

1,3-Bis(ethoxycarbonyl)-5,6-dimethoxy-2-methylindole (25). (a) From 5,6-dimethoxy-2-methylindole (23). To a 3 M solution of methylmagnesium bromide (0.5 mL, 1.5 mmol) in 20 mL of dry THF was added indole 23 (200 mg, 1.04 mmol) in 2 mL of dry THF. The mixture was warmed on a hot water bath for 0.5 h. The solution was cooled with an ice bath, and ethyl chloroformate (0.3 mL, 2.8 mmol) was added. The reaction mixture was heated to reflux for 5 h and after cooling was treated with 1 mL of water, dried (MgSO₄), and evaporated to yield an oily material. ¹H NMR revealed a 50:40:10 ratio of diester 25 to starting material (23) to monoester product 24. When this material was allowed to stand at room temperature, crystals formed. These were suction filtered and washed with a cold ethanol/hexane mixture to give 81 mg (23%) of 25 as a white solid: mp 140–141 °C; ¹H NMR (CDCl₃) δ 7.74 (s, 1 H, Ar H), 7.62 (s, 1 H, Ar H), 4.43 (m, 4 H, CH₂CH₃), 3.95 (s, 3 H, OCH₃), 3.94 (s, 3 H, OCH₃), 2.95 (s, 3 H, CH₃), 1.50 (m, 6 H, CH₂CH₃). Anal. Calcd for C₁₇H₂₁NO₆: C, 60.88; H, 6.31; N, 4.18. Found: C, 60.49; H, 6.33; N, 4.08.

(b) From Ethyl 5,6-Dimethoxy-2-methylindole-3-carboxylate (11B). Indole 11B (13 mg, 0.05 mmol), 3 M methylmagnesium bromide (0.03 mL, 0.09 mmol), and ethyl chloroformate (0.02 mL, 0.18 mmol) were allowed to react in the same way as described for the preparation of 25 from 23. The product was crystallized from ethanol to yield 12 mg (73%) of 25: mp 140–141 °C; ¹H NMR spectrum was identical with the product obtained from 23.

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Registry No. 2, 6014-30-8; 7, 75014-12-9; 8B, 83634-09-7; 9B, 83634-10-0; 11A, 16381-44-5; 11B, 24608-62-6; 12, 83634-11-1; 13, 83634-12-2; 14, 93-17-4; 15, 17354-04-0; 16, 14430-23-0; 17, 5446-82-2; 18, 73396-98-2; 19, 83634-13-3; 20, 83634-17-7; 21, 83634-14-4; 22, 83634-15-5; 23, 57330-45-7; 24, 83634-18-8; 25, 83634-16-6; thiophenol, 108-98-5; ethyl 3-aminocrotonate, 7318-00-5; hydroxy-*p*-quinone, 2474-72-8.

Preparation and Properties of *endo,endo*-7,8-Diphenylbicyclo[4.1.1]octa-2,4-diene

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endo,endo-7,8-Diphenylbicyclo[4.1.1]octa-2,4-diene (10) has been prepared in ten steps from ϵ -truxillic acid. If the pendant phenyl substituents in this hydrocarbon could adopt conformations where they become approximately coplanar with the diene segment, the possibility for substantive electronic delocalization through the cyclobutane relay orbitals exists. Three-dimensional X-ray crystal structure analysis of 10 reveals that while the unsaturated four-carbon bridge is essentially planar, one of the aryl rings is twisted 20° out of plane because proximity factors prohibit parallel stacking. Additionally, photoelectron spectroscopic analysis of 10 and several model compounds (17, 18, and 23) shed no light on the question of through-bond interaction because of high-level interference arising from electron promotion out of the benzene rings. Nonetheless, the chemical reactivity of 10 is very high, it being very prone to thermolysis and photolysis. Interestingly, the reactions which occur under these conditions find no parallel with the behavior of lesser substituted prototype structures.

The effects of inserting one or more carbon atoms of tetrahedral geometry between the p orbital networks of classical π systems have received considerable study. In homoaromatic cations,^{2,3} the resulting gap does not pro-

hibit charge delocalization. However, decreased overlap integrals lead to substantive dropoffs in interaction, the levels of which are apparently inadequate to support homoconjugation in neutral⁴ and anionic analogues.⁵ When two π systems are linked together in mutually perpendicular planes, spiroconjugation can result.⁶ However, such through-space electronic delocalization manifests itself only when the interacting π components have degenerate or nearly degenerate basis orbital energies. This condition stipulates that spiroconjugation should be most important in those molecules which possess identical pairs of perpendicular, planar π segments. The available experimental results are in full agreement.^{6a,d,7}

In the last few years, an awareness has developed that four-membered rings are capable of strong interaction with pendant vinyl groups. By means of photoelectron spec-

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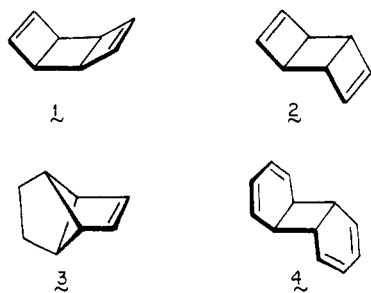
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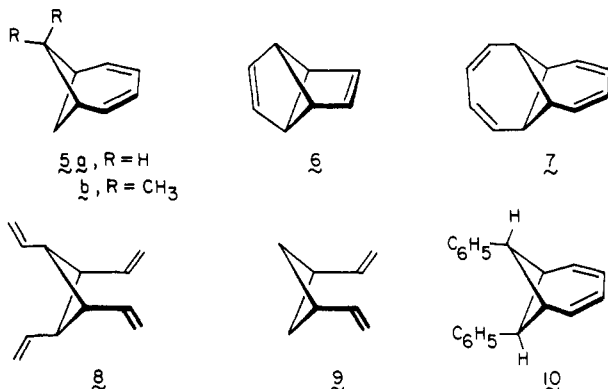
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troscopy, large through-bond effects have been observed in *syn*- (1) and *anti*-tricyclo[4.2.0.0^{2,5}]octadienes (2),⁸ tri-

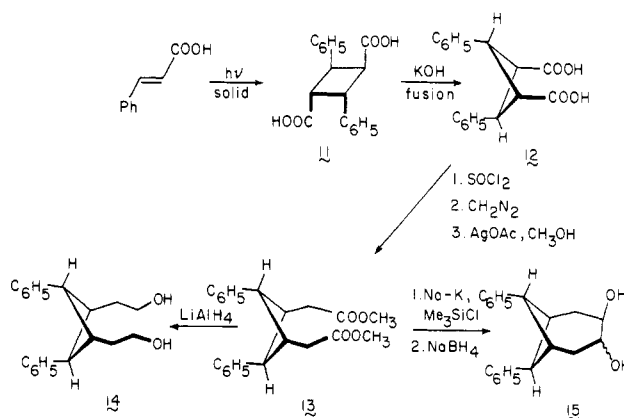


cyclo[3.3.0.0^{2,6}]octene (3),⁹ and *anti*-tricyclo[6.4.0.0^{2,7}]dodecatetraene (4).¹⁰ Almost simultaneously, Hogeveen¹¹ and Borden¹² recognized major differences in the Diels-Alder reactivities of bicyclobutane- and cyclobutane-bridged dienes. With the successful synthesis of bicyclo[4.1.1]octa-2,4-diene (5a) came the realization that re-



placement of a spiro center by a four-membered ring should lead to appreciably stronger electronic interaction.¹³ The resonance integral (β) for 5a was found to equal -1.9 eV. This observation led to a theoretical study by Bischof, Gleiter, and Haider on the ability of cyclobutane Walsh orbitals to function as relays.¹⁴ The previously described limitation of spiroconjugated systems was found to be lifted for doubly bridged molecules such as 6 and 7, chiefly because of a reversal in orbital sequencing. Experimental support for these conclusions was available in the case of tricyclo[3.3.0.0^{2,6}]octa-3,7-diene (6) which contains a destabilized relay orbital network and therefore weakened cyclobutane bonds.¹⁵ The physical and chemical characteristics of 6 are highlighted by a first transition of unusually low energy (300 nm) and rapid isomerization to

Scheme I



semibullvalene at room temperature.¹⁶ Biradical intermediates are thought to be involved.¹⁷

Clearly, however, additional evidence in support of relay orbital interaction through cyclobutyl bonds would be highly desirable. Supportive photoelectron spectroscopic measurements on vinylcyclobutane,¹⁸ the isomeric 1,2- and 1,3-divinylcyclobutanes,¹⁹ and 8^{20,21} have recently been completed. The thermochemical²² and photochemical behavior of 9²³ has also been elucidated. A synthesis of 5b has been reported²⁴ and its response to pyrolysis and photolysis detailed.²⁵

As a prelude to a synthesis of 7, we have prepared *endo,endo*-7,8-diphenylbicyclo[4.1.1]octa-2,4-diene (10) and detail herein our synthetic approach to this hydrocarbon as well as certain of its physical and chemical properties.

