

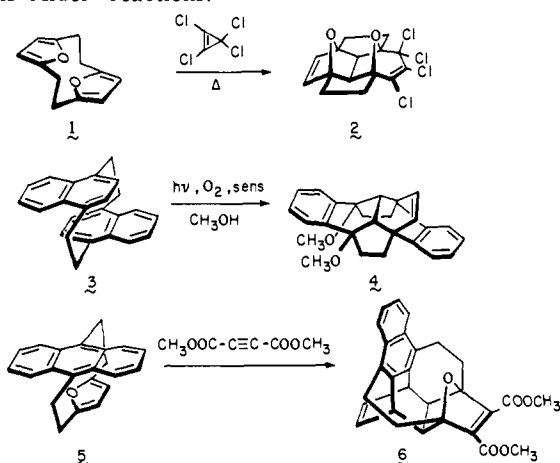
# Domino Diels-Alder Cycloadditions to 9,10-Dihydrofulvalene and 11,12-Dihydrosesquifulvalene. A Synthetic Tool for the Elaboration of Polycondensed Alicyclic Systems<sup>1</sup>

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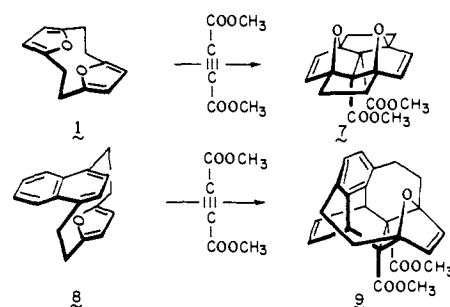
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**Abstract:** The practicality of constructing highly condensed alicyclic frameworks through multiple Diels-Alder cycloaddition reactions (of the domino or pincer type) involving 9,10-dihydrofulvalene, decachloro-9,10-dihydrofulvalene, and 11,12-dihydrosesquifulvalene is presented in full detail. Illustrative of the synthetic potential of the method are efficient syntheses of hexahydro-3,4,7-methenocyclopenta[*a*]pentalene (**10**), octahydro-3,6-dimethylenedicyclopenta[*cd,gh*]pentalene (**11**), triquinacene (**12**), and a number of previously unknown (CH)<sub>12</sub> isomers. The greatly enhanced 4π donor reactivity of cyclopentadiene relative to cycloheptatriene rings does not permit the isolation of intermediate stage adducts in those instances where only five-membered cycles are involved. When the larger rings are present, temperatures in excess of 130 °C are required to complete the overall formation of four new σ bonds. Decachloro-9,10-dihydrofulvalene exhibits greatly reduced reactivity relative to its hydrocarbon analogue and consequently is of limited practical utility. The varied responses of four somewhat related polycyclic azo compounds (**37**, **48**, **49**, and **63**) to thermal and photochemical activation are also demonstrated.

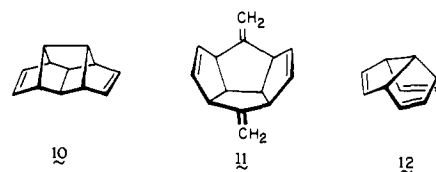
Those structural features unique to the [2.2]- and [3.3]-paracyclophanes rather tightly compress transannularly disposed π networks and beget a modicum of interaction between them.<sup>4</sup> Of particular relevance to the present investigation are those two-stage cycloadditions which lead to polycyclic products. There are formally two ways in which such multistage C-C bond forming reactions can occur. Illustrative of the first type are the efficient condensation of [2.2](2,5)furanophane (**1**) with tetrachlorocyclopropene to give **2**,<sup>5</sup> the reaction of *anti*-[2.2]naphthalenophane (**3**) with singlet oxygen in methanol to provide **4**,<sup>6</sup> and the capture of dimethyl acetylenedicarboxylate by anthracenophane **5**.<sup>7</sup> Here initial *intermolecular* cycloaddition of a dienophile to a 1,3-diene part structure generates a new olefinic center which subsequently becomes directly involved as a dienophile in an ensuing *intramolecular* (π<sub>4</sub> + π<sub>2</sub>) bonding scheme.<sup>8</sup> We shall hereafter refer to such multiple cycloaddition processes as "domino Diels-Alder" reactions.<sup>9</sup>



The second cyclocondensation pathway requires that the dienophile be originally acetylenic and proceeds by utilization of both degrees of unsaturation in the triple bond to achieve two-stage cyclization. The reactivity of **1**<sup>10</sup> and naphthalenofuranophane **8**<sup>11</sup> toward dimethyl acetylenedicarboxylate serves as prototypical examples. Their classification as "pincer Diels-Alder reactions" would seem appropriate since this term clearly connotes that compression of a dienophile between two diene components has transpired.



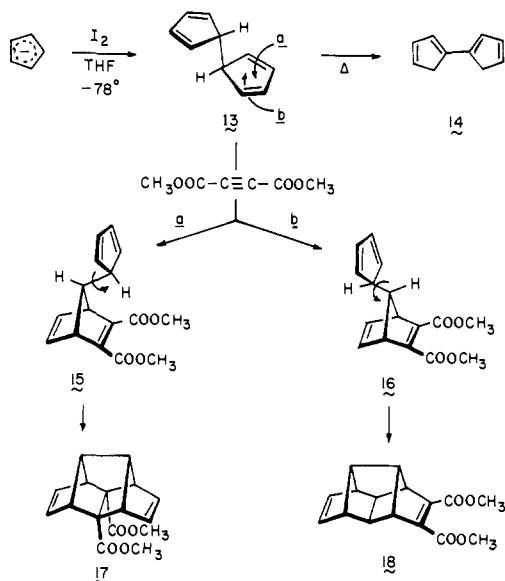
Either process is seen to lend itself readily to the formation of four new C-C bonds and to the construction of a rather elaborate polycyclic structure in a *single* laboratory manipulation. Clearly, if less sterically compressed polyolefins were to enter into analogous multiple cycloadditions, facile synthetic routes to a variety of new functionalized alicyclic systems would become available. At the inception of these studies, no examples of this chemistry had appeared in the literature.<sup>12</sup> Among several reasons for our interest in this potentially valuable synthetic tool was the likelihood that access to a number of highly condensed molecules might be conveniently realized. This paper provides a detailed report of the synthesis of hexahydro-3,4,7-methenocyclopenta[*a*]pentalene (**10**), octahydro-3,6-dimethylenedicyclopenta[*cd,gh*]pentalene (**11**), triquinacene (**12**), certain other new (CH)<sub>12</sub> hydrocarbons, and related molecules by this versatile technique. Elsewhere we have documented its application to the preparation of C<sub>16</sub>-hexaquinacene<sup>1b</sup> and several pentagonal dodecahedrane precursors.<sup>13,14</sup>



## Results and Discussion

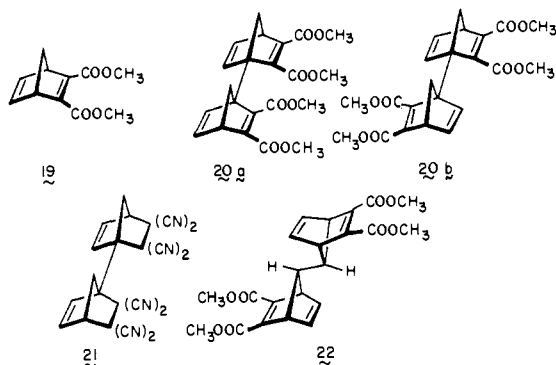
**9,10-Dihydrofulvalene.** Although 9,10-dihydrofulvalene (**13**) is directly accessible by flash vacuum pyrolysis of nickelocene,<sup>15</sup> the expense and other limitations of this method led us to exploit Doering and Matzner's earlier observation that sodium cyclopentadienide could be oxidatively coupled with 0.5

equiv of iodine in tetrahydrofuran solution at  $-78^{\circ}\text{C}$ .<sup>16,17</sup> In the first step of this reaction, nucleophilic attack of cyclopentadienide on elemental iodine (with loss of  $\text{I}^-$ ) presumably generates the highly reactive 5-iodocyclopentadiene,<sup>18</sup> the halogen in which undergoes displacement by a second anion molecule. If solutions of **13** are allowed to warm, 1,5-hydrogen shifts result in the formation of unwanted, but thermodynamically favored, 1,5-dihydrofulvalene (**14**).<sup>15-17</sup> However, Hedaya and co-workers astutely recognized that solutions of **13** could be generated without difficulty by constantly main-



taining the temperature at  $-70^{\circ}\text{C}$  and below.<sup>12</sup> Accordingly, this methodology was adapted to the present study. Since **13** is a molecule of  $C_{2v}$  symmetry (when fully eclipsed) which likely prefers to adopt the conformation shown ( $C_{2h}$ ), bonding of a dienophile can in principle occur either by "inside" or "outside" approach to the two equivalent cyclopentadiene rings. For example, attack by dimethyl acetylenedicarboxylate along the *a* coordinate would afford intermediate **15** which by subsequent bond rotation and intramolecular closure could provide **17**. Use of coordinate *b* would give rise to **16**, the anticipated precursor of **18**.

Guided by the earlier findings of the Union Carbide group, we treated a cold solution of **13** with the acetylenic diester and obtained a mixture of the pincer (**17**) and domino Diels-Alder adducts (**18**) in approximately equal amounts. In addition to these desired products, there was also isolated **19** and the bis



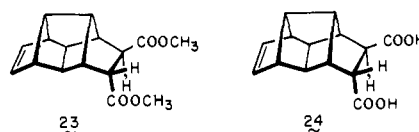
adducts **20a** and **20b** in low yield. The latter two are the result of the cycloaddition of 2 equiv of the dienophile to **14**. Two possible bis adducts are represented here, but no effort was made to characterize them separately. A similar bis adduct (**21**) was obtained by Doering and Matzner through reaction of **14** with TCNE.<sup>16</sup> The absence of compounds such as **22** is of some interest. However, to be certain that its nondetection

was not due to the workup procedure employed, crude reaction mixtures were also carefully chromatographed. Again, no **22** could be found. The absence of **22** suggests that the rate of intramolecular cycloaddition in **15** and **16** is faster than bonding of a second external dienophile to these intermediates.

Diesters **17** and **18** can be separated by fractional distillation through a Teflon-coated spinning-band column, but a significant amount of decomposition does accompany this workup procedure. Alternatively, at Hedaya's suggestion the selective removal of **18** by partial saponification was attempted and found to permit ready separation of the two diesters because of the significantly more hindered nature of the carbomethoxyl groups in **17**.

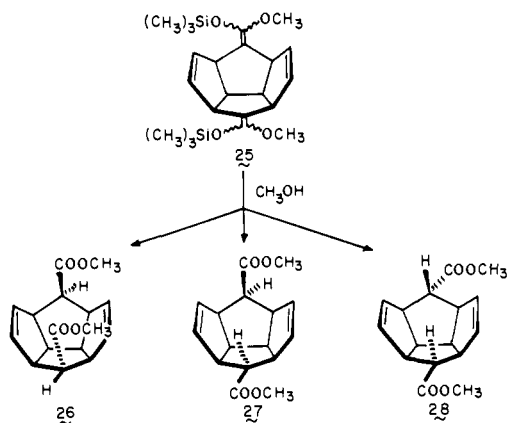
The  $^1\text{H}$  NMR spectrum of **17** in  $\text{CDCl}_3$  shows a methoxyl singlet ( $\delta$  3.56, 6 H) and three other absorptions at 6.02 (t,  $J = 2$  Hz, 4 H), 3.28 (m, 4 H), and 2.48 (m, 2 H) as expected of its  $C_{2v}$  symmetry. The  $^{13}\text{C}$  NMR spectrum is characterized by six peaks at 172.6, 132.7, 69.5, 64.4, 58.8, and 51.5 ppm. The lessened symmetry ( $C_s$ ) of **18** follows from its  $^1\text{H}$  ( $\delta$  5.83 (t,  $J = 2$  Hz, 2 H), 3.72 (s, 6 H), 3.25 (d,  $J = 2.8$  Hz, 2 H), 2.97 (m, 2 H), 2.58 (v br, 2 H), and 2.13 (m, 2 H)) and  $^{13}\text{C}$  spectral parameters (165.2, 140.4, 132.2, 62.4, 61.2, 60.7 (2 C), 51.8, and 49.4 ppm).

