Experimental and Theoretical Analysis of the Effects of Strain Diminution on the Stereoselectivity of Dienophilic Capture by π-Facially Nonequivalent Homologues of Isodicyclopentadiene

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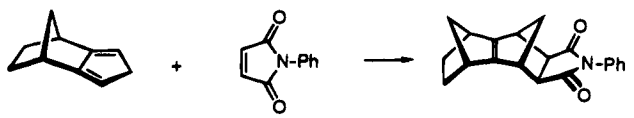
Abstract: Four new cyclic dienes, constructed such that their conjugated π networks are fused to bicyclic frameworks, viz. **6**−**9**, have been prepared. All four are less strained than isodicyclopentadiene (**1**) and therefore lack the high-lying σ orbital energy levels that presumably give rise to π orbital tilting found uniquely in **1**. The addition of various dienophiles to these dienes results in predominant Diels−Alder reaction from the top face, in contradistinction to the behavior of **1**, which reacts with high below-plane π-facial diastereoselectivity. The structures of the adducts were determined almost entirely by NOE methods as applied directly to the products themselves, their dihydro derivatives, or quadricyclane photoisomers. The relative energies of the two principal transition states for **6**−**9** were calculated by means of an MM2 model. The features uncovered by this means showed larger torsional angles between H(1) and C(4) to be invariably associated with bottom-face dienophile capture. Since this ordering of torsional strain effects does not conform with the experimental facts, such contributions cannot be responsible for controlling the stereoselectivity of these cycloadditions. Rather, in the absence of σ/π interaction, steric approach control operates, and dienophiles attack preferentially from the sterically less crowded π surface.

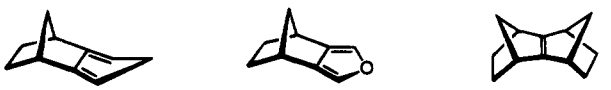
Introduction

The Diels−Alder cycloaddition chemistry of isodicyclopentadiene (**1**) has intrigued and puzzled chemists for many years.[1] The stereoselectivity exhibited by **1** toward many dienophiles is quite unique in that bond formation occurs from the sterically more hindered bottom face of the cyclopentadiene ring.[2] For example, *N*-phenylmaleimide reacts with **1** to give uniquely **2**, the product of a below-plane, exo transition-state orientation.[3] Several rationalizations of this phenomenon have been advanced.



1 **2**

An early proposal by Rondan, Paddon-Row, Caramella, and Houk[4] arose as an extension of their π-orbital distortion arguments for norbornene. Ab initio STO-3G calculations, which indicated the terminal olefinic hydrogens in 2-methylenenorbornane to be pyramidalized in the exo direction, were extrapolated to **1**. A corresponding upward bend as in **3** would, if present, accommodate below-plane attack and deter approach of a dienophile from the top face. This hypothesis was later invalidated when various fulvene analogs of **1**, confirmed by X-ray crystallographic analysis to possess fully planar five-membered rings, were shown to undergo fully controlled below-plane capture as well.[5]



3 **4** **5**

At about the same time, Vogel invoked the Bell−Evans−Polanyi principle[6] and suggested that the observed stereoselectivity was dictated by product stability.[7] Due to the aromaticity of the furan ring in **4**, equilibration between the possible stereoisomeric adducts was anticipated but not found. On this basis, the below-plane isomers were calculated to be approximately 2.5 kcal/mol more stable than their facial isomers. The thermodynamic preference of *syn*-sesquinorbornene (**5**) derivatives was loosely attributed to an electronic effect first observed in norbornadiene.[8−10] Indeed, **5** and related compounds having this framework are well recognized to exhibit strong downward pyramidalization.[11,12] Notwithstanding, Vogel's arguments were refuted on the basis of the stereoselectivity

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Figure 1. (a) End-on view of **1** to show the effects of σ/π mixing on the π_s lobes. (b) Contour plot showing the actual rotation calculated for the terminal π lobes in ψ_1.[1c]

of Diels–Alder cycloadditions to *anti,anti*-2,3-diethylidenenorbornane.[11f] Because the products in this instance do not contain the sesquinorbornene framework, little thermodynamic difference between above-plane and below-plane attack would be anticipated. However, an overwhelming preference for dienophile capture from the bottom face persisted.

In their first papers involving the chemistry of **1**, Paquette and Gleiter advanced for consideration the possibility that the stereochemical course of additions to **1** was a consequence of disrotary tilting of the π orbitals in ψ_1 brought on because of admixing of the π orbitals of the diene with the high-lying σ orbitals of the adjoining norbornyl framework (Figure 1).[2b,c] With the electron density more intense on the top face of the diene, antibonding (repulsive) interaction with the HOMO of an approaching dienophile causes top-face cycloaddition to be less kinetically favorable.[13] Semiempirical methods (INDO, SPINDO) applied to **1** were shown to generate energy levels that correlate well with its PE spectrum. This proposal is

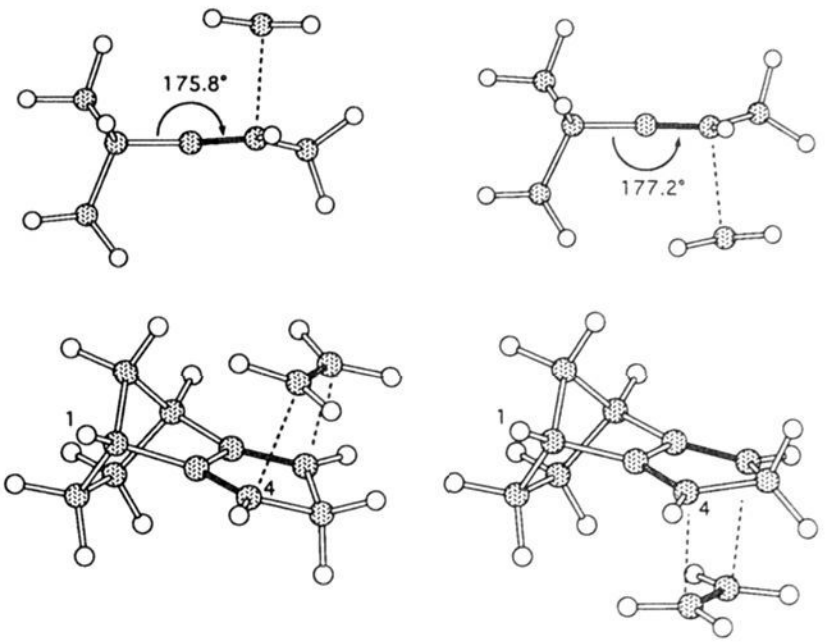
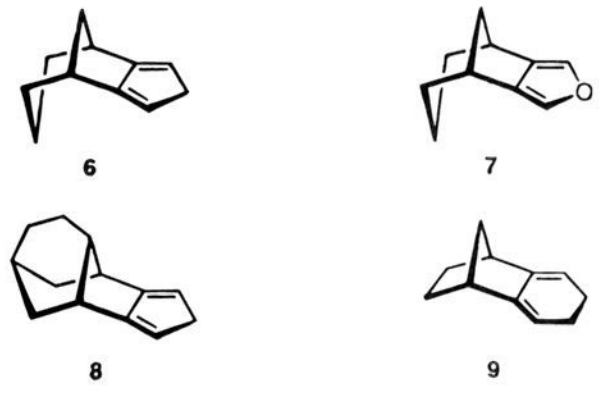


Figure 2. Transition-state geometries for above- and below-plane attack of ethylene on **1** using the MNDO theoretical model.[4]

founded on the ground-state electronic features. As a consequence, the earlier the transition state, the more pronounced should be the effects of σ/π interaction. Dienophiles that strongly perturb the MO's of the diene in opposition to the tilting would not be expected to conform to the trend otherwise observed.[2g,h]

Houk's second proposal is based on a torsional angle transition-state effect.[14] A readily recognized characteristic of the (4 + 2) cycloaddition transition states involving **1** is the degree of bending. The side view provided at the top of Figure 2 shows that the carbon centers of both the diene and ethylene are pyramidalized. When the ethylene fragments are removed from the two structures and the energies of the remaining pyramidalized isodicyclopentadienes are determined, that which participated in the below-plane transition state was found to be 0.4 kcal/mol more stable than its top-face counterpart. The respective energies correlate directly with the torsional energy involving H(1) and C(4) (Table 1). Since the larger torsion angle is said to lessen the overall energy of the associated transition state, the preferred product should arise from bottom-face attack.

In an effort to distinguish between the latter two proposals in a reasonably definitive manner, we have presently synthesized the substrates **6**–**9** and examined the stereochemistry of their Diels–Alder reactions with several dienophiles.[15] Whereas **6**,



7, and **8** no longer possess the norbornane framework, **9** has been designed to be relieved of strain at the opposite end of the molecule. In all four cases, the ring enlargement essentially eliminates σ/π mixing (see Figure 3), because the σ energy levels fall too far below that of the lowest π. On the other

(9) Theoretical calculations on the π anisotropy of norbornene: (a) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345. (b) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435. (c) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703. (d) Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482. (e) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445. (f) Inagaki, S.; Fugimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054. (g) Liotta, C. L. *Tetrahedron Lett.* **1975**, 523. (h) Liotta, C. L. *Tetrahedron Lett.* **1975**, 519. (i) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: Heidelberg, 1975. (j) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509.

(10) Other articles relating to norbornene: (a) Rondan, N. G.; Paddon-Row, M. N.; Caramella, P.; Mareda, J.; Mueller, P. H.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 4974. (b) Paddon-Row, M. N.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 7162. (c) Tee, O. S.; Altmann, J. A.; Yates, K. *J. Am. Chem. Soc.* **1974**, *96*, 3141. (d) Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *J. Am. Chem. Soc.* **1973**, *95*, 2209. (e) Brown, H. C.; Hammar, W. J.; Kawakami, J., H.; Rothberg, I.; Vander Jagt, D. L. *J. Am. Chem. Soc.* **1967**, *89*, 6381. (f) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

(11) Crystallographic studies: (a) Reference 2e. (b) Paquette, L. A.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *J. Org. Chem.* **1980**, *45*, 4922. (c) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095. (d) Reference 7. (e) Bartlett, P. D.; Combs, G. L., Jr.; Le, A.-X. T.; Watson, W. H.; Galloy, J.; Kimura, M. *J. Am. Chem. Soc.* **1982**, *104*, 3131. (f) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642. (g) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. A.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136. (h) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148. (i) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232. (j) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625. (k) Watson, W. H.; Galloy, J.; Grossie, D. A.; Bartlett, P. D.; Combs, G. L. *Acta Crystallogr.* **1984**, *C40*, 1050. (l) Paquette, L. A.; Shen, C.-C.; Krause, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2351. (m) Paquette, L. A.; Shen, C.-C. *J. Am. Chem. Soc.* **1990**, *112*, 1159. (n) Irngartinger, H.; Deuter, J.; Charumilind, P.; Paquette, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 9236.

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(13) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* **1983**, *16*, 328.

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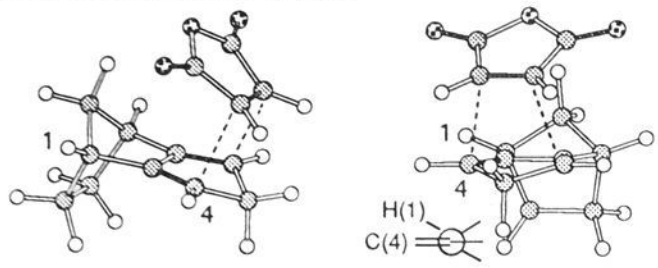
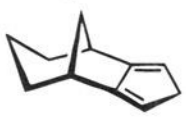
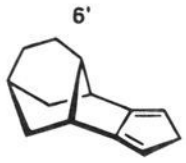
Table 1. Calculated H(1)−C(4) Torsion Angles (deg) for Dienes **1**, **6**, **6′**, **8**, and **9** in Their Ground States and Their Transition-State Structures Corresponding to Top- and Bottom-Face Attack with Maleic Anhydride as the Dienophile[a,b]



diene	ground state	transition state: top-face, endo	transition state: bottom-face, exo	ΔE^c (kcal/mol)
 **1**	21.5	20.1	26.2	0.80
 **6**	34.7	33.4	37.1	−3.19
 **6'**	33.8	32.8	36.3	−3.01
 **8**	33.8	32.3	35.6	−3.16
 **9**	21.1	18.6	26.8	2.09

[a] The transition states were not constrained to have C_s symmetry. [b] These data are based on results using the MM2 force field. [c] $\Delta E = E_{(top)} - E_{(bottom)}$.

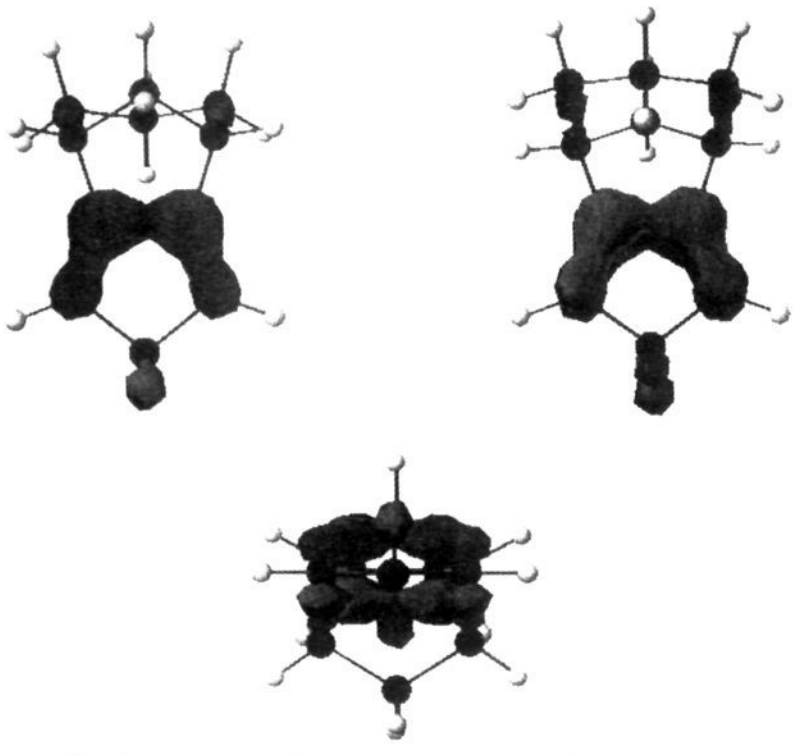
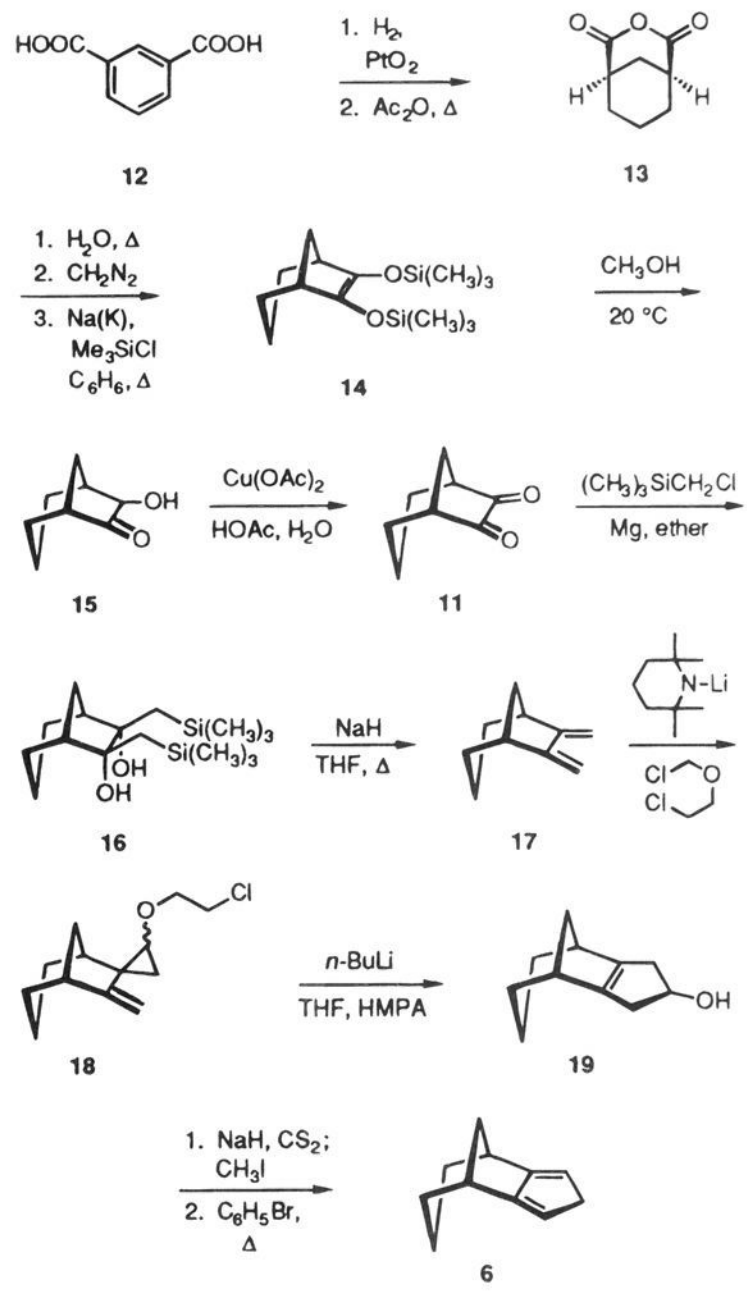


