threo); MS (relative intensity) m/e 196 (2), 150 (100), 140 (3), 137 (2), 123 (12), 121 (5), 109 (10), 93 (2), 91 (2), 77 (7), 65 (4); M^+ 352.1427; ^1H NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 3.76 (s, 6 H), 3.80 (s, 3 H), 3.90 (dd, J = 5 Hz, J = 11 Hz, 2 H), 4.40 (m, 1 H), 4.92 (d, J = 5 H, 1 H), 6.78–7.00 (m, 6 H); ^{13}C NMR ($(CD_3)_2CO/D_2O$, 9:1) δ 56.3, 56.4, 61.8, 73.9, 85.6, 105.5, 113.6, 118.4, 122.1, 123.1, 133.3, 148.5, 148.9, 151.5.

Acknowledgment. We thank Conselho Nacional de-Desenvolbimento Científico e Tecnológico (CBOq) for a scholarship (R.R.V.), Fundaçao de Amparo à Pesquisa do Estado de Sao Paulo (FAPESP), the programme Universidade de Sao Paulo (USP-Banco Interamericano de Desenvolvimento, BID), and The British Council for supporting the collaboration between Queen Mary and Westfield College and the Instituto de Quimica, USP. We wish to thank Mr. P. R. Haycock of the University of London Intercollegiate Research Service (ULIRS) in high field NMR at Queen Mary and Westfield College for measuring the ^1H and ^{13}C spectra (Bruker WH-400).

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Registry No. **1a**, 17078-88-5; **1b**, 67015-29-6; **1c**, 1835-10-5; **1d**, 20679-57-6; **1e**, 7382-59-4; **1f**, 136863-16-6; **1g**, 10535-17-8; **1h**, 7572-96-5; **1i**, 58497-34-0; **1i** ketone, 7572-91-0; **1j**, 136863-17-7; **2a**, 22675-96-3; **2b**, 22317-29-9; **2c**, 1835-09-2; **3a**, 121-33-5; **3b**, 120-14-9; **3c**, 2426-87-1; **3d**, 134-96-3; **3e**, 6527-32-8; **4a**, 93-07-2; **4b**, 121-34-6; **5**, 90-05-1; lignin, 9005-53-2.

The Triplex Diels–Alder Reaction: Intramolecular Cycloaddition of Phenyl-Substituted Alkenes to 1,3-Dienes

Ingrid Wölfle, Samantha Chan, and Gary B. Schuster*

Department of Chemistry, University of Illinois, Roger Adams Laboratory, Urbana, Illinois 61801

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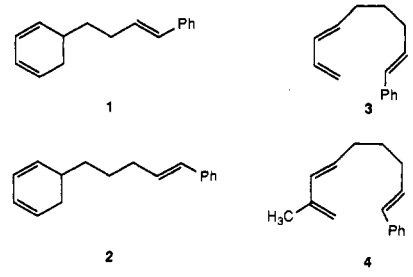
The triplex Diels–Alder reaction of dienes and styrene-like dienophiles that are covalently linked with a flexible alkyl chain was investigated. Sensitization with 9,10-dicyanoanthracene in benzene solution leads to good yields of [4 + 2] adducts when the diene is a derivative of cyclohexadiene and the linking chain contains two atoms. If the linking chain contains three atoms, dyotropic transfer of hydrogens occurs. When acyclic dienes are employed, it is believed that conformational isomers lead to mixtures containing considerable yields of both [4 + 2] and [2 + 2] cycloadducts.

Introduction

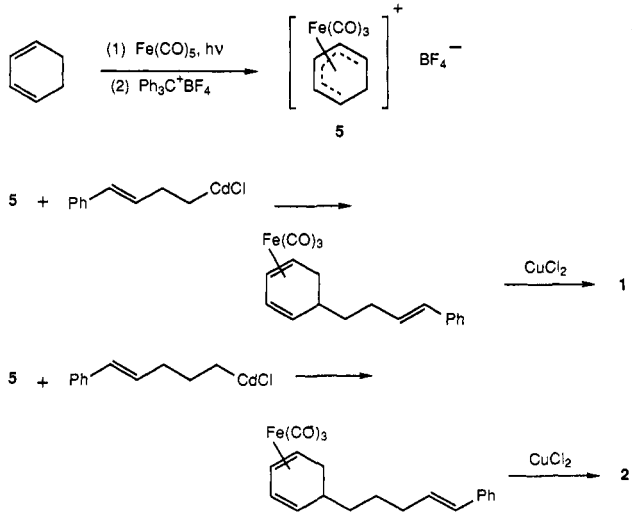
The triplex Diels–Alder reaction provides a useful photochemical adjutant to the conventional thermal, Lewis acid-catalyzed, and radical cation modalities of this cycloaddition reaction when both the diene and dienophile are electron-rich.[1] In recent reports we described the application of this approach to the stereospecific cycloaddition of methylstyrenes to 1,3-cyclohexadiene[2] and its expansion to the intermolecular addition of 1,3-dienes to enolic, alkenyl, and acetylenic dienophiles.[3] Additional interest in this reaction has been sparked by the discovery that irradiation of the optically active, electron-deficient catalyst (−)-1,1′-bis(2,4-dicyanonaphthalene) gives the endo-trans-[4 + 2] cycloadduct of *trans*-β-methylstyrene and 1,3-cyclohexadiene in 15% enantiomeric excess.[4]

There are significant limitations to application of the triplex Diels–Alder reaction. Two of these are competing dimerization of the diene when its concentration is high and troublesome [2 + 2] cycloaddition of the diene to the dienophile. We sought to overcome these problems by covalently linking the diene and the dienophile. In this intramolecular version, we hoped that the local concentration of diene would be high enough to intercept a short-lived exciplex of sensitizer and dienophile without production of diene dimers. Similarly, it was postulated that conformational and ring strain related restriction associated with the linking group might require exclusive operation of the [4 + 2] cycloaddition mode. These hypotheses were tested by examination of the intramolecular triplex Diels–Alder reaction of phenyl-substituted alkenes linked to acyclic 1,3-dienes and to a linked cyclohexadiene. The results of this investigation reveal certain advantages and restrictions of the intramolecular triplex reaction.

