Palladium-Catalyzed Addition of Alkyne to Norbornene Derivatives. Unusual Ring Formation and Expansion Reactions

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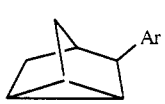
Treatment of norbornadiene (NBD) with BrCCPh and HCCPh in the presence of $Pd(PPh_3)_4$ and triethylamine gave the multiple-ring product **5a**, which is constructed from two NBD and two PhCC groups. Norbornene (NBE) reacts similarly with BrCCPh and HCCPh and with $BrCCCH_2OCH_3$ and $HCCCH_2OCH_3$ to afford **5b,c**, respectively. The structure of **5b** was determined by X-ray diffraction. Crystal data for **5b**: orthorhombic, *Pbca*, a = 11.329(7) Å, b = 16.218(12) Å, c = 24.297(8) Å, Z = 8. In the presence of formic acid and triethylamine, the reaction of 1-bromoalkyne with NBD or its derivative catalyzed by $Pd(PPh_3)_4$ afforded product **6** (NBD and BrCCPh, **6a**; NBE and BrCCPh, **6b**; NBE and $BrCCCH_2OCH_3$, **6c**). The skeleton of **6** is the same as that of **5** except that the alkynyl substituent in **5** is replaced by a hydrogen atom in **6**. The reaction of 1,4-epoxy-1,4-dihydronaphthalene (EHN) and 5,8-$(CH_3O)_2$EHN with HCCPh under conditions similar to those for **5a** afforded **8a** and **8b**, respectively. Treatment of EHN, 5,8-$(CH_3O)_2$EHN, and *exo*-dimethyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate with BrCCPh under conditions similar to those for **6a** gave products **9a–c**, respectively. Both **8** and **9** contain two EHN and an alkyne molecule. The structure of **8b** was also determined by X-ray diffraction. Crystal data for this compound: triclinic, $P\bar{1}$, $C_{32}O_6H_{30}$, a = 9.2000(23) Å, b = 9.912(4) Å, c = 15.164(6) Å, α = 83.73(3)°, β = 76.60(3)°, γ = 77.00(3)°, Z = 2. Mechanisms involving multiple insertions are proposed to account for the formation of **5–9** and the stereochemistry of these compounds.

Introduction

While carbon–carbon bond formation mediated by transition-metal complexes is an important field in organometallic chemistry,[1] the reverse metal-catalyzed carbon–carbon bond-breaking reactions are less well documented.[1a] There are few catalytic reactions known that involve both carbon–carbon bond formation and breaking.[2,3] Recently, we observed a palladium-catalyzed reaction of norbornadiene with aryl halide to give the three-membered aryl-substituted nortricyclene **1**.[4] Under similar



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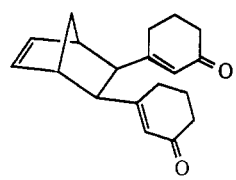

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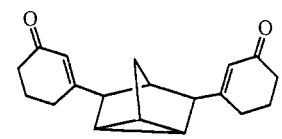
conditions, the reaction of norbornadiene with 3-iodo-2-cyclohexen-1-one afforded different types of products. Depending on the reaction conditions, the reaction may selectively lead to a cis exo 2,3-disubstituted norbornene (**2**),[5] a 3,5-disubstituted nortricyclene (**3**),[6] or a monosubstituted nortricyclene (**4**). The rich chemistry of norbornadiene with various organic halides mediated by palladium complexes prompts us to investigate the reaction of 1-haloalkyne with norbornene and its derivatives. In this paper, we report the results of these reactions that involve both extensive carbon–carbon bond formation and breakage steps leading to ring formation and ring expansion in the products.



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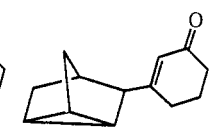

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Results and Discussion

Reaction of Norbornene and Norbornadiene with Alkyne. Treatment of norbornadiene with 1-bromo-2-phenylacetylene and phenylacetylene in the presence of $Pd(PPh_3)_4$ and triethylamine gave the product **5a** in 53% yield based on phenylacetylene used (eq 1). The mass spectral data for **5a** indicate that it consists of two norbornadiene and two phenylacetylenyl (PhC≡C) groups. Under similar conditions, norbornene reacts with 1-bromo-2-phenylacetylene and phenylacetylene to yield **5b** and with $BrC{\equiv}CCH_2OCH_3$ and $HCCCH_2OCH_3$ to give **5c**. Due

† National Tsing Hua University.
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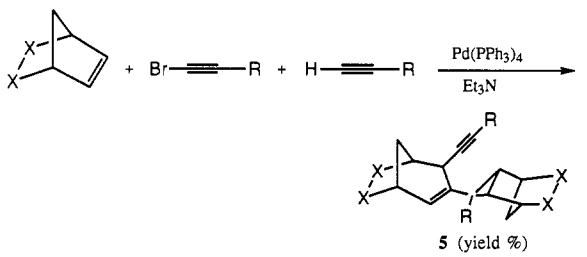


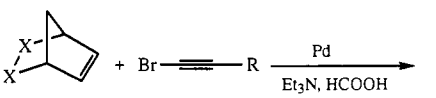
5 (yield %) (1)

XX = C_2H_2	R = Ph	**5a** (53)
XX = C_2H_4	R = Ph	**5b** (66)
XX = C_2H_4	R = CH_2OCH_3	**5c** (38)

to the complexity of these compounds, their mass and ^1H and ^{13}C NMR spectral data are insufficient to unambiguously determine the structures. Consequently, the crystal structure of a representative of these compounds, **5b**, was determined by X-ray diffraction. A molecular drawing with selected bond distances and angles of this compound is displayed in Figure 1. In agreement with the mass spectral data, the results of X-ray structure analysis indicate that **5b** consists of two norbornene and two phenylacetylenyl groups, although some of these groups underwent skeletal rearrangement during formation of this product. The norbornene fragments are linked to each other via the alkyne carbons (C1 and C2) of the phenylacetylenyl group. One alkyne carbon (C1) is connected to a norbornene by forming a cyclopropane ring (C1–C18–C19), while the other alkyne carbon (C2) is inserted into the carbon–carbon double bond of the second norbornene, leading to a ring expansion reaction. The cyclopropane ring of **5b** is exo to the first norbornene fragment, and the phenyl group points toward the bridging carbon (C24). The phenylacetylenyl group on the second norbornene fragment is also cis to the bridging carbon (C8). The formation of the cyclopropane ring (C1–C18–C19) is evidenced by the angles between the carbon–carbon bonds in the ring (∠C18–C1–C19 = 59.7°, ∠C1–C18–C19 = 60.1°, ∠C1–C19–C18 = 60.2°), which are all close to the ideal value of 60°. The presence of a carbon–carbon double bond (C2–C3) in the six-membered ring is supported by the observed bond distance between C2 and C3 of 1.322 Å and bond angles ∠C3–C2–C9 = 120°, ∠C2–C3–C4 = 124°, and ∠C1–C2–C9 = 116° (see Figure 1). The observed angles around C2 are near the expected value of 120° for an sp^2 carbon.

