was passed through a cold (-40 °C) Florisil column (elution with hexane). There was obtained a colorless oil, the ^{1}H NMR spectrum of which showed it to be a mixture of **20**, **22**, and **23** (ratio differed somewhat from run to run).

Comparable treatment of **24** afforded a mixture of **22** and **23** in a 1:1 ratio.

Procedure for Determining the Rates of Electrocyclic Ring Opening in 20 and Bond Shifting in 22 ⇄ 23. A small amount (about 25 mg) of the hydrocarbon prepared as above was dissolved in $CDCl_3$ and transferred to an NMR tube. The solution was degassed by three freeze-thaw cycles, sealed under vacuum, and placed in the thermally equilibrated constant-temperature probe of a Bruker HX-90 NMR spectrometer. After allowance was made for thermal equilibration (several minutes), FT spectra (four scans) were taken at appropriate time intervals. The olefinic proton region was recorded on fully expanded scale and the peaks were machine integrated.

Estimated values of the rate constants k_2 and k_3 were obtained using a nonlinear least squares fit of eq 4 to be experimental data. In this procedure, a measure of "goodness of fit" χ^2 was minimized with respect to each of the parameters k_2 and k_3 simultaneously (eq 5). The calculations were carried out using an appropriately modified version of the routine CURFIT.[46]

$$\chi^2 = \sum\{[y_i - y_i(x_i)]^2/\sigma_i^2\} \qquad (5)$$

Single-Crystal X-ray Analysis of 17*. A single crystal ~0.3 mm^3 was chosen for diffraction work. Preliminary X-ray photographs showed orthorhombic symmetry. Accurate lattice constants, obtained by a least-squares fit of 15 moderate 2θ values, were: **a** = 10.8527 (9), **b** = 15.1095 (13), and **c** = 15.9280 (13) Å. Systematic extinctions and the presence of chirality were uniquely accommodated by space group $P2_12_12_1$ and density considerations suggested one molecule of composition $C_{28}H_{41}N_3O_2$ formed the asymmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using a variable speed, 1° ω-scan and graphite monochromated Cu Kα radiation (1.54178 Å). Of the 2043 reflections collected in this manner, 1969 (95%) were judged observed after correction for Lorentz, polarization, and background effects ($F_o^2 \geq 3\sigma(F_o^2)$).

A phasing model was achieved using a multisolution weighted tangent formula approach in which four special and one general reflection served as a starting set for 200 E's.[47] An E synthesis calculated from the most favorable solution showed 30 plausible nonhydrogen atoms. The remaining nonhydrogen atoms were found on a subsequent F synthesis and the hydrogens on a ΔF synthesis after partial refinement. Full-matrix, least-squares refinements with anisotropic nonhydrogen atoms and fixed isotropic hydrogens have currently converged to a standard crystallographic residual of 0.095. Further crystallographic information can be found in the Supplementary Material.

Acknowledgment. This research was supported in part with funds provided by the National Science Foundation (CHE-790033) and NIH-NCI (CA-24487). The authors are also indebted to Mr. Gregory Wells for his early pioneering experiments and to Professor N. L. Allinger for enlightening correspondence.

Supplementary Material Available: Racemization rate data and activation parameters for (+)-**7**, polarimetric data obtained for the racemization of (+)-**7***, exemplary rate data for the conversion **20** → **22** ⇌ **23** at 36 °C and 46 °C, bicyclooctatriene electrocyclic ring opening and bond shifting rate data for **12** ≈ **20** and **7** ≈ **22** ≈ **23**, a compilation of racemization, bond shifting, and ring inversion rate data for 1,3-(t-Bu)$_2$COT, and fractional coordinates, temperature factors, bond distances, bond angles, and structure factors for **17*** (17 pages). Ordering information is given on any current masthead page.

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Bond Fixation in Annulenes. 12. Effect of Vicinal Di-*tert*-butyl Substitution on Cyclooctatetraene Valence Isomerization.