Figure 3. Contour plot of the π lobes in ψ_1 of **6** (top view) showing that no π orbital tilting is extent. The MOPAC module within CAChe (version 2.7) was used.

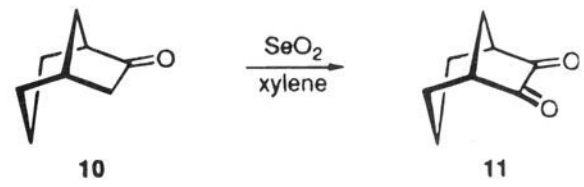
hand, the torsional effects in **6**−**9** continue to parallel the ordering present in **1**.

Scheme 1



Results

Synthesis of 2,4,5,6,7,8-Hexahydro-4,8-methanoazulene (6). Although the selenium dioxide oxidation of ketone **10**[16,17] to α-diketone **11** had been reported earlier,[17] unattractively low yields were invariably realized by us under a variety of conditions. An alternative, more reliable route to this key



intermediate was therefore developed (Scheme 1). A modification of Smith and Byrne's hydrogenation of isophthalic acid (**12**) over Adams's catalyst[18] gave the hexahydro product enriched in the cis isomer. Heating this mixture in acetic anhydride resulted in near-quantitative conversion to anhydride **13**. Following conversion to the *cis*-dimethyl ester, cyclization was accomplished under acyloin conditions[19] to make **14** available. Hydrolysis of this bis(silyl enol ether) was realized simply by stirring in deoxygenated methanol at 20 °C (66% overall). When **15** was exposed to copper(II) acetate monohydrate in aqueous acetic acid,[20] there was obtained a 77% yield of **11**, the spectral properties of which were already well known to us.

(16) Sauers, R. R.; Swithenbank, C. *J. Org. Chem.* **1964**, *29*, 3469.
(17) Wiberg, K. B.; Hess, B. A., Jr. *J. Org. Chem.* **1966**, *31*, 2250.
(18) Smith, H. A.; Byrne, F. P. *J. Am. Chem. Soc.* **1950**, *72*, 4406.
(19) Bloomfield, J. J.; Owsley, D. C.; Nelke, J. M. *Org. React.* **1976**, *23*, 259.
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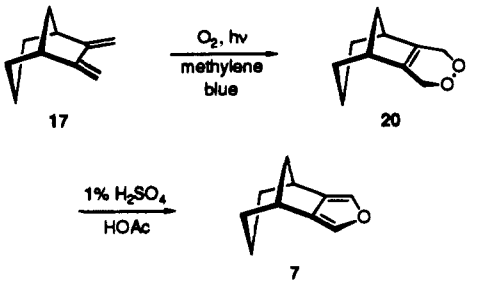
Scheme 2



High stereoselectivity was achieved upon addition of excess [(trimethylsilyl)methyl]magnesium chloride[21] to **11**; the only diastereomer detected was **16**. The choice of ether as the reaction solvent proved crucial to the realization of a respectable yield (72%) in this twofold Grignard reaction. In eight of the success enjoyed by many researchers in application of the Peterson olefination procedure,[22] **16** was heated with sodium hydride in THF. Twofold elimination occurred smoothly to provide diene **17** in 93% yield after purification.

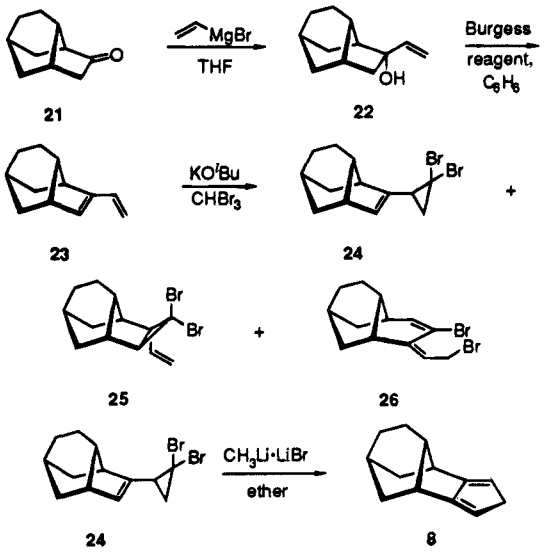
Controlled addition to **17** of chloromethyl β-chloroethyl ether in the presence of lithium 2,2,6,6-tetramethylpiperidide[23] gave rise to a 1:1 mixture of the diastereomeric vinylcyclopropyl ethers **18** (41%) alongside 37% of recovered diene. In line with precedent, treatment of **18** with *n*-butyllithium in THF containing HMPA liberated ethylene and produced the lithium salt of the vinylcyclopropanol, which underwent an alkoxide-accelerated 1,3-shift[24] to give cyclopentenol **19** in 61% yield after workup. Dehydration leading to **6** was accomplished in 70% yield by heating the xanthate in freshly distilled bromobenzene. Since **6** proved to be a highly labile compound, its purification consisted of rapid flash chromatography on silica gel with pentane elution, evaporation of the pentane, and direct use of the resulting bromobenzene solution in the ensuing Diels–Alder reactions. In this manner, its rapid decomposition by either polymerization or air oxidation could be conveniently skirted.

Other routes to **6** were examined.[25] Only that outlined in Scheme 1 succeeded in delivering the necessary quantities of this diene.

Synthesis of 5,6,7,8-Tetrahydro-4,8-methano-4*H*-cyclohepta[*c*]furan (7). When photooxygenated in the presence of methylene blue, diene **17** was transformed efficiently into the highly crystalline endoperoxide **20** (Scheme 2).

Several methods have been reported for furan formation from compounds related to **20**.[7,26] Most of these proved unsatisfactory. For example, heating **20** with 1% acetic anhydride in acetic acid at 80 °C required at least 48 h before an appreciable quantity of the endoperoxide was consumed. Although the presence of **7** could be detected, the yield was poor. *p*-Toluenesulfonic acid in refluxing benzene afforded many products. Amberlyst-15 and Dowex resins were more tolerant but gave **7** in 1% yield after 7 days of heating in benzene. The less acidic procedures developed by Magnus, Herz, Matsumoto, and Berchtold were similarly ineffective. Finally, stirring **20** with 1% H_2SO_4 in acetic acid was found to generate the desired furan reproducibly in 19% yield. Under these conditions, **7** was easily isolated and freed from major impurities.

Scheme 3



Synthesis of 2,3b,4,5,6,7,7a,8-Octahydro-5,8-methanocyclopent[*a*]indene (8). Our selection of ketone **21** as a precursor of diene **8** was founded on its ease of preparation in quantity.[27] Conversion of **21** to allylic alcohol **22** was followed by dehydration with the Burgess reagent.[28] Although the efficiency of this last step was only 57%, the convenience encountered during workup was welcomed (Scheme 3). The rigid conformational features of **23** were expected to be conducive to profitable application of the Skattebøl rearrangement[29] for cyclopentadiene ring annulation. Although the formation of **25** was originally expected to be disfavored for the usual steric reasons, dibromocarbene reacted with **23** to give the three products **24** (30%), **25** (13%), and **26** (13%). Cyclopropane **25** was only transiently stable following its isolation, with isomerization to **26** and other unidentified products occurring on standing at room temperature for only a few minutes. For reasons of ring strain, **25** was not considered to be a viable precursor to **8** in any event.[11i,30]

Notwithstanding, **24** could be readily separated in pure condition by silica gel chromatography and reacted with the CH_3Li·LiBr complex in ether. This transformation was conducive to providing ample quantities of **8** in yields averaging 50%.

Synthesis of 1,2,3,4,6,7-Hexahydro-1,4-methanonaphthalene (9). A straightforward means for gaining access to **9** was developed by taking advantage of the remarkable ease with which 1,2,3-cyclohexatriene can be generated from triflate **27** and cesium fluoride in anhydrous DMSO.[31] When this highly reactive intermediate was trapped with cyclopentadiene, triene **28** could be isolated in 74% yield (Scheme 4). In light of the high air-sensitivity of **28**, its diimide reduction to **9** was invariably performed without delay. The rate of oxidation of

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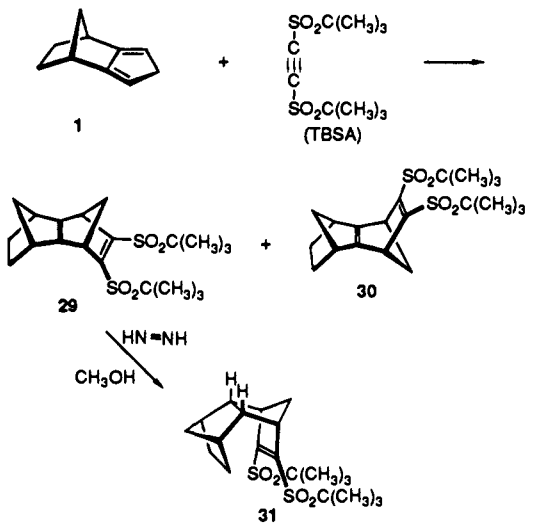
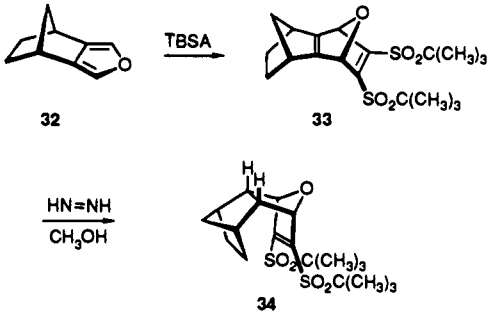
(24) Wilson, S. R. *Org. React.* **1993**, *43*, 93.
(25) Hickey, E. R. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 1993.
(26) (a) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1969**, 1664. (b) Harirchian, B.; Magnus, P. D. *Synth. Commun.* **1977**, *7*, 119. (c) Kondo, K.; Matsumoto, M. *Chem. Lett.* **1974**, 701. (d) Turner, J. A.; Herz, W. *J. Org. Chem.* **1977**, *42*, 1900. (e) Foster, C. H.; Berchtold, G. A. *J. Org. Chem.* **1975**, *40*, 3743.
(27) Tichy, M.; Sicher, J. *Collect. Czech. Chem. Commun.* **1972**, *37*, 3106.
(28) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26.
(29) (a) Holm, K. H.; Skattebøl, L. *Acta Chem. Scand. B* **1985**, *39*, 549. (b) Holm, K. H.; Skattebøl, L. *Acta Chem. Scand. B* **1984**, *38*, 783. (c) Skattebøl, L. *Tetrahedron* **1967**, *23*, 1107. (d) Skattebøl, L. *J. Org. Chem.* **1964**, *29*, 2951.
(30) McLaughlin, M. L.; McKinney, J. A.; Paquette, L. A. *Tetrahedron Lett.* **1986**, *27*, 5595.
(31) Shakespeare, W. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1990**, *112*, 8578.

9 did not approximate that of **28**, but its storage under an inert atmosphere is mandatory to preclude conversion to the known arene. The π-facial stereoselectivity for **28** was not studied.

Diels–Alder Cycloaddition Studies. Although the list of dienophiles that have been added to **1** is extensive, bis(*tert*-butylsulfonyl)acetylene (TBSA)[32] has presently been included for two reasons. Its reactivity appeared to be sufficiently elevated as to engage the entire group of dienes **6**–**9** in Diels–Alder reaction. Also, the absence of endo and exo geometries in the two possible cycloadducts would serve to simplify the analysis of product distribution. In practice, **1** reacts exothermically with TBSA in $CDCl_3$ solution to give adducts **29** and **30** in a 3:1 ratio (^{1}H NMR analysis). When chromatographically



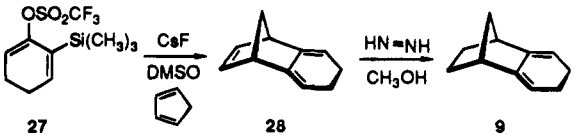
separated, these disulfones were obtained in isolated yields of 74% and 23%, respectively. Since the stereochemistries of **29** and **30** could not be unequivocally resolved by NOE measurements, both products were individually subjected to diimide reduction. As expected for a *syn*-sesquinorbornadiene, **29** was smoothly transformed into **31**. Disulfone **30** did not react since its central double bond is not pyramidalized. The structural features of **31** were convincingly corroborated by NOE measurements.[25] 4-Oxatricyclo[5.2.1.0^{2,6}]deca-2,5-diene (**32**) reacted with TBSA under identical conditions to give only **33** (93% isolated). This adduct likewise consumed diimide rapidly to afford the dihydro derivative **34**.



