Acetylenic Vinyllithiums: Consecutive Cycloisomerization−[4 + 2] Cycloaddition Reactions

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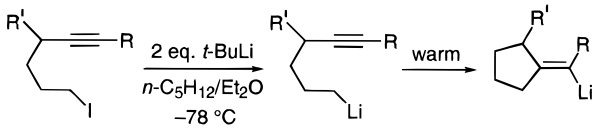
Acetylenic vinyllithiums (**2**), which were generated from the corresponding acetylenic vinyl bromides (**3**) by low-temperature lithium−bromine exchange, cyclize on warming to give, following quench with water, isomerically pure conjugated bis-exocyclic 1,3-dienes (**1**) in good to excellent yield. Both five-membered and six-membered outer-ring dienes may be prepared: 5-exo closure of an acetylenic vinyllithium, which proceeds with total stereocontrol via syn-addition to give the *E*-isomer of a five-membered outer-ring diene, tolerates aryl-, silyl-, or alkyl-substituents at the distal acetylenic carbon; the corresponding 6-exo process is less facile and seems to be confined to substrates bearing an anion-stabilizing substituent, such as phenyl or trimethylsilyl, at the terminal acetylenic carbon. The highly reactive bis-exocyclic 1,3-dienes serve as precursors to polycyclic materials through subsequent Diels−Alder reaction with a wide variety of dienophiles. The consecutive exchange−cyclization−cycloaddition methodology, which can be conducted in one pot without isolation of intermediates, provides an efficient, operationally simple, and diastereoselective route to diverse polycyclic ring systems.

Intramolecular addition of an organolithium to an unactivated olefinic π-bond affords a convenient route to a variety of carbocyclic and heterocyclic products.[2−4] "Anionic" cyclizations[5] of organolithiums bearing a remote carbon-carbon triple bond have also been investigated but the chemistry of such acetylenic systems is less well developed than that of their olefinic counterparts.[2] Studies of acetylenic alkyllithiums have established that the ring closure proceeds, as shown below, in a stereoselectively syn-fashion to give exocyclic vinyllithiums in good yield.[6,7]



In light of the excellent regio- and stereocontrol observed in ring closures of acetylenic alkyllithiums, we were prompted to investigate the synthetic utility of the cyclization of acetylenic vinyllithiums. As detailed below, exo-dig cycloisomerization of a vinyllithium tethered to an acetylenic unit provides an experimentally simple method for the preparation of synthetically useful bis-exocyclic 1,3-dienes.[8]

A variety of bis-exocyclic 1,3-dienes have long been known, and the rich cycloaddition chemistry of these molecules has been well documented.[9] More recently, a number of transition-metal-catalyzed routes to such "outer-ring" dienes have been developed,[10] and these approaches have largely supplanted classical elimination

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(5) It should be noted that, although the ring closure of an olefinic or acetylenic organolithium is often termed an anionic cyclization, the lithium atom is intimately involved in the process and undoubtedly serves to facilitate the cyclization. For a discussion of the unique role of lithium in the cyclization of 5-hexenylalkalies, see: Bailey, W. F.; Punzalan, E. R. *J. Am. Chem. Soc.* **1994**, *116*, 6577.

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(8) A preliminary account of this investigation has appeared, see: Ovaska, T. V.; Warren, R. R.; Lewis, C. E.; Wachter-Jurcsak, N. M.; Bailey, W. F. *J. Org. Chem.* **1994**, *59*, 5868.

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(10) (a) Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422. (b) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (c) Trost, B. M.; Lee, D. C. *J. Org. Chem.* **1989**, *54*, 2271. (d) Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 12491. (e) Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 24 and references therein. (f) Meyer, F. E.; Ang, K. H.; Steinig, A. G.; de Meijere, A. *Synlett* **1994**, 191. (g) Grigg, R.; Sukirthalingam, S.; Sirdharan, V. *Tetrahedron Lett.* **1991**, *32*, 2545 and references therein.

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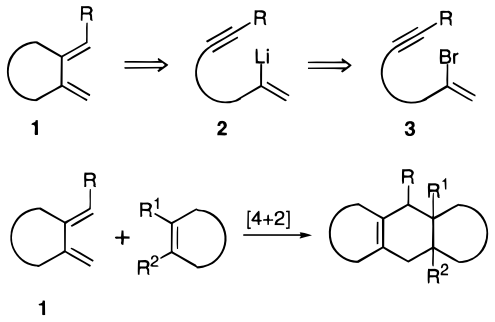
sequences[11] for the preparation of these very useful intermediates. At the inception of the present study it was anticipated, as illustrated below, that a bis-exocyclic 1,3-diene (**1**) could be constructed by cyclization of a suitably constituted acetylenic vinyllithium (**2**) which, in turn, would be generated from an acetylenic vinyl bromide (**3**) by low-temperature lithium−halogen exchange. A major impetus for this approach was the realization that the cyclization strategy, once reduced to practice, could be coupled with the powerful Diels−Alder reaction[12] to provide a highly efficient and experimentally simple route to a wide variety of complex polycyclic systems. As demonstrated by the model studies described below, this expectation was fully realized.



Results and Discussion

Preparation and Cyclization of Acetylenic Vinyllithiums. A representative selection of acetylenic vinyl bromides (**4**−**14**), prepared for the most part in straightforward fashion by standard acetylide displacement procedures,[13] were selected to access the scope of the cycloisomerization route to bis-exocyclic 1,3-dienes. Acetylenic vinyllithiums **2** were generated at low-temperature by addition of 2.0−2.2 molar equiv of *tert*-butyllithium (*t*-BuLi) in pentane to an approximately 0.1 M solution of the appropriate vinyl bromide (**4**−**14**) in a mixture of *n*-pentane−diethyl ether. In the initial stages of this investigation,[8] the acetylenic vinyllithiums were prepared at ∼−100 °C using a solvent system composed of *n*-pentane−diethyl ether in an effort to avoid unwanted dehydrohalogenation of the base-sensitive substrates. Indeed, pioneering studies by Seebach's group of the reaction of *t*-BuLi with vinyl bromides in solvent systems containing THF have demonstrated that it is often necessary to perform the exchange at temperatures below −110 °C to minimize alkyne formation.[14] For this reason, we were delighted to subsequently discover that the acetylenic vinyllithiums (**2**) may be cleanly generated by lithium−bromine exchange at a more experimentally convenient temperature of −78 °C following our general protocol[15] provided that the solvent system is free of THF: there was no evidence of dehydrohalogenation when the vinyl bromide substrates (**4**−**14**) were treated with *t*-BuLi using these conditions,[16] and this is the recommended procedure for production of **2**. As would be expected,[7] the acetylenic vinyllithiums derived from bromides **4**−**14** are stable at low-temperature; quench of each reaction mixture at −78 °C with oxygen-free MeOH delivered the corresponding enyne in virtually quantitative yield.

With a convenient method in hand for the conversion of acetylenic vinyl bromides to organolithiums, conditions necessary to effect carbocyclization of the acetylenic vinyllithiums were investigated. At the outset it was clear that the facility of the cyclization would be dependent on two factors: (1) the nature of the substituent attached to the distal acetylenic carbon, and (2) the length of the tether joining the vinyllithium to the acetylenic unit. Studies of acetylenic alkyllithiums had demonstrated that aryl- and silyl-substituted substrates cyclize much more rapidly than do alkyl-substituted analogs and that 5-exo-dig closures are invariably more facile than 6-exo processes.[7] Indeed, whereas the ring closure of 6-phenyl-5-hexynyllithium is quite rapid even at −50 °C, the analogous alkyl-substituted material, 5-decynyllithium, cyclizes some 10^6 times more slowly at this low temperature.[17] In view of the anticipated sluggish isomerization of alkyl-substituted acetylenic vinyllithiums and the expected difficulty of effecting 6-exo-dig closures, acetylenic vinyllithiums bearing alkyl groups, as well as those giving a six-membered ring on closure, were generated in solutions containing less diethyl ether (i.e., 10:1 or 14:1 by vol of *n*-pentane−diethyl ether) than is normally employed for the exchange reaction[15] so as to minimize inadvertent quench of the organolithium by proton abstraction from the ether solvent.

Cycloisomerizations were effected by simply allowing solutions of the acetylenic vinyllithiums to warm and stand for a period of time at an appropriate temperature under an atmosphere of argon prior to the addition of oxygen-free MeOH or water. Isomerization conditions and the results of the cyclization experiments are summarized in Table 1. Cursory inspection of the data presented in Table 1 reveals that both five- and six-membered bis-exocyclic 1,3-dienes may be generated by this approach. Moreover, in all but one instance (vide infra; Table 1, entry 10), the ring closures proceed in a totally stereoselective fashion, via syn-addition of the vinyllithium to the acetylenic moiety, to give an isomerically pure *E*-outer-ring diene. It should be noted that the only byproduct detected in any of these reactions was the open-chain enyne.

More detailed analysis of the results presented in Table 1 indicates that the facility of the ring closure of an acetylenic vinyllithium (**2**) is a strong function of the group appended to the π-system. Thus, 5-exo cyclization of substrates bearing either an aryl substituent (Table 1, entries 1, 4, and 5) or a trimethylsilyl-substituent (Table 1, entries 2 and 3) proceed rapidly to give conjugated, five-membered outer-ring dienes in 84−94% isolated yield. The alkyl-substituted acetylenic vinyllithiums derived from 7-alkyl-2-bromo-1-hepten-4-ynes

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(12) The vast primary literature on the Diels−Alder reaction has spawned an extensive number of reviews. A representative selection of monographs may be found in: (a) Smith, M. B. *Organic Synthesis*; McGraw-Hill: New York, 1994. (b) March, J. A. *Advanced Organic Chemistry*, 4th ed.; Wiley Interscience: New York, 1992; pp 839−852. (c) Holmes, H. L. *Org. React.* **1958**, *4*, 60.

(13) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam, 1988.

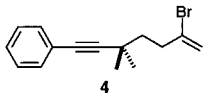
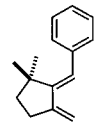
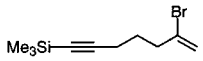
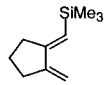
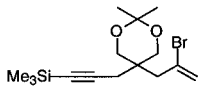
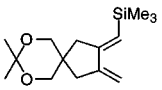
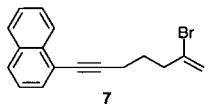
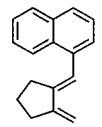
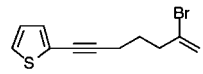
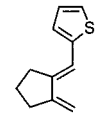
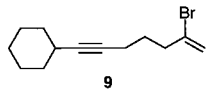
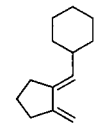
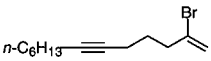
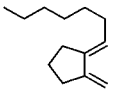
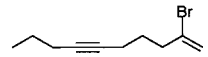
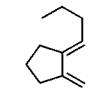
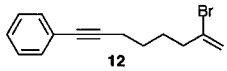
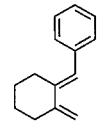
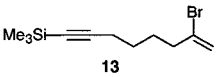
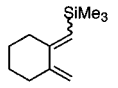
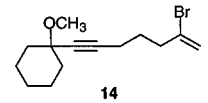
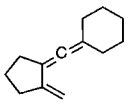
(14) (a) Seebach, D.; Neumann, H. *Chem Ber.* **1974**, *107*, 847. (b) Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

(15) Bailey, W. F.; Punzalan, E. R. *J. Org. Chem.* **1990**, *55*, 5405.

(16) It would appear that the dehydrohalogenation reaction observed by Seebach's group[14] when vinyl bromides are treated with *t*-BuLi at −78 °C is a consequence of the presence of THF in such reaction mixtures. The fact that alkyne formation is completely suppressed when the exchange is conducted in solvent systems composed of hydrocarbon and diethyl ether suggests that ether-solvated dimeric *t*-BuLi may be responsible for the exchange while the THF-solvated monomer may be responsible for the elimination reaction.[15]

(17) Bailey, W. F.; Ovaska, T. V. *Organometallics* **1990**, *9*, 1694.

Table 1. Cyclization of Acetylenic Vinyllithiums

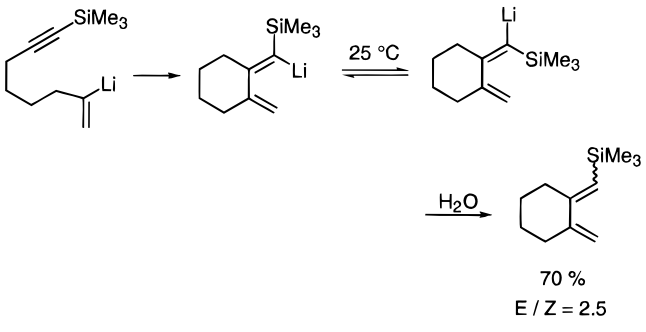
entry	substrate	exchange;[a] n-C_5H_{12}–Et_2O vol ratio/ temp, °C	cyclization;[b] temp, °C / time, h	product	yield,[c] %
1	 **4**	4:1 / –100	0 / 1		94
2	 **5**				87
3	 **6**				94
4	 **7**	10:1 / –100			84
5	 **8**	10:1 / –78	23 / 2		84
6	 **9**	10:1 / –78	TMEDA,[d] 24 / 40		61
7	 **10**				76
8	 **11**		TMEDA,[d] 25 / 24		51
9	 **12**	14:1 / –100	40 / 3		80
10	 **13**	10:1 / –78	25 / 6		70[e]
11	 **14**		24 / 2		97

[a] Acetylenic vinyllithiums were generated at the indicated temperature by addition of 2 equiv of *t*-BuLi in pentane to a solution of the acetylenic vinyl bromide in the indicated proportions (by volume) of dry, oxygen-free *n*-pentane – diethyl ether. [b] Reaction mixtures were allowed to warm and stand under argon at the indicated temperature for the specified time to effect cycloisomerization prior to quench with water or methanol. [c] Isolated yield of crude 1,3-diene. [d] Oxygen-free TMEDA (2 molar equiv) was added to the reaction mixture prior to warming. [e] Product was an approximately 2.5:1 mixture of the E- and Z-isomers, respectively.