7,8-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene[1]

Yuji Hanzawa[2] and Leo A. Paquette*

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210. *Received July 28, 1980*

Abstract: 7,8-Di-*tert*-butylbicyclo[4.2.0]octa-2,4,7-triene (**3**) has been prepared by Diels-Alder addition of cyclobutadiene to 3,4-di-*tert*-butylcyclopentadienone and pyrolysis of the adduct. Because of unusually high levels of peripheral steric strain, **3** does not undergo observable ring opening to the cyclooctatetraene. This example is the first where the less stable [8]annulene valence tautomer is seen to be thermodynamically favored in the absence of constraining influences (e.g., bridged systems). Flash vacuum pyrolysis of the title compound at 550 °C gave both bond shift isomers of 1,4-di-*tert*-butylcyclooctatetraene.

During the past 2 decades, studies conducted in several leading international laboratories have demonstrated that cyclooctatetraene is capable of three fundamental structural changes, the energetic demands of which for the parent hydrocarbon fall in the order: ring inversion < bond shifting ≪ valence isomerization.[3,4] While the first two phenomena are related in their common dependence on the attainment of a planar transition state, the conversion to bicyclo[4.2.0]octa-2,4,7-triene requires disrotatory cyclization of three contiguous double bonds. Despite the richness of cyclooctatetraene's dynamic behavior, little attention has previously

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[1] Part 11. Paquette, L. A.; Hanzawa, Y.; McCullough, K. J.; Tagle, B.; Swenson, W.; Clardy, J. preceding paper in this issue.

[2] Graduate School Postdoctoral Fellow, 1979-1980.

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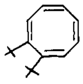
been directed to an analysis of the manner in which these processes might deal with *exceptionally high levels* of steric strain.

The mechanics by which acyclic and simple cyclic molecules cope with strain effects is presently rather well understood.[5] As molecules become increasingly rigid, their ability to accommodate this type of excess energy is lessened and striking alterations in physical and chemical properties can frequently be seen. For example, the 22 kcal/mol of strain energy present in *o*-di-*tert*-butylbenzene[6] does not result in any serious perturbation of benzenoid aromaticity, but is manifested in bond angle distortion[7] and facile extrusion of a *tert*-butyl group.[6,8] In 1,8-di-*tert*-butylnaphthalenes, the peri substituents reside on opposite sides of the mean plane of the aromatic ring, exhibit a heightened barrier to ring flipping (> 24 kcal/mol), and find it possible to rotate about the C_{alkyl}–C_{aryl} bonds with increased facility (~6.5 kcal/mol).[9]

Our interest in [8] annulenes such as **1** and **2** follow directly from the preceding considerations. Because of the tub-shaped molecular conformation of such systems, the *tert*-butyl substituents in **1** can in principle maintain a reasonable distance. However,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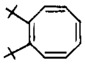
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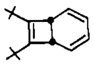
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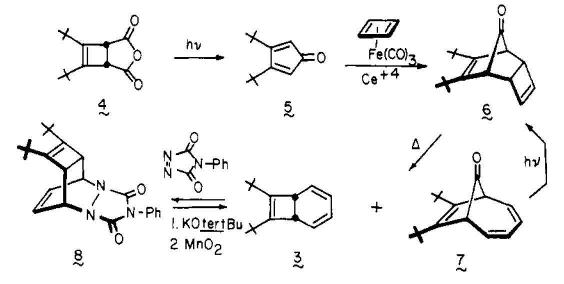
there is anticipated to exist a reluctance for involvement in any conformational change that would compress the dihedral angle by which these groups would be separated. In contrast, **2** shares in part the character of *cis*-di-*tert*-butylethylene,[10] an olefin of established high strain energy.[11] As the cyclooctatetraene ring progresses from its preferred puckered form toward a planar conformation, there occurs an expansion of its internal bond angles from 126° to approximately 135°.[12] Since this structural perturbation necessarily leads to enhanced steric compression of the peripheral substituents,[1,13-15] **2** should prove recalcitrant to both bond shifting and ring inversion. In this paper, we describe a convenient synthesis of **3** and report on the dramatic discovery that **3**, unlike all previously known bicyclo[4.2.0]octatrienes,[1,16-20] exhibits no observable tendency to undergo electrocyclic ring opening, forcing conditions notwithstanding.

Results

Photolysis of anhydride **4** in ether solution through Vycor with a 450-W Hanovia lamp, in line with a prior disclosure by Maier and co-workers,[21] gave 3,4-di-*tert*-butylcyclopentadienone (**5**).