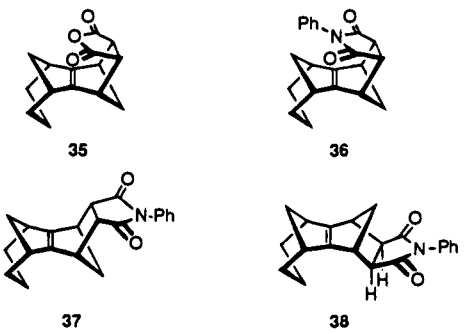
When maleic anhydride (MA) was added to a bromobenzene solution of **6**, cycloaddition was complete in less than 5 h at 20 °C, and **35** emerged as the only reaction product (92%). With *N*-phenylmaleimide (NPM), a somewhat slower cycloaddition occurred (8 h). Following chromatographic separation, the three adducts **36** (66%), **37** (15%), and **38** (19%) were obtained in

(32) (a) Riera, A.; Cabré, F.; Moyano, A.; Pericas, M. A.; Santamaria, J. *Tetrahedron Lett.* **1990**, *31*, 2169. (b) Riera, A.; Marti, M.; Moyano, A.; Pericas, M. A.; Santamaria, J. *Tetrahedron Lett.* **1990**, *31*, 2173.

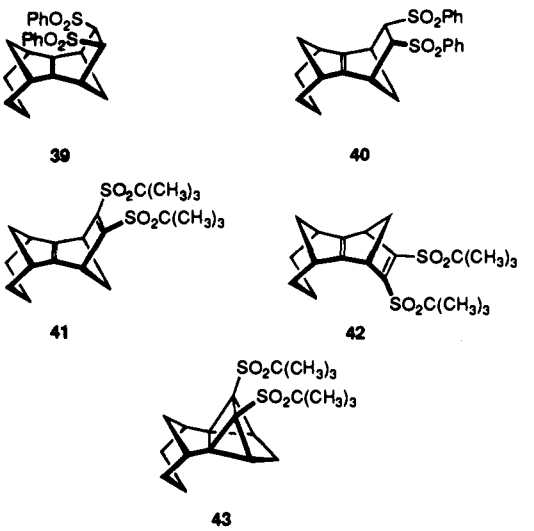
Scheme 4



pure condition. ^{1}H NMR assignments to all four compounds followed from earlier precedent and the results of NOE measurements.



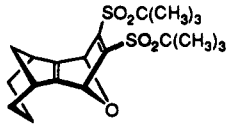
A return to complete top-face attack was seen with (*Z*)-1,2-bis(phenylsulfonyl)ethylene (PSE).[33] The top-face, endo nature of **39** (78%) was ascertained by means of the NOE interactions between the α-sulfonyl protons and the syn apical hydrogen of the proximate methano bridge. In **40** (20%), the interaction of



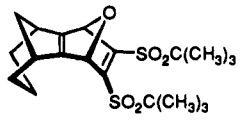
consequence was to the apical hydrogen on the more remote, syn-disposed methano bridge. TBSA reacted much more rapidly with **6** to give a mixture of **41** (74%) and **42** (24%) within 5 min. Since this pair of cycloadducts proved to be inseparable, the mixture was allowed to stand in ordinary light. Under these conditions, **41** undergoes [2 + 2] photocyclization to give **43**. This more highly caged compound proved to be separable from the mixture and amenable to structural verification by ^{1}H NMR.

Furan **7** proved unreactive toward NPM, PSE, maleonitrile, tetracyanoethylene, and other dienophiles under a variety of conditions, including high pressure. In contrast, cycloaddition involving TBSA was complete within 10 h at 20 °C. Two products were isolated in 70% and 24% yields. The minor constituent **45** was transformed quantitatively into **46**, thereby confirming that top-face attack was again kinetically dominant.

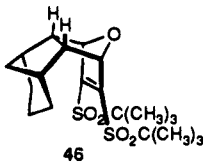
(33) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. *J. Org. Chem.* **1984**, *49*, 596.



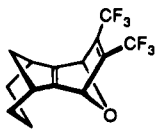
44



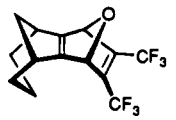
45



46



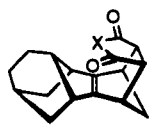
47



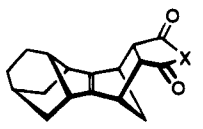
48

On standing with an excess of hexafluoro-2-butyne in $CDCl_3$ solution (sealed tube), **7** reacted completely within 18 h to give a closely comparable mixture of **47** (68%) and **48** (27%). Although the sensitivity of **47** and **48** prevented their derivatization, useful similarities with **44** and **45** were manifested in their ^1H NMR spectra. The chemical shifts of the bridgehead protons geminal to oxygen appear more upfield in the major adduct (δ 5.52) than in the minor isomer (δ 5.56). For **44** and **45**, the related protons are seen at δ 5.65 and 5.67, respectively, in $CDCl_3$ solution. The same trends are manifested in the carbon resonances: **47** (83.21 ppm)/**48** (83.74 ppm) as compared to **44** (87.90 ppm)/**45** (88.24 ppm). This evidence and the very similar product ratios in the two examples form the exclusive basis of our stereochemical assignments to **47** and **48**.

On standing with maleic anhydride or *N*-phenylmaleimide for 10 or 24 h, respectively, in CH_2Cl_2 solution at 20 °C, **8** was transformed into three adducts. In the first instance, the major product **49a** (72%) could easily be separated from the mixture and identified as before. Although the two minor components



49



50

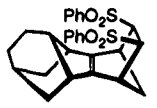
MA: a, X = O (72%) (<20%)
NPM: b, X = NPh (42%) (26%)

51

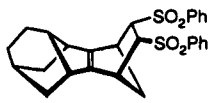
a, X = O (<20%)
b, X = NPh (13%)

50a and **51a** proved to be inseparable, NOE studies performed on the mixture provided clear indication that both cycloaddition products were the result of anti-Alder addition, although they could not be distinguished. All three NPM adducts were isolated in chromatographically pure condition. The major and minor constituents **49b** and **51b** were positively identified by NOE studies. In the case of **50b**, complete stereochemical definition was not realized under analogous conditions. Since the exo relationship of the dienophile to the remainder of the molecule was evident, this adduct was considered to be the product of top-face, exo bonding by simple deduction.

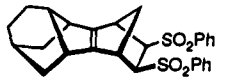
BSE added to **8** in a manner closely comparable to the pattern exhibited by NPM. Thus, **52** was likewise isolated in 42% yield.



52



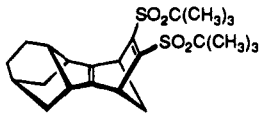
53



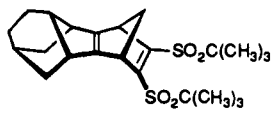
54

Although the ratio of **53** to **54** was closer to 4:1 than to the 2:1 value seen for **50b** and **51b**, this difference may not be significant in light of the greater difficulty associated with the purification of the minor disulfones.

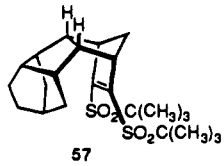
With TBSA as the dienophile, two cycloadducts were formed in a 3.6:1 ratio as determined by ^1H NMR integration of the two new proton resonances monitored at δ 4.08 and 4.05. In order to simplify the structural determinations, derivatization was undertaken directly. Exposure of the mixture to diimide afforded a small quantity of the reduced cycloadduct **57**. In



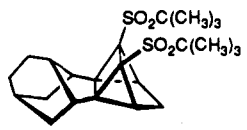
55



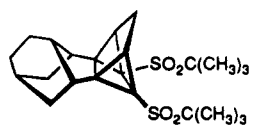
56



57



58



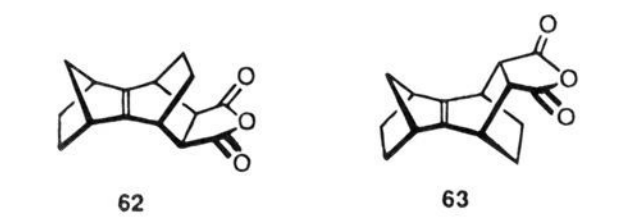
59

addition, **55/56** dissolved in a small quantity of CH_2Cl_2 was left in sunlight for 12 h. Separation of the product mixture gave pure samples of the substituted quadricyclanes **58** (major) and **59** (minor). Since NOE studies on **58** revealed the above-plane locus of the two *tert*-butyl groups, exo adduct **55** was necessarily the predominating Diels–Alder addend.

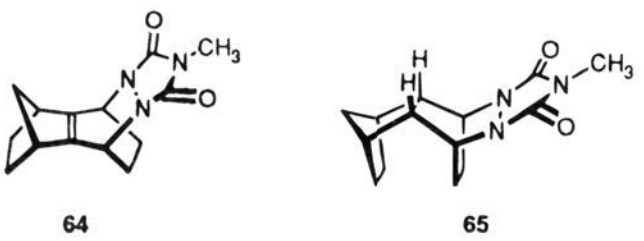
As expected, cyclohexadiene **9** was considerably less reactive than its cyclopentadiene counterparts. In fact, NPM, PSE, TBSA, and phenyl vinyl sulfone did not cycloadd to **9** even under forcing conditions (175 000 psi). Maleic anhydride did react with **9** when coerced to do so (175 000 psi, 4 days). Of the four adducts produced, the structures of **60** (52%), **61** (37%), and **62** (8%) were positively confirmed by NOE methods. The stereochemistry of **63** (3%) was arrived at by the process of elimination.

As a consequence of the limited number of dienophiles amenable to Diels–Alder cycloaddition to **9**, attention was turned to the highly reactive reagents *N*-methyltriazolinedione and hexafluoro-2-butyne. In the first instance, the red color of the dienophile was completely discharged within minutes as the CH_2Cl_2 solution was warmed to room temperature. ^1H NMR analysis revealed that only a single product had formed. Its identity as **64**, the product of above-plane attack, was revealed following diimide reduction to **65** and NOE studies on this compound. The condensation of hexafluoro-2-butyne with **9**

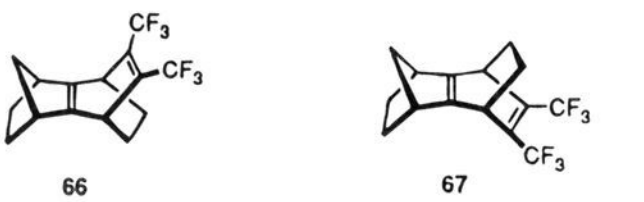
60 61



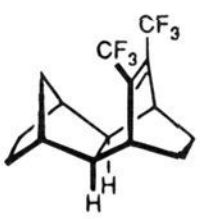
62 63



64 65



66 67



68

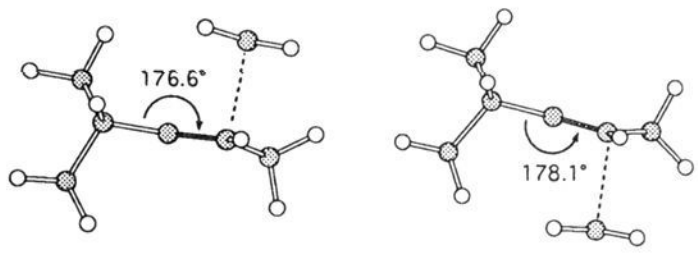
proceeded only to 63% completion after 72 h at room temperature. MPLC separation of major adduct **66** (50%) from its endo isomer **67** (12%) was followed by diimide reduction of **66**. NOE studies on the dihydro derivative indicated it to be **68**. Interestingly, the delivery of hydrogen to the central double bond in **66** occurred from the face opposite that occupied by the fluorine atoms.

All of the Diels–Alder reactions described above were performed under strict kinetic control. All attempts made to force equilibration between π-facially stereoisomeric adducts were to no avail, irrespective of whether they were formed from **6**, **7**, **8**, or **9**.

Transition-State Modeling. Houk's investigation into the below-plane preference exhibited by isodicyclopentadiene (**1**) in its Diels–Alder cycloaddition with various dienophiles led him to examine the transition states of these reactions by means of the MM2 force field.[14] The use of two separate programs was implemented when semiempirical (MNDO) methods alone incorrectly calculated the ground-state energies and geometries of the two possible [4 + 2] adducts from the reaction of **1** with ethylene.

In subsequent correspondence, Houk suggested that desired starting transition-state geometries "should be easy to obtain by doing an AM1 transition search with enforced C_s symmetry."[34] Indeed, authentic transition-state structures for the cycloaddition of ethylene to cyclopentadiene could be obtained from semiempirical (AM1) and ab initio (6-31G*) methods with the software packages MOPAC 6.0[35a] and Gaussian 92[35b] when these calculations were performed on a CRAY Y-MP8/864 supercomputer. The derived structures closely resembled each other and those previously reported by Houk (3-21G)[36] and Jorgensen (6-31G*).[37]

(34) Personal communication to E.R.H. (June 2, 1992).



69 70

Figure 4. Side views of the MM2-generated transition-state structures for the top- and bottom-face Diels–Alder cycloaddition of ethylene to isodicyclopentadiene, showing the pyramidalized nature of those sp^2-hybridized carbon centers participating in the reaction.

When all attempts to extend these techniques (viz., AM1 and MM2) to the above- and below-plane transition-state structures for the ethylene–isodicyclopentadiene reaction generated dihedral angles widely divergent from the reported values,[14] we bypassed this unfortunate limitation by selecting minimization protocols that were grounded instead in molecular mechanics. The new approach involved adaptation of Allinger's MM2 code within the MODEL software package.[38] The MNDO-generated transition structures of the isodicyclopentadiene/ethylene system were used as the starting geometry for each MM2 calculation. Seventeen atoms corresponding to the seven carbon atoms of the cyclopentadiene and ethylene fragments and the atoms directly bound to each of these seven carbon atoms were fixed in space to preserve the highly pyramidalized MNDO geometry of each transition structure. The positions of all other atoms were fully optimized with the normal parameters of Allinger's MM2 force field.[14] The minimized transition-state structures realized in this fashion (Figure 4) featured "reactive centers" which were 2.251 and 2.250 Å apart for top-face and bottom-face dienophilic capture, respectively. The pyramidalized carbon atoms of the diene and dienophile along with the nonparallel approach of the two reactants from either face of the diene noted earlier[36a,39] were also quite apparent. The H(1)–C(4) dihedral angles within **69** (16.20°) and **70** (25.24°) were likewise found to be in close agreement with those reported by Houk.[14]

When maleic anhydride was substituted for ethylene at the same reactive distance (2.20 Å), the transition-state geometries **71** and **72** (Figure 5) were likewise significantly pyramidalized at each sp^2-hybridized carbon center. The energy difference between **71** and **72** was 0.8 kcal/mol in favor of **72**. Houk reported a 1.0 kcal/mol bottom preference for this specific cycloaddition.[14]

In light of the evident workability of this model, comparable procedures were applied to **6**, **8**, and **9**, and entirely similar features were seen. As before, each transition state distinguished itself on the basis of its H(1)–C(4) dihedral angles and the

(35) (a) MOPAC 6.0, Quantum Chemistry Program Exchange (QCPE), Department of Chemistry, Indiana University, Bloomington, IN. (b) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binckley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Revision B; *Gaussian 92*, Gaussian Inc.: Pittsburgh, PA, 1992.

(36) Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172. See also: Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682.

(37) Jorgensen, W. L.; Lim, D.; Blake, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 2936.

(38) MODEL version KS 2.96 provided by W. C. Still and K. Steliou. See: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; ACS Monograph 177; American Chemical Society: Washington, DC, 1982. All of the illustrations were generated with CHEM-3D PLUS (Cambridge Scientific Co., Inc., Cambridge, MA, 1990).

(39) Brown, F. K.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 4609.

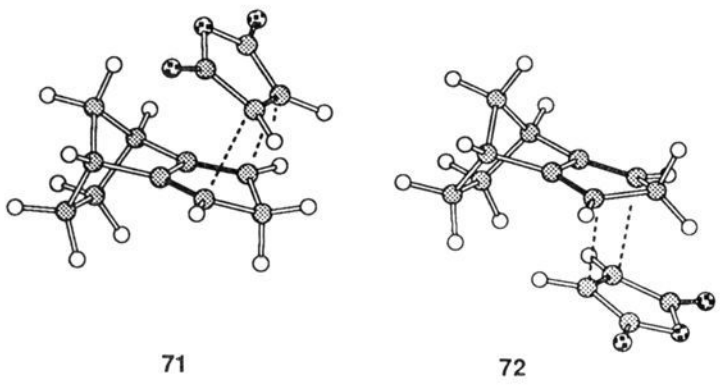


Figure 5. Changes in the MM2 energy for the isodicyclopentadiene–maleic anhydride reaction via top- and bottom-side approach.

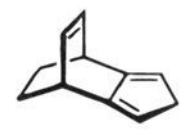
differences in the energies of its facial isomers (Table 1). According to Houk,[14] the smaller dihedral angles should induce an increase in the overall strain of the associated transition state. If this were the actual controlling element underlying π-facial stereoselectivity, bottom-face, exo attack should be kinetically preferred in all cases since approach along this trajectory generates the larger dihedral angle. One might argue, however, that the dihedral angles calculated for **6**, the boat conformer of **6**, and **8** are quite large (>30°) and that a torsional angle of 10–15° is more constraining to a system.

For this reason, the differences in the MM2 energies (ΔE) of the facially isomeric transition-state structures within this series were also evaluated (Table 1). A positive ΔE denotes the top-face, endo approach to be higher in energy content than the bottom-face, endo orientation. Consequently, **1** and **9** should experience bonding to a dienophile primarily from below. While **1** does follow this reaction course in most instances, **9** does not despite the fact that its ΔE is more than twice as large as that of **1**. Dienes **6** and **8** likewise prefer to react from their top surface. It is noteworthy that the conformational change that distinguished **6** from **6′** has little impact on the projected dominant stereofacial isomer.

Discussion

Each new diene examined in this study was designed for a particular purpose. Cyclopentadiene **6** and furan **7** do not possess the norbornyl framework that is present in **1**. In **8**, the propano bridge is locked into a boatlike conformation in order to guarantee that steric interference with below-plane attack cannot operate. Ring homologation of the norbornyl skeleton was implemented to release the strain inherent in **1**. Cyclohexadiene **9** experiences strain release in the other sector of the molecule. Once either steric constraint is released, the σ orbital energies are expected to fall off rather steeply, such that σ/π mixing no longer operates as it does in **1**. The stereoelectronic control gained by **1** as a consequence of this orbital interaction would therefore not be expected to operate. According to the Paquette–Gleiter theory, dienes **6**–**9** should participate in Diels–Alder chemistry by preferred attack on the less sterically encumbered top face since directive influences that would dictate otherwise are inherently absent. The experimental results conform fully to these expectations.

In an attempt to rationalize the stereoreversed Diels–Alder facial selectivity in terms of Houk's theory, an MM2 model was developed that closely parallels his earlier work. A common prediction that bottom attack should occur in **1** as well as in **6**, **8**, and **9** was arrived at because all four dienes give rise to transition states having larger H(1)–C(4) torsional angles when bonding occurs below-plane. These conclusions run counter to experimental fact. Neither are they in agreement with the cycloaddition behavior of **73**, a hydrocarbon earlier examined by us.[2b,2c,11b] In this system, the torsional angles of



73

consequence at 8.5° (bottom) and 2.4° (top) are much smaller than those calculated in Table 1. Nonetheless, fundamental adherence to facial selectivity identical to that predicted in the other frameworks is to be expected. Experimentally, dienophiles add to **73** predominantly from the top (79–100%). Thus, Houk's theory appears to survive neither these decade-old observations nor the latest experimental challenge detailed herein.

Torsional angle decompression is not the source of facial selectivity in Diels–Alder cycloadditions involving cyclic dienes fused to bicyclic frameworks. Rather, further evidence has accrued in support of the proposal that π orbital tilting may well serve as the key determinant of contrasteric π-facial stereoselectivity in the case of isodicyclopentadiene.

Experimental Section

All manipulations were performed under an inert (nitrogen unless otherwise noted) atmosphere. Solvents were dried over 4 Å molecular sieves before their distillation. Benzene, diethyl ether (ether), tetrahydrofuran (THF), and toluene were distilled from sodium or sodium/benzophenone ketyl. Chlorotrimethylsilane (TMSCl), dichloromethane (CH_2Cl_2), diisopropylamine, dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), and triethylamine were each distilled from calcium hydride. Chloroform was distilled from phosphorus pentoxide. All reagents were reagent grade and purified where necessary.

Melting points are uncorrected. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Exact mass measurements were performed with either a Kratos MS-30 or a VG 70-250S mass spectrometer at The Ohio State University Chemical Instrumentation Center.

(Bicyclo[3.2.1]oct-6-en-6,7-ylenedioxy)bis[trimethylsilane] (14). Into a flame-dried three-necked 2 L Morton flask equipped with an overhead stirrer (glass stir paddle), addition funnel, reflux condenser, and nitrogen inlet were placed anhydrous benzene (600 mL), sodium (12.77 g, 0.555 mol), and potassium (12.77 g, 0.327 mol). The mixture was heated slowly and eventually refluxed gently for 45 min, whereupon a fine "silver-sand" was produced. Dimethyl *cis*-1,3-cyclohexanedicarboxylate (15.21 g, 76.0 mmol) and chlorotrimethylsilane (56.0 mL, 0.441 mol) were dissolved in anhydrous benzene (100 mL) and transferred to the addition funnel via syringe. The warm flask was cooled to room temperature, and dropwise addition of the benzene solution was commenced. The reaction mixture developed a purple color during the addition process. The slurry was heated for an additional 5 h upon completion of the addition and stirred at ambient temperature overnight. The purple slurry was (carefully!) filtered through Celite, and the residue was washed with anhydrous benzene and subsequently deactivated under an inert atmosphere with isopropyl alcohol while the solvent was being removed from the filtrate. The remaining yellow liquid was distilled (0.10 mmHg, 65 °C) to give **14** as a colorless oil (16.01 g, 74%): IR (CH_2Cl_2, cm^{-1}) 1725, 1680, 1365, 1340, 1315, 1275, 1255, 1225, 1055, 1045, 845; ^1H NMR (300 MHz, $CDCl_3$) δ 2.20 (s, 2H), 2.02–1.95 (m, 1H), 1.75–1.60 (m, 1H), 1.60–1.46 (m, 3H), 1.37–1.27 (m, 2H), 1.23 (d, J = 9.5 Hz, 1H), 0.19 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.7, 40.0, 39.4, 24.2, 18.8, 0.8; MS *m/z* (M^+) calcd 284.1627, obsd 284.1605.

(1*S*,5*R*)-7-Hydroxybicyclo[3.2.1]octan-6-one (15). Dry nitrogen was bubbled through anhydrous methanol (175 mL) for 1 h. A 16.01 g (56.3 mmol) sample of **14** was transferred in via syringe, and the solution was stirred at ambient temperature for 24 h. Evaporation of the solvent afforded a pale yellow solid which was recrystallized from petroleum ether to give **15** as a colorless solid (7.78 g, 100%): mp

162−166 °C; IR (CH_2Cl_2, cm^{-1}) 3525, 1740; ^1H NMR (300 MHz, $CDCl_3$) δ 4.04 (dd, J = 6.9, 1.7 Hz, 1H), 3.08 (s, 1H), 2.63 (q, J = 1.2 Hz, 1H), 2.41 (m, 1H), 1.98−1.78 (m, 3H), 1.68−1.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 221.6, 78.1, 43.6, 36.6, 31.6, 31.1, 25.3, 19.0; MS m/z (M^+) calcd 140.0838, obsd 140.0828.

Bicyclo[3.2.1]octane-6,7-dione (11). A solution of **15** (5.62 g, 40.1 mmol) in methanol (6.4 mL) was diluted with glacial acetic acid and water (1:1, 56.2 mL) and treated with copper(II) acetate monohydrate (17.99 g, 90.1 mmol). The blue slurry was refluxed for 6 h, at which time the reaction mixture had developed a red color. The slurry was cooled to room temperature and filtered through a pad of Celite. The aqueous layer was extracted with CH_2Cl_2 until the extracts were colorless. The organic phases were combined and washed with brine, 50% $NaHCO_3$ solution, brine, and water (70 mL each). The organic layer was dried and concentrated to leave an orange oil, distillation of which afforded an orange-yellow solid in the distillation head (4.29 g, 77%). An additional sublimation (20 mmHg, 140 °C) afforded pure **11** (4.16 g, 75%): mp 156−157 °C; IR ($CHCl_3$, cm^{-1}) 1735, 1175; ^1H NMR (300 MHz, $CDCl_3$) δ 2.54 (br s, 1H), 2.27−2.16 (m, 2H), 2.05−1.83 (m, 2H), 1.79−1.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 222.0, 46.1, 43.5, 37.1, 32.1, 30.6, 30.4, 18.7; MS m/z (M^+) calcd 138.0681, obsd 138.0674.

(1*R*,5*S*,6*S*,7*R*)-6,7-Bis[(trimethylsilyl)methyl]bicyclo[3.2.1]octane-6,7-diol (16). A 100 mL three-necked flask charged with Mg (1.42 g, 58.4 mmol) and fitted with an addition funnel, reflux condenser, and gas inlet was flame-dried. Ether (5 mL) was added. Into the addition funnel was dissolved (chloromethyl)trimethylsilane (6.85 mL, 49.1 mmol) in ether (10 mL). Three milliliters of this solution was added to the reaction vessel. External heating with a heat gun initiated the Grignard reaction. The remaining solution was added dropwise at a rate that maintained the reaction mixture at a gentle reflux. Once the addition was complete, the slurry was refluxed for 1 h. During this time, a second 100 mL three-necked round-bottom flask fitted with an addition funnel, gas inlet, and reflux condenser was flame-dried. Bicyclo[3.2.1]octane-6,7-dione (**11**, 0.50 g, 3.62 mmol) and ether (7 mL) were stirred in this flask until a clear solution resulted. The ethereal solution of [(trimethylsilyl)methyl]magnesium chloride was transferred at ambient temperature via cannula to the latter addition funnel and added dropwise. Once addition was completed, the solution was stirred at reflux for 48 h and cooled to room temperature before being poured slowly into 75 g of ice water. Next, 5 N HCl was added with stirring until all the salts were dissolved. The separated aqueous layer was extracted with ether (3 × 50 mL). The ether solutions were combined, dried, and evaporated to leave a light yellow oil. Silica gel chromatography (elution with 5% ethyl acetate in petroleum ether) afforded **16** as a colorless solid, mp 67.5−69.5 °C (from pentane), (0.81 g, 72%): IR (CH_2Cl_2, cm^{-1}) 3530, 865, 845; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 2H), 2.03 (s, 2H), 1.91−1.87 (m, 2H), 1.71−1.55 (m, 1H), 1.52−1.37 (m, 3H), 1.37 (ABq, J_{AB} = 12.1 Hz, v_{AB} = 65.0 Hz, 2H), 0.99 (ABq, J_{AB} = 14.5 Hz, v_{AB} = 122.5 Hz, 4H), 0.08 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 83.4, 45.0, 33.3, 29.6, 27.5, 19.9, 0.8; MS m/z (M^+) calcd 314.2097, obsd 296.1922. Anal. Calcd for $C_{16}H_{34}O_2Si_2$: C, 61.08; H, 10.89. Found: C, 61.22; H, 10.92.

6,7-Dimethylenebicyclo[3.2.1]octane (17). A cold (0 °C), magnetically stirred slurry of NaH (0.80 g of 97%, 33.3 mmol) in THF (20 mL) was treated dropwise with **16** (1.01 g, 3.21 mmol) dissolved in THF (20 mL). The reaction mixture was stirred at ambient temperature for 2 h before being heated at reflux for 15 h. The brownish-orange slurry was cooled to 0 °C, and water (70 mL) was added dropwise until all of the excess NaH had been consumed, and then the remaining water was added all in one portion. The aqueous phase was extracted with pentane (3 × 50 mL). The combined organic phases were washed with water and brine (50 mL each), dried, and evaporated without heating. MPLC purification (silica gel, pentane elution) afforded **17** as a colorless oil (0.40 g, 93%): IR (CH_2Cl_2, cm^{-1}) 1610, 1445, 1435, 1080, 885; ^1H NMR (300 MHz, $CDCl_3$) δ 5.35 (s, 2H), 4.84 (s, 2H), 2.71 (m, 2H), 1.69 (m, 1H), 1.62 (m, 5H), 1.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.2, 101.7, 42.9, 38.3, 33.7, 18.6; MS m/z (M^+) calcd 134.1096, obsd 134.1123. Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.81; H, 10.45.

(1*R*,5*S*)-2′-(2-Chloroethoxy)-7-methylenespiro[bicyclo[3.2.1]octane-6,1′-cyclopropane] (18). A three-necked 250 mL round-bottom flask fitted with two reflux condensers was flame-dried before the addition of **17** (2.00 g, 14.9 mmol) dissolved in ether (10 mL). Into one addition funnel was placed a 1.0 M LiTMP slurry (prepared from 2,2,6,6-tetramethylpiperidine (3.05 mL, 18.1 mmol) and *n*-butyllithium (1.3 M in hexanes, 12.60 mL, 16.4 mmol)). The second addition funnel was charged with a solution of chloromethyl β-chloroethyl ether (2.15 g, 16.7 mmol) dissolved in ether (14 mL, approximately 1.0 M). The reaction flask was cooled to 0 °C, and equal volumes were added dropwise from the two addition funnels over a 30 min period. The reaction mixture was stirred at 0 °C for 3 h and at ambient temperature overnight. Water (100 mL) was introduced, and the separated aqueous solution was extracted with ether (3 × 50 mL). The combined organic phases were washed with water and brine (50 mL each), dried, and evaporated. MPLC purification of the residue (silica gel, elution with 1% ethyl acetate in petroleum ether) afforded recovered **17** (0.74 g, 37%), followed by **79** as a colorless oil (1.37 g, 41%, 1:1 mixture of diastereomers): IR (CH_2Cl_2, cm^{-1}) 1640, 1430, 1360, 1340, 1295, 1150, 1075, 805; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71 (s, 1H), 4.63 (s, 1H), 4.47 (s, 1H), 4.10 (s, 1H), 3.70 (t, J = 5.8 Hz, 2H), 3.66−3.54 (m, 6H), 3.26 (dd, J = 6.3, 4.3 Hz, 1H), 3.21 (dd, J = 6.6, 4.0 Hz, 1H), 2.77 (s, 2H), 2.06 (br s, 1H), 1.87−1.77 (m, 2H), 1.71−1.41 (m, 14H), 1.03−0.99 (m, 3H), 0.9 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 154.3, 100.3, 95.7, 70.8, 70.6, 67.7, 66.4, 44.3, 44.2, 42.6, 42.4, 42.0, 39.6, 38.5, 34.9, 34.8, 34.6, 34.1, 33.9, 30.1, 28.6, 19.4, 19.3, 18.0, 16.9; MS m/z (M^+) calcd 226.1124, obsd 226.1123. Anal. Calcd for $C_{13}H_{19}ClO$: C, 68.86; H, 8.45. Found: C, 69.09; H, 8.54.