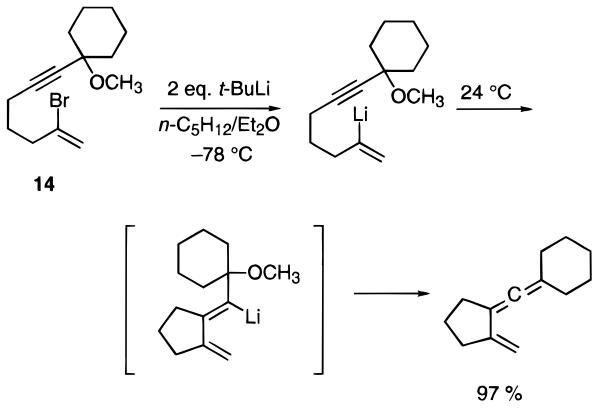
(**9**–**11**) were far more resistant to rearrangement than were the aryl- or silyl-substrates. Indeed, as detailed in our preliminary report,[8] 5-exo cyclization of an alkyl-substituted system does not proceed to an appreciable extent when the acetylenic vinyllithiums are warmed to room temperature in *n*-pentane–diethyl ether solution.

Fortunately, the ring closure of an alkyl-bearing acetylenic vinyllithium is more facile when *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) is added prior to warming. As demonstrated by the data presented in Table 1 (entries 6−8), reasonable yields of isomerically pure (*E*)-1-alkylidene-2-methylenecyclopentanes may be realized by conducting the isomerization of the alkyl-substituted systems in the presence of 2 molar equiv of scrupulously dry and oxygen-free TMEDA at room temperature for an extended period of time. It is perhaps worth noting explicitly that rigorous exclusion of oxygen and moisture is imperative to the success of ring closures requiring day-long warming at room temperature.

The relative ease with which five-membered outer-rings may be constructed via intramolecular carbolithiation (Table 1, entries 1−8) prompted us to explore the possibility of preparing six-membered rings by 6-exo-dig cyclization. Not unexpectedly,[7] this mode of ring closure was more difficult to achieve than 5-exo cyclization to a five-membered ring. Indeed, the 6-exo mode of ring closure appears to be confined to substrates bearing an anion-stabilizing aryl- or silyl-substituent on the terminal acetylenic carbon; to date we have been unable to find conditions that result in synthetically useful 6-exo-dig cyclization of alkyl-substituted acetylenic vinyllithiums. Be that as it may, cycloisomerization of the acetylenic vinyllithiums derived from 2-bromo-8-phenyl-1-octen-7-yne (**12**) and 2-bromo-8-(trimethylsilyl)-1-octen-7-yne (**13**) were effected in good yield by simply allowing solutions of the organolithiums in *n*-pentane−diethyl ether to warm and stand at room temperature for several hours under an atmosphere of argon (Table 1, entries 9, 10). Cyclization of the organolithium prepared from **13** afforded the expected, isomerically pure, (*E*)-1-benzylidene-2-methylenecyclohexane; however, 6-exo closure of the silyl-substituted system gave an approximately 70:30 mixture of the diastereoisomeric *E*- and *Z*-outer-ring dienes upon quench with water (Table 1, entry 10). As illustrated below, the isolation of a mixture of isomeric products from the later cyclization is undoubtedly a consequence of cis-trans isomerization of the initially formed *E*-isomer upon standing at 25 °C for 6 h. There is ample precedent for the equilibration of silyl-substituted vinyllithiums at room temperature in ethereal solvents and just such behavior has been documented in studies of the cyclization of acetylenic alkyllithiums.[7]



The cyclization methodology described above may be slightly modified to allow preparation of otherwise relatively inaccessible exocyclic, conjugated allenenes[18] (s-annulated 1,2,4-trienes) by simple incorporation of a leaving-group at the distal propargylic position of the acetylenic vinyllithium.[19] Thus, as illustrated below, the



vinyllithium generated from bromide **14** cleanly cyclizes with expulsion of the propargylic methoxy group to afford the five-membered exocyclic allenene in 97% isolated yield (Table 1, entry 11). This remarkably high-yield intramolecular S_N' reaction is clearly the most direct route to such exocyclic 1,2,4-trienes, and we are currently exploring the possibility of preparing related conjugated systems by this approach.

Diels−Alder Reactions of 1,3-Bis-Exocyclic Dienes. The efficient preparation of isomerically pure outer-ring dienes provided by cycloisomerization of acetylenic vinyllithiums may be easily coupled with well-explored Diels−Alder methodology to provide a simple, direct route to more complex polycyclic ring systems. Intermolecular Diels−Alder reactions of bis-exocyclic 1,3-dienes are well precedented[9−12] and the representative selection of [4 + 2] cycloaddition reactions presented in Table 2 further illustrates the utility of these reactive dienes for the synthesis of diverse ring structures. It might be noted that no attempt was made to optimize conditions for individual Diels−Alder reactions; adducts were prepared by adding the dienophile (1 equiv) to the crude outer-ring diene (1.1−1.5 equiv) in toluene or methylene chloride solution. Indeed, an operationally important feature of this methodology for the preparation of polycyclic materials is the ability to conduct the entire three-step operation (exchange−cycloisomerization−cycloaddition) in one pot without purification (or even isolation) of the intermediate bis-exocyclic 1,3-dienes. Although yields are tabulated for intermediate dienes in Table 1, the adducts listed in Table 2 were often prepared in one flask by simply replacing the pentane−ether solvent with toluene and adding the appropriate dienophile to the crude bis-exocyclic 1,3-diene. In practice, isolation and purification of the often crystalline cycloadduct is normally a fairly simple matter since the major byproducts are variable amounts of the enyne formed by formal reduction of the acetylenic vinyl bromide.

The intermolecular Diels−Alder reactions presented in Table 2 proceeded in unexceptional fashion with the expected cis-endo stereochemistry.[9−12] The structures of the adducts were for the most part established by standard one- and two-dimensional NMR spectroscopy, including NOE difference spectra and phase sensitive

(18) For reviews of the preparation and reactions of conjugated allenenes, see: (a) Landor, P. D. In *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: New York, 1982; Vol. 1, pp 205−222. (b) Hopf, H. *Ibid*. Vol. 2, pp 563−576.

(19) The preparation of alkenylidenecycloalkanes by cyclization of acetylenic alkyllithiums bearing a propargylic leaving group has been described: see, Bailey, W. F.; Aspris, P. H. *J. Org. Chem.* **1995**, *60*, 754.

Table 2. Diels–Alder Reactions of Bis-1,3-Exocyclic Dienes

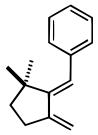
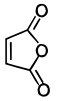
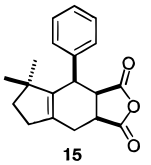
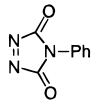
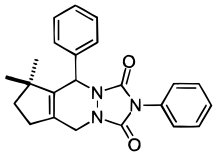
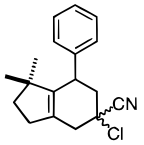
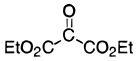
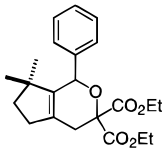
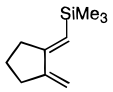
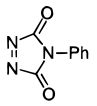
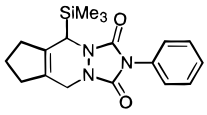
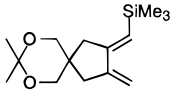
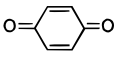
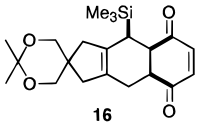
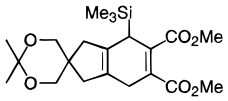
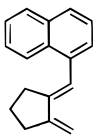
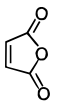
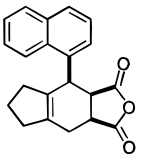
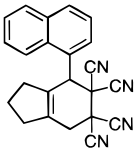
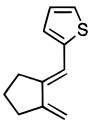
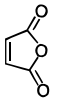
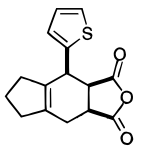
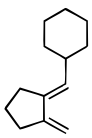
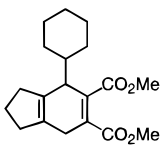
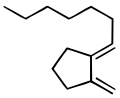
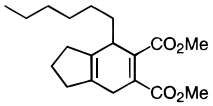
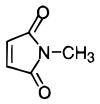
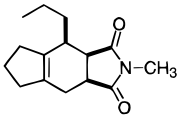
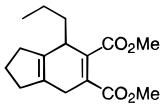
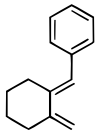
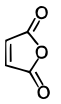
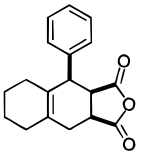
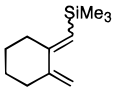
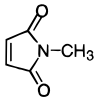
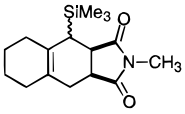
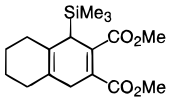
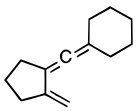
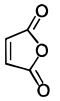
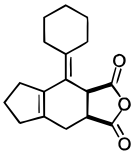
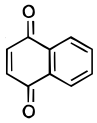
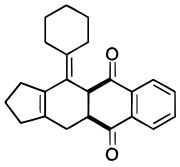
entry	diene	dienophile	conditions[a]	adduct	yield,[b] %
1			$PhCH_3$ reflux, 3 h	 **15**	80
2			CH_2Cl_2 0 °C, 10 min		75
3			$PhCH_3$ reflux, 18 h		85
4			$PhCH_3$ reflux, 2 h		86
5			CH_2Cl_2 0 °C, 10 min		83
6			$PhCH_3$ reflux, 4 h	 **16**	89
7		$MeO_2C-C\equiv C-CO_2Me$	$PhCH_3$ reflux, 3 h		91
8			$PhCH_3$ reflux, 1.5 h		75
9			$PhCH_3$ reflux, 2 h		71
10			$PhCH_3$ reflux, 2 h		58
11		$MeO_2C-C\equiv C-CO_2Me$	$PhCH_3$ reflux, 3 h		74

Table 2 (Continued)

entry	diene	dienophile	conditions[a]	adduct	yield,[b] %
12		$MeO_2C-C\equiv C-CO_2Me$	$PhCH_3$ reflux, 2 h		63
13			$PhCH_3$ reflux, 2 h		71
14		$MeO_2C-C\equiv C-CO_2Me$	$PhCH_3$ reflux, 3 h		70
15			$PhCH_3$ reflux, 1.5 h		85
16			$PhCH_3$ reflux, 2 h		66
17		$MeO_2C-C\equiv C-CO_2Me$	$PhCH_3$ reflux, 3 h		68
18			$PhCH_3$ reflux, 2 h		90
19			$PhCH_3$ reflux, 2 h		80

[a] Cycloadditions were conducted by adding 1.0 equiv of the dienophile to 1.1 - 1.5 equiv of the bis-exocyclic 1,3-diene. [b] Isolated yield of analytically pure product.

NOESY experiments,[20a] and confirmed in the case of adducts **15** (Table 2, entry 1) and **16** (Table 2, entry 6) by single-crystal X-ray analyses[8,20b] (Figure 1).

