Synthesis of Bicyclic Enediynes from Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]acetylene: A Tandem Diels−Alder/Palladium(II)- and Copper(I)-Cocatalyzed Cross-Coupling Approach

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The reaction of bicycloalkenylbis(phenyliodonium) triflates **1a** or **b** (available via the Diels−Alder reaction of bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]acetylene with cyclopentadiene or furan, respectively) with alkynylstannanes **2a**−**g** at room temperature in DMF in the presence of catalytic amounts of *trans*-benzyl(chloro)bis(triphenylphosphine)palladium(II) and copper(I) iodide proceeds smoothly and with selectivity to afford good to excellent yields of bicyclic enediynes **3a**−**k**.

Introduction

The discovery of new potent antitumor antibiotics, such as calicheamicins, esperamicins, dynemicin, and more recently, the kedarcidin and C-1027 chromophores, which contain *cis*-enediynes, has sparked renewed interest in the chemistry of enediynes with both open chain and cyclic structures.[1] It is widely recognized that Bergman cyclization[2]—the cycloaromatization of conjugated *cis*-enediynes to 1,4-benzenoid diradicals—within these compounds is responsible for their biological activity.[3] Furthermore, conjugated *cis*-enediynes are useful starting materials in the synthesis of various carbocyclic compounds such as tetrahydronaphthalenes,[4] naphthoquinones,[5] dihydroindene,[6] and dihydrobenzindene systems.[7]

A number of interesting strategies have been recently developed for the direct construction of hex-3-ene-1,5-diyne systems that involve installation of the ene part of *cis*-enediynes as the final step;[8] however, the more traditional and common syntheses involve metal-catalyzed cross-coupling of halo enynes, 1,2-dihaloalkenes,[9] and 1,2-dihalobenzenes[10] with alkynes, alkynylstannanes, or alkynylzinc reagents.[11,12] These procedures are usually performed in polar solvents (e.g., DMF or THF) at elevated temperatures over a period of 1−8 h and generally proceed in good yields (with retention of dihaloalkene stereochemistry). Unfortunately, few of these methods allow for the installation of substituents (e.g., a carbocyclic framework) on the olefin of the enediyne.[8d] Furthermore, few examples of coupling with unprotected alkynes bearing an electron-withdrawing functionality, such as a carbonyl group, have appeared.

In recent years, a great variety of stable, crystalline alkenyl(phenyl)iodonium salts have become readily available and are employed as versatile intermediates in chemical synthesis.[13] They undergo a large number of carbon−carbon bond-forming reactions by nucleophilic substitution of the iodobenzene moiety with organocuprates[14] and soft enolates[14] and by palladium-catalyzed carbonylation[14a] and coupling of alkenyl(phenyl)iodonium salts with olefins.[15] More recently, we exploited the electron-deficient character of these iodonium compounds in a palladium(II)- and copper(I)-cocatalyzed coupling of stereodefined alkenyl(phenyl)iodonium triflates with unsaturated tri-*n*-butylstannanes.[16] A variety of stannanes, including alkenylstannanes and simple and functional-

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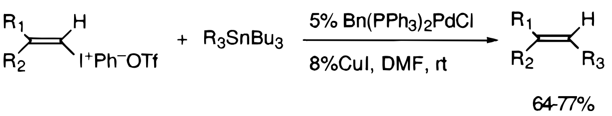
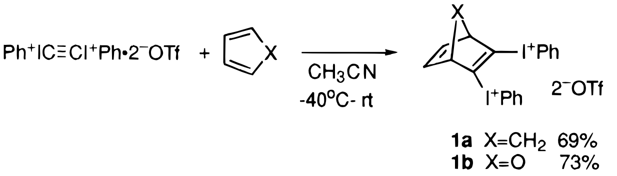
ized alkynylstannanes, couple in good yields under exceedingly mild conditions and afford stereodefined products (eq 1).



(1)

In 1991, we reported a general approach to the synthesis of bicycloalkenylbis(phenyliodonium) bistriflates **1** by the Diels–Alder reaction of bis(phenyliodonio)acetylene bistriflate[17] with dienes such as cyclopentadiene and furan (eq 2).[17a] This new class of alkenyl diiodonium salts undergoes reaction with a range of nucleophiles in the presence of copper(I) salts,[18] and in almost all cases, the products observed are those resulting from vinylic nucleophilic substitution of the iodobenzene moiety. In particular, the coupling reaction of the bicycloalkenyldiiodonium salts with simple lithium–alkynyl cuprates results in selective nucleophilic substitution of the two iodobenzene groups with the alkynes (eq 3).[18b] These reactions occur under mild conditions to afford the respective bicyclic enediynes substituted by alkyl, trimethylsilyl, or aryl groups; however, in some cases the yields are only moderate. This methodology is also restricted to using those alkynes that will form stable alkynyl cuprates. In contrast, a wide variety of alkynylstannanes are known,[19] including those substituted by electron-withdrawing groups. In this paper, we report that the palladium(II) and copper(I) cocatalyzed double coupling reaction of alkenyl bis(phenyliodonium)triflates with a variety of alkynylstannanes proceeds under mild conditions to give good to excellent yields of bicyclic enediynes, including those with functionalized substituents.



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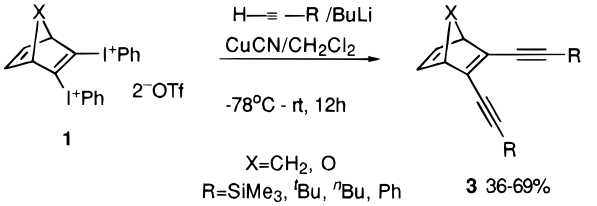


(3)

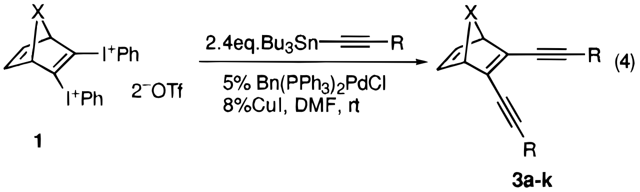
Results and Discussion

Reaction of the bicycloalkenylbis(phenyliodonio) bistriflates **1**[17] with alkynylstannanes **2**[19] in the presence of 5 mol % of *trans*-benzyl(chloro)bis(triphenylphosphine)palladium(II)[20] and 8 mol % of copper iodide in degassed DMF at room temperature results in rapid formation of the desired enediynes in good to excellent yields (eq 4, Table 1). ^{1}H NMR and analytical TLC analyses of the crude reaction products indicated that clean coupling had occurred; the major components were iodobenzene, the enediyne **3**, and small amounts of the starting tributyltin acetylene (even after KF treatment). Importantly, competitive coupling of iodobenzene (produced as a byproduct of the reaction) with the alkynylstannanes occurs to less than 5%, which is in accord with our earlier observations associated with alkenyl(phenyliodonium) triflates.[16] However longer reaction times do result in the formation of varying amounts (10–20%) of such undesired, coupled products. Both the palladium(II) and copper(I) catalysts are necessary for the reaction to occur. The lower yields observed for the 3,5-epoxy-1,4-cyclohexadienes **3c,e,g,i,j** are thought to be due to their instability in the reaction mixtures. Indeed, the ratios of iodobenzene to enediyne in the crude reaction products were much lower than the expected 2:1, as determined by ^{1}H NMR analyses.

Table 1. Palladium(II)/Copper(I)-Cocatalyzed Coupling of Alkenylbis(phenyliodonium) Bistriflates 1a,b with Alkynylstannanes 2a–g

entry	diiodonium salt	X	alkynyl-stannane	R	product	yield[a] (%)
1	**1a**	CH_2	**2a**	CH_3	**3a**	82
2	**1a**	CH_2	**2b**	*n*Bu	**3b**	76
3	**1b**	O	**2b**	*n*Bu	**3c**	55
4	**1a**	CH_2	**2c**	$SiMe_3$	**3d**	60
5	**1b**	O	**2c**	$SiMe_3$	**3e**	63
6	**1a**	CH_2	**2d**	Ph	**3f**	92
7	**1b**	O	**2d**	Ph	**3g**	54
8	**1a**	CH_2	**2e**	$(CO)N(CH_2)_5$	**3h**	77
9	**1b**	O	**2e**	$(CO)N(CH_2)_5$	**3i**	53
10	**1a**	CH_2	**2f**	$(CO)^t$Bu	**3j**	52
11	**1a**	CH_2	**2g**	$(CO)C_{10}H_{15}$	**3k**	86

[a] Isolated yields of pure compounds based on the starting diiodonium salts.



(4)

Analytically pure enediynes **3** were isolated as viscous yellow oils by column or radial chromatography, on silica gel. Those containing electron-withdrawing substituents **3h–k** were markedly less stable than the alkyl-, (trimethylsilyl)-, and aryl-substituted compounds; however, all could be stored for weeks, as dilute solutions, at −20 °C with only minimal deterioration.

The products were identified by the IR, UV, NMR and high-resolution mass spectral data and in the cases of **3b–f** agreed closely with literature data.[18b] The IR spectra all show the triple bond absorption at 2215–2125 cm^{-1}. Frequently, these bands resolved into two separate absorptions, a phenomenon also observed in the case of the parent *cis*-hex-3-ene-1,5-diyne[21] and expected with compounds of such symmetry.[22] The UV spectra all contain an absorption maximum between 284 and 364 nm. As expected, the λ_{max} increases with extent of

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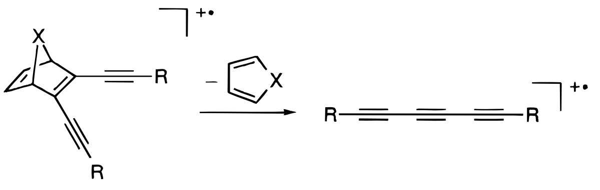
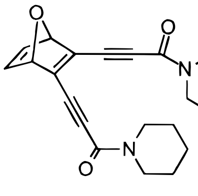
conjugation and polarization of the enediyne system in order of alkyl < trimethylsilyl < amido < carbonyl < phenyl.[23] In addition, for any given R group, the λ_{max} for the oxy-bridged analogues is 10−15 nm greater than the corresponding methylene-bridged compounds. The ^1H NMR spectra display patterns indicative of 1,2-disubstituted norbornadienes[24] or 3,5-epoxy-1,4-cyclohexadienes along with the corresponding signals of the alkynyl R groups. For **3a,b,d,f,h,j,k**, the olefinic protons are found at 6.90−6.78 ppm, the allylic bridgehead protons at 3.84−3.53 ppm, and the geminally-coupled ($J \sim 7$ Hz), bridging, methylene protons at 2.33−2.05 ppm. Similarly, for **3c,e,g,i**, the olefinic protons resonate at 7.21−7.10 ppm and the allylic, bridgehead protons at 5.58−5.33 ppm. Particularly characteristic in the ^{13}C NMR spectra are the signals due to the acetylenic carbons at 76−114 ppm and olefinic carbons at 140−143 ppm. For **3a,b,d,f,h,j,k**, the signals at *ca.* 56 ppm and *ca.* 72 ppm are due to the bridgehead-methine and bridging-methylene carbons, respectively, whereas for **3c,e,g,i**, the oxygenated, bridgehead methine is found at 87 ppm. The mass spectra afford, in most cases, the appropriate molecular ions. For compounds **3j** and **3k**, no molecular ion was observed under a variety of conditions; however, the fragmentation pattern and all other spectroscopic data are in accord with the proposed structures. For compounds **3a,c,f,g**, an interesting fragmentation takes place under EI conditions; the molecular ion loses C_4H_4X, presumably due to a retro Diels−Alder reaction (eq 5).[25]



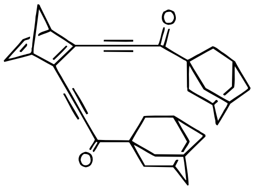
3a,c,f,g

(5)

The yields of bicyclic enediynes using the palladium(II)- and copper(I)-cocatalyzed double coupling of bicyclic alkenylbis(phenyliodonium) bistriflates with alkynylstannanes are generally higher than those observed for the corresponding coupling reaction with lithium alkynylcuprates.[18b] More importantly, the current work allows for the formation and isolation of the sensitive, functionalized enediynes, such as **3i** and **3k**. Little is known about such compounds in terms of their properties and reactivity (e.g., Bergman cyclization) since these species would be difficult to obtain via more traditional methods, e.g., the coupling of dihaloalkenes, which require, amongst other things, elevated temperatures. Such compounds are of interest because it has been shown that substitution of one of the propargyl positions of an enediyne, by an electron-withdrawing group, such as a carbonyl, causes an increase in the rate of Bergman cyclization.[26]



3i



3k

In conclusion, we have developed a two-step synthesis of functionalized bicyclic enediynes starting from bis(phenyliodonio)acetylene bistriflate utilizing a tandem Diels−Alder/metal-catalyzed cross-coupling approach. The second step, the focus of this paper, is the first example of a 2-fold, metal-catalyzed, cross-coupling reaction of alkenyldiiodonium salts and illustrates the emergence of such compounds as useful synthons for bifunctional electrophilic alkenes. In contrast to the great variety of nucleophiles available for metal-catalyzed cross-coupling reactions, only a few types of biselectrophiles (e.g, dihaloalkenes and benzenes) are available.[11] The stable alkenyldiiodonium salts can be thought of as new, highly reactive members of this select group of bifunctional electrophilic alkenes.

Experimental Section

General Methods. Reactions were generally performed in flame-dried glassware under an atmosphere of argon, using anhydrous solvents. DMF was distilled under reduced pressure from CaH_2, stored over 4 Å molecular sieves, and purged with argon for 15 min before use. Starting diiodonium salts **1a,b** were prepared according to the known procedure[17b] and dried for 2 h under vacuum prior to use. Alkynylstannanes **2a−g** were prepared according to known methods from the corresponding terminal acetylenes.[19a,27] Analytical thin layer chromatography (TLC) was conducted on aluminum-backed UV_{254} TLC plates. Column chromatography was performed in the usual manner[28] using silica gel (230−400 mesh). Radial chromatography (silica gel, 200−400 mesh) was performed with a Harrison Research chromatotron, Model 7924T. Infrared spectra were recorded using neat samples on NaCl plates. UV spectra were recorded as dilute solutions in a 1 cm pathlength cell. Proton and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 and 75 MHz, respectively, and were calibrated against internal standards (residual $CHCl_3$ (7.27 ppm) for ^1H NMR and the central peak of $CDCl_3$ (77.23 ppm) for ^{13}C NMR). Mass spectra were obtained under electron impact (EI) conditions at 70 eV, and perfluorokerosine was used as a reference for peak-matching.

General Procedure for the Preparation of Bicyclic Enediynes. To degassed DMF (2.5−5 mL) at room temperature under an atmosphere of argon was added diiodonoium salt **1** (0.5−1.0 mmol) followed by alkynylstannane **2** (1.2−2.4 mmol), *trans*-benzyl(chloro)bis(triphenylphosphine)palladium(II) (5 mol %), 0.025−0.050 mmol), and copper iodide (8 mol %, 0.04−0.08 mmol). After the mixture had stirred at rt for 30 min it was worked up as follows: The reaction mixture was poured into saturated NH_4Cl (20 mL) and extracted with ether (3 × 10 mL). The combined ether extracts were stirred vigorously with KF (10% aqueous, 10 mL) for 15 min, the mixture was filtered to remove precipitated Bu_3SnF, and then the phases were separated. The organic phase was washed with water (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated to give the crude product, which was subjected to chromatographic purification.

2,3-Di-1′-propynylbicyclo[2.2.1]hepta-2,5-diene (3a). The reaction of diiodonium **1a** (796 mg, 1.00 mmol) with alkynylstannane **2a** (823 mg, 2.4 mmol) under the usual conditions gave an orange oil that was subjected to column chromatography (hexanes). Concentration of the fractions (R_f 0.20) afforded **3a** (138 mg, 82%) as a light yellow oil: ^1H NMR δ 6.79 (dd, J = 1.9, 1.9 Hz, 2H), 3.57−3.54 (m, 2H), 2.15 (dt, J = 6.5, 1.5 Hz, 1H), 2.11 (s, 6H), 2.04 (dt, J = 6.5, 1.6 Hz, 1H);

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^{13}C NMR δ 142.0, 140.4, 98.9, 76.3, 71.6, 56.1, 5.6; IR ν_{max} 3080, 2993, 2931, 2866, 2209, 1448, 1375, 1297 cm^{-1}; UV−vis λ_{max} (log ϵ, chloroform) 284 (3.7) nm; MS 168 (100), 102 (49); HRMS calcd for $C_{13}H_{12}$ 168.0939, found 168.0928.

2,3-Di-1′-hexynylbicyclo[2.2.1]hepta-2,5-diene (3b).[18b] The reaction of diiodonium **1a** (796 mg, 1.00 mmol) with alkynylstannane **2a** (891 mg, 2.4 mmol) under the usual conditions gave an orange oil which was subjected to column chromatography (hexanes). Concentration of the fractions (R_f 0.25) afforded **3a** (190 mg, 76%) as a light yellow oil: ^{1}H NMR δ 6.79 (dd, J = 2.0, 2.0 Hz, 2H), 3.57−3.53 (m, 2H), 2.46 (t, J = 7.0 Hz, 4H), 2.17 (dt, J = 6.5, 1.7 Hz, 1H), 2.05 (dt, J = 6.5, 1.6 Hz, 1H), 1.62−1.42 (m, 8H), 0.93 (t, J = 7.2 Hz, 6H); ^{13}C NMR δ 142.0, 140.6, 103.4, 77.1, 71.6, 56.0, 31.1, 22.2, 20.2, 13.9; IR ν_{max} 3070, 2961, 2932, 2871, 2205, 1466, 1458, 1296 cm^{-1}; UV−vis λ_{max} (log ϵ, cyclohexane) 302 (3.7) nm; MS 252 (100); HRMS calcd for $C_{19}H_{24}$ 252.1878, found 252.1891.

2,3-Di-1′-hexynyl-7-oxabicyclo[2.2.1]hepta-2,5-diene (3c).[18b] The reaction of diiodonium **1b** (399 mg, 0.50 mmol) with alkynylstannane **2b** (446 mg, 1.2 mmol) under the usual conditions gave an orange oil that was subjected to radial chromatography (1:40 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.20) afforded **3c** (70 mg, 55%) as a light yellow oil: ^{1}H NMR δ 7.10 (dd, J = 1.1, 1.1 Hz, 2H), 5.33 (dd, J =1.1, 1.1 Hz, 2H), 2.48 (t, J = 3.1 Hz, 4H), 1.62−1.41 (m, 8H), 0.94 (t, J = 7.3 Hz, 6H); ^{13}C NMR δ 143.2, 140.5, 107.4, 86.7, 74.7, 30.9, 22.2, 20.3, 13.9; IR ν_{max} 3017, 2934, 2873, 2215, 2203, 1733, 1466, 1273, 1031, 879, 707 cm^{-1}; UV−vis λ_{max} (log ϵ, cyclohexane) 314 (3.5) nm; MS 254 (87), 186 (69), 129 (100); HRMS calcd for $C_{18}H_{22}O$ 254.1671, found 254.1682.

2,3-Bis[(trimethylsilyl)ethynyl]bicyclo[2.2.1]hepta-2,5-diene (3d).[18b] The reaction of diiodonium **1a** (796 mg, 1.00 mmol) with alkynylstannane **2c** (929 mg, 2.4 mmol) under the usual conditions gave an orange oil that was subjected to column chromatography (1:40 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.21) afforded **3d** (170 mg, 60%) as a light yellow oil: ^{1}H NMR δ 6.80 (dd, J = 1.9, 1.9 Hz, 2H), 3.67−3.63 (m, 2H), 2.19 (dt, J = 6.6, 1.6 Hz, 1H), 2.09 (dt, J = 6.6, 1.5 Hz, 1H), 0.22 (s, 18H); ^{13}C NMR δ 143.5, 142.0, 109.1, 100.7, 71.9, 55.9, 0.2; IR ν_{max} 3070, 2997, 2961, 2900, 2871, 2142, 2127, 1250, 846, 759, 742, 623 cm^{-1}; UV−vis (hexanes) λ_{max} (log ϵ, cyclohexane) 314 (4.0) nm; MS 284 (88), 203 (100); HRMS calcd for $C_{17}H_{24}Si_2$ 284.1417, found 284.1397.

2,3-Bis[(trimethylsilyl)ethynyl]-7-oxabicyclo[2.2.1]hepta-2,5-diene (3e).[18b] The reaction of diiodonium **1b** (399 mg, 0.50 mmol) with alkynylstannane **2c** (465 mg, 1.2 mmol) under the usual conditions gave an orange oil that was subjected to radial chromatography (1:1 CH_2Cl_2/hexanes). Concentration of the fractions (R_f 0.35) afforded **3e** (90 mg, 63%) as a light yellow oil: ^{1}H NMR δ 7.11 (dd, J = 1.0, 1.0 Hz, 2H), 5.42 (dd, J = 1.1, 1.0 Hz, 2H), 0.24 (s, 18H); ^{13}C NMR δ 143.1, 143.1, 113.6, 97.9, 86.6, 0.1; IR ν_{max} 3020, 2961, 2900, 2143, 2125, 1409, 1291, 1251, 1187, 1032, 959, 849 cm^{-1}; UV−vis (hexanes) λ_{max} (log ϵ, cyclohexane) 328 (3.4) nm; MS 286 (70), 218 (60), 203 (100), 73 (31).

2,3-Bis(phenylethynyl)bicyclo[2.2.1]hepta-2,5-diene (3f).[18b] The reaction of diiodonium **1a** (796 mg, 1.00 mmol) with alkynylstannane **2d** (939 mg, 2.4 mmol) under the usual conditions gave an orange oil that was subjected to column chromatography (1:99 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.30) afforded **3f** (270 mg, 92%) as a light yellow oil: ^{1}H NMR δ 7.52−7.49 (m, 4H), 7.39−7.31 (m, 6H), 6.90 (dd, J = 1.9, 1.9 Hz, 2H), 3.82−3.78 (m, 2H), 2.33 (dt, J = 6.7, 1.5 Hz, 1H), 2.19 (dt, J = 6.7, 1.5 Hz, 1H); ^{13}C NMR δ 142.2, 141.8, 131.6, 128.5, 128.5, 123.7, 103.4, 86.2, 71.6, 56.3; IR ν_{max} 3061, 2993, 2942, 2868, 2187, 1484, 1443, 1297, 754, 720, 689, 617 cm^{-1}; UV−vis (hexane) λ_{max} (log ϵ, cyclohexane) 350 (4.3) nm; MS 292 (62), 226 (100); HRMS calcd for $C_{23}H_{16}$ 292.1252, found 292.1259; calcd for M − C_5H_6 ($C_{18}H_{10}$) 226.0783, found 226.0799.

2,3-Bis(phenylethynyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene (3g). The reaction of diiodonium **1b** (399 mg, 0.50 mmol) with alkynylstannane **2d** (469 mg, 1.2 mmol) under the usual conditions gave an orange oil that was subjected to radial chromatography (1:40 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.25) afforded **3g** (80 mg, 54%) as a light yellow oil: ^{1}H NMR δ 7.55−7.50 (m, 4H), 7.40−7.34 (m, 6H), 7.21 (dd, J = 1.0, 1.0 Hz, 2H), 5.58 (dd, J = 1.0 Hz, 2H); ^{13}C NMR δ 143.2, 141.2, 131.7, 129.0, 128.6, 123.1, 106.9, 86.9, 83.6; IR ν_{max} 3061, 3024, 2931, 2194, 2172, 1596, 1484, 1443, 1288, 1273, 1031, 910, 880, 850, 755, 731, 709, 689 cm^{-1}; UV−vis (hexane) λ_{max} (log ϵ, cyclohexane) 364 (4.7) nm; MS 294 (17), 226 (100); HRMS calcd for $C_{22}H_{14}O$ 294.1045, found 294.1063; calcd for M − C_4H_4O ($C_{18}H_{10}$) 226.0783, found 226.0771.

2,3-Bis[[(*N*,*N*-pentamethyleneamino)carbonyl]ethynyl]bicyclo[2.2.1]hepta-2,5-diene (3h). The reaction of bis iodonium **1a** (798 mg, 1.00 mmol) with alkynylstannane **2e** (1.02g, 2.4 mmol) under the usual conditions gave an orange oil that was subjected to column chromatography (1:1 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.3) afforded **3h** (280 mg, 77%) as an unstable yellow oil: ^{1}H NMR δ 6.78 (dd, J = 1.9, 1.9 Hz, 2H), 3.79−3.75 (m, 2H), 3.67 (t, J = 5.4H), 4H), 3.55 (t, J = 5.6 Hz, 4H), 2.23 (dt, J = 6.9, 1.6 Hz, 1H), 2.15 (dt, J = 6.9, 1.6 Hz, 1H), 1.70 −1.48 (m, 12H); ^{13}C NMR δ 152.6, 144.4, 141.8, 95.4, 85.3, 72.5, 56.0, 48.4, 42.5, 26.6, 25.6, 24.6; IR ν_{max} 3071, 2981, 2956, 2930, 2869, 2198, 1623, 1448, 1260, 1213, 1130, 1021, 668 cm^{-1}; UV−vis (hexanes) λ_{max} (log ϵ, cyclohexane) 330 (4.0) nm; MS 363 (9), 279 (28), 86 (63), 84 (100); HRMS calcd for $C_{23}H_{26}N_2O_2$ 363.2073, found 363.2090.

2,3-Bis[[(*N*,*N*-pentamethyleneamino)carbonyl]ethynyl]-7-oxabicyclo[2.2.1]hepta-2,5-diene (3i). The reaction of diiodonium **1b** (399 mg, 0.50 mmol) with alkynylstannane **2e** (511 mg, 1.2 mmol) occurred under the usual conditions except that the crude black reaction mixture was subjected directly to column chromatography (ethyl acetate) rather than aqueous workup. Concentration of the fractions (R_f 0.4) afforded **3i** (110 mg, 53%) as an unstable yellow oil: ^{1}H NMR δ 7.13 (dd, J = 1.1, 1.1 Hz, 2H), 5.56 (dd, J = 1.1, 1.1 Hz, 2H), 3.71−3.65 (m, 4H), 3.60 (dt, J = 7.7, 5.0 Hz, 4H), 1.71−1.53 (m, 12H); ^{13}C NMR δ 152.2, 144.3, 143.1, 98.9, 86.6, 82.7, 48.5, 42.7, 26.7, 25.6, 24.7; IR ν_{max} 2941, 2860, 2199, 2185, 1613, 1434, 1258, 1137, 1014, 912, 848, 724 cm^{-1}; UV−vis λ_{max} (log ϵ, chloroform) 340 (3.8); MS 277 (4), 113 (10), 84 (100).

2,3-Bis[(*tert*-butylcarbonyl)ethynyl]bicyclo[2.2.1]hepta-2,5-diene (3j). The reaction of diiodonium **1a** (798 mg, 1.00 mmol) with alkynylstannane **2e** (958 mg, 2.4 mmol) under the usual conditions gave a dark brown oil that was subjected to column chromatography (1:20 ethyl acetate/hexanes). Concentration of the fractions (R_f 0.4) afforded **3j** (160 mg, 52%) as an unstable yellow oil: ^{1}H NMR δ 6.85 (dd, J = 1.9, 1.9 Hz, 2H), 3.86−3.82 (m, 2H), 2.31 (dt, J = 6.9, 1.6 Hz, 1H), 2.22 (dt, J = 6.9, 1.5 Hz, 1H), 1.24 (s, 18H); ^{13}C NMR δ 194.1, 145.9, 142.0, 100.3, 86.4, 72.6, 56.6, 45.1, 26.3; IR ν_{max} 2968, 2957, 2187, 2170, 1655, 1478, 1458, 1171, 1084, 1066, 1045, 1017, 1002, 703 cm^{-1}; UV−vis λ_{max} (log ϵ, hexanes) 338 (3.7) nm; MS 308 (36), 280 (36), 252 (46), 223 (74), 196 (39), 181 (33), 167 (37), 157 (33), 69 (61), 57 (100); HRMS calcd for $C_{21}H_{24}O_2$ 308.1776. Found 308.1777.

2,3-Bis[(adamantylcarbonyl)ethynyl]bicyclo[2.2.1]hepta-2,5-diene (3k). The reaction of diiodonium **1a** (798 mg, 1.00 mmol) with alkynylstannane **2e** (1.15g, 2.4 mmol) under the usual conditions gave a dark brown oil that was subjected to column chromatography (2:1 CH_2Cl_2/hexanes). Concentration of the fractions (R_f 0.35) afforded **3k** (400 mg, 86%) as an unstable yellow oil: ^{1}H NMR δ 6.85 (dd, J = 1.9, 1.9 Hz, 2H), 3.84−3.82 (m, 2H), 2.31 (dt, J = 6.9, 1.5 Hz, 1H), 2.21 (dt, J = 6.9, 1.5 Hz, 1H), 2.07(m, 6H), 1.93−1.84 (m, 10H), 1.79−1.62 (m, 14H); ^{13}C NMR δ 193.6, 145.5, 141.9, 100.4, 86.5, 72.6, 56.6, 47.1. 38.2, 36.7, 28.1; IR ν_{max} 2959, 2937, 2928, 2917, 2907, 2872, 2853, 2177, 2170, 1659, 1452, 1232, 1224, 1022, 736, 657 cm^{-1}; UV−vis λ_{max} (log ϵ, hexanes) 334 (3.7) nm; MS 136 (100) 135 (52).

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Supporting Information Available: ^{13}C NMR spectra of compounds **3a**−**k** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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