1,2,3,4,5,6,7,8-Octahydro-4,8-methanoazulen-2-ol (19). A solution of **18** (0.61 g, 2.69 mmol) in THF (10 mL) and HMPA (10 mL) was cooled to 0 °C and treated with *n*-butyllithium (1.3 M in hexanes, 10 mL, 13.0 mmol) via syringe. The mixture was stirred at 0 °C for 15 min before being warmed to room temperature and stirred overnight. Water (100 mL) was introduced, and the separated aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were washed with water and brine (50 mL each), dried, and evaporated. MPLC purification of the residue (silica gel, elution with 5 → 20% ethyl acetate in petroleum ether) afforded **19** as a colorless solid (0.27 g, 61%): mp 65−66.5 °C; IR (CH_2Cl_2, cm^{-1}) 3620; ^1H NMR (300 MHz, $CDCl_3$) δ 4.84 (tt, J = 7.0, 5.7 Hz, 1H), 2.84 (s, 1H), 2.64 (m, 2H), 2.32 (br s, 2H), 2.09 (m, 3H), 1.50 (d, J = 9.9 Hz, 1H), 1.41−1.18 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 143.7, 77.1, 76.4, 47.5, 47.1, 38.6, 37.9, 37.7, 37.5, 24.6, 24.6, 19.4, 19.2; MS m/z (M^+) calcd 164.1201, obsd 164.1189. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.48; H, 9.88.

2,4,5,6,7,8-Hexahydro-4,8-methanoazulene (6). A mixture of sodium hydride (1.34 g, 55.8 mmol), carbon disulfide (35 mL), and **19** (0.77 g, 4.69 mmol) was refluxed for 12 h, treated with methyl iodide (excess), and heated for an additional 6 h. Water (50 mL) was added, and the separated aqueous layer was extracted with ether (3 × 50 mL). The combined organic phases were washed with water and brine (50 mL each), dried, and evaporated. MPLC purification of the residue (silica gel, elution with pentane) afforded the xanthate as a colorless oil (0.78 g, 65%): IR (CH_2Cl_2, cm^{-1}) 1450, 1320, 1230, 1180, 1080, 1060, 1030; ^1H NMR (300 MHz, $CDCl_3$) δ 6.28 (tt, J = 7.2, 4.5 Hz, 1H), 2.92 (m, 2H), 2.56 (s, 3H), 2.40 (m, 3H), 2.34 (d, J = 4.5 Hz, 0.5H), 2.33 (d, J = 4.4 Hz, 0.5H), 2.24 (m, 1H), 1.58 (d, J = 10.0 Hz, 1H), 1.50−1.22 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 143.8, 88.7, 47.5, 37.7, 34.8, 24.5, 19.2, 19.0; FAB MS m/z (M^+ + 1) calcd 254.08, obsd 254.03. Anal. Calcd for $C_{13}H_{18}OS_2$: C, 61.38; H, 7.13. Found: C, 61.52; H, 7.22.

A solution of the xanthate (0.20 g, 0.77 mmol) in freshly distilled bromobenzene (5 mL) was refluxed for 6 h, cooled to ambient temperature, and flashed down a silica gel column (pentane elution). Evaporation of the pentane (30 Torr, no heating) afforded a colorless bromobenzene solution which contained approximately 70 mol % (80 mg) of **6**: IR (C_6H_5Br, cm^{-1}) 1680, 1370; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (t, J = 1.2 Hz, 2H), 3.28 (br s, 2H), 2.83 (br s, 2H), 2.00 (br s, 2H), 1.78 (s, 1H), 1.74 (s, 1H), 1.67−1.30 (m, 4H); MS m/z (M^+) calcd 146.1096, obsd 146.1099.

4,5,6,7,8,9-Hexahydro-5,9-methano-1*H*-cyclohepta[*d*][1,2]-dioxin (20). A solution of **17** (0.10 g, 0.75 mmol) and methylene blue (10 mg) in CH_2Cl_2 (250 mL) was irradiated at 0 °C with a Radias 600 W tungsten halogen lamp for 1.5 h with continuous bubbling of oxygen.

Concentration of the solvent and flash chromatography of the blue-green solid through a silica gel plug (CH_2Cl_2 elution) afforded a colorless solid, recrystallization of which from petroleum ether gave **20** as colorless irregular prisms (90 mg, 73%), mp 61−63 °C; IR (CH_2Cl_2, cm^{-1}) 1350, 1030, 980, 960, 910; ^1H NMR (300 MHz, $CDCl_3$) δ 4.62 (m, 4H), 2.51 (d, J = 2.4 Hz, 2H), 2.05 (m, 1H), 1.48−1.39 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.9, 70.4, 44.1, 39.7, 24.2, 18.9; MS m/z (M^+) calcd 166.0994, obsd 166.1039. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.11; H, 8.44.

5,6,7,8-Tetrahydro-4,8-methano-4H-cyclohepta[c]furan (7). Acetic acid (100 mL) containing 1% sulfuric acid and **20** (0.10 g, 0.60 mmol) was stirred at room temperature for 5.5 h. Water (100 mL) and pentane (50 mL) were quickly introduced, the layers were separated, and the aqueous phase was extracted with pentane (3 × 50 mL). The combined organic layers were washed with water, saturated $NaHCO_3$ solution, and brine (50 mL each), and then dried and concentrated (30 Torr, no heating) to give **7** as a yellow oil (17 mg, 19%); IR ($CHCl_3$, cm^{-1}) 1680, 1570, 1260; ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 2H), 3.03 (m, 2H), 2.32 (m, 1H), 1.82, (d, J = 10.5 Hz, 1H), 1.70−1.39 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 131.6, 48.8, 33.6, 30.6, 19.4; MS m/z (M^+) calcd 148.0888, obsd 148.0891.

(1*S*,2*S*,3a*S*,5*R*,7a*S*)-Octahydro-2-vinyl-1,5-methanoinden-2-ol (22). A THF solution (50 mL) of **21** (8.00 g, 53.3 mmol) was cooled to 0 °C and treated with a solution of vinylmagnesium bromide (1.0 *M* in THF, 110 mL, 0.11 mol). The reaction mixture was stirred at 0 °C for 30 min and heated at gentle reflux for 6 h before being returned to ambient temperature. Ice water (200 mL) was added, followed by sufficient 10% HCl to dissolve the salts. Once the organic layer was decanted, the aqueous layer was extracted with ether (3 × 75 mL). The combined organic phases were washed with water and brine, dried, and evaporated. Column chromatography of the residue (silica gel, elution with 5% ethyl acetate in petroleum ether) afforded **22** as a colorless solid (9.01 g, 95%), mp 51−52.5 °C; IR (CH_2Cl_2, cm^{-1}) 3600; ^1H NMR (300 MHz, $CDCl_3$) δ 6.13 (dd, J = 17.2, 10.7 Hz, 1H), 5.17 (dd, J = 17.2, 1.0 Hz, 1H), 4.96 (dd, J = 10.7, 1.0 Hz, 1H), 2.26 (dd, J = 14.0, 7.2 Hz, 1H), 2.16 (dm, J = 13.8 Hz, 1H), 1.98 (m, 1H), 1.83 (m, 2H), 1.75 (m, 1H), 1.63 (m, 3H), 1.48−1.35 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.4, 109.4, 81.0, 49.4, 46.0, 37.6, 35.2, 34.9, 27.2, 26.3, 23.1, 19.5; MS m/z (M^+) calcd 178.1358, obsd 178.1358. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 81.01; H, 10.24.

(1*S*,3a*R*,5*R*,7a*S*)-3a,4,5,6,7,7a-Hexahydro-2-vinyl-1,5-methanoindene (23). A solution of **22** (2.00 g, 11.2 mmol) in benzene (120 mL) was treated dropwise with a solution of the Burgess reagent (4.00 g, 16.8 mmol) in the same solvent (30 mL). The mixture was stirred at room temperature for 15 min before being heated at reflux for 2.5 h, cooled to ambient temperature, filtered, and flashed down a column of basic alumina (pentane elution). Solvent evaporation afforded a colorless oil which was further purified by MPLC (silica gel, pentane elution) to provide **23** as a colorless liquid (1.03 g, 57%): IR ($CHCl_3$, cm^{-1}) 1630, 1460, 1375, 990, 900, 830; ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (dd, J = 17.4, 10.5 Hz, 1H), 5.87 (d, J = 3.1 Hz, 1H), 4.92 (m, 2H), 2.40 (dd, J = 8.3, 4.6 Hz, 1H), 2.29 (m, 1H), 2.00 (m, 1H), 1.72 (m, 3H), 1.52−1.34 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 138.4, 132.6, 112.7, 40.0, 39.9, 38.3, 29.5, 29.4, 28.2, 27.1, 19.6; MS m/z (M^+) calcd 160.1252, obsd 160.1236.

This compound should not be stored.

(1*S*,3a*R*,5*R*,7a*S*)-2-(2,2-Dibromocyclopropyl)-3a,4,5,6,7,7a-hexahydro-1,5-methanoindene (24). A mixture of deoxygenated pentane (100 mL), diene **23** (0.84 g, 5.24 mmol), and freshly prepared potassium *tert*-butoxide (2.40 g, 21.4 mmol) was cooled to 0 °C. Bromoform (0.16 mL, 1.83 mmol) was introduced via syringe, and stirring was maintained at 0 °C for 1 h and at room temperature for 2 h. Addition of water (100 mL) was followed by extraction of the aqueous layer with pentane (3 × 75 mL). The combined organic phases were washed with water (45 mL), dried, and evaporated. MPLC purification of the residue (silica gel, pentane elution) afforded dibromide **24** (0.53 g, 30%) and recovered diene **23** (16 mg, 2%) in addition to **25** (0.232 g, 13%) and **26** (224 mg, 13%), all as colorless liquids. The desired dibromocyclopropane **24** develops a brown color on standing at room temperature or 0 °C for a few hours and should be used immediately.

For **24**: colorless oil; IR ($CHCl_3$, cm^{-1}) 1450, 1360, 1140, 1110, 1090, 1040, 990, 910; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90 (d, J = 2.9 Hz, 1H), 2.38−2.20 (m, 4H), 2.06−1.07 (series of m, 10H), 0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.7, 138.2, 42.2, 40.1, 31.6, 29.2, 28.2, 27.9, 27.7, 27.6, 25.2, 22.6, 19.5; MS m/z (M^+) calcd 329.9619, 331.9598, 333.9578, obsd 329.9605, 331.9610 , 333.9581.

2,3b,4,5,6,7,7a,8-Octahydro-5,8-methanocyclopent[*a*]indene (8). A cold (0 °C) solution of **24** (0.50 g, 1.51 mmol) in ether (175 mL) was treated dropwise with methylliithium (1.20 M in ether, 5.10 mL, 6.12 mmol) via syringe. Stirring was continued at 0 °C for 3 h before the reaction mixture was quenched with water (40 mL). The separated aqueous layer was extracted with pentane (3 × 20 mL). The combined organic phases were washed with water (25 mL), dried, and evaporated. Column chromatography of the residue (basic alumina, elution with pentane) afforded **8** as a colorless liquid (0.13 g, 50%): IR ($CHCl_3$, cm^{-1}) 1470, 1450, 1385, 1350, 1340, 1320, 1240, 1030, 970 , 960; ^1H NMR (250 MHz, $CDCl_3$) δ 5.73 (t, J = 1.4 Hz, 2H), 3.21 (s, 2H), 2.68 (dd, J = 9.7, 4.0 Hz, 2H), 2.07 (m, 1H), 1.86 (m, 3H), 1.65 (m, 2H), 1.59−1.51 (m, 3H), 1.37 (m, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 160.1, 115.5, 45.7, 41.6, 35.1, 34.3, 27.0, 24.3, 19.8; MS m/z (M^+) calcd 172.1252, obsd 172.1254.

This diene should be used immediately.

1,4,6,7-Tetrahydro-1,4-methanonaphthalene (28). To a solution of **27** (4.89 g, 16.3 mmol) in anhydrous DMSO (20 mL) was introduced freshly distilled cyclopentadiene (1.13 mL, 16.9 mmol) via syringe, followed immediately by finely ground cesium fluoride (5.02 g, 33.0 mmol) which had been stirred in DMSO (5 mL) for 30 min. A deep green color developed after 5 min, and the dark solution was stirred for 12 h at ambient temperature. Water (100 mL) was added, and the separated aqueous layer was extracted with pentane (3 × 50 mL). The combined organic phases were washed with water and brine (50 mL each), dried, and evaporated (30 Torr, no heating). MPLC purification of the residue (silica gel, elution with pentane) afforded **28** as a colorless oil (1.73 g, 74%): IR ($CHCl_3$, cm^{-1}) 1440, 1340, 1310, 1240, 1230, 1170, 960, 830, 810, 680; ^1H NMR (200 MHz, $CDCl_3$) δ 6.17 (t, J = 1.7 Hz, 2H), 5.54 (s, 2H), 3.32 (t, J = 1.7 Hz, 2H), 2.22 (m, 4H), 1.83 (dt, J = 7.9, 1.4 Hz, 1H), 1.56 (d, J = 7.9 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.4, 135.6, 112.6, 52.9, 47.3, 23.1; MS m/z (M^+) calcd 144.0939, obsd 144.0928.

1,2,3,4,6,7-Hexahydro-1,4-methanonaphthalene (9). A mixture of potassium azodicarboxylate (2.56 g, 13.2 mmol) and **28** (1.73 g, 12.0 mmol) in methanol (40 mL) was cooled to 0 °C before glacial acetic acid (1.37 mL, 23.9 mmol) was introduced dropwise via syringe. The slurry was stirred at 0 °C for 2 h and at room temperature overnight. Water (100 mL) and pentane (50 mL) were added, and the separated aqueous layer was extracted with pentane (3 × 50 mL). The organic phases were combined, washed with water and brine (75 mL each), dried, and evaporated (30 Torr, no heating). MPLC purification of the residue (silica gel, elution with pentane) afforded **9** as a colorless oil (1.10 g, 63%): IR ($CHCl_3$, cm^{-1}) 1450, 1350, 1280, 1080, 1030, 965, 950, 890, 830, 810; ^1H NMR (200 MHz, $CDCl_3$) δ 5.32 (s, 2H), 2.75 (s, 2H), 2.14 (m, 4H), 1.66 (m, 2H), 1.35 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.7, 110.5, 42.2, 40.7, 28.9, 22.8; MS m/z (M^+) calcd 146.1096, obsd 146.1080.

