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Stereocontrolled Synthesis, Conformational Features, and Response to Thermal Activation of the Seven Possible Bis- and Trishomocycloheptatrienes

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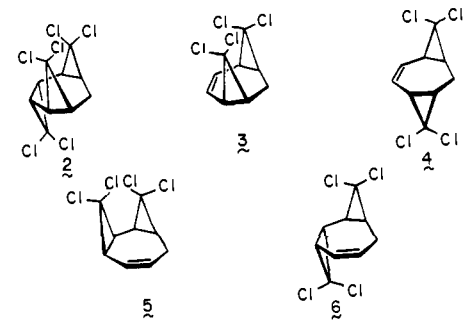
Abstract: The stereocontrolled synthesis of the seven possible bis- and trishomocycloheptatrienes is detailed. Reaction of cycloheptatriene with dichlorocarbene and subsequent reductive dechlorination has afforded *syn*- (**8**) and *anti*-1,5-bishomocycloheptadienes (**9**) together with the anti,anti-trishomo derivative **7**. Sequential treatment of **9** with dibromocarbene and sodium in *tert*-butyl alcohol/tetrahydrofuran provided exclusively the anti,syn-trishomo framework (**11**). Preparation of the stereoisomeric 1,3-bishomocycloheptadienes **20** and **23** began by exhaustive cyclopropanation of 3,5-cycloheptadienol. Following Collins oxidation to the derived ketones, the requisite olefinic units were introduced by lithium–ammonia reduction of the enol phosphates. The remaining trishomo derivative **24** was obtained by cyclopropanation of **20** with methylene iodide and zinc–silver couple. The conformational populations of these tri- and tetracyclic systems were revealed by detailed NMR examination which included variable-temperature studies. The most interesting compound proved to be **9** which undergoes facile degenerate ring inversion with E_a = 8.13 kcal/mol and $\Delta H^{\ddagger}$ = 7.74 kcal/mol. A decrease in conformational flexibility relative to cycloheptatriene (by ca. 2.3 kcal/mol) was thereby revealed. Lastly, the susceptibility of all seven hydrocarbons to thermal rearrangement was assessed.

Although the concepts of homoconjugation and homoaromaticity have elicited much interest in recent times,[2] the interactions which are so strikingly manifested in monohomo examples have less frequently been sought in systems having the intrinsic structural capability for more extended electronic delocalization.[3] Bis- and trishomocycloheptatrienes, for example, potentially bring this dimension to the chemistry of the familiar tropylium ion. Yet, none of the seven possible hydrocarbons which belong to this series have been reported to this time.[4] The primary goal of the present study was to devise unequivocal routes to these molecules such that all possible stereoisomers were fully characterized. Ancillary objectives were examination of the conformational characteristics of the title hydrocarbons and determination of their susceptibility to thermal bond reorganization. The success of the synthetic schemes to be described has provided substrates directly relevant to mechanistic studies of long-range cyclopropyl interaction,[5a,b] photoelectron spectroscopic analysis of extended cyclopropane interaction,[6] and the general question of stereochemical requirements for trishomoaromaticity.[5c]

Synthetic Considerations

The consequences of adding dichlorocarbene to cycloheptatriene (**1**) under conditions of phase transfer catalysis were first examined. Contrary to the report of Sasaki and coworkers,[7] one tricyclopropanated (**2**) and two biscyclopropanated compounds (**3** and **4**) were produced and readily separated by a combination of column chromatography on silica gel and fractional crystallization. Rigorous stereochemical assignments to these adducts could, of course, not be made on the basis of their ^{1}H NMR spectra. However, because the cyclopropyl protons in **2** appear as a narrow signal at δ 1.80 and the pair of methylene protons gives rise to multiplets centered at 2.36 and 1.18, a symmetrical structure is seemingly implicated for this product. The level of anisotropic shielding operating on the latter of these hydrogens is particularly noteworthy. The spectra of **3** and **4** also reveal symmetrical patterns consistent with molecular frameworks having either C_s or C_2 symmetry (see Experimental Section).