Chart I. 1,3-Dienes Linked to *trans*-Styrene Dienophiles



Scheme I. Syntheses of Compounds 1 and 2



(1) Brieger, G.; Bennet, J. M. *Chem. Rev.* **1980**, *80*, 63.
(2) Hartsough, D.; Schuster, G. B. *J. Org. Chem.* **1989**, *54*, 3. Calhoun, G. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 6870.
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0022-3263/91/1956-7313$02.50/0

Scheme II. Syntheses of Compounds 3 and 4

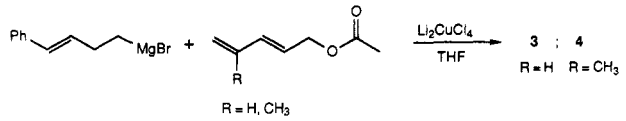


Table I. Reactions of Triene 1

		% yield (relative)			
sensitizer	solvent	[4 + 2]6	major [2 + 2]7	minor [2 + 2]	% conversion
DCA	benzene	88	12		92
DCN	benzene	45	53	2	98
DCN	CH_3CN	66	30	4	94
BP	benzene		94	6	94
none	benzene		100		100
thermal	toluene	100			100
Ar_3N^+ [a]	CH_2Cl_2	59			82
Ar_3N^+/pyr [b]	CH_2Cl_2	44			50

[a] ArN^+ = tris(*p*-bromophenyl)aminium hexachloroantimonate, pyr = 2,6-di-*tert*-butylpyridine; 10 mol %. [b] 50 mol % Ar_3N^+/60 mol % pyr.

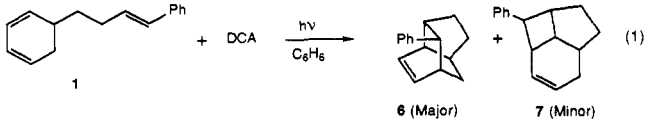
Results

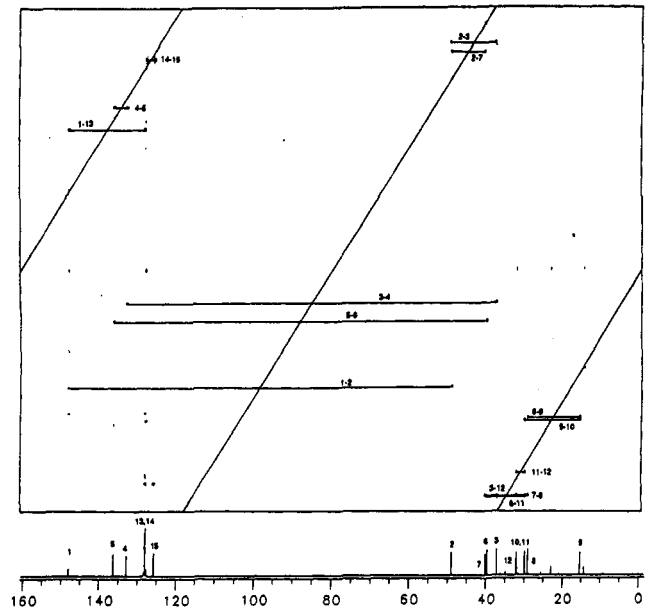
(1) Preparation of Covalently Linked Electron-Rich Dienes and Dienophiles. Shown in Chart I is the set of linked dienes and dienophiles prepared for the examination of the intramolecular triplex Diels–Alder reaction.

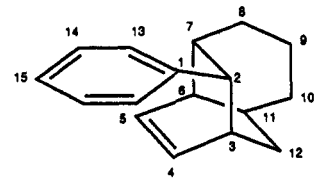
The route for preparation of substituted cyclohexadienes 1 (5-(*trans*-4-phenylbutenyl)cyclohexa-1,3-diene) and 2 (5-(*trans*-5-phenylpentenyl)cyclohexa-1,3-diene) is shown in Scheme I. Detailed descriptions of these reactions are presented in the Experimental Section. The key step of these convergent syntheses is the use of cyclohexadienyl iron tricarbonyl tetrafluoroborate as an electrophilic cyclohexadiene synthon. The cyclohexadienyl iron salt is prepared in good yield by photolysis of iron pentacarbonyl in the presence of 1,3-cyclohexadiene and then hydride abstraction with triphenylcarbenium tetrafluoroborate. Reaction of the cyclohexadienyl iron salt with organocadmium reagents[5] followed by oxidative demetalation of the adduct gives the desired cyclohexadienes 1 and 2.

The synthetic sequence used for the preparation of 3 (9-phenyl-1-*trans*-3-*trans*-8-nonatriene) and 4 (2-methyl-9-phenyl-1-*trans*-3-*trans*-8-nonatriene) is shown in Scheme II. The key step in their syntheses is the cuprate-mediated coupling of the pentadienyl acetates with the Grignard reagent formed from 4-bromo-1-phenyl-1-*trans*-butene.

(2) Photochemistry of Cyclohexadiene Derivative 1. Irradiation of an air-saturated benzene solution of 1 containing a catalytic amount of 9,10-dicyanoanthracene (DCA) at 350 nm (the light is absorbed by the DCA) gives two products in a 7.5:1 ratio that were shown by GC/MS to be isomeric with the starting material, see eq 1. The major product from the DCA-photosensitized reaction is formed exclusively when 1 is heated in a refluxing toluene solution. When the photochemical reaction of 1 is sensitized with benzophenone instead of DCA, isomeric products are again formed, but in this case neither is that obtained from the thermolysis and the ratio is 1:18. These related results are summarized in Table I.



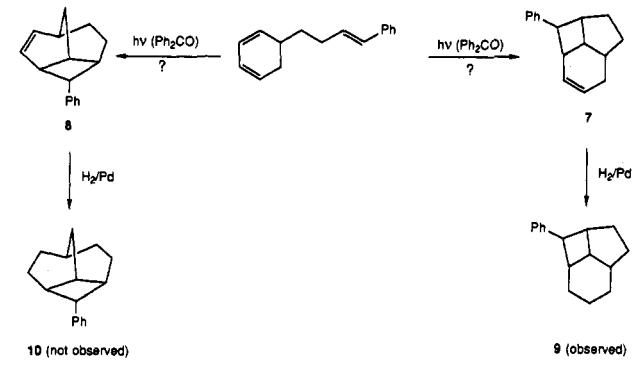




11

Figure 1. ^{13}C-INADEQUATE spectrum of 11.

Scheme III. Identification of [2 + 2] Adduct



The product formed from thermolysis of 1, the major product from its DCA-photosensitized reaction, was isolated by chromatography and shown to be the intramolecular [4 + 2] cycloaddition product endo-trans-tricyclic hydrocarbon 6 by spectral methods. In particular, comparison of the ^{13}C and ^1H NMR spectra of 6 with independently prepared *endo-trans*-6-methyl-5-phenylbicyclo[2.2.2]oct-2-ene confirms the major ring structure and the stereochemical assignments.[2,3] Analysis of the ^{13}C-INADEQUATE spectrum[6] (Figure 1) of the analogous adduct from 2 (see below) shows that this product arises from the normal "parallel" cycloaddition route rather than the energetically more demanding "crossed" cycloaddition path.

(5) Pearson, A. J.; Yoon, J. *Tetrahedron Lett.* **1985**, *26*, 2399. Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954.