Results

The solid-state photodimerization of *trans*-cinnamic acid to produce α -truxillic acid (11) and the subsequent isomerization of 11 to ϵ -truxillic acid (12) have been described previously.²⁶ This two-step sequence provides a desirable and otherwise difficultly accessible cyclobutane substitution pattern in which carbons 1 and 3 and carbons 2 and 4 bear like substituents which are mutually *cis* oriented. Treatment of 12 with thionyl chloride and reaction of the resultant diacid chloride with diazomethane afforded a crystalline didiazo ketone which smoothly underwent Wolff rearrangement to produce 13. This diester proved to be a direct link to diols 14 and 15 as shown in Scheme I.

Before an acyloin condensation was attempted on 13, its response to base-promoted cyclization was explored. Under a variety of conditions (Na in CH₃OH, K in *t*-BuOH, LDA in THF, Na-K in benzene), only the starting diester was recovered. This lack of reactivity was construed to reflect a significant level of nonbonded steric

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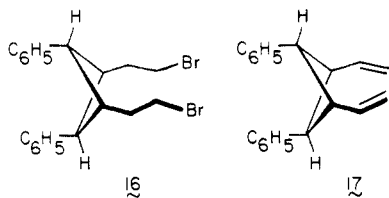
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interaction between the phenyl groups as incipient C–C bond formation becomes advanced. In fact, molecular models suggest that free rotation of both phenyl groups is highly unlikely when a 3-carbon bridge is fixed on the opposite side of the molecule. Severe restraints on rotation continue to persist when a four-carbon bridge is in place as in 15. Not surprisingly, therefore, the acyloin conditions which allow synthetic access to 5a¹³ gave no evidence of monomeric product when applied to 13. This complication was subsequently overcome through use of a motor-driven syringe pump to introduce 13. In this manner, locally high concentrations of diester were avoided, and intramolecular ring closure was given an opportunity to occur. Our best conditions involved adding 13 at a rate of approximately 100 mg/h to a refluxing benzene solution containing chlorotrimethylsilane and a dispersion of sodium–potassium alloy. Direct treatment of the cyclization product mixture with sodium borohydride in methanol provided 15 in yields of 40% or better.

A mixture of diol isomers was evident from the ¹³C NMR spectrum which exhibited nine different aliphatic carbon signals (five for the cis isomer and four for the trans). The constitution of this mixture was determined by quantitative conversion (2,2-dimethoxypropane, pyridinium *p*-toluenesulfonate, dichloromethane) to the corresponding acetones and comparison of the relative areas of the methyl singlets in the ¹H NMR spectrum. Invariably, the cis isomer was favored by a factor of at least 3. Clearly, the steric problems presented by the phenyl groups could be overcome and entry to the desired bicyclo[4.1.1]octane system realized in this manner.

Hydride reduction of 13 readily afforded 14. Conversion of this diol to dibromide 16 was conveniently performed



with triphenylphosphine dibromide. Subsequent dehydrobromination with potassium *tert*-butoxide in tetrahydrofuran gave diene 17.

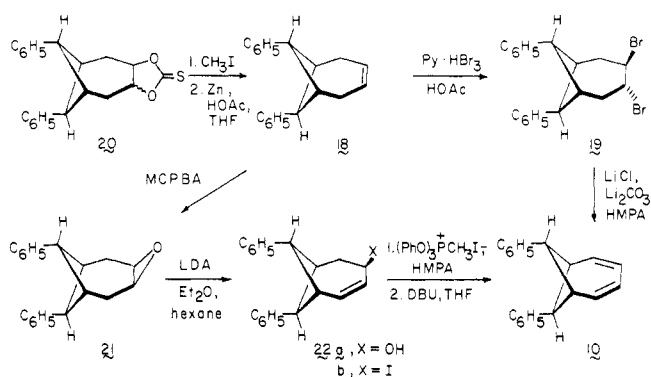
Analogous efforts to dehydrate 15 proved unsuccessful. Thus, although the dimesylate could be prepared in quantitative yield, it did not give rise to diene under a variety of conditions (*t*-BuOK in Me₂SO, *t*-BuOK in C₆H₆, DBU in THF). This inability to proceed directly from an acyloin-derived dimesylate to a 1,3-diene has been encountered before²⁷ and may arise because of increased acidity of the hydrogens on those carbon atoms which carry the sulfonate groups. If so, elimination can occur in the wrong direction. The more hindered ditosylate could be prepared in 67% yield. Although molecular models suggested that those alignments necessary for syn elimination were quite feasible, no olefinic products were isolated when this derivative was stirred with neutral alumina (Woelm, activity grade Super I) in refluxing dichloromethane.²⁸ When the bis(*O*-4-methylphenyl) chlorothioformate was generated (80%) and pyrolyzed (180 °C, 30 mm),²⁹ a mixture of unsaturated products having lost the cyclobutane ring was obtained. This result suggested that 10, if indeed formed, might be thermally labile (see below).

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Scheme II



When attention was turned to preparation of the vicinal dihalide, we discovered that S_N2 displacement could not be efficiently carried out. Although 15 proved unreactive to 48% hydrobromic acid in refluxing chloroform or ethanol, two new compounds identified as 18 (40%) and 19 (10%) were isolated from its exposure to 3.3 equiv of triphenylphosphine dibromide in dichloromethane at 25 °C for 48 h. When epoxide 21 was subjected to the same conditions, no reaction occurred. This suggests that the deoxygenation of 21 is not the source of 18. Rather, this olefin may arise by reductive elimination of an intermediate alkoxyphosphonium salt. In any event, the desired conversion to 19 did not predominate.

At this juncture, the decision was made to utilize 18 as the precursor to 10. Although a variety of sequences are available for the conversion of 1,2-diols to olefins, many of these protocols involve concerted rearrangements which would be uniquely applicable to the cis isomer in our case. Surprisingly, a number of the remaining procedures which were attempted proved unsuccessful. For example, exposure of the dimesylate to sodium amalgam or the anthracene radical anion³⁰ failed to give 18. When the dixanthate of 15 was treated with tri-*n*-butyltin hydride,³¹ olefin formation was again not observed. In contrast, direct treatment of diol 15 with potassium/titanium trichloride in refluxing tetrahydrofuran³² did furnish 18 in 46% yield. However, isolation of the desired product from these reaction mixtures proved unusually troublesome.

In our hands, the most efficient and reproducible scheme to arrive at 18 involved use of the isomeric thionocarbonates 20 (Scheme II). The thermal decomposition of such derivatives with triethyl phosphite is well-known.³³ However, to accommodate a mixture such as is represented by 20, an alternative route which entails alkylation with methyl iodide and reductive elimination of the resultant vicinal iodo thionocarbonate has been developed.³⁴ Thus, following preparation of 20 by treatment of 15 in refluxing benzene with *N,N'*-thiocarbonyldiimidazole, this mixture was alkylated under sealed-tube conditions and subsequently treated with zinc. Symmetric olefin 18 was isolated in 76% yield.

