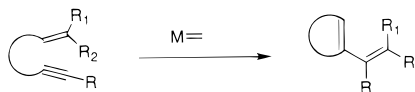
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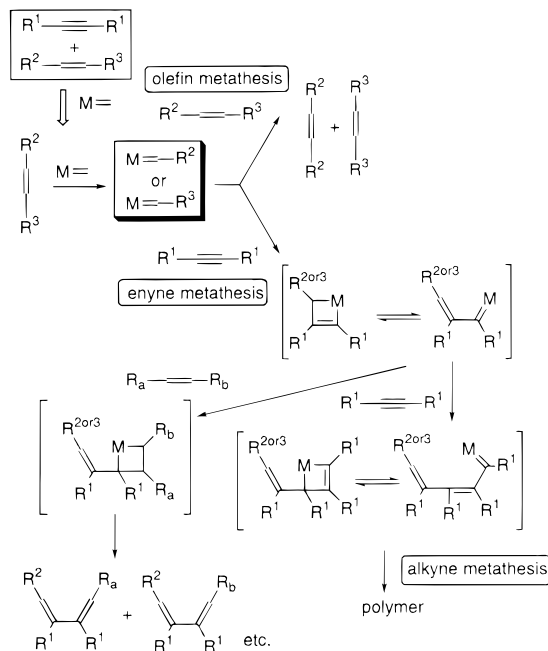
Scheme 1. 1,3-Diene Synthesis from Alkyne and Ethylene



Scheme 2. Intramolecular Enyne Metathesis



Scheme 3. Reaction Course of Intermolecular Enyne Metathesis



Intramolecular-enyne metathesis is a very unique reaction. It seems likely that the alkylidene part of the alkene migrates to the alkyne carbon. Thus, the resultant cyclized product has diene moiety.⁷

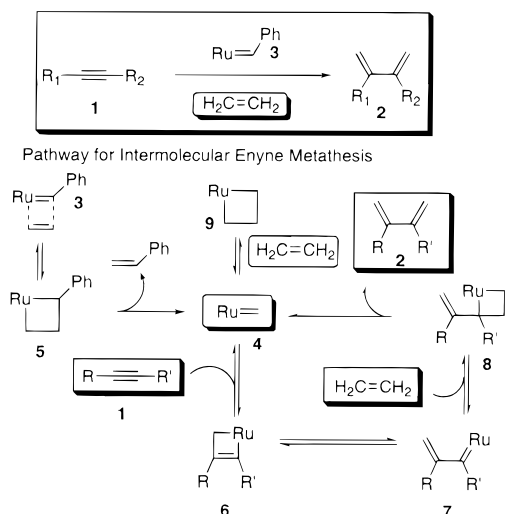
However, intermolecular enyne metathesis is more complicated than intermolecular diene metathesis, because three kinds of metatheses, intermolecular diene metathesis, intermolecular alkyne metathesis, and intermolecular enyne metathesis, are included in this reaction and they produce many olefins, dienes, and polymers as shown in Scheme 3.

Moreover, these products are further metathesized by carbene complex to give a complicated mixture. Thus, it seems that it is impossible to use this reaction in synthetic organic chemistry.

We planned 1,3-diene synthesis by intermolecular ruthenium-catalyzed enyne metathesis. In this pathway, we used ethylene gas as the alkene. The possible pathway is shown in Scheme 4.

The real catalyst **4** is generated from ruthenium carbene complex **3** and ethylene *via* ruthenacyclobutane **5**.⁸ It reacts

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Scheme 4. Our Plan for 1,3-Diene Synthesis Using Intermolecular Enyne Metathesis


with alkyne **1** to produce ruthenacyclobutene **6**, which converts into vinylmethylidene ruthenium complex **7**. It should react with ethylene, not alkyne **1**, to produce diene **2** via ruthenacyclobutane **8**, and ruthenium methylidene complex **4** would be regenerated. If ruthenium methylidene complex **4** reacts with ethylene, ruthenacyclobutane **9** is produced. However, this process is a so-called nonproductive process, and ethylene and ruthenium methylidene complex **4** is reproduced. Thus, the desired diene **2** should be obtained.

When a CH_2Cl_2 solution of **1a** and ruthenium carbene complex **3** (3 mol %) was stirred at room temperature for 45 h under ethylene gas, the desired diene was obtained in 66% yield (conversion yield, 89%). The use of 10 mol % of ruthenium complex **3** slightly improved the yield of the diene.

In a similar manner, the reactions of various alkynes under ethylene gas were carried out in the presence of ruthenium catalyst **3**, and the results are shown in Table 1. The dienes having functional groups such as keto-carbonyl group, silyloxy group, ester, and ketal were synthesized from the corresponding alkyne and ethylene. It was quite interesting that the terminal alkyne could be converted into diene in high yield (run 7). The yields were good to moderate and the conversion yields were high.

The results indicate that the novel synthetic method of 1,3-diene from alkyne and ethylene could be developed using

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Table 1. 1,3-Diene Synthesis of Intermolecular Enyne Metathesis^c

Run	Substrate	Ru (mol %)	Product	Yield ^{d)}
1	 1a	3	 2a	66% (89%)
		10	 2a	71% (90%)
2	 1b	3	 2b	62% (100%)
3	 1c	10 ^{b)}	 2c	53% (82%)
4	 1d	10 ^{b)}	 2d	60% (86%)
5	 1e	3	 2e	74% (89%)
6	 1f	3	 2f	48% (84%)
7	 1g	5	 2g	81% (100%)

^a Yields in parentheses are conversion yields. ^b 5 mol % of ruthenium catalyst **3** was used. After 40 h, 5 mol % of **3** was re-added. ^c All reactions were carried out in CH_2Cl_2 under ethylene gas using ruthenium catalyst at room temperature for 45 h.

ruthenium-catalyzed enyne metathesis. The remarkable characteristic for this procedure is that the synthetic procedure is very simple, namely, the CH_2Cl_2 solution of alkyne was stirred at room temperature under ethylene gas (1 atm) in the presence of a catalytic amount of ruthenium benzylidene catalyst (3–10 mol %).

Further studies are in progress.

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Supporting Information Available: Experimental details for compounds **1b–g** and **2a–g** (5 pages). See any current masthead page for ordering and Internet access instructions.

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