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Table II. Reactions of Triene 2

sensitizer/solvent	yields (%) based on conversion: [4 + 2] adduct 11	12	[2 + 2] adducts: unidentified isomers		other[a]	% conversion	mass balance
DCA/PhH	30	10			15	90	60
TriCa/PhH[d]	22	25			8	96	57
TCA/PhH[d]	17	24			3	95	46
DCN/PhH	30	11	9	7	12	96	67
DCN/CH_3CN	8	trace	15	31		96	56
thermal	95[b]						
BP/PhH[c]	1		3	6	some	7	30

[a] Dimerized and aromatized starting material and adducts to the sensitizer. [b] A minor isomeric product is detected, but it was not identified. [c] GC ratios of products. Absolute yields were not determined. [d] TriCA is 2,9,10-tricyanoanthracene and TCA is 2,6,9,10-tetracyanoanthracene.

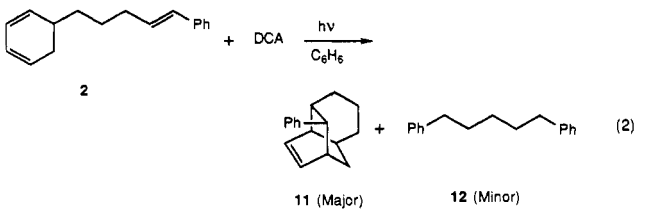
Table III. Reactions of Trienes 3 and 4

triene	sensitizer	solvent	yields (%) based on conversion: 13	14	15 (two isomers)
3	DCN	benzene	6	9	54, 33
3	DCN	dioxane	14	22	50, 24
3	DCA	benzene	36		10, 7
3	DCA	dioxane	20		13, 6
3	thermal	benzene	50	50	
3	Ph_2CO	benzene			60, 40
4	DCN	benzene	8	16	21
4	DCA	benzene	25		5
4	thermal	benzene	70	30	
4	Ph_2CO	benzene			72

The minor product formed in the DCA-sensitized reaction is the major product obtained when benzophenone is the sensitizer. It was isolated by preparative gas chromatography. Since cycloaddition reactions sensitized by triplet benzophenone are known to give predominantly [2 + 2] adducts,[7] we considered that the minor product formed in the DCA-sensitized reaction could be either of the tricyclic alkenes (**7**, **8**) shown in Scheme III. These isomers cannot be easily distinguished by their spectral properties. However, hydrogenation of **8** should give **10**, which has a plane of symmetry, while hydrogenation of **7** gives **9**, which lacks this symmetry element. The tricyclic alkanes thus may be distinguished by means of ^{13}C NMR spectroscopy. Hydrogenation of the minor photoproduct from the DCA-sensitized reaction of **1** gives a tricyclic alkane having 10 unique aliphatic-region ^{13}C resonances. On this basis we tentatively assign the structure of the minor product to tricyclic alkene **7**. The details of the spectral analyses are given in the Experimental Section.

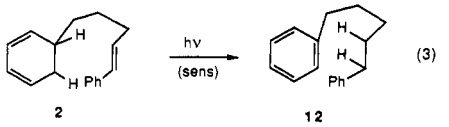
(3) Intramolecular Cycloaddition of 1 under Radical Cation Conditions. The triplex Diels–Alder reaction operates only in nonpolar solvents where dissociation of the intermediary exciplex to radical ions is energetically unfavorable. In contrast, 1,4-dicyanonaphthalene (DCN) sensitized Diels–Alder reactions carried out in acetonitrile solution have been shown to proceed through radical ion intermediates.[2] The reaction of **1** under these conditions gives [4 + 2] adduct **6** and [2 + 2] adduct **7** in a ratio of 2:1. Similarly, Bauld and co-workers have shown that the radical cation Diels–Alder reaction can be initiated with triarylaminium salts in methylene chloride solution.[8] Under these conditions, **1** gives adduct **6** in 48% yield. When 2,6-di-*tert*-butylpyridine (a scavenger Gassman and co-workers have shown to be effective in preventing acid-catalyzed reactions in the presence of aminium salts)[9] is present in the reaction solution, the yield of adduct **6** decreases to 22%. These results are summarized in Table I.

(4) Photochemistry of Cyclohexadiene Derivative 2. The pentenyl-substituted cyclohexadiene derivative **2** was prepared to probe the significance of chain length on the intramolecular triplex Diels–Alder reaction. Irradiation of DCA in a benzene solution containing **2** gives two products in a ratio of 3:1 that are isomeric with the starting material. The major product was identified as the endo,trans-tricyclic hydrocarbon **11** (see eq 2) by com-



(2)

parison with the cycloadduct formed in the thermal intramolecular Diels–Alder reaction of **2** (see below). The minor product from the photochemical reaction was identified as 1,5-diphenylpentane (**12**) by comparison with an independently prepared, authentic sample. Formation of **12** occurs by transfer of hydrogens from the cyclohexadiene-like portion of **2** to its styrene-like group as shown in eq 3. Related dyotropic reactions have previ-



(3)

ously been observed under thermal conditions,[10] but to the best of our knowledge, the rearrangement of **2** to **12** would be the first photochemical example of this process. Alternatively, **12** might be formed by a stepwise transfer of hydrogen atoms. The effects of sensitizer and conditions on the reaction of **2** were examined; the results are summarized in Table II.

Thermolysis of **2** in benzene solution at 200 °C for 24 h gives two products that are isomeric with the starting material in ratio of 18:1. The major product was isolated by preparative gas chromatography and shown to be cycloadduct **11** by analysis of its NMR spectra. In particular, consideration of its ^{13}C-INADEQUATE spectrum (Figure 1)

(7) Valentine, D.; Turro, N. J.; Hammond, G. S. *J. Am. Chem. Soc.* **1964**, *86*, 5202.
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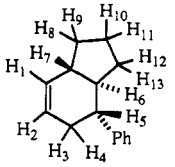
Table IV. Correlation of ^1H and ^{13}C Resonances of 13 from HETCOR Experiment

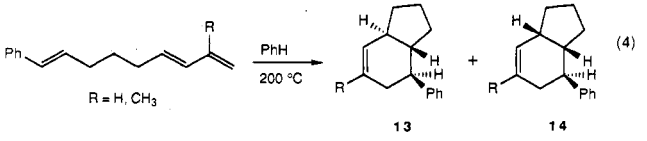


^{13}C NMR (δ)	assignment	^1H NMR (δ)
28.5	C-H_{12} or C-H_{13}	0.99–1.13 (quin, 1 H)
29.7	C-H_8 or C-H_9	1.22–1.35 (quin, 1 H)
28.5	C-H_{12} or C-H_{13}	1.51 (m, 1 H)
49.1, 22.0	C-H_6, C-H_{10}, C-H_{11}	1.63–1.80 (m, 3 H)
29.7	C-H_8 or C-H_9	1.93 (m, 1 H)
45.6	C-H_7	2.06 (m, 1 H)
36.8	C-H_4	2.22 (m, 1 H)
36.8	C-H_3	2.47 (m, 1 H)
46.8	C-H_5	2.76 (m, 1 H)
127.4	C-H_2	5.70 (m, 1 H)
130.2	C-H_1	5.94 (d, 1 H)
126.1	C-H_{phenyl}	7.21–7.35 (m, 5 H)
128.5		
146.3		

confirms a carbon atom connectivity that permits discrimination between the normal "parallel" [4 + 2] cycloaddition to form 11 from a "crossed" addition mode. The details of the structure analysis are presented in the Experimental Section.