All the ^1H NMR spectra of compounds **5a–c** show characteristic AB type resonances at δ 1.64 and 1.83 for the two protons on the cyclopropane ring and a doublet at δ 6.12 for the olefin proton on the six-membered ring. For **5a,b**, the resonances for the bridging methylene protons near the cyclopropane group at *ca.* δ 0.5 are the most upfield proton signals of these compounds, presumably due to the effect of ring currents in the phenyl and cyclopropane groups (Figure 1). Interestingly, for **5c** only the bridging methylene proton at the same side of the cyclopropane group shows its NMR signal at a position <1 ppm; the resonance for the other bridging methylene proton is buried in the region 1–2 ppm, in which the proton signals cannot be clearly assigned due to overlapping. In the ^{13}C NMR spectra, the signals for the cyclopropane carbons appear at *ca.* δ 31 and 58 (attached to Ph), while the resonances for alkyne carbons occur at about δ 80 and 95.

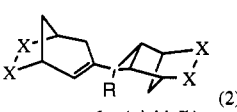
Attempts to prepare **5** which contains two different alkynes by treating a mixture of $BrC{\equiv}CC_6H_5$ and $HC{\equiv}CCH_2OCH_3$ (or $HC{\equiv}C(CH_2)_3CH_3$) with norbornene resulted in the isolation of the phenyl-substituted product **5b**. There is no product that contains a substituent from $HC{\equiv}CCH_2OCH_3$ (or $HC{\equiv}C(CH_2)_3CH_3$). Careful examination of the reactions of norbornadiene with 1-bromo-2-phenylacetylene and phenylacetylene showed that, in addition to **5a**, the hydrogenolysis product **6a** in ca. 2% yield (see eq 2)and a coupling product of 1-bromo-2-



XX = C_2H_2, R = Ph

XX = C_2H_4, R = Ph

XX = C_2H_4, R = CH_2OCH_3



6 (yield %) (2)

6a (49)

6b (86)

6c (35)

phenylacetylene and phenylacetylene, 1,4-diphenylbutadiyne (**7a**; 26% yield),were also formed. Similarly,

7a

in the reaction of norbornene with 1-bromo-2-phenylacetylene and phenylacetylene, the corresponding hydrogenolysis product **6b** in 3% yield and the diyne **7a** in 25% yield were observed. Compound **7a** was readily identified by comparing its mass and NMR spectra with those of an

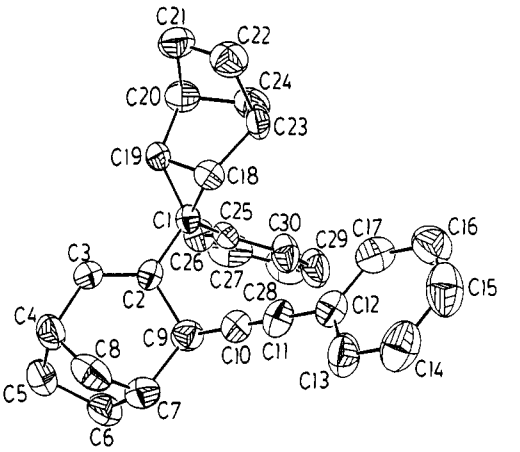
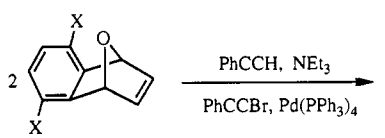


Figure 1. Molecular structure of **5b** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): C1–C2 = 1.518(10), C1–C18 = 1.523(10), C1–C19 = 1.522(10), C2–C3 = 1.322(11), C2–C9 = 1.518(10), C5–C6 = 1.537(12), C9–C10 = 1.494(12), C10–C11 = 1.168(12), C11–C12 = 1.431(12), C18–C19 = 1.515(10), C21–C22 = 1.539(11); C2–C1–C18 = 112.2(6), C2–C1–C19 = 115.3(6), C2–C1–C25 = 111.7(6), C18–C1–C19 = 59.7(4), C18–C1–C25 = 125.2(6), C19–C1–C25 = 123.5(6), C1–C2–C3 = 124.2(6), C1–C2–C9 = 116.2(6), C3–C2–C9 = 119.7(7), C2–C3–C4 = 123.6(6), C9–C10–C11 = 177.5(9), C10–C11–C12 = 179.6(9), C1–C18–C19 = 60.1(5), C1–C19–C18 = 60.2(4).

authentic sample,[7] while the structures of compounds **6** were assigned on the basis of their spectral data and by comparison with those of compounds **5**. The details of the structure analysis of **6** follow.

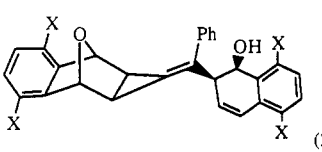
In the presence of formic acid and triethylamine, the reaction of 1-bromo-2-phenylacetylene with norbornadiene catalyzed by $Pd(PPh_3)_4$ selectively gave the hydrogenolysis product **6a**. The corresponding product **5a** was not observed under the reaction conditions. Presumably, formic acid served as the hydride source in the reactions. Metal-catalyzed hydride transfer using formic acid as the hydride source is well-known.[8] Norbornene also reacts with 1-bromo-2-phenylacetylene to afford the corresponding product **6b**. The product yield for norbornene is higher than that for norbornadiene. Under conditions similar to those for **6a**, the reaction of methyl 1-bromopropargyl ether with norbornene afforded product **6c**. The coupling patterns of ^1H and ^{13}C NMR signals of compound **5** and **6** are similar. For comparison, the resonances for the two protons on the cyclopropane ring appear at δ 1.28 and 1.48 and that for the olefin proton on the six-membered ring occurs at δ 6.01 for **6a**, while the corresponding values for **5a** appear at δ 1.64 and 1.83 and at δ 6.12, respectively. On the basis of the NMR and mass spectra of **6a–c**, the structures as shown in eq 2 are proposed.

Reaction of 1,4-Epoxy-1,4-dihydronaphthalene with Alkyne. The reaction of 1,4-epoxy-1,4-dihydronaphthalene (EHN) with phenylacetylene in the presence of 1-bromo-2-phenylacetylene, $Pd(PPh_3)_4$, and triethylamine afforded products **8a** in ca. 60% yield and **7a** in 35% yield. While in the absence of phenylacetylene the reaction produced only a trace of **8a**, the omission of 1-bromo-2-phenylacetylene gave no product **8a**. If $Pd(PPh_3)_4$ was replaced by $Pd(PPh_3)_2Cl_2$ and 2 equiv of PPh_3, the same product yields (58% of **8a** and 35% of **7a**) were obtained within experimental error. Similarly, treating 5,8-dimethoxy-1,4-epoxy-1,4-dihydronaphthalene (5,8-$(CH_3O)_2$-EHN) with phenylacetylene under conditions similar to those for the formation of **8a** gave **8b** (eq 3). Because the



X = H

X = OCH_3



(3)

8 (yield %)

8a (61)