The selection of **18** as a precursor to the unknown  $(\text{CH})_{12}$  diene **10** was obvious and this conversion was initiated by selective reduction of the carbonyl conjugated double bond. To this end, **18** was treated with aqueous chromous sulfate under an inert atmosphere<sup>19</sup> and was thereby transformed in 94%



yield to the desired dihydro product with trans isomer **23** predominating by a wide margin (77%). Saponification of the unpurified mixture, followed by electrolytic decarboxylation of the diacids in 10% aqueous pyridine<sup>20</sup> gave **10** in 20-45% purified yield. The yields of **10** were reproducibly increased to >55% and the purity of the hydrocarbon was significantly enhanced when **24** was heated at 180-185  $^{\circ}\text{C}$  with 2 equiv each of  $\text{Cu}_2\text{O}$  and 2,2'-bipyridyl in quinoline solution.<sup>21</sup> The novel structural features of **10** consist of two fused norbornene rings and contain no less than six five-membered rings within its molecular framework. The  $C_{2v}$  symmetry of this compound is reflected in the simplified nature of its  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals (see Experimental Section).<sup>22</sup>

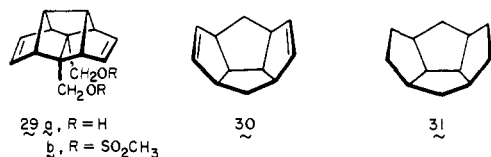
With the development of an efficient synthesis of **17**, efforts subsequently became directed toward cleavage of its central bond as a means of elaborating **11**. Two methods were given particular attention. In the first, **17** was heated overnight in toluene with a dispersion of sodium and chlorotrimethylsilane.<sup>23</sup> This procedure led efficiently to **25**, hydrolysis of which with dry methanol (kinetic quenching) resulted in production of a mixture of dihydro diesters (95%) consisting ( $^1\text{H}$  NMR analysis) of di-endo isomer **26** (77%), exo,endo isomer **27** (22%), and di-exo isomer **28** (1%). Fractional crystallization from hexane afforded pure **26**. Its  $^1\text{H}$  (a single methyl ester absorption) and  $^{13}\text{C}$  NMR (six lines) spectra are fully consistent with retention of  $C_{2v}$  symmetry. Equilibration of **26** with a catalytic quantity of sodium methoxide in methanol at room temperature resulted in formation of a mixture of **27** (20%) and **28** (80%). Pure di-exo isomer **28** ( $C_{2v}$  symmetry) was obtained free of its isomers by repeated recrystallization of this mixture from hexane. The endo,exo isomer (**27**) was not obtained in a pure state. Assignment of its structure was based upon the equilibration studies and the appearance of an AB quartet in the olefinic proton region. When recourse was made



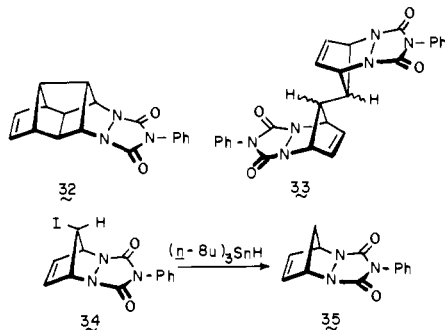
to sodium in liquid ammonia at  $-78\text{ }^{\circ}\text{C}$ <sup>24</sup> and the resulting dienolate was quenched with aqueous ammonium chloride solution, little kinetic control of protonation was observed. Instead, a mixture of **26–28** (79%) was produced with no single isomer predominating; a fourth unidentified substance was also formed in low yield under these conditions.

An alternate solution to this problem has no stereochemical ramifications. Thus, lithium aluminum hydride reduction of **17** to diol **29a** (95%) was followed by treatment with sulfene<sup>25</sup> to give dimesylate **29b** (85%). Subsequent heating of **29b** with sodium iodide in anhydrous hexamethylphosphoramide at  $130\text{ }^{\circ}\text{C}$  for 48 h afforded tetraene **11** directly in good yield together with a small amount of an unsymmetrical diiodide. In contrast to a number of closely related reactions,<sup>26</sup> **29b** did not give a symmetrical dihalogenated product. In our opinion, this reactivity is a reflection of the rather strained nature of the central bond in these intermediates.

The eight olefinic protons of **11** are seen as two singlets of area 4 at  $\delta$  5.28 and 4.83, the remaining six hydrogens appearing as a rather narrow multiplet at 3.80–3.35 ( $\text{CDCl}_3$  solution). The inherent symmetry ( $C_{2v}$ ) is further substantiated by its  $^{13}\text{C}$  NMR spectrum (five lines). The molecular framework of **11** consists of four fused cyclopentane rings having all syn-cis stereochemistry and is therefore closely related to the recently described diene **30**.<sup>27</sup> Unlike **30** which is reported to be air sensitive, **11** is stable to the atmosphere, a property it apparently shares with the fully saturated parent ring system **31**.<sup>27</sup>



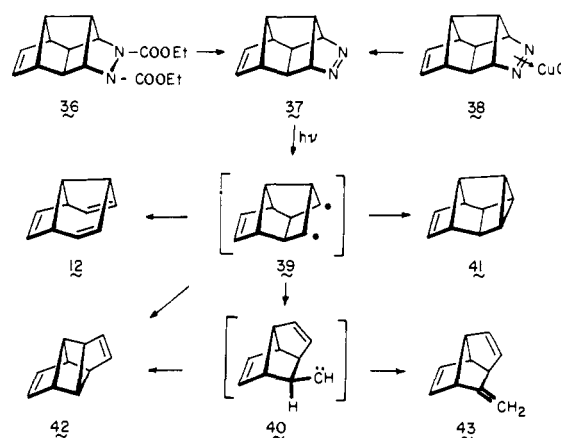
To establish the generality of the domino Diels–Alder reactivity of 9,10-dihydrofulvalene, its behavior toward several additional dienophiles was examined. Treatment of cold ( $-78\text{ }^{\circ}\text{C}$ ) tetrahydrofuran solutions of **13** with the highly reactive *N*-phenyltriazolinedione, followed by warming to room temperature and chromatography on silica gel, led to the isolation of adducts **32–35**. The  $^1\text{H}$  NMR spectra of **34**<sup>18</sup> and **35**<sup>28</sup>



proved identical with those given in the literature and their structural interrelationship was further substantiated by tri-*n*-butyltin hydride reduction of **34** to **35**.

The third adduct (3%) was expectedly polycondensed. Its  $^1\text{H}$  NMR spectrum showed it to be the domino adduct of  $C_2$  symmetry (**32**) by virtue of the appearance of paired signals at  $\delta$  5.87 (t,  $J = 2\text{ Hz}$ , 2 H), 4.6 (m, 2 H), 2.9 (m, 2 H), 2.5 (m, 2 H), and 2.2 (m, 2 H).<sup>29</sup> Elemental and  $^1\text{H}$  NMR analyses showed the final and major product to be a bis adduct of the triazolinedione and unrearranged **13**. Because several stereoisomeric formulations for **33** are possible, its precise stereochemistry, or, indeed, the possibility that a mixture was in hand have not been elucidated. In this instance, the competitive rates of intra- and intermolecular cycloaddition (by a second dienophile molecule) cannot be ascertained because initial bonding along coordinate *a* in **13** now provides a first-stage adduct which cannot undergo intramolecular bonding and is therefore forced to generate bis adduct(s).

Nonetheless, a reduction in the reactivity of the azo dienophile should allow that intramolecular cycloaddition which normally follows initial bonding from direction *b* to become increasingly competitive with bis adduct formation. Indeed, when recourse was made to the less reactive diethyl azodicarboxylate reagent, no iodine-containing or multiple addition products were isolated and acquisition of **36** was consequently made more practical. Hydrolysis of either **32** or **36** and subsequent manganese dioxide oxidation afforded the stable and highly crystalline azo compound **37** in 64–79% yield after sublimation. In the case of **32**, the aniline by-product caused purification problems. This difficulty was bypassed through hydrolysis in the presence of cupric chloride<sup>30</sup> and subsequent liberation of **37** from the brick-red azo complex **38**.



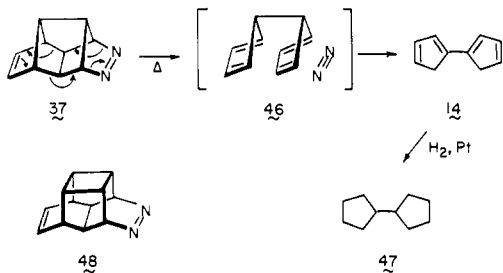
Irradiation of **37** through Pyrex in purified pentane solutions (0.0025–0.01 M) at room temperature with a Hanovia 450-W lamp gave a mixture of hydrocarbons consisting of triquinacene (**12**, 58–61%), the novel  $(\text{CH})_{10}$  hydrocarbon **41** (25–30%), diene **42** (9–10%), and triene **43** (3%). The individual hydrocarbons were separated gas chromatographically or, more conveniently, by column chromatography on silica gel.

The genesis of the several products can be economically rationalized in terms of intermediate biradical **39**. Cleavage of this 1,4 biradical in a Grob-type fragmentation directly affords triquinacene ( $\delta$  5.62 (s, 6 H) and 3.73 (s, 4 H)).<sup>29–32</sup> Collapse of this same biradical to form a C–C bond produces the bicyclo[2.1.0]pentane derivative **41**. The  $^1\text{H}$  NMR spectrum of this stable oily hydrocarbon shows the customary downfield triplet at  $\delta$  5.52 (2 H) in addition to multiplets centered at 2.94 (1 H), 2.83 (2 H), 2.21 (2 H), 2.05 (2 H), and 1.27 (1 H). Double irradiation studies at 100 MHz established that the 2.94 absorption arises from the apical proton proximal to the  $\pi$  bond, the 2.83, 2.21, and 2.05 multiplets from the allylic, bicyclopentyl, and homoallylic hydrogen pairs, respec-

tively, and the most upfield signal (1.27) from the remaining cyclopropyl proton. Recently, **41** has been observed among other products in the photoisomerization of triquinacene.<sup>33</sup> A 1,2 shift of the remote apical carbon in **39** can lead directly to **42** which has previously been characterized as the (CH)<sub>10</sub> system into which hypostrophene is thermally converted.<sup>34</sup> This identity was substantiated through rearrangement of an authentic sample of hypostrophene (**44**)<sup>35</sup> in the injector port of a gas chromatograph. The volatile product was identical with **43** (<sup>1</sup>H NMR, VPC retention times). Structural assignment to minor product **43** is based solely upon its spectral properties which include a terminal spin-isolated methylene group ( $\delta$  4.74 (s)), a pair of additional olefinic absorptions at 6.20 (2 H) and 5.67 (2 H) which are nearly identical in multiplicity with the comparable signals exhibited by lumibullvalene (**45**),<sup>36</sup> and two likewise paired allylic methine transitions at 3.03 and 2.65 which agree with the symmetry of the molecule. The formation of **43** may be envisioned as the result of electronic reorganization within **39** with formation of unsaturated carbene **40** and a subsequent 1,2-hydride shift. Parallel transformations occur frequently in 1,3 biradicals.<sup>37</sup>

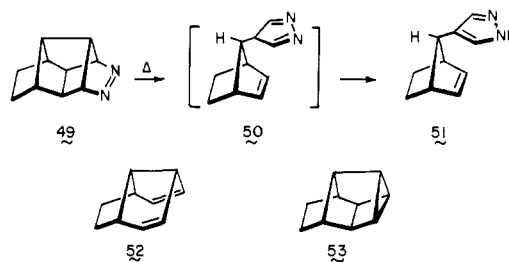


When pyrolyzed in a flow system at 380 °C, azo compound **37** extruded nitrogen with conversion to a mixture of dihydrofulvenes in which **14** predominated. Catalytic hydrogenation of this labile mixture afforded bicyclopentyl (**47**) exclusively, the spectroscopic properties of which were identical with those reported.<sup>38</sup> Examination of the reported experimental conditions for the photolysis<sup>33</sup> and thermolysis<sup>39</sup> of triquinacene serves convincingly to show that secondary processes are not likely involved in the formation of **41** and **14** from **37**.