(5) Photochemistry of 9-Phenylnonatrienes 3 and 4. The sensitivity of the intramolecular triplex Diels–Alder reaction to constraint of the diene component in a ring was examined by studying acyclic trienes 3 and the 4. Irradiation of a benzene solution of triene 3 and DCN at 350 nm gives two [4 + 2] cycloaddition products in a ratio of 2:3 and two [2 + 2] cycloaddition products in a ratio of 18:11. When DCA is the sensitizer, only one of the two [4 + 2] cycloaddition products is observed, but both [2 + 2] addition products are formed. The ratio of cycloaddition products under these conditions is 10:0:6:3. The results of these experiments and those carried out under related reaction conditions are summarized in Table III.

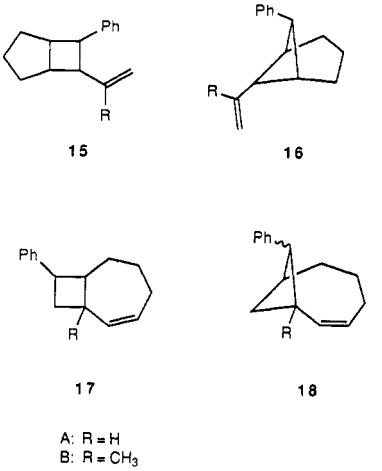
The products from the sensitized irradiations of 3 were identified by comparison with materials formed by alternative synthetic routes. Thermolysis of triene 3 at 200 °C in benzene solution gives two compounds in a 1:1 ratio that were shown to be identical with those assigned as the [4 + 2] adducts in the DCN photosensitized reaction of 3. These compounds were identified as *trans*- and *cis*-4-phenylhexahydroindenes 13 and 14 (see eq 4) by chemical and spectroscopic means.



(4)

Aromatization of the mixture formed in the thermolysis of 3 with DDQ converts both cycloaddition products to 7-phenylindene. This assures the operation of a parallel [4 + 2] cycloaddition route in the reactions of 3. Isomers 13 and 14 were separated by preparative gas chromatography and analyzed by ^1H and ^{13}C NMR spectroscopy. Application of COSY and HETCOR (Table IV) spectral techniques[11] permits the assignment of the proton and carbon resonances for these compounds. These results are described in the Experimental Section.

Chart II. Possible [2 + 2] Cycloaddcts Formed from Trienes 3 and 4



The stereochemistry of the ring juncture for 13 and 14 is assigned by reference to the common observation that bridgehead carbon atoms with a cis structure generally absorb upfield of the corresponding carbon atoms in the trans isomer[12] and from assumption of retention of dienophile configuration in the thermolysis of 3. The stereochemistry of the benzylic carbon atoms of 13 and 14 is assumed to be that shown in eq 4 since we have previously observed retention of dienophile stereochemistry in the triplex Diels–Alder reaction of *cis*- and *trans*-β-methylstyrene. From these chemical and spectroscopic studies, the major product formed in the DCA-sensitized triplex Diels–Alder reaction of 3 is identified as *trans*-hexahydroindene 13.

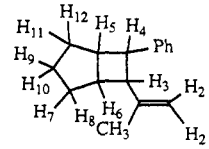
The two other products formed in the DCA-sensitized reaction of 3 are identified as [2 + 2] products by comparison with the products formed in the benzophenone sensitized reaction of the triene. Irradiation of a benzene solution of 3 containing benzophenone as a triplet sensitizer gives two products isomeric with the starting triene which were shown by GC/MS analysis to be identical with the products designated [2 + 2] cycloadducts formed in the DCN- or DCA-sensitized reaction of 3. Shown in Chart II are four possible structurally isomeric compounds that can be formed by [2 + 2] cycloaddition of 3.

The cycloadducts formed in the benzophenone-sensitized reaction were separated by preparative gas chromatography and analyzed by spectroscopic methods. Both compounds show a terminal vinyl group in their ^1H NMR spectra. These observations eliminate structures 17 and 18 from consideration. Cycloadducts 15 and 16 were distinguished on the basis of their ^{13}C NMR spectra: structure 16 possesses a plane of symmetry that is absent in 15. The ^{13}C NMR spectra of the products formed in the benzophenone-sensitized reaction each reveal 13 unique carbon atoms. This observation is consistent with structure 15 but not with 16. Further support for this assignment comes from analysis of the HETCOR NMR spectrum (Table V) which is presented in the Experimental Section. On the basis of these experiments we cannot distinguish with certainty between the possible stereoisomeric forms of the bicyclo[3.2.0]heptane 15. However, it is reasonable to presume a cis ring juncture and to suggest that these [2 + 2] cycloadducts are isomeric

(11) Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH: New York, 1988.

(12) Metzger, P.; Casadevall, E.; Pouet, M. J. *J. Org. Magn. Reson.* **1982**, *19*, 229. Metzger, P.; Cabestaing, C.; Casadeval, E.; Casadevall, A. *J. Org. Magn. Reson.* **1982**, *19*, 144.

Table V. Correlation of ^1H and ^{13}C Resonances of 15b from HETCOR Experiment



^{13}C NMR (δ)	assignment	^1H NMR (δ)
21.9	C–H	1.14 (s, 3 H)
32.8 or 32.9	C–H_7, C–H_8, C–H_{11}, or C–H_{12}	1.60 (m, 3 H)
		1.72 (m, 1 H)
		1.89 (m, 1 H)
		1.97 (m, 1 H)
42.6	C–H_6	2.70 (m, 1 H)
48.8	C–H_3	2.78 (m, 1 H)
38.9	C–H_5	2.99 (q, 1 H)
47.4	C–H_4	3.17 (dd, 1 H)
110.2	C–H_2	4.78 (d, 2 H)
125.6	C–H_{phenyl}	7.14–7.26 (m, 5 H)
127.5		
128.5		

with respect to the phenyl and vinyl substituents on the four-membered ring.

The triplex Diels–Alder reaction of **4** was investigated to analyze the effect of alkyl substitution on the diene portion. In particular, 2-methyl-substituted triene **4** was anticipated to have a higher population of s-cis component than unalkylated triene **3**. However, low-temperature NMR spectral analysis of **4** does not reveal more than one stereoisomer, and the triplex Diels–Alder reaction of **4** gives results qualitatively similar to the obtained with **3**. These findings are summarized in Table III.