8b (58)

spectral data for **8a,b** are insufficient for unambiguous assignment of the structures of these compounds, the crystal structure of **8b** was determined by X-ray diffraction. A molecular drawing of **8b** and selected bond distances and angles are presented in Figure 2. As indicated in the structure, **8b** is stoichiometrically composed of a phenylacetylene and two 5,8-$(CH_3O)_2$EHN molecules. The former serves as a bridge connecting the two 5,8-$(CH_3O)_2$-EHN fragments. In one 5,8-$(CH_3O)_2$EHN molecule, the carbons of the olefin double bond are all connected to the terminal carbon of the phenylacetylenyl group, forming an exo three-membered cyclic group, while in the second 5,8-$(CH_3O)_2$EHN molecule only one carbon of the carbon–carbon double bond is linked to the internal alkyne carbon of phenylacetylene. Furthermore, one oxygen–carbon bond is cleaved, leading to the formation of a hydroxycyclohexadiene ring in which the hydroxy and the alkenyl substituents are cis to each other. The presence of carbon–carbon double bonds between C11 and C12 and between C21 and C22 (Figure 2) in **8b** is supported by the observed bond distances 1.316 and 1.317 Å, respectively, while the formation of a three-membered ring (C9–C10–C11) is evidenced by the angles near 60° between the carbon–carbon bonds in the ring ($\angle$C9–C10–C11 = 58.2°, $\angle$C9–C11–C10 = 63.2°, $\angle$C10–C9–C11 = 58.7°). The bond angles centered at C12, C21, and C22, which are all close to 120°, further indicate the existence of double bonds between C11 and C12 and between C21 and C22. In the ^1H NMR spectra of **8b**, the two endo protons on the cyclopropane ring appear at δ 2.11 and 2.23, while the signals for the olefin protons on the hydroxycyclohexadiene ring occur at δ 6.25 (d, J = 9.8 Hz) and 7.15 (dd, J = 9.8 and 2.9 Hz). The two protons attached to the sp^3 carbons on the hydroxycyclohexadiene ring appear at δ 4.05 (b) and 5.02 (m). The observed chemical shifts are comparable to those reported for 2-substituted *cis*-1,2-dihydro-1-naphthol.[9]

Treatment of 7-oxanorbornene with 1-bromo-2-phenylacetylene in the presence of $Pd(PPh_3)_4$, formic acid, and triethylamine afforded product **9** (eq 4), which according

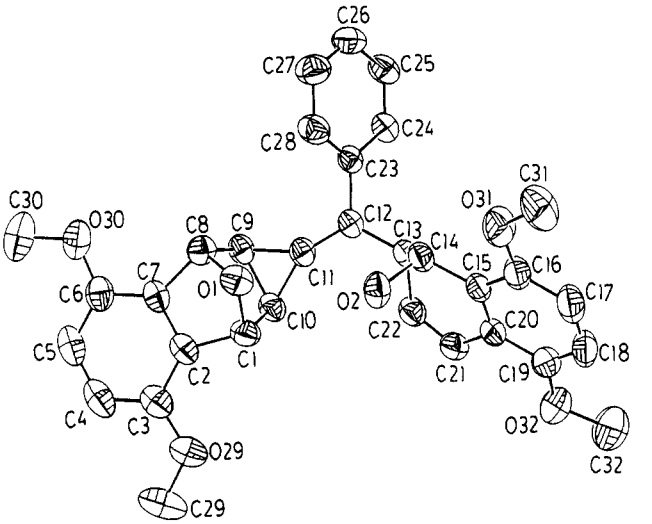


Figure 2. Molecular structure of **8b** showing the atom-labeling scheme. Selected bond distances (Å) and angles (deg): O2–C14 = 1.433(3), C9–C10 = 1.540(4), C9–C11 = 1.467(4), C11–C12 = 1.316(4), C12–C13 = 1.504(4), C12–C23 = 1.491(4), C13–C14 = 1.531(4), C13–C22 = 1.500(4), C14–C15 = 1.500(4), C15–C20 = 1.394(4), C20–C21 = 1.456(4), C21–C22 = 1.317(4); C8–C9–C11 = 115.96(21), C10–C9–C11 = 58.65(17), C1–C10–C11 = 115.73(22), C9–C10–C11 = 58.20-(17), C9–C11–C10 = 63.15(18), C11–C12–C13 = 122.73(23), C11–C12–C23 = 119.93(23), C14–C13–C22 = 110.34(21), C13–C14–C15 = 110.62(22), C14–C15–C20 = 119.14(24), C15–C20–C21 = 118.94(25), C20–C21–C22 = 121.4(3), C13–C22–C21 = 120.18(24).

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(8) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613.
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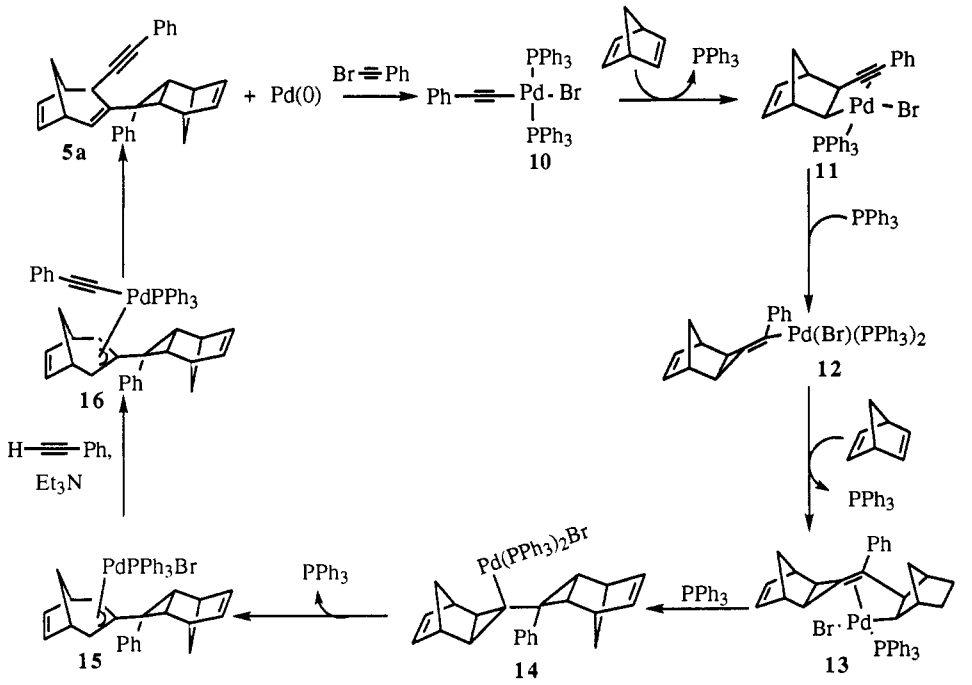
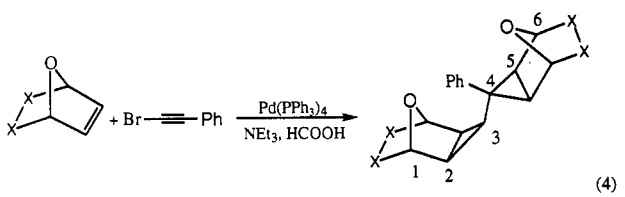
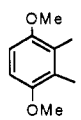
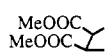
Scheme 1



to the NMR and mass spectra may be considered to be



(4)

