JOC Article

Palladium-Catalyzed [2 + 2 + 2] Cocyclotrimerization of Benzynes with Bicyclic Alkenes: An Efficient Route to Anellated 9,10-Dihydrophenanthrene Derivatives and Polyaromatic Compounds

Thiruvellore Thatai Jayanth, Masilamani Jeganmohan, and Chien-Hong Cheng*

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30013, ROC

chcheng@mx.nthu.edu.tw

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An efficient method for the cocyclotrimerization of bicyclic alkenes and benzynes catalyzed by palladium phosphine complexes to give the corresponding norbornane anellated 9,10-dihydrophenanthrene derivatives is described. Bicyclic alkenes **1a**−**i** undergo [2 + 2 + 2] cocyclotrimerization with benzynes generated from precursors **2a**−**d** [2-(trimethylsilyl)phenyl triflate (**2a**), 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**2b**), 6-(trimethylsilyl)-2,3-dihydro-1H-5-indenyl triflate (**2c**), 4-methyl-2-(trimethylsilyl)phenyl triflate (**2d**)] in the presence of $PdCl_2(PPh_3)_2$ in acetonitrile at ambient temperature to yield anellated 9,10-dihydrophenanthrene products **3a**−**r** in moderate to excellent yields. The [2 + 2 + 2] cocyclotrimerization products from oxa- and azabicyclic alkenes can be applied for the synthesis of polyaromatics, substituted benzo[*b*]triphenylenes (**8a**−**f**), via a simple Lewis acid mediated deoxyaromatization in good yields. In addition the [2 + 2 + 2] products undergo retro Diels−Alder reaction readily, providing a new method for the synthesis of substituted phenanthrenes and for generating isobenzofurans. A plausible mechanism is proposed to account for the catalytic [2 + 2 + 2] cycloaddition reaction.

Introduction

Transition-metal-catalyzed [2 + 2 + 2] cyclotrimerization reactions have been an area of extensive investigation and have played a crucial role in the development of synthetic methodology in organic synthesis.[1] The utility of arynes in this type of reaction has generated a special interest in the past 5 years. Even though benzynes in metal-mediated cycloaddition chemistry are well-known, their use has been restricted to only stoichiometric reactions.[2] However, the development of new methods for the generation of arynes under mild conditions[3] has led to the exploration of aryne as a potential cycloaddition partner in metal-catalyzed reactions. In 1998, Pena et al. reported a palladium-catalyzed trimerization of benzynes to give triphenylenes.[4] Later, the same group showed that benzynes underwent [2 + 2 + 2] cocyclotrimerization with alkynes[5] (alkyne-benzyne-benzyne) to give the corresponding aromatic products. Yamamoto and co-workers also reported similar cocyclizations of arynes with alkynes[6] and with allyl chlorides[7] using palladium complexes as catalysts. In this context, we very recently have developed a nickel-catalyzed highly chemoselective cocyclotrimerization of benzynes with allenes.[8] Although several types of copartners such as alkynes, allylic chlorides, and allenes have been used, bicyclic alkene as a copartner for the [2 + 2 + 2] cocyclotrimerization with benzyne derivatives has not been explored.

Our continuous interest in metal-mediated cyclotrimerization reaction[9] and bicyclic alkene chemistry[10] prompted us to explore the possibility of the cocyclotrimerization of bicyclic alkenes with benzynes. In this

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[2] (a) Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992. (b) Bennett, M. A.; Wenger, E. *Organometallics* **1995**, *14*, 1267. (c) Bennett, M. A.; Hockless, D. C. R.; Wenger, E. *Organometallics* **1995**, *14*, 2091. (d) Bennett, M. A.; Wenger, E. *Organometallics* **1996**, *15*, 5536. (e) Deaton, K. R.; Gin, M. S. *Org Lett.* **2003**, *5*, 2477. For reviews, see: (f) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (g) Buchwald, S. L.; Broene, R. D. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Willkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, pp 771−784. (h) Bennett, M. A.; Schwemlein, H. P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296. (i) Bennett, M. A.; Wenger, E. *Chem. Ber.* **1997**, *130*, 1029.

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[5] (a) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Am. Chem. Soc.* **1999**, *121*, 5827. (b) Peña, D.; Pérez, D.; Guitián, E.; Castedo, L. *J. Org. Chem.* **2000**, *65*, 6944.