Discussion

The primary impetus for studying the intramolecular version of the triplex Diels–Alder reaction was to learn if covalent linkage of the two participating functional groups would inhibit cyclodimerization of the diene and influence the regiochemistry of the reaction. Additionally, we hoped to gain insight about the structure of the triplex by restricting its accessible geometries.

In the proposed mechanism for the triplex Diels–Alder reaction, an exciplex of the sensitizer[2,3] and the dienophile is captured by the diene. In intermolecular versions of this reaction, we have detected exciplex emission when DCN is the sensitizer. The lifetimes of these exciplexes are generally ca. 20 ns, and time-resolved fluorescence experiments reveal that their rate constants for reaction with 1,3-cyclohexadiene are ca. 9×10^8 M^{-1} s^{-1}.

We are unable to detect exciplex emission under any conditions from trienes **1–4**. This observation, coupled with the fact that these compounds undergo the triplex Diels–Alder reaction (particularly **1** and **2**), implies that exciplexes are formed in these cases but that the high local concentration of diene quenches the emission and prohibits their detection. This is apparently a consequence of linking the diene and dienophile since it enforces a high local diene concentration. Likewise, the absence of detected emission is consistent with the presence of the linking groups creating no special inhibition to triplex formation.

Of the four trienes examined, **1** gives the best yield of [4 + 2] cycloadduct under triplex conditions. When DCA is the sensitizer, the yield of this product is nearly 90%. However, even for this triene, there is competition from the [2 + 2] cycloaddition mode. The ratio of the products from these two paths is more than 7.5:1 when DCA is the sensitizer. But, when DCN is used this ratio changes to ca. 1:1. This may be evidence for a relatively slow reaction leading to cyclization of the triplex in comparison with intersystem crossing to a triplet state. We have suggested previously that the higher yield of [2 + 2] cycloaddition product is connected to the triplet energies of the sensitizers: DCN can generate the triplet of the diene or dienophile, but triplet DCA cannot. Alternatively, both the [4 + 2] and [2 + 2] cycloadducts could originate from triplexes that may differ in the sequence of components or in the nature of dienophile participation. Some evidence for this latter suggestion comes from the examination of trienes **3** and **4**.

Comparison of the results obtained for trienes **1** and **2** reveals a potential limitation to the intramolecular version of the triplex Diels–Alder reaction. Apparently, a substantial side reaction occurs when low-energy conformations of the triplex permit transfer of hydrogen atoms to the dienophile. This is seen in the formation of **12** from **2** and might occur generally when the diene is a derivative of 1,3-cyclohexadiene and the linking group contains a flexible chain of three atoms. This restriction may be serious since we find that acyclic dienes are only modestly useful in this reaction.

The sensitized photochemical reactions of acyclic trienes **3** and **4** give complex mixtures of cycloaddition products. Both [4 + 2] and [2 + 2] cycloaddition products are obtained with DCN and DCA as the sensitizer, and the composition of the product mixture appears to be relatively resistant to alkyl substitution on the diene. We attribute the complexity of this process to the presence of both s-cis and s-trans conformations of the diene. If the exciplexes and triplexes are formed irreversibly from different conformations of the diene, these probably lead to different products.

In conclusion, our examination of the intramolecular triplex Diels–Alder reaction reveals certain advantages and limitations to this approach. Covalent linkage of the diene and dienophile portions removes the necessity of high dienophile concentrations to prevent the dimerization of the diene. When the diene is cyclic and the linking alkyl group contains a flexible chain of three atoms, hydrogen atoms are transferred to the diene in competition with cycloaddition. Finally, acyclic dienes having multiple conformations lead to complex mixtures of products.

Experimental Section

General. ^1H and ^{13}C NMR spectra were recorded on General Electric QE 300 or GN 500 FT spectrometers and are referenced to $CHCl_3$. IR spectra were recorded on an IBM FT-IR 32 instrument. Gas chromatographic analyses were done on a Hewlett-Packard 5790A gas chromatograph using an OV-17 megabore column with tetradecane or nonadecane as internal standards for yield calculations. Preparative gas chromatographic separations were carried out on a Varian Aerograph 90-P instrument fitted with a thermal conductivity detector by means of either a 2.5 m × 0.95 cm column packed with 19% SE-30 on Chromosorb A or with 22% OV-17 on Chromosorb A. Mass spectrometric data were obtained by GC/MS on a Hewlett-Packard 5890 GC with a Hewlett-Packard 5970 mass selective detector (EI, 70 eV). High-resolution electron impact mass spectra (HREI) were obtained on a Varian 731 mass spectrometer. Elemental analyses were performed by the microanalysis laboratory of the University of Illinois. Photolyses were carried out in Pyrex containers with a Rayonet photoreactor equipped with 350-nm broadband lamps, a 450-W mercury lamp, or a 1000-W mercury lamp using a 400-nm cutoff filter.

Materials. All solvents were freshly distilled and dried before use according to standard procedures. Tris(*p*-bromophenyl)-aminium hexachlorostibnate was purchased from Aldrich and purified by precipitation from CH_2Cl_2 with dry diethyl ether immediately prior to use. All other reagents were used as received, unless otherwise specified.

Photolyses. Benzene solutions of reagents **1**, **2**, **3**, or **4** (typically 3×10^{-2} M) and sensitizer (saturated solutions for DCA and TCA, ca. 10^{-3} M for DCN and benzophenone) were placed in Pyrex test tubes equipped with magnetic stirring bars. The tubes were sealed with septa and purged with N_2 at 0 °C for 5 min. The samples containing DCN or benzophenone sensitizers were irradiated in a Rayonet photoreactor equipped with 350-nm lamps. Those having DCA or TCA sensitizer were irradiated through a 400-nm cutoff filter with a mercury lamp.

5-Bromo-1-phenyl-*trans*-1-pentene. To an ice-cold stirred suspension of lithium aluminum hydride (2 g, 52 mmol) in dry ether (50 mL) was added dropwise a solution of γ-benzylidenebutyric acid[13] (7.3 g, 41 mmol) in dry ether (20 mL). After complete addition, the mixture was stirred for 1 h at 0 °C. Workup afforded 1-phenyl-*trans*-1-penten-5-ol as a clear, viscous liquid (5.6 g, 82%). To an ice-cold stirred solution of the alcohol (5.6 g, 35 mmol) and pyridine (0.5 mL) in dry ether (50 mL) was added dropwise a solution of PBr_3 (3.52 g, 13 mmol) in dry ether (10 mL). The solution was stirred at room temperature for 12 h and then quenched by addition of water. Workup and distillation afforded the bromide as a clear liquid. The spectral data agree with those previously published.[14]

General Procedure for Preparation of 5-Alkenyl-Substituted 1,3-Cyclohexadienes. To a stirred, ice-cold suspension of iron tricarbonylcyclohexadienyl tetrafluoroborate[15] in dry THF under N_2 was added via cannula a freshly prepared solution of the organocadmium reagent[16] (1.2 equiv of iron salt). After complete addition, the mixture was stirred for 1 h at 0 °C and then partitioned between ether and an aqueous NH_4Cl solution. The organic phase was washed with water and then brine. After drying ($MgSO_4$) and evaporation of the solvent, the residue was stirred with ethanolic $CuCl_2$ at room temperature for 1 h. The solution was then extracted with hexane, washed with brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by flash chromatography on silica gel with hexane. The purity of the collected fractions was monitored by GC, and the pure fractions were combined.