Two routes to 10 from 18 were developed. In the first, 18 was subjected to a bromination–dehydrobromination sequence.³⁵ Initial attempts to add elemental bromine in carbon tetrachloride or glyme unexpectedly gave rise to multiple products and a persistence of red color in the

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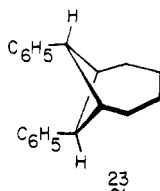
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reaction mixture. It was subsequently determined that the double bond in 18 was particularly sluggish in its reaction with Br₂. Optimum conditions for conversion to 19 consisted in treatment with pyridinium hydrobromide perbromide in acetic acid with one or more equivalents of added lithium bromide. While a 98% yield of *trans*-dibromide 19 was obtained, it is noteworthy that as long as 1 week was often required to achieve the total consumption of 18. Similarly, catalytic hydrogenation of 18 required an unusually extended period of time to produce 23;



peracid epoxidation of 18 also proceeded slowly. These results may be indicative of steric hindrance imposed by those benzylic hydrogens positioned on the cyclobutane ring.

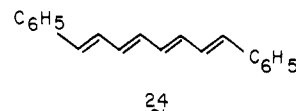
When dibromide 19 was treated at 80 °C in hexamethylphosphoramide containing lithium chloride, lithium carbonate, and ground glass,³⁵ no reaction was seen to occur. Elevation of the temperature to 110 °C was necessary before dehydrohalogenation became observable. At this temperature, preparative-scale experiments gave the desired diene along with unidentified yellow contaminants which were sometimes present in significant amounts. Chromatographic purification attempts on 10 by using basic alumina were frustrated by the difficulties encountered after 10 was placed in solution. Additional yellowing was always evident. However, the diene was found to be soluble in hot methanol and could thus be separated from the oily yellow residues by simple decantation of the warm methanolic solution. In this manner, a concentrated solution afforded crystalline 10 when chilled. Because of its lability, 10 was purified on a small scale prior to each use. It was estimated that the dehydrohalogenation reaction afforded the diene in at least 60% yield.

In an effort to examine alternate methods for the introduction of the 1,3-diene unit at lower temperatures, allylic alcohol 22a was prepared in 77% yield by ring opening of epoxide 21 with lithium diisopropylamide (Scheme II). However, attempts at preparation of the corresponding allylic mesylate or allylic tosylate resulted in formation of a multitude of products as indicated by thin-layer chromatographic analysis. Approaches aimed at the allylic bromide were similarly thwarted. Although a 16% yield of the corresponding allylic selenide (o-nitrophenyl selenocyanate, tri-*n*-butylphosphine³⁶) was obtained, it had become evident that positioning of a good leaving group at this site was not particularly desirable. With generation of the corresponding allylic cation intermediate comes the possibility of ready access to a number of unwanted reaction channels.

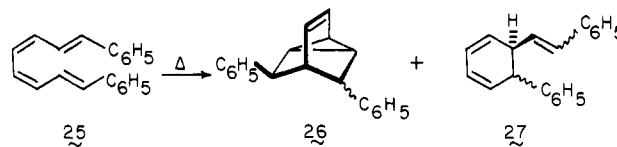
Diene 10 could also be isolated in low yield from 22a by utilization of the methyltriphenoxyphosphonium iodide reagent.^{37,38} However, because this transformation is mediated by allylic iodide 22b, it suffers from analogous complications. It appears, then, that dehydrobromination of 19 is the most efficient route to 10.

In the ultraviolet spectrum of 10, bands are seen between 250 and 300 nm which correspond closely to those exhibited by 5a and 5b. However, the extinction coefficients are somewhat lower (factor of 3–4). The extent to which the phenyl groups perturb this diene system is not known, but no Diels–Alder cycloaddition attempts with this molecule were successful. Forcing reaction conditions with dimethyl acetylenedicarboxylate and maleic anhydride gave no characterizable products. In the case of tetracyanoethylene in either chloroform or acetonitrile at 80 °C, an orange complex quickly formed, but the color did not give way to a new component. Similarly, while 10 was very slowly consumed at room temperature by both *N*-methyl- and *N*-phenyltriazolinedione, no monomeric cycloadduct was formed. It appeared from the broad, non-descript ¹H NMR signals of the reaction mixtures and their mass spectra that polymeric materials had been produced.

When a glyme solution of 10 was irradiated through Pyrex or quartz, a yellow color developed immediately, and yellow platelets soon precipitated from solution. This yellow crystalline precipitate (46%) was identified as the all-*trans* isomer of 1,8-diphenyl-1,3,5,7-octatetraene (24).³⁹ Neither solvent deoxygenation prior to irradiation nor the use of acetonitrile-*d*₃ altered the reaction course.



Because of the already mentioned complex mixture obtained from thermolysis of the bis(dithiocarbonate) of 15, little further work was done regarding isolation of products from the thermolysis of 10. It is of interest to call attention to the fact that slow heating of a sealed capillary containing this diene caused marked yellowing to begin at 130 °C. As the temperature was gradually increased to 190 °C, the color darkened to orange, and some solidification occurred. This behavior contrasts with the behavior of 5b which required a temperature of 225 °C before rearrangement took place.²⁵ The complex nature of our pyrolysate may have its origins in the lability of 24 and its isomers to thermal rearrangement. For example, simple heating of 25 in ethyl acetate at 175 °C leads to two tricyclooctenes 26 in a combined yield of 45% and a mixture of 1,3-cyclohexadienes 27 (15%).⁴⁰



The diphenyldivinylcyclobutane 17 exhibited no photochemical reactivity upon either direct or sensitized irradiation for comparable periods of time. It was also unreactive when heated for 6 h at 285 °C in an evacuated sealed tube.

X-ray Crystal Structure Analysis

To date, 10 represents the only crystalline example of a bicyclo[4.1.1]octa-2,4-diene. The framework of such molecules is seen to be closely related to that of norcaradiene (28) with its weak central cyclopropane bond replaced by a methylene group. In a formal sense, therefore, 5a, 5b, and 10 may be considered to be [1,1]-

(36) Grieco, P. A.; Gilman, S.; Nishizawa, M. *J. Org. Chem.* **1976**, *41*, 1485.

(37) Hutchins, R. O.; Hutchins, M. G.; Milewski, C. A. *J. Org. Chem.* **1972**, *37*, 4190.

(38) Spangler, C. W.; Hartford, T. W. *Synthesis* **1976**, 108.

(39) Akhtar, M.; Richards, T. A.; Weedon, B. C. L. *J. Chem. Soc.* **1959**, 933.

(40) Marvell, E. N.; Suebert, J.; Vogt, A.; Zimmer, G.; Moy, G.; Siegmann, J. R. *Tetrahedron* **1978**, *34*, 1323.



28

dihomobenzene derivatives.⁴¹ For this and the reasons discussed earlier, determination of the molecular structure of **10** was expected to provide key information on the extent to which the diene moiety is planar, the relative lengths of the cyclobutane ring bonds, the magnitude of the puckering within the four-membered ring, and the dihedral angle relationships adopted by the two pendant phenyl substituents. To achieve maximum electronic interaction through the relay orbitals, the aryl rings should populate those conformations where they are approximately coplanar or perpendicular to the diene component.

The bond lengths, bond angles, and torsion angles for **10** are summarized in Tables I–III. Figure 1 is a stereopair drawing of the molecule which also indicates the numbering scheme. The final atomic and anisotropic thermal parameters (Tables IV and V) are provided as supplementary material.

In actual fact, the conjugated diene unit is seen to be an essentially planar belt about the cyclobutane ring, with no atom deviating from the least-squares plane by more than 1.4°. The exaggerated puckering effect which this 1,3-bridge might be expected to convey to the four-membered ring is apparently offset by the steric compression induced between the two cis-locked phenyl groups. Thus, the C₁–C₄–C₅, C₃–C₄–C₅, C₁–C₂–C₈, and C₃–C₂–C₈ angles are relatively normal and strikingly similar at 112.3–112.9°. This translates to a dihedral angle of 22.3–22.6°, a value quite similar to those exhibited by simple substituted cyclobutanes (23–33°),⁴³ except when they are cis-fused in a 1,2-fashion to other rings. The latter structural condition causes the level of puckering to be greatly reduced (8–12.6°).⁴⁴

Although the opposed C₁–C₄ (1.554 Å) and C₂–C₃ (1.555 Å) bonds of the four-membered ring compare favorably in length with the average value observed for cyclobutanes (1.550 Å),⁴³ the alternate two bonds represented by C₁–C₂ (1.572 Å) and C₃–C₄ (1.569 Å) are significantly longer. These unexpected characteristics provide for an alternating short bond–long bond arrangement, thereby causing **10** to approach twofold rotational symmetry more closely than mirror symmetry, at least in the crystalline state.

The decidedly nonparallel relationship of the two phenyl rings is also clearly seen, there being a 20° difference in the orientation of C₁₁–C₁₆ vs. C₂₁–C₂₆ relative to the bicy-

Table I. Bond Lengths (Å) in **10** with Standard Deviations in Parentheses

C(1)–C(2)	1.572 (2)	C(11)–C(16)	1.381 (3)
C(1)–C(4)	1.554 (2)	C(12)–C(13)	1.379 (4)
C(1)–C(11)	1.501 (3)	C(13)–C(14)	1.368 (5)
C(2)–C(3)	1.555 (2)	C(14)–C(15)	1.363 (5)
C(2)–C(8)	1.496 (3)	C(15)–C(16)	1.384 (3)
C(3)–C(4)	1.569 (2)	C(21)–C(22)	1.385 (3)
C(3)–C(21)	1.508 (3)	C(21)–C(26)	1.385 (3)
C(4)–C(5)	1.498 (3)	C(22)–C(23)	1.382 (3)
C(5)–C(6)	1.323 (3)	C(23)–C(24)	1.362 (4)
C(6)–C(7)	1.461 (3)	C(24)–C(25)	1.375 (4)
C(7)–C(8)	1.324 (3)	C(25)–C(26)	1.375 (3)
C(11)–C(12)	1.384 (3)		

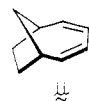
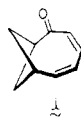
Table II. Bond Angles (in Degrees) in **10** with Standard Deviations in Parentheses

C(2)–C(1)–C(4)	87.9 (1)
C(2)–C(1)–C(11)	114.5 (1)
C(4)–C(1)–C(11)	118.9 (1)
C(1)–C(2)–C(3)	88.1 (1)
C(1)–C(2)–C(8)	112.3 (1)
C(3)–C(2)–C(8)	112.9 (1)
C(2)–C(3)–C(4)	87.9 (1)
C(2)–C(3)–C(21)	118.0 (1)
C(4)–C(3)–C(21)	114.8 (1)
C(1)–C(4)–C(3)	88.2 (1)
C(1)–C(4)–C(5)	112.4 (1)
C(3)–C(4)–C(5)	112.3 (1)
C(4)–C(5)–C(6)	126.0 (2)
C(5)–C(6)–C(7)	127.1 (2)
C(6)–C(7)–C(8)	126.5 (2)
C(2)–C(8)–C(7)	126.1 (2)
C(1)–C(11)–C(12)	117.9 (2)
C(1)–C(11)–C(16)	125.0 (2)
C(12)–C(11)–C(16)	117.1 (2)
C(11)–C(12)–C(13)	121.7 (2)
C(12)–C(13)–C(14)	120.4 (3)
C(13)–C(14)–C(15)	118.8 (3)
C(14)–C(15)–C(16)	121.2 (3)
C(11)–C(16)–C(15)	120.8 (2)
C(3)–C(21)–C(22)	123.2 (2)
C(3)–C(21)–C(26)	119.3 (2)
C(22)–C(21)–C(26)	117.4 (2)
C(21)–C(22)–C(23)	120.8 (2)
C(22)–C(23)–C(24)	120.7 (2)
C(23)–C(24)–C(25)	119.5 (2)
C(24)–C(25)–C(26)	119.8 (2)
C(21)–C(26)–C(25)	121.7 (2)

Table III. Torsion Angles (in Degrees) in **10** with Standard Deviations in Parentheses

C(1)–C(4)–C(5)–C(6)	–48.3 (2)
C(4)–C(5)–C(6)–C(7)	–0.2 (3)
C(5)–C(6)–C(7)–C(8)	–1.2 (3)
C(6)–C(7)–C(8)–C(2)	1.4 (3)
C(7)–C(8)–C(2)–C(1)	48.1 (2)
C(8)–C(2)–C(1)–C(4)	–92.8 (2)
C(2)–C(1)–C(4)–C(5)	92.4 (2)
C(3)–C(4)–C(5)–C(6)	49.3 (2)
C(4)–C(5)–C(6)–C(7)	–0.2 (3)
C(5)–C(6)–C(7)–C(8)	–1.2 (3)
C(6)–C(7)–C(8)–C(2)	1.4 (3)
C(7)–C(8)–C(2)–C(3)	–49.6 (2)
C(8)–C(2)–C(3)–C(4)	92.4 (2)
C(2)–C(3)–C(4)–C(5)	–92.3 (2)
C(1)–C(2)–C(3)–C(4)	–21.0 (1)
C(2)–C(3)–C(4)–C(1)	21.3 (1)
C(3)–C(4)–C(1)–C(2)	–21.0 (1)
C(4)–C(1)–C(2)–C(3)	21.2 (1)

(41) The term dihomobenzene is not meant to convey any sense of closed-shell electron delocalization. Rather, it constitutes a simple way to indicate that the widely recognized 6π6C cyclic unsaturated carbon framework has been interrupted by two bridges along a common unsaturated edge. Furthermore, this trivial system of nomenclature is readily adaptable to many ring systems. The numerical prefixes merely connote the number of atoms in the individual bridges. Thus, *i* becomes [1,1]-dihomo[*b*]tropone, *ii* is termed [2,1]-dihomobenzene, and *iii* emerges as the [1,1]-dihomotropylium cation.



(42) Structures *i* and *iii* are currently unknown and their synthesis constitutes an active area of research in these laboratories.

(43) (a) Cotton, F. A.; Frenz, B. A. *Tetrahedron* 1974, 30, 1587. (b) Moriarty, R. M. *Top. Stereochem.* 1974, 8, 271.

(44) (a) Anderson, B.; Fernolt, L. *Acta Chem. Scand.* 1970, 24, 445. (b) Anderson, B.; Srinivasan, R. *Ibid.* 1972, 26, 3468. (c) Wiberg, K. B.; Olli, L. K.; Golombeski, N.; Adams, R. D. *J. Am. Chem. Soc.* 1980, 102, 7467.

clo[4.1.1]octadiene nucleus. The associated carbon atoms of the cyclobutane ring (C₁ and C₃) are simply too close (approximately 2.1 Å) to permit parallel stacking of the aryl substituents. In our judgment, they should be about 3.5 Å apart before one might anticipate coplanarity be-

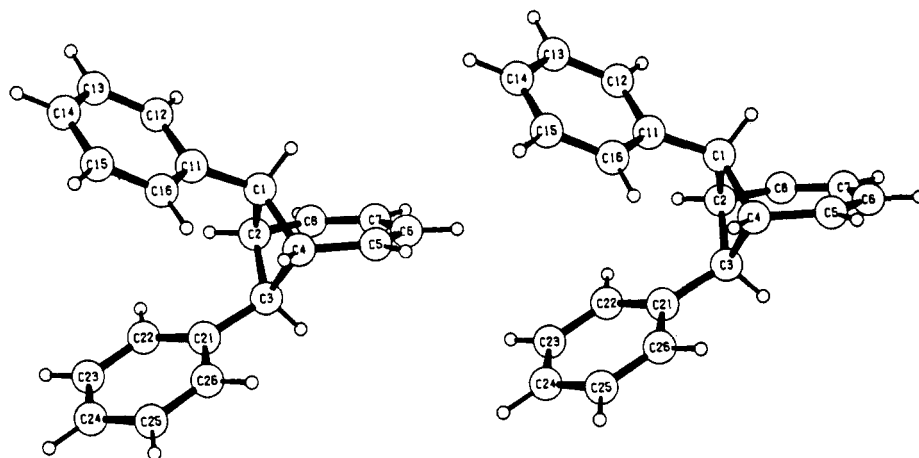
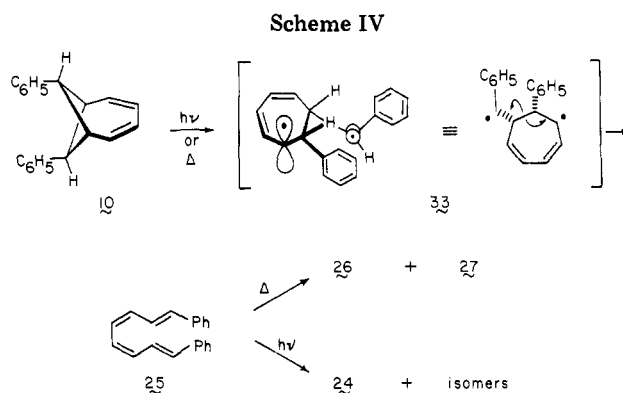
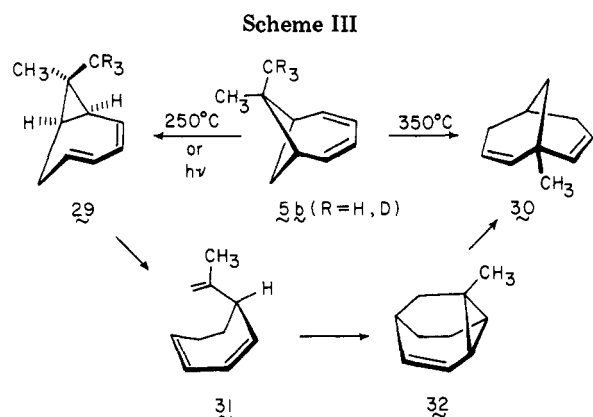