(1*R*,4*S*,5*R*,8*S*)- and (1*R*,4*S*,5*S*,8*R*)-2,3-Bis(*tert*-butylsulfonyl)-1,4,5,6,7,8-hexahydro-1,4:5,8-dimethanonaphthalene (29 and 30). A dried NMR tube was charged with **1** (10 mg, 75.6 μmol) dissolved in $CDCl_3$ (0.5 mL), followed by bis(*tert*-butylsulfonyl)acetylene (45 mg, 0.17 mmol). Upon mixing, an exothermic reaction was apparent. The tube stood for 2 h, after which reaction was judged to be 100% complete by ^1H NMR analysis. Solvent evaporation followed by MPLC purification on silica gel (elution with 20% ethyl acetate in petroleum ether) gave pure **29** (22 mg, 74%) and **30** (7 mg, 23%).

For **29**: colorless irregular prisms, mp > 200 °C; IR ($CHCl_3$, cm^{-1}) 1480, 1310, 1270, 1120, 970, 950; ^1H NMR (300 MHz, $CDCl_3$) δ 4.09 (s, 2H), 3.18 (s, 2H), 2.70 (dd, J = 7.0, 1.6 Hz, 1H), 2.23 (m, 1H), 1.68 (m, 2H), 1.45 (s, 18H), 1.30 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 159.0, 75.3, 62.0, 58.2, 52.0, 42.9, 24.0, 23.8; MS m/z (M^+) calcd 398.1585, obsd 398.1577. Anal. Calcd for $C_{20}H_{30}O_4S_2$: C, 60.27; H, 7.59. Found: C, 60.07; H, 7.47.

For **30**: colorless irregular prisms, mp > 200 °C; IR ($CHCl_3$, cm^{-1}) 1470, 1360, 1290, 1270, 1110, 960; ^1H NMR (300 MHz, $CDCl_3$) δ 4.07 (s, 2H), 3.26 (s, 2H), 2.82 (d, J = 6.6 Hz, 1H), 2.18 (m, 1H),

1.79 (m, 2H), 1.44 (s, 18H), 1.26 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 160.7, 79.2, 62.1, 57.0, 50.9, 43.7, 25.7, 23.9; MS *m/z* (M^+) calcd 398.1585, obsd 398.1599). Anal. Calcd for $C_{20}H_{30}O_4S_2$: C, 60.27; H, 7.59. Found: C, 60.29; H, 7.74.

(1*R*,4*S*,4a*R*,5*R*,8*S*,8a*S*)-2,3-Bis(*tert*-butylsulfonyl)-1,4,4a,5,6,7,8,-8a-octahydro-1,4:5,8-dimethanonaphthalene (31). A mixture of potassium azodicarboxylate (28 mg, 0.14 mmol), **29** (6 mg, 14.3 mmol), and MeOH (5 mL) was cooled to 0 °C prior to the dropwise addition of HOAc (16 μL) in MeOH (1 mL). The slurry was stirred for 4 h, water (100 mL) and CH_2Cl_2 (10 mL) were added, and the separated aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The organic phases were combined, washed with water and brine (25 mL each), dried, and evaporated. MPLC purification of the residue (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded **31** as colorless irregular prisms (6 mg, 98%): mp 168 °C dec; IR ($CHCl_3$, cm^{-1}) 1480, 1310, 1190, 1130; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.30 (t, J = 1.6 Hz, 2H), 2.74 (s, 2H), 2.34 (dq, J = 8.5, 1.2 Hz, 1H), 2.28 (s, 2H), 1.77 (dt, J = 8.5, 1.3 Hz, 1H), 1.73−1.63 (m, 2H), 1.58−1.41 (m, 4H), 1.51 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 86.0, 64.5, 51.3, 46.7, 34.5, 26.7, 24.6, 16.5; FAB MS *m/z* (M^+ + 1) calcd 401.18, obsd 401.20. Anal. Calcd for $C_{20}H_{32}O_4S_2$: C, 59.97; H, 8.05. Found: C, 59.83; H, 8.06.

(1*R*,4*S*,5*R*,8*S*)-6,7-Bis(*tert*-butylsulfonyl)-1,2,3,4,5,8-hexahydro-5,8-epoxy-1,4-methanonaphthalene (33). To a solution of **32** (15 mg, 0.11 mmol) in $CDCl_3$ (1.5 mL was added bis(*tert*-butylsulfonyl)-acetylene (29 mg, 0.11 mmol) likewise dissolved in $CDCl_3$ (0.5 mL). An exothermic reaction commenced. After 5 min at ambient temperature, ^{1}H NMR analysis revealed complete reaction and the formation of only one cycloadduct. The $CDCl_3$ was evaporated, and the yellow solid was purified using MPLC (silica gel, elution with CH_2Cl_2) to afford **33** as a colorless solid (42 mg, 93%), mp 147 °C dec; IR ($CHCl_3$, cm^{-1}) 1620, 1310 1120; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (s, 2H), 3.29 (s, 2H), 1.71 (m, 4H), 1.47 (s, 18H), 1.35 (dt, J = 8.3, 1.3 Hz, 1H), 1.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 160.9, 88.2, 62.4, 51.6, 42.5, 23.8, 23.3; FAB MS *m/z* (M^+ + 1) calcd 401.15, obsd 401.17.

(1*R*,4*S*,4a*S*,5*R*,8*S*,8a*R*)-6,7-Bis(*tert*-butylsulfonyl)-1,2,3,4,4a,5,8,-8a-octahydro-5,8-epoxy-1,4-methanonaphthalene (34). A mixture of potassium azodicarboxylate (80 mg, 0.41 mmol) and **33** (21 mg, 52.7 mmol) in MeOH (5 mL) was cooled to 0 °C prior to the dropwise addition of HOAc (45 μL). The slurry was stirred at 0 °C for 3 h and at room temperature overnight. The usual workup and purification gave **34** as a colorless solid (17 mg, 82%): mp 131°C dec; IR ($CHCl_3$, cm^{-1}) 1720, 1630, 1320, 1125; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08 (t, J = 2.5 Hz, 2H), 2.87 (s, 2H), 2.34 (s, 2H), 1.83 (d, J = 9.4 Hz, 1H), 1.65 (m, 3H), 1.55 (s, 18H), 1.45 (d, J = 2.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 85.5, 64.4, 49.6, 48.8, 37.7, 25.1, 24.6; FAB MS *m/z* (M^+ + 1) calcd 403.16, obsd 403.01.

(1*R*,2*R*,3*S*,4*S*,5*R*,9*S*)-2,3,4,5,6,7,8,9-Octahydro-1,4:5,9-dimethano-1*H*-benzocycloheptene-2,3-dicarboxylic Anhydride (35). Maleic anhydride (37 mg, 0.38 mmol) was added directly to a bromobenzene solution (4 mL) containing **6** (55 mg, 0.379 mmol). The reaction mixture was stirred at room temperature for 5 h, at which time TLC analysis indicated consumption of the diene. Column chromatography (silica gel, elution with a mixture of petroleum ether (150 mL) and then ethyl acetate (200 mL). When concentrated, the ethyl acetate fraction afforded a residue, MPLC purification of which (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded the single colorless cycloadduct **35** (81 mg, 92%): mp 98−99.5 °C; IR (CH_2Cl_2, cm^{-1}) 1860, 1810, 1780, 1225, 1075, 940, 915; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (dd, J = 2.9, 1.6 Hz, 2H), 3.48 (dd, J = 2.9, 1.5 Hz, 2H), 2.48 (dd, J = 4.7, 3.1 Hz, 2H), 2.22 (dt, J = 8.9, 1.4 Hz, 1H), 2.08 (m, 1H), 1.83 (dd, J = 8.8, 1.0 Hz, 1H), 1.56−1.40 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 150.9, 56.9, 50.5, 48.6, 45.5, 38.2, 24.8, 19.8; MS *m/z* (M^+) calcd 244.1099, obsd 244.1111. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.64; H, 6.59.

***N*-Phenylmaleimide Addition to 6.** A bromobenzene solution (5 mL) of **6** (96 mg, 0.65 mmol) was stirred at ambient temperature while *N*-phenylmaleimide (0.14 g, 0.79 mmol) was added. The reaction mixture was allowed to stir for 8 h under an inert atmosphere before being subjected to flash chromatography (silica gel, elution with petroleum ether (225 mL) and then ethyl acetate (200 mL)). Those fractions containing ethyl acetate were combined and concentrated to leave a residue that was purified by MPLC techniques (silica gel, elution with 20% ethyl acetate in petroleum ether). Three cycloadducts were obtained from the column in the following order and quantities: **38** (48 mg, 19%), **37** (37 mg, 15%), and **36** (166 mg, 66%).

For **36**: colorless irregular prisms, mp > 225 °C; IR ($CHCl_3$, cm^{-1}) 1770, 1710, 1500, 1370, 1180; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.20 (m, 5H), 3.57 (dd, J = 2.9, 1.6 Hz, 2H), 3.47 (m , 2H), 2.49 (m, 2H), 2.30 (dt, J = 8.6, 1.5 Hz, 1H), 1.93 (m, 1H), 1.91 (dd, J = 8.6, 1.0 Hz, 1H), 1.57−1.42 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.6, 150.1, 131.8, 128.7, 127.9, 125.7, 57.0, 50.1, 47.7, 44.4, 38.1, 24.9, 19.8; MS *m/z* (M^+) calcd 319.1572, obsd 319.1544. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63 Found: C, 78.79; H, 6.58.

For **37**: colorless irregular prisms, mp 185−200 °C dec; IR ($CHCl_3$, cm^{-1}) 1760, 1710, 1370, 1180; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48−7.24 (m, 5H), 3.37 (s, 2H), 2.97 (s, 2H), 2.55 (dd, J = 2.8, 1.5 Hz, 2H), 2.06 (dd, J = 9.6, 1.5 Hz, 2H), 1.77 (d, J = 9.6 Hz, 1H), 1.61 (d, J = 9.6 Hz, 1H), 1.58−1.43 (m, 3H), 1.26 (m, 1H), 0.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 154.0, 132.0, 129.2, 128.6, 126.4, 51.9, 49.9, 46.7, 45.2, 37.7, 25.1, 19.9; MS *m/z* (M^+) calcd 319.1572, obsd 319.1576. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63. Found: C, 79.32; H, 6.74.

For **38**: colorless irregular prisms, mp 142−143 °C; IR ($CHCl_3$, cm^{-1}) 1765, 1700, 1490, 1370, 1280, 1170; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.36 (m, 3H), 7.29−7.26 (m, 2H), 3.46 (s, 2H), 3.02 (d, J = 1.3 Hz, 2H), 2.72 (m, 1H), 1.76 (dt, J = 9.6, 1.5 Hz, 1H), 1.66 (dt, J = 9.6, 1.5 Hz, 1H), 1.56−1.40 (m, 7H), 1.25 (t, J = 7.2 Hz, 1H), 1.07−0.99 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 153.8, 132.0, 129.2, 128.6, 126.4, 49.3, 48.6, 46.5, 46.0, 39.0, 24.3, 19.5; MS *m/z* (M^+) calcd 319.1572, obsd 319.1580. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63. Found: C, 79.13; H, 6.58.

(1*R*,2*S*,3*R*,4*S*,5*S*,9*R*)- and (1*R*,2*R*,3*S*,4*S*,5*S*,9*R*)-2,3,4,5,6,7,8,9-Octahydro-2,3-bis(phenylsulfonyl)-1,4:5,9-dimethano-1*H*-benzocycloheptene (39 and 40). To a solution of **6** (96 mg, 0.65 mmol) dissolved in bromobenzene (5 mL) was added *cis*-1,2-bis(phenylsulfonyl)ethylene (0.20 g, 0.65 mmol). To increase solubility, CH_2Cl_2 (2 mL) was introduced, and the reaction mixture was stirred at room temperature for 12 h, at which time TLC suggested consumption of the diene. After solvent evaporation, the residue was subjected to column chromatography (silica gel, elution with petroleum ether (250 mL) and then ethyl acetate (500 mL)) and MPLC purification of the residue from the ethyl acetate fraction (silica gel, elution with 30% ethyl acetate in petroleum ether) to give **40** (60 mg, 20%) and **39** (231 mg, 78%).

For **39**: colorless irregular prisms, mp 213.5−215 °C; IR (CH_2Cl_2, cm^{-1}) 1440, 1325, 1300, 1140, 1075; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.1 Hz, 4H), 7.61 (m, 2H), 7.52 (m, 4H), 4.22 (s, 2H), 3.13 (s, 2H), 2.96 (m, 1H), 2.86 (s, 2H), 1.97 (dt, J = 9.0, 1.2 Hz, 1H), 1.64 (d, J = 9.0 Hz, 1H), 1.59−1.45 (m, 6H), 0.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 141.5, 133.3, 128.8, 128.6, 71.3, 52.4, 49.3, 46.8, 39.0, 25.4, 20.3; MS *m/z* (M^+) calcd 454.1273, obsd 454.1324. Anal. Calcd for $C_{25}H_{26}O_4S_2$: C, 66.05; H, 5.76. Found: C, 66.02; H, 6.25.

For **40**: colorless irregular prisms, mp 227−228 °C; IR (CH_2Cl_2, cm^{-1}) 1440, 1330, 1255, 1150, 1080; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, J = 7.4 Hz, 4H), 7.64 (t, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 4H), 3.55 (d, J = 1.7 Hz, 2H), 3.25 (s, 2H), 2.83 (d, J = 9.4 Hz, 1H), 2.31 (m, 2H), 2.06 (d, J = 9.4 Hz, 1H), 1.92 (m, 1H), 1.70 (br s, 2H), 1.52 (m, 2H), 1.45−1.25 (m, 2H), 0.88 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 140.3, 133.5, 128.9, 128.7, 69.9, 51.7, 49.6, 45.7, 37.6, 24.7, 19.6; MS *m/z* (M^+) calcd 454.1273, obsd 454.1265. Anal. Calcd for $C_{25}H_{26}O_4S_2$: C, 66.05; H, 5.76. Found: C, 66.28; H, 5.89.

Bis(*tert*-butylsulfonyl)acetylene Addition to 6. Diene **6** (43 mg, 0.291 mmol) dissolved in bromobenzene (2 mL) was stirred at ambient temperature while bis(*tert*-butylsulfonyl)acetylene (0.10 g, 0.375 mmol) was added. After 5 min, when TLC indicated the total consumption of **6**, the solvent was evaporated, and the residue was subjected sequentially to flash chromatography (silica gel, elution with ethyl acetate) and MPLC (silica gel, elution with 20% ethyl acetate in petroleum ether) to give **41** and **42** as an inseparable mixture in a 2.7:1.0 ratio (107 mg, 90%), **43** (9 mg, 8%), and some recovered dienophile.

For **41** and **42**: colorless solid, mp 132−136.5 °C dec; IR (CH_2Cl_2, cm^{-1}) 1475, 1455, 1300, 1270, 1115, 950; ^{1}H NMR (300 MHz, $CDCl_3$)

δ 4.11 (t, J = 1.4 Hz, 2H), 4.05 (t, J = 1.4 Hz, 1H), 2.88 (d, J = 7.4 Hz, 1H), 2.78 (m 7H), 2.63 (m, 1H), 2.31 (m, 2H), 2.15 (m, 1H), 1.63 (m, 8H), 1.47 (s, 18H), 1.42 (s, 18H), 1.24 (m, 2H), 0.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 163.5, 159.2, 158.5, 78.0, 75.9, 62.0, 61.8, 58.3, 57.3, 51.4, 50.5, 39.4, 39.0, 29.6, 24.9, 24.4, 24.0, 23.9, 20.4; MS *m/z* (M^+) calcd 412.1742, obsd 412.1735.