[6] (a) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533. (b) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *Tetrahedron Lett.* **2000**, *41*, 729. (c) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280.

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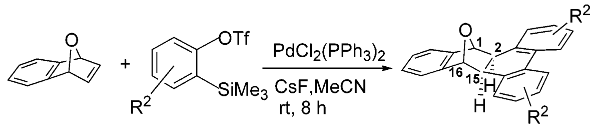
10.1021/jo048702k CCC: $27.50

SCHEME 1



1a **2a**: $R^2 = H$ **3**

2b: $R^2 = 3,4\text{-}Me_2$

2c: $R^2 = 3,4\text{-}(CH_2)_3\text{-}$

2d: $R^2 = 4\text{-}Me$

paper we wish to report the first synthesis of anellated 9,10-dihydrophenanthrene derivatives from the cycloaddition reaction of two benzynes with a bicyclic alkene. Furthermore, we wish to demonstrate that the products from oxa- and azabicyclic alkenes and benzyne derivatives are very useful precursors for the synthesis of polycyclic aromatic hydrocarbons and for the generation of isobenzofurans as well as phenanthrene derivatives.

Results and Discussion

Treatment of oxabenzonorbornadiene (0.50 mmol) (**1a**), benzyne precursor 2-(trimethylsilyl)phenyl triflate (1.0 mmol) (**2a**), CsF (1.5 mmol), and $PdCl_2(PPh_3)_2$ (0.025 mmol, 5 mol %) in acetonitrile at ambient temperature for 8 h yielded [2 + 2 + 2] cocyclotrimerization product **3a** in 94% yield (Scheme 1). The structure of **3a** was thoroughly characterized by its spectral data. Control experiments revealed that in the absence of palladium catalyst, no desired product was observed. The catalytic reaction is highly stereoselective, giving the exo isomer as the exclusive product. Exo stereochemistry of this product was established on the basis of the coupling constant of protons H-2 and H-15 on the norbornane-phenanthrene ring junction and bridgehead protons H-1 and H-16 (see Scheme 1). It is well-known that for norbornene derivatives the coupling constant between an endo proton at C-15 and a bridgehead proton at C-16 is nearly zero, whereas the value between the exo and a bridgehead proton is ca. 3 Hz and can be clearly observed. For compound **3a**, both sets of protons appear as singlets in its ^1H NMR spectrum at δ 5.40 and 3.42, thereby confirming the exo stereochemistry.[10d,11]

To optimize the present catalytic reaction, the reaction of **1a** and **2a** in the presence of CsF was carried out under different reaction conditions. The catalytic activities of various palladium complexes in CH_3CN for the [2 + 2 + 2] cocyclotrimerization were first examined. Phosphine-free palladium complexes $PdCl_2$, $Pd(OAc)_2$, $Pd(dba)_2$, and $PdCl_2(CH_3CN)_2$ in CH_3CN were active for the reaction but gave **3a** in low yields (42−46%). The use of palladium phosphine complexes such as $Pd(PPh_3)_4$ and $PdCl_2(dppe)$ greatly improved the catalytic efficiency, affording **3a** in 82% and 76% yield, respectively. $PdCl_2(PPh_3)_2$ shows the highest catalytic activity, giving **3a** in 94% yields. A brief examination of the effect of solvent using $PdCl_2(PPh_3)_2$ as the catalyst on the yield of **3a** revealed that CH_3CN was the solvent of choice. Other solvents such as THF, dioxane, toluene, and CH_2Cl_2 were totally ineffective for the [2 + 2 + 2] cycloaddition reaction. The reaction of **1a** and **2a** in the absence of any metal catalyst system gave the [2 + 2] cycloaddition product in quantitative yields.[12] When $NiCl_2(PPh_3)_2/Zn$ was used as the catalyst system the [2 + 2 + 2] cyclotrimerization product was obtained in only 4% yield. The [2+2] cycloaddition of **1a** and benzyne appeared to be the major reaction in this case.