X-X	9 (yield%)
	9a (78)
	9b (80)
	9c (97)

constructed of two oxanorbornenes and one phenylacetylene molecule. It is interesting to note that both **8** and **9** have exactly the same chemical formula, although their skeletons are different. The two epoxy molecules are linked to each other via a phenylacetylene fragment. Each alkyne carbon is connected to the olefin carbons of an epoxy molecule, forming a cyclopropane ring. The presence of two cyclopropane rings in **9a** is evidenced by the observation of characteristic ^{13}C NMR resonances at δ 28.46, 33.57, and 37.30 for the three tertiary carbons and at δ 44.89 for the quaternary carbon of the two cyclopropane rings and the ^1H NMR signals at δ 1.40 (d), 1.67 (s), and 2.44 (t) for the protons on the rings. These ^1H and ^{13}C NMR resonances are relatively upfield compared to those signals with the same degree of substituents. The observed coupling constant of 7.4 Hz between the protons (at δ 1.40 (d) and 2.44 (t)) on one of the cyclopropane rings supports the notion that the three hydrogens on this ring are all cis to each other.[10] The cis stereochemistry is further verified by NOE experiments. Irradiation of the signal at δ 1.40 (H2) led to an increase in intensity of the signals at δ 2.44 (H3) by 18.1%, but by only 3.2% at δ 5.50 (H1). The larger NOE for H3 than for H1 indicates that the distance between H1 and H2 which are staggered to each other is longer than that between H2 and H3. It appears that only a cis arrangement of H2 and H3 would result in a shorter distance between H2 and H3 than that between H2 and H1. Similarly, **9b** and **9c** were prepared in good to excellent yields from the reaction of 1-bromo-2-phenylacetylene with the corresponding oxanorbornene derivatives in the presence of $Pd(PPh_3)_4$, formic acid, and triethylamine. The structural assignments of these products are also based on the mass and NMR spectral data and comparison of these data with those for the corresponding compound **8**. In all products **5**, **6**, **8**, and **9**, one or two cyclopropane rings are included. The formation of cyclopropane rings from the reaction of norbornadiene or norbornene with alkenyl halides or with internal acetylenes in the presence of palladium complexes was observed previously.[11]

Mechanistic Considerations. In spite of the complexity of observed products **5–9**, the mechanisms for these catalytic reactions may be proposed on the basis of established principles of organometallic chemistry. Scheme 1 presents the proposed mechanism for the catalysis of reaction 1 that produces compound **5a**. The first step of the reaction is expected to be an oxidative addition of 1-bromo-2-phenylacetylene to $Pd(PPh_3)_4$ to give the trans square-planar complex $Pd(C{\equiv}CR)Br(PPh_3)_2$ (**10**).[12] Exo coordination of norbornadiene and insertion of the olefin double bond in the norbornadiene molecule into the

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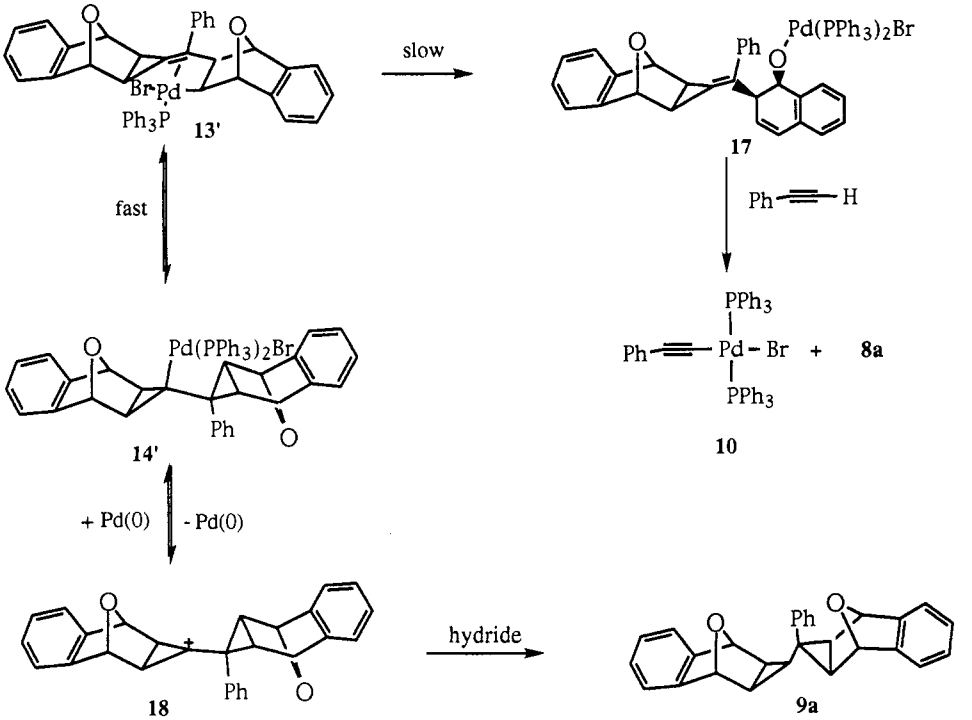
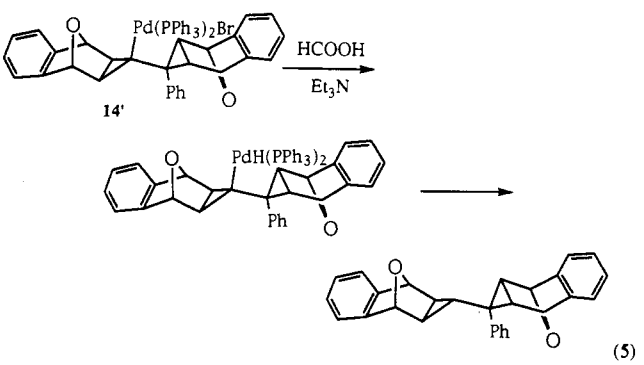
Scheme 2



Pd—CCPh bond leads to the formation of Pd(II) intermediate **11**, in which an intramolecular η^2-alkyne coordination occurs. Intramolecular η^2-alkene complexes of a similar type were isolated previously by us.[13] Successive intramolecular and intermolecular insertions result in the Pd(II) species **14**, which consists of two cyclopropane groups. Ring opening of this cyclopropyl–palladium species affords the palladium π-allylic complex **15**, which then reacts with phenylacetylene in the presence of a base to give **16**. Reductive elimination of Pd(II) yields the final product **5a**. The stereochemistry of the phenylacetylenyl group in **5a** predicted on the basis of the mechanism is in agreement with that determined by X-ray diffraction (Figure 1). This palladium-mediated cyclopropane ring opening to give a (π-allyl)palladium intermediate has been observed previously.[14] The reaction pathways for the formation of compound **6** (reaction 2) are likely similar to those for reaction 1, except the last steps. The reaction of **15** in Scheme 1 with a hydride source to give a palladium(II) hydride followed by reductive elimination affords product **6**. For the formation of **8** and **9**, the first few steps, including oxidative addition and successive olefin and alkyne insertions to yield intermediate **13'** (Scheme 2), are similar to those in Scheme 1 for reaction 1. In the catalytic reaction that leads to **8a**, the intermediate **13'** undergoes β-oxygen elimination to afford ring-opening intermediate **17**. Several pathways may be proposed for the transformation of **17** to **8a**. For example, **17** may be protonated by $HNEt_3Br$ to give product **8a** and a palladium(II) species. Reaction of the latter with phenylacetylene in the presence of triethylamine regenerates **10**. Another possibility is that **17** reacts directly with phenylacetylene to give **10** and **8a** (Scheme 2). The ring-opening reaction was observed previously by us in the reaction of aryl halide with 1,4-epoxy-1,4-dihydronaphthalenes.[9]