For **43**: colorless irregular prisms, mp 184.5−186 °C; IR (CH_2Cl_2, cm^{-1}) 1480, 1460, 1365, 1290, 1260, 1120, 1100, 1070, 1040, 950; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.91 (s, 2H), 2.87 (m, 1H), 2.63 (s, 2H), 2.65 (d, J = 12.9 Hz, 1H), 2.53 (d, J = 12.9 Hz, 1H), 1.93 (d, J = 11.6 Hz, 1H), 1.68−1.62 (m, 4H), 1.47 (s, 18H), 1.52−1.42 (m, 1H), 1.06 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.0, 52.7, 47.2, 43.7, 38.2, 34.6, 32.8, 30.7, 24.5, 20.0; MS *m/z* (M^+) calcd 412.1742, obsd 412.1732. Anal. Calcd for $C_{21}H_{32}O_4S_2$: C, 61.13; H, 7.82. Found: C, 61.14; H, 7.83.

(1*R*,4*S*,5*S*,9*R*)- and (1*R*,4*S*,5*R*,9*S*)-2,3-Bis(*tert*-butylsulfonyl)-4,5,6,7,8,9-hexahydro-1,4-epoxy-5,9-methano-1*H*-benzocycloheptene (44 and 45). A dried NMR tube was charged with **7** (17 mg, 0.11 mmol) dissolved in $CDCl_3$ (0.5 mL) and bis(*tert*-butylsulfonyl)-acetylene (40 mg, 0.15 mmol). This solution stood for 10 h, after which time the reaction was judged to be 100% complete by ^{1}H NMR analysis, which indicated two cycloadducts to be formed in a ratio of 2.9:1.0. Evaporation of the solvent and MPLC purification (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded **44** (33 mg, 70%) and **45** (11 mg, 24%).

For **44**: off-white solid, mp 153 °C dec; FT-IR (CH_2Cl_2, cm^{-1}) 1602, 1303, 1127; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (s, 2H), 2.90 (m, 2H), 2.20 (dt, J = 5.0, 5.0 Hz, 1H), 1.71 (d, J = 10.2 Hz, 2H), 1.50−1.47 (m, 5H), 1.44 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 163.7, 87.9, 62.2, 48.8, 39.5, 24.4, 23.7, 19.2; MS *m/z* (M^+) calcd 414.1535, obsd 414.1493.

For **45**: off-white solid, mp 127 °C dec; FT-IR (CH_2Cl_2, cm^{-1}) 1597, 1459, 1299, 1119; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (s, 2H), 2.96 (s, 2H), 2.48 (m, 1H), 1.74 (d, J = 10.0 Hz, 1H), 1.68−1.52 (m, 5H), 1.50 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 162.0, 88.2, 62.3, 51.5, 39.0, 24.2, 23.8, 19.9; MS *m/z* (M^+) calcd 414.1535, obsd 414.1436.

(1*R*,4*S*,4a*R*,5*R*,9*S*,9a*S*)-2,3-Bis(*tert*-butylsulfonyl)-4,4a,5,6,7,8,9,-9a-octahydro-1,4-epoxy-5,9-methano-1*H*-benzocycloheptene (46). To a mixture of potassium azodicarboxylate (90 mg, 0.46 mmol), **45** (7 mg, 16.6 mmol), and MeOH (5 mL) cooled to 0 °C was added HOAc (50 μL, 0.87 mmol) in MeOH (1 mL) dropwise. The slurry was stirred for 4 h and worked up in the predescribed manner. MPLC purification of the residue (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded **46** (6 mg, 97%): mp 154−155 °C; IR (CH_2Cl_2, cm^{-1}) 1600, 1450, 1310, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (m, 2H), 3.09 (m, 2H), 2.32 (br s, 2H), 2.26−2.22 (m, 2H), 2.00 (m, 1H), 1.69−1.60 (m, 4H), 1.56 (s, 18H), 1.53−1.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 86.0, 64.5, 51.3, 46.7, 34.5, 26.7, 24.6, 16.5; FAB MS *m/z* ($M^+ + 1$) calcd 417.18, obsd 417.02.

(1*R*,4*S*,5*S*,9*R*)- and (1*R*,4*S*,5*R*,9*S*)-4,5,6,7,8,9-Hexahydro-2,3-bis-(trifluoromethyl)-1,4-epoxy-5,9-methano-1*H*-benzocycloheptene (47 and 48). Furan **7** (20 mg, 0.135 mmol) was dissolved in $CDCl_3$ (0.5 mL) and placed in a thick-walled NMR tube. This solution was cooled to −78 °C, and hexafluoro-2-butyne (0.50 g, 3.09 mmol) was condensed therein. The tube was sealed before being warmed to ambient temperature. After 18 h, reaction was judged to be 100% complete by ^{1}H NMR analysis, which indicated the formation of two adducts in a ratio of 2.5:1.0. The tube was recooled to −78 °C and opened. Evaporation of the solvent and MPLC purification of the residue (silica gel, elution with pentane and then 5% ethyl acetate in petroleum ether) afforded **47** (28 mg, 68%) and **48** (11 mg, 27%).

For **47**: colorless oil; FT-IR (CH_2Cl_2, cm^{-1}) 1604, 1458, 1152; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (s, 2H), 2.85 (d, J = 4.9 Hz, 2H), 2.20 (m, 1H), 1.69 (d, J = 10.1 Hz, 1H), 1.60−0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 83.2, 49.9, 38.4, 24.5, 19.2; MS *m/z* (M^+) calcd 310.0792, obsd 310.0795.

For **48**: colorless oil; FT-IR (CH_2Cl_2, cm^{-1}) 1600, 1459, 1121, 1073; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (s, 2H), 2.93 (m, 2H), 2.45 (m, 1H), 1.71 (d, J = 10.1 Hz, 1H), 1.60−0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0, 83.7, 49.7, 38.4, 23.5, 18.8; MS *m/z* (M^+) calcd 310.0792, obsd 310.0789.

Maleic Anhydride Addition to 8. A CH_2Cl_2 solution (10 mL) of **8** (37 mg, 0.21 mmol) was stirred at ambient temperature while maleic anhydride (21 mg, 0.21 mmol) was added. The reaction mixture was allowed to stir for 10 h under an inert atmosphere before the solvent was removed. The remaining solid was purified by MPLC (silica gel, elution with 20% ethyl acetate in petroleum ether). Three cycloadducts were obtained in the following quantities: pure **49a** (42 mg, 72%) and an inseparable mixture of **50a** and **51a** (12 mg, 20%).

For **49a**: colorless irregular prisms, mp 124.5−125 °C; IR (CH_2Cl_2, cm^{-1}) 1780, 1720; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (dd, J = 3.0, 1.6 Hz, 2H), 3.49 (m, 2H), 2.28 (m, 2H), 2.18 (m, 1H), 2.08 (dt, J = 8.6, 1.6 Hz, 1H), 1.85 (dt, J = 8.6, 1.6 Hz, 1H), 1.83 (m, 1H), 1.72 (m, 2H), 1.53 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 158.3, 59.2, 48.5, 45.7, 45.3, 37.9, 29.2, 28.0, 27.8, 19.7; MS *m/z* (M^+) calcd 270.1256, obsd 270.1259. Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.23; H, 6.70.

For the mixture of **50a** and **51a**: colorless solid, mp 159−163 °C; IR (CH_2Cl_2, cm^{-1}) 1780, 1710; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.48 (s, 2H), 3.43 (t, J = 1.2 Hz, 2H), 3.32 (d, J = 1.52 Hz, 2H), 3.00 (d, J = 1.4 Hz, 2H), 2.55 (dd, J = 8.6, 4.2 Hz, 2H), 2.33 (m, 2H), 2.24 (m, 1H), 2.07 (m, 1H), 1.97 (dt, J = 9.8, 1.5 Hz, 1H), 1.84 (m, 2H), 1.76−1.71 (m, 4H), 1.64−1.36 (m, 14H), 1.26 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.7, 161.3, 50.5, 50.2, 49.7, 47.7, 47.4, 46.3, 46.2, 38.7, 37.4, 29.4, 28.4, 27.9, 27.5, 27.0, 20.0, 19.7; MS *m/z* (M^+) calcd 270.1256, obsd 270.1259.

***N*-Phenylmaleimide Addition to 8.** To a solution of **8** (0.13 g, 72.6 mmol) in CH_2Cl_2 (10 mL) was added *N*-phenylmaleimide (0.13 g, 72.2 mmol), and the reaction mixture was stirred at room temperature for 24 h. Evaporation of the solvent and MPLC purification (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded in order of elution: **51b** (17 mg, 13%), **50b** (32 mg, 26%), and **49b** (52 mg, 42%), corresponding to a 1.0:1.9:3.1 ratio.

For **49b**: colorless irregular prisms, mp 164−165 °C; IR (CH_2Cl_2, cm^{-1}) 1710, 1430, 1380, 1270, 1180; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.29 (m, 3H), 7.19−7.16 (m, 2H), 3.53 (dd, J = 3.0, 1.6 Hz, 2H), 3.46 (m, 2H), 2.29 (dd, J = 8.2, 4.4 Hz, 2H), 2.15 (dt, J = 8.4, 1.5 Hz, 1H), 1.99 (m, 1H), 1.94 (dt, J = 8.4, 1.5 Hz, 1H), 1.82 (br s, 1H), 1.64 (m, 2H), 1.59−1.43 (series of m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 157.6, 131.9, 128.8, 128.0, 125.8, 59.7, 47.6, 45.1, 44.3, 37.9, 29.2, 28.2, 27.8, 19.7; MS *m/z* (M^+) calcd 345.1729, obsd 345.1730. Anal. Calcd for $C_{23}H_{23}NO_2$: C, 79.97; H, 6.71. Found: C, 79.46; H, 6.79.

For **50b**: colorless irregular prisms, mp 209−210 °C; IR (CH_2Cl_2, cm^{-1}) 1710, 1375; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49−7.35 (m, 3H), 7.28−7.24 (m, 2H), 3.37 (s, 2H), 2.88 (d, J = 1.0 Hz, 2H), 2.35 (m, 2H), 2.12 (m, 1H), 1.93 (dt, J = 9.5, 1.4 Hz, 1H), 1.84 (m, 1H), 1.79 (dt, J = 9.5, 1.4 Hz, 1H), 1.74 (m, 3H), 1.56 (m, 4H), 1.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 161.4, 132.0, 129.1, 128.5, 126.4, 49.4, 48.6, 47.4, 45.1, 37.5, 29.6, 28.9, 27.6, 20.2; MS *m/z* (M^+) calcd 345.1729, obsd 345.1722.

For **51b**: colorless irregular prisms, mp > 225 °C; IR (CH_2Cl_2, cm^{-1}) 1710, 1380; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50−7.36 (m, 3H), 7.28−7.25 (m, 2H), 3.46 (s, 2H), 3.23 (d, J = 1.0 Hz, 2H), 2.56 (dt, J = 6.1, 4.0 Hz, 2H), 2.25 (m, 1H), 1.86 (m, 2H), 1.72 (m, 1H), 1.65−1.51 (m, 3H), 1.39 (dd, J = 6.4, 2.5 Hz, 4H), 1.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 158.7, 131.9, 129.2, 128.6, 126.4, 49.9, 46.5, 45.0, 44.3, 38.9, 28.6, 27.2, 27.0, 19.9; MS *m/z* (M^+) calcd 345.1729, obsd 345.1729.

Addition of (*Z*)-1,2-Bis(phenylsulfonyl)ethylene to 8. A solution of **8** (81 mg, 0.47 mmol) in CH_2Cl_2 (2 mL) was treated with (*Z*)-1,2-bis(phenylsulfonyl)ethylene (0.15 g, 0.49 mmol), and a deep purple color developed within 5 s. The reaction mixture was stirred at room temperature for 12 h and subjected directly to column chromatography (silica gel, elution with pentane (250 mL) and then ethyl acetate (500 mL)). Evaporation of the latter fraction and MPLC purification of the slightly colored residue (silica gel, elution with 30% ethyl acetate in petroleum ether) afforded in order of elution: **54** (7 mg, 3%), **53** (24 mg, 11%), and **52** (95 mg, 42%), corresponding to a 1.0:3.3:12.9 ratio.

For **52**: colorless irregular prisms, mp > 210 °C; IR (CH_2Cl_2, cm^{-1}) 1450), 1340, 1310, 1160, 1090; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 7.0 Hz, 4H), 7.62 (m, 2H), 7.53 (t, J = 1.2 Hz, 4H), 4.17 (s, 2H), 3.14 (s, 2H), 3.01 (m, 1H), 2.64 (m, 2H), 1.83 (m, 4H), 1.56 (m,

7H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 141.4, 133.3, 128.8, 128.6, 71.0, 54.9, 46.6, 43.6, 38.5, 30.2, 28.4, 27.9, 20.0; MS *m/z* (M^+) calcd 480.1429, obsd 480.1451.

For **53**: colorless irregular prisms, mp > 210 °C; IR ($CHCl_3$, cm^{-1}) 1460, 1430, 1340, 1320, 1270, 1160, 910; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 (d, J = 7.2 Hz, 4H), 7.66−7.52 (series of m, 6H), 3.44 (d, J = 1.8 Hz, 2H), 3.23 (s, 2H), 2.82 (d, J = 9.3 Hz, 1H), 2.08 (m, 2H), 1.95 (m, 1H), 1.89 (d, J = 9.3 Hz, 1H), 1.75 (m 1H), 1.62 (m, 2H), 1.51 (m, 2H), 1.40 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2, 140.9, 133.5, 128.9, 128.6, 69.5, 51.5, 47.7, 45.6, 37.3, 29.1, 27.8, 27.4, 20.0; MS *m/z* (M^+) calcd 480.1429, obsd 480.1433. Anal. Calcd for $C_{27}H_{28}O_4S_2$: C, 67.47; H, 5.87. Found: C, 67.52; H, 6.01.

For **54**: colorless irregular prisms, mp > 210 °C; IR ($CHCl_3$, cm^{-1}) 1460, 1340, 1310, 1275, 1160; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04−8.00 (m, 4H), 7.68−7.54 (m, 6H), 3.78 (d, J = 2.2 Hz, 2H), 3.28 (s, 2H), 2.60 (dt, J = 9.4, 1.7 Hz, 1H), 2.33 (dd, J = 8.7, 4.2 Hz, 2H), 2.11 (m, 1H), 1.74 (m, 2H), 1.66 (s, 1H), 1.55 (m, 4H), 1.26 (m, 2H), 1.02 (dd, J = 13.7, 3.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 140.9, 133.6, 129.0, 128.6, 69.7, 47.9, 47.2, 44.2, 38.7, 28.5, 27.0, 26.8, 19.6; MS *m/z* (M^+) calcd 480.1429, obsd 480.1431.