This palladium-catalyzed [2 + 2 + 2] cocyclotrimerization reaction was successfully extended to different bicyclic alkenes and substituted benzynes (Table 1). The reaction of 2-(trimethylsilyl)phenyl triflate (**2a**) with norbornene[13] (**1b**), norbornadiene (**1c**), benzonorbornadiene (**1d**), and 2,5-norbornadiene-2,3-dicarboxylic acid diethyl ester (**1e**) gave the corresponding cyclotrimerization products **3b**, **3c**, **3d**, and **3e** in 87%, 85%, 89%, and 54% yields, respectively (entries 2−5). Azabenzonorbornadiene (**1f**) also reacted with benzyne to give the [2 + 2 + 2] cocyclotrimerization product **3f** in 72% yield. Under similar reaction conditions, the cocyclotrimerization of bicyclic alkenes with substituted benzynes also proceeded smoothly to give the corresponding anellated 9,10-dihydrophenanthrene derivatives. Thus, oxabenzonorbornadiene (**1a**) reacted with substituted benzynes **2b** and **2c** to give anellated 9,10-dihydrophenanthrene derivatives **3g** and **3h** in good yields (entries 7 and 8). 6,7-Methylenedioxy-oxabenzonorbornadiene (**1g**) underwent cocyclotrimerization with benzynes **2a**−**c** to afford products **3i**, **3j**, and **3k** in 82%, 78%, and 71% yields, respectively (entries 9−11). Similarly, treating 6,7-dimethoxy-oxabenzonorbornadiene (**1h**) and 6-methyloxabenzonorbornadiene (**1i**) with **2a**, and **2b** afforded the corresponding [2 + 2 + 2] products (entries 12−15) **3l**−**o** in 77−88% yields. When 4-methyl-substituted benzyne precursor **2d** was employed in the cocyclotrimerization with **1a**, a mixture of regioisomers as shown in Scheme 3 was obtained, as expected for a cycloaddition reaction using 4-methylbenzyne as a substrate. Thus the present [2 + 2 + 2] cyclotrimerization reaction was found to be compatible with a variety of bicyclic alkenes and benzyne precursors.

On the basis of the known chemistry of palladium,[4−10] bicyclic alkenes, and arynes, we propose the mechanism in Scheme 2 to account for the present palladium-catalyzed [2 + 2 + 2] cocyclotrimerization reaction. The

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(9) (a) Rayabarapu, D. K.; Sambaiah, T.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2001**, *40*, 1286. (b) Huang, D.-J.; Rayabarapu, D. K.; Li, L.-P.; Sambaiah, T.; Cheng, C.-H. *Chem. Eur. J.* **2000**, *6*, 3706. (c) Duan, J. P.; Cheng, C. H. *Tetrahedron Lett.* **1993**, *34*, 4019. (d) Duan, J. P.; Cheng, C. H. *Organometallics*. **1995**, *14*, 1608. (e) Feng, C. C.; Nandi, M.; Sambaiah, T.; Cheng, C. H. *J. Org. Chem.* **1999**, *64*, 3538. (f). Rayabarapu, D. K.; Chiou, C. F.; Cheng, C. H. *Org. Lett.* **2002**, *4*, 1679.

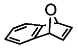
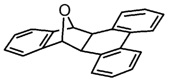
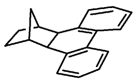
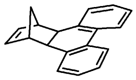
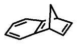
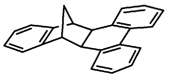
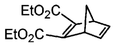
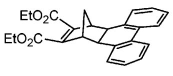
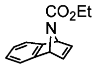
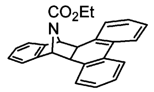
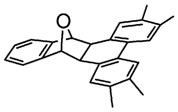
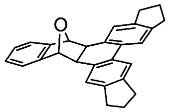
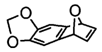
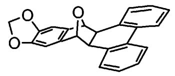
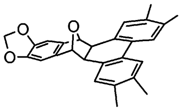
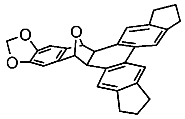
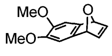
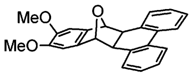
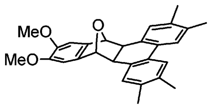
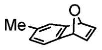
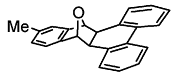
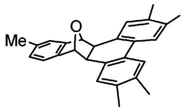
(10) (a) Hsiao, T.-Y.; Santhosh, K. C.; Liou, K.-F.; Cheng, C.-H. *J. Am. Chem. Soc.* **1998**, *120*, 12232. (b) Huang, D.-J.; Sambaiah, T.; Cheng, C.-H. *New. J. Chem.* **1998**, *22*, 1147. (c) Sambaiah, T.; Li, L.-P.; Huang, D.-J.; Lin, C.-H.; Rayabarapu, D. K.; Cheng, C.-H. *J. Org. Chem.* **1999**, *64*, 3663. (d) Sambaiah, T.; Huang, D.-J.; Cheng, C.-H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 195. (e) Shanmugasundaram, M.; Wu, M.-S.; Jeganmohan, M.; Huang, C.-H.; Cheng, C.-H. *J. Org. Chem.* **2002**, *67*, 7724.