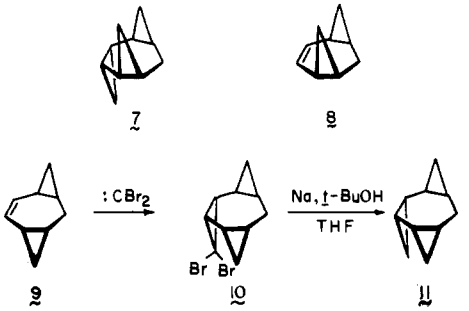


From the demonstrated absence of **5** and **6** (vide infra), the preferred initial site of dichlorocarbene attack on cycloheptatriene is inferred to be the C(1)–C(2) double bond. Subse-

quent reaction occurs at C(5)-C(6) with little stereochemical discrimination. This point was established by resubjecting both **3** and **4** to the original experimental conditions. While **3** entered readily into further reaction, **4** proved stable to further cyclopropanation. Since **3** was converted uniquely to **2**, the two flanking cyclopropane rings in the tris adduct must be stereodisposed as in the precursor molecule. Furthermore, the combined isolated yield of this pair ofihroductsi(29%) is seen to be roughly comparable with that realized for **4** (23%).

Reductive dechlorination of **2–4** with sodium and *tert*-butyl alcohol in ammonia/ether led smoothly to the structurally related hydrocarbons **7–9.** The ^{13}C NMR spectrum of **7** consists of six signals and is therefore that of a symmetrical molecule. Although the most direct proof for the anti,anti arrangement of the three-membered rings in **7** comes from its independent synthesis (vide infra), the rather complex ^{1}H NMR spectrum also attests to this stereochemistry. Thus, in addition to the cycloheptyl methylene protons which are characterized by widely divergent chemical shifts ($\Delta\delta \sim 2$ ppm), the twelve cyclopropyl protons appear as three quite differently weighted multiplets centered at δ 0.70 (9 H), 0.10 (1 H), and −0.05 (2 H). This pattern conforms to that expected for (a) the sum of the six peripheral and three "exo" cyclopropyl hydrogens, (b) the "endo" proton of the central cyclopropane ring, and (c) the remaining two shielded protons, respectively.

Assignment of structure to **8** rests upon its definitive ^{13}C (five peaks) and ^{1}H NMR spectra. In $CDCl_3$, the olefinic protons appear as a sharp singlet (δ 5.55), and the cycloheptyl methylene protons are now narrowly spaced (multiplets at 2.50 and 2.30). A rather broad multiplet in the 1.53–1.03 region due to the four remaining peripheral hydrogens is accompanied by two other complex absorptions attributable to the "exo" (0.78) and mutually shielded "endo" protons (0.00). These data are to be compared with those recorded for **9** whose ^{13}C spectrum

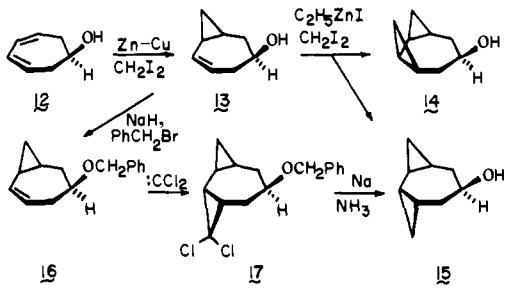


features four signals in the intensity ratio 2:1:4:2 and whose ^{1}H spectrum is characterized by an AA'BB' multiplet centered at δ 5.56 (2 H), a broadened triplet at 1.92 (2 H), and an intricate pattern ranging from 1.40 to 0.5 (8 H). Relevantly, the cycloheptyl methylene protons have now gained equivalence due to axial symmetry, and no anisotropic shielding is in evidence.

Dibromocarbene addition to **9** in pentane solution (KO-*t*-Bu, $HCBr_3$) or by means of phase transfer catalysis in a benzene-water mixture (NaOH, $HCBr_3$) provided the desired tetracyclic adduct **10.** Reductive debromination gave rise to anti,syn trishomo derivative **11.** Since this hydrocarbon lacks symmetry, all of its unique hydrogens combine to generate an exceedingly complex spectrum.

Exposure of **8** to ethylzinc iodide and methylene iodide proceeded stereospecifically to provide an alternate synthesis of **7.**

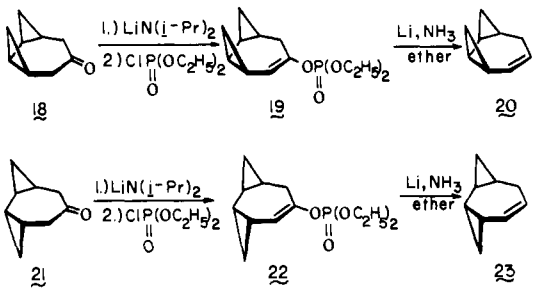
Preparation of the stereoisomeric 1,3-bishomocycloheptatrienes began by sodium borohydride reduction of tropone to form 3,5-cycloheptadienol (**12**).[8] That Simmons-Smith cyclopropanation of **12** leads to *cis*-bicyclo[5.1.0]oct-5-en-3-ol