Figure 1. Three-dimensional stereopair view of 10 as determined by X-ray analysis.



tween the C_6H_5 substituents.

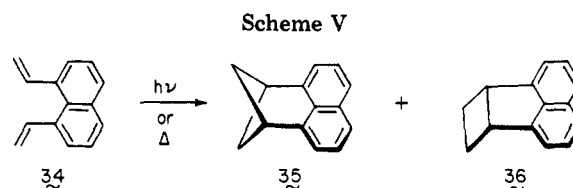
Finally, note should be taken of the fact that the value of a torsion angle, say that for $C_5-C_6-C_7-C_8$, is not the same as the angle between the two vectors $[C_6 \rightarrow C_5]$ and $C_7 \rightarrow C_8]$.

Discussion

Diene 10 has been found to be particularly susceptible to thermolysis and photolysis and to differ significantly from prototypical examples in the course of its ensuing rearrangements. For example, direct irradiation of 5b or pyrolysis at 250 °C has been reported to lead to 29 (Scheme III).²⁵ Suitable deuterium labeling has revealed the [1,5] sigmatropic shift to proceed predominantly with inversion of configuration under both sets of conditions. When 5b is subjected to higher temperatures (350 °C) in a flow system, clean isomerization to 30 is seen. On the basis of careful studies, intermediates 31 and 32 were isolated and their involvement in the four-step conversion to 30 experimentally established.²⁵

Undoubtedly, prevailing steric factors within 10 and the extended conjugation available to both free radical centers following cyclobutane ring homolysis (cf. 33, Scheme IV) foster conversion to 25 and thence to 24, 26, or 27. The initial formation of terminal double bonds having trans geometry as in 25 is anticipated if the phenyl ring of the benzyl substituent in 33 becomes conformationally oriented as far as possible from the cycloheptadienyl radical.

The photochemical and thermal interconversions of the stereoisomeric 1,8-diphenyl-1,3,5,7-octatetraenes have been well studied.^{39,40,45} In particular, all-trans isomer 24 has been shown to be capable of photoisomerization to three



different mono- and dicis isomers.⁴⁵ In view of this, our high-yield recovery of crystalline 24 requires that its deposition from the reaction mixture under the reaction conditions preclude subsequent rearrangement. The chromophore-containing components obtainable from the chilled photolysates following the removal of 24 may well consist of these isomers.

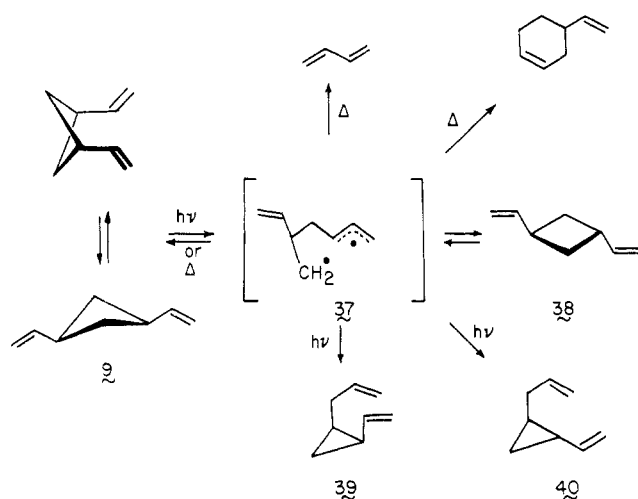
It would be erroneous to conclude that benzylic radicals of the type under discussion are by their very nature uniquely prone to fragmentation with formation of styrene-like products. In at least one example where the reverse behavior has been noted, Meinwald and Kapecki observed that the heating of 34 to 150 °C in various solvents produced the cyclized products 35 and 36 in a 3:1 ratio (Scheme V).⁴⁶ The same two products arise upon irradiation, although 35 now dominates still more (10:1).

The pair of double bonds in 34 are not originally linked together in a conjugated diene arrangement. When this structural feature is placed in a cyclobutane context as in 9, more classical behavior returns. Thus, the thermolysis of 9 at 300 °C proceeds via diradical 37 to give butadiene, 4-vinylcyclohexene, and a small amount of trans isomer 38 (Scheme VI).²² Under conditions of irradiation, 9 undergoes no intramolecular photocycloaddition. Instead, rearrangement to cis- (39) and trans-allylvinylcyclopropane (40) is observed.²³

(45) Zechmeister, L.; Pinckard, J. H. *J. Am. Chem. Soc.* 1954, 76, 4144.

(46) Meinwald, J.; Kapecki, J. A. *J. Am. Chem. Soc.* 1972, 94, 6234.

Scheme VI



What can be said about the existence of relay orbital effects within 10? Our attempts to gain insight into this question by photoelectron spectroscopic analysis of 10 vis-à-vis 17, 18, and 23 as model compounds confirmed fears that electron promotions from orbitals contained within the phenyl rings of these molecules would seriously obliterate the relevant portions of their PE spectra.⁴⁷ As noted earlier, the electronic spectrum of 10 is similarly complicated.⁴⁸ Consequently, we must await the synthesis of 7 and/or related *stable* analogues before gaining suitable experimental verification of relay-orbital interaction involving perpendicular π components.

Experimental Section

Melting points were determined in open capillaries with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. Proton magnetic resonance spectra were recorded with Varian EM-390, EM-360, and T-60 spectrometers as well as with a Bruker WP-200 spectrometer. Carbon spectra were recorded with Bruker WP-80 and WP-200 spectrometers. Ultraviolet spectra were recorded on a Cary Model 14 spectrometer. Mass spectra were determined on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Dimethyl (1 α ,2 β ,3 α ,4 β)-2,4-Diphenyl-1,3-cyclobutanediacetate (13). A solution containing ϵ -truxillic acid (12; 3.00 g, 10.1 mmol) and thionyl chloride (4 mL, 55.4 mmol) in 50 mL of chloroform was stirred under a reflux condenser equipped with a drying tube for 2 h at room temperature and an additional 3 h at 50 °C. Solvent and excess thionyl chloride were removed on a rotary evaporator and the resultant crystalline acid chloride [mp 106–108 °C; IR (KBr) ν_{\max} 1805 cm⁻¹] was dissolved in 50 mL of anhydrous tetrahydrofuran and added dropwise over 10 min to a well stirred, ice-cold ethereal solution of diazomethane (80 mmol in 200 mL of ether). This solution was kept at 0 °C for 2 h and allowed to warm to room temperature. Removal of solvent furnished the diazo ketone as a yellow, crystalline solid [IR (KBr) ν_{\max} 2100 and 1630 cm⁻¹]. This material was dissolved in 100 mL of absolute methanol, treated dropwise at 50 °C with a catalyst solution consisting of 100 mg of silver acetate in 5 mL of 1:1 methanol-triethylamine, and stirred until nitrogen evolution ceased. The reaction mixture was filtered through Celite and concentrated. The remaining oil was dissolved in 150 mL of ethyl ether and washed sequentially with 1 N hydrochloric acid, saturated sodium bicarbonate solution, and brine (150 mL each). Drying and evaporation left diester 13 as a pale yellow oil. An

analytical sample was obtained as a colorless oil by filtration of a small amount through silica gel (elution with dichloromethane): IR (neat) ν_{\max} 3030, 2950, 1735, 1600, 1495, 1435, 740, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 7.29 (s, 10 H), 3.27 (s, 6 H), 2.97–2.36 (series of m, 8 H); ¹³C NMR (CDCl₃) 171.9, 141.5, 128.4, 127.2, 126.7, 51.0, 49.9, 44.8, 38.9 ppm; mass spectrum, calcd *m/e* 352.1674, obsd 352.1680.

Anal. Calcd for C₂₂H₂₄O₄: C, 74.97; H, 6.86. Found: C, 74.85; H, 6.94.

endo,endo-7,8-Diphenylbicyclo[4.1.1]octane-3,4-diol (15). A 1-L, three-necked, round-bottomed flask was equipped with a nichrome wire stirrer, mercury seal, mechanical stirrer, and two condensers (6 and 12 in. in length). A motor-driven syringe pump was mounted beside the shorter condenser, such that a 12-in. syringe needle could be inserted through a rubber septum in the top and down the shaft toward the reaction mixture. The larger condenser was fitted with an argon inlet. The flask was charged with sodium (2.75 g, 0.12 mol) and potassium (4.69 g, 0.12 mol) in 600 mL of anhydrous benzene, and the mixture was heated with rapid stirring to generate a dispersion. Two syringes were charged with benzene solutions (30 mL) of chlorotrimethylsilane (15 mL, 0.118 mol) and unpurified diester 13 (from 3.0 g of 12), respectively. Simultaneous addition of these solutions was made over 30 h, and an additional 4-h reflux period followed. The reaction mixture was cooled and rapidly filtered through a Celite pad under a constant flow of argon (Caution: the filterables are pyrophoric). The resultant pale yellow solution was concentrated to a total volume of 20 mL and added dropwise over 1 h to a stirred suspension of sodium borohydride (1.70 g, 44.9 mmol) in 100 mL of absolute ethanol which was maintained at 65 °C under an argon atmosphere. After the addition was complete, the mixture was heated at reflux for 2 h, cooled, and evaporated. The residue was treated with ice-cold 1.5 N hydrochloric acid (150 mL). Extraction of this aqueous phase with ethyl acetate (3 × 100 mL) was followed by washing of the combined organic layers with brine prior to drying. Removal of the solvent and silica gel chromatography of the residue (elution with 2:1 dichloromethane-ethyl acetate) afforded 1.32 g (44% overall from ϵ -truxillic acid) of 15 as a crystalline mixture of the two isomeric diols: mp 125–133 °C (from hexane-ethyl acetate); IR (KBr) ν_{\max} 3360, 3020, 2920, 1600, 1490, 1440, 1020, 740, 690 cm⁻¹; ¹H NMR (C₅D₅N) δ 7.10 (s, 10 H), 5.90 (s, 2 H), 4.90–4.30 (m, 2 H), 3.40–2.10 (series of m, 8 H); ¹³C NMR (CDCl₃, 9-line aliphatic region) 74.7, 73.8, 46.1, 45.2, 45.0, 41.8, 41.2, 38.7, 36.3 ppm; mass spectrum, calcd *m/e* 294.1619, obsd 294.1626.

(1 α ,2 β ,3 α ,4 β)-2,4-Diphenyl-1,3-cyclobutanediethanol (14). A solution containing diester 13 (1.13 g, 3.20 mmol) in 10 mL of tetrahydrofuran was added dropwise over 40 min to a refluxing slurry of lithium aluminum hydride (182 mg, 4.79 mmol) in 30 mL of tetrahydrofuran, and reflux was maintained for 5 h under a nitrogen atmosphere. After the reaction mixture was cooled to room temperature, the excess hydride reagent was destroyed with ethyl acetate, and hydrolysis was carried out by using saturated sodium sulfate solution. Finally, the mixture was filtered, and the resultant solution was dried and evaporated to yield 900 mg (94%) of 14 as a pale yellow oil which crystallized on standing. Recrystallization from 1:1 hexane-dichloromethane gave colorless crystals: mp 105–106 °C; IR (KBr) ν_{\max} 3300, 3020, 2920, 1600, 1490, 1440, 1025, 745, 700 cm⁻¹; ¹H NMR (C₅D₅N) δ 7.60–7.15 (m, 10 H), 5.28 (br s, 2 H), 3.67 (t, *J* = 6 Hz, 4 H), 2.95–2.55 (m, 4 H), 2.20–1.80 (m, 4 H); ¹³C NMR (CDCl₃) 143.4, 128.7, 127.2, 126.6, 60.7, 50.8, 46.3, 38.4 ppm; mass spectrum, calcd *m/e* 296.1776, obsd 296.1782.

Anal. Calcd for C₂₀H₂₄O₂: C, 81.10; H, 8.16. Found: C, 80.94; H, 8.15.

(1 α ,2 β ,3 α ,4 β)-1,1'-[2,4-Bis(2-bromoethyl)-1,3-cyclobutanediyl]bis[benzene] (16). A solution of diol 14 (333 mg, 1.11 mmol) in 10 mL of dichloromethane was added dropwise over 15 min to an ice-cold solution containing a 35% excess of triphenylphosphine dibromide in 20 mL of dichloromethane (prepared from 790 mg of triphenylphosphine and 480 mg of bromine). The resultant solution was warmed to room temperature and stirred overnight. Filtration of the concentrated reaction mixture through silica gel (elution with 1:1 hexane-dichloromethane) afforded 276 mg (58%) of 16 as a pale yellow oil: IR (neat) ν_{\max} 3030, 2925, 1600, 1495, 1445, 740, 695 cm⁻¹; ¹H NMR (CDCl₃) δ

(47) Gleiter, R., private communication.

(48) The PE spectrum of an isomer of 7 has been measured and does show a strong interaction of the butadiene groups through the cyclobutane ring: Borden, W. T.; Young, S. D.; Frost, D. C.; Westwood, N. P. C.; Jorgensen, W. L. *J. Org. Chem.* 1979, 44, 737.

7.32 (s, 10 H), 3.05 (t, $J = 7$ Hz, 4 H), 2.65–1.85 (series of m, 8 H); ^{13}C NMR (CDCl_3) 142.6, 128.8, 127.1, 126.9, 50.6, 47.4, 39.4, 30.0 ppm; mass spectrum, calcd m/e 420.0089, obsd 420.0099.

(1 α ,2 β ,3 α ,4 β)-1,1'-(2,4-Diethenyl-1,3-cyclobutanediyl)bis[benzene] (17). A 10-mL solution containing potassium *tert*-butoxide (450 mg, 4.01 mmol) in anhydrous tetrahydrofuran was maintained at gentle reflux under nitrogen as a solution of dibromide 16 (150 mg, 0.35 mmol) in 8 mL of tetrahydrofuran was added dropwise over the course of 2 min. The resultant mixture was kept at the reflux temperature for 1.5 h, cooled to room temperature, treated with 1 mL of saturated ammonium chloride solution, stirred for 2 h, and decanted. The solid residue was washed with ethyl ether, the total organic layer was concentrated in vacuo, and the residue was dissolved in 20 mL of ethyl ether and washed with water and brine (20 mL each) prior to drying. Evaporation left 77 mg of crude 17. Silica gel purification on a thick-layer plate (elution with 3:2 hexane–dichloromethane) afforded 71 mg (76%) of pure 17 as a colorless oil: IR (neat) ν_{max} 3050, 2930, 1635, 1600, 1495, 1460, 1000, 920, 750, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.23 (s, 10 H), 6.35–4.85 (m, 6 H), 3.15–2.85 (m, 4 H); ^{13}C NMR (CDCl_3) 142.9, 140.2, 128.4, 126.7, 126.4, 115.0, 50.6, 49.0 ppm; mass spectrum, calcd m/e 260.1564, obsd 260.1571; UV (isooctane) 256 nm (ϵ 720), 262 (820), 267 (700), 272 (670).

Anal. Calcd for $\text{C}_{20}\text{H}_{20}$: C, 92.25; H, 7.75. Found: C, 92.25; H, 7.75.