(11) (a) Smith, C. D. *J. Am. Chem. Soc.* **1966**, *88*, 4273.

(12) The formal triple bond of benzyne is unique with regard to its ability to undergo thermal [2 + 2] cycloaddition reaction with an olefinic bond; this exception is accounted for by invoking a pseudo excitation effect due to the unusually low lying LUMO of benzyne. (a) Hayes, D. M.; Hoffmann, R. *J. Phys. Chem.* **1972**, *76*, 656. (b) Epiotis, N. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 751.

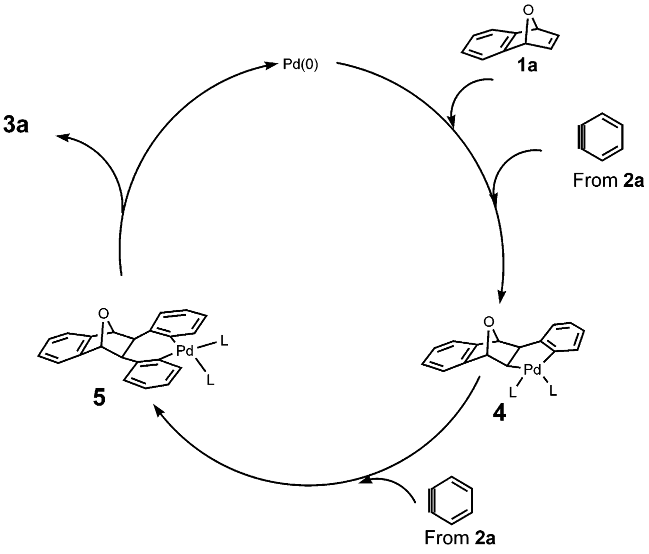
(13) A product similar to **3b** has been reported by the coupling of aryl halides and norbornene catalyzed by palladium complexes in the presence of a base. (a) Catellani, M.; Chiusoli, G. P. *J. Org. Met. Chem.* **1985**, 286, *C13*. For a Domino coupling of aryl halides and norbornene see, Albrecht, K.; Reiser, O.; Weber, M.; Knieriem, K.; de Meijere, A. *Tetrahedron* **1999**, *50*, 383.

TABLE 1. Results of Palladium-Catalyzed [2 + 2 + 2] Cocyclotrimerization of Bicyclic Alkenes and Benzynes[a]

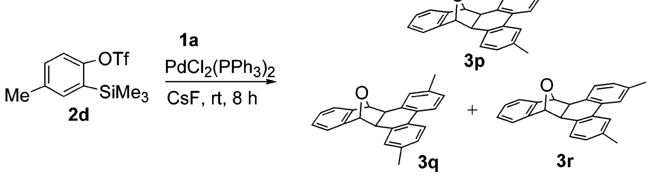
Entry	**1**	**2**	Product		Yield (%)[b]
1	 **1a**	**2a**		**3a**	90 (94)
2	 **1b**	**2a**		**3b**	87
3	 **1c**	**2a**		**3c**	85
4	 **1d**	**2a**		**3d**	89
5	 **1e**	**2a**		**3e**	54
6	 **1f**	**2a**		**3f**	72
7	**1a**	**2b**		**3g**	82
8	**1a**	**2c**		**3h**	73
9	 **1g**	**2a**		**3i**	82
10	**1g**	**2b**		**3j**	78
11	**1g**	**2c**		**3k**	71
12	 **1h**	**2a**		**3l**	79
13	**1h**	**2b**		**3m**	77
14	 **1i**	**2a**		**3n**	88
15	**1i**	**2b**		**3o**	86

[a] All reactions were carried out under the following conditions: bicyclic alkene (**1**, 0.50 mmol), benzyne precursor (**2**, 1.00 mmol), $PdCl_2(PPh_3)_2$ (0.025 mmol), CsF (1.50 mmol), and CH_3CN (2 mL) for 8 h. [b] Isolated yields; yield in parentheses was determined by ^1H NMR integration method using mesitylene as an internal standard.