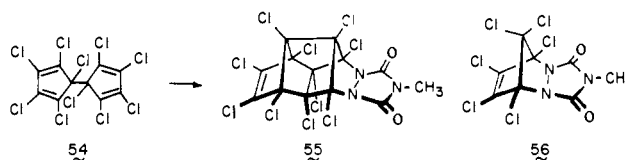


This ready fragmentation, which contrasts strikingly with the reported thermal stability of **48**,<sup>40</sup> can be viewed as the result of a concerted ( $2\pi_s + 2\sigma_s + 2\sigma_s + 2\sigma_s + 2\sigma_s$ ) fragmentation. To test the validity of this assumption, the  $2\pi_s$  element was removed by simply hydrogenating the double bond. When the resulting azo compound **49**<sup>41</sup> was pyrolyzed under conditions identical with those employed for **37**, loss of nitrogen was not observed. Instead, pyrazole **51** was isolated in quantitative yield. There was no evidence for the presence of hydrocarbons **52** and **53**<sup>41</sup> in the pyrolysate (VPC analysis). In this instance, thermal excitation of the strained polycondensed framework resulted in a net retrocycloaddition leading to **50** which subsequently experiences net 1,3-hydrogen shift to afford the aromatic heterocycle. Pyrazoles of the type **51** generally exist as a mixture of tautomers.<sup>42</sup> Since these tautomers are in rapid equilibrium with each other on the NMR time scale, the simplified proton and carbon spectra of **51** are consistent with its virtual C<sub>s</sub> symmetry. The widely divergent thermal responses of **37** and **49** should be compared with that of **63** (vide infra). The photochemistry of **49** has been discussed separately.<sup>41</sup>

The attempted domino Diels–Alder reactions of **13** with 1,4-benzoquinone and methyl propiolate failed to yield any recognizable polycondensed adducts.



**Decachloro-9,10-dihydrofulvalene.** Given the interesting facets of the chemistry of **13**, experimental scrutiny of the response of its perchlorinated derivative **54** to reactive dienophiles was undertaken. McBee and coworkers had previously described this readily available chlorocarbon<sup>43,44</sup> as recalcitrant, “rigorous attempts to effect Diels–Alder reaction with maleic anhydride and other dienophiles” having apparently failed.<sup>43</sup> They chose to focus attention on steric inhibition to bonding. It has also been noted that **54** is subject to isomerization at temperatures in excess of its melting point (125 °C).<sup>45</sup> As a result, the temperature range available to achieve the desired cycloaddition is rather limited. Not surprisingly, therefore, such electron-deficient dienophiles as tetracyanoethylene, dicyanomaleimide, diethyl azodicarboxylate, and dimethyl acetylenedicarboxylate afforded only recovered **54** under our chosen reaction conditions. Use of more elevated temperatures to promote cycloaddition led to polymer formation and/or adducts only indirectly related to **54**.



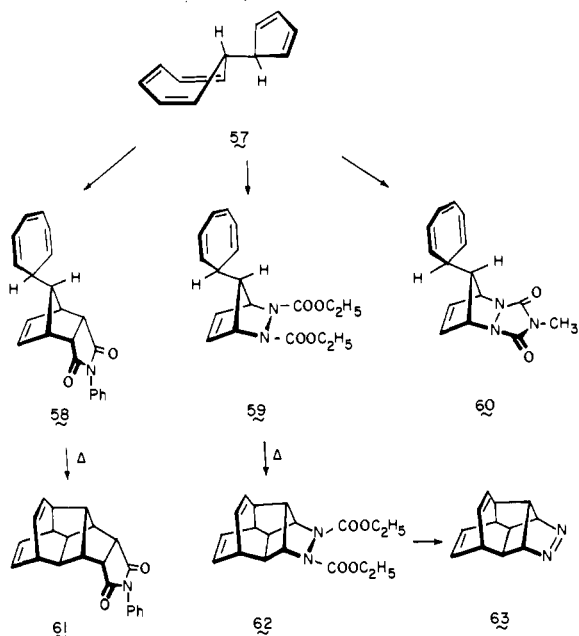
However, heating of **54** with *N*-methyltriazolinedione in refluxing ethyl acetate for 3 days successfully gave rise to adduct **55** as a sparkling white, quite insoluble solid in 63% yield. The highly condensed nature of **55** follows principally from its UV and NQR spectra.<sup>46</sup> Thus, its electronic absorption curve ( $\lambda_{\text{max}}^{\text{dioxane}}$  216 nm ( $\epsilon$   $6.9 \times 10^3$ ) and 230 ( $5.8 \times 10^3$ )) is quite similar to that given by **56** ( $\lambda_{\text{max}}^{\text{dioxane}}$  213 nm ( $\epsilon$   $5.8 \times 10^3$ ), 228 (sh) ( $5.1 \times 10^3$ ), and 252 (sh) ( $2.5 \times 10^3$ )), but very unlike those exhibited by **54**, hexachlorocyclopentadiene, or octachlorocyclopentene.<sup>43</sup> The NQR spectrum of **55** measured at 77 K is characterized by ten lines, all of which are of equal intensity. This pattern remains essentially invariant up to 195 K, as expected for a rigid molecule. Because good model systems are lacking, the NQR data must be viewed as hardly conclusive. Yet, available correlations do permit logical assignment to the observed frequencies (see Experimental Section).

Unfortunately, **55** could not be transformed by standard procedures into the corresponding azo compound, a possible precursor of perchlorotriquinacene.<sup>30</sup> Also, attempts to remove reductively the chlorine substituents proved futile. Thus, the use of **54** in the preparation of polycondensed adducts is limited.

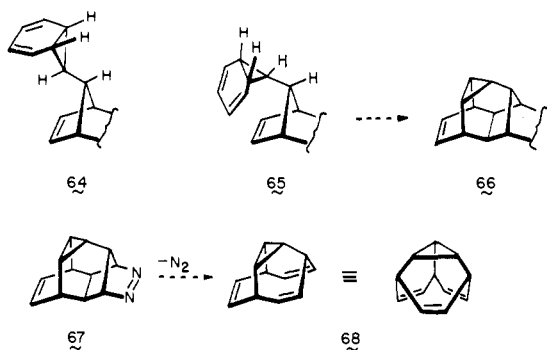
**11,12-Dihydrodesquifulvalene.** To this point, only cycloadditions of dienophiles to multiple cyclopentadienoid dienes have been examined. Extension of these principles suggests that, by merely varying the nature of the coupled multiple dienes, other novel carbocyclic systems may be efficiently constructed. Two interesting candidates are 11,12-dihydrodesquifulvalene (**57**)<sup>47</sup> and *cis*-<sup>8,9,9'</sup>-bicyclonona-1,3,5,7-tetraene.<sup>48</sup> The first of these polyolefins, which is available in high yield by coupling of thallos cyclopentadienide with tropylium tetrafluoroborate at low temperatures, has now been investigated for its ability to undergo multiple cycloadditions and shown to provide a facile route to (CH)<sub>12</sub> hydrocarbons.

Exposure of **57** to equimolar quantities of *N*-phenylmaleimide or diethyl azodicarboxylate at  $-30\text{ }^{\circ}\text{C}$  proceeded exclusively by addition to the cyclopentadiene ring with apparent steric approach control to give **58** (81%)<sup>47</sup> or **59** (72%). The stereochemistry of these adducts, which could only be inferred from the otherwise definitive spectral data, was established by subsequent intramolecular reaction involving the isolated double bond and the cycloheptatriene ring (*vide infra*). When the more reactive *N*-methyltriazolinedione was employed, less stereochemical discrimination was noted. Although anti isomer **60** did predominate, the presence of its syn counterpart was now evident in the mother liquors.

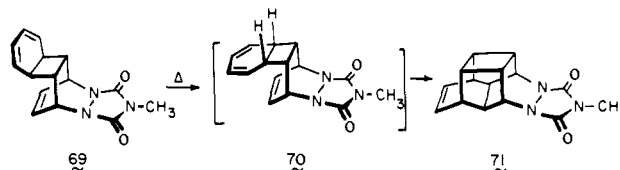
In general, when a cycloheptatriene derivative functions as a  $4\pi$  component in cycloaddition reactions, prior valence isomerization to its norcaradiene tautomer gains importance. This is because the triene lacks the planar 1,3-diene moiety which allows its valence isomer to gain the kinetic advantage. If such factors were to become important in further intramolecular reactions of **58–60**, then the transient formation of **64**



and/or **65** must be considered. Although **64** is considerably less strained than **65**, interaction with the norbornene double bond cannot occur because of geometrical constraints. This difficulty is not present in **65** which, if formed to a small extent, might be expected to close rapidly and provide the multiply condensed framework **66**. Should this possibility be realized with either **59** or **60**, then a route to azo compound **67** would become available. Our intention was to determine if **67** would serve as



a precursor to the most interesting, yet elusive,  $(\text{CH})_{12}$  hydrocarbon **68**. Some degree of credibility was given to this line of thinking by Berson and Davis' finding that heating of **69** at  $160\text{ }^{\circ}\text{C}$  triggered bicyclooctadiene  $\rightarrow$  cyclooctatriene valence tautomerism followed by reclosure to **70** (an assumed tran-



sient) having syn stereochemistry. Intramolecular Diels–Alder reaction within **70** afforded the polycondensed adduct **71**.<sup>40</sup>

In actuality, an interesting contrast was noted between the mode of reaction of **69** on the one hand and **58** and **59** on the other. Heating of the last two compounds in chlorobenzene led efficiently to **61** and **62**, respectively. It is clear from spectral data that both adducts possess four distinct olefinic protons and are unsymmetrical. In addition, the various allylic and bridgehead protons can be discerned. Attempts to promote intramolecular cycloaddition in **60** yielded polymeric material, chiefly because of the apparent facility with which retrograde cycloaddition occurs in this example. Clearly, therefore, norcaradiene form **65** is of no kinetic consequence, direct trapping of the seven-membered ring in **58** and **59** being overwhelmingly favored.

Domino adduct **62** could be converted without difficulty to the polycondensed azo compound **63**. When samples of **63** were pyrolyzed in a flow system at  $450\text{ }^{\circ}\text{C}$  ( $\text{N}_2$  entrainment), 80% conversion to a single  $(\text{CH})_{12}$  product was observed. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Chart I) of this hydrocarbon show signals indicating that both original double bonds have been retained and that bicyclopentane ring formation had occurred. Accordingly, fragmentation of the central bond in **63** to give the known **72**<sup>49</sup> did not operate. Rather, biradical collapse (or the equivalent) leading to **73** had taken place.

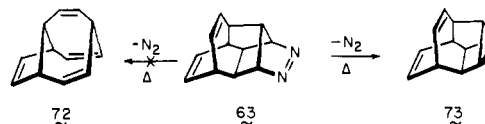
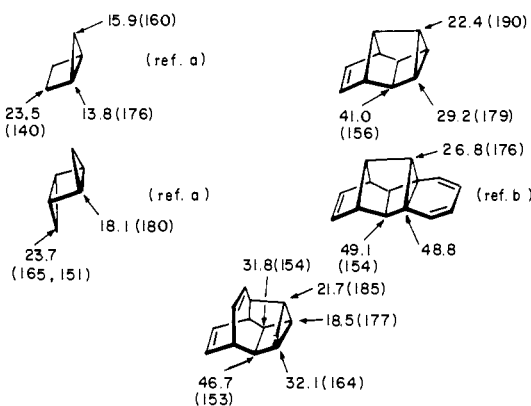


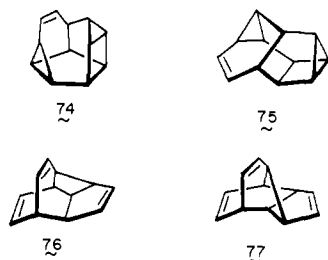
Chart I.  $^{13}\text{C}$  NMR Shift Data for Selected Bicyclopentanes (Parts per Million from  $\text{Me}_4\text{Si}$ )



<sup>a</sup> M. Christl, *Chem. Ber.*, **108**, 2781 (1975). <sup>b</sup> B. Trost and W. Herdle, *J. Am. Chem. Soc.*, **98**, 1989 (1976). The values in parentheses refer to  $J_{13\text{C}-\text{H}}$ .

Photolysis of **63** in purified pentane solution ( $6.8 \times 10^{-3}\text{ M}$ ) through Pyrex with a Hanovia 450-W lamp afforded three major products along with two minor components which were not further investigated because of their low relative concentrations (5.9 and 2.7%). The major component of the mixture (46%) proved to be **73**. The next most abundant hydrocarbon (23%), which was shown by  $^{13}\text{C}$  off-resonance decoupling and elemental analysis to also be a  $(\text{CH})_{12}$  isomer, exhibits a  $^1\text{H}$  NMR spectrum indicating its olefinic/saturated proton ratio to be 1:5. Accordingly, its framework must contain but one site

of unsaturation and be the result of skeletal rearrangement. By making recourse to Balaban's compilation of all possible valence isomers of [12]annulene,<sup>50</sup> we were able to reduce the vast number of structural possibilities to 16 realistic choices. Of these candidates, there exists precedent for the selection of **74** or **75** (vide infra). These isomers can in principle be derived from **63** by di- $\pi$ -methane rearrangement, and loss of nitrogen. In a separate experiment, it was demonstrated that **73** is stable to the conditions of photolysis and consequently does not serve as precursor. Unfortunately, no conclusive evidence is available to confirm this photoproduct as **74** or **75**. Therefore, we emphasize the tentative nature of our assignment.



The third component (9.2%), likewise a member of the (CH)<sub>12</sub> subset (<sup>13</sup>C off-resonance decoupling and combustion analysis), displays an olefinic/saturated proton ratio of 1:1 and is therefore triply unsaturated. Although unambiguous assignment of structure has likewise not yet proven possible in this instance, the available spectral data is most consistent with either **76** or **77**. Mechanistically, these molecules can arise by precedented<sup>9b</sup> electronic reorganization within the putative 1,3-biradical intermediate.

In spite of these inconclusive results, we see that azo compound **63** can serve as precursor to a widely diverse group of (CH)<sub>12</sub> hydrocarbons.

## Conclusion

Our results suggest that multistage cycloaddition reactions of  $\sigma$ -coupled cyclopolyolefins show great potential for the synthesis of highly condensed carbocyclic structures. More extensive elaboration of these concepts should thus be a fruitful research activity. It would appear that the high reactivity of cyclopentadiene rings may not allow for the routine isolation of intermediate adducts. Since the second stages of the domino or pincer Diels-Alder process proceed intramolecularly and therefore have greatly reduced entropy complications, the rates associated with such [ $\pi_4 + \pi_2$ ] bonding are likely to be substantially enhanced over the norm. In the two examples of domino Diels-Alder cycloaddition to 11,12-dihydropseudovalene described herein, not only were single stage adducts isolable, but closure to **61** and **62** required rather elevated temperatures. This steep falloff in rate appears to be associated with involvement of the intact cycloheptatriene ring as the diene partner. Can structural frameworks be found where the tautomeric norcaradiene forms would be kinetically favored? If so, the scope of these reactions would be still further widened.

The chemistry of this paper illustrates that conformationally flexible molecules can indeed be made to undergo reactions comparable with those witnessed with more rigid structures. Although high steric compression, bond angle deformation, and stretched bonds are not available as driving forces to the more relaxed molecules, those proximity effects which can be realized through conformational interconversion with more stable three-dimensional arrangements can certainly be manipulated to advantage. For those who are fascinated by symmetry and its consequences, the domino and pincer Diels-Alder reactions can in principle provide a variety of imaginative art forms, a few of which are exemplified herein.

## Experimental Section

Melting points and boiling points are uncorrected. Proton magnetic resonance spectra were obtained with Varian A-60A, Varian HA-100, and Bruker HX-90 spectrometers; apparent splittings are given in all cases. Carbon spectra were recorded with the Bruker unit. Infrared spectra were determined on Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector.

**Dimethyl 3,3a,3b,4,6a,7a-Hexahydro-3,4,7-metheno-7H-cyclopenta[a]pentalene-7,8-dicarboxylate (17) and Dimethyl 3a,3b,4,6a,7,7a-Hexahydro-3,4,7-metheno-3H-cyclopenta[a]pentalene-1,2-dicarboxylate (18).** In a 3-L three-necked flask (previously flame-dried under high vacuum), equipped with a Hershberg stirrer and a nitrogen inlet, were placed 275 g of Woelm basic alumina (which had been dried at 300 °C for at least 12 h and cooled in a vacuum desiccator over phosphorus pentoxide) and 62 g (2.70 g-atoms) of freshly cut sodium. The mixture was heated with a mantle under a stream of deoxygenated nitrogen. As the sodium melted, the alumina was stirred slowly at first and then rapidly until a fine black dispersion was formed. After slow cooling of the dispersion, 1.3 L of dry, degassed tetrahydrofuran was added and stirred for 10 min. A cold (-78 °C) solution of cyclopentadiene (100 g, 1.51 mol) in 80 mL of dry, degassed tetrahydrofuran was added dropwise to the ice-cooled sodium dispersion. After completion of the addition, the sodium cyclopentadienide solution was stirred at room temperature for 1 h. During this period a 5-L three-necked flask was dried under high vacuum with a flame and, upon cooling, was filled with an inert gas (nitrogen or argon). After the reaction flask had been equipped with a dry Hershberg stirrer and a dry transfer (gas dispersion) tube, the two flasks were connected together via the transfer tube. After the dispersion had been permitted to settle, the transfer was accomplished by exerting a positive pressure of argon (mercury bubbler) on the flask containing the sodium dispersion and a controlled vacuum on the receiving flask which was kept at -20 °C during the transfer. After completion of the transfer, the receiving flask was filled with nitrogen again. The dispersion was rinsed with 125 mL of dry, degassed tetrahydrofuran, stirred, and transferred as before.

The grayish sodium cyclopentadienide solution was cooled to -78 °C to form a white slurry to which was added dropwise with stirring a degassed solution of sublimed iodine (192 g, 0.756 mol) in 320 mL of dry tetrahydrofuran over a period of 50 min. During reaction, the solution developed a greenish color which darkened as the addition of iodine continued. When the solution exhibited a dark reddish brown color, the addition of iodine (generally 90-98% of the solution was added) was terminated. The reaction mixture was maintained at -78 °C while a solution of distilled dimethyl acetylenedicarboxylate (113 g, 0.795 mol) in 100 mL of dry, degassed tetrahydrofuran was added dropwise during 30 min. After stirring for 15 min at -78 °C, the mixture was permitted to warm to room temperature.

After 3 h, the heterogeneous reaction mixture was concentrated under reduced pressure (25-30 °C (35 mm)). The resulting yellow slurry was diluted with 1 L of ether and the mixture stirred for a few minutes. Filtration of the ethereal solution through a Celite pad removed the precipitated sodium iodide and undissolved bis adducts. The dark, ethereal filtrate was stored overnight at 0 °C.

**Workup A.** Upon concentration of the ethereal solution, there was obtained 230 g of a black viscous oil which was distilled under vacuum (0.3 mm) by slow addition to an evacuated flask heated at 200-220 °C by a Wood's metal bath. A greenish viscous oil (65.4 g) was collected. The relative percentages of diesters **17**, **18**, and **19** as determined from the <sup>1</sup>H NMR spectrum of the distillate were 38.5, 34.2, and 27.3%, respectively. A solution of the distillate in 1 L of absolute methanol was treated with a solution of potassium hydroxide (43.4 g, 0.672 mol) in 200 mL of water under nitrogen. The dark solution was stirred for 1.5 h at room temperature at which point most of the methanol was removed under reduced pressure over an additional 1.5-h period. The concentrate was diluted with 1 L of water and the resulting mixture was extracted with ether (5 × 150 mL). The combined ethereal layers were washed with water (3 × 150 mL) and brine (1 × 150 mL) before drying. Removal of the solvent yielded 21.96 g (10.7%) of **17**. Recrystallization from hexane afforded white crystals: mp 62.0-62.5 °C;  $\nu_{\text{max}}^{\text{KBr}}$ : 1727 and 1288 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.02 (t, *J* = 2 Hz, 4 H), 3.56 (s, 6 H), 3.28 (m, 4 H), and 2.48 (m, 2

H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ), 172.65, 132.67, 69.49, 64.39, 58.84, and 51.50; *m/e* 272.1048, observed 272.1052. Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4$ : C, 70.57; H, 5.92. Found: C, 70.56; H, 6.07.

Acidification of the alkaline aqueous layer with 30% sulfuric or hydrochloric acid followed by filtration and air drying overnight yielded 22.76 g of brownish carboxylic acids. A mixture of the carboxylic acids, 25 mL of absolute methanol, 2.5 g of concentrated sulfuric acid, and 60 mL of benzene was heated at reflux for 9 h under nitrogen. With cooling, 200 mL of water was added and the layers were separated. The aqueous layer was extracted with ether ( $3 \times 100$  mL) and the combined organic layers were washed with dilute aqueous sodium bicarbonate solution ( $1 \times 100$  mL) and water ( $3 \times 100$  mL) and dried. Concentration yielded 19.9 g of a reddish oil, distillation of which yielded three fractions: one of bp 115–117 °C (0.05 mm), 0.243 g of **19**, slightly contaminated by **18**; bp 120–128 °C (0.05 mm), 7.24 g of **18**, slightly contaminated by **17**; one of bp 128–134 °C (0.05 mm), and 5.56 g of pure **18**. The total yield of **18** was 6.2%. The analytical sample was prepared by first passing the diester through an alumina column (ethyl acetate elution) followed by molecular distillation at 85 °C (0.2 mm):  $\nu_{\text{max}}^{\text{neat}}$  1720, 1631, and 1285  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.83 (t,  $J = 2$  Hz, 2 H), 3.72 (s, 6 H), 3.25 (d,  $J = 2.8$  Hz, 2 H), 2.97 (m, 2 H), 2.58 (m, 2 H), and 2.13 (m, 2 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 165.23, 140.44, 132.16, 62.37, 61.18, 60.72 (2C), 51.82, and 49.37; *m/e* calcd 272.1048, observed 272.1052. Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4$ : C, 70.57; H, 5.92. Found: C, 70.36; H, 6.03.

**Workup B.** Upon concentration of the ethereal solution, the resulting viscous oil (230 g) was dissolved in 1 L of methanol and treated with a solution of 91 g (1.38 mol) of potassium hydroxide in 200 mL of water at ice temperature under nitrogen. After the initial exothermic reaction had subsided, the solution was stirred at room temperature for 1.5 h. The basic mixture was then filtered through a Celite pad to remove polymeric material. The filtrate was concentrated under reduced pressure for 1.5–2 h at room temperature. This concentrate was diluted with 1 L of water and the resulting aqueous mixture extracted with petroleum ether. The combined organic layers were washed with water and brine before drying. Concentration yielded 24.0 g of slightly yellow crystalline **17**. Continuous extraction of the aqueous mixture for 24 h with petroleum ether increased the total yield to 25.2 g (12.3%).

The basic aqueous mixture was acidified with 50% aqueous sulfuric acid with stirring. The dark viscous oil which formed above the water was extracted with dichloromethane ( $3 \times 500$  mL). Concentration yielded a black oil which was esterified with 10.0 g of concentrated sulfuric acid and 200 mL of methanol in 300 mL of benzene by refluxing the mixture under nitrogen for 14.5 h. Following dilution with 1 L of water, the acidic mixture was extracted with petroleum ether ( $3 \times 600$  mL). The combined organic layers were washed with aqueous sodium bicarbonate solution ( $2 \times 500$  mL) and water (500 mL), dried, and concentrated to give 29.33 g of a mixture of **17**, **18**, **19**, and **20** which was chromatographed on Florisil. Elution with 5% ether/petroleum ether yielded 16 g of slightly impure diester **18**. Distillation as before permitted a 60% recovery of **18**, thereby lowering the overall yield to 4.7%.

The bis adducts **20** were isolated by two methods. Extraction of the precipitated sodium iodide salts with dichloromethane produced varying amounts of bis adducts (1–3%). Alternatively, the crude product was chromatographed on silica gel. After removing diesters **17**, **18**, and **19** from the column with 10% ether/petroleum ether, the bis adducts (5.8 g, 3.5%) were recovered with ethyl acetate: mp 146.5–152 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1732, 1715, 1620, 1435, 1256, and 721  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 6.90 (m, 4 H), 3.93 (m, 2 H), 3.70 (s, 12 H), and 2.33 (m, 4 H); *m/e* calcd 414.1315, observed 414.1323.

**Dimethyl 2,3,3a,3b,4,6a,7,7a-Octahydro-3,4,7-metheno-1H-cyclopenta[a]pentalene-1,2-endo,exo-dicarboxylate (23).** To an aqueous 0.581 N chromous sulfate solution (50 mL, 29 mmol) was added dropwise under nitrogen a solution of diester **18** (2.52 g, 9.24 mmol) in 50 mL of distilled dimethylformamide. After being stirred for an additional 5–10 min, the dark green reaction mixture was diluted with 200 mL of water and extracted with ether. The ethereal extracts were combined and washed with water and brine, dried, and concentrated to give 2.37 g (93.5%) of a mixture of isomeric dihydro diesters. Fractional recrystallization from pentane/ether yielded pure endo,exo isomer **23**: mp 94–94.5 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1728, 1187, 1174, and 730  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.80 (t,  $J = 1.8$  Hz, 2 H), 3.70 (s, 3 H), 3.68 (s, 3 H), 3.30 (m, 2 H), 2.75 (m, 4 H), 2.50 (m, 1 H), 2.20 (m, 1 H), and 1.68 (m, 2 H). Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_4$ : C, 70.05; H, 6.61.

Found: C, 70.04; H, 6.64.

**2,3,3a,3b,4,6a,7,7a-Octahydro-3,4,7-metheno-1H-cyclopenta[a]pentalene-1,2-endo,exo-dicarboxylic Acid (24).** To a solution of diester **23** (1.42 g, 5.18 mmol) in 25 mL of methanol was added under nitrogen a solution of potassium hydroxide (3.06 g, 47.3 mmol) in 10 mL of water. The reaction mixture was stirred at room temperature for 8 h. Most of the solvent was removed under reduced pressure. The residue was diluted with 25 mL of water and acidified with 30% sulfuric acid. The slightly tan colored precipitate was filtered, washed with water ( $2 \times$ ), and dried to yield 1.25 g (96.5%) of diacid **24**: mp 235–240 °C dec;  $\nu_{\text{max}}^{\text{KBr}}$  1700, 1421, 1319, 1256, and 1209  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{Me}_2\text{SO}-d_6$ ) 12.19 (br s, 2 H), 5.75 (5,  $J = 1.8$  Hz, 2 H), 2.24–3.24 (br m, 7 H), 2.08 (br s, 1 H), and 1.58 (br s, 2 H).

**3a,3b,4,6a,7,7a-Hexahydro-3,4,7-metheno-3H-cyclopenta[a]pentalene (10). A. Electrolytic Decarboxylation.** Diacid **24** (1.23 g, 5.01 mmol) was dissolved in 100 mL of a 10% aqueous pyridine solution containing 1.3 mL of triethylamine. The electrolysis was conducted at 20–23 °C for 6 h with stirring. The temperature was maintained by passage of a coolant through the walls of the cell by means of a varistatic pump (Manostat). The initial amperage of 0.5 A had fallen off to 0.2 A when the electrolysis was terminated. The dark reaction mixture was diluted with 250 mL of water and extracted with pentane (followed by VPC analysis). The pentane extracts were combined and washed with dilute hydrochloric acid and dilute sodium bicarbonate solution before drying over anhydrous sodium sulfate. The pentane was removed through a vacuum-jacketed Vigreux column at atmospheric pressure. The last traces of the pentane were removed under reduced pressure (25 mm) to yield 364 mg (46.5%) of crude **10**, slightly contaminated by an unknown side product. Preparative VPC purification at 115 °C (6 ft  $\times$  0.25 in. 5% SE-30 on Chromosorb G) separated the components. The diene **10** was isolated in 11.5% yield (89 mg);  $\nu_{\text{max}}^{\text{neat}}$  3061, 2970, 724, and 681  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.79 (t,  $J = 2$  Hz, 4 H), 2.83 (m, 4 H), 2.42 (m, 2 H), and 1.79 (t,  $J = 2$  Hz, 2 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 132.51, 61.70, 60.62, and 49.12; *m/e* calcd for 156.0939, observed 156.0941. Anal. Calcd for  $\text{C}_{12}\text{H}_{12}$ : C, 92.26; H, 7.74. Found: C, 92.01; H, 7.79.

The crude product could also be directly distilled at 95–100 °C (35 mm) to afford pure **10** in 20% yield.

**B. Copper(I)-Promoted Oxidative Decarboxylation.**<sup>51</sup> Into a 50-mL flask equipped with a magnetic stirrer and reflux condenser was placed 2.474 g (10.05 mmol) of **24**, 3.274 g (22.9 mmol) of red cuprous oxide, 3.421 g (21.90 mmol) of 2,2'-bipyridyl, 300 mg of powdered soft glass, and 15 mL of quinoline. The contents were thoroughly mixed, flushed with nitrogen, and heated first at 155 °C for 2 h with efficient stirring, and then at 185 °C for 32 h. After cooling at ambient temperature, the mixture was poured onto 200 g of ice containing 2 N hydrochloric acid adequate to dissolve the amine. The cold suspension was covered with 50 mL of pentane, the mixture was filtered through Celite, and the insolubles were washed thoroughly with hot pentane. The filtrate layers were separated and the aqueous layer was extracted with pentane ( $2 \times 30$  mL). The combined organic layers were washed twice with 0.5 N hydrochloric acid (50 mL), twice with water (50 mL), and once with 5% sodium bicarbonate solution prior to drying and careful distillation of solvent. The residue was vacuum transferred at 65 °C (0.2 mm) to an ice-cooled receiver to give 0.897 g (57%) of pure **10**.

**Dimethyl 2a,3,3a,5a,6,6a,6b,6c-Octahydrodicyclopenta[cd,gh]pentalene-3,6-endo,endo-dicarboxylate (26).** In a dry 250-mL three-necked flask, which was equipped with condenser, Hershberg stirrer, and nitrogen inlet, freshly cut sodium (3.4 g, 0.148 g-atom) in 90 mL of dry toluene was heated with rapid stirring under nitrogen until a fine dispersion was formed. Trimethylchlorosilane (20 mL, 0.157 mol) was added via a syringe at the top of the condenser. A solution of diester **17** (1.028 g, 3.77 mmol) in 10 mL of dry toluene was added dropwise. After being stirred at reflux for 13.5 h, the dark solution was filtered through Celite. Excess trimethylchlorosilane was removed by concentration of the filtrate at atmospheric pressure to  $\sim 20$  mL. The concentrated toluene solution was then added dropwise to 100 mL of dry methanol with stirring under nitrogen. After dilution of the methanolic solution with 500 mL of water, the layers were separated. The aqueous layer was extracted with pentane ( $3 \times 100$  mL), after which the combined organic layers were washed with water ( $3 \times 200$  mL) and dried. Concentration yielded a yellow oil which was chromatographed on silica gel. Hexane elution removed silylated products, while 20% ether/hexane afforded 0.977 g (95%) of the diester mixture, which consisted of 77% di-endo **26**, 22% endo,exo **27**, and 1% di-exo



**28** ( $^1\text{H}$  NMR analysis). Repeated recrystallizations from hexane afforded pure di-endo isomer **26**; mp 84–84.5 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1738 and 1195  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.66 (s, 4 H), 3.70 (s, 6 H), and 2.91–3.64 (m, 8 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 173.19, 134.08, 53.09, 51.52, 51.31, and 49.04;  $m/e$  calcd 274.1205, observed 274.1210. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_4$ : C, 70.05; H, 6.61. Found: C, 70.10; H, 6.78.

**Dimethyl 2a,3,3a,5a,6,6a,6b,6c-Octahydrodicyclopenta[cd,gh]pentalene-3,6-exo,exo-dicarboxylate (28)**. The crude mixture of diesters **26–28** (0.62 g, 2.26 mmol) was treated with a catalytic amount of sodium methoxide in 30 mL of dry methanol at room temperature for 4.5 days under nitrogen. After the addition of 10 mL of saturated aqueous ammonium chloride, the reaction mixture was diluted with 300 mL of water and extracted with ether (3  $\times$  100 mL). The combined ethereal layers were washed with water (1  $\times$  200 mL) and brine (1  $\times$  200 mL) and dried. Removal of the solvent yielded a yellow oil which was chromatographed on silica gel. The diester mixture (0.58 g) was recovered in 94% yield from the column with 40% ether/hexane. The composition was determined to be 80% di-endo **28** and 20% endo,exo **27** by  $^1\text{H}$  NMR analysis. Repeated recrystallizations from hexane afforded pure di-endo isomer **28**; mp 75.5–77 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1738, 1175, and 740  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.37 (s, 4 H), 3.68 (s, 6 H), 3.33–3.68 (m, 6 H), and 2.91 (s, 2 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 176.37, 135.15, 56.08, 54.55, 52.66, and 51.80;  $m/e$  calcd 274.1205, observed 274.1210. Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_4$ : C, 70.05; H, 6.61. Found: C, 69.96; H, 6.71.

Partial  $^1\text{H}$  NMR data for endo, exo isomer **27** ( $\delta$ ,  $\text{CDCl}_3$ ): 5.45 (AB q,  $J_{\text{AB}} = 5.5$  Hz,  $\Delta V_{\text{AB}} = 15.6$  Hz, 4 H).

**3,3a,3b,4,6a,7a-Hexahydro-3,4,7-metheno-7H-cyclopenta[a]pentalene-7,8-dimethanol (29a)**. A solution of **17** (398 mg, 1.46 mmol) in 10 mL of anhydrous ether was added slowly to a mixture of lithium aluminum hydride (171 mg, 4.39 mmol) in 40 mL of ether and heated at reflux under nitrogen for 12 h. Excess hydride was destroyed by the addition of 0.5 mL of water, 0.5 mL of a 10% sodium hydroxide solution, and 1.5 mL of water in that order. An additional 30 mL of ether was added and the solution was filtered through a Celite pad. The precipitated salts were thoroughly washed with ether. After drying, the combined filtrates were concentrated to yield 302 mg (95%) of **29a** which was recrystallized from ether: mp 255–240 °C dec;  $\nu_{\text{max}}^{\text{KBr}}$  3280, 3070, and 1025  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.94 (t,  $J = 2$  Hz, 4 H), 3.59 (s, 4 H), 2.90 (m, 4 H), 2.48 (m, 2 H), and 2.07 (br s, 2H, -OH). Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_2$ : C, 77.75; H, 7.46. Found: C, 77.63; H, 7.43.

**3,3a,3b,4,6a,7a-Hexahydro-3,4,7-metheno-7H-cyclopenta[a]pentalene-7,8-dimethanol Dimethanesulfonate (29b)**. To a solution of **29a** (199 mg, 0.924 mmol) in 30 mL of dichloromethane containing 3.70 mmol of triethylamine (100% molar excess) cooled to  $-10$  °C was added methanesulfonyl chloride (317 mg, 2.77 mmol). The resulting solution was stirred for 30 min under nitrogen. The reaction mixture was transferred to a chilled separatory funnel and extracted with ice water, cold 10% hydrochloric acid, saturated sodium bicarbonate solution, and brine. After drying, the organic layer yielded 291 mg (85%) of **29b** upon concentration. Recrystallization from ethyl acetate/ether produced white needles: mp 130–130.5 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1344, 1173, 949 and 696  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 6.00 (t,  $J = 1.8$  Hz, 4 H), 3.95 (s, 4 H), 3.00–3.15 (m, 4 H), 2.97 (s, 6 H), and 2.55–2.70 (m, 2 H). Anal. Calcd for  $\text{C}_{16}\text{H}_{20}\text{S}_2\text{O}_6$ : C, 51.59; H, 5.41; S, 17.22. Found: C, 51.46; H, 5.40; S, 17.06.

**2a,3,3a,5a,6,6a,6b,6c-Octahydro-3,6-dimethylenedicyclopenta[cd,gh]pentalene (11)**. A mixture of crude dimesylate **29b** (1.72 g, 4.61 mmol) and sodium iodide (7.1 g, 47.4 mmol) in 45 mL of anhydrous hexamethylphosphoramide was stirred under nitrogen for 2 days at 130 °C. With cooling, the reaction mixture was diluted with 600 mL of water and extracted with pentane (9  $\times$  100 mL). The combined organic layers were washed with water (3  $\times$  150 mL) and brine (1  $\times$  150 mL) before drying. The pentane was removed at atmospheric pressure to yield 938 mg of a yellow oil. The crude product consisted of 81% tetraene **11** and 19% unsymmetrical diiodide. The product was chromatographed on Florisil (72  $\times$  2 cm column) and eluted with pentane. Tetraene **11** was isolated in 51% yield (427 mg) as a white crystalline solid. The analytical sample was obtained by sublimation at 60 °C (30 mm): mp 53.2–53.5 °C;  $\nu_{\text{max}}^{\text{neat}}$  3055, 2974, 2889, 1651, 881, and 747  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.28 (s, 4 H), 4.83 (s, 4 H), and 3.35–3.80 (m, 6 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 155.58, 135.32, 106.45, 58.78, and 52.20;  $m/e$  calcd 182.1095, observed 182.1098. Anal. Calcd for  $\text{C}_{14}\text{H}_{14}$ : C, 92.26; H, 7.74. Found: C, 92.26; H, 7.81.

The diiodide was recovered from the column by continued pentane

elution as a slightly contaminated solid: 160 mg; mp 112–113 °C;  $\nu_{\text{max}}^{\text{KBr}}$  3046, 1322, 896, and 702  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ , 100 MHz) 5.97 (m, 4 H), 3.34 (m, 2 H), 2.87 (br s, 6 H), and 2.47 (s, 2 H) (impurity present as a singlet at 3.10);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 134.51, 134.29, 132.29, 67.06, 66.79, 59.73, 57.89, 53.36, 49.48, 45.38, 43.49, and 13.87;  $m/e$  calcd 435.9188, observed 435.9153. Its structure was not established.

**4a,5,5a,8a,8b,9-Hexahydro-2-phenyl-5,8,9-metheno-1H,8H-pentaleno[2',1':3,4]pyrazolo[1,2-a]-s-triazole-1,3(2H)-dione (32)**. In a 250-mL three-necked flask (previously flame-dried), which was equipped with a transfer tube containing a glass wool plug, a Hershberg stirrer, and a nitrogen inlet, were placed 15 g of Woelm basic alumina (which had been dried at 300 °C overnight and cooled in a vacuum desiccator over phosphorus pentoxide) and 3.48 g of sodium metal. The mixture was heated with a mantle under a stream of deoxygenated nitrogen. As the sodium melted, the alumina was stirred slowly at first and then rapidly until a fine black dispersion was formed. After slow cooling of the dispersion, 75 mL of dry, degassed tetrahydrofuran was added and stirred for 10 min. A solution of cyclopentadiene (5.0 g, 0.0756 mol) in 10 mL of dry, degassed tetrahydrofuran was added dropwise to the ice-cooled sodium dispersion. After completion of the addition, the sodium cyclopentadienide solution was stirred at room temperature for 1 h. A second 250-mL three-necked reaction flask (previously flame-dried) was equipped with a magnetic stirring bar, low-temperature thermometer, and a nitrogen inlet. After the dispersion had been permitted to settle, the two flasks were connected together and the transfer was accomplished by exerting a positive pressure (mercury bubbler) of nitrogen (or argon) on the flask containing the sodium dispersion and cooling the receiving flask to  $-20$  °C. After completion of the transfer, the dispersion was rinsed with 25 mL of dry, degassed tetrahydrofuran, stirred, and then transferred as before.

The grayish sodium cyclopentadienide solution was cooled to  $-78$  °C to form a white slurry to which was added dropwise with stirring a degassed solution of sublimed iodine (9.6 g, 0.0378 mol) in 25 mL of dry tetrahydrofuran over a period of 30 min. During reaction, the solution developed a greenish color which darkened as the addition of iodine proceeded. When the solution exhibited a dark reddish brown color, the addition of iodine was terminated. The reaction mixture was maintained at  $-78$  °C, while a solution of sublimed *N*-phenyltriazolinedione (6.62 g, 0.0378 mol) in 50 mL of dry, degassed tetrahydrofuran was added dropwise over a 30-min period. After being stirred for 15 min at  $-78$  °C, the mixture was permitted to warm to room temperature.

After 3 h, the heterogeneous reaction mixture was concentrated under reduced pressure (25–30 °C (35 mm)) to produce a dark greenish brown solid. The residue was dissolved in dichloromethane and filtered through a Celite pad, thereby removing the precipitated sodium iodide and polymeric material. The filtrate was coated on 7 g of silica gel and placed on a silica gel column (150 g). The monoadducts were eluted from the column with 30% ether/hexane in the following order. **34** (210–261 mg): mp 117–125 °C dec;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.40 (s, 5 H), 6.5 (t,  $J = 2$  Hz, 2 H), 5.2 (m, 2 H), and 4.40 (m, 1 H);  $^{18}\text{m/e}$  calcd 366.9820, observed 366.9825. **32** (127–312 mg, 1.1–3.0%), recrystallized from 2-propanol to yield white needles: mp 228.5–229 °C;  $\nu_{\text{max}}^{\text{KBr}}$  1774, 1713, 1496, and 1399  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.40 (s, 5 H), 5.87 (t,  $J = 2$  Hz, 2 H), 4.60 (m, 2 H), 2.90 (m, 2 H), 2.5 (m, 2 H), and 2.2 (m, 2 H). Anal. Calcd for  $\text{C}_{18}\text{H}_{15}\text{N}_3\text{O}_2$ : C, 70.80; H, 4.95; N, 13.76. Found: C, 70.97; H, 5.13; N, 13.52. **35** (0.69–1.27 g): mp 140–144 °C (lit.<sup>28</sup> mp 142–144 °C);  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.37 (s, 5 H), 6.44 (t,  $J = 1.8$  Hz, 2 H), 5.12 (t,  $J = 1.8$  Hz, 2 H), 2.23 and 1.91 (ABX<sub>2</sub> system,  $J_{\text{AB}} = 9.0$  Hz,  $J_{\text{AX}} = J_{\text{DX}} = 1.8$  Hz, 1 H and 1 H).<sup>28</sup>

Bis adduct **33** (2.75 g) was recovered from the column by elution with ethyl acetate. Recrystallization from ethyl acetate yielded white needles: mp 209–216 °C dec (rapid heating);  $\nu_{\text{max}}^{\text{KBr}}$  1775, 1722, 1395, and 781  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 7.40 (s, 10 H), 6.45 (m, 4 H), 5.18 (m, 2 H), 4.85 (m, 2 H), 3.07 (br d,  $J \approx 8$  Hz, 1 H) and 2.50 (br d,  $J \approx 8$  Hz, 1 H);  $m/e$  305 (parent – PTAD). Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{O}_4\text{N}_6$ : C, 64.99; H, 4.20; N, 17.49. Found: C, 64.47; H, 4.13; N, 17.28.

**Reduction of 34 with Tri-*n*-butyltin Hydride. Formation of 4-Phenyl-2,4,6-triaza[5.2.1.0<sup>2,6</sup>]tricyclodec-8-ene-3,5-dione (35)**. A magnetically stirred solution of **34** (153 mg, 0.417 mmol) and 0.294 g (1.012 mmol) of tri-*n*-butyltin hydride in 5 mL of dry benzene was warmed on a steam bath under nitrogen until the solution became



homogeneous. With cooling, azobisisobutyronitrile (4.6 mg) was added and the mixture was stirred at room temperature for 12 h. After heating of the reaction mixture at 60 °C for 3.5 h, the solvent was removed under reduced pressure. The crude product was chromatographed on silica gel. After the tin-containing by-products were removed with 20% ether/petroleum ether, adduct **35** was collected with 50% ether/petroleum ether in 84.5% yield (81 mg).

**Diethyl 3a,3b,4,6a,7,7a-Hexahydro-3,4,7-metheno-1H-pentaleno[2,1-c]pyrazole-1,2(3H)-dicarboxylate (36).** A sodium (31 g, 1.35 g-atoms) dispersion on alumina (136 g) was prepared as described above and treated with 50 g (0.76 mol) of cyclopentadiene in 50 mL of dry, degassed tetrahydrofuran. The resulting sodium cyclopentadienide stirred with a degassed solution of sublimed iodine (96.5 g, 0.38 mol) in 200 mL of dry tetrahydrofuran over a period of 1 h. The reaction mixture was maintained at –78 °C, while a solution of diethyl azodicarboxylate (55 g, 0.304 mol) in 50 mL of dry, degassed tetrahydrofuran was added dropwise over a 30-min period. After slow warming (cooling bath not removed), the mixture was stirred at room temperature under nitrogen for 12 h.

After removal of the precipitated salts, the filtrate was concentrated under reduced pressure (25–30 °C (35 mm)) to yield a dark viscous oil. After the addition of 500 mL of dichloromethane to the oil, the heterogeneous mixture was filtered once more. The total recovery of sodium iodide was 108.58 g (96%). The filtrate was concentrated to yield 122.89 g of a viscous oil which was coated onto 125 g of silica gel and placed on a silica gel column (310 g). Elution with 5% ether/petroleum ether afforded a reddish, labile oil (26.20 g) whose <sup>1</sup>H NMR spectrum (CS<sub>2</sub>) was reminiscent of that of 1,5-dihydrofulvalene (**14**). A mixture of **36** and the cyclopentadiene adduct (13.61 g) was obtained by eluting the column with 35% ether/petroleum ether. This mixture was rechromatographed on silica gel (30% ether/petroleum ether elution) until complete separation was achieved. **36** (5.06 g, 5.47%) was recrystallized from ether/pentane to yield two crystal types: cubic, mp 78–79.5 °C, and rosette (mp 70–71.5 °C;  $\nu_{\max}^{\text{CCl}_4}$  1746 and 1712 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 5.82 (t, *J* = 2 Hz, 2 H), 4.56 (d, *J* = 3 Hz, 2 H), 4.18 (q, *J* = 7 Hz, 4 H), 2.90 (m, 2 H), 2.30 (br m, 2 H), 2.03 (m, 2 H), and 1.28 (t, *J* = 7 Hz, 6 H). Anal. Calcd for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>: C, 63.14; H, 6.62; N, 9.21. Found: C, 63.07; H, 6.69; N, 9.31.

**3a,3b,4,6a,7,7a-Hexahydro-3,4,7-metheno-3H-pentaleno[2,1-c]pyrazole (37).** **A. Manganese Dioxide Procedure.** In a 250-mL three-necked flask, a solution of **36** (1.025 g, 3.37 mmol) and 2.21 g of potassium hydroxide (86.6%, 0.034 mol) in 125 mL of reagent grade 2-propanol was heated at reflux for 1.5 h under nitrogen. The heterogeneous mixture was acidified at 0 °C to a pH of 2 with 3 N hydrochloric acid. The acidic mixture was neutralized at room temperature with an aqueous 3 N ammonium hydroxide solution. To this heterogeneous mixture, 2.92 g (0.034 mol) of manganese dioxide (94%) was added. After being stirred at room temperature for 3 h, the mixture was treated with 100 mL of dichloromethane and filtered. After dilution with 600 mL of water and separation of the layers, the aqueous phase was extracted repeatedly with dichloromethane. The combined organic layers were washed with water (3 × 125 mL) and brine (1 × 125 mL) prior to drying. The solvent was removed at atmospheric pressure to yield 539 mg of a yellow solid, which upon sublimation at 80 °C (35 mm) afforded 419 mg (79%) of **37** as white needles: mp 66.8–67.5 °C (sealed tube);  $\nu_{\max}^{\text{CCl}_4}$  3064, 1265, 1248, 710, and 674 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 100 MHz) 5.86 (t, *J* = 2 Hz, 2 H), 5.21 (d, *J* = 3 Hz, 2 H), 3.02 (m, 2 H), 2.56 (m, 1 H), 2.44 (m, 1 H), and 1.96 (m, 2 H); *m/e* calcd 158.0844, observed 158.0847, and *m/e* (P – N<sub>2</sub>) calcd 130.0782, observed 130.0784. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.93; H, 6.46; N, 17.71.

**B. Cupric Chloride Procedure.** In a 100-mL three-necked flask, a solution of **32** (201 mg, 0.659 mmol) and 420 mg of potassium hydroxide (86.6%, 6.51 mmol) in 35 mL of reagent grade 2-propanol was heated at reflux for 1.5 h under nitrogen. The dark heterogeneous mixture was acidified at 0 °C to a pH of 2 with 3 N hydrochloric acid. After warming, the acidic mixture was neutralized at room temperature with an aqueous 3 N ammonium hydroxide solution. The reaction mixture was diluted with 200 mL of water and extracted with dichloromethane (4 × 50 mL). The combined organic layers were washed with water (1 × 100 mL) and brine (1 × 100 mL). After removal of the solvent, the residue was dissolved in 12 mL of methanol and 1 mL of water. A methanolic solution of cupric chloride dihydrate (457 mg, 0.268 mmol in 1.5 mL) was added to the semicarbazide so-

lution. Immediately, a brick red precipitate formed and was separated by filtration. The methanolic solution was diluted with 100 mL of water and then extracted with dichloromethane. The combined organic layers were washed with water and brine before drying. After concentration, the residue was dissolved in 2 mL of methanol and solid cuprous chloride was added until further addition failed to yield more of the brick red complex. To a heterogeneous mixture of the collected azo complex **38** in 5 mL of water, an aqueous 3 N sodium hydroxide solution was added dropwise until the complex had been completely decomposed. After dilution with an additional 10 mL of water, the solution was extracted with ether. The combined ethereal layers were washed with water and brine, dried, and concentrated at atmospheric pressure to give 88 mg (84%) of pure **37** (free of aniline). Sublimation at 80 °C (35 mm) afforded 66 mg (64%) of the azo product.

**Photolysis of 37.** A stirred, degassed 0.009 M solution of **37** (635 mg, 4.014 mmol) in purified pentane (440 mL) was irradiated through Pyrex with a medium-pressure Hanovia light source (450 W) under nitrogen for 10 h. After filtration, the pentane solution was concentrated through a vacuum-jacketed Vigreux column at atmospheric pressure. The concentrate was passed through a small silica gel column. Pentane elution afforded the hydrocarbons, while unreacted **37** (154 mg) was recovered with 5% ether/pentane.

The mixture of hydrocarbons was shown by VPC analysis on the SE-30 column (75 °C) to consist 58–61% triquinacene (**12**), 25–30% 1a,1b,2,4a,5,5a-hexahydro-1,2,5-metheno-1H-cyclopropa[*a*]pentalene (**41**), 9–10% 3a,4,7,7a-tetrahydro-1,4,7-methenoindene (**42**), and 3% 1,3a,4,6a-tetrahydro-7-methylene-1,4-methanopentalene (**43**). The hydrocarbons were separated by preparative VPC on SE-30 (70 °C) or by column chromatography on silica gel (pentane elution) (elution order: **41**, **42**, and then a mixture of **12** and **43**). Generally, the hydrocarbons were isolated by preparative VPC. **12** (58 mg, 11%: <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 5.62 (s, 6 H) and 3.73 (s, 4 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 132.89, 57.68, and 47.96. **41**:  $\nu_{\max}^{\text{neat}}$  3061, 1246, 718, and 688 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 100 MHz) 5.52 (t, *J* = 2.0 Hz, 2 H), 2.94 (m, 1 H), 2.85 (m, 2 H), 2.21 (m, 2 H), 2.05 (m, 2 H), and 1.27 (m, 1 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 128.84, 64.70, 58.49, 41.17, 29.24, and 22.39; *m/e* calcd 130.0782, observed 130.0784. Anal. Calcd for C<sub>10</sub>H<sub>10</sub>: C, 92.26; H, 7.74. Found: C, 92.10; H, 8.05. **42**: <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.30 (m, 2 H), 5.70 (m, 2 H), 2.95 (m, 2 H), 2.55 (m, 2 H), and 2.00 (m, 2 H). **43**: <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>, 100 MHz) 6.20 (m, 2 H), 5.67 (m, 2 H), 4.74 (s, 2 H), 3.03 (m, 2 H), and 2.65 (m, 2 H); *m/e* calcd 130.0782, observed 130.0784.

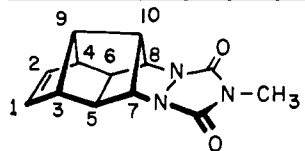
**Thermal Rearrangement of Hypostrophene. Conversion into 3a,4,7,7a-Tetrahydro-1,4,7-methenoindene (42).** An authentic sample of hypostrophene<sup>35</sup> was thermally rearranged on a gas chromatograph fitted with the SE-30 column heated to 75 °C. The injector port which was heated to 190–270 °C effected 20–40% conversion, respectively. The rearranged product has identical <sup>1</sup>H NMR spectral data and VPC retention times as photoproduct **42** from the irradiation of **37**.

**Pyrolysis of 37.** Pyrolysis of **37** (35.2 mg, 0.222 mmol) was effected by subliming the material into a nitrogen flow system (4 cm<sup>3</sup>/min) and passage through a quartz chip packed quartz reactor<sup>52</sup> (28 cm × 1.6 cm) at 380 °C (40 mm). A reddish liquid was collected in a dry ice–acetone trap: <sup>1</sup>H NMR ( $\delta$ , C<sub>6</sub>D<sub>6</sub>) 6.0–6.6 and 2.0–3.1, fully consistent with a mixture of dihydrofulvalenes.<sup>53</sup>

**Hydrogenation of the Dihydrofulvalene Pyrolysis Mixture. Formation of Bicyclopentyl (47).** The pyrolysate (in C<sub>6</sub>D<sub>6</sub>) was hydrogenated over Adams' catalyst (8 mg) in 2 mL of absolute methanol at atmospheric pressure for 19 h. After dilution of the methanolic solution with 30 mL of water, the mixture was extracted with pentane (4 × 10 mL). The combined organic layers were washed with water (3 × 10 mL) and dried. Concentration of the pentane solution was accomplished through a vacuum-jacketed Vigreux column at atmospheric pressure. Preparative VPC isolation on the SE-30 column at 85 °C of the only product gave pure **47**:  $\nu_{\max}^{\text{neat}}$  2920, 1452, 1367, 1331, 1020, 925, and 892 cm<sup>-1</sup>; <sup>38</sup> *m/e* (rel intensity) 138 (39), 109 (26), 96 (88), 95 (82), 82 (100), 81 (63), 79 (22).<sup>38</sup>

**Pyrolysis of 49.** Pyrolysis of **49** (270 mg, 1.685 mmol) was effected by subliming the material into a nitrogen flow system (13 cm<sup>3</sup>/min) and passage through a quartz chip packed quartz reactor<sup>52</sup> (28 cm × 1.6 cm) at 370 °C (3 mm). A white, crystalline material (275 mg) was collected in the –78 °C trap. VPC analysis of the pyrolysate indicated the absence of hydrocarbons **52** and **53**. The crude pyrolysate was chromatographed on silica gel. Elution with 70% ether/hexane afforded 257 mg (95%) of pure **51** which was recrystallized from ether/hexane: mp 124–125 °C;  $\nu_{\max}^{\text{KBr}}$  3119 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>)

Table I. NQR Assignments of 55

	frequency, MHz	chlorine assignment	comments
	37.746, 37.763	Cl <sub>1</sub> and Cl <sub>2</sub>	normal shift for vinylic chlorines
	37.919, 38.064	Cl <sub>3</sub> and Cl <sub>4</sub>	allylic chlorines
	38.694, 39.353	Cl <sub>5</sub> , Cl <sub>6</sub> , Cl <sub>9</sub> , and Cl <sub>10</sub>	shifts of the unsaturated chlorines are upfield of those in the hexachlorocyclohexanes due to strain
	39.712, 39.785		attached to carbons bearing nitrogen having lone-pair electrons orthogonal to the C-Cl bond $\sigma$
	40.633, 41.409	Cl <sub>7</sub> and Cl <sub>8</sub>	

10.2 (br s, 1 H, >NH), 7.27 (s, 2 H), 5.88 (t,  $J = 1.8$  Hz, 2 H), 2.93 (m, 2 H), 2.71 (br s, 1 H), 1.58–2.02 (m, 2 H), and 0.83–1.24 (m, 2 H) <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 133.10 (d), 132.73 (d), 120.48 (s), 54.44 (d), 47.43 (d), and 25.41 (t);  $m/e$  calcd 160.1000, observed 160.1003. Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>2</sub>: C, 74.96; H, 7.55. Found: C, 74.98; H, 7.42.

**Domino Diels-Alder Reaction of 54 with *N*-Methyltriazolinedione.** A solution of **54** (8.2 g, 0.018 mol) and *N*-methyltriazolinedione (2.0 g, 0.018 mol) in ethyl acetate (125 mL) was heated under a nitrogen atmosphere at the reflux temperature for 3 days. The solution was cooled and partially concentrated to give 4.0 g of adduct, mp 251–252 °C. Chromatography of the residue on silica gel (elution with 30% ether in pentane) furnished an additional gram of product (total yield 63%). Recrystallization from ethanol afforded pure **55**: mp 251.5–252 °C;  $\nu_{\max}^{\text{KBr}}$  1730, 1430, 1378, and 1240 cm<sup>-1</sup>;  $m/e$  calcd 582.7110, observed 582.7112. Anal. Calcd for C<sub>13</sub>H<sub>3</sub>Cl<sub>10</sub>N<sub>3</sub>O<sub>2</sub>: C, 26.57; H, 0.51; N, 7.15. Found: C, 26.72; H, 0.74; N, 7.11.

The NQR assignments of **55** are given in Table I.

**Adduct 56.** A solution of hexachlorocyclopentadiene (300 mg) and *N*-methyltriazolinedione (115 mg) in ethyl acetate (10 mL) was heated at reflux under nitrogen for 20 h. The solvent was evaporated and the residue was recrystallized from ethanol to give pure **56**: mp 166.5–167 °C;  $\nu_{\max}^{\text{CH}_2\text{Cl}_2}$  1750, 1380, 1130, 1090, and 900 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 3.00 (N-CH<sub>3</sub>);  $m/e$  calcd 382.8356, found 382.8359. Anal. Calcd for C<sub>8</sub>H<sub>3</sub>Cl<sub>6</sub>N<sub>3</sub>O<sub>2</sub>: C, 24.91; H, 0.78; N, 10.89. Found: C, 25.18; H, 0.96; N, 10.90.

**Cycloaddition of 57 and *N*-Phenylmaleimide.** To a stirred suspension of thallos cyclopentadiene (1.31 g, 4.87 mmol) in dry acetonitrile (20 mL) maintained at –30 °C under nitrogen was added tropylium tetrafluoroborate (870 mg, 4.92 mmol). The resulting suspension was stirred at –30 °C for 15 min prior to addition of a solution of *N*-phenylmaleimide (840 mg, 4.86 mmol) in acetonitrile (10 mL) during 10 min. After warming to room temperature during 1 h, the mixture was filtered and the filtrate evaporated. The residual tan solid (2.78 g) was taken up in dichloromethane and filtered through a short column of Florisil to remove residual thallium salts. Recrystallization of the residue from ethyl acetate gave **58** (1.29 g, 81%) as a colorless crystalline solid: mp 197–198 °C (lit.<sup>47</sup> mp 197–198 °C); <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.5–7.0 (m, 5 H), 6.6 (m, 2 H), 6.3–6.0 (m, 4 H), 5.08 (4-line m, 2 H), 3.65–3.3 (m, 4 H), 2.3 (d,  $J = 11$  Hz, 1 H), and 1.9–1.55 (m, 1 H);  $m/e$  calcd 329.1416, observed 329.1420. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.10; H, 5.77; N, 4.28.

**Diethyl anti-7-(7-Cycloheptatrienyl)-2,3-diazanorborn-5-ene-2,3-dicarboxylate (59).** A solution of 11,12-dihydrosequisulfolvalene in dry acetonitrile was prepared as described above from 11.1 g (41.4 mmol) of thallos cyclopentadiene and 7.33 g (41.4 mmol) of tropylium tetrafluoroborate. While maintained at –30 °C, a solution of diethyl azodicarboxylate (7.20 g, 41.4 mmol) in 20 mL of dry acetonitrile was added dropwise. The suspension was stirred at –30 °C for 1 h and allowed to warm to room temperature during an additional hour. The solids were separated by filtration and the filtrate was evaporated. This viscous brown gum was dissolved in chloroform and filtered through a short column of Florisil. Recrystallization of the residue from ethyl acetate afforded 9.8 g (72%) of **59** as colorless crystals: mp 125–126 °C;  $\nu_{\max}^{\text{KBr}}$  3010, 1740, and 1600 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.65–5.95 (m, 6 H), 5.25–4.9 (m, 4 H), 4.20 (q,  $J = 7.5$  Hz, 4 H), 2.5 (br d,  $J = 11$  Hz, 1 H), 1.9–1.6 (m, 1 H), and 1.27 (t,  $J = 7.5$  Hz, 6 H);  $m/e$  calcd 330.1579, observed 330.1584. Anal. Calcd for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.44; H, 6.76; N, 8.49.

**anti-10-(7-Cycloheptatrienyl)-4-methyl-2,4,6-triazol[5.2.1.0<sup>2,6</sup>]tricyclodec-8-ene-3,5-dione (60).** A cold (–80 °C) stirred slurry of thallos cyclopentadiene (1.31 g, 4.87 mmol) in dry dichloromethane maintained under an atmosphere of nitrogen was treated with

tropylium tetrafluoroborate (868 mg, 4.88 mmol) in one portion. The suspension was stirred at this temperature for 45 min prior to dropwise addition of a solution of *N*-methyltriazolinedione (552 mg, 4.89 mmol) in dry dichloromethane (10 mL). Upon completion of the addition, the mixture was stirred for 15 min more and then filtered while being maintained at –80 °C. The thallium residues were washed with the same solvent, the combined filtrates were kept at room temperature for 1 day, and the solvent volume was reduced to ~5 mL. Chromatography on Florisil (chloroform elution) furnished 834 mg (64%) of **60**: mp 182–183 °C (from ethyl acetate/hexane);  $\nu_{\max}^{\text{KBr}}$  3040, 3030, 1775, 1710, 1450, 1400, 1200, 740, 600, and 590 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.70–6.55 (m, 2 H), 6.40–6.30 (m, 2 H), 6.30–6.16 (m, 2 H), 5.40–5.15 (4-line m, 2 H), 4.87 (m, 2 H), 2.90 (s, 3 H), and 2.5–2.2 (m, 2 H);  $m/e$  calcd 269.1164, observed 269.1169. Anal. Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 66.90; H, 5.61; N, 15.61. Found: C, 66.88; H, 5.65; N, 15.53.

**Thermal Cyclization of 58.** A solution of **58** (451 mg, 1.37 mmol) in purified chlorobenzene (15 mL) was heated at the reflux temperature for 30 h. Evaporation of solvent left an off-white solid, recrystallization of which from benzene/hexane (decolorization with charcoal) furnished 410 mg (91.2%) of **61** as colorless crystals: mp 216–217 °C;  $\nu_{\max}^{\text{Nujol}}$  1770, 1705, 1495, 760, 720, and 690 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 7.5–7.0 (m, 5 H), 6.5–6.0 (4-line m, 2 H), 5.9–5.2 (br m, 2 H), 3.4–2.3 (m, 8 H), 2.2–2.0 (m, 1 H), and 1.9–1.6 (m, 1 H);  $m/e$  calcd 329.1416, observed 329.1420. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub>: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.10; H, 5.77; N, 4.28.

**Thermal Cyclization of 59. Generation of Azo Compound 63.** A solution of **59** (7.0 g, 21.2 mmol) in purified chlorobenzene (175 mL) was heated at reflux under a nitrogen atmosphere for 30 h. Evaporation of the solvent left **62** as a colorless to pale brown oil which failed to crystallize: <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.5–6.1 (m, 2 H), 5.9–5.2 (br m, 2 H), 4.4–3.9 (m consisting of two overlapping q,  $J = 7.5$  Hz, 4 H, and a br s, 2 H, 3.2–1.8 (br m, 6 H), and 1.25 (pair of overlapping t,  $J = 7.5$  Hz, 6 H).

The above oil dissolved in anhydrous isopropyl alcohol (25 mL) was treated with sodium hydroxide pellets (7.0 g, 175 mmol) and the solution was heated at the reflux temperature for 2.5 h. The major portion of the solvent was removed under reduced pressure and replaced by 75 mL of water. Adjustment of the pH to ~2 was made with concentrated hydrochloric acid, the solution was stirred for 1 h, and then the pH was adjusted to 9 with ammonium hydroxide. The product was extracted into dichloromethane (3 × 30 mL) and the combined organic phases were washed with water (2 × 100 mL), dried, and evaporated. The resulting brown solid weighed 3.05 g. Continuous extraction (24 h) of the aqueous layer with dichloromethane afforded an additional 400 mg of the hydrazine.

The combined solids dissolved in methanol (10 mL) were treated with a solution of cupric chloride (3.14 g) in methanol (10 mL). After 30 min, the solvent was removed under reduced pressure, water (20 mL) was added, and 3 N sodium hydroxide was introduced until pH 9 was attained. After the addition of dichloromethane (30 mL), the insoluble copper salts were removed by filtration. The layers were separated and the aqueous phase was again extracted with dichloromethane (2 × 30 mL). The insoluble solids were placed in a Soxhlet extractor and leached with dichloromethane. The combined organic layers were dried and concentrated to afford 3.22 g (83%) of **63**. Recrystallization from hexane furnished colorless needles: mp 97–99 °C; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 6.7–6.1 (m, 2 H), 5.95–5.3 (m, 2 H), 5.08 (br s, 1 H), 4.42 (br s, 1 H), 3.3–2.4 (m, 4 H), and 2.1–1.25 (m, 2 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 138.69, 137.37, 128.76, 128.60, 84.46, 79.66, 59.24, 44.59, 44.38, 35.15, 35.02, and 34.50;  $m/e$  calcd 184.1000, observed 184.1003. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>: C, 78.22; H, 6.57. Found: C, 78.35; H, 6.64.

**Pyrolysis of 63.** Pyrolysis of **63** (109 mg) was effected by subliming the material into a nitrogen flow system at a pressure of 3 mm and

passage through the quartz chip packed quartz reactor described above at 450 °C. The yellowish semisolid which was collected in the dry ice-acetone trap was leached with hexane. Evaporation of the hexane left **73** (97% pure by VPC analysis). Analytically pure hydrocarbon was obtained as a waxy semisolid by preparative VPC purification on a 5 ft × 0.25 in. 10% SE-30 column at 130 °C (25 mg, 23%): <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>) 6.43–6.15 (m, 2 H), 6.0–5.58 (m, 2 H), 3.28–1.97 (m, 6 H), 1.95–1.7 (m, 1 H), and 1.65–1.2 (m, 1 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 137.69, 137.26, 134.94, 128.49, 49.64, 46.72, 37.98, 36.28, 32.13, 31.83, 21.72, and 18.53; *m/e* calcd 156.0939, observed 156.0941. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.95.

**Photolysis of 63.** A solution of **63** (321 mg) in purified pentane (400 mL) was irradiated at room temperature with a 450-W medium-pressure Hanovia lamp housed in a water-cooled Hanovia immersion type apparatus. Agitation was provided by a slow stream of nitrogen introduced at the bottom of the well. After 48 h, the solvent was carefully evaporated at atmospheric pressure to leave a yellow oil. VPC analysis (5 ft × 0.25 in. 10% SE-30 on Chromosorb W, 130 °C) revealed ~95% conversion to products. Two minor components (total 8.6%) were available in inadequate quantity for characterization. The two major components (70 and 20%) were collected under preparative conditions to give 133 and 40 mg, respectively, of waxy semisolids. Because <sup>1</sup>H NMR analysis showed the dominant fraction to still consist of two products, it was subjected to further separation on a 6 ft × 0.25 in. 10% Carbowax 20M column (Chromosorb W, 130 °C). In this way, **73** (46%) could be efficiently separated from the triply unsaturated (CH)<sub>12</sub> isomer tentatively formulated as **76** or **77**. **74** or **75**: <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>) 6.55–6.2 (m, 1 H), 6.1–5.75 (m, 1 H), 3.75–3.35 (m, 1 H), 3.15–2.65 (m, 2 H), and 2.55–1.1 (br m, 7 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 127.87, 125.33, 66.69, 41.06, 40.36, 40.14, 39.17, 35.99, 29.46, 27.52, 20.61, and 18.67 (all doublets in the off-resonance spectrum); *m/e* calcd 136.0939, observed 136.0941. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>: C, 92.26; H, 7.74. Found: C, 92.18; H, 7.85. **76** or **77**: <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>) 6.3–5.17 (br m, 6 H), 3.05–2.45 (br m, 3 H), and 2.0–1.4 (br m, 3 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 136.50, 135.75, 131.86, 126.79, 126.25, 125.93, 47.86, 46.51, 38.90, 28.16, 26.17, and 18.78 (all doublets in the off-resonance spectrum); *m/e* calcd 156.0939, observed 156.0941. Anal. Calcd for C<sub>12</sub>H<sub>12</sub>: C, 92.26; H, 7.74. Found: C, 92.25; H, 7.95.

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