Hexahydro-endo,endo-6,9-diphenyl-5,7-methano-4H-cyclohepta[d]-1,3-dioxole-2-thione (20). A solution containing isomeric diols 15 (1.79 g, 6.08 mmol) and *N,N'*-thiocarbonyldiimidazole (1.14 g, 6.40 mmol) in 125 mL of benzene was heated at the reflux temperature for 20 h under a nitrogen atmosphere. Concentration of the cooled solution and silica gel chromatography of the residue (elution with dichloromethane) gave a crystalline mixture of the corresponding thionocarbonates. Further elution with 1:1 dichloromethane–ethyl acetate gave a small amount of unreacted diol which was recycled as above. The combined yield of 20 was 1.75 g (85%). One recrystallization from hexane–dichloromethane furnished material with the following: mp 158–159 °C; IR (KBr) ν_{max} 3020, 2940, 1790, 1595, 1490, 1440, 1370–1260 (br), 1195, 1160, 1140, 920, 760, 690 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.45–6.70 (br s, 10 H), 5.60–5.20 (m, 2 H), 3.45–2.30 (series of m, 8 H); ^{13}C NMR (CDCl_3 , 5-line aliphatic region for the predominant isomer) 84.3, 46.8, 46.0, 40.8, 34.0 ppm; mass spectrum, calcd m/e 336.1183, obsd 336.1189.

Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{S}$: C, 74.83; H, 5.98. Found: C, 75.13; H, 6.08.

endo,endo-7,8-Diphenylbicyclo[4.1.1]oct-3-ene (18). Alkylation of 20 was performed in an evacuated sealed tube. The thionocarbonate (1.75 g, 5.20 mmol) was dissolved in 20 mL of glyme, 15 mL of methyl iodide was added, and the contents were heated at 90 °C for 5 h. The reaction mixture was cooled, and the volatiles were evaporated. The crude product was dissolved in 50 mL of tetrahydrofuran, and 6.5 g of zinc dust and 1 mL of glacial acetic acid were added. This mixture was stirred overnight at room temperature under nitrogen and filtered through Celite. The filtrate was evaporated, and the residue was dissolved in 200 mL of ethyl ether. This solution was washed sequentially with water, saturated sodium bicarbonate solution, and brine (100 mL each) and passed through a cone of magnesium sulfate. Evaporation of the resultant solution and filtration of the residue through silica gel (elution with 9:2 hexane–dichloromethane) gave 1.03 g (76%) of 18 as a colorless oil which solidified on standing: mp 64 °C; IR (KBr) ν_{max} 3060, 3000, 2940, 2860, 1640, 1600, 1490, 1450, 1440, 750, 700, 670 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.20–7.04 (m, 10 H), 5.77 (s, 2 H), 3.15 (s, 2 H), 3.01 (s, 2 H), 2.56 (s, 4 H); ^{13}C NMR (CDCl_3) 144.7, 128.0, 127.1, 126.0, 125.3, 45.1, 42.0, 35.1 ppm; mass spectrum, calcd m/e 260.1564, obsd 260.1571; UV (isooctane) 265 nm (ϵ 6.9×10^3), 272 (6.0×10^3).

Anal. Calcd for $\text{C}_{20}\text{H}_{20}$: C, 92.25; H, 7.75. Found: C, 91.87; H, 7.68.

trans-3,4-Dibromo-endo,endo-7,8-diphenylbicyclo[4.1.1]octane (19). A solution containing 18 (331 mg, 1.27 mmol) and anhydrous lithium bromide (217 mg) in 10 mL of anhydrous glacial acetic acid was stirred at room temperature (in the dark under argon) as a total of 450 mg (1.1 equiv) of pyridinium hydrobromide perbromide was added in sequential fashion ($t = 0$, 0.3 equiv; $t = 12$ h, 0.3 equiv; $t = 21$ h, 0.15 equiv; $t = 37$ h, 0.35 equiv). The

dibromide precipitated as it was formed, and after 90 h TLC analysis showed the olefin to be absent. The reaction mixture was poured into 100 mL of water and extracted with ether (2×100 mL). The organic layer was washed consecutively with water (2×100 mL), saturated sodium bicarbonate solution (2×100 mL), and brine (100 mL) prior to drying. Evaporation of solvent and silica gel purification (thick-layer plate, elution with 2:1 hexane–dichloromethane) gave 524 mg (98%) of 19 as colorless crystals: mp 173 °C (from ether–ethanol); IR (KBr) ν_{max} 3020, 2940, 1595, 1490, 1440, 1430, 1170, 750, 720, 695 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.03 (br s, 10 H), 5.00–4.65 (m, 2 H), 3.50–2.20 (series of m, 8 H); ^{13}C NMR (CDCl_3) 142.2, 128.1, 126.8, 125.7, 56.8, 44.9, 43.8, 43.4 ppm; mass spectrum, calcd m/e 417.9932, obsd 417.9943.

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{Br}_2$: C, 57.16; H, 4.79. Found: C, 57.07; H, 4.86.

endo,endo-7,8-Diphenylbicyclo[4.1.1]octane (23). A solution containing 18 (286 mg, 1.1 mmol) in 5 mL of ethyl acetate was added to a mixture of 50 mg of 10% palladium on charcoal in 5 mL of ethyl acetate and hydrogenated at a pressure of 1 atm with vigorous stirring. After 53 h, the required amount of hydrogen had been consumed. The reaction mixture was filtered through Celite and concentrated on a rotary evaporator. Final traces of solvent were removed in vacuo, and the resultant opaque syrup was crystallized with external dry ice cooling. Recrystallization from a minimal amount of benzene afforded 284 mg (98%) of 23: mp 36 °C; IR (CHCl_3) ν_{max} 3020, 2940, 1600, 1500, 1450, 720, 700, 670 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.05 (s, 10 H), 3.26–2.90 (m, 4 H), 1.92 (br s, 8 H); ^{13}C NMR (CDCl_3) 144.8, 127.8, 127.1, 125.0, 44.8, 43.6, 30.9, 25.2 ppm; mass spectrum, calcd m/e 262.1721, obsd 262.1726; UV (isooctane) 265 nm (ϵ 6.4×10^3), 272 (5.5×10^3).

Anal. Calcd for $\text{C}_{20}\text{H}_{22}$: C, 91.55; H, 8.45. Found: C, 91.38; H, 8.49.

endo,endo-8,9-Diphenyl-4-oxatricyclo[5.1.1.0^{3,5}]nonane (21). To a solution containing 195 mg of 18 (0.75 mmol) in 10 mL of dichloromethane at 0 °C was added 200 mg of *m*-chloroperbenzoic acid (80–90% purity, 1.23–1.39 equiv). The solution was allowed to warm to room temperature with continued stirring under nitrogen. After 24 h, the oxidation was judged complete by TLC analysis. The reaction mixture was washed with saturated sodium bicarbonate solution and water (20 mL each), filtered through a cone of magnesium sulfate, and concentrated. Filtration of the residue through silica gel (elution with dichloromethane) gave a quantitative yield of the epoxide as a crystalline solid: mp 84–85 °C (from hexane–ether); IR (KBr) ν_{max} 3060, 3030, 2970, 2920, 1600, 1495, 1445, 1425, 1020, 760, 730, 700 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.07 (s, 10 H), 3.70–2.00 (series of m, 10 H); mass spectrum, calcd m/e 276.1514, obsd 276.1519.

Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{O}$: C, 86.91; H, 7.29. Found: C, 86.52; H, 7.28.

endo,endo-7,8-Diphenylbicyclo[4.1.1]oct-4-en-3-ol (22a). A solution of lithium diisopropylamide corresponding to an excess of approximately 12-fold was prepared by mixing diisopropylamine (2.80 mL, 20 mmol) and *n*-butyllithium (10 mL of 1.6 M in hexane, 16 mmol) in 12 mL of anhydrous ether at –30 °C under an atmosphere of nitrogen. This solution was allowed to warm to room temperature and cooled to 0 °C prior to addition of a solution containing 21 (349 mg, 1.26 mmol) in 12 mL of ether. The reaction mixture was kept at room temperature for 60 h and cooled again to 0 °C before being quenched with 2 mL of saturated ammonium chloride solution. The reaction mixture was then diluted with 50 mL of ether, transferred to a separatory funnel, and washed sequentially with water, 2 M hydrochloric acid, and water (50 mL each). The resultant solution was filtered through a plug of magnesium sulfate and evaporated. Purification of the residue on silica gel (thick-layer plate, double elution with dichloromethane) afforded 272 mg (77%) of 22a as a colorless oil: IR (neat) ν_{max} 3360, 3020, 2920, 1640, 1600, 1490, 1440, 1260, 1070, 1030, 710 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.05 (br s, 10 H), 6.70–6.20 (m, 1 H), 6.05–5.70 (m, 1 H), 5.25–4.80 (m, 1 H), 3.50–3.10 (m, 4 H), 2.95–2.55 (m, 1 H), 2.50–2.10 (m, 2 H); mass spectrum (for $\text{M}^+ - \text{H}_2\text{O}$), calcd m/e 258.1408, obsd 258.1402.

endo,endo-7,8-Diphenylbicyclo[4.1.1]octa-2,4-diene (10). Method A. A mixture consisting of dibromide 19 (930 mg, 1.21 mmol), lithium carbonate (1.50 g, 20.30 mmol), lithium chloride (1.10 g, 25.95 mmol), and 30 mg of finely ground soft glass in 6

mL of hexamethylphosphoramide was vigorously stirred under nitrogen while being heated at 110 °C for 7 h. After being cooled to room temperature, the reaction mixture was poured into 150 mL of water and extracted with ether (2 × 250 mL). The combined extracts were washed with an equal volume of water and dried. The residue left upon evaporation of the ether was passed through a column of basic alumina (3 cm × 3 cm, elution with 125 mL of 9:1 hexane-ether). Concentration of the eluate afforded a colorless oil that solidified with external dry ice cooling, leaving 457 mg of a crystalline mass. Several recrystallizations of a small sample of the above from methanol furnished the diene in pure form: mp 74 °C; IR (CDCl₃) ν_{max} 3020, 2960, 1600, 1490, 1440, 1070, 1030, 900 cm⁻¹; 200 MHz ¹H NMR (CDCl₃) δ 7.13-6.95 (m, 10 H), 6.56-6.47 (m, 2 H), 6.02-5.96 (m, 2 H), 3.45 (s, 2 H), 3.39-3.36 (m, 2 H); ¹³C NMR (CDCl₃) 142.4, 137.6, 127.8, 126.8, 125.4, 124.5, 44.0, 39.8 ppm; mass spectrum, calcd *m/e* 258.1408, obsd 258.1402; UV (isooctane) 268 nm (ϵ 550), 273 (950), 286 (1300), 295 (960). This material yellowed rapidly when in solution and exposed to light. It was therefore expedient to purify samples immediately before use.

Method B. A solution containing allylic alcohol **22a** (240 mg, 0.86 mmol) in 1.5 mL of hexamethylphosphoramide was stirred at 60 °C under nitrogen while methyltriphenoxyposphonium iodide (780 mg, 1.73 mmol) was added in one portion. After 2 h at 60 °C, the resultant solution was heated for an additional 5 h at 105 °C. The contents were cooled to room temperature, poured into 15 mL of 2.7 M aqueous potassium hydroxide solution, and extracted with 1:1 pentane-ether (2 × 250 mL). The total organic layer was washed once with brine (100 mL), dried, and evaporated. The remaining oil was chromatographed on neutral alumina (thick-layer plate, double elution with hexane). This served to separate most of the yellow chromophoric material and afforded a broad band which amounted to 136 mg and whose composition was indicated by analytical TLC to consist mostly of the desired diene and a slower moving component (presumed to be **22b**). This material was dissolved in 2 mL of tetrahydrofuran, an excess of 1,8-diazabicyclo[5.4.0]undec-7-ene was added, and the solution was magnetically stirred at room temperature under nitrogen. After 36 h, the lower *R_f* spot had disappeared. Silica gel chromatography of the residue (thick-layer plate, elution with hexane) afforded 20 mg (9%) of **10** as a colorless oil. This material crystallized after standing overnight at 0 °C and was identical with those samples of **10** prepared above. For allylic iodide **22b**: ¹H NMR (CDCl₃) δ 7.33-6.76 (br m, 10 H), 6.26-5.33 (series of m, 3 H), 3.46-3.13 (m, 2 H), 3.13-2.83 (m, 2 H), 2.70-2.40 (m, 2 H).

Photolysis of 10: *all-trans*-1,8-Diphenyl-1,3,5,7-octa-tetraene (**24**). Into a quartz NMR tube was placed **10** (46 mg) as a solution in 0.5 mL of glyme-*d*₁₀. Irradiation for 10 min in a Rayonet chamber equipped with a bank of ten 254-nm bulbs

left a yellow solution whose NMR spectrum already showed a scattering of the phenyl signals. Additional irradiation occasioned the deposition of bright yellow platelets. After a total of 150 min, the irradiation was halted. More precipitation was prompted by cooling the tube at 0 °C for several minutes. The crystals so obtained amounted to 18.6 mg: mp 221-229 °C (lit.^{39,40} mp 232 °C); ¹H NMR (CDCl₃) multiplets at δ 7.39-7.26 and 6.64-6.42 with a ratio of 10:8, respectively; mass spectrum, calcd *m/e* 258.1408, obsd 258.1415. The decanted portion of the reaction mixture was chromatographed on silica gel to afford 6 mg of unreacted diene and a complex mixture of other yellow materials.

Crystal Data, Data Collection, Structural Solution, and Refinement. The crystals of **10** were orthorhombic, space group *Pcab*, with *a* = 10.489 (4), *b* = 10.677 (3), and *c* = 26.524 (7) Å and with *d*_{calcd} = 1.155 g cm⁻³ for *Z* = 8 (C₂₀H₁₈, *M_r* = 258.36). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu K α radiation, θ -2 θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.20 × 0.5 × 0.6 mm. A total of 2004 independent reflections were measured for $\theta < 57^\circ$, of which 1597 were considered to be observed [*I* > 2.5 σ (*I*)]. The structure was solved by a multiple-solution procedure⁴⁹ and was refined by full-matrix least-squares methods. Three reflections which were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms, and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations, but their parameters were not refined. The final discrepancy indices are *R* = 0.040 and *R_w* = 0.046 for the remaining 1594 observed reflections. The final difference map has no peaks greater than ± 0.1 eÅ⁻³.

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Registry No. **10**, 83681-47-4; **12**, 528-38-1; **12** dichloride, 20324-70-3; **13**, 83729-96-8; **14**, 83681-42-9; **15** (isomer 1), 83681-41-8; **15** (isomer 2), 83709-52-8; **16**, 83692-50-6; **17**, 83681-43-0; **18**, 83681-45-2; **19**, 83681-46-3; **20** (isomer 1), 83729-99-1; **20** (isomer 2), 83681-44-1; **21**, 83681-49-6; **22a**, 83681-50-9; **22b**, 83681-51-0; **23**, 83681-48-5; **24**, 22828-29-1.

Supplementary Material Available: Final atomic (Table IV) and anisotropic thermal parameters (Table V) for **10** (2 pages). Ordering information is given on any current masthead page.

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Formation of Nonaromatic Products in the Chlorination of Simple Substituted Aromatic Ethers

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The neat chlorination of 4-chloroanisole produces 1,3,4,5,6-pentachloro-4-methoxycyclohexene in 35% yield. Mono- and dichlorinated anisoles and a variety of simple substituted anisoles were chlorinated to determine the generality of nonaromatic product formation. 3,4-Dichloroanisole, 4-fluoroanisole, 4-bromoanisole, 4-methylanisole, and 4-chlorophenetole form similar products based on their spectral properties. These products are proposed to form by a *cis*-1,2 chlorine addition followed by a rapid *cis*-1,4 chlorine addition. On the basis of the NMR data, a predominate configuration is proposed.

Previously we reported that during the neat chlorination of anisole there is, in addition to the expected aromatic products, a nonaromatic product, 1,3,4,5,6-pentachloro-4-

methoxycyclohexene, **2**, which forms in 28% yield (Scheme I). The formation of **2** was determined to originate not from anisole but from 4-chloroanisole, **1**, in 35% yield.¹