(1*R*,4*S*,4b*S*,9*R*)- and (1*R*,4*S*,4b*R*,9*S*)-2,3-Bis(*tert*-butylsulfonyl)-1,4,4b,5,6,7,8,8a-octahydro-1,4:6,9-dimethanofluorene (55 and 56). A solution of **8** (80 mg, 0.46 mmol) in CH_2Cl_2 (15 mL) was treated with bis(*tert*-butylsulfonyl)acetylene (0.12 g, 0.46 mmol) and stirred for 2 h at room temperature. Solvent evaporation and MPLC purification of the residue (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded an inseparable 3.6:1 mixture of **55** and **56** as a colorless solid (0.19 g, 98%): mp 139−140 °C; IR (CH_2Cl_2, cm^{-1}) 1320, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.08 (t, J = 1.4 Hz, 2H), 4.05 (t, J = 1.4 Hz, 2H), 2.95 (dt, J = 6.9, 1.5 Hz, 1H), 2.72 (dt, J = 6.6, 1.7 Hz, 1H), 2.59 (m, 5H), 2.47 (m, 1H), 2.24 (m, 1H), 2.15 (dt, J = 6.6, 1.7 Hz, 1H), 1.86−1.70 (m, 6H), 1.64−1.25 (m, 11H), 1.49 (s, 18H), 1.41 (s, 18H), 0.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 164.7, 164.0, 163.8, 79.5, 77.1, 62.0, 61.8, 58.2, 56.9, 47.2, 45.5, 38.8, 38.4, 28.2, 28.2, 27.8, 27.6, 26.6, 24.0, 23.9, 20.3, 20.0; MS *m/z* (M^+) calcd 438.1899, obsd 438.1895.

(1*R*,4*S*,4a*R*,4b*R*,9*S*,9a*S*)-2,3-Bis(*tert*-butylsulfonyl)-1,4,4a,-4b,5,6,7,8, 8a,9a-decahydro-1,4:6,9-dimethanofluorene (57). A mixture of potassium azodicarboxylate (0.33 g, 1.70 mmol), the mixture of cycloadducts **55** and **56** (75 mg, 0.17 mmol, ratio of 2.4:1.0), and methanol (5 mL) was cooled to 0 °C before the dropwise addition of glacial acetic acid (193 μL, 3.36 mmol). The slurry was stirred for 2 h at 0 °C and at room temperature for 1 h prior to the usual workup. MPLC purification of the residue (silica gel, elution with 20% ethyl acetate in petroleum ether) separated 16 mg (21%) of reduced cycloadduct **57** from unreacted starting material as a colorless solid: mp 152.5−154 °C; IR (CH_2Cl_2, cm^{-1}) 1330, 1130; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38 (s, 2H), 3.05 (d, J = 2.3 Hz, 2H), 2.30 (dt, J = 8.3, 1.1 Hz, 1H), 2.21 (br d, J = 8.0 Hz, 2H), 1.97 (dd, J = 14.7, 3.4 Hz, 2H), 1.86 (d, J = 8.3 Hz, 1H), 1.81 (t, J = 3.4 Hz, 1H), 1.68 (m, 2H), 1.54 (m, 1H), 1.53 (m, 18H), 1.50−1.31 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 64.0, 61.6, 53.5, 52.1, 45.4, 36.4, 28.6, 28.0, 24.7, 21.9, 20.3; FAB MS *m/z* (M^+ + 1) calcd 441.21, obsd 441.08.

(1*R*,1a*S*,3*R*,3a*R*,3b*R*,8*S*,8a*S*,10*S*)- and (1*R*,1a*S*,3*R*,3a*R*,3b*S*,8*R*,-8a*S*,10*S*)-1,10-Bis-(*tert*-butylsulfonyl)decahydro-5*H*-5,8-methano-1,3,3a-methanocyclo-propa[2,3]cyclopent[1,2-*a*]Indene (58 and 59). A CH_2Cl_2 (2 mL) solution of the **55/56** mixture (10 mg, 22.8 μmol, ratio 1.8:1.0) was stirred on the benchtop for 24 h. Following evaporation, MPLC purification of the residue (silica gel, elution with 30% ethyl acetate in petroleum ether) afforded two difficultly separable products **58** (6 mg, 62%) and **59** (3 mg, 35%).

For **58**: colorless irregular prisms, mp 123.5−124.5 °C; IR (CH_2Cl_2, cm^{-1}) 1270; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94 (s, 2H), 2.79 (m, 1H), 2.52 (dd, J = 9.2, 3.9 Hz, 2H), 2.49 (d, J =12.6 Hz, 1H), 2.29 (d, J = 12.6 Hz, 1H), 1.94−1.77 (m, 4H), 1.56−1.50 (m, 2H), 1.46 (s, 18H), 1.24 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.0, 55.1, 48.0, 41.3, 38.4, 34.9, 34.0, 33.1, 26.5, 24.5, 22.2, 19.1; MS *m/z* (M^+) calcd 438.1899, obsd 438.1898. Anal. Calcd for $C_{23}H_{34}O_4S_2$: C, 62.98; H, 7.81. Found: C, 62.72; H, 8.13.

For **59**: colorless irregular prisms, mp > 200 °C; IR (CH_2Cl_2, cm^{-1}) 1330, 1270, 1110; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.79 (s, 2H), 2.51 (dd, J = 9.4, 3.8 Hz, 2H), 2.34 (m, 3H), 2.16 (d, J = 11.2 Hz, 1H), 1.92 (m, 1H), 1.82 (m, 3H), 1.79−1.49 (m, 2H), 1.46 (s, 18H), 1.39 (m, 1H), 1.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 63.3, 54.0, 47.8, 40.2, 37.8, 36.0, 33.9, 33.1, 26.1, 25.2, 22.9, 18.4; MS *m/z* (M^+) calcd 438.1899, obsd 438.1890.

Maleic Anhydride Addition to 9. Cyclohexadiene **9** (0.10 g, 0.684 mmol) and maleic anhydride (62 mg, 0.629 mmol) were dissolved in ethyl acetate (**4** mL), sealed in a Teflon tube, and placed in a high-pressure reactor at 175 000 psi for 4 days. Evaporation of the solvent and MPLC purification of the residue afforded three fractions containing four cycloadducts in the following quantities: **62** and **63** (an inseparable mixture in a 3.1:1 ratio, 17 mg, 11%), **61** (57 mg, 37%), and **60** (80 mg, 52%).

For **60**: colorless irregular prisms, mp 145−146 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.41 (s, 2H), 3.08 (s, 2H), 2.96 (s, 2H), 1.66−1.57 (m, 4H), 1.29−1.25 (m, 2H), 1.11−1.04 (m, 2H), 0.90−0.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 145.4, 49.1, 45.3, 44.7, 33.4, 25.3, 24.8; MS *m/z* (M^+) calcd 244.1099, obsd 244.1102. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.76; H, 6.66.

For **61**: colorless irregular prisms, mp 137.5−138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.44 (s, 2H), 3.09 (t, J = 1.6 Hz, 2H), 2.92 (t, J = 1.6 Hz, 2H), 1.67 (m, 2H), 1.62−1.53 (m, 2H), 1.41−1.31 (m, 1H), 1.26 (s, 1H), 1.19 (dt, J = 6.3, 1.5 Hz, 1H), 0.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.3, 145.9, 53.3, 45.8, 44.2, 33.2, 25.2, 24.7; MS *m/z* (M^+) calcd 244.1099, obsd 244.1098. Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.42; H, 6.57.

For **62/63**: colorless solid, mp 109−118 °C; IR ($CHCl_3$, cm^{-1}) 1360, 1120, 1060, 1020; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.30 (s, 2H), 3.26 (s, 2H), 3.06 (m, 4H), 2.81 (d, J =1.3 Hz, 2H), 1.69 (m, 8H), 1.54 (m, 1H), 1.41 (d, J = 1.2 Hz, 4H), 1.36 (m, 1H), 1.33 (t, J = 2.1 Hz, 1H), 1.26 (s, 1H), 1.12 (dt, J = 8.2, 1.4 Hz, 1H), 1.03 (dm, J = 9.0 Hz, 1H), 0.98−0.83 (series m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 171.8, 146.5, 145.8, 49.0, 48.6, 48.0, 46.4, 44.8, 44.7, 32.6, 32.5, 25.5, 25.3, 22.7, 21.6; MS *m/z* (M^+) calcd 244.1099, obsd 244.1101.

(1*R*,4*S*,5*S*,8*R*)-1,4,5,6,7,8-Hexahydro-*N*-methyl-1,4-ethano-5,8-methanophthalazine-2,3-dicarboximide (64). A solution of **9** (0.10 g, 0.68 mmol) in CH_2Cl_2 (5 mL) was cooled to −78 °C and treated with 4-methyl-1,2,4-triazoline-3,5-dione (76 mg, 0.67 mmol). The bright red color gradually faded as the reaction mixture warmed slowly to room temperature. Evaporation of the solvent left a tan solid, MPLC purification of which (silica gel, elution with 20% ethyl acetate in petroleum ether) afforded **64** as a colorless solid (0.17 g, 98%): mp 151 °C; IR ($CHCl_3$, cm^{-1}) 1770, 1720, 1470, 1405, 1275, 1220, 1175; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.02 (s, 2H), 3.07 (s, 2H), 2.98 (s, 3H), 2.14 (m, 2H), 1.69 (m, 2H), 1.28 (dt, J = 8.4, 1.8 Hz, 1H), 1.19 (m, 2H), 1.12 (dt, J = 8.4, 1.5 Hz, 1H), 0.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 143.5, 51.5, 50.2, 43.7, 25.2, 25.1, 24.3; MS *m/z* (M^+) calcd 259.1321, obsd 259.1319. Anal. Calcd for $C_{14}H_{17}N_3O_2$: C, 64.85; H, 6.61. Found: C, 64.78; H, 6.79.

(1*R*,4*S*,4a*S*,5*S*,8*R*,8a*R*)-Octahydro-*N*-methyl-1,4-ethano-5,8-methano-phthalazine-2,3-dicarboximide (65). A mixture of potassium azodicarboxylate (26 mg, 0.13 mmol), **64** (17 mg, 66.7 mmol), and methanol (5 mL) was cooled to 0 °C before glacial acetic acid (15.3 μL, 0.27 mmol) was introduced dropwise. The slurry was stirred for 2 h and worked up in the predescribed manner. MPLC purification of the residue (silica gel, elution with 55% ethyl acetate in petroleum ether) afforded recovered **64** (10 mg, 65%) and the reduced cycloadduct **65** as a colorless solid (5 mg, 30%): mp 155−156 °C dec; IR (CH_2Cl_2, cm^{-1}) 1760, 1700, 1460; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (s, 2H), 3.05 (s, 3H), 2.44 (s, 2H), 2.60 (d, J = 9.3 Hz, 2H), 2.20 (s, 2H), 1.94 (d, J = 8.8 Hz, 2H), 1.84 (d, J = 8.8 Hz, 2H), 1.50 (d, J = 8.8 Hz, 2H), 1.42 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 52.4, 43.5, 42.2, 40.6, 25.3, 24.7, 22.5; MS *m/z* (M^+) calcd 261.1477, obsd 261.1473. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33. Found: C, 64.17; H, 7.37.

(1*R*,4*S*,5*S*,8*R*)- and (1*R*,4*S*,5*R*,8*S*)-1,4,5,6,7,8-Hexahydro-2,3-bis-(trifluoro-methyl)-1,4-ethano-5,8-methanonaphthalene (66 and 67). Diene **9** (0.10 g, 0.68 mmol) was dissolved in $CDCl_3$ (0.50 mL) and placed in a thick-walled NMR tube. This solution was cooled to −78 °C before the condensation of hexafluoro-2-butyne (ca. 0.50 g, 3.09 mmol). The tube was sealed and allowed to warm to ambient temperature. After 72 h, reaction was judged to be 63% complete by ^{1}H NMR analysis. There was evidence of two cycloadducts in a ratio

of **4**.3 (**66**):1.0 (**67**). The tube was recooled to −78 °C and opened. Evaporation of the solvent left a yellowish oil, MPLC purification of which (silica gel, elution with pentane) afforded unreacted **9** (36 mg, 36%), **66** (105 mg, 50%), and **67** (26 mg, 12%).

For **66**: colorless oil; FT-IR (CH_2Cl_2, cm^{-1}) 1290, 1123; ^1H NMR (300 MHz, $CDCl_3$) δ 3.97 (t, J = 1.2 Hz, 2H), 2.98 (t, J = 1.5 Hz, 2H), 1.68 (d, J = 6.4 Hz, 2H), 1.54−1.50 (m, 4H), 1.32−1.27 (m, 1H), 1.07 (dt, J = 8.3, 1.5 Hz, 1H), 0.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 122.3 (q, J = 272.8 Hz, CF_3), 47.8, 44.1, 37.9, 25.0, 23.6; MS m/z (M^+) calcd 308.1000, obsd 308.1010. Anal. Calcd for $C_{15}H_{14}F_6$: C, 58.44; H, 4.58. Found: C, 58.73; H, 4.76.

For **67**: colorless oil; FT-IR (CH_2Cl_2, cm^{-1}) 1291, 1123; ^1H NMR (300 MHz, $CDCl_3$) δ 4.02 (s, 2H), 3.07 (d, J = 1.2 Hz, 2H), 1.65 (d, J = 7.4 Hz, 2H), 1.43 (d, J = 6.9 Hz, 2H), 1.35−1.25 (m, 4H), 1.13−1.06 (m, 2H), 0.89−0.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.0, 49.9, 44.6, 38.4, 29.7, 25.3; MS m/z (M^+) calcd 308.1000, obsd 308.1007.

(1*R*,4*S*,4a*R*,5*S*,8*R*,8a*S*)-1,4,4a,5,6,7,8,8a-Octahydro-2,3-bis(trifluoromethyl)-1,4-ethano-5,8-methanonaphthalene (68). A mixture of potassium azodicarboxylate (0.79 g, 4.07 mmol), **66** (0.12 g, 0.39 mmol), and methanol (5 mL) was cooled to 0 °C before the dropwise addition of glacial acetic acid (230 μL, 4.02 mmol) in MeOH (1 mL). The slurry was stirred for 2 h at 0 °C and at room temperature overnight and then worked up in the predescribed fashion. MPLC purification (silica gel, elution with pentane) afforded **68** as colorless needles (0.11g, 92%): mp 67−68 °C; IR ($CHCl_3$, cm^{-1}) 1290, 1260, 1190, 1140, 1110; ^1H NMR (300 MHz, $CDCl_3$) δ 2.98 (s, 2H), 2.16 (s, 2H), 2.03 (s, 2H), 1.59 (m, 2H), 1.40−1.23 (m, 6H), 1.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.7 (q, J = 273.2 Hz, CF_3), 46.7, 42.6, 40.6, 33.3, 27.0, 23.8; MS m/z (M^+) calcd 310.1156, obsd 310.1108. Anal. Calcd for $C_{15}H_{16}F_6$: C, 58.06; H, 5.20. Found: C, 57.65; H, 5.17.

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Supplementary Material Available: Final *XYZ* coordinates for those structures involved in the molecular modeling studies (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.