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# Ruthenium-Catalyzed Cyclization of Alkyne−Epoxide Functionalities through Alternation of the Substituent and Structural Skeleton of Epoxides

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Treatment of 1-(*o*-ethynylphenyl)-2-alkyl-2-aryl epoxides with $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst (10 mol %) in hot toluene (100 °C, 12 h) led to an atypical cyclization and gave 1-aryl-2-alkyl-1*H*-indene derivatives and carbon monoxide efficiently. The cyclization of 1-*cis*-enynyl-2-alkyl epoxides with this catalyst in hot toluene (10 mol %, 100 °C, 12 h) gave 2,5-disubstituted phenols in 45−72% yields. Under the same conditions, 1-*cis*-enynyl- 2,2-dialkyl epoxides and 1-*cis*-enynyl- 2-alkyl-2-aryl epoxides gave the corresponding 6,6-disubstituted cyclohexa-2,4-dien-1-ones in good yields (85−91%). Mechanisms for these new cyclization reactions are proposed on the basis of trapping experiments and isotope labeling experiments. The formation of 1*H*-indene products likely involves ruthenium−acyl intermediates whereas cyclohexa-2,4-dien-1-ones are thought to derive from ruthenium−ketene intermediates.

## Introduction

Transition-metal-catalyzed cyclization is a powerful tool for the construction of complex carbocyclic and heterocyclic molecules.[1,2] The reaction generally involves formation of two or three carbon−carbon bonds among molecules of $\pi$-type such as alkene, alkyne, 1,3-diene, methylenecyclopropane, carbon monoxide, ketone, aldehyde, allene, and imine. Although the hybridization of an epoxide molecule lies between $sp^2$ and $sp^3$ character,[3] metal-mediated coupling reaction on organic epoxides is less studied.[4,5] Several metal salts effect the coupling of epoxide with alkyne via a one-electron radical process[6] or acid-mediated ring opening of epoxides,[7] but the reaction generally requires an excess amount of metal or Lewis acid reagents. Only a few examples have been reported for catalytic epoxide−alkyne coupling reaction.[4,5]

Recently, we reported[8] a cascade alkyne−epoxide cyclization of (*o*-ethynyl)phenyl epoxides catalyzed by $TpRuPPh_3(CH_3CN)_2PF_6$.[9] This cyclization led to a complete oxygen transfer from epoxide to terminal alkyne to give cationic ruthenium ketene−alkene intermediate (**I**), further leading to intramolecular cyclization.[8] The reaction products are highly dependent on the epoxide substituents: 1,2-disubstituted epoxides gave 2-naphthol product **A** whereas 1,2,2-trisubstituted epoxides afforded 1-alkylidene-2-indanones **B** (Scheme 1). These two cyclized products arise from attack of the alkene of intermediate **I** at the tethered ketene functionality via 6-*endo-dig* and 5-*endo-dig* cyclizations, respectively. For such a cationic cyclization, we envisage that the substituents of epoxide substrate are crucial for the cyclization chemoselectivity because they affect the location of cationic charge of reaction intermediates **I**. In this continuing work, we discovered new patterns of alkyne−epoxide cyclization

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(4) (a) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363. (b) Gansauer, A.; Bluhm, H.; Pierobon, M. *J. Am. Chem. Soc.* **1998**, *120*, 12849. (c) Lo, C.-Y.; Guo, H.-Y.; Lian, J.-J.; Liu, R.-S. *J. Org. Chem.* **2002**, *67*, 3930

(5) Molinaro, C.; Jamison, T. F. *J. Am. Chem. Soc.* **2003**, *125*, 8076.

(6) (a) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986. (b) Gansauer, A.; Pierobon, M.; Bluhm, H. *Angew. Chem., Int. Eng.* **1998**, *37*, 101.

(7) (a) Chou, W.-N.; White, J. B. *Tetrahedron Lett.* **1991**, *32*, 7637. (b) Gaebert, C.; Mattaay, I. *Tetrahedron Lett.* **1997**, *53*, 14297. (c) Palomino, E.; Schaap, A. P.; Heeg, M. J. *Tetrahedron Lett.* **1989**, *30*, 6801. (d) Madhushaw, R. J.; Li, C.-L.; Shen, K.-H.; Hu, C.-C.; Liu, R.-S. *J. Am. Chem. Soc.* **2001**, *123*, 7427.

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(9) For catalytic reactions that use this ruthenium catalyst, see: (a) Yeh, K.-L.; Liu, B.; Lo, C.-Y.; Liu, R.-S. *J. Am. Chem. Soc.* **2002**, *124*, 6510. (b) Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294. (c) Shen, H.-C.; Pal, S.; Lian, J.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 15762. (d) Lo, C.-Y.; Guo, H.-Y.; Lian, J.-J.; Liu, R.-S. *J. Org. Chem.* **2002**, *67*, 3930. (e) Chang, C.-L.; Kumar, M. P.; Liu, R.-S. *J. Org. Chem.* **2004**, 69, 2793.