SCHEME 2

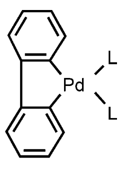


SCHEME 3



catalysis is likely initiated by the reaction of Pd(0) with bicyclic alkene and benzyne to form palladacycle **4**. A second benzyne insertion into **4** gives palladacycloheptadiene **5**. Reductive elimination of **5** yields the final product and regenerates the Pd(0) catalyst. Complexes similar to palladacycle **4** have been isolated and characterized previously by the addition of a (phenyl)iodopalladium complex to norbornene followed by cyclometalated deprotonation.[14]

An alternative pathway via the cyclometalation of two benzyne molecules to yield palladacyclopentadiene complex **7** as the first step is also possible, but it is less likely considering that an excess amount of alkene exists in the reaction medium while benzyne is being generated. Moreover, if at all complex **7** is formed then it is highly feasible that a third benzyne can insert into the palladacycle to give triphenylene. Under our reaction conditions, the formation of triphenylene was not observed.



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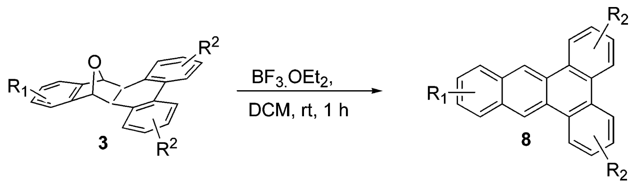
The involvement of the benzyne moiety in the present catalytic reaction is strongly supported by the results of the cocyclotrimerization reaction of **1a** and **2d** affording a mixture of three regioisomeric products **3p**, **3q**, and **3r** in approximately a 2:1:1 ratio as determined by GC−MS and ^{1}H NMR. The observation indicated that the two carbons originally attached to the silyl and the OTf groups of **2d** have the same reactivity toward oxabicyclic alkene **1a**, in agreement with the formation of a benzyne moiety from **2d** prior to the reaction with **1a**.

SCHEME 4



The present [2 + 2 + 2] cocyclotrimerization products undergo deoxyaromatization readily with the help of a Lewis acid at room temperature, providing a simple yet extremely efficient route to various substituted polycyclic aromatic hydrocarbons. Several reports of the synthesis of benzo[*b*]triphenylenes are known in the literature,[15] but complicated procedures, harsh reaction conditions, poor yields, and numerous synthetic steps limit the traditional methods for the synthesis of polycyclic aromatic hydrocarbons having five or more benzene rings.[16] Treatment of product **3a** with 1.5 equiv of $BF_3{\cdot}OEt_2$ in dichloromethane at room temperature for 1 h afforded benzo[*b*]triphenylene (1,2,5,6-dibenzoanthracene) (**8a**) in 85% yield (Scheme 4). Similarly, **3i**, **3j**, **3k**, **3m**, and **3o** underwent deoxyaromatization on treatment with 1.5 equiv of $BF_3{\cdot}OEt_2$ to afford the corresponding substituted benzo[*b*]triphenylenes **8a**−**f** in 81%, 83%, 76%, 78%, and 80% yields, respectively, as shown in Table 2, entries 2−6. It is interesting to note that most of these polycyclic aromatic hydrocarbons show strong photoluminescence in the solid state and in solutions and are potentially useful as electroluminescent and photoluminescent materials.[17] The application of these materials in an organic light-emitting diode is underway.

The generation of isobenzofurans has been a subject of interest in organic synthesis.[18] They have been widely used as dienes in the Diels−Alder reactions to provide substituted 7-oxabicyclo[2.2.1]heptanes, which are key intermediates in natural product synthesis.[19,20] As a

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[15] (a) Harvey, R. G.; Lebya, C.; Konieczny, M.; Fu, P. P.; Sukumaran, K. B. *J. Org. Chem.* **1978**, *43*, 3423. (b) Minsky, A.; Rabinowitz, M. *Synthesis* **1983**, 497. (c) Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1981**, *46*, 2740. (d) Moursounidis, J.; Wege, D. *Aus. J. Chem.* **1988**, *41*, 235. (e) Fitzgerald, J. J.; Drysdale, N. E.; Olofson, R. A. *J. Org. Chem.* **1992**, *57*, 7122. (f) Yang, C.; Yang, D. T. C.; Harvey, R. G. *Synth. Lett.* **1992**, *10*, 799.