5-(4-Phenyl-*trans*-3-butenyl)cyclohexa-1,3-diene (1). The organocadmium reagent prepared from 4-bromo-1-phenyl-*trans*-1-butene[16] (12.65 g, 60 mmol) afforded **1** as a clear liquid (0.89 g, 10%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.69 (m, 2 H), 2.01–2.07 (m, 1 H), 2.27–2.41 (m, 4 H), 5.75–5.79 (m, 1 H), 3.80–5.83 (m, 1 H), 5.91–5.94 (m, 2 H), 6.23–6.38 (m, 1 H), 6.43 (d, 1 H, J = 16 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.70 (CH_2), 30.46 (CH_2), 32.40 (CH), 34.23 (CH_2), 123.93 (CH), 124.17 (CH), 125.99 (CH), 126.05 (CH), 126.98 (CH), 128.61 (CH), 130.11 (CH), 130.84 (CH), 131.35 (CH), 137.94 (C); GC/MS m/e (rel. abundance) 210 (29), 117 (69), 115 (36), 92 (63), 91 (100); HRMS (EI) for $C_{16}H_{18}$ calcd 210.14085, found 210.14082; IR ($CDCl_3$) 3033, 2926, 2857, 1653, 1599, 1495, 1449, 967, 930 cm^{-1}.

5-(5-Phenyl-*trans*-4-pentenyl)cyclohexa-1,3-diene (2). The organocadmium reagent prepared from 5-bromo-1-phenyl-*trans*-1-pentene (8.35 g, 38 mmol) afforded **2** as a clear liquid (1.84 g, 25%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45–1.61 (m, 4 H), 1.98–2.08 (m, 1 H), 2.25–2.37 (m, 4 H), 5.75–5.78 (m, 2 H), 5.82–5.85 (m, 2 H), 6.28 (dt, 1 H, J_1 = 15.5 Hz, J_2 = 7 Hz), 6.44 (d, 1 H, J = 7 Hz), 7.25 (t, 1 H, J = 7 Hz), 7.35 (t, 1 H, J = 7.5 Hz), 7.40 (d, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.62 (CH_2), 28.61 (CH_2), 32.71 (CH), 33.14 (CH_2), 34.02 (CH_2), 123.58 (CH), 123.96 (CH), 125.85 (CH), 125.91 (CH), 126.74 (CH), 128.42 (CH), 129.84 (CH) 130.77 (CH), 131.45 (CH), 137.75 (C); GC/MS m/e (rel. abundance) 224 (10), 133 (20), 117 (22), 115 (24), 92 (50), 91 (100); HRMS (EI) for $C_{17}H_{20}$ calcd 224.15650, found 224.15627.

Preparation and Identification of 6. A solution of **1** (77.8 mg) was heated at reflux in dry toluene (10 mL) under N_2 for 38 h. The solvent was removed, and the residue was eluted through basic alumina with hexane. Evaporation of the solvent gave **6** as a clear liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33–1.40 (m), 1.49–1.72 (m), 1.89–2.19 (m), 2.26 (s, broad), 2.56–2.66 (m), 6.21 (dd, 1 H, $J_1 = J_2$ = 7.5 Hz), 6.39 (dd, 1 H, $J_1 = J_2$ = 7.5 Hz), 7.19–7.30 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 32.16 (CH_2), 32.40 (CH_2), 43.14 (CH_2), 36.72 (CH_2), 39.81 (CH_2), 42.72 (CH), 45.37 (CH), 54.90 (CH), 125.64 (CH), 127.88 (CH), 128.35 (CH), 131.23 (CH), 133.55 (CH), 147.64 (C); GC/MS m/e (rel. abundance) 210 (87), 117 (33), 115 (32), 104 (36), 92 (80), 91 (100); HRMS (EI) for $C_{16}H_{18}$ calcd 210.14085, found 210.14102; IR ($CDCl_3$) 3035 (d), 2942 (br), 2870, 1615, 1500, 1445, 1380, 909 cm^{-1}.

Preparation and Identification of 7. A solution of **1** (83.1 mg) in benzene (6 mL) was placed in a Pyrex cell and purged with N_2 for 15 min. The sample was then irradiated with 350-nm light for 50 h. The solvent was removed, and the residue was eluted through a column of basic alumina with hexane. Solvent removal afforded **7** as a clear liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.66–1.74 (m, 2 H), 1.91–1.95 (m, 2 H), 2.11–2.16 (m, 1 H), 2.28–2.33 (m, 2 H), 2.69–2.71 (m, 1 H), 2.80–2.90 (m, 3 H), 5.73–5.77 (m, 1 H), 5.82–5.85 (m, 1 H), 7.33–7.40 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.20 (CH_2), 31.75 (CH_2), 32.92 (CH_2), 34.78 (CH), 35.00 (CH), 36.61 (CH), 44.97 (CH), 50.88 (CH), 124.38 (CH), 125.90 (CH), 126.84 (CH), 128.54 (CH), 146.70 (C); GC/MS m/e (rel. abundance) 210 (38), 117 (32), 115 (32), 104 (34), 92 (73), 91 (100); HRMS (EI) for $C_{16}H_{18}$ calcd 210.14085, found 210.14123; IR ($CDCl_3$) 3085, 3062, 2940 (br), 1643, 1601, 1495, 1451 cm^{-1}.

Hydrogenation of 7: Preparation of the Hydrogenated [2 + 2] Adduct 9. To a solution of **7** (approximately 80 mg) in ethyl acetate (5 mL) was added a small amount of Pd/C hydrogenation catalyst. The mixture was hydrogenated at 50 psi pressure in a Parr apparatus. Gravity filtration and solvent removal afforded the hydrogenated adduct as a clear liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.3–2.1 (m), 2.3 (s, broad), 2.7 (s, broad), 2.8 (s, broad), 7.1–7.6 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.99 (CH_2), 26.20 (CH_2), 26.67 (CH_2), 30.37 (CH_2), 32.42 (CH_2), 35.02 (CH_2) 35.55 (CH), 36.20 (CH), 43.40 (CH), 45.79 (CH), 125.70 (CH), 126.82 (CH), 128.34 (CH), 146.52 (C); GC/MS m/e (rel. abundance) 212 (100), 121 (50), 117 (64), 115 (66), 94 (83), 91 (74), 70 (61); HRMS (EI) for $C_{16}H_{20}$ calcd 212.1565, found 212.15709; IR ($CDCl_3$) 3084, 3029, 2942 (br), 1717, 1603, 1495, 1453 cm^{-1}.