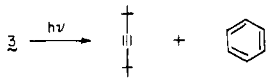
Diels–Alder addition of cyclobutadiene to **5** proceeded efficiently to deliver **6**, the stereochemistry of which conforms to its ^{1}H NMR spectral features (see Experimental Section) and the well-known adherence of cyclobutadiene to secondary orbital overlap control.

Contrary to existing precedent,[22,23] the photochemical activation of **6** under a variety of conditions invariably provided very complex product mixtures. When diglyme-d_{14} solutions of **6** were heated to 160–170 °C, comparable difficulties were encountered. However, recourse to flash vacuum pyrolysis at 200–210 °C and 1–1.5 Torr led to the formation of hydrocarbon **3**, bicyclic ketone **7**, and several minor unidentified aromatic compounds whose separation was readily achieved by chromagraphic means.

The structural assignment to **7** follows from its ^{1}H and ^{13}C NMR spectra (see Experimental Section) and its quantitative reconversion to **6** upon irradiation at 2537, 3000, or 3500 Å. Informatively, **7** proved stable to the conditions utilized for the thermolysis of **6**. Consequently, **7** does not serve as a precursor to **3**. This observation implies that the bicyclo[4.2.0]octatriene may arise by direct [$_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s$] cleavage within **6**.

Triene **3** proved to be an air-sensitive oil which reacted readily with *N*-phenyltriazolinedione to give adduct **8** from which it could be regenerated. The location of the pair of *tert*-butyl groups in both **3** and **8** was easily recognized from their ^{1}H NMR spectra. The four cyclohexadiene vinylic protons in **3** which appear as a multiplet at δ 5.82–5.4 become well separated in **8** (δ 6.13 and 5.0) owing to the generation of two bridgehead sites adjacent to nitrogen. In neither case were cyclobutene vinylic protons in evidence.

Furthermore, irradiation of **3** in a Rayonet reactor fitted with a bank of 2537-Å lamps resulted in facile retrograde [2 + 2] cycloaddition[24] to give benzene and di-*tert*-butylacetylene in quantitative yield. No evidence was found for transitory opening to **2** during this transformation.



Bicyclo[4.2.0]octatriene **3** proved to be rather thermally stable. Flash vacuum pyrolyses conducted below 400 °C at 0.1 Torr led to efficient recovery of starting material. Above this temperature, the formation of products became detectable. For preparative purposes, the isomerizations were performed at 550 °C and 0.1–0.25 Torr. Under these conditions, low yield conversion to a mixture of the bond shift isomers of 1,4-di-*tert*-butylcyclooctatetraene (**11** $\rightleftarrows$ **12**) took place. An independent synthesis of **11** and **12** was subsequently achieved and will be reported sepa-

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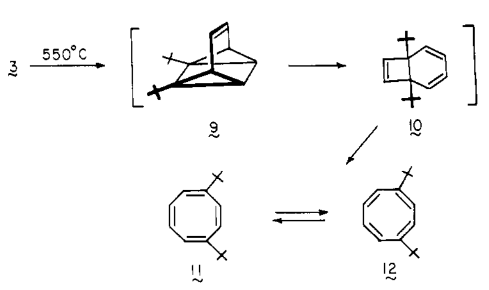
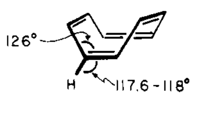


rately. Subsequent to preparative VPC purification and isolation (column temp 150 °C), the ^{1}H NMR spectrum of the **11** ⇄ **12** mixture was seen to consist of two high-field singlets at δ 1.11 and 1.10 (ratio 1:2) and vinylic proton signals at δ 6.03, 5.96, 5.9, 5.7, and 5.6. The relative ratio of the two regions was 1:3, weighted, of course, in favor of the *tert*-butyl resonances. Thin layer chromatography of this sample on silica gel (hexane elution) showed two spots. Recovery of the major (lower R_f) component showed it to consist of one of these isomers: ^{1}H NMR (δ, $CDCl_3$) 6.03 (s, 2 H), 5.7 (m, 2 H), 5.6 (m, 2 H), and 1.11 (s, 18 H). When allowed to stand at room temperature, such solutions gradually developed the spectral characteristics of the **11** ⇄ **12** mixture. The change was complete in less than 2 h. Subsequent to recovery of the minor component from the silica gel plate, a ^{1}H NMR spectrum identical with that of the mixture was recorded. Evidently, the rate of bond shifting in this isomer is faster than that in its more polar counterpart.

The conversion of **3** to **11** and **12** is precedented[24,25] and is most concisely rationalized in terms of intramolecular Diels–Alder cycloaddition within the bicyclo[4.2.0]octatriene to give the tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octene intermediate **9**. Subsequent [$_\sigma 2_s$ + $_\sigma 2_s$ + $_\pi 2_s$] ring opening of this *cis*^{2}-bishomobenzene leads to the new bicyclo[4.2.0]octatriene **10** which is not sterically hampered from opening to the observed products.

Discussion

With the stability of **3** relative to its [8]annulene form (**2**) established, it becomes of interest to assess the relative importance of various strain contributions which come into play in establishing the equilibrium position of this valence tautomerization. X-ray[26] and electron diffraction[27] studies of the parent cyclooctatetraene molecule have revealed the ring to be tub-shaped with a relevant external bond angle of 117.6–118° (see **13**) and a torsion angle about the C–C single bonds of 56–58°. By way of comparison, X-ray structural determinations of non-benzo-fused cyclobutene systems[28] such as **14**,[29] **15**,[30] and **16**[31] predictably show that a four-membered unsaturated ring projects the sp^2-bound substituents at substantially wider angles away from each other (128–135°). Therefore, the steric compression of two *tert*-butyl groups positioned 1,2 on the cyclooctatetraene frame as in **2** will be better satisfied by conversion to **3**. However, the existence of a cyclobutene ring in **3** is not without energetic costs of its own. Huisgen has established the energy of activation for electrocyclization within cyclooctatetraene to be 27.2 kcal/mol.[32] The reversal of this process in bicyclo[4.2.0]octatriene requires an E_{act} of 18.7 kcal/mol.[33,34] Thus, a rough estimate of the energy difference between the mono- and bicyclic forms is 8.5 kcal/mol. The present data suggest that the strain relief which materializes in **3** is of a degree adequate to preserve the bicyclooctatriene characteristics of the system.



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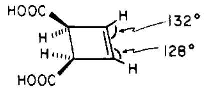

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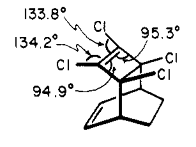

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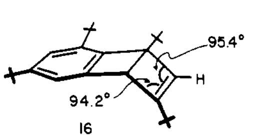

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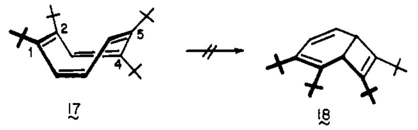
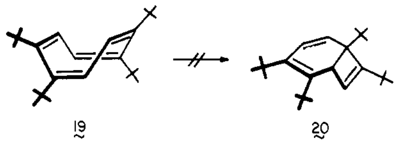
Some appreciation of the upper limit of these energetics can be gained by consideration of the properties of two tetra-*tert*-butyl cyclooctatetraenes prepared by Maier and co-workers.[35] In **17**, for example, there is observed no tendency on the part of the [8]annulene for ring closure to **18**, the release of nonbonded interactions between the 1,2-substituents notwithstanding. This is undoubtedly because the neighboring, but relatively remote *tert*-butyl groups at C-4 and C-5 in **17** must experience substantial steric compression in **18** where they now must share the space available external to a cyclohexene double bond. The level of strain experienced by 1,2 substituents in **17** and the 4,5 groups in **18** are probably closely compensatory, and the destabilization present in the bicyclooctatriene nucleus regains the equilibrium-dictating position.





Comparable analysis of **19** shows that the [8]annulene frame so nicely accommodates the four *tert*-butyl groups that electrocyclization to **20** could not possibly offer a more sterically advantageous situation.