[16] (a) Harvey, R. G. In *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH: New York, 1997.

[17] (a) Shih, H.-T.; Shih, H.-S.; Cheng, C.-H. *Org. Lett.* **2001**, *6*, 881. (b) Shih, H.-T.; Lin, C.-H.; Shih, H.-H.; Cheng, C.-H. *Adv. Mater.* **2002**, *14*, 1409.

[18] (a) Haddadin, M. J. *Heterocycles* **1978**, *9*, 865. (b) Friedrichsen, W. *Adv. Heterocycl. Chem.* **1980**, *26*, 135. (b) Rickborn, B. *Advances in Theoretically Interesting Molecules*; Thummel, R. P., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, Chapter 1. (c) Chan, S.-H.; Yick, C.-Y.; Wong, H. N. C. *Tetrahedron* **2002**, *58*, 9413.

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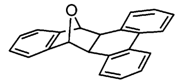
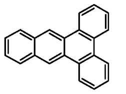
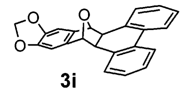
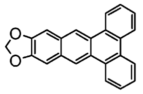
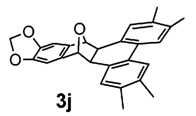
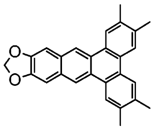
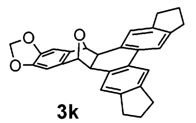
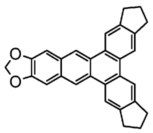
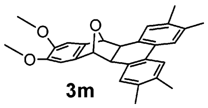
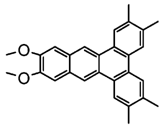
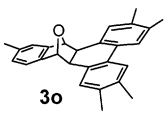
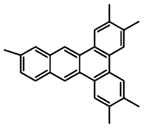
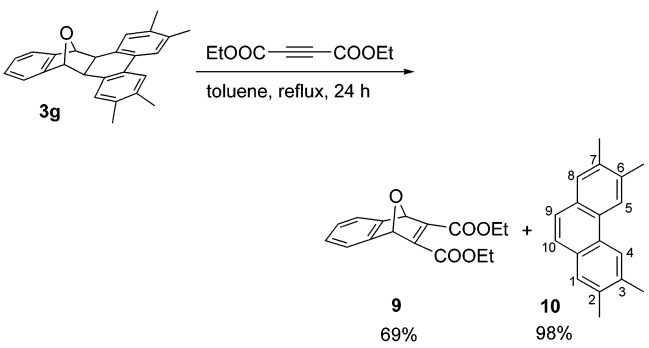
TABLE 2. Results of Deoxyaromatization of [2 + 2 + 2] Cocyclotrimerization Products 3[a]

Entry	3	Product		Yield (%)[b]
1	 **3a**		**8a**	85(94)
2	 **3i**		**8b**	81
3	 **3j**		**8c**	83
4	 **3k**		**8d**	76
5	 **3m**		**8e**	78
6	 **3o**		**8f**	80

[a] All reactions were carried out under the following conditions: **3** (1.00 mmol), $BF_3{\cdot}OEt_2$(1.5 mmol), and CH_2Cl_2 (2.0 mL) for 1 h. [b] Isolated yields; yield in parentheses was determined by ^1H NMR integration method using mesitylene as an internal standard.

SCHEME 5



result of the high reactivity and readily polymerizing nature at room temperature, their generation has been a challenge to organic chemists.[21]

When product **3g** was refluxed in toluene for 24 h in the presence of diethyl acetylenedicarboxylate, the corresponding cycloadduct product **9** and the substituted phenanthrene **10** were obtained in high yields (Scheme 5). The present method appears to provide a convenient route for new precursors of isobenzofurans and for the synthesis of phenanthrenes with no substituent at the 9- and 10-positions. It is noteworthy that all previously reported constructions of phenanthrene via benzyne invariably have substituents at the 9- and 10-positions of the phenanthrene ring in addition to the other substituents.[5-7] The reaction shown in Scheme 5 is complementary to the previously reported method in this respect.