Preparation and Identification of 11. A solution of **2** (60 mg, 0.3 mmol) in dry benzene (2 mL) was placed in a thick-wall Pyrex tube and, after three freeze–pump–thaw cycles, sealed under vacuum. The tube was placed in an oven heated to 200 °C for 45 h. Solvent removal afforded adduct **11** as a clear liquid: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37–1.57 (m, 5 H), 1.66–1.81 (m, 4 H), 1.96 (s, br, 1 H), 2.24 (m, 1 H), 2.66 (m, 1 H), 6.21 (t, 1 H, J = 7 Hz), 6.50 (t, 1 H, J = 7.5 Hz), 7.18–7.27 (m, 5 H); ^{13}C NMR (125 MHz, C_6D_6) δ 15.28 (CH_2), 28.98 (CH_2), 29.75 (CH), 29.83 (CH_2), 31.96 (CH_2), 37.06 (CH), 39.51 (CH), 40.08 (CH), 48.83 (CH), 125.71 (CH), 127.92 (CH), 128.09 (CH), 132.75 (CH), 136.18 (CH), 147.96 (C); GC/MS m/e (rel. abundance 224 (34), 133 (42), 117 (19), 115 (21), 92 (61), 91 (100); HRMS (EI) for $C_{17}H_{20}$ calcd 224.15650, found 224.156527.

^{13}C-INADEQUATE Spectrum of 11. The question of "parallel" versus "crossed" [4 + 2] cycloadduct was answered by determining the connectivity of C3. For the parallel cycloaddct, C3 is connected to the benzylic carbon C2, a vinylic carbon, and a methylene carbon. For the crossed adduct the methylene carbon is replaced by a methine carbon. Analysis of the ^{13}C-INADEQUATE spectrum (Figure 1) shows that C3 is connected to C12, which was shown by APT to be a methylene carbon. We therefore assigned the structure to be the parallel adduct **11**.

9-Phenyl-1,3(*E*),8(*E*)-nonatriene (3). This compound was prepared using the procedure of Roush[17] using 4-bromo-1-phenyl-1-*trans*-butene (1.00 g, 4.74 mmol) and 2(*E*),4-pentadienyl acetate[18] (399 mg, 3.16 mmol) to afford the desired diene in 20% yield: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (m, 2 H), 2.17 (m, 4 H), 5.02 (dd, 2 H), 5.70 (m, 1 H), 6.00–6.45 (m, 3 H), 7.30 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.81, 32.02, 32.50, 114.89, 125.91, 126.84, 128.49, 130.11, 131.29, 134.97, 138.00; GC/MS m/e (relative abundance) 198 (14), 129 (68), 115 (83), 91 (100), 79 (97). Anal. Calcd for $C_{15}H_{18}$: C, 90.84; H, 9.16. Found: C, 90.86; H, 9.13.

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Table VI. ^{13}C NMR Shifts (ppm) of Possible Bridgehead Carbon Atoms

13	45.64, 46.84, 49.08
14	41.22, 42.28, 43.37
13a	46.10, 46.75, 49.14
14a	41.48, 41.92, 43.73

4-Methyl-2(*E*),4-pentadienyl Acetate. This compound was prepared by means of the procedure of Oida and Ohki[18] with 4-methyl-2(*E*),4-pentadienol (11.6 g, 0.118 mol) to afford the product. Bulb-to-bulb distillation yielded the product containing a small amount of ether.

2-Methyl-9-phenyl-1,3(*E*),8(*E*)-nonatriene (4). This compound was prepared by means of the procedure of Roush[17] with 4-bromo-1-phenyl-1-*trans*-butene (4.50 g, 21.4 mmol) and 4-methyl-2(*E*),4-pentadienyl acetate (2.00 g, 14.3 mmol) to afford the desired triene: ^1H NMR (300 MHz, $CDCl_3$) δ 1.50 (m, 2 H), 1.76 (s, 3 H), 2.12 (m, 4 H), 4.79 (s, 2 H), 5.59 (dt, J = 9, 18 Hz, 1 H), 6.12 (m, 2 H), 6.31 (d, J = 18 Hz, 1 H), 7.18 (m, 5 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.72, 29.05, 32.24, 32.53, 114.36, 125.91, 125.91, 126.83, 128.48, 130.08, 130.45, 130.66, 133.19, 137.83, 142.00; HRMS calcd for $C_{16}H_{20}$ 212.1565, found 212.1574. Anal. Calcd for $C_{16}H_{20}$: C, 90.50; H, 9.50. Found: C, 90.59; H, 9.52.

Thermal Products. A benzene solution of the triene (2 mL, ca. 10^{-2} M) in a thick walled Pyrex tube was degassed (freeze–pump–thaw, three times) and sealed under vacuum. The solution was heated in a sand bath at 200 °C for 48 h, and then the solvent was removed from the reaction mixture. The resulting yellow oil contained two products that were separated by preparative GC:

4-Phenyl-*trans*-2,3,3a,4,5,7a-hexahydroindene (13): ^1H NMR (500 MHz, $CDCl_3$) δ 0.99–1.13 (m, 1 H), 1.22–1.35 (m, 1 H), 1.51 (m, 1 H), 1.63–1.80 (m, 3 H), 1.93 (m, 1 H), 2.06 (m, 1 H), 2.22 (m, 1 H), 2.44–2.50 (m, 1 H), 2.76 (m, 1 H), 5.704 (m, 1 H), 5.94 (d, 1 H), 7.21–7.35 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.00, 28.48, 29.74, 36.84, 45.64, 46.84, 49.08, 126.11, 127.37, 128.49, 130.23, 146.26; HRMS calcd for $C_{15}H_{18}$ 198.1409, found 198.1392.

4-Phenyl-*cis*-2,3,3a,4,5,7a-hexahydroindene (14): ^1H NMR (500 MHz, $CDCl_3$) δ 1.28–1.42 (m, 2 H), 1.48–1.55 (m, 1 H), 1.60–1.74 (m, 2 H), 1.91–1.96 (m, 1 H), 2.15–2.21 (m, 2 H), 2.31–2.38 (m, 1 H), 2.43–2.52 (m, 2 H), 5.81–5.86 (m, 2 H), 7.22–7.34 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.19, 30.52, 32.78, 33.91, 41.22, 42.28, 43.37, 126.05, 128.10, 128.41, 130.79, 146.35; HRMS calcd for $C_{15}H_{18}$ 198.1409, found 198.1412.