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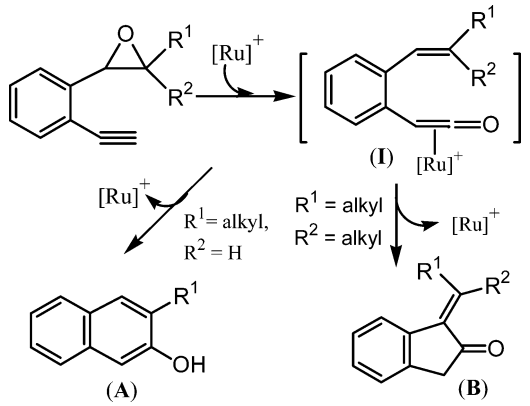
**SCHEME 1**




reactions upon modification of the substrate frameworks and substituents.

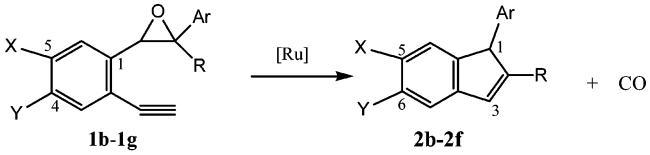
## Results and Discussion

Although 2,2-disubstituted epoxides gave 1-alkylidene-2-indanones **B**, treatment of 2-methyl-2-phenyl epoxide **1a** with $TpRuPPh_3(CH_3CN)_2PF_6$[10] catalyst (10 mol %) in hot toluene (100 °C, 12 h) gave 1-phenyl-2-methyl-1*H*-indene species **2a** in 78% yield. GC analysis of the gaseous mixture above the reaction solution showed the presence of carbon monoxide. High-resolution mass spectra of compound **2a** indicate loss of carbon monoxide relative to its starting epoxide **1a**. The structure is confirmed by $^{13}C$ NMR spectra, which shows 14 carbon peaks with one carbon less than the expectation. The proposed structure is also supported by the $^1H$ NOE effect.[11]

We prepared various 2-alkyl-2-aryl epoxides **1b**−**g** to examine the generality of this atypical cyclization. These epoxides were present as either the *E*-isomer or a mixture of *E*- and *Z*-isomers. Entries 2−4 (Table 1) show the suitability of this cyclization to the variation of alkyl and aryl substituents of epoxides with ethyl, 4-tolyl, and 4-fluorophenyl groups, and the corresponding indene products **2b**−**d** were obtained in 72−77% yields. Entries 4−6 show the cyclization of epoxides **1e**−**g** bearing a fluoro substituent at their phenyl C4 or C5 carbons respectively; the resulting indenes **2e**−**f** were obtained in 71−80% yields. The regiochemistry of indene **2e** (entry 4) was determined by $^1H$ NOE spectra.[11] Notably, the indene product generated from epoxide **1g** is identical to that given from epoxide **1e** even though these two epoxides have a fluoro substituent at different phenyl positions. This information suggests that the cyclizations of epoxide **1e** and **1g** proceed through the same intermediate.

With these encouraging results, we further examined the effects of epoxide skeletons on the cyclization chemoselectivity. We prepared various 1,2-disubstituted **3a**−**c** and 1,2,2-trisubstituted epoxides **5a**−**h** bearing a *cis*-enynyl substituent. As shown in Table 2, epoxides **3a**−**c** gave 2,5-disubstituted phenols **4a**−**c** in 45−72% yields

**TABLE 1. Ruthenium-Catalyzed Cyclization of 2,2-Alkylaryl Epoxides**



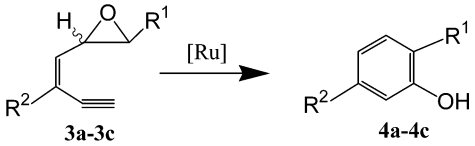

**1b-1g** **2b-2f**

[Ru] = 10 mol% $TpRuPPh_3(CH_3CN)_2PF_6$

| entries | expoxides[a] | indenes[b] |
|---|---|---|
| 1 | X = Y = H, Ar = Ph, R = Et (**1b**, *E*/*Z* = 1.3) | **2b** (77%) |
| 2 | X = Y = H, Ar = *p*-MePh, R = Me (**1c**, *E*/*Z* = 2.5 | **2c** (76%) |
| 3 | X = Y = H, Ar = *p*-FPh, R = Me (**1d**, *E*/*Z* = 2.6) | **2d** (72%) |
| 4 | X = H, Y = F, Ar = Ph, R = Me (**1e**, *E*-form only) | **2e** (75%) |
| 5 | X = H, Y = F, Ar = p-MePh, R = Me (**1f**, *E*-form only) | **2f** (71%) |
| 6 | X = F, Y = H, Ar = Ph, R = Me (**1g**, *E*-form only) | **2e** (80%) X = H, Y = F |

[a] Conditions: [substrate] = 0.75 M, 100 °C, 12 h, toluene. [b] Yields were reported after elution from a silica column.

**TABLE 2.**




**3a-3c** **4a-4c**

[Ru] = 10 mol%$TpRuPPh_3(CH_3CN)_2PF_6$

| entries | epoxides[a] | phenols[b] |
|---|---|---|
| 1 | $R^1 = {}^i$Pr, $R^2 = n$Bu (**3a**) | **4a** (72%) |
| 2 | $R^1 = {}^n$Bu, $R^2 = {}^nC_6H_{13}$ (**3b**) | **4b** (65%) |
| 3 | $R^1$ = Ph, $R^2 = {}^nC_6H_{13}$ (**3c**) | **4c** (45%) |

[a] Conditions: [substrate] = 0.75 M, 100 °C, 12 h, toluene. [b] Yields were reported after elution from a silica column.

in the presence of ruthenium catalyst (10 mol %). The structures of phenols **4a**−**c** were confirmed by $^1H$, $^{13}C$, and high-resolution mass spectra,[11] although the outcomes of cyclization of epoxides **3a**−**c** are essentially the same as those observed for *o*-ethynylphenyl epoxides (Scheme 1) that gave 2-naphthols **A**.

As shown in Table 3, treatment of 1-*cis*-ethynyl-2,2-dialkyl epoxide **5a** (*E*/*Z* = 0.9) with ruthenium catalyst (10 mol %) afforded 6,6-disubstituted cyclohexa-2,4-dien-1-one **6a** with 90% yield. The proposed structure is compatible with its $^1H$-NOE[11] and $^{13}C$ NMR spectra and by high-resolution mass spectra. This chemoselectivity is distinct from what is observed for their *o*-ethynylphenyl epoxide analogues that gave 1-alkylidene-2-indanones **B** (Scheme 1). We prepared various epoxide analogues with various *E*/*Z* ratios[12] to examine the generality of this cyclization. Entries 2−7 show the suitability of this cyclization with variation of the $R^3$ and $R^4$ substituents; the resulting cyclic ketones **6b**−**g** were obtained in 85−92% yields. We also prepared 2,2-disubstituted epoxide **5h** bearing geminal methyl and phenyl groups to examine a possible alternation of reaction selectivity like those

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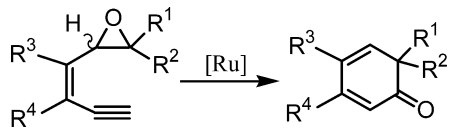
(11) The $^1H$ NOE NMR spectra of key compounds **2a**, **2e**, and **6a** are shown in either the Experimental Section or the Supporting Information.

(12) The *E*/*Z* ratios of epoxides **3a**−**c** and **5a**−**h** are given in the Supporting Information.

**TABLE 3. Cyclization of 1-*cis*-Enynyl-2,2-dialkyl Epoxides**

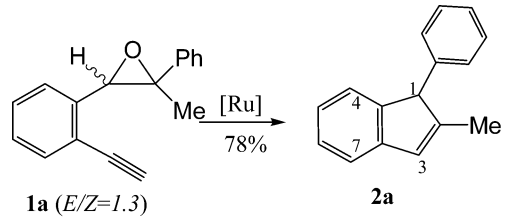


[Ru] = 10mol%
$TpRuPPh_3(CH_3CN)_2PF_6$

| entries | epoxides[a] | ketones[b] |
|---|---|---|
| 1 | $R^1 = {}^nPr$, $R^2 = Me$<br>$R^3 = H$, $R^4 = Ph$ (**5a**) | **6a** (90%) |
| 2 | $R^1 = {}^nC_5H_{11}$, $R^2 = Me$<br>$R^3 = H$, $R^4 = Ph$ (**5b**) | **6b** (92%) |
| 3 | $R^1 = R^2 = Me$<br>$R^3 = H$, $R^4 = {}^nC_6H_{13}$ (**5c**) | **6c** (90%) |
| 4 | $R^1 = Et$, $R^2 = Me$<br>$R^3 = H$, $R^4 = {}^nC_6H_{13}$ (**5d**) | **6d** (85%) |
| 5 | $R^1 = R^2 = Me$<br>$R^3 = H$, $R^4 = Ph$ (**5e**) | **6e** (85%) |
| 6 | $R^1 = Me$, $R^2 = Et$<br>$R^3 = H$, $R^4 = Ph$ (**5f**) | **6f** (88%) |
| 7 | $R^1 = R^2 = Me$<br>$R^3 = R^4 = -C_4H_8-$ (**5g**) | **6g** (92%) |
| 8 | $R^1 = Ph$, $R^2 = Me$<br>$R^3 = H$, $R^4 = {}^nC_6H_{13}$ (**5h**) | **6h** (89%) |

[a] Conditions: [substrate] = 0.75 M, 100 °C, 12 h, toluene. [b] Yields were reported after elution from a silica column.

**SCHEME 2**



**1a** (*E/Z=1.3*) **2a**

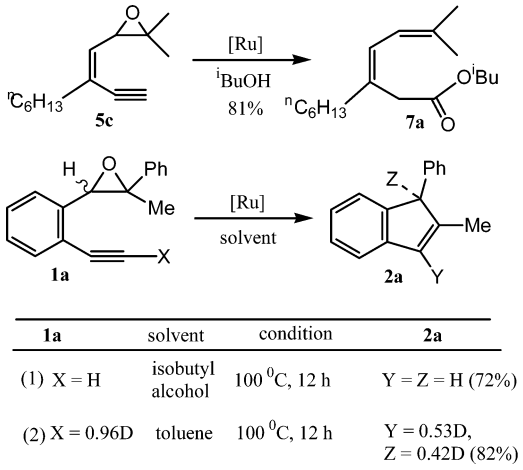
[Ru] = 10 mol% $TpRuPPh_3(CH_3CN)_2PF_6$

described in Scheme 2 and Table 1. Treatment of this epoxide with ruthenium catalyst in hot toluene (100 °C, 12 h) gave the same ketone **6h** in 89% yield (entry 8), and the electronic effect of the phenyl substituent of epoxide **5h** failed to alter the chemoselectivity in the way that we observed for their *o*-(ethynyl)phenyl epoxide analogues **1a**−**g**.

To examine the nature of reaction mechanism, we selected isobutyl alcohol as the reaction solvent. Epoxides **1a** and **5c** were chosen because they gave indene and cyclohexa-2,4-dien-1-one derivatives, distinct from our previous observations.[8] As shown in Scheme 3, treatment of epoxide **5c** with ruthenium catalyst (10 mol %) in hot isobutyl alcohol gave the ester **7a** in 81% yield. In contrast, the catalytic reaction of **1a** still gave indene **2a** in 72% yield. These results reveal that ruthenium−ketene intermediate (**I**) was generated for epoxide **5c** but not for compound **1a**. Notably, for the deuterated sample **1a**, its alkynyl deuterium was transferred to the C1 and C3 protons of indene **2a** with 42% and 53% deuterium contents, respectively.[13]

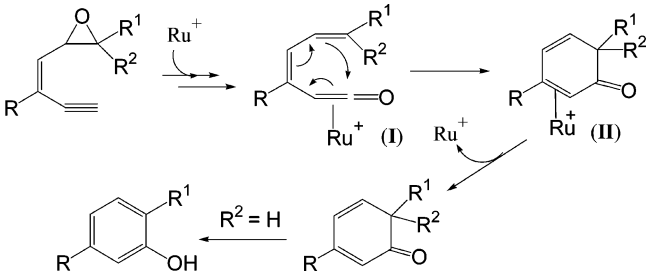
We propose two plausible mechanisms in Schemes 4 and 5, which account for the formation of 2,4-cyclohexadien-1-one and indene products, respectively. The mechanism of formation of 2,4-cyclohexadien-1-one seems straightforward because the trapping experiment indicates that ruthenium−ketene species **I** is likely the reaction intermediate. The transformation from starting epoxide to intermediate **I** has been elucidated in our previous study.[8] As shown in Scheme 4, the 6-*endo-dig* cyclization of the terminal alkenyl carbon of species **I** at the ketene moiety[14] gave ruthenium−$\pi$-cyclohexadienone species **II** and ultimately afforded the observed cyclic ketones.

**SCHEME 3**



| 1a | solvent | condition | 2a |
|---|---|---|---|
| (1) X = H | isobutyl alcohol | 100 $^0$C, 12 h | Y = Z = H (72%) |
| (2) X = 0.96D | toluene | 100 $^0$C, 12 h | Y = 0.53D, Z = 0.42D (82%) |

**SCHEME 4**



In Scheme 5, the epoxide **1a** is catalyzed by ruthenium complex to form ruthenium−vinylidenium species **III** and further to yield ruthenium−acyl species **IV** rather than the ruthenium−ketene **I** as we failed to trap species **I** with isobutyl alcohol. Species **C** equilibrates with species **V** because of the stability of a tertiary benzyl cation. This species subsequently forms ruthenium−acyl species **VI** via intramolecular attack of ruthenium at the tertiary cationic center. TpRu(IV)−acyl species **VI** is prone to decarbonylation reaction; we expect that species **VI** easily loses one CO molecule to give ruthenium−cyclohexadiene intermediate **VII** and further produces species **VIII** via reductive elimination. Addition of $H^+$ or the cationic $Ru^+$ species (M = H or Ru) to species **VIII** is expected to yield benzyl cations **IX** and **IX′**. The chemoselectivity in the

(13) The deuterium contents of 1*H*-indene **2a** were calculated by the crude products given from deutertated **1a** because purification of indene **2a** on a $Et_3N$-pretreated silica column led to a loss of deuterium content at the C1 and C3-indene proton. The C1H and C3-H deuterium contents were estimated to be 30% and 46%, respectively.

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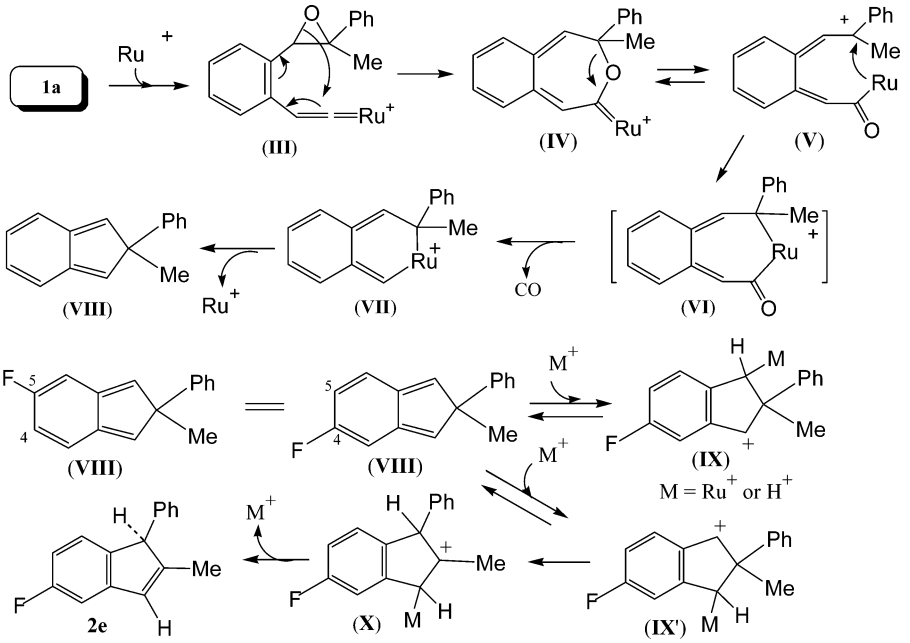
**SCHEME 5**



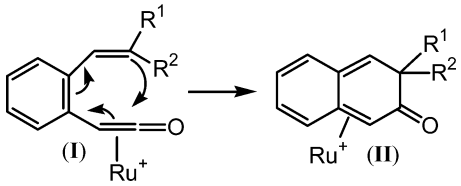

cyclization of fluorophenyl epoxides **1e** and **1g** depends on the relative stability of benzyl cations **IX** and **IX′**; a $\pi$-donor group such as fluoro prefers cation **IX′** through $\pi$-conjugation to induce 1,2-phenyl migration to give tertiary cation **X** and ultimately yields the observed product **2e**. Residual water and the acid catalyst TpRu-$PPh_3(CH_3CN)_2PF_6$ likely generate a small amount of protons to catalyzed the conversion of species **G** to indene **2e**.

Although we obtained no direct evidence for formation of ruthenium−ketene intermediate **I**, the loss of CO indicates the formation of ruthenium(IV)−acyl intermediates.[9b] In our previous study, the TpRu(IV)−acyl species was shown to undergo decarbonylation even in the presence of alcohol or a CO atmosphere under pressure.[9b] The symmetric character of species **VIII** provides a rationale that both 5-fluoro- and 6-fluoro-substituted epoxide species **1e** and **1g** should give the same product, consistent with our observations (Table 1, entries 4 and 6). This species is also compatible with the deuterium labeling experiment in Scheme 3 that the alkynyl deuterium of **1a** was transferred equally to the at C1 and C3 protons of indene **2a**.

It is interesting to note the different chemoselectivities in the cyclization of 1-(*o*-ethynylphenyl)-2,2-dialkyl epoxides and 1-(enynyl)-2,2-disubstituted epoxides **5a**−**h** which gave 1-alkylidene-2-indanones **B** and 2,4-cyclohexadien-1-ones **6a**−**h**, respectively. This discrimination is probably due to a higher energy in the transformation of ketene species **I** to the ruthenium−dieneone **II**, which sacrifices the aromatic energy of species **I** (Scheme 6).

**Conclusions**. We report new patterns of the epoxide−alkyne cyclizations with alternation of the substituent and structural skeleton of the epoxide substrates. With $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst, 1-(*o*-ethynylphenyl)-2-alkyl-2-aryl epoxides gave 1-aryl-2-alkyl-1*H*-indene derivatives and carbon monoxide in hot toluene whereas 1-*cis*-enynyl-2,2-disubstituted epoxides produced the corresponding 6,6-disubstituted cyclohexa-2,4-dien-1-ones

**SCHEME 6**



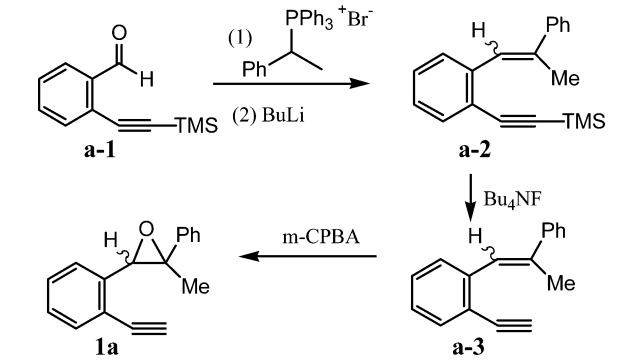

efficiently. The former is proposed to involve TpRu(IV)−acyl intermediates while the latter likely involves ruthenium−ketene species according to deuterium labeling and isobutyl alcohol trapping experiments. 6,6-Disubstituted cyclohexa-2,4-dien-1-ones are a useful building block in constructing complex molecular framework through Diels−Alder or Michael reaction.[15] This method has been applied to synthesis of naturally occurring compounds. Further application of our synthetic method for the synthesis of complex bioactive molecule is under current investigation.

## Experimental Section

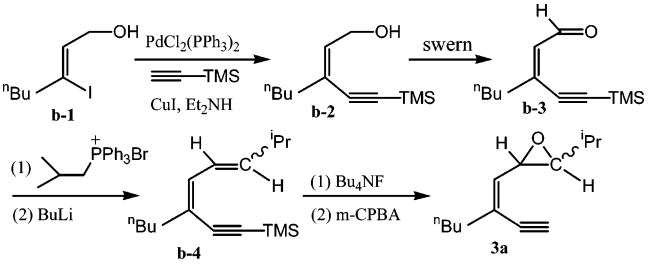
**(1) Typical Procedure for the Synthesis of 1-(*o*-Ethynylphenyl)-2-methyl-2-phenyl Epoxides (1a).** The synthetic protocol of epoxide **1a** is depicted in Scheme 7. To a THF solution (20 mL) of (α-methylbenzyl)triphenylphosphonium bromide (3.32 g, 7.42 mmol) at 0 °C was added $^n$BuLi (2.5 mL, 2.5 M, 6.43 mmol), and the mixture was stirred at 0 °C for 1.0 h. To this solution was added *o*-(2′-trimethylsilylethynyl)-benzaldehyde **a-1** (1.00 g, 4.95 mmol), and the mixture was stirred at 28 °C for 4 h. The solution was quenched with water and concentrated in vacuo. The organic layer was extracted with diethyl ether, dried over $MgSO_4$, and chromatographed (hexane, $R_f = 0.75$) over a silica column to give the olefination product **a-2** as a colorless oil (1.22 g, 4.20 mmol, 85%). This silyl compound was then dissolved in THF (10 mL) and added with $Bu_4NF$ (1.0 M, THF, 4.65 mL, 4.60 mmol), and the mixture was stirred at 26 °C for 8 h before addition of water (10 mL). The solution was concentrated, extracted with diethyl ether, and chromatographed on a silica column (hexane, $R_f =$

(15) Liao, C.-C.; Peddinti, R. K. *Acc. Chem. Res.* **2002**, *35*, 856.

**SCHEME 7**




**SCHEME 8**



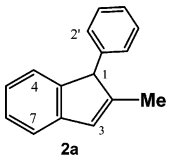

0.86) to give an enyne **a-3** (0.83 g, 3.78 mmol, 90%) as colorless oil. To a $CH_2Cl_2$ solution (15 mL) of this enyne (0.50 g, 2.29 mmol) was added *m*-chloroperbenzoic acid (0.52 g, 3.02 mmol), and the mixture was stirred for 3 h at 28 °C. The resulting solution was quenched with an aqueous $NaHCO_3$ solution, extracted with diethyl ether, and dried over anhydrous $MgSO_4$. The resulting solution filtered through a small basic $Al_2O_3$ bed, concentrated, and eluted through a $Et_3N$-pretreated silica column (diethyl ether−hexane, 1:1) to afford epoxide **1a** as a colorless oil (0.47 g, 2.00 mmol, 87%).

**(2) Experimental Procedure for Cyclization of (*o*-Ethynyl)phenyl Epoxide (1a) to Indene 2a.** A long tube containing $TpRuPPh_3(CH_3CN)_2PF_6$ (32 mg, 0.042 mmol) was dried in vacuo for 2 h before it was charged with epoxide **1a** (100 mg, 0.42 mmol) and toluene (0.56 mL). The mixture was heated at 100 °C for 12 h before cooling to room temperature. The solution was concentrated and eluted through a silica column (hexane/diethyl ether = 5/1) to afford indene **2a** (68 mg, 3.32 mmol, 78%) as a yellow oil.

**(3) Typical procedure for the Synthesis of 1-*cis*-Enynyl-2-(isopropyl) Epoxide (3a).** As shown in Scheme 8, to a diethylamine solution (30 mL) of *Z*-3-iodohept- 2-en-1-ol (**b-1**) (2.00 g, 8.33 mmol) were added trimethylsilylacetylene, $PdCl_2(PPh_3)_2$ (110 mg, 0.16 mmol), and CuI (15 mg, 0.80 mmol); the mixture was stirred for 28 °C for 12 h. The solution was concentrated and eluted through a silica column to afford an enynyl alcohol **b-2** as an oil (1.56 g, 7.42 mmol). To a dichloromethane solution of this alcohol (1.00 g, 4.75 mmol) were added oxalic chloride (0.50 mL, 5.9 mmol) and dimethyl sulfoxide (0.80 mL, 11.2 mmol) at −78 °C, and the mixture was stirred for 1 h before addition of $Et_3N$ (6.6 mL, 47.6 mmol). The solution was continued to stir for 1 h before treatment with $H_2O$, and the organic layer was extracted with diethyl ether and chromatographed over a silica column to give aldehyde **b-3** as an oil (0.86 g, 4.14 mmol, 87%). To a THF solution (25 mL) of isobutyltriphenyl phosphonium bromide (2.30 g, 5.76 mmol) was added BuLi (2.0 mL, 2.5 M, 5.0 mmol) at 0 °C, and the mixture was stirred for 1 h before treatment with aldehyde **b-3**. The mixture was stirred for 12 h before it was added excess hexane (30 mL) to precipitate more triphenylphosphine oxide. The solution was filtered, and the filtrate was concentrated and eluted through a silica column to give the olefination product **b-4** (840 mg, 3.38 mmol, 88%) as a colorless oil. This olefination compound was converted to the epoxide **3a** in an overall 65% yield following the same $Bu_4$-NF-desilylation and *m*-CPBA oxidation procedures as described in Scheme 7.

**(4) Spectral Data for 1-(*o*-Ethynylphenyl)-2-methyl-2-phenyl Epoxides (1a):** IR (Nujol, $cm^{-1}$): 3330 (s), 3100 (s), 3065 (s), 2258 (m), 2119 (s), 1625 (w), 1250 (m). $^1H$ NMR (400 MHz, $CDCl_3$): (major-*E*-isomer) $\delta$ 7.53−7.44 (m, 3 H), 7.41 (dt, $J$ = 8.0, 1.0 Hz, 3 H), 7.38 (dt, $J$ = 7.5, 1.0 Hz, 2 H), 7.25 (d, $J$ = 7.5 Hz, 1 H), 4.20 (s, 1 H), 3.25 (s, 1 H), 1.41 (s, 3 H); (selected peaks, minor-*Z*-isomer) $\delta$ 7.43 (dt, $J$ = 7.5, 1.0 Hz, 3 H), 7.18 (dt, $J$ = 7.5, 1.0 Hz, 2 H), 7.13 (dt, $J$ = 8.0, 1.0 Hz, 2 H), 4.45 (s, 1 H), 3.42 (s, 1 H), 1.85 (s, 3 H), the remaining peaks are overlapped with those of the major isomer. $^{13}C$ NMR (100 MHz, $CDCl_3$): (major *E*-isomer) $\delta$ 142.5, 139.5, 132.2, 128.6, 128.4, 127.8, 127.6, 126.7, 125.6, 121.5, 82.4, 81.8, 64.9, 64.0, 17.9. MS (75 eV, *m*/*z*): 234 ($M^+$). HRMS: calcd for $C_{17}H_{14}O$ 234.1045, found 234.1042.

**(5) Spectral Data for 2-Methyl-1-phenyl-1*H*-indene (2a).** IR (Nujol, $cm^{-1}$): 3030 (s), 3008 (s), 3065 (s), 2258 (m), 1625 (m), 1685 (s). $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.27−7.25 (m, 3 H), 7.20 (dt, $J$ = 7.5, 1.5 Hz, 2 H), 7.10 (d, $J$ = 8.0 Hz, 1 H), 7.04 (d, $J$ = 7.5 Hz, 1 H), 7.01(d, $J$ = 7.5 Hz, 2 H), 6.53 (s, 1 H), 4.28 (s, 1 H), 1.91 (s, 3 H). $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ 149.9, 148.5, 144.7, 139.7, 128.6, 128.1, 127.1, 127.0, 126.6, 124.1, 123.7, 119.7, 59.3, 15.1. HRMS: calcd for $C_{16}H_{14}$ 206.1096, found 206.1098.




| irradiation | intensity increase |
|---|---|
| $H^1$ ($\delta$ 4.28) | Me ($\delta$ 1.91, 1.7 %), $H^4$ ($\delta$ 7.25, 1.0 %) $H^{2'}$ ($\delta$ 7.01, 1.5 %) |
| $H^3$ ($\delta$ 6.53) | $H^7$ ($\delta$ 7.27, 1.0 %), Me (1.4 %) |
| Me ($\delta$ 1.91) | $H^1$ (2.8%), $H^3$ (4.1%) |

**(6) Spectral Data for 2-(2-Ethynylhex-1-enyl)-3-isopropyloxirane (3a).** IR (Nujol, $cm^{-1}$): 2256 (m), 1620 (w), 1225 (m). $^1H$ NMR (400 MHz, $CDCl_3$): (major *trans*-isomer) $\delta$ 5.36 (d, $J$ = 8.7 Hz, 1 H), 3.17 (s, 1 H), 2.77 (dd, $J$ = 8.6, 4.3 Hz, 1 H), 2.63 (dd, $J$ = 6.8, 1.2 Hz, 1 H), 2.13 (t, $J$ = 7.6 Hz, 2 H), 1.60−1.54 (m, 1 H), 1.52−1.44 (m, 2 H), 1.32−1.25 (m, 2 H), 0.96 (d, $J$ = 6.8 Hz, 3 H), 0.90 (d, $J$ = 6.8 Hz, 3 H), 0.86 (t, $J$ = 6.5 Hz, 3 H); (minor *cis*-isomer) $\delta$ 5.54 (d, $J$ = 8.7 Hz, 1 H), 3.89 (dd, $J$ = 8.7, 4.3 Hz, 1 H), 3.63 (dd, $J$ = 8.7, 1.4 Hz, 1 H), 3.17 (s, 1 H), 2.16 (t, $J$ = 7.4 Hz, 2 H), 1.60−1.54 (m, 1 H), 1.52−1.44 (m, 2 H), 1.32−1.25 (m, 2 H), 1.09 (d, $J$ = 6.7 Hz, 3 H), 1.00 (d, $J$ = 6.7 Hz, 3 H), 0.86 (t, $J$ = 6.5 Hz, 3 H). $^{13}C$ NMR (150 MHz, $CDCl_3$): (major *trans*-isomer) $\delta$ 135.6, 128.8, 82.9, 81.2, 65.4, 55.5, 36.9, 36.6, 30.5, 30.0, 21.9, 20.2, 18.3; (minor *cis*-isomer) $\delta$ 132.6, 127.6, 82.5, 81.1, 64.8, 55.4, 36.9, 36.6, 30.0, 28.1, 21.8, 18.9, 13.8. MS (75 eV, *m*/*z*): 192 ($M^+$). HRMS: calcd for $C_{13}H_{20}O$ 192.1514, found 192.1520.

**(7) Spectral Data for 5-Butyl-2-isopropyl-phenol (4a).** IR (Nujol, $cm^{-1}$): 3610 (s), 1580 (m), 1625 (w), 1225 (m). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 7.08 (d, $J$ = 8.0 Hz, 1 H), 6.73 (d, $J$ = 8.0 Hz, 1 H), 6.57 (s, 1 H), 4.84 (bs, OH), 3.19−3.12 (m, 1 H), 2.51 (t, $J$ = 7.6 Hz, 2 H), 1.58−1.53 (m, 2 H), 1.37−1.32 (m, 2 H), 1.24 (s, 3 H), 1.23 (s, 3 H), 0.91 (t, $J$ = 7.4 Hz, 3 H). $^{13}C$ NMR (150 MHz,$CDCl_3$): $\delta$ 152.5, 141.6, 131.4, 126.1, 120.9, 115.2, 35.0, 33.4, 26.7, 22.7, 22.6, 22.3, 13.9. HRMS: for $C_{13}H_{20}O$ calcd 192.1514, found 192.1518.

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**Supporting Information Available:** Spectral data of compounds **1a**−**g**, **2b**−**f**, **3b**,**c**, **4b**,**c**, **5a**−**h**, **6a**−**h**, and **7a** in repetitive experiments; $^1H$ and $^{13}C$ NMR spectra of key compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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