Conclusion

In conclusion, this work has successfully demonstrated a [2 + 2 + 2] cocyclotrimerization of benzyne with a bicyclic alkene, yielding the norbornane anellated 9,10-dihydrophenanthrene units in good yields. In addition, the [2 + 2 + 2] cocyclotrimerization products readily undergo aromatization and retro Diels−Alder reactions, providing a convenient route for the synthesis of polyaromatic hydrocarbons and phenanthrenes and for the generation of isobenzofurans. Further studies into the possibility of novel cyclotrimerization partner for benzynes and also on various possible synthetic transformations of the products described above are underway in our laboratories.

Experimental Section

Procedure for [2 + 2 +2] Cocyclotrimerization of Bicyclic Alkene with Benzyne. A round-bottom sidearm flask (25 mL) containing bicyclic alkene (0.500 mmol), $PdCl_2(PPh_3)_2$ (0.0175 g, 5 mol %), and CsF (0.226 g, 1.50 mmol) was evacuated and purged with nitrogen gas three times. Freshly distilled dry acetonitrile (2.0 mL) and benzyne precursor 2-(trimethylsilyl)aryl triflate (2.0 mmol) were added. The

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reaction mixture was stirred at room temperature for 8 h. The reaction mixture was then filtered through Celite and silica gel and eluted with dichloromethane. The filtrate was concentrated, and the residue was purified on a silica gel column using hexanes−ethyl acetate as eluent to afford the desired products.

Products **3a**−**o** were obtained according to this procedure. Product yields of these reactions are listed in Table 1, and the spectral data of representative products are listed below. All of these products decomposed during melting point determination, likely undergoing retro Diels−Alder reactions, at temperature >130 °C.

(2*R,15*S**)-23-Oxahexacyclo[14.6.1.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,22}]tricosa-3(8),4,6,9(14),10,12,17,19,21-nonaene (3a).** ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.94 (d, J = 6.6 Hz, 2 H), 7.44−7.41 (m, 4 H), 7.32−7.25 (m, 6 H), 5.40 (s, 2 H), 3.42 (s, 2 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 145.7, 135.0, 131.8, 129.9, 128.0, 127.0, 126.9, 122.7, 119.2, 90.3, 43.9. HRMS calcd for $C_{22}H_{16}O$ 296.1201, found 296.1213.

(2*R,15*S**)Pentacyclo[14.2.1.0^{2,15}.0^{3,8}.0^{9,14}]nonadeca-3(8),4,6,9(14),10,12-hexaene (3b).** ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.87 (d, J = 6.6 Hz, 2 H), 7.26−7.21 (m, 6 H), 3.24 (s, 2 H), 2.41 (s, 2 H), 1.73−1.72 (m, 2 H), 1.66−1.65(m, 2 H), 1.44 (d, J = 12.0 Hz, 1 H), 1.06 (d, J = 12.0 Hz, 1H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 137.6, 131.3, 130.1, 127.6, 126.2, 122.0, 49.5, 45.8, 33.2, 30.2. HRMS calcd for $C_{19}H_{18}$ 246.1409, found 246.1404.

(2*R,15*S**)Pentacyclo[14.2.1.0^{2,15}.0^{3,8}.0^{9,14}]nonadeca-3(8),4,6,9(14),10,12,17-heptaene (3c).** ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.95 (d, J = 12.0 Hz, 2 H), 7.37 (d, J = 8.4 Hz, 2 H), 7.30−7.27 (m, 4 H), 6.41 (s, 2 H), 3.11 (s, 2 H), 3.04 (s, 2 H), 1.44 (d, J = 12.0 Hz, 1 H), 1.21 (d, J = 12.0 Hz, 1 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 137.8, 137.6, 131.8, 130.2, 127.6, 126.2, 122.3, 55.4, 42.7, 41.2. HRMS calcd for $C_{19}H_{16}$ 244.1252, found 244.1255.

Ethyl (2*R,15*S**)-23-Azahexacyclo[14.6.1.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,22}]tricosa-3(8),4,6,9(14),10,12,17(22),18,20-nonaene-23-carboxylate (3f).** ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.88 (d, J = 7.8 Hz, 2 H), 7.45 (d, J = 7.2 Hz, 4 H), 7.31−7.21 (m, 6 H), 5.27 (bd, 2 H), 3.66 (bd, 2 H), 3.60 (s, 2 H), 0.84 (s, 3 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 155.3, 145.3, 134.3, 131.6, 130.2, 128.1, 127.5, 126.5, 122.5, 119.8, 71.8, 60.9, 44.1, 14.1. HRMS calcd for $C_{25}H_{21}N0_2$ 367.1572, found 367.1569.