Accordingly, the substitution plan of the title bicyclo[4.2.0]-octatriene (**3**) is presently unique in that it best minimizes steric interaction between the peripheral substituents and allows the less stable nucleus to be thermodynamically favored.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with a Varian T-60 instrument and apparent splittings are given in all cases. The ^{13}C NMR spectra were recorded on a Bruker HX-90 instrument. Mass spectra were measured with an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

1,2-Di-*tert*-butylcyclobutenedicarboxylic Acid Anhydride (4).[36] A solution of maleic anhydride (10 g, 0.10 mol), di-*tert*-butylacetylene[37] (30

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[36] Described in the Fritschi thesis, ref 35b.

g, 0.22 mol), and benzophenone (4 g) in 300 mL of dry acetone was irradiated at room temperature through Pyrex with a 450-W Hanovia lamp for 40 h. Following solvent evaporation, the residue was sublimed at 100 °C and 0.4 Torr and recrystallized from pentane. There was isolated 10 g of **4** as colorless crystals, mp 125 °C (lit.[36] mp 125 °C): IR (CCl_4, cm^{-1}) 1860 and 1780; ^1H NMR (δ, CCl_4) 3.71 (s, 2 H) and 1.23 (s, 18 H).

3,4-Di-*tert*-butylcyclopentadienone (5).[20] Anhydride **4** (3.302 g, 0.014 mol) in ether (600 mL, freshly distilled from benzophenone ketyl) was irradiated through Vycor with a 450-W Hanovia lamp for 2 h. The pale yellow solution was concentrated to dryness and the residual oil was passed through a silica gel column (40 × 2.5 cm) with pentane–ether (100:1) elution. There was isolated 486 mg (18%) of a pale yellow oil which slowly crystallized (lit.[20] mp 47.5–48.5 °C): IR (CCl_4, cm^{-1}) 1708 cm^{-1}; ^1H NMR (δ, CCl_4) 5.35 (s, 2 H) and 1.36 (s, 18 H).

***endo*-7,8-Di-*tert*-butyltricyclo[4.2.1.0^{2,5}]nona-3,7-dien-9-one (6).** To a cold (−5 °C) magnetically stirred solution of **5** (89 mg, 0.46 mmol) and cyclobutadieneiron tricarbonyl (152 mg, 0.79 mmol) was slowly added 2.13 g of ceric ammonium nitrate in portions during 1 h under an argon atmosphere. Upon completion of the addition, ether was added and the precipitated solid was removed by filtration. The filtrate was washed with water and brine, dried, and evaporated. The residual oil was purified by preparative thin layer chromatography on silica gel (elution with hexane–ether 10:1) to give 81 mg (72%) of **6** as colorless crystals, mp 80 °C (preparative VPC on 5% FFAP, 160 °C): IR (CCl_4, cm^{-1}) 1770; ^1H NMR (δ $CDCl_3$) 5.75 (pseudo-s, 2 H), 3.0 (narrow m, 4 H), and 1.28 (s, 18 H); ^{13}C NMR (ppm, $CDCl_3$) 199.84, 143.58, 136.18, 53,86, 39.39, 32.95, and 32.53; *m/e* calcd 244.1827, obsd 244.1832.

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.47; H, 10.01.

Flash Vacuum Pyrolysis of 6. In a typical experiment, a 318-mg (1.3 mmol) sample of **6** was subjected to flash vacuum pyrolysis on a quartz apparatus heated to 200–210 °C at a pressure of 1–1.5 Torr. The thermolysate was collected at −78 °C by placement of the cold finger directly at the exit port of the pyrolysis chamber. The resulting mixture was separted into its components by preparative thin layer chromatography on silica gel (elution with hexane–ether 30:1). In addition to recovered **6** (25 mg) and several unidentified aromatic components (total of 29 mg), there was isolated 27 mg of **3** which proved to be a somewhat sensitive colorless oil: ^1H NMR (δ, $CDCl_3$) 5.82–5.4 (m, 4 H), 3.2 (narrow m, 2 H), and 1.2 (s, 18 H); ^{13}C NMR (ppm, $CDCl_3$) 129.87, 128.36, 121.08, 38.50, 31.36, and 30.63; *m/e* calcd 216.1878, obsd 216.1882.