(**13**) has been reported previously by Lambert.[9] Exposure of **13** to an excess of zinc-copper couple and methylene iodide in ether did not result in further reaction even after prolonged periods of reflux (up to 6 days). Although recourse to zinc-silver couple[10] and diethylzinc[11] proved somewhat more efficacious (47–48% conversion to biscyclopropanated products), ethylzinc iodide[12] emerged as the reagent of choice. After a reaction period of 23 h, **13** was transformed quantitatively into a mixture of bisadducts **14** and **15** (70:30). The two alcohols were readily separated by column chromatography on silica gel or by preparative scale VPC on SE-30.

In agreement with the established directing effect of the hydroxyl group,[13] the major product has all syn geometry. The C_s symmetry of **14** is clearly revealed by its ^{13}C (five signals) and ^{1}H NMR spectra supported by appropriate Eu(fod)$_3$ shift studies.[14] The stereochemical reversal which results in the formation of **15** appears to be the result of steric congestion on the syn face of **13** and not to unusual conformational factors such as those encountered in medium-ring allylic alcohols.[15] If this hypothesis is correct, the problem of reversing the directionality of this reaction so as to obtain **15** with high stereochemical control reduces to substitution of the hydroxyl function. In actuality, reaction of benzyl ether **16,** which is available from **13** in 97.5% yield, with dichlorocarbene under phase transfer conditions followed by reduction with sodium in ethereal liquid ammonia furnished **15** in 80% overall yield. The ^{13}C spectrum of this alcohol shows nine signals indicative of its unsymmetrical nature. The ^{1}H spectrum consists of a multiplet at δ 4.10 (1 H), a broad one-proton singlet at 1.08, multiplets of area 2 centered at 2.13, 1.27, and 0.00, and a four-proton multiplet at 0.72.

Collins oxidation[16] of **14** and **15** led essentially quantitatively to ketones **18** and **21.** Conversion of **18** to enol phosphate **19**



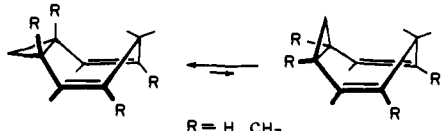
and subsequent treatment with lithium in ammonia gave syn bishomocycloheptatriene **20** in greater than 80% overall yield. Comparable application of the Ireland procedure[17] to **21** likewise resulted in smooth conversion to stereoisomeric olefin **23.** Cyclopropanation of **20** with methylene iodide and zinc-silver couple gave a 65:35 mixture of **11** and **24,** the third and final trishomocycloheptatriene. The final step in the synthesis of **24** involves a reaction so transparent that structural as-

signment hardly requires more elaborate justification. Notwithstanding, recognition of the simplicity of the ^{13}C spectrum (six peaks) and the anisotropic shielding effects prevailing upon all three "endo" cyclopropyl hydrogens [δ −0.05 (m, 2 H) and −0.38 (m, 1 H)] conforms uniquely with the syn,syn orientation of the three-membered rings.

Conformational Features

Detailed NMR studies have established that cycloheptatriene[18] and a number of its derivatives[19] exist as interconverting pairs of nonplanar conformers.[20] For the parent hydrocarbon, the two conformers are isoenergetic with an energy barrier separating them of approximately 6 kcal/mol.[18] In terms of experimental observation, the methylene protons are seen to remain isochronous down to −140 °C at 60 MHz. Below this temperature, the "axial" and "equatorial" H_7 protons gain individual identity and appear as two bands with the "axial" proton experiencing the greater shielding.[19] As substituents are introduced onto the ring, the barrier to conformational inversion may be decreased or enhanced depending upon their nature and position. For example, the trifluoromethyl groups in 7,7-bis(trifluoromethyl)cycloheptatriene remain isochronous down to −185 °C, presumably because the ring in this instance is rendered more planar and can invert more readily.[19b] In contrast, 7-*tert*-butyl-1-methylcycloheptatriene undergoes slow inversion at room temperature and prefers to exist in that conformation where the *tert*-butyl group is axially disposed.[19c]

Clearly, the conformational populations of such systems are delicately balanced by a number of factors. Any perturbation of the prevailing interactions produces a marked change not only in conformational distribution but also in the facility of the inversion process. Additional informative examples are the 3,4-homocycloheptatrienes **25**.[21] Although the barrier to interconversion of **25a** to **25b** