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Ruthenium-Catalyzed Cyclization of Epoxide with a Tethered Alkyne: Formation of Ketene Intermediates via Oxygen Transfer from Epoxides to Terminal Alkynes

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Abstract: Treatment of (*o*-ethynyl)phenyl epoxides with $TpRuPPh_3(CH_3CN)_2PF_6$ (10 mol %) in hot toluene (100 °C, 3−6 h) gave 2-naphthols or 1-alkylidene-2-indanones very selectively with isolated yields exceeding 72%, depending on the nature of the epoxide substituents. Surprisingly, the reaction intermediate proved to be a ruthenium-π-ketene species that can be trapped efficiently by alcohol to give an ester compound. This phenomenon indicates a novel oxygen transfer from epoxide to its terminal alkyne catalyzed by a ruthenium complex. A plausible mechanism is proposed on the basis of reaction products and the deuterium-labeling experiment. The 2-naphthol products are thought to derive from 6-*endo-dig* cyclization of (*o*-alkenyl)-phenyl ketene intermediates, whereas 1-alkylidene-2-indanones are given from the 5-*endo-dig* cyclization pathway.

Introduction

One current trend in catalytic reactions is the formation of carbon−carbon bonds among two or three π-typed molecules such as alkyne, alkene, 1,3-diene, methylenecyclopropane, carbon monoxide, imines, allene, ketone, and aldehyde.[1,2] Few studies are focused on the metal-mediated coupling reaction on σ-typed epoxide molecules.[3,4] Although several metal salts effect the coupling of epoxide with alkyne via a one-electron radical process[3a−c] or acid-induced opening of epoxides,[4c] the reaction generally requires an excess amount of metal reagents (>1.0 equiv). Gansauer reported that a catalytic amount of titanium-(III) complexes sufficed to implement radical epoxide-alkyne[3c] cyclization in the presence of excess manganese powder. McDonald and co-workers achieved the synthesis of furans via $W(CO)_6$-catalyzed cyclization of α-ethynyl epoxides.[4] The first intermolecular alkyne-epoxide coupling was recently reported by Jamison[5] with the use of $Ni(0)-PBu_3$ catalyst. To our best knowledge, there is no precedent for a catalytic epoxide-alkyne coupling leading to a complete transfer of an oxygen atom from epoxide[6] to alkyne to generate a ketene intermediate (Scheme 1, eq 1), ultimately giving useful cyclized products.

Recently, we reported the aromatization of (*o*-alkenyl)-ethynylbenzene with a 1,2-shift of halo and aryl substituents,[7c] and the mechanism involves ruthenium−vinylidenium intermediates.[8] We now extend the ruthenium-catalyzed electrocyclization to α-ethynylphenyl epoxides to assess the feasibility of the electrocyclization of epoxide-olefin-vinylidenium functionalities. Such an electrocyclization is still unknown and very interesting in mechanistic aspects. The reaction pathway possibly leads to cleavage of the carbon−carbon or carbon−oxygen bond of an epoxide.[3−5,9] We are delighted to discover that the cyclization generates a ruthenium-ketene intermediate via an oxygen transfer process (Scheme 1, eq 2); here, we report details of this remarkable phenomenon.

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(2) For selected examples, see: (a) Brummond, K. M.; Lu, J. *J. Am. Chem. Soc.* **1999**, *121*, 5087. (b) Tobisu, M.; Chatani, N.; Asaumi, T.; Amako, K.; Ie, Y.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **2000**, *122*, 12633. (c) Kablaoui, N. M.; Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 5818. (d) Chatani, N.; Morimoto, T.; Fukumoto, Y.; Murai, S. *J. Am. Chem. Soc.* **1996**, *118*, 5335. (e) Chatani, N.; Tobisu, M.; Asaumi, T.; Murai, S. *Synthesis* **2000**, 925. (f) Shibata, T.; Toshida, N.; Takagi, K. *Org. Lett.* **2002**, *4*, 1619. (g) Seo, J.; Chui, H. M. P.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 476. (h) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008. (i) Yamamoto, Y.; Takagishi, H.; Itoh, K. *J. Am. Chem. Soc.* **2002**, *124*, 6844.

(3) (a) RajanBabu, T. V.; Nugent, W. A. *J. Am. Chem. Soc.* **1994**, *116*, 986. (b) Gansauer, A.; Pierobon, M.; Bluhm, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 101. (c) Gansauer, A.; Bluhm, H.; Pierobon, M. *J. Am. Chem. Soc.* **1998**, *120*, 12849. (d) Odedra, A.; Wu, C.-J.; Madhushaw, R. J.; Wang, S. L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9610.

(4) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363.

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

(6) For reviews of the metal-catalyzed oxygen transfer reaction, see: *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Joughe, C. R. H. I., Eds.; Plenum: New York, 1986.

(7) 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.

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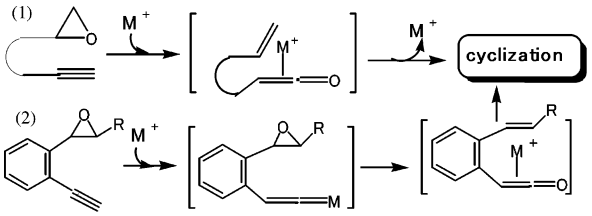
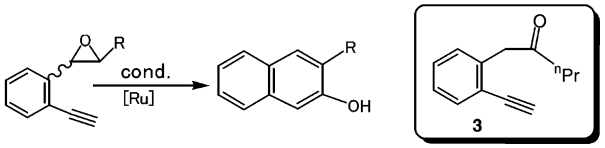
(9) For coupling of epoxide with alkyne and alkene via cleavage of the C−C bond of epoxide, see selective examples: (a) Chou, W.-N.; White, J. B. *Tetrahedron Lett.* **1991**, *32*, 7637. (b) Gaebert, C.; Mattaay, J. *Tetrahedron* **1997**, *53*, 14297. (c) Palomino, E.; Schaap, A. P.; Heeg, M. J. *Tetrahedron Lett.* **1989**, *30*, 6801.

10.1021/ja049943c CCC: $27.50

Scheme 1



Scheme 2



epoxide	time	naphthol (yield)
(1) R = H (**1a**)	24 h	0 %
(2) R = Me (**1b**)	24 h	0 %
(3) R = ^{n}Pr (**1c**)	3 h	**2c** (91%)

[Ru] = $TpRuPPh_3(CH_3CN)_2PF_6$
cond. toluene, 100 ^{0}C

Results and Discussion

$TpRuPPh_3(CH_3CN)_2PF_6$[10] [Tp = tris(1-pyrazolyl)borate] was chosen as a catalyst because it readily reacted with terminal alkyne[7] to produce a cationic and highly electrophilic ruthenium-vinylidenium species.[7,8] This characteristic is responsible for catalytic reactions including transfer hydrogenation,[7a] cleavage of a carbon−carbon triple bond,[7b] and cyclization of (*o*-alkenyl)-ethynylbenzene with a skeletal rearrangement.[7c] This catalyst was prepared from heating $TpRu(PPh_3)_2Cl$ with $LiPF_6$ in CH_3CN.[10] We first examined the structural effect of epoxides on catalytic reactions. As shown in Scheme 2, treatment of (*o*-ethynyl)phenyl epoxides **1a** and **1b** (*E*/*Z* = 1.6) with this ruthenium catalyst (10 mol %) in hot toluene (100 °C, 24 h) failed to give any noticeable product. However, the epoxide **1c** bearing a long *n*-propyl group gave naphthol **2c** in 91% yield (toluene, 100 °C, 3 h). Under similar conditions, ketone **3** failed to give the same product, but gave an enyne (*Z*/*E* = 2.1) via dimerization of its terminal alkyne.[11] This information suggests that the epoxy−ketone isomerization[12] is not operable under catalytic conditions. The yields of naphthol **2c** are highly dependent on reaction solvents, shown in the results as follows: dichloroethane (58%, 90 °C, 36 h), dimethoxyethane (53%, 85 °C, 35 h), acetonitrile (25%, 90 °C, 48 h), 3-pentanone (27%, 100 °C, 5.5 h), and DMF (12%, 100 °C, 6 h). No activity was observed for related ruthenium catalysts including $C_5H_5RuPPh_3(CH_3CN)_2PF_6$[13] and $TpRuPPh_3(CH_3CN)Cl$.[10] This information suggests that the basic tris(1-pyzarolyl)borate ligand and two vacant sites in $TpRuPPh_3(CH_3CN)_2PF_6$ are crucial for the catalytic activity.

We prepared various (*o*-ethynyl)phenyl epoxides **4**−**15** to examine the generality of this cyclization. As shown in Table 1, these epoxides contained a mixture of *E*- and *Z*-isomers (*E*/*Z* = 0.71−2.9)[14] except for styryl oxide derivative **6** (entry 3) that was obtained as *E*-isomer. All substrates bear a long or bulky 2′-alkyl substituent to ensure the catalytic activity. 1′,2′-Disubstituted epoxides **4**−**6** bearing a *n*-pentyl, isopropyl, and phenyl group were compatible with this cyclization (10 mol % catalyst, toluene, 100 °C, 3 h), giving the products **16**−**18** in yields of 72−95%. The reaction proceeds well with naphthyl epoxide **7** to deliver 3-phenanthrol **19** in 83% yield. The alkyne-epoxide coupling is very effective for compounds **8**,**9** bearing a 5-fluoro substituent (entries 5,6) and extended well to the substrates **10**−**13** bearing a π-donor group (X = F, Cl, Br, OMe) at the phenyl C(4) carbon (entries 7−10). The corresponding products **20**−**25** were obtained in as high as 87−93% yields without the formation of byproducts. Electron-rich benzene species **14**,**15** gave 85−88% yields of cyclized products **26**,**27**. The structures of compounds **21** and **22** were unambiguously confirmed by ^{1}H NOE spectra (see the Supporting Information).[15]

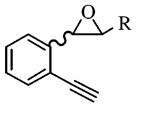
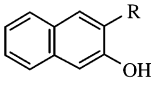
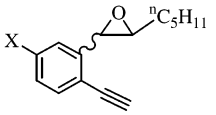
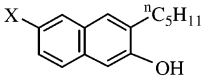
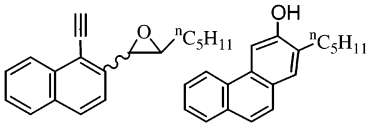
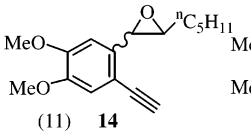
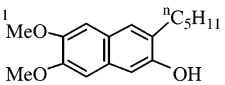
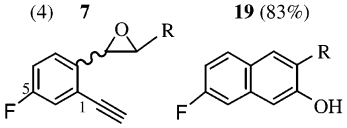
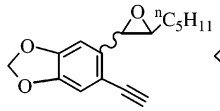
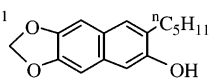
As shown in Table 2, we prepared various 1′,2′,2′-epoxide substrates **28**−**35** to examine the possible formation of naphthol products bearing a tertiary carbon. Notably, 1′,2′,2′-trisubstituted epoxide **28** gave 1-alkylidene-2-indenone **36** in 89% yield under similar conditions (entry 1). This transformation involves a complicated reorganization of the molecular skeleton. Assignment of the structure of indanone **36** was made on the basis of ^{13}C−^{1}H HMBC spectra.[15] The proposed structure was reconfirmed by the match of the ^{1}H NMR spectra with those of an authentic sample which we prepared according to the literature method[16] as depicted in Scheme 3. This framework is envisaged to derive from the bond connection between the epoxide C1′ and terminal acetylene carbons, whereas the oxygen atom migrates to the same acetylene carbon. Additional examples are provided in entries 2−10 to illustrate the generality. Entries 2,3 show efficient cyclization of epoxides **29** and **30** which bear different 2′,2′-epoxide alkyl substituents, to give 2-indanones **37** and **38** in 83−86% yields. NMR signals of *Z*- and *E*-isomers of indanone **37** were assigned on the basis of ^{1}H NMR NOE spectra.[15] Naphthyl epoxide **31** gave the analogous product **39** in 72% yield. The cyclization also works well with the substrates **32**−**35** bearing a 5-fluoro-, 4-fluoro-, 4-methoxy, and 4,5-methylenedioxy substituent, respectively, giving 72−91% yields of the cyclized products **40**−**43**.

Scheme 4 shows crucial experiments to better understand the reaction mechanism. We were delighted to discover that a key reaction intermediate can be trapped using isobutyl alcohol as a solvent. Heating epoxide **1a** in hot isobutyl alcohol in the presence of 10 mol % ruthenium catalyst gave ester **44a** in low yield (21%) over a long period (100 °C, 48 h). In contrast, heating epoxides **5**, **9**, and **28** in hot isobutyl alcohol (100 °C) for 6 h gave esters **44b**, **44c**, and **45** in respective yields of 71%, 79%, and 90%. Only the *trans*-isomer of compound **44b** and **44c** was obtained despite the different *E*/*Z* ratios of the starting epoxides **5** and **9** (*E*/*Z* = 4.2 and 0.53).

We prepared deuterated samples ***d*-1c** and ***d*-28** for the isotope-labeling experiment, and the results are given in Scheme

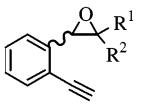
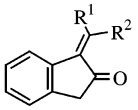
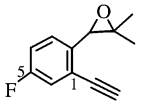
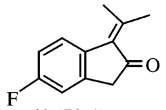
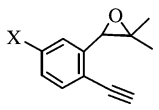
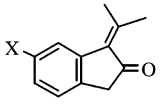
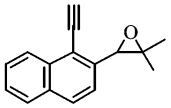
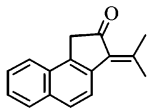
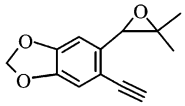
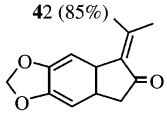
(10) Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34.
(11) See the related reaction: Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275.
(12) Okuda, K.; Katsura, T.; Tanino, H.; Kakoi, H.; Inoue, S. *Chem. Lett.* **1994**, 197.
(13) This complex was prepared by treatment of $CpRu(CH_3CN)_3PF_6$ with PPh_3 in equal molar proportion.
(14) The *E*/*Z* ratios of epoxides **4**−**15** were described in the Supporting Information.
(15) The ^{1}H NOE spectra of compounds **21**−**22**, **37** and ^{13}C−^{1}H HMBC NMR spectra of compound **36** were provided in the Supporting Information.
(16) Ensley, H. E.; Balakrishnan, P.; Hogan, C. *Tetrahedron Lett.* **1989**, *30*, 1625.

Table 1. Ruthenium-Catalyzed Cyclization of (*o*-Ethynyl)phenyl Epoxides

substrates[a]	products[b]	substrates	products
			
(1) R = $^{n}C_5H_{11}$ (**4**)	**16** (81%)	(7) X = F (**10**)	**22** (90%)
(2) R = $^{i}C_3H_7$ (**5**)	**17** (72%)	(8) X = Cl (**11**)	**23** (91%)
(3) R = *E*-Ph (**6**)	**18** (95%)	(9) X = Br (**12**)	**24** (93%)
		(10) X = OMe (**13**)	**25** (87%)
			
(4) **7**	**19** (83%)	(11) **14**	**26** (85%)
			
(5) R = $^{i}C_3H_7$ (**8**)	**20** (89%)	(12) **15**	**27** (88%)
(6) R = $^{n}C_5H_{11}$ (**9**)	**21** (84%)		

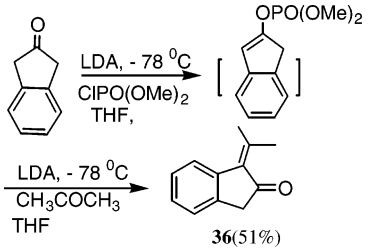
[a] 10 mol % catalyst, [substrate] = 1.2 M, 100 °C, 3 h. [b] Yields were reported after separation from column chromatograph. [c] The *E*/*Z* ratios of the epoxides are provided in the Supporting Information.

Table 2. Ruthenium-Catalyzed Synthesis of 1-Alkylidene-2-indanone

substrates[a]	products[b]	substrates	products
			
(1) R^1=R^2=Me (**28**)	**36** (89%)	(5) **32**	**40** (72%)
(2) R^1=Me, R^2=Et (**29**)	**37** (Z/E=2.8, 86%)		
(3) R^1=R^2=Et (**30**)	**38** (83%)	(6) X = F (**33**)	**41** (91%)
		(7) X = OMe (**34**)	**42** (85%)
			
(4) **31**	**39** (72%)	(9) **35**	**43** (86%)

[a] 10 mol % catalyst, [substrate] = 1.2 M, 100 °C, 3 h. [b] Yields were reported after separation from column chromatograph.

Scheme 3

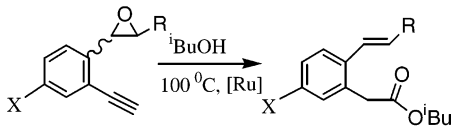


5. The alkynyl deuterium of species ***d*-1c** was transferred exclusively to the naphthyl C1 carbon of naphthol **2c**, whereas the corresponding proton of epoxide ***d*-28** was located at one of the methylene protons of indanone ***d*-36**. Both cases show a 1,2-shift for the alkynyl deuterium of epoxides ***d*-1c** and ***d*-28** as compared to their respective products ***d*-2c** and ***d*-36**. This information indicates the involvement of ruthenium-vinylidenium intermediates in the reaction mechanism.[17]

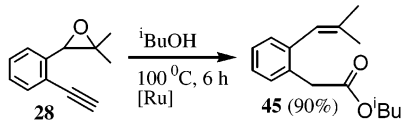
The formation of esters **44b**,**c** and **45** strongly indicates that a ruthenium-π-ketene intermediate **D** is the key reaction intermediate (Scheme 6).[18] We propose that the ruthenium catalyst first forms vinylidene-ruthenium species **A**,[7,8] which is also supported by deuterium-labeling experiments given in Scheme 5. Intramolecular electrocyclization via attack of the epoxide of species **A** at its central allene carbon produces seven-membered ether ring **B**, which is stabilized by extensive cationic delocalization. This species undergoes subsequent cleavage of the ether ring to give ruthenium-π-ketene species **C** that is in

(17) (a) Merlic, C. A.; Pauly, M. E. *J. Am. Chem. Soc*. **1996**, *118*, 11319. (b) Maeyama, K.; Iwasa, N. *J. Org. Chem*. **1999**, *64*, 1344. (c) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc*. **2002**, *124*, 518.
(18) Tidwell, T. T. *Ketene*; John Wiley: New York, 1995.

Scheme 4

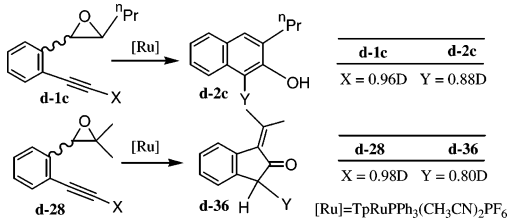


epoxide	time	products
(1) X=H, R=H (**1a**)	48 h	**44a** (18%)
(2) X=H, R=^{i}Pr **5**, (E/Z=4.2)	6 h	**44b** (71%)
(3) X=F, R=$^{n}C_5H_{11}$ **9**, (E/Z=0.53)	6 h	**44c** (79%)



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

Scheme 5



equilibrium with isomeric species **D**. In the case of 1′,2′-disubstituted olefin (R^2 = H), species **D** undergoes 6-*endo-dig* electrocyclization (path **a**)[19] to form six-membered ketone species **E**, and ultimately gives naphthol **2c**, **16**−**18** via loss of a proton and subsequent reprotonation. For 1′,2′,2′-trisubstituted olefin (R^2 = alkyl), species **D** undergoes 5-*endo-dig* cyclization (path **b**) to give species **F**, and finally gives 1-alkylidene-2-indanones **36**−**38**. According to this mechanism, the *E*/*Z* ratios of resulting styrene **44**,**45** are expected to follow their thermal equilibrium values, in favor of *E*-styrene derivatives.

The 6-*endo-dig* (path **a**) cyclization in the proposed mechanism was strongly supported by literature reports.[18,19] 1,3-Dienyl-4-ketenes readily formed similar 2-naphthols via 6-*endo-dig* cyclization at ambient conditions.[19] Although 5-*endo-dig* cyclization (path **b**) is little known in ketene chemistry, we observed similar behavior in the aromatization of (*o*-styryl)-ethynylbenzene[7c] in which the styryl C′1-carbon attacks at the central ruthenium-vinylidenium carbon in a 5-*endo-dig* fashion. The dimethyl substituents of epoxide species **D** enhance the 5-*endo-dig* cyclization via formation of a stable tertiary carbocation **F**.

The success of this catalytic reaction relies on the cleavage of the ether ring of the Fischer-typed ruthenium-oxacarbenium **B**. We believe that a long alkyl or bulky R^1 substituent is required to weaken this carbon−oxygen bond because of increasing steric hindrance. This hypothesis accounts well for the catalytic inactivity of epoxides **1a** and **1b** (Scheme 2) bearing a small hydrogen and methyl group, respectively. Generation of ester **44a** from epoxide **1a** is presumably generated from nucleophilic attack of isobutyl alcohol at the carbenium C_α-carbon of intermediate **B**, to generate species **G** that ultimately gives the observed product (Scheme 7). This catalytic pathway is shown to be inefficient possibly due to the difficulty of the nucleophilic attack.

The esters **44**,**45** are unlikely generated from the reaction of TpRu-acyl intermediates with isobutyl alcohol. According to our previous studies,[7b] TpRu-vinylacyl species readily underwent decarbonylation to liberate carbon monoxide and alkene even in the presence of carbon monoxide (10 atm).[20,21] The decarbonylation was so rapid that TpRu-acyl intermediates could not be trapped by aliphatic alcohols to form esters.[7b,20,21]

Conclusion

In summary, we have reported a cascade alkyne-epoxide cyclization of (*o*-ethynyl)phenyl epoxides catalyzed by ruthenium complexes. The reaction products are highly dependent on the epoxide substituents. 1′,2′-Disubstituted epoxides gave 2-naphthol derivatives efficiently, whereas 1′,2′,2′-trisubstituted produced 1-alkylidene-2-indanones in good yields. We propose a plausible mechanism involving ketene-alkene intermediates, generated from an oxygen migration from epoxide to terminal alkyne. The 2-naphthol products are thought to derive from 6-*endo-dig* cyclization of ketene-alkene intermediates, whereas 1-alkylidene-2-indanones are given from the 5-*endo-dig* cyclization pathway. This proposed mechanism is supported by trapping experiments using isobutyl alcohol as well as the deuterium-labeling experiment. Examination of this reaction on molecules bearing various alkyne-epoxide functionalities is under investigation.

Experimental Section

(1) General. Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst was prepared by heating $TpRu(PPh_3)_2Cl$ with $LiPF_6$ in CH_3CN.[10] 2-Bromobenzaldehyde was obtained commercially and used without purification. *o*-(2′-Trimethylsilylethynyl)benzaldehyde was obtained by the Sonogashira coupling reaction of 2-bromobenzaldehyde with trimethylsilylacetylene.[22]

(2) Typical Procedure for the Synthesis of (*o*-Ethynyl)phenyl Epoxide (1c). To a THF solution (20 mL) of *n*-butyltriphenylphosphonium bromide (2.96 g, 7.42 mmol) at 0 °C was added *n*-BuLi (2.5 mL, 6.43 mmol), and the mixture was stirred at 0 °C for 0.5 h. To this solution was added *o*-(2′-trimethylsilylethynyl)benzaldehyde (1.0 g, 4.95 mmol), and the mixture was stirred at room temperature 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 = 0.71) over a silica column to give the olefination product as a colorless oil (1.01 g, 4.17 mmol, 85%). This silyl compound was then dissolved in THF (10 mL) and added to Bu_4NF (1 M) (4.6 mL, 4.58 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 = 0.86) to give an enyne (0.67 g, 3.94 mmol,

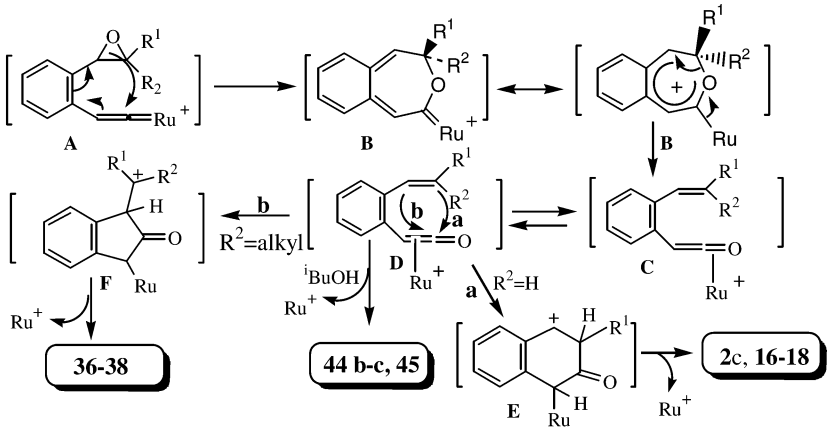
(19) (a) Danheiser, R. L.; Brisbois, R. G.; Kowalczyk, J. J.; Miller, R. T. *J. Am. Chem. Soc*. **1990**, *112*, 3093. (b) Merlic, C. A.; Xu, D. *J. Am. Chem. Soc*. **1991**, *113*, 7418. (c) Masamune, S.; Fukumoto, K. *Tetrahedron Lett*. **1965**, 4647. (d) Mayr, H.; Huisgen, R. *J. Chem. Soc., Chem. Commun*. **1976**, 57.

(20) We previously reported the ruthenium-catalyzed transformation of ethynyl alcohol into alkene and carbon monoxide.[7b] This catalytic reaction proceeded via formation of TpRu-vinylacyl intermediates that cannot be trapped by isobutyl alcohol. The reaction was not inhibited by carbon monoxide (10 atm) because of its facile decarbonylation.

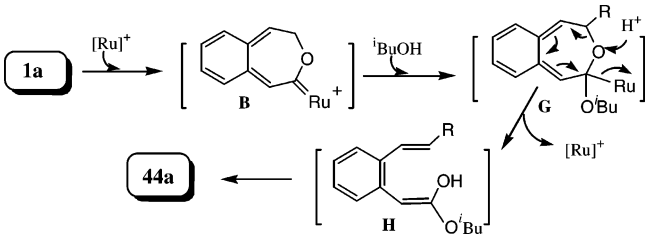
(21) Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S., unpublished results.

(22) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett*. **1975**, 4467.

Scheme 6



Scheme 7



95%) as colorless oil. To a CH_2Cl_2 solution (15 mL) of this enyne (0.5 g, 2.94 mmol) was added *m*-chloroperbenzoic acid (0.65 g, 3.82 mmol), and the mixtures were 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 was 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 (*o*-ethynyl)phenyl epoxide (**1c**) as a colorless oil (0.41 g, 2.20 mmol, 75%).

(3) Experimental Procedure for Cyclization of (*o*-Ethynyl)phenyl Epoxide (1c) to Naphthanol. A long tube containing $TpRu(PPh_3)(CH_3CN)_2PF_6$ (41.0 mg, 0.054 mmol) was dried in vacuo for 2 h before it was charged with epoxide **1** (100 mg, 0.54 mmol) and toluene (0.45 mL). The mixture was heated at 100 °C for 4 h before cooling to room temperature. The solution was concentrated and eluted through a silica column (hexane/diether = 5/1) to afford naphthol **2c** (91 mg, 0.49 mmol, 91%) as a yellow oil.

(4) 2-(2-Ethynylphenyl)-3-propyloxirane (1c). IR (Nujol, cm^{-1}) 3330(s), 3100(s), 3065(s), 2258(m), 2119(s), 1625(w), 1250(m); ^1H NMR (400 MHz, $CDCl_3$) (*E*/*Z* = 1.8), *E*-isomer, δ 7.46 (d, J = 7.3 Hz, 1H), 7.31−7.19 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 4.06 (d, J = 2.4 Hz, 1H), 3.30 (s, 1H), 2.83 (dt, J = 5.5, 2.4 Hz, 1H), 1.72−1.50 (m, 2H), 1.43−1.18 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H), minor *Z*-isomer (selected peaks), δ 7.46 (d, J = 7.3 Hz, 1H), 7.31−7.19 (m, 2H), 7.17 (d, J = 8.0 Hz, 1H), 4.29 (d, J = 4.4 Hz, 1H), 3.30−3.29 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H), the rest peaks are overlapped with those of the major *E*-isomer; ^{13}C NMR (100 MHz, $CDCl_3$) major *E*-isomer δ 140.4, 138.4, 132.4, 129.1, 127.2, 123.7, 81.8, 81.0, 63.0, 56.7, 34.3, 19.1, 13.9; HRMS calcd for $C_{13}H_{14}O$, 186.1045; found, 186.1041.

(5) 3-Propylnaphthalen-2-ol (2c). IR (Nujol, cm^{-1}) 3610(s), 3100(s), 3067(s), 2258(m), 2119(s), 1624(w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.55 (s, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.10 (s, 1H), 2.73 (t, J = 8.0 Hz, 2H), 1.77−1.67 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 131.6, 129.1, 128.9, 127.5, 126.1, 126.0, 125.8, 123.6, 109.6, 33.0, 23.2, 14.4; HRMS calcd for $C_{13}H_{14}O$, 186.1045; found, 186.1047.

Acknowledgment. We wish to thank the National Science Council, Taiwan for supporting this work.

Supporting Information Available: Synthetic schemes and spectral data of compounds **1a**,**1b** and **3**−**45** in repetitive experiments and $^1H-^{13}C$ NMBC spectra of compound **36**. This material is available free of charge via the Internet at http://pubs.acs.org.

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