Aromatization of 13 and 14. A benzene solution containing the hexahydroindenes and dicyanodichloroquinone (DDQ, 3 equiv) was heated at reflux. The extent of reaction was monitored by GC/MS. After 1 h, both a partially oxidized phenylindane and fully oxidized phenylidene were detected. The indene was identified as 7-phenylindene by means of independent synthesis.

7-Phenylindene. 7-Phenylindene was prepared by a method similar to those of Albrecht[19] and Adamczyk and Netzel[20] starting from 2-(bromomethyl)biphenyl: ^1H NMR (300 MHz, $CDCl_3$) δ 3.56 (t, 2 H, J = 1.65 Hz), 6.66 (m, 1 H), 7.03 (m, 1 H), 7.31–7.65 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.07, 120.18, 125.30, 127.01, 127.13, 128.44, 128.49, 128.92, 131.14, 132.06, 134.45, 141.24, 145.38; GC/MS m/e (rel. abundance) 192 (100), 191 (51), 189 (25), 165 (16); HRMS calcd for $C_{15}H_{12}$ 192.0960, found 192.0934. Anal. Calcd for $C_{15}H_{12}$: C, 93.75; H, 6.25. Found: C, 93.27; H, 6.30.

6-Methyl-7-phenyl-*trans*-2,3,3a,4,5,7a-hexahydroindene (13a): ^1H NMR (500 MHz, $CDCl_3$) δ 1.02 (quin, J = 9.5 Hz, 1 H), 1.22 (quin, J = 9.5 Hz, 1 H), 1.46–1.49 (m, 1 H), 1.59–1.70 (m, 3 H), 1.67 (s, 3 H), 1.87 (m, 1 H), 2.01 (m, 1 H), 2.14 (m, 1 H), 2.30 (m, 1 H), 2.71 (m, 1 H), 5.61 (s, 1 H), 7.17–7.31 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.20, 23.18, 28.25, 30.02, 41.89, 46.10, 46.75, 49.14, 124.66, 126.05, 127.34, 128.46; HRMS calcd for $C_{16}H_{20}$ 212.1560, found 212.1565.

6-Methyl-7-phenyl-*cis*-2,3,3a,4,5,7a-hexahydroindene (14a): ^1H NMR (500 MHz, $CDCl_3$) δ 1.25–1.36 (m, 2 H), 1.48–1.53 (m, 1 H), 1.60–1.69 (m, 2 H), 1.71 (s, 3 H), 1.86 (m, 1 H), 2.04 (dd, J = 5, 7 Hz, 1 H), 2.15 (br d, J = 11.5 Hz, 1 H), 2.25 (m, 1 H), 2.44 (m, 1 H), 2.50 (td, 1 H), 5.54 (s, 1 H), 7.18–7.30 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 23.65, 24.26, 30.18, 32.87, 38.89, 41.48, 41.92, 43.73, 124.63, 126.00, 128.02, 128.36, 133.35, 146.39; HRMS calcd for $C_{16}H_{20}$ 212.1560, found 212.1565.

The stereochemistry of the ring junction was decided using the ^{13}C NMR shifts of the bridgehead carbons. Metzger[12] showed empirically that the shifts of the carbons at a cis junction are more shielded than those of a trans junction. The data that support the assignment are shown in Table VI.

Benzophenone-Sensitized Reactions. The trienes in benzene solutions containing benzophenone (7.20×10^{-3} M) were purged with N_2 for 15 min and irradiated (350 nm, Rayonet) for 1 h. The reaction mixtures were concentrated and then eluted through neutral alumina with hexane to remove the benzophenone. The products were isolated by means of preparative GC.

7-Ethylene-6-phenyl[3.2.0]bicycloheptane (15a). Isomer A: ^1H NMR (500 MHz, $CDCl_3$) δ 1.66–1.72 (m, 2 H), 1.74–1.79 (m, 2 H), 1.97 (m, 1 H), 2.03 (m, 1 H), 2.75 (q, 1 H), 2.86 (m, 1 H), 3.03 (q, 1 H), 3.26 (dd, 1 H), 4.86 (d, 1 H), 4.94 (d, 1 H), 5.57 (m, 1 H), 7.21–7.37 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.78, 32.64, 33.08, 41.43, 41.58, 46.08, 46.99, 113.64, 125.79, 128.05, 128.58, 140.38, 142.53.

7-Ethylene-6-phenyl[3.2.0]bicycloheptane (15a). Isomer B: ^1H NMR (500 MHz, $CDCl_3$) δ 1.48–1.56 (m, 2 H), 1.70 (dd, 1 H), 1.77–1.85 (m, 3 H), 2.86 (m, 2 H), 2.94 (m, 1 H), 3.12 (m, 1 H), 5.06 (dd, 2 H), 5.94 (m, 1 H), 7.18–7.31 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.38, 27.03, 32.58, 39.14, 44.23, 44.99, 46.70, 114.53, 125.78, 126.55, 128.38, 138.46, 146.08.

7-(1-Methylethylene)-6-phenyl[3.2.0]bicycloheptane (15b): ^1H NMR (500 MHz, $CDCl_3$) δ 1.14 (s, 3 H), 1.60–1.66 (m, 3 H), 1.92 (m, 1 H), 1.89 (m, 1 H), 1.97 (m, 1 H), 2.70 (m, 1 H), 2.78 (m, 1 H), 2.99 (q, 1 H), 3.17 (dd, 1 H), 4.78 (d, 2 H), 7.14–7.26 (m, 5 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.94, 25.64, 32.76, 32.85, 38.92, 42.58, 47.41, 48.76, 110.24, 125.59, 127.53, 128.33; HRMS calcd for $C_{16}H_{20}$ 212.1560, found 212.1565.

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Registry No. **1**, 136824-27-6; **2**, 136824-28-7; **3**, 136824-29-8; **4**, 136824-30-1; **6**, 136824-31-2; **7**, 136824-32-3; **9**, 136824-33-4; **11**, 136824-34-5; **13**, 136824-35-6; **13a**, 136824-38-9; **14**, 136824-36-7; **14a**, 136824-39-0; **15a**, 136824-37-8; **15b**, 136824-40-3; (*E*)-PhCH=CH(CH$_2$)Br, 57238-67-2; PHCH=CH(CH$_2$)$_2$CO$_2$H, 28525-69-1; (*E*)-PhCH=CH(CH$_2$)$_3$OH, 13159-16-5; (*E*)-PhCH=CH(CH$_2$)$_2$Br, 7515-41-5; (*E*)-HOCH$_2$CH=CHC(CH$_3$)=CH$_2$, 67065-89-8; (*E*)-AcOCH=CHCH=CH$_2$, 35694-20-3; (*E*)-AcOCH$_2$CH=CHC(CH$_3$)=CH$_2$, 136824-41-4; 7-phenylindene, 78383-19-4; iron tricarbonylcyclohexadienyl tetrafluoroborate, 12308-69-9.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of all compounds for which analyses were not obtained (31 pages). Ordering information is given on any current masthead page.

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