Substrates suitable for intramolecular Diels–Alder reaction[21] may also be easily constructed by acetylenic vinyllithium cyclization as illustrated by the example presented in Scheme 1. The preparation of vinyl bromide **17** required for the generation of the acetylenic vinyl-

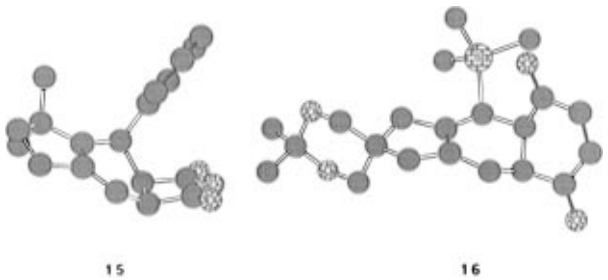
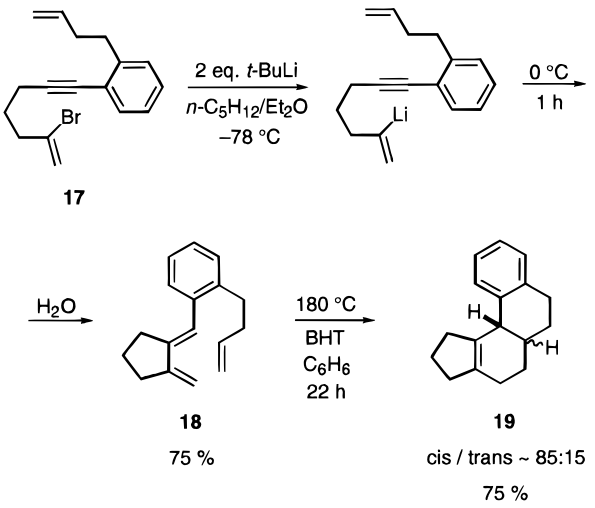


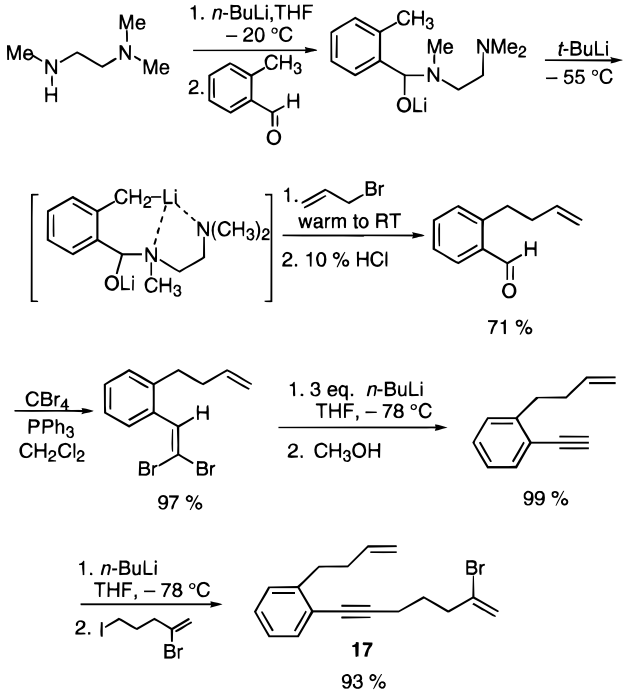
Figure 1. Computer-generated rendering of the structures of compounds **15** and **16** as determined by single-crystal X-ray crystallography.[20b]

(20) (a) Full details are available in the Ph.D. Dissertation of Nanette M. Wachter-Jurcsak, University of Connecticut, Storrs, CT, 1995. (b) Crystallographic data for **15**: $C_{19}H_{20}O_3$, $a = 10.448(2)$ Å, $b = 12.119(2)$ Å, $c = 12.929(3)$ Å, $\alpha = 74.84(3)°$, $\beta = 86.36(3)°$, $\gamma = 89.30(3)°$, $V = 1576.9(5)$ Å^3, space group = $P1$, molecules/unit cell = 4, density (calcd) = 1.248 g cm^{-3}, linear absorption factor = 0.668 mm^{-1}. Crystallographic data for **16** appear in footnote 14 of ref 8. The structures were solved by direct methods. The authors have deposited atomic coordinates for **15** and **16** with the Cambridge Crystallographic Data Center. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 1



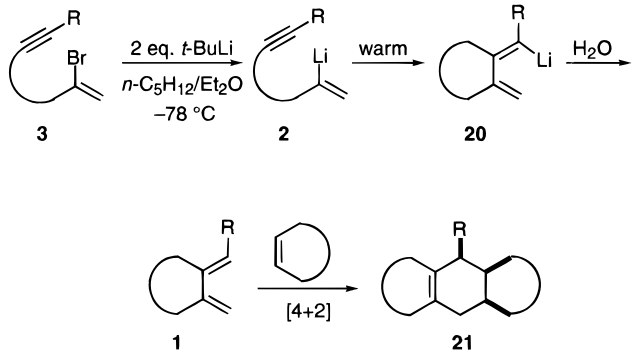
Scheme 2



lithium was accomplished in 63% overall yield from *o*-tolualdehyde as outlined in Scheme 2. Thus, allylation of *o*-tolualdehyde following the elegant general procedure of Comins and Brown[22] gave the known 2-(3-butenyl)-benzaldehyde[23] which was then converted to **17** in straightforward fashion (Scheme 2). Lithium−bromine exchange between **17** and *t*-BuLi in *n*-pentane−diethyl ether (4:1 by vol) solution at −78 °C afforded the corresponding vinyllithium which cyclized upon warming to 0 °C for 1 h (Scheme 1). Quench of the reaction mixture with water delivered triene **18** in 75% yield. Intramolecular [4 + 2]-cycloaddition, accomplished by heating a benzene solution of **18** at 180 °C for 22 h, proceeded in 75% yield to give tetracycle **19** as an approximately 6:1 mixture of diastereoisomers (Scheme 1). The major product of the intramolecular cycloaddition is tentatively assigned the cis-stereochemistry on the basis of NMR data and literature precedent.[10b,21]

Conclusions

The results summarized in Table 1 demonstrate that cycloisomerization of a vinyllithium tethered to an acetylenic unit provides a convenient, efficient route to five- and six-membered bis-exocyclic 1,3-dienes. The 5-exo closure, which proceeds with total stereocontrol to give the *E*-isomer of a five-membered outer-ring diene, tolerates aryl-, silyl-, or alkyl-substituents at the distal acetylenic carbon; the corresponding 6-exo process is less facile and seems to be confined to substrates bearing an anion-stabilizing substituent at the terminal acetylenic carbon. As expected on the basis of prior art,[9−12] the outer-ring dienes react stereoselectively with a wide range of dienophiles to give diastereoisomerically pure polycyclic ring systems in good to excellent yield (Table 2). As a practical matter, it should be noted that preparation of polycyclic products can be accomplished without isolation of intermediates. As illustrated below, the consecutive operations of exchange−cycloisomerization−quench−cycloaddition (**3** → **2** → **20** → **1** → **21**) may be conducted in one pot to deliver pure adducts in good overall yield.



Experimental Section

General Procedures. General spectroscopic and chromatographic procedures have been previously described.[3g] NMR spectra were recorded as solutions in $CDCl_3$, and all chemical shifts are reported relative to Me_4Si at $\delta = 0.00$. Product mixtures were analyzed by GC on a 19-m × 0.25-mm methyl phenyl (20%) silicone fused-silica capillary column and by GC-MS on a 25-m × 0.20-mm cross-linked methyl silicone fused-silica capillary column.

All operations involving organolithiums were performed in flame-dried glassware using standard syringe/cannula techniques under an atmosphere of dry, oxygen-free argon that had been passed through a column containing an activated BASF R3-11 copper catalyst. All liquids used for the preparation and quench of organolithiums that had not been freshly distilled were rendered essentially oxygen free immediately prior to use by bubbling dry, deoxygenated argon through the neat liquid for a minimum of 5 min. The concentration of commercial solutions of alkyllithium reagents (FMC) were determined immediately prior to use by titration with standard 2-butanol in xylene using 1,10-phenanthroline as indicator following the method of Watson and Eastham.[24] Diethyl ether and THF were freshly distilled from dark-purple solutions of sodium/benzophenone. Dry, olefin-free *n*-pentane was obtained by repeated washings of technical-grade *n*-pentane with concentrated sulfuric acid until the acid layer remained clear, followed by washing with water and saturated aqueous sodium

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(22) Comins, D. L.; Brown, J. D. *J. Org. Chem.* **1984**, *49*, 1078.
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bicarbonate, drying over $MgSO_4$, and distillation of the purified pentane under nitrogen from lithium aluminum hydride.

Literature procedures, incorporating some minor modifications, were followed for the preparation of 4-bromo-4-penten-1-ol,[25] ethyl 4-bromo-4-pentenoate,[26] diethyl 2-(2-bromo-2-propenyl)-2-(3-(trimethylsilyl)-2-propynyl)propanedioate,[27] 6-iodo-1-hexyne,[28] and 1-ethynyl-1-methoxycyclohexane.[29] The previously reported *gem*-dibromides, 1-(2,2-dibromoethenyl)-naphthalene,[30] 2-(2,2-dibromoethenyl)thiophene,[31] and (2,2-dibromoethenyl)cyclohexane,[30] were converted, using the general procedure of Corey and Fuchs,[32] to the following known acetylenes: 1-ethynylnaphthalene,[33] 2-ethynylthiophene,[31] and ethynylcyclohexane.[30]

2-Bromo-5-iodo-1-pentene. Following the general procedure of Crossland and Servis,[34] 6.926 g (49.1 mmol) of 4-bromo-4-penten-1-ol[25] was converted into its mesylate. The crude mesylate was added to a solution of 15.0 g (100 mmol) of dry sodium iodide in 150 mL of dry acetone, and the mixture was stirred overnight at room temperature under an atmosphere of nitrogen and then at gentle reflux for 2 h. The mixture was cooled, inorganic salts were removed by filtration, and the precipitate was washed with three 50-mL portions of dry acetone. The combined filtrate and washings were concentrated at reduced pressure, taken up in pentane, and washed with 5% aqueous sodium thiosulfate. The organic layer was dried ($MgSO_4$) and concentrated at reduced pressure to give 10.804 g (94%) of the iodide as a colorless liquid: bp 77 °C (2.2 mm); ^{1}H NMR δ 2.06 (apparent pentet, J = 6.82 Hz, 2 H), 2.56 (t, J = 7.13 Hz, 2 H), 3.19 (t, J = 6.67 Hz, 2 H), 5.47 (s, 1 H), 5.68 (s, 1 H); ^{13}C NMR δ 4.88, 30.87, 41.56, 118.20, 132.04. Anal. Calcd for C_5H_8BrI: C, 21.84; H, 2.93. Found: C, 22.07; H, 2.60.

2-Bromo-6-iodo-1-hexene. The general procedure of Suzuki and co-workers[35] was followed to prepare the vinyl bromide. Thus, 5.23 g (25.1 mmol) of 6-iodo-1-hexyne[28] was added at 0 °C under an atmosphere of nitrogen to 150 mL of a solution of *B*-bromo-9-BBN prepared by adding 150 mL of methylene chloride to 37.5 mL of a commercial 1.0 M solution of *B*-bromo-9-BBN in methylene chloride. The solution was stirred at 0 °C for 3 h, 15 mL of glacial acetic acid was then added, and the mixture was stirred for an additional 1 h prior to the sequential addition of 200 mL of 3 M aqueous sodium hydroxide and 35 mL of 30% hydrogen peroxide. The mixture was stirred for 1 h, the layers were separated, and the aqueous layer was extracted with three 50-mL portions of hexanes. The combined extracts were washed sequentially with 100 mL of water, 100 mL of saturated, aqueous sodium bicarbonate, and 100 mL water. The organic layer was dried ($MgSO_4$) and concentrated at reduced pressure, and the residue was eluted from a column of silica gel with hexanes to give 5.21 g (72%) of the product: ^{1}H NMR δ 1.62−1.71 (m, 2 H), 1.81 (apparent pentet, J = 6.79 Hz, 2 H), 2.43 (t, J = 7.12 Hz, 2 H), 3.17 (t, J = 6.79 Hz, 2 H), 5.39 and 5.56 (AB pattern, J_{AB} = 1.37 Hz, 2 H); ^{13}C NMR δ 5.97, 28.66, 32.05, 40.18, 116.99, 133.73. Anal. Calcd for $C_6H_{10}BrI$: C, 24.94; H, 3.49. Found: C, 25.23; H, 3.55.

5-Bromo-2-methyl-5-hexen-2-ol. A solution of 5.00 g (24.2 mmol) of ethyl 4-bromo-4-pentenoate[26] in 13 mL of dry diethyl ether was added to a solution of 52.5 mmol of methylmagnesium bromide in diethyl ether (prepared by adding 17.5 mL of a 3.00 M solution of the Grignard reagent to 26 mL of anhydrous diethyl ether) at such a rate as to maintain gentle reflux of the reaction mixture. After the addition was complete, the mixture was heated at gentle reflux for 30 min. The cooled reaction mixture was quenched with 9.00 mL of aqueous, saturated NH_4Cl, the clear ethereal layer was separated, and the white precipitate was continuously extracted with diethyl ether for 14 h in a Soxhlet apparatus. The combined ethereal extracts were concentrated at reduced pressure to give 4.04 g (87%) of product as a clear oil: ^{1}H NMR δ 1.20 (s, 6 H), 1.60 (br s, 1 H), 1.66−1.72 (5 lines, 2 H), 2.46−2.52 (5 lines, 2 H), 5.34 (d, 1.62 Hz, 1 H), 5.54−5.57 (m, 1 H); ^{13}C NMR δ 29.25, 36.55, 42.01, 70.34, 116.20, 134.79; IR (neat) 3394, 2972, 1629, 1467, 1377, 1150, 885 cm^{-1}; HRMS calcd for $C_6H_{10}BrO$ ($M^+ - CH_3$) 176.9915, found 176.9912.

2,5-Dibromo-5-methyl-1-hexene. A mixture of 3.51 g (18.2 mmol) of 5-bromo-2-methyl-5-hexen-2-ol and 0.384 g (4.85 mmol) of pyridine was placed in a 100 mL three-necked, round-bottom equipped with a mechanical stirrer and a calcium chloride drying tube, and the flask was immersed in an ice-bath. To this cold solution was added 1.86 g (6.87 mmol) of phosphorus tribromide via syringe over a period of 15 min. After the addition was complete, the mixture was allowed to warm and stir at room temperature for additional 30 min. The apparatus was then set for downward distillation under reduced pressure (3 mm) and the distillate boiling below 100 °C was collected. Redistillation of the crude product afforded 3.06 g (67%) of the dibromide as a clear liquid: bp 65−68 °C (2.3 mm); ^{1}H NMR δ 1.75 (s, 6 H), 2.01 (m, 2 H), 2.65 (m, 2 H), 5.39 (1 H, d, J = 1.62 Hz); ^{13}C NMR δ 35.0, 39.7, 46.6, 67.1, 117.9, 134.3; IR (neat) 2990, 2803, 1630, 1466, 1444, 1388, 1369, 1238, 1206, 1090, 880, 836 cm^{-1}; HRMS calcd for $C_7H_{12}Br_2$ 253.9306, found 253.9306.

2-Bromo-5,5-dimethyl-7-phenyl-1-hepten-6-yne (4). The general procedure of Negishi and Baba[36] was followed for the preparation of this compound. Thus, a solution of 3.38 g (33.1 mmol) of freshly distilled phenyl acetylene and 55 mL of dry pentane was cooled under argon in an ice-bath, and 10.72 mL of a 3.11 M solution of *n*-BuLi in hexane (33.35 mmol) was slowly added via syringe. The mixture was stirred for 30 min at 0 °C, and 1.47 g (11.04 mmol) of aluminum chloride was then added in small portions over a period of 30 min. The mixture was stirred for an additional 30 min period, and solvents were then removed by rotary evaporation under an atmosphere of dry nitrogen. The solid residue was cooled in an ice-bath, 30 mL of dry methylene chloride was added to dissolve the powdery solid, and 2.477 g (9.673 mmol) of 2,5-dibromo-5-methyl-1-hexene in 55 mL of dry methylene chloride was added in a dropwise fashion. The mixture was stirred at 0 °C for 1 h and then poured into 55 mL of ice-cold 10% aqueous HCl. The aqueous layer was extracted with three 40-mL portions of diethyl ether, and the combined organic layers were washed once with brine and dried over $MgSO_4$. Concentration at reduced pressure afforded a brown liquid which was purified by column chromatography (hexanes, R_f = 0.14) to give 2.10 g (78%) of product: bp (Kugelrohr) 135−140 °C (0.2 mm); ^{1}H NMR δ 1.31 (s, 6 H), 1.70−1.78 (m, 2 H), 2.63−2.71 (m, 2 H), 5.40 (d, J = 1.68 Hz, 1 H), 5.95−5.61 (m, 1 H), 7.25−7.39 (m, 5 H); ^{13}C NMR δ 29.20, 31.25, 38.03, 41.80, 81.05, 96.07, 116.23, 123.72, 127.57, 128.14, 131.54, 134.77; IR (neat) 3057, 2968, 2867, 1630, 1598, 1468, 1383, 1365, 1292, 1028, 886, 756, 692 cm^{-1}. Anal. Calcd for $C_{15}H_{17}Br$: C, 64.99; H, 6.18. Found: C, 64.72; H, 6.48.

2-Bromo-7-(trimethylsilyl)-1-hepten-6-yne (5). A solution of 0.804 g (8.19 mmol) of (trimethylsilyl)acetylene in 25 mL of anhydrous THF was cooled to −78 °C under an atmosphere of nitrogen, and 4.66 mL of a 1.56 M solution of *n*-BuLi in hexane (7.27 mmol) was added over a period of 10 min. After stirring the reaction mixture at −78 °C for an additional hour, 2.00 g (7.27 mmol) of 2-bromo-5-iodo-1-pentene was added rapidly. The cooling bath was then removed, and the mixture was allowed to warm to room temperature and then heated at gentle reflux overnight. The mixture was concentrated at reduced pressure, the residue was partitioned between 20 mL of water and 20 mL of diethyl ether, and the aqueous layer was extracted with three 15-mL portions of diethyl ether. The combined organic layers were

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(29) Reference 13, p 263.
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(36) Negishi, E.; Baba, S. *J. Am. Chem. Soc.* **1975**, *97*, 7385.

dried ($MgSO_4$) and concentrated to give an oil which was passed through a short plug of alumina eluting with pentane to give, after solvent removal, 1.54 g (94%) of product: ^{1}H NMR δ 0.12 (s, 9 H), 1.73 (quintet, J = 7.06 Hz, 2 H), 2.22 (t, J = 6.98 Hz, 2 H), 2.50 (apparent td, J_t = 7.16 Hz, J_d = 0.92 Hz, 2 H), 5.39 (apparent d, J = 2.63 Hz, 1 H), 5.57−5.81 (m, 1 H); ^{13}C NMR δ 0.09, 18.39, 26.46, 40.06, 85.26, 106.17, 117.31, 133.36; IR (neat) 2940, 2895, 2190, 1640, 1440, 1260, 850, 750 cm^{-1}; HRMS calcd for C_7H_8Br ($M^+ - Me_3Si$) 170.9809, found 170.9806.

2-(2-Bromo-2-propenyl)-2-(3-(trimethylsilyl)-2-propynyl)-1,3-propanediol. A solution of 3.80 g (9.76 mmol) of diethyl 2-(2-bromo-2-propenyl)-2-(3-(trimethylsilyl)-2-propynyl)propanedioate[27] in 15 mL of diethyl ether was added over a 30 min period to a suspension of 1.65 g (43.6 mmol) of lithium aluminum hydride in 75 mL of dry diethyl ether, and the mixture was stirred for 30 min at room temperature. The reaction mixture was cautiously hydrolyzed by sequential, dropwise addition of 2.0 mL of water, 2.0 mL of 15% aqueous sodium hydroxide, and 6.0 mL of water. The mixture was filtered by gravity, and the white precipitate was washed well with ether. Concentration of the combined filtrate and washings gave 2.98 g of diol (~100% crude yield) which was used for subsequent reactions: ^{1}H NMR δ 0.11 (s, 9 H), 2.28 (s, 2 H), 2.63 (s, 2 H), 2.74 (broad s, 2 H), 3.65 (s, 2 H), 3.66 (s, 2 H), 5.58 (d, J = 1.41 Hz, 1 H), 5.71−5.76 (m, 1 H); ^{13}C NMR δ −0.03, 22.85, 41.84, 43.25, 66.18, 88.38, 103.13, 121.90, 127.53; IR (neat) 3380, 2957, 2174, 1622, 1431, 1250, 1083, 1035, 842 cm^{-1}; HRMS calcd for $C_{12}H_{21}BrSiO_2$ 304.0494, found 304.0495.

5-(2-Bromo-2-propenyl)-2,2-dimethyl-5-(3-(trimethylsilyl)-2-propynyl)-1,3-dioxane (6). A solution of 1.52 g (4.98 mmol) of 2-(2-bromo-2-propenyl)-2-(3-(trimethylsilyl)-2-propynyl)-1,3-propanediol, 0.620 g (5.96 mmol) of 2,2-dimethoxypropane, and 2.4 mg of TsOH in 13 mL of benzene was distilled until the still-head temperature reached 75 °C. The mixture was then allowed to cool, and a small amount of anhydrous potassium carbonate (~10 mg) was added to neutralize the acid catalyst. The mixture was filtered, the filtrate was concentrated, and the residue was chromatographed over silica gel (5% EtOAc/hexanes, R_f = 0.14) to afford 1.50 g (87%) of product: ^{1}H NMR δ 0.13 (s, 9 H), 1.40 (s, 3H), 1.41 (s, 3 H), 2.50 (s, 2 H), 2.65 (s, 2 H), 3.77 (s, 4 H), 5.60 (d, J = 1.38 Hz, 1 H), 5.72−5.76 (m, 1 H); ^{13}C NMR δ 0.04, 22.50, 23.60, 25.04, 36.29, 43.57, 66.43, 88.29, 98.14, 103.13, 121.93, 127.07; IR (neat) 2992, 2958, 2174, 1623, 1429, 1372, 1250, 1198, 1097, 843, 760 cm^{-1}; HRMS calcd for $C_{12}H_{16}BrO_2$ ($M^+ - Me_3Si$) 271.0333, found 271.0329.

2-Bromo-7-(1-naphthyl)-1-hepten-6-yne (7). A solution of 3.406 g (22.4 mmol) of 1-ethynylnaphthalene in 20 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 16.0 mL of a 1.39 M solution of *n*-BuLi in hexanes (22.2 mmol) was added. The cooling bath was then removed, and the reaction mixture was stirred at room temperature 30 min prior to the addition of 5.48 g (19.9 mmol) of 2-bromo-5-iodo-1-pentene. The mixture was heated at gentle reflux for 17 h, cooled to room temperature, and then quenched with 15 mL of water. The mixture was extracted with three 15-mL portions of diethyl ether, the combined ethereal extract were dried ($MgSO_4$) and concentrated, and the residue was distilled to give 4.31 g (72%) of product: bp 175 °C (0.6 mm); ^{1}H NMR δ 1.97 (pentet, J = 7.15 Hz, 2 H), 2.61 (t, J = 6.93, 2 H), 2.69 (t, J = 7.20 Hz, 2 H), 5.47 (d, J = 1.49 Hz), 5.68 (d, J = 1.49 Hz, 1 H), 7.37−7.85 (m, 6 H), 8.33 (apparent d, J = 8.02 Hz, 1 H); ^{13}C NMR δ 18.42, 26.99, 40.40, 79.39, 94.11, 117.43, 121.50, 125.21, 126.19, 126.24, 126.54, 128.07, 128.22, 130.09, 133.21, 133.50; IR (neat) 3065, 2980, 2220, 1613, 1570, 1410, 1378, 1098, 870, 780, 758 cm^{-1}. Anal. Calcd for $C_{17}H_{15}Br$: C, 68.24; H, 5.05. Found: C, 67.89; H, 5.02.

2-Bromo-7-(2-thienyl)-1-hepten-6-yne (8). A solution of 4.08 g (37.8 mmol) of 2-ethynylthiophene in 45 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen and 29.8 mL of a 1.61 M solution of *n*-BuLi in hexanes (48.0 mmol) was added. The cooling bath was then removed, and the solution was stirred at room temperature 30 min prior to the addition of 10.4 g (37.9 mmol) of 2-bromo-5-iodo-1-pentene. The mixture was heated at gentle reflux for 18 h, cooled to room temperature, and then quenched with 25 mL of water. The mixture was extracted with three 15-mL portions of diethyl ether, the combined ethereal extracts were dried ($MgSO_4$) and concentrated, and the residue was distilled to give 8.02 g (83%) of the product as a oil: bp 118−120 °C (0.7 mm); ^{1}H NMR δ 1.78 (pentet, J = 7.07 Hz, 2 H), 2.45 (t, J = 7.07 Hz, 2 H), 2.58 (t of d, J = 7.07, J = 0.67 Hz, 2 H), 5.37 and 5.56 (AB pattern, J_{AB} = 1.53 Hz, 2 H), 6.85−6.87 (m, 1 H), 7.04−7.10 (m, 2 H); ^{13}C NMR δ 18.28, 26.52, 40.22, 74.44, 93.11, 117.39, 123.87, 126.01, 126.73, 131.02, 133.31. Anal. Calcd for $C_{11}H_{11}BrS$: C, 51.78; H, 4.35. Found: C, 51.89; H, 4.44.

2-Bromo-7-cyclohexyl-1-hepten-6-yne (9). A solution of 2.69 g (24.9 mmol) of ethynylcyclohexane in 25 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 19.0 mL of a 1.37 M solution of *n*-BuLi in hexanes (26.0 mmol) was added. The cooling bath was removed, and the reaction mixture was stirred at room temperature 1 h prior to the addition of 5.92 g (21.5 mmol) of 2-bromo-5-iodo-1-pentene. The mixture was then heated at gentle reflux for 14 h, cooled to room temperature, and then partitioned between 10 mL of 5% aqueous sodium thiosulfate and 40 mL of diethyl ether. The aqueous layer was extracted with three 10-mL portions of diethyl ether, and the combined ethereal layers were dried ($MgSO_4$) and concentrated at reduced pressure. The residue was passed through a short silica gel column eluting with hexanes (R_f = 0.70) to afford 4.26 g (78%) of product: ^{1}H NMR δ 1.25−1.39 (m, 6 H), 1.65−1.77 (m, 6 H), 2.14−2.20 (t of d, J = 6.88 Hz, J = 2.16 Hz, 2 H), 2.38 (bs, 1 H), 2.51 (t, J = 6.88 Hz, 2 H), 5.38 and 5.57 (AB pattern, J_{AB} = 1.40 Hz, 2 H); ^{13}C NMR δ 17.42, 24.90, 25.94, 27.19, 29.11, 33.12, 40.21, 78.80, 85.49, 116.98, 133.79. Anal. Calcd for $C_{13}H_{19}Br$: C, 61.19; H, 7.50. Found: C, 61.03; H, 7.22.

2-Bromo-1-tridecen-6-yne (10). A solution of 2.10 g (19.1 mmol) of 1-octyne in 20 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 13.6 mL of a 1.37 M solution of *n*-BuLi in hexanes (18.6 mmol) was added. The cooling bath was then removed, and the solution was stirred at room temperature 30 min prior to the addition of 4.61 g (16.8 mmol) of 2-bromo-5-iodo-1-pentene in 3 mL of dry HMPA. The mixture was heated at gentle reflux for 16 h, cooled to room temperature, and then partitioned between 10 mL of 5% aqueous sodium thiosulfate and 40 mL of diethyl ether. The aqueous layer was extracted with three 10-mL portions of diethyl ether, the combined ethereal layers were dried ($MgSO_4$) and concentrated at reduced pressure, and the residue was distilled to afford 3.54 g (82%) of product: bp 132−133 °C (2.4 mm); ^{1}H NMR δ 0.85 (t, J = 6.63 Hz, 3 H), 1.23−1.43 (m, 8 H), 1.69 (pentet, J = 6.96 Hz, 2 H), 2.07−2.17 (m, 4 H), 2.50 (t, J = 7.21 Hz, 2 H), 5.37 (apparent s, 1 H), 5.56 (apparent s, 1 H); ^{13}C NMR δ 13.99, 17.45, 18.69, 22.54, 27.16, 28.52, 29.05, 31.34, 40.26, 78.90, 81.09, 116.93, 133.77. Anal. Calcd for $C_{13}H_{21}Br$: C, 60.71; H, 8.23. Found: C, 60.73; H, 8.13.

2-Bromo-1-decen-6-yne (11). A solution of 856 mg (12.6 mmol) of 1-pentyne in 11 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 4.40 mL of a 3.46 M solution of *n*-BuLi in hexanes (15.2 mmol) was added. The cooling bath was removed, and the solution was stirred at room temperature 30 min prior to the addition of 2.67 g (9.71 mmol) of 2-bromo-5-iodo-1-pentene. The mixture was heated at gentle reflux for 14 h, cooled to room temperature, and then partitioned between 10 mL of 5% aqueous sodium thiosulfate and 40 mL of diethyl ether. The aqueous layer was extracted with three 10-mL portions of diethyl ether, the combined ethereal layers were dried ($MgSO_4$) and concentrated at reduced pressure, and the residue was distilled to afford 1.90 g (92%) of product: bp 82 °C (1.5 mm); ^{1}H NMR δ 0.95 (t, J = 7.33 Hz, 3 H), 1.50 (sextet, J = 7.14 Hz, 2 H), 1.74 (pentet, J = 7.16 Hz, 2 H), 2.16 (m, 4 H), 2.54 (t of d, J = 7.24 Hz, J = 1.03 Hz, 2 H), 5.39 and 5.58 (AB pattern, J_{AB} = 1.52 Hz, 2 H); ^{13}C NMR δ 13.43, 17.43, 20.71, 22.47, 27.16, 40.25, 79.07, 80.88, 116.98, 133.75. Anal. Calcd for $C_{10}H_{15}Br$: C, 55.83; H, 7.03. Found: C, 55.89; H, 7.16.

2-Bromo-8-phenyl-1-octen-7-yne (12). A solution of 2.07 g (20.3 mmol) of phenylacetylene in 15 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 13.0 mL of a 1.50 M solution of *n*-BuLi in hexanes (19.5 mmol) was

added. The cooling bath was then removed, and the solution was stirred at room temperature for 30 min prior to the addition of 5.47 g (18.9 mmol) of 2-bromo-6-iodo-1-hexene. The reaction mixture was heated at gentle reflux for 18 h, cooled to room temperature, and then quenched with 15 mL water. The mixture was extracted with three 10-mL portions of diethyl ether, the combined ethereal extracts were dried ($MgSO_4$) and concentrated, and the residue was distilled to give 4.66 g (94%) of the product as a pale yellow oil: bp 118−120 °C (0.7 mm); ^{1}H NMR δ 1.50−1.69 (m, 4 H), 2.36 (t, J = 6.80 Hz, 2 H), 2.41 (t, J = 6.94 Hz, 2 H), 5.34 and 5.52 (AB pattern, J_{AB} = 1.19 Hz, 2 H), 7.19−7.36 (m, 5 H); ^{13}C NMR δ 19.13, 27.02, 27.36, 40.85, 80.94, 89.68, 116.66, 123.89, 127.54, 128.17, 131.52, 134.30. Anal. Calcd for $C_{14}H_{15}Br$: C, 63.89; H, 5.74. Found: C, 64.10; H, 5.75.

2-Bromo-8-(trimethylsilyl)-1-octen-7-yne (13). A solution of 2.66 g (27.1 mmol) of (trimethylsilyl)acetylene in 25 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 17.0 mL of a 1.77 M solution of *n*-BuLi in hexanes (30.1 mmol) was added. The cooling bath was then removed, and the solution was stirred at room temperature for 30 min prior to the addition of 5.15 g (17.8 mmol) of 2-bromo-6-iodo-1-hexene. The mixture was heated at gentle reflux for 17 h, cooled to room temperature, and then quenched with 15 mL water. The mixture was extracted with three 15-mL portions of diethyl ether, the combined ethereal extracts were dried ($MgSO_4$) and concentrated, and the residue was distilled to give 4.39 g (96%) of product: bp 110−111 °C (2.5 mm); ^{1}H NMR δ 0.12 (s, 9 H), 1.47−1.56 (m, 2 H), 1.59−1.68 (m, 2 H), 2.22 (t, J = 6.92 Hz, 2 H), 2.42 (t, J = 6.81 Hz, 2 H), 5.37 and 5.55 (AB pattern, J_{AB} = 1.46 Hz, 2 H); ^{13}C NMR δ 0.14, 19.56, 26.90, 27.20, 40.81, 84.83, 106.90, 116.58, 134.31. Anal. Calcd for $C_{11}H_{19}BrSi$: C, 50.96; H, 7.39. Found: C, 50.94; H, 7.63.

2-Bromo-7-(1-methoxycyclohexyl)-1-hepten-6-yne (14). A solution of 3.14 g (22.7 mmol) of 1-ethynyl-1-methoxycyclohexane[29] in 25 mL of dry THF was added to 14.0 mL of a 1.77 M solution of *n*-BuLi in hexanes (24.8 mmol) at room temperature under an atmosphere of nitrogen, and the resulting solution was warmed at gentle reflux for 1 h. The mixture was then allowed to cool to room temperature, 4.96 g (18.1 mmol) of 2-bromo-5-iodo-1-pentene was added, and the resulting mixture was heated at reflux for 15 h. The reaction was quenched with 20 mL of water and extracted with three 30-mL portions of diethyl ether. The combined ethereal extracts were dried ($MgSO_4$) and concentrated, and the residue was distilled to give 3.91 g (60%) of product: bp 147−149 °C (2.0 mm); ^{1}H NMR δ 1.45−1.55 (m, 8 H), 1.72−1.82 (m, 4 H), 2.25 (t, J = 6.87 Hz, 2 H), 2.53 (t, J = 6.87 Hz, 2 H), 3.31 (s, 3 H), 5.39 and 5.57 (AB pattern, J_{AB} = 1.44 Hz, 2 H); ^{13}C NMR δ 17.33, 22.87, 25.50, 26.94, 36.97, 40.20, 50.44, 73.94, 81.94, 85.11, 117.22, 133.52. Anal. Calcd for $C_{14}H_{21}BrO$: C, 58.96; H, 7.42. Found: C, 59.29; H, 7.16.

2-(3-Butenyl)-1-ethynylbenzene. Following the general procedure of Comins,[22] a solution of 1.64 mL (12.8 mmol) of *N*,*N*,*N*′-trimethylethylenediamine in 32 mL of anhydrous THF was cooled to −78 °C, and 8.05 mL of 1.54 M solution of *n*-BuLi in hexane (12.4 mmol) was added under an atmosphere of argon. After 30 min of stirring at −78 °C, 1.44 g (12.0 mmol) of *o*-tolualdehyde was added and the solution was allowed to warm to −20 °C over a period of 20 min. The mixture was then cooled to −55 °C, and 21.8 mL of a 1.64 M solution of *t*-BuLi in pentane (36.0 mmol) was added. The resulting dark-red solution was stirred at −55 °C for 2.5 h and then recooled to −78 °C, and 8.71 g (72.0 mmol) of allyl bromide was added rapidly. The cooling bath was then removed, the colorless reaction mixture was allowed to warm and stir at room temperature for 30 min, and the mixture was then poured into 75 mL of cold 10% aqueous hydrochloric acid. The resulting two-phase mixture was stirred rapidly for 10 min, and the layers were separated. The aqueous layer was extracted with three 50-mL portions of diethyl ether, and the combined ethereal layers were washed with brine, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed over silica gel (5% EtOAc/*n*-pentane, R_f = 0.26) to give 1.36 g (71%) of the known[23] **2-(3-butenyl)benzaldehyde** as a clear oil: ^{1}H NMR δ 2.33−2.39 (4 lines, 2 H), 3.14 (t, J = 7.75 Hz, 2 H), 4.98−5.07 (m, 2 H), 5.80−6.00 (complex pattern, 1 H), 7.25−7.90 (m, 4 H), 10.27 (s, 1 H); ^{13}C NMR δ 31.91, 35.95, 114.43, 126.55, 131.04, 131.95, 133.63, 133.69, 137.36, 144.48, 192.34.

The aldehyde (3.08 g, 19.2 mmol) was added at 0 °C to a solution of 12.4 g (37.5 mmol) of carbon tetrabromide and 19.6 g (103 mmol) of triphenylphosphine in 150 mL of methylene chloride, and the mixture was stirred at 0 °C for 30 min and then at room temperature for 40 min. Pentane (120 mL) was then added, and the precipitate was removed by vacuum filtration. The filtrate was concentrated under reduced pressure, and the residue was passed through a short column of silica gel using pentane as the eluent to give 5.89 g (97%) of 2-(3-butenyl)-1-(2,2-dibromoethenyl)benzene as a clear oil. The dibromide (5.51 g, 17.4 mmol) was dissolved in 120 mL of anhydrous THF, cooled to −78 °C, and treated with 36.2 mL of a 1.80 M solution of *n*-BuLi in hexane (65.1 mmol). The resulting mixture was stirred at −78 °C for 1 h. The reaction was quenched by the addition of 0.60 mL of methanol followed by 1.20 mL of water, the cooling bath was then removed, and the mixture was allowed to warm to room temperature. The bulk of the solvent was removed under reduced pressure, the residue was partitioned between 20 mL of water and 100 mL of pentane, the layers were separated, and the aqueous phase was extracted with pentane. The combined pentane extracts were dried ($MgSO_4$) and concentrated to afford 2.76 g (∼100%) of essentially pure title compound that was used as such for subsequent reactions: ^{1}H NMR δ 2.39 (apparent q, J = 7.06 Hz, 2 H), 2.89 (apparent t, J = 7.84 Hz, 2 H), 3.25 (s, 1 H), 4.95−5.08 (m, 2 H), 5.80−5.98 (complex pattern, 1 H), 7.11−7.29 (m, 3 H), 7.46 (d, J = 7.48 Hz, 1 H); ^{13}C NMR δ 33.92, 34.52, 80.70, 82.24, 114.90, 121.48, 125.79, 128.78, 128.78, 132.88, 138.01, 144.44; IR (neat) 3295, 3072, 2927, 2104, 1641, 912, 756 cm^{-1}; HRMS calcd for $C_{12}H_{12}$ 156.0939, found 56.0935.

2-Bromo-7-[2-(3-butenyl)phenyl]-1-hepten-6-yne (17). A solution of 2.33 g (14.9 mmol) of 2-(3-butenyl)-1-ethynylbenzene in 53 mL of dry THF was cooled to −78 °C under an atmosphere of nitrogen, and 8.29 mL of a 1.80 M solution of *n*-BuLi in hexanes (14.9 mmol) was added. The cooling bath was then removed, and the solution was stirred at room temperature for 1 h prior to the addition of 4.10 g (14.9 mmol) of 2-bromo-5-iodo-1-pentene. The mixture was heated at gentle reflux for 16 h, cooled to room temperature, and then quenched with water. The mixture was extracted well with diethyl ether, the combined ethereal extracts were dried ($MgSO_4$) and concentrated, and the residue was purified by column chromatography on silica gel using petroleum ether (R_f = 0.20) as eluent to afford 4.20 g (93%) of the product as a clear oil: ^{1}H NMR δ 1.86 (quintet, J = 7.05 Hz, 2 H), 2.34−2.43 (m, 2 H), 2.47 (t, J = 6.93 Hz, 2 H), 2.61 (t, J = 7.22 Hz, 2 H), 2.85 (m, 2 H), 4.94−5.10 (m, 2 H), 5.44 (apparent d, J = 1.39 Hz, 1 H), 5.62−5.64 (m, 1 H), 5.80−5.96 (10 lines, 1 H), 7.08−7.22 (m, 3 H), 7.36 (d, J = 7.30 Hz, 1 H); ^{13}C NMR δ 18.14, 26.85, 34.08, 34.55, 40.23, 79.86, 92.61, 114.76, 117.29, 123.07, 125.69, 127.65, 128.61, 132.15, 133.43, 138.08, 143.51; HRMS calcd for $C_{17}H_{19}$ (M^+ − Br) 223.1487, found 223.1484.

General Procedure for the Generation and Cyclization of Acetylenic Vinyllithiums. An approximately 0.1 M solution of the appropriate acetylenic vinyl bromide (**4**−**14**, **17**) in *n*-pentane−diethyl ether (proportions as given in Table 1) was cooled under an atmosphere of argon to either −100 °C (bath temperature; MeOH−liq N_2) or −78 °C (bath temperature; acetone−solid CO_2) as indicated in Table 1, and, with stirring, 2.0−2.2 molar equiv of commercial *t*-BuLi in pentane was added via syringe over a 5 min period. The reaction mixture was stirred for an additional 5 min at low temperature, and 2.0 molar equiv of dry, deoxygenated TMEDA was added at −78 °C to reaction mixtures prepared from substrates **9**−**11** bearing an alkyl substituent on the triple bond (Table 1, entries 6−8). The reaction mixtures were then allowed to stand under argon for a period of time at the appropriate temperature to effect the isomerization: specific conditions of time and temperature used to complete the cyclization of various substrates are given in Table 1. Reaction mixtures were quenched with either deoxygenated water or MeOH, washed with water, dried ($MgSO_4$), and concentrated. The crude bis-exocyclic 1,3-dienes were used in subsequent Diels−

Alder reactions: the yields reported in Table 1 are those of the dienes; the balance of the product, assayed by GC and ^{1}H NMR, was the isomeric uncyclized enyne. The dienes exhibited the spectroscopic data presented below.

(*E*)-1-Benzylidene-5,5-dimethyl-2-methylenecyclopentane (Table 1, entry 1): ^{1}H NMR δ 1.05 (s, 6 H), 1.53 (t, J = 7.49 Hz, 2 H), 2.47 (tt, J = 7.49 Hz, J = 2.39 Hz, 2 H), 4.88 (t, J = 2.09 Hz, 1 H), 5.40 (t, J = 2.34 Hz, 1H), 6.99 (apparent s, 1 H), 7.21−7.32 (m, 5 H); ^{13}C NMR δ 27.78, 29.25, 29.86, 41.74, 103.28, 120.27, 126.40, 127.60, 129.31, 138.27, 149.75, 151.54; IR (neat) 3100, 3043, 2970, 2880, 1601, 1498, 1370, 963, 763, 701 cm^{-1}; HRMS calcd for $C_{15}H_{18}$ 198.1409, found 198.1409.

(3aα,4*β*,8aα)-5,5-Dimethyl-4-phenyl-4,5,6,7,8,8a-hexahydro-3a*H*-2-oxa-5-indacene-1,3-dione (15) (Table 2, entry 1). A solution of 103 mg (0.519 mmol) of (*E*)-1-benzylidene-5,5-dimethyl-2-methylenecyclopentane and 33.9 mg (0.346 mmol) of maleic anhydride in 3 mL of toluene was heated at reflux for 3 h. Removal of solvent at reduced pressure gave an off-white solid which was recrystallized from hexanes to give 82 mg (80%) of product as colorless crystals: mp 157−158 °C; ^{1}H NMR δ 0.58 (s, 3 H), 1.06 (s, 3 H), 1.66−1.84 (m, 2 H), 2.28−2.64 (m, 3 H), 2.94 (dd, J = 18.23 Hz, J = 1.58 Hz, 1 H), 3.30−3.43 (m, 2 H), 3.93 (d, J = 5.78 Hz, 1 H), 7.10−7.40 (m, 5 H); ^{13}C NMR δ 21.85, 26.65, 27.21, 33.06, 38.05, 38.97, 39.46, 46.72, 47.04, 128.22, 128.52, 128.77, 133.20, 137.45, 141.85, 171.43, 173.83; IR (KBr) 3055, 3020, 2954, 1856, 1779, 1489, 1453, 1220, 1072, 746, 707 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O_3$: C, 76.99; H, 6.81. Found: C, 76.68; H, 7.05.

5,5-Dimethyl-2,4-diphenyl-5,6,7,8-tetrahydro-4*H*-2,3a,-8a-triaza-5-indacene-1,3-dione (Table 2, entry 2). To a bright-red solution of 83.4 mg (0.476 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 3 mL of methylene chloride at 0 °C was added 113 mg (0.570 mmol) of (*E*)-1-benzylidene-5,5-dimethyl-2-methylenecyclopentane, and the resulting pale yellow mixture was stirred at 0 °C for 10 min. Removal of solvent at reduced pressure gave a tan-colored solid which was recrystallized from acetone to give 133 mg (75%) of the cycloadduct: mp 179−180 °C; ^{1}H NMR δ 0.56 (s, 3 H), 1.17 (s, 3 H), 1.80−1.92 (m, 2 H), 2.41−2.56 (m, 2 H), 4.08 (d, J = 16.64 Hz, 1 H), 4.55 (d, J = 16.64 Hz, 1 H), 5.51 (s, 1 H), 7.25−7.45 (m, 10 H); ^{13}C NMR δ 26.55, 27.39, 30.49, 40.44, 45.80, 56.96, 125.16, 127.80, 128.25, 128.43, 128.52, 128.76, 128.87, 131.09, 136.12, 139.90, 150.96, 152.68; IR (KBr) 3064, 2950, 2860, 1776, 1708, 1504, 1458, 1412, 1290, 1135, 767, 719, 697 cm^{-1}. Anal. Calcd for $C_{23}H_{23}N_3O_2$ C, 73.96; H, 6.21; N, 11.26. Found: C, 73.60; H, 6.25; N, 11.08.

5-Chloro-1,1-dimethyl-7-phenyl-2,3,4,5,6,7-hexahydro-1*H*-indene-5-carbonitrile (Table 2, entry 3). A solution of 83.3 mg (0.420 mmol) of (*E*)-1-benzylidene-5,5-dimethyl-2-methylenecyclopentane and 24.5 mg (0.280 mmol) of 2-chloroacrylonitrile in 5 mL of toluene was heated at gentle reflux for 18 h. Solvent was removed at reduced pressure, and the residue was chromatographed over silica gel (5% EtOAc/hexanes; R_f = 0.29) to give 68.0 mg (85%) of the cycloadduct as a 7.2:1 mixture of diastereoisomers. The pale-yellow, viscous liquid crystallized on standing: mp = 81−83 °C; ^{1}H NMR (major diastereoisomer) δ 0.57 (s, 3 H), 0.93 (s, 3 H), 1.60−1.78 (m, 2 H), 2.08−2.18 (m, 1 H), 2.25−2.37 (m, 5 H), 3.37 (s, 1 H), 7.25−7.37 (m, 5 H); ^{13}C NMR 22.09, 25.46, 27.62, 29.68, 32.91, 39.49, 46.36, 50.82, 60.11, 118.97, 127.75, 128.35, 128.40, 133.45, 136.92, 137.85; HRMS calcd for $C_{18}H_{20}ClN$ 285.1284, found 285.1288.

7,7-Dimethyl-1-phenyl-4,5,6,7-tetrahydro-1*H*-cyclopenta[*c*]pyran-3,3-dicarboxylic Acid Diethyl Ester (Table 2, entry 4). A solution of 112.2 mg (0.566 mmol) of (*E*)-1-benzylidene-5,5-dimethyl-2-methylenecyclopentane, 70.2 mg (0.403 mmol) of diethyl ketomalonate, and 5.80 mg of 4-hydroxyphenol in 5 mL of toluene was heated at gentle reflux for 2 h. Solvent was removed at reduced pressure, and the residue was chromatographed over silica gel (15% EtOAc/hexanes; R_f = 0.20) to give 129 mg (86%) of the adduct as a single regioisomer: ^{1}H NMR δ 0.37 (s, 3 H), 0.97 (s, 3 H), 1.22 (t, J = 7.12 Hz, 3 H), 1.30 (t, J = 7.12 Hz, 3 H), 1.53−1.71 (m, 2 H), 2.13−2.28 (m, 1 H), 2.37−2.50 (m, 1 H), 2.81−2.84 (three lines, 2 H), 4.10−4.31 (overlapping patterns, 4 H), 5.52 (apparent quintet, J = 2.56 Hz, 1 H), 7.24−7.36 (m, 5 H); ^{13}C NMR δ 13.91, 14.25, 26.87, 27.21, 31.30, 33.24, 40.43, 45.83, 61.73, 62.08, 77.11, 80.84, 128.11, 128.24, 128.90, 130.61, 140.33, 141.75, 168.00, 168.93; IR (neat) 3087, 2954, 1746, 1495, 1456, 1364, 1259, 1182, 1043, 967, 858, 745, 700 cm^{-1}; HRMS calcd for $C_{22}H_{28}O_5$ 372.1937, found 372.1933.

(*E*)-1-((Trimethylsilyl)methylidene)-2-methylenecyclopentane (Table 1, entry 2): ^{1}H NMR δ 0.11 (s, 9 H), 1.67 (apparent quintet, J = 7.26 Hz, 2 H), 2.35−2.48 (m, 4 H), 4.86 (br s, 1 H), 5.34 (apparent t, J = 2.26 Hz, 1H), 5.94 (t, J = 2.26 Hz, 1 H); ^{13}C NMR δ 0.45, 24.04, 33.47, 33.58, 103.56, 116.85, 150.19, 156.48; IR (neat) 2954, 1595, 1312, 1247, 1043, 868, 841 cm^{-1}; HRMS calcd for $C_{10}H_{18}Si$ 166.1178, found 166.1175.

2-Phenyl-4-(trimethylsilyl)-5,6,7,8-tetrahydro-4*H*-2,3a,-8a-triaza-5-indacene-1,3-dione (Table 2, entry 5). To a bright red solution of 54.5 mg (0.311 mmol) of 4-phenyl-1,2,4-triazoline-3,5-dione in 3 mL of methylene chloride at 0 °C was added 60.7 mg (0.365 mmol) of (*E*)-1-((trimethylsilyl)methylidene)-2-methylenecyclopentane and the resulting pale yellow mixture was stirred at 0 °C for 10 min. Removal of solvent at reduced pressure gave a tan-colored solid which was recrystallized from acetone to give 88.1 mg (83%) of the cycloadduct: mp 123−124 °C; ^{1}H NMR δ 0.12 (s, 9H), 2.00 (5 line pattern, J = 7.10 Hz, 2 H), 2.40 (t, J = 7.10, 4 H), 4.00 (d, J = 15.87 Hz, 1 H), 4.25 (d, J = 15.87 Hz, 1 H), 4.31 (s, 1 H), 7.08−7.21 (m, 5 H); ^{13}C NMR δ −1.77, 22.86, 32.96, 34.24, 46.30, 48.95, 125.37, 125.63, 127.93, 129.08, 131.49, 133.01, 149.68, 153.77; IR (KBr) 3014, 2954, 2899, 2848, 1772, 1711, 1600, 1502, 1455, 1417, 1250, 844, 762, 690 cm^{-1}. Anal. Calcd for $C_{18}H_{23}N_3O_2Si$: C, 63.31; H, 6.79; N, 12.30. Found: C, 63.18; H, 6.93; N, 12.35.

(*E*)-2-((Trimethylsilyl)methylidene)-3-methylene-7,9-dioxaspiro[4.5]decane (Table 1, entry 3): ^{1}H NMR δ 0.10 (s, 9 H), 1.39 (s, 3 H), 1.41 (s, 3 H), 2.35 (d, J = 2.23 Hz, 2 H), 2.38 (t, J = 2.18 Hz, 2 H), 3.58 (apparent s, 4 H), 4.85−4.89 (m, 1 H), 5.36 (t, J = 2.28 Hz, 1 H), 5.96 (t, J = 2.32 Hz, 1 H); ^{13}C NMR δ −0.48, 23.32, 24.25, 38.93, 39.88, 40.11, 68.05, 97.87, 105.72, 119.32, 147.57, 153.69; IR (neat) 2953, 1640, 1600, 1370, 1248, 1198, 1100, 1063, 835 cm^{-1}; HRMS calcd for $C_{15}H_{26}O_2Si$ 266.1702, found 266.1701.

(4*β*,4aα,8aα)-2′,2′-Dimethyl-4-(trimethylsilyl)spiro(1,3,4,-4a,5,8,8a,9-octahydrocyclopenta[*b*]naphthalene-2,5′-[1,3]-dioxane)-5,8-dione (16) (Table 2, entry 6). A solution of 76.7 mg (0.288 mmol) of (*E*)-2-((trimethylsilyl)methylidene)-3-methylene-7,9-dioxaspiro[4.5]decane and 208 mg (0.192 mmol) of 1,4-benzoquinone in 3 mL of toluene was heated at reflux for 4 h. Removal of solvent at reduced pressure gave a solid which was recrystallized from a mixture of benzene and hexane to give 64 mg (89%) of product as pale-yellow crystals: mp 152−154 °C; ^{1}H NMR δ 0.13 (s, 9 H), 1.39 (s, 3 H), 1.41 (s, 3 H), 1.61−1.69 (m, 1 H), 1.96−2.25 (m, 5 H), 2.38 (d, J = 15.48 Hz, 1 H), 2.94−3.06 (m, 1 H), 3.48 (t, J = 4.84 Hz, 1 H), 3.69−3.85 (m, 4 H), 6.56 (dd, J = 10.27 Hz, J = 1.66 Hz, 1 H), 6.65 (d, J = 10.27 Hz, 1 H); ^{13}C NMR δ 0.62, 23.53, 24.11, 28.00, 28.47, 30.89, 42.75, 42.94, 50.52, 69.15, 69.37, 97,69, 127.77, 132.13, 137.85, 140.59, 199.59, 202.42; IR (KBr) 2992, 2944, 2852, 1687, 1601, 1452, 1381, 1249, 1199, 1088, 1068, 835, 755 cm^{-1}. Anal. Calcd for $C_{21}H_{30}O_4Si$: C, 67.35; H, 8.08. Found: C, 66.99; H, 8.45.

2′,2′-Dimethyl-4-(trimethylsilyl)spiro(4,7-dihydro-1*H*-indene-2,5′-[1,3]dioxane)-5,6-dicarboxylic Acid Dimethyl Ester (Table 2, entry 7). A solution of 77.7 mg (0.291 mmol) of (*E*)-2-((trimethylsilyl)methylidene)-3-methylene-7,9-dioxaspiro[4.5]decane and 28.1 mg (0.198 mmol) of dimethyl acetylenedicarboxylate in 3 mL of toluene was heated at reflux for 3 h. Removal of the solvent at reduced pressure and chromatography of the residue over silica gel (20 % EtOAc/hexanes; R_f = 0.40) gave 74.0 mg (91%) of a clear oil which crystallized slowly on standing: mp 66−67 °C; ^{1}H NMR δ −0.01 (s, 9 H), 1.38 (s, 6 H), 2.03−2.34 (m, 4 H), 2.75−2.92 (m, 3 H), 2.63 (s, 2 H), 3.64 (s, 2 H), 3.69 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR δ −1.57, 23.65, 23.83, 29.71, 34.73, 40.97, 42.32, 42.86, 51.96, 52.00, 69.13, 69.33, 97.65, 126.27, 130.69, 132.44, 137.58, 168.54, 168.97; IR (neat) 2992, 2951, 1728, 1437, 1384, 1265, 1198, 875, 833 cm^{-1}. Anal. Calcd for $C_{21}H_{32}O_6Si$: C, 61.74; H, 7.89. Found: C, 61.46; H, 8.02.

(*E*)-2-(1-Naphthylmethylidene)-1-methylenecyclopentane (Table 1, entry 4): ^{1}H NMR δ 1.74 (5 line pattern, J =

7.15 Hz, 2 H), 2.55−2.66 (m, 4 H), 5.07 (apparent s, 1 H), 5.66 (apparent s, 1 H), 7.48−7.88 (m, 8 H); ^{13}C NMR δ 24.52, 32.60, 33.76, 102.91, 116.67, 124.58, 125.26, 125.68, 125.79, 126.19, 127.18, 128.47, 131.96, 133.63, 135.22, 143.91, 150.33; HRMS calcd for $C_{17}H_{16}$ 220.1250, found 220.1252.

(3aα,4*β*,8aα)-4-(Naphthalen-1-yl)-4,5,6,7,8,8a-hexahydro-3a*H*-2-oxa-5-indacene-1,3-dione (Table 2, entry 8). A solution of 189 mg (0.86 mmol) of (*E*)-2-(1-naphthylmethylidene)-1-methylenecyclopentane and 75.4 mg (0.769 mmol) of maleic anhydride in 5 mL of toluene was heated at gentle reflux for 1.5 h. Evaporation of the solvent left a yellow solid which was recrystallized from benzene to afford 184 mg (75%) of bone-white crystals: mp 165−166 °C; ^{1}H NMR δ 1.87 (5 line pattern, J = 7.48 Hz, 2 H), 2.12 (m, 2 H), 2.48−2.62 (m, 3 H), 3.02 (d, J = 17.85 Hz, 1 H), 3.45 (t of d, J = 8.70 Hz, J = 2.05 Hz 1 H), 3.72 (t, J = 8.70 Hz, 1 H), 4.87 (d, J = 7.57, 1 H), 7.02−7.84 (m, 6 H), 8.20 (d, J = 8.37 Hz, 1 H); ^{13}C NMR δ 19.72, 21.30, 21.66, 34.78, 35.86, 38.85, 45.08, 123.52, 125.17, 125.40, 125.87, 126.09, 128.83, 128.92, 132.21, 133.58, 134.16, 134.39, 170.63, 173.64. Anal. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 78.93; H, 5.83.

4-Naphthalen-1-yl-2,3,4,5,6,7-hexahydro-1*H*-indene-5,5,6,6-tetracarbonitrile (Table 2, entry 9). A solution of 185 mg (0.84 mmol) of (*E*)-2-(1-naphthylmethylidene)-1-methylenecyclopentane and 98.3 mg (0.767 mmol) of recrystallized tetracyanoethylene in 5 mL of toluene was heated at gentle reflux for 2 h. The reaction mixture was filtered through a short plug of neutral alumina using diethyl ether as the eluent, the solution was concentrated, and the residue triturated with pentane to give a yellow solid. Recrystallization from pentane afforded 189 mg (71%) of product: mp 153−154 °C; ^{1}H NMR δ 1.93−2.02 (m, 2 H), 2.09 (d, J = 2.88 Hz, 1 H), 2.25 (d, J = 2.88 Hz, 1 H), 2.51 (m, 1 H), 2.64 (m, 1 H), 3.19 (d, J = 17.43 Hz, 1 H), 3.40 (d, J = 17.43 Hz, 1 H), 5.36 (s, 1 H), 7.45−7.66 (m, 4 H), 7.96 (m, 2 H), 8.19 (d, J = 8.44 Hz); ^{13}C NMR δ 21.78, 33.85, 34.03, 36.25, 40.49, 42.35, 46.26, 109.74, 111.05, 122.00, 124.99, 126.58, 126.91, 127.45, 128.46, 129.44, 130.88, 131.81, 132.51, 134.29, 134.64, 142.08. Anal. Calcd for $C_{23}H_{16}N_4$: C, 79.29; H, 4.63; N, 16.08. Found: C, 78.85; H, 4.87; N, 15.70.

(*E*)-2-(2-Thienylmethylidene)-1-methylenecyclopentane (Table 1, entry 5): ^{1}H NMR δ 1.82 (5 line pattern, J = 7.30 Hz, 2 H), 2.41−2.51 (m, 2 H), 2.69 (dt, J = 7.24 Hz, 2.40 Hz, 2 H), 4.93 (apparent s, 1H), 5.39 (apparent s, 1 H), 6.91−7.27 (m, 4 H); ^{13}C NMR δ 24.20, 32.53, 34.13, 102.30, 113.23, 125.15, 126.77, 127.12, 130.90, 142.44, 150.45; HRMS for calcd $C_{11}H_{12}S$ 176.0660, found 176.0662.

(3aα,4*β*,8aα)-4-(Thiophen-2-yl)-4,5,6,7,8,8a-hexahydro-3a*H*-2-oxa-5-indacene-1,3-dione (Table 2, entry 10). A solution of 190.3 mg (1.08 mmol) of (*E*)-2-(2-thienylmethylidene)-1-methylenecyclopentane and 107.7 mg (1.10 mmol) of maleic anhydride in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure and chromatography of the burgundy-colored residue over silica gel using diethyl ether as eluent gave 173 mg (58%) of the product as an oil: ^{1}H NMR δ 1.87 (5 line pattern, J = 7.81 Hz, 2 H), 2.28−2.46 (m, 5 H), 2.84 (d, J = 16.86 Hz, 1 H), 3.41−3.49 (m, 2 H), 4.18 (d, J = 5.44 Hz, 1 H), 6.74 (d, J = 3.41 Hz, 1 H), 6.89 (dd, J = 5.12 Hz, J = 3.41 Hz, 1 H), 7.12 (dd, J = 5.12 Hz, J = 1.04 Hz, 1 H); ^{13}C NMR δ 21.24, 21.76, 34.45, 35.61, 36.08, 37.73, 46.60, 125.44, 127.21, 127.64, 134.63, 135.58, 140.47, 171.26, 173.58; HRMS calcd for $C_{15}H_{14}O_3S$ 274.0664, found 274.0660.

(*E*)-2-(Cyclohexylmethylidene)-1-methylenecyclopentane (Table 1, entry 6): ^{1}H NMR δ 0.85−0.92 (m, 4 H), 1.10−1.40 (m, 6 H), 1.53 (t, J = 7.11 Hz, 1 H), 2.05 (t of d, J = 14.88, J = 8.09 Hz, 2 H), 2.14−2.26 (m, 2 H), 2.33−2.41 (m, 2 H), 4.74 (apparent s, 1 H), 5.19 (apparent s, 1 H), 5.81−5.85 (m, 1 H); ^{13}C NMR δ 14.19, 22.76, 29.24, 29.60, 29.82, 31.92, 34.63, 100.62, 120.83, 139.89, 149.80; HRMS calcd for $C_{13}H_{20}$ 176.1565, found 176.1567.

4-Cyclohexyl-2,3,4,7-tetrahydro-1*H*-indene-5,6-dicarboxylic Acid Dimethyl Ester (Table 2, entry 11). A solution of 116.1 mg (0.659 mmol) of (*E*)-2-(cyclohexylmethylidene)-1-methylenecyclopentane and 69.0 mg (0.485 mmol) of dimethyl acetylenedicarboxylate in 5 mL of toluene was heated at gentle reflux for 3 h. Removal of the solvent at reduced pressure and chromatography of the pale-yellow residue over silica gel (10% EtOAc/hexanes; R_f = 0.56) gave 114.7 mg (74%) of the adduct as an oil: ^{1}H NMR δ 0.77−0.90 (m, 2 H), 1.00−1.25 (m, 4 H), 1.43−1.71 (m, 4 H), 1.79−1.89 (m, 2 H), 2.11−2.19 (m, 2 H), 2.27−2.46 (m, 3 H), 2.75−2.93 (m, 2 H), 3.15 (bs, 1 H), 3.68 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR δ 22.87, 26.77, 27.03, 28.90, 29.32, 30.93, 35.09, 35.57, 42.62, 45.65, 51.98, 132.86, 133.16, 133.93, 138.97, 168.24, 169.76; HRMS calcd for $C_{19}H_{26}O_4$ 318.1821, found 318.1824.

(*E*)-2-Heptylidene-1-methylenecyclopentane (Table 1, entry 7): ^{1}H NMR δ 0.85−0.99 (m, 3 H), 1.25−1.38 (m, 10 H), 1.79−1.45 (m, 2 H), 2.08 (t of d, J = 6.97, J = 14.32 Hz, 2 H), 2.31−2.42 (m, 2 H), 4.74 (s, 1 H), 5.19 (s, 1 H), 5.81−5.85 (m, 1 H); HRMS calcd for $C_{13}H_{22}$ 178.1721, found 178.1721.

4-Hexyl-2,3,4,7-tetrahydro-1*H*-indene-5,6-dicarboxylic Acid Dimethyl Ester (Table 2, entry 12). A solution of 170.8 mg (0.958 mmol) of (*E*)-2-heptylidene-1-methylenecyclopentane and 131.3 mg (0.924 mmol) of dimethyl acetylenedicarboxylate in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure and chromatography of the pale-yellow residue over silica gel (20% EtOAc/hexanes; R_f = 0.78) gave 186.0 mg (63%) of the adduct: ^{1}H NMR δ 0.83−0.95 (m, 3 H), 1.11−1.29 (m, 8 H), 1.44−1.63 (m, 2 H), 1.90 (5 line pattern, 2 H), 2.14−2.40 (m, 4 H), 2.78−3.10 (m, 2 H), 3.32 (bs, 1 H), 3.76 (s, 3 H), 3.79 (s, 3 H); ^{13}C NMR δ 14.02, 22.09, 22.60, 24.17, 28.62, 29.48, 30.77, 31.64, 33.22, 35.17, 39.53, 51.99, 52.04, 130.71, 131.86, 133.50, 140.94, 167.73, 169.80; HRMS calcd for $C_{19}H_{28}O_4$ 320.1988, found 320.1989.

(*E*)-2-Butylidene-1-methylenecyclopentane (Table 1, entry 8): ^{1}H NMR δ 0.82−1.01 (m, 3 H), 1.16−1.27 (m, 2 H), 1.37−1.45 (m, 2 H), 1.65 (t, J = 7.24 Hz, 2 H), 2.02−2.38 (m, 4 H), 4.74 (apparent s, 1 H), 5.19 (apparent s, 1 H), 5.80−5.88 (m, 1 H); ^{13}C NMR δ 14.05, 22.61, 23.97, 29.04, 31.91, 34.52, 100.54, 120.40, 140.00, 149.65; HRMS calcd for $C_{10}H_{16}$ 136.1252, found 136.1256.

(3aα,4*β*,8aα)-2-Methyl-4-propyl-5,6,7,8,8a-hexahydro-3a*H*-2-aza-5-indacene-1,3-dione (Table 2, entry 13). A solution of 84.1 mg (0.617 mmol) of (*E*)-2-butylidene-1-methylenecyclopentane and 61.0 mg (0.549 mmol) of *N*-methylmaleimide in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure and chromatography of the residue over silica gel (hexanes; R_f = 0.47) gave 96.3 mg (71%) of the isomerically pure product as a yellow oil: ^{1}H NMR δ 0.92 (t, J = 7.00 Hz, 3 H), 1.39−1.43 (m, 3 H), 1.61−1.64 (m, 2 H), 1.76−1.86 (m, 2 H), 2.25−2.40 (m, 5 H), 2.52−2.60 (m, 2 H), 2.94 (s, 3 H), 3.09−3.11 (m, 1 H); ^{13}C NMR δ 14.18, 21.38, 22.47, 24.10, 24.54, 31.72, 34.29, 35.72, 36.48, 40.20, 43.91, 134.62, 139.25, 178.57, 180.26; HRMS calcd for $C_{15}H_{21}NO_2$ 247.1572, found 247.1571.

4-Propyl-2,3,4,7-tetrahydro-1*H*-indene-5,6-dicarboxylic Acid Dimethyl Ester (Table 2, entry 14). A solution of 104.2 mg (0.765 mmol) of (*E*)-2-butylidene-1-methylenecyclopentane and 103.8 mg (0.730 mmol) of dimethyl acetylenedicarboxylate in 5 mL of toluene was heated at gentle reflux for 3 h. Removal of the solvent at reduced pressure and chromatography of the residue over silica gel (5% EtOAc/hexanes; R_f = 0.53) gave 142.8 mg (70%) of the product as an oil: ^{1}H NMR δ 0.82−0.98 (m, 3 H), 1.20−1.30 (m, 2 H), 1.47−1.61 (m, 2 H), 1.86−1.94 (m, 2 H), 2.10−2.40 (m, 4 H), 2.80−3.15 (m, 2 H), 3.32 (bs, 1 H), 3.76 (s, 3 H), 3.80 (s, 3 H); ^{13}C NMR δ 14.27, 17.66, 22.07, 28.64, 33.14, 33.20, 35.14, 39.49, 52.02, 127.96, 130.92, 131.78, 133.56, 140.70, 167.77, 169.71; HRMS calcd for $C_{16}H_{22}O_4$ 278.1518, found 278.1518.

(*E*)-2-Benzylidene-1-methylenecyclohexane (Table 1, entry 9): ^{1}H NMR δ 1.63 - 1.79 (m, 4 H), 2.41 (t, J = 6.02 Hz, 2 H), 2.61 (t, J = 6.13 Hz, 2 H), 4.79 (d, J = 1.58 Hz, 1 H), 5.07 (d, J = 1.58 Hz, 1 H), 6.64 (s, 1 H), 7.27−7.39 (m, 5 H); ^{13}C NMR δ 26.33, 26.88, 29.62, 35.47, 108.75, 123.21, 126.36, 128.07, 129.43, 131.60, 142.86, 151.25; HRMS calcd for $C_{14}H_{16}$ 184.1252, found 184.1249.

(3aα,4*β*,9aα)-4-Phenyl-1,3-dioxo-3,a,4,5,6,7,8,9,9a-octahydronaptho[2,3-*c*]furan (Table 2, entry 15). A solution of 191.6 mg (1.04 mmol) of (*E*)-2-benzylidene-1-methylenecyclohexane and 67.0 mg (0.683 mmol) of maleic anhydride in 5 mL of toluene was heated at gentle reflux for 1.5 h. Removal of solvent at reduced pressure afforded a solid which was recrystallized from heptane to give 164 mg (86%) of bone-white

crystals: mp 137−138 °C; ^{1}H NMR δ 1.49−1.65 (m, 4 H), 1.86 (t, J = 6.97 Hz, 2 H), 2.09 (t, J = 5.63 Hz, 2 H), 2.38 (dd, J = 18.16 Hz, J = 11.17 Hz, 1 H), 2.76 (d, J = 18.16 Hz, 1 H), 3.35 (dd, J = 11.17 Hz, J = 3.08 Hz, 1 H), 3.44 (dd, J = 9.37 Hz, J = 7.16 Hz, 1 H), 3.63 (d, J = 7.16 Hz, 1 H), 7.02−7.05 (m, 3 H), 7.23−7.25 (m, 2 H); ^{13}C NMR δ 22.64, 22.93, 25.58, 29.43, 30.13, 37.23, 44.99, 45.32, 128.07, 128.22 (two carbons), 128.69, 129.09, 136.84, 171.60, 173.94. Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.33; H, 6.09.

(*E*)- and (*Z*)-2-((Trimethylsilyl)methylidene)-1-methylenecyclohexane (Table 1, entry 10): GC analysis indicated that the product consisted of 70% of the bis-exocyclic diene as a 2.5:1 mixture of the *E*- and *Z*-isomers along with 30% of the known[37] trimethyl(oct-7-en-1-yne)silane; ^{1}H NMR [major diastereoisomer] δ 0.10 (s, 9 H), 0.97−1.00 (m, 2 H), 1.67−1.85 (m, 4 H), 2.20−2.38 (m, 2 H), 4.59 (apparent s, 1 H), 4.88 (apparent s, 1 H), 5.47 (apparent s, 1H); HRMS calcd for $C_{11}H_{20}Si$ 180.1334, found 180.1334.

(3aα,4α and 4*β*,9aα)-2-Methyl-4-(trimethylsilyl)-1,3-dioxo-2,3,3a,4,5,6,7,8,9,9a-decahydro-1*H*-benz[*f*]isoindole (Table 2, entry 16). A solution of 127.5 mg (0.707 mmol) of a 2.5:1 mixture of the *E*- and *Z*-isomers of 2-((trimethylsilyl)-methylidene)-1-methylenecyclohexane and 94.7 mg (0.852 mmol) of *N*-methylmaleimide in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure gave a solid which was recrystallized from heptane to afford 136.5 mg (66%) of bone-white crystals of the adduct as a 4:1 ratio of diastereoisomers: mp 41−44 °C; ^{1}H NMR [major diastereoisomer] δ 0.03 (s, 9 H), 1.53 (m, 4 H), 1.87−1.97 (m, 4 H), 2.14−2.23 (m, 2 H), 2.91 (s, 2 H), 2.95 (d, J = Hz, 1 H), 3.15 (t, J = Hz, 1 H); ^{13}C NMR [mixture of diastereoisomers] δ 0.82, 0.99, 22.98, 23.04, 23.16, 24.53, 28.12, 29.22, 29.62, 30.48, 31.00, 31.71, 31.84, 32.49, 40.19, 41.10, 41.15, 42.63, 125.86, 128.55, 130.75, 133.03, 179.77, 180.33, 180.87, 181.52. Anal. [mixture of diastereoisomers] Calcd for $C_{16}H_{25}NO_2Si$: C, 65.93; H, 8.65. Found: C, 66.19; H, 8.57.

1-(Trimethylsilyl)-1,4,5,6,7,8-hexahydronaphthalene-2,3-dicarboxylic Acid Dimethyl Ester (Table 2, entry 17). A solution of 130.0 mg (0.721 mmol) of a 2.5:1 mixture of the *E*- and *Z*-isomers of 2-((trimethylsilyl)methylidene)-1-methylenecyclohexane and 64.6 mg (0.455 mmol) of dimethyl acetylenedicarboxylate in 5 mL of toluene was heated at gentle reflux for 3 h. Concentration of the product mixture gave an oil which was purified by flash chromatography on silica gel (10% EtOAc/hexanes; R_f = 0.57) to afford 96.3 mg (68%) of the product as a yellow oil: ^{1}H NMR δ −0.13 (s, 9 H), 1.38−1.46 (m, 4 H), 1.67−1.89 (m, 4 H), 2.47 (d, 1 H), 2. 64 (s, 1 H), 3.48−3.70 [overlapping patterns, i.e. 3.57 (s, 3 H), 3.47−3.63 (m, 1 H), 3.66 (s, 3 H)]; ^{13}C NMR δ −0.94, 22.86, 23.01, 29.62, 30.35, 34.00, 39.34, 51.87, 53.31, 122.14, 128.60, 130.02, 138.26, 168.43, 168.71; HRMS calcd for $C_{17}H_{26}O_4Si$ 322.1600, found 322.1598.

(*E*)-2-(Cyclohexylidenemethylidene)-1-methylenecyclopentane (Table 1, entry 11): ^{1}H NMR δ 0.84−0.88 (m, 2 H), 1.51−1.59 (m, 6 H), 1.65 (pentet, J = 7.22 Hz, 2 H), 2.08−2.23 (m, 4 H), 2.35−2.45 (m, 2 H), 4.88 (apparent s, 1 H), 5.04 (apparent s, 1 H); ^{13}C NMR δ 25.09, 26.25, 28.17, 31.67, 32.03, 33.95, 103.49, 103.80, 106.84, 148.60, 192.19; HRMS calcd for $C_{13}H_{18}$ 174.1409, found 174.1410.

4-Cyclohexylidene-4,5,6,7,8,8a-hexahydro-3a*H*-5-indacene-1,3-dione (Table 2, entry 18). A solution of 115.5 mg (0.662 mmol) of (*E*)-2-(cyclohexylidenemethylidene)-1-methylenecyclopentane and 64.7 mg (0.660 mmol) of maleic anhydride in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure gave a yellow solid which was recrystallized from benzene to afford 162.0 mg (90%) of bone-white crystals: mp 131−132 °C; ^{1}H NMR δ 1.55−1.80 (m, 8 H), 1.83−1.94 (m, 2 H), 2.10−2.15 (m, 2 H), 2.21−2.31 (m, 2 H), 2.37−2.53 (m, 2 H), 2.65 (d, J = 15.89 Hz, 1 H), 2.78−2.88 (m, 1H), 3.44−3.51 (m, 1 H), 4.33 (d, J = 9.35 Hz, 1 H); ^{13}C NMR δ 23.77, 24.87, 26.53, 28.25, 28.44, 32.46, 32.93, 36.30, 37.03, 41.91, 43.95, 116.86, 137.23, 139.73, 142.57, 171.93, 173.64. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.96; H, 7.41. Found: C, 74.56; H, 7.23.

4-Cyclohexylidene-2,3,4,4a,10a,11-hexahydro-1*H*-cyclopenta[*b*]anthracene-5,10-dione (Table 2, entry 19). A solution of 105.4 mg (0.605 mmol) of (*E*)-2-(cyclohexylidenemethylidene)-1-methylenecyclopentane and 80.0 mg (0.506 mmol) of 1,4-naphthoquinone in 5 mL of toluene was heated at gentle reflux for 2 h. Removal of the solvent at reduced pressure gave a yellow solid which was recrystallized from hexanes to afford 134.5 mg (80%) of bone-white crystals: mp 201 °C; ^{1}H NMR δ 1.58 (t, J = 3.58 Hz, 2 H), 1.68−1.79 (m, 6 H), 1.82−1.91 (m, 2 H), 2.10−2.41 (m, 5 H), 2.63 (dd, J = 13.14 Hz, J = 7.64 Hz, 2 H), 2.83−2.99 (m, 1 H), 3.37 (apparent pentet, J = 6.56 Hz, 1H), 4.39 (d, J = 4.90 Hz, 1 H), 7.69−7.73 (m, 2 H), 7.97−8.07 (m, 2 H); ^{13}C NMR δ 23.31, 26.88, 28.83, 32.64, 32.71, 35.39, 37.19, 50.04, 51.41, 120.01, 126.67, 127.20, 133.26, 134.04, 134.24, 135.12, 136.98, 140.44, 195.99, 199.51. Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.84; H, 6.97.

(*E*)-2-[2-(3-Butenyl)benzylidene]-1-methylenecyclopentane (18): ^{1}H NMR δ 1.72 (apparent quintet, J = 7.15 Hz, 2 H), 2.29−2.39 (m, 2 H), 2.51 (tt, J = 7.25 Hz, J = 2.31 Hz, 2 H), 2.59 (td, J = 2.31, J = 7.09 Hz, 2 H), 2.71−2.81 (m, 2 H), 4.94−5.10 (m, 3 H), 5.47 (apparent t, J = 2.14 Hz, 1 H), 5.80−5.97 (m, 1 H), 7.01 (br s, 1 H), 7.16−7.45 (m, 4 H); ^{13}C NMR δ 24.53, 32.32, 33.69, 34.87, 102.44, 114.79, 117.34, 125.66, 126.72, 128.63, 128.81, 129.06, 132.12, 138.15, 140.23, 142.45, 150.32; HRMS calcd for $C_{17}H_{20}$ 224.1565, found 224.1563.

(5aα,11bα)-2,3,4,5,5a,6,7,11b-Octahydro-1*H*-cyclopenta[*c*]phenanthrene (19). A solution of 42.1 mg (0.187 mmol) of (*E*)-2-[2-(3-butenyl)benzylidene]-1-methylenecyclopentane (**18**) and 4.0 mg of BHT in 4 mL of deoxygenated benzene was heated at 180 °C for 22 h in a screw-capped pressure tube. The solvent was then removed, and the residue was purified by flash chromatography on silica gel (hexanes; R_f = 0.37) to give 31.5 mg (75%) of the cycloadduct as an approximately 6:1 mixture of diastereoisomers: ^{1}H NMR [major diastereoisomer] δ 1.40−1.60 (m, 3 H), 1.80−1.92 (m, 4H), 2.02−2.15 (m, 2 H), 2.21−2.38 (m, 2 H), 2.42−2.60 (m, 1 H), 2.74−2.88 (m, 3 H), 3.08−3.17 (m, 1 H), 7.05−7.15 (m, 3 H), 7.30−7.38 (m, 1 H); ^{13}C NMR [major diastereoisomer] δ 22.70, 26.67, 28.56, 29.24, 30.80, 35.96, 36.36, 40.25, 43.99, 125.18, 125.27, 125.92, 128.43, 135.01, 138.28, 138.68, 141.56; [minor diastereoisomer] δ 21.44, 23.10, 24.58, 28.49, 29.34, 29.69, 33.07, 35.56, 41.11, 124.90, 125.60, 128.54, 130.31, 133.84, 134.97, 137.50, 138.99; HRMS calcd for $C_{17}H_{20}$ 224.1565, found 224.1564.

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Supporting Information Available: Copies of ^{1}H or ^{13}C NMR spectra for all new compounds for which combustion analytical data are not available (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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