Similar to the formation of **8**, intermediates **13'** and **14'** are involved in the formation of **9**. However, it is not completely clear how **14'** is transformed into the final product **9a**. A reasonable pathway as shown in eq 5 is the



(5)

reaction of **14'** with formic acid and triethylamine to give a palladium hydride followed by reductive elimination to yield the product. However, this mechanism predicts an organic product with stereochemistry different from **9** (eq 5) and thus can be discarded. Another possible pathway (Scheme 2) involves the decomposition of **14'** to give the cyclopropyl cation **18**. Hydride addition to this species from the endo side affords **9**. Model studies of cation **18** clearly indicate that the endo side is less hindered than the exo side for nucleophilic addition. It should be noted that in the mechanism for the formation of compounds **5** and **6** (Scheme 1), a cyclopropyl cation similar to **18** might also be involved. The proposed intermediate **14** first decomposes to give a cyclopropyl cation, which then rearranges to an allylic cation. Trapping of this cation by palladium(0) affords **15**. Cyclopropyl and allylic cations were proposed as intermediates for the solvolysis of cyclopropyl-*p*-toluenesulfonates.[10,15] Due to the electron-

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withdrawing ability of the bridging oxygen on **14'**, further rearrangement of the cyclopropyl cation **18** (Scheme 2) to the corresponding allylic cation is prohibited, resulting in the formation of products different from **5** and **6**.

As indicated in Scheme 2, the formation of **8** and **9** involves the common intermediate **13'**. To account for the observation that **8** is formed in the absence of formic acid and triethylamine, while **9** is produced in the presence of these two species, it is necessary to propose a mechanism (Scheme 2) that involves rapid and reversible insertion of olefin into the palladium–carbon bond and formation of a cyclopropane ring in **13'** to yield **14'** and reversible formation of cationic species **18**. In the presence of formic acid and triethylamine, **18** is trapped by a hydride to give **9a**, while in the absence of formic acid and triethylamine, the reaction path to give **9a** is terminated and slow ring opening of **13'** followed by protonation affords **8a**.

According to the above mechanistic discussion, we expect that all catalytic reactions of alkynes with norbornene derivatives follow similar reaction pathways. Exo coordination of norbornene substrates before insertion into the palladium–carbon bond is the origin of the formation of exo cyclopropane rings in the intermediates and in the final products. The observed different final products are determined by the number of insertion steps and by the type of termination process. Four olefin or alkyne insertions proceed prior to termination steps in the preparation of products **5**, **6**, or **9**. For compounds **8**, only three insertion steps are required before ring-opening termination.

With respect to the formation of diyne **7**, the steps including substitution of the bromide ligand in the intermediate **10** by an acetylide and reductive elimination of the resulting intermediate are expected to take place. Oxidative coupling of terminal alkynes to 1,3-diynes by palladium complexes and other metal species were reported previously.[16] It should be noted that in the reaction of 1,4-epoxy-1,4-dihydronaphthalene with phenylacetylene (eq 3) to give product **8a**, the formation of side product **7** was accompanied by production of a palladium(0) species which is unable to further catalyze the reaction. The addition of 1-bromo-2-phenylacetylene converts this palladium(0) species back to intermediate **10** and hence regenerates the catalytic activity. This explains why a substantial amount of 1-bromo-2-phenylacetylene is required for reaction 3, although stoichiometrically the reaction does not need the substrate.

Conclusion

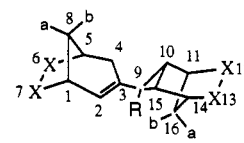
We have demonstrated several unusual multiple-ring formation and ring-opening processes from the reactions of alkynes with norbornene and its derivatives. All these reactions involve the addition of alkynyl groups to norbornene or its derivatives to give intermediates that readily undergo successive insertions, cyclizations, and ring-opening reactions. Cyclization selectively leads to three-membered rings, although four-membered-ring products are expected to be more stable thermodynamically. The one-carbon ring expansion during the formation of **5** and **6**, presumably via a cyclopropyl cation, is interesting and should be useful in organic synthesis. Applications of this type of cyclization and one-carbon ring expansion to other systems are currently under investigation.

Experimental Section

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. ^1H and ^{13}C NMR experiments were performed on a Varian Gemini 300 instrument at 300 MHz. Infrared spectra were obtained on a Bomem MB-100 spectrometer. Mass spectra at low resolution and high resolution were recorded on JEOL JMS-D100 and JMS-HX110 instruments, respectively.

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noted. The following compounds were prepared according to the published procedures: $Pd(PPh_3)_4$;[17] $Pd(PPh_3)_2Cl_2$;[18a] 1-bromo-2-phenylacetylene, methyl 1-bromopropargyl ether, and 1-bromoheptyne.[18]

Reaction of Norbornadiene with 1-Bromo-2-phenylacetylene and Phenylacetylene. A round-bottom flask containing $Pd(PPh_3)_4$ (0.120 g, 0.104 mmol) was purged with nitrogen three times. To the flask were added sequentially 1-bromo-2-phenylacetylene (0.455 g, 2.50 mmol), phenylacetylene (0.255 g, 2.50 mmol), norbornadiene (0.920 g, 10.0 mmol), toluene (10 mL), and triethylamine (1.01 g, 10.0 mmol). The solution was then stirred at 80 °C for 24 h. During this period, the solution changed gradually from orange to red-brown. After filtration through Celite, the filtrate was concentrated and then separated on a silica gel column using a mixture of hexanes and ethyl acetate (30/1, v/v) as the eluent to give products **5a** (0.512 g, 1.33 mmol) in 53% yield and **7a** (0.131 g, 0.65 mmol) in 26% yield. The spectral data for **5a** are as follows. (In order to clearly assign the NMR signals, the general atom-labeling scheme **18** is employed



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for compounds **5** and **6**. This atom-labeling scheme is different from that used in the molecular drawing of **5b** in Figure 1.) ^1H NMR (300 MHz, $CDCl_3$): δ 0.54 (d, J = 9.4 Hz, 1 H, H(16a)), 0.63 (d, J = 9.4 Hz, 1 H, H(16b)), 1.64 (d, J = 7.8 Hz, 1 H, H(15)), 1.78–1.83 (m, 1 H, H(8a)), 1.83 (d, J = 7.8 Hz, 1 H, H(10)), 1.92 (d, J = 9.4 Hz, 1 H, H(8b)), 2.71–2.75 (m, 2 H, H(1), H(5)), 2.82 (br s, 2 H, H(11), H(14)), 2.98 (br s, 1 H, H(4)), 5.46 (dd, J = 5.6 Hz, J = 2.9 Hz, 1 H, H(7)), 6.12 (d, J = 6.6 Hz, 1 H, H(2)), 6.16 (dd, J = 5.6 Hz, J = 2.9 Hz, 1 H, H(6)), 6.48 (br s, 2 H, H(12), H(13)), 7.10–7.53 (m, 10 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 31.54 (d, C(15)), 31.86 (d, C(10)), 38.44 (d, C(4)), 38.71 (t, C(16)), 41.07 (t, C(8)), 42.15 (d, C(1)), 42.84 (d, C(5)), 45.23 (d, C(11), C(14)), 58.02 (s, C(9)), 81.56 (s, CC), 93.46 (s, CC), 124.66 (s), 126.00 (d), 127.68 (d, C(2)), 128.27 (d), 128.47 (d), 128.57 (d), 128.81 (d), 129.00 (d), 129.49 (d), 129.62 (d), 131.62 (d, C(7)), 137.32 (s, C(3)), 141.27 (d, C(6)), 142.28 (d, C(12), C(13)). IR (KBr): 2950, 2220, 1490, 1440, 1320, 1048, 760, 700 cm^{-1}. HRMS: calcd for $C_{30}H_{26}$ 386.2036, found 386.2033. Mp: 140 °C.