(2*R,15*S**)-5,6,11,12-Tetramethyl-23-oxahexacyclo[14.6.1.0^{2,15}.0^{3,8}.0^{9,14}.0^{17,22}]tricosa-3(8),4,6,9(14),10,12,17(22),18,20-nonaene (3g).** ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.72 (s, 2 H), 7.48 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.4 Hz, 2 H), 7.20 (s, 2 H), 5.41 (s, 2 H), 3.55 (s, 2 H), 2.36 (s, 12 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 145.9, 136.0, 135.0, 132.2, 131.0, 129.6, 126.8, 123.5, 119.1, 90.1, 43.4, 19.7, 19.5. HRMS calcd for $C_{26}H_{24}O$ 352.1827, found 352.1831.

Procedure for Deoxyaromatization of 3 to Benzo[*b*]triphenylenes (8). A round-bottom sidearm flask (25 mL) containing **3** (0.500 mmol) was evacuated and purged with nitrogen gas three times. Dichloromethane (2.0 mL) and $BF_3\cdot OEt_2$ (0.090 mL, 0.750 mmol) were added. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then poured into a saturated aqueous $NaHCO_3$ solution and extracted with dichloromethane. The organic layer was washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was recrystallized from a mixture of dichloromethane and hexanes to afford the desired products.

Products **8a**−**f** were obtained according to this procedure. Product yields of these reactions are listed in Tables 2, and the spectral data of representative products are listed below.

2,3,6,7-Tetramethyldibenzo[5,6:7,8]anthra[2,3-*d*][1,3]dioxole (8c). Colorless needles, mp 274−275 °C. ^{1}H NMR (600 MHz, d_6-DMSO): δ 9.05 (s, 2 H), 8.54 (s, 2 H), 8.43 (s, 2 H), 7.48 (s, 2 H), 6.16 (s, 2 H), 2.48 (s, 12 H). ^{13}C NMR (150 MHz, d_6-DMSO): δ 147.7, 136.1, 135.8, 129.3, 127.3, 127.2, 126.3, 124.0, 123.9, 120.6, 102.9, 101.3,19.8, 19.7. HRMS calcd for $C_{27}H_{22}O_2$ 378.1620, found 378.1618.

1,2,3,6,7,8-Hexahydrodiindeno[5′,6′:5,6:5′,6′:7,8]anthra[2,3-*d*][1,3]dioxole (8d). Colorless needles, mp 269−270 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 8.81 (s, 2 H), 8.53 (s, 2 H), 8.40 (s, 2 H), 7.28 (s, 2 H), 6.05 (s, 2 H), 3.12 (m, 8 H), 2.19 (m, 4 H). ^{13}C NMR (150 MHz, CDCl$_3$): δ 147.8, 143.9, 143.6, 129.4, 128.9, 128.3, 127.6, 120.6, 118.5, 118.2, 103.2, 100.9, 33.0, 25.8. HRMS calcd for $C_{29}H_{22}O_2$ 402.1620, found 402.1618.

Diels−Alder Cycloaddition of in Situ Generated Isobenzofuran from 3g with Diethyl Acetylenedicarboxylate. A round-bottom sidearm flask (25 mL) containing **3g** (0.500 mmol, 0.176 g) and diethyl acetylenedicarboxylate (1.00 mmol, 0.170 g) in dry toluene was refluxed for 24 h under nitrogen atmosphere. The reaction mixture was cooled and concentrated, and the residue was purified on a silica gel column using hexanes−ethyl acetate as eluent to give **9** in 69% yield (0.099 g) and **10** in 98% yield (0.115 g).

Acknowledgment. We thank the National Science Council of the Republic of China (NSC 92-2113-M-007-044) for support of this research.

Supporting Information Available: Spectral data for compounds **3d**, **3e**, **3h**−**o**, **8a**, **8b**, **8e**, **8f**, **9**, and **10** and ^{1}H NMR spectra for all compounds **3a**−**o**, **8a**−**f**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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