The most polar product proved to be ketone **7**, mp 107–108.5 °C, after sublimation at 60–70 °C and 0.1 Torr: IR (CCl_4, cm^{-1}) 1760; ^1H NMR (δ, $CDCl_3$) 5.8–5.6 (m, 4 H), 3.4–3.16 (m, 2 H), and 1.33 (s, 18 H); ^{13}C NMR (ppm, $CDCl_3$) 215.56, 146.02, 132.43, 124.15, 58.85, 34.64, and 33.25; *m/e* calcd 244.1827, obsd 244.1834.

***N*-Phenyltriazolinedione Addition to 3.** A solution of **3** (27.1 mg, 0.13 mmol) in $CDCl_3$ was treated with *N*-phenyltriazolinedione until the red color persisted. Evaporation of solvent and short-path chromatography on silica gel (chlorofrom elution) afforded **8** in quantitative yield. Colorless needles, mp 209–211 °C, were obtained upon recrystallization from ethyl acetate: ^1H NMR (δ, $CDCl_3$) 7.36 (m, 5 H), 6.13 (m, 2 H), 5.0 (m, 2 H), 2.95 (m, 2 H), and 1.13 (s, 18 H); *m/e* calcd 391.2260, obsd 391.2265.

Anal. Calcd for $C_{24}H_{29}N_3O_2$: C, 73.63; H, 7.47. Found: C, 73.48; H, 7.49.

Hydrolysis–Oxidation of 8. A solution of **8** (147 mg, 0.38 mmol) in isopropyl alcohol (15 mL) was heated to the reflux temperature with sodium hydroxide (300 mg) under a nitrogen atmosphere for 20 h. The mixture was cooled in ice–water and acidified with 3 N hydrochloric acid. Ammonium hydroxide (3 N) was introduced to make the solution basic. Hexane (20 mL) and activated manganese dioxide (300 mg) were added and the mixture was stirred at room temperature for 30 min. The organic phase was separated and the aqueous layer was extracted with hexane (2 × 100 mL). The combined organic layers were washed with water and brine prior to drying and solvent evaporation. The residual oil was passed through a Florisil column with hexane elution. There was isolated 73 mg (89%) of **3**.

Photoisomerization of 7. A solution of **7** (10 mg) in anhydrous ether (10 mL) was irradiated in a Rayonet reactor fitted with a bank of 2537-Å lamps for 20 min. Following removal of solvent, the ^1H NMR spectrum of the product was recorded in $CDCl_3$ solution. Tricyclic ketone **6** was seen to be formed completely.

Several additional irradiations were conducted in NMR tubes ($CDCl_3$ solutions) at 3000 and 3500 Å. Longer reaction times were required (1.5 h), but complete conversion to **6** was again seen.

Photolysis of 3. A THF-d_8 solution of **3** (14 mg) contained in a quartz NMR tube was flushed with argon and irradiated in a Rayonet reactor fitted with 2537-Å lamps. The progress of reaction was checked at 10-min intervals and found to be complete after 1 h. Clean quantitative conversion to benzene and di-*tert*-butylacetylene was observed.

Thermal Rearrangement of 3. The bicyclo[4.2.0]octatriene (0.30 g, 1.43 mmol) was subjected to flash vacuum pyrolysis at 550 °C and 0.1 Torr. The pyrolysate (ca. 100 mg) was collected on a cold finger (dry ice–ether bath) positioned at the exit of the pyrolysis tube. This material was dissolved in a small amount of ether and directly subjected to preparative VPC purification (8 ft × 0.25 in. 15% DEGS on Chromosorb W, 150 °C). Collection of the major component gave 16 mg of colorless oil: ^1H NMR (δ, $CDCl_3$) 1.10 and 1.11 (ratio 1:2), 5.6, 5.7, 5.9, 5.96, and 6.03. The ratio of the vinyl proton absorptions to the *tert*-butyl peaks was 1:3.

Thin layer chromatography on silica gel (hexane elution) showed two clean spots and gave 4.2 mg of the higher R_f component and 7.3 mg of the low R_f component. The first of these exhibited a ^1H NMR spectrum identical with the above. The latter substance was characterized by three olefinic absorptions (6.03, 5.7, and 5.6) and a sharp singlet at δ 1.11. On standing at room temperature, this spectrum gradually changed into that previously observed; *m/e* calcd 216.1878, obsd 216.1872.

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