Synthesis of 5b from the Reaction of Norbornene with 1-Bromo-2-phenylacetylene and Phenylacetylene. 5b was prepared in 66% yield by following a procedure similar to that described for **5a**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.33 (d, J = 10.9 Hz, 1 H, H(16a)), 0.44 (d, J = 10.9 Hz, 1 H, H(16b)), 0.78–0.96 (m, 1 H), 1.25–1.65 (m, 10 H), 1.95 (d, J = 10.9 Hz, 1 H), 2.32 (s, 1 H), 2.40–2.46 (m, 3 H), 2.79 (br s, 1 H), 5.95 (d, J = 6.7 Hz, 1 H, H(2)), 7.13–7.5 (m, 10 H) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 26.89 (d), 28.37 (t), 30.31 (t), 30.51 (t), 30.86 (d), 31.05

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(t), 32.71 (t), 34.20 (t), 35.49 (d), 36.09 (d), 36.55 (s), 36.62 (d), 39.19 (d), 39.52 (d), 81.40 (s), 93.76 (s), 124.54 (s), 125.63 (d), 127.33 (d), 127.89 (d), 128.19 (d), 128.47 (d), 129.15 (d), 129.62 (d), 129.85 (d), 131.35 (d), 137.95 (s), 141.97 (s). IR (KBr): 3028, 2942, 2862, 2218, 1487, 1435, 1356, 1272, 753, 702 cm^{-1}. HRMS: calcd for $C_{30}H_{30}$ 390.2349, found 390.2349. Mp: 95 °C.

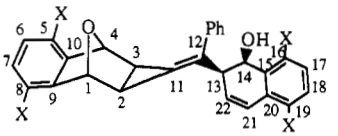
Synthesis of 5c from the Reaction of Norbornene with 1-Bromo-3-methoxypropyne and Methyl Propargyl Ether. **5c** was prepared in 38% yield by following a procedure similar to that described for **5a**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (d, J = 10.4 Hz, 1 H, H(16b)), 0.93 (d, J = 7.6 Hz, 1 H, H(15)), 1.17 (d, J = 7.6 Hz, 1 H, H(10)), 1.22–1.87 (m, 10 H), 1.92 (d, J = 10.4 Hz, 1 H), 2.35–2.40 (m, 1 H), 2.46 (br s, 3 H), 2.90 (br s, 1 H), 3.26 (s, 3 H), 3.40 (s, 3 H), 3.61 (s, 2 H), 4.14 (s, 2 H), 5.77 (d, J = 6.6 Hz, 1 H, H(2)). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 27.03 (d), 28.55 (t), 30.21 (t), 30.43 (t), 30.93 (s), 30.98 (t), 31.27 (d), 32.49 (t), 34.35 (t), 35.25 (d), 36.78 (d), 39.58 (d), 40.00 (d), 57.25 (q), 58.12 (q), 60.34 (t), 74.22 (t), 76.34 (s), 90.34 (s), 130.32 (d), 138.73 (s). IR (neat): 2948, 2225, 1714, 1449, 1093, 735 cm^{-1}. HRMS: calcd for $C_{22}H_{30}O_2$ 326.2247, found 326.2252.

Reaction of Norbornadiene with 1-Bromo-2-phenylacetylene in the Presence of Formic Acid. A round-bottom flask containing $Pd(PPh_3)_4$ (0.120 g, 0.104 mmol), 1-bromo-2-phenylacetylene (0.455 g, 2.50 mmol), norbornadiene (0.920 g, 10.0 mmol), and toluene (10 mL) was purged with nitrogen three times. To the flask were added triethylamine (1.01 g, 10.0 mmol) and formic acid (0.46 g, 10 mmol). The solution was then stirred at 60 °C for 12 h. Addition of ether (15 mL) was followed by extraction with water four times. The organic layer was dried by anhydrous $MgSO_4$, filtered, concentrated, and then separated on a silica gel column using a mixture of hexanes and ethyl acetate (50/1, v/v) as the eluent to give **6a** (0.351 g, 1.23 mmol) in 49% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.57 (d, J = 9.5 Hz, 1 H, H(16a)), 0.65 (d, J = 9.5 Hz, 1 H, H(16b)), 1.28 (d, J = 7.8 Hz, 1 H, H(15)), 1.43 (d, J = 9.3 Hz, 1 H, H(8a)), 1.48 (d, J = 7.8 Hz, 1 H, H(10)), 1.73 (d, J = 17.9 Hz, 1 H, H(4) endo), 1.80 (dd, J = 9.3 Hz, J = 4.8 Hz, 1 H, H(8b)), 2.18 (ddd, J = 17.9 Hz, J = 5.3 Hz, J = 1.9 Hz, 1 H, H(4) exo), 2.63–2.66 (m, 2 H, H(1), H(5)), 2.89 (br s, 2 H, H(11), H(14)), 5.60 (dd, J = 5.5 Hz, J = 2.7 Hz, 1 H, H(7)), 6.01 (d, J = 6.5 Hz, 1 H, H(2)), 6.10 (d, J = 5.5 Hz, J = 2.7 Hz, 1 H, H(6)), 6.50 (br s, 2 H, H(12), H(13)), 7.16–7.32 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 29.08 (t, C(4)), 34.42 (d, C(15)), 34.68 (d, C(10)), 37.96 (d, C(1)), 38.32 (d, C(5)), 41.05 (t, C(16)), 41.23 (t, C(8)), 42.53 (d, C(11)), 42.57 (d, C(14)), 59.48 (s, C(9)), 125.57 (d), 126.84 (d, C(2)), 128.18 (d), 128.33 (d), 128.89 (d), 130.21 (d, C(7)), 138.77 (d, C(6)), 139.23 (s, C(3)), 141.95 (d, C(12), C(13)), 142.05 (s). IR (KBr): 2967, 1598, 1491, 1444, 1311, 1048, 703 cm^{-1}. HRMS: calcd for $C_{22}H_{22}$ 286.1723, found 286.1743.

Synthesis of 6b from the Reaction of Norbornene with 1-Bromo-2-phenylacetylene in the Presence of Formic Acid. **6b** was prepared in 86% yield by following a procedure similar to that described for **6a**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.28 (d, J = 10.4 Hz, 1 H, H(16a)), 0.36 (d, J = 10.4 Hz, 1 H, H(16b)), 1.07 (d, J = 7.5 Hz, 1 H, H(15)), 1.12 (d, J = 7.5 Hz, 1 H, H(10)), 1.22–1.74 (m, 12 H), 2.17–2.32 (m, 4 H), 6.81 (d, J = 6.6 Hz, 1 H, H(2)), 7.12–7.24 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 28.66 (d), 29.25 (d), 30.08 (t), 30.38 (t), 30.96 (t), 33.14 (d), 35.22 (d), 35.73 (t), 36.39 (d), 37.59 (s), 38.27 (t), 125.35 (d), 128.00 (d), 128.04 (d), 128.43 (d), 129.32 (d), 129.39 (d), 139.76 (s), 142.17 (s). IR (neat): 3021, 2939, 1599, 1492, 1310, 876, 750, 701, 635 cm^{-1}. HRMS: calcd for $C_{22}H_{26}$ 290.2035, found 290.2028.

Synthesis of 6c from the Reaction of Norbornene with 1-Bromo-3-methoxypropyne in the Presence of Formic Acid. **6c** was prepared in 35% yield by following a procedure similar to that described for **6a**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.73 (d, J = 10.5 Hz, 1 H, H(16b)), 0.77 (d, J = 7.6 Hz, 1 H, H(15)), 0.86 (d, J = 7.6 Hz, 1 H, H(10)), 1.23–1.89 (m, 13 H), 2.29–2.43 (m, 4 H), 3.26 (s, 3 H), 3.52 (s, 2 H), 5.62 (d, J = 6.6 Hz, 1 H, H(2)). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 28.86 (d), 28.96 (d), 29.01 (t), 30.31 (t), 30.81 (t), 31.35 (s), 33.15 (d), 34.93 (d), 35.29 (t), 35.71 (t), 36.80 (d), 39.01 (t), 58.16 (q), 74.36 (t), 127.47 (d), 140.73 (s). IR (neat): 2949, 1653, 1559, 1451, 721 cm^{-1}. HRMS: calcd for $C_{18}H_{26}O$ 258.1984, found 258.1979.

Reaction of 1,4-Epoxy-1,4-dihydronaphthalene with Phenylacetylene. To a solution of $Pd(PPh_3)_4$ (0.120 g, 0.104 mmol), phenylacetylene (0.255 g, 2.50 mmol), 1-bromo-2-phenylacetylene (0.455 g, 2.50 mmol), and 1,4-epoxy-1,4-dihydronaphthalene (0.720 g, 5.00 mmol) under N_2 was added a solution of toluene (10 mL) and triethylamine (1.01 g, 10.0 mmol). The system was continuously stirred for 24 h at 80 °C. The solvent was removed and the residue was separated on a silica gel column using a mixture of hexanes and ethyl acetate (10/1, v/v) as the eluent to give **8a** (0.595 g, 1.53 mmol) in 61% yield and **7a** (0.177 g, 0.88 mmol) in 35% yield. The spectral data for **8a** are as follows. (The general atomic labeling scheme **19** is employed for compounds 8. This atomic labeling is different from that used in Figure 2.)



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^1H NMR (300 MHz, $CDCl_3$): δ 2.04 (d, J = 6.8 Hz, 1 H, H(2) or H(3)), 2.10 (d, J = 6.8 Hz, 1 H, H(2) or H(3)), 2.89 (br s, 1 H, –OH), 4.17 (br s, 1 H, H(14)), 4.60–4.62 (m, 1 H, H(13)), 5.23 (s, 1 H, H(1) or H(4)), 5.48 (s, 1 H, H(1) or H(4)), 6.20 (d, J = 9.6 Hz, 1 H, H(22)), 6.73 (dd, J = 9.6 Hz, J = 2.8 Hz, 1 H, H(21)), 7.17–7.38 (m, 9 H), 7.44 (t, J = 7.1 Hz, 2 H), 7.64 (d, J = 7.6 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 24.36 (d, C(2) or C(3)), 25.67 (d, C(2) or C(3)), 46.55 (d, C(14)), 68.27 (d, C(13)), 80.01 (d, C(1), C(4)), 119.65 (d, C(21)), 126.50 (d), 126.70 (d), 127.03 (d), 127.59 (d), 127.75 (d), 128.65 (d, C(22)), 128.79 (d), 128.97 (d), 129.13 (d), 129.79 (s), 132.12 (s), 132.81 (s), 134.72 (s), 139.38 (s), 146.15 (s), 146.18 (s). IR (neat): 3472, 3027, 1638, 1491, 1452, 1215, 1189, 756, 696 cm^{-1}. HRMS: calcd for $C_{28}H_{22}O_2$ 390.1621, found 390.1599.

Synthesis of 8b from the Reaction of 5,8-Dimethoxy-1,4-epoxy-1,4-dihydronaphthalene with Phenylacetylene. **8b** was prepared in 58% yield by following a procedure similar to that described for **8a**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.11 (d, J = 7.0 Hz, 1 H, H(2) or H(3)), 2.23 (d, J = 7.0 Hz, 1 H, H(2) or H(3)), 2.81 (s, 1 H, –OH), 3.80 (s, 3 H, –OMe), 3.82 (s, 3 H, –OMe), 3.86 (s, 3 H, –OMe), 3.88 (s, 3 H, –OMe), 4.05 (br s, 1 H, H(14)), 5.02 (m, 1 H, H(13)), 5.61 (s, 1 H, H(1) or H(4)), 5.68 (s, 1 H, H(1) or H(4)), 6.25 (d, J = 9.8 Hz, 1 H, H(22)), 6.72 (s, 2 H, H(6), H(7)), 6.81 (d, J = 9.0 Hz, 1 H, H(17) or H(18)), 6.87 (d, J = 9.0 Hz, 1 H, H(17) or H(18)), 7.15 (dd, J = 9.8 Hz, J = 2.9 Hz, 1 H, H(21)), 7.36 (t, J = 7.5 Hz, 1 H), 7.45 (t, J = 7.3 Hz, 2 H), 7.66 (d, J = 7.7 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 23.89 (d, C(2) or C(3)), 25.14 (d, C(2) or C(3)), 46.04 (d, C(14)), 56.14 (q, –OMe), 56.27 (q, –OMe), 56.49 (q, –OMe), 61.06 (d, C(13)), 78.13 (d, C(1) or C(4)), 78.28 (d, C(1) or C(4)), 110.85 (d), 111.37 (d), 111.55 (d), 112.09 (d), 120.82 (d, C(21)), 123.08 (s), 123.60 (s), 126.57 (d), 127.59 (d, C(22)), 128.58 (d), 129.03 (d), 129.68 (s), 132.20 (s), 135.37 (s), 135.51 (s), 139.22 (s), 147.49 (s), 147.62 (s), 149.65 (s), 151.37 (s). IR (KBr): 3494, 2934, 2834, 1596, 1493, 1259, 1004, 989, 811, 694 cm^{-1}. HRMS: calcd for $C_{32}H_{30}O_6$ 510.2045, found 510.2045. Mp: 130 °C.

Reaction of 1,4-Epoxy-1,4-dihydronaphthalene with 1-Bromo-2-phenylacetylene in the Presence of Formic Acid. A round-bottom flask containing $Pd(PPh_3)_4$ (0.120 g, 0.104 mmol), 1-bromo-2-phenylacetylene (0.455 g, 2.50 mmol), 1,4-epoxy-1,4-dihydronaphthalene (1.44 g, 10.0 mmol), and toluene (10 mL) was purged with nitrogen three times. To the flask were added triethylamine (1.01 g, 10.0 mmol) and formic acid (0.46 g, 10 mmol). The solution was then stirred at 60 °C for 8 h. Addition of ether (15 mL) was followed by extraction with water four times. The organic layer was dried by anhydrous $MgSO_4$, filtered, concentrated, and then separated on a silica gel column using a mixture of hexanes and ethyl acetate (10/1, v/v) as the eluent to

Table 1. Crystal and Data Collection Parameters

	5b	8b
empirical formula	$C_{30}H_{30}$	$C_{32}O_6H_{30}$
fw	390.57	510.59
cryst size, mm	0.20 × 0.30 × 0.40	0.40 × 0.45 × 0.45
cryst syst	orthorhombic	triclinic
space group	*Pbca*	$P\bar{1}$
a, Å	11.329(7)	9.2000(23)
b, Å	16.218(12)	9.912(4)
c, Å	24.297(8)	15.164(6)
α, deg		83.73(3)
β, deg		76.60(3)
γ, deg		77.00(3)
cell vol, Å^3	4464(4)	1308.2(9)
Z	8	2
D(calcd), Mg m^{-3}	1.162	1.296
abs coeff, mm^{-1}		0.08
F(000)	1682	540
scan type	$\theta/2\theta$	$\theta/2\theta$
scan speed, deg/min	2.06–8.24	2.06–8.24
2θ range, deg	18.78–23.20	18.68–23.18
index ranges	$0 \le h \le 12, 0 \le k \le 17, 0 \le l \le 26$	$-9 \le h \le 9, 0 \le k \le 10, -15 \le l \le 16$
no. of rflns collected	2909	3419
no. of indep rflns	2909 (1146 > 2.0 $\sigma(I)$)	3409 (2489 > 2.0 $\sigma(I)$)
R	0.046	0.037
R_w	0.041	0.035
goodness of fit	1.31	2.22
largest diff peak/hole, e Å^{-3}	0.170/–0.16	0.170/–0.190

give **9a** (0.761 g, 1.95 mmol) in 78% yield. The spectral data for **9a** are as follows. (For clear signal assignments, the atom-labeling scheme shown in eq 4 is used for compound **9**.) ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, J = 7.4 Hz, 2 H, H(2)), 1.67 (br s, 2 H, H(5)), 2.44 (t, J = 7.4 Hz, 1H, H(3)), 4.70 (br s, 2 H, H(6)), 5.50 (s, 2 H, H(1)), 7.05–7.48 (m, 13 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 28.46 (d, C(2)), 33.57 (d, C(5)), 37.30 (d, C(3)), 44.89 (s, C(4)), 78.21 (d, C(1)), 78.73 (d, C(6)), 119.26 (d), 119.31 (d), 125.40 (d), 125.61 (d), 125.80 (d), 127.48 (d), 128.41 (d), 146.16 (s), 147.94 (s), 148.21 (s). IR (KBr): 3007, 1452, 993, 906, 839, 752, 700 cm^{-1}. HRMS: calcd for $C_{28}H_{22}O_2$ 390.1622, found 390.1624. Mp: 235 °C.

Synthesis of 9b from 5,8-Dimethoxy-1,4-epoxy-1,4-dihydronaphthalene and 1-Bromo-2-phenylacetylene in the Presence of Formic Acid. 9b was prepared in 80% yield by following a procedure similar to that described for **9a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.46 (d, J = 7.3 Hz, 2 H, H(2)), 1.72 (br s, 2 H, H(5)), 2.41 (t, J = 7.3 Hz, 1 H, H(3)), 3.77 (s, 6 H, –OMe), 3.85 (s, 6 H, –OMe), 4.95 (br s, 2 H, H(6)), 5.73 (s, 2 H, H(1)), 6.61 (s, 2 H), 6.66 (s, 2 H), 7.17 (t, J = 7.2 Hz, 1 H), 7.24 (t, J = 7.6 Hz, 2 H), 7.36 (d, J = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 27.97 (d, C(2)), 33.20 (d, C(5)), 36.97 (d, C(3)), 44.82 (s, C(4)), 56.15 (q, –OMe), 56.19 (q, –OMe), 76.35 (d, C(1)), 76.93 (d, C(6)), 111.06 (d), 125.31 (d), 127.41 (d), 128.35 (d), 137.16 (s), 137.44 (s), 146.09 (s), 147.19 (s), 147.23 (s). IR (KBr): 2939, 2832, 1496, 1452, 1255, 1080, 994, 906, 802, 708 cm^{-1}. HRMS: calcd for $C_{32}H_{30}O_6$ 510.2043, found 510.2054. Mp: 130 °C.

Synthesis of 9c from *exo*-Dimethyl 7-Oxabicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate and 1-Bromo-2-phenylacetylene in the Presence of Formic Acid. 9c was prepared in 97% yield by following a procedure similar to that described for **9a**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (d, J = 7.6 Hz, 2 H, H(2)), 1.37 (t, J = 7.6 Hz, 1 H, H(3)), 1.52 (br s, 2 H, H(5)), 2.94 (br s, 2 H), 3.09 (br s, 2 H), 3.62 (s, 6 H, –OMe), 3.70 (s, 6 H, –OMe), 4.28 (br s, 2 H, H(6)), 5.04 (s, 2 H, H(1)), 7.14 (t, J = 7.2 Hz, 1 H), 7.22 (t, J = 7.1 Hz, 2 H), 7.31 (d, J = 7.0 Hz, 2 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 21.10 (d, C(2)), 23.75 (d, C(3)), 28.35 (s, C(4)), 28.52 (d, C(5)), 51.98 (q, –OMe), 52.13 (q, –OMe), 52.43 (d), 52.74 (d), 78.16 (d, C(6)), 78.55 (d, C(1)), 125.79 (d), 127.71 (d), 128.72 (d), 145.07 (s), 171.38 (s), 171.50 (s). IR (KBr): 3450, 2952, 1738, 1437, 1353, 1193, 938, 701 cm^{-1}. HRMS: calcd for $C_{28}H_{30}O_{10}$ 526.1841, found 526.1812. Mp: 182 °C.

X-ray Structure Determinations. All data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo source (Kα radiation, 0.7093 Å). The structures were solved by direct methods and refined by a full-matrix least-squares method based on F values. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were positioned on geometric grounds (C–H = 0.96 Å). Atomic scattering factors were taken from ref 19. Crystallographic computations were carried out on a Micro VAX III computer using the NRCC-SDP-VAX structure determination package.[20] Relevant crystallographic parameters are assembled in Table 1.

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Supplementary Material Available: Tables of atomic coordinates, complete bond lengths and angles, and anisotropic thermal parameters for **5b** and **8b** (8 pages). Ordering information is given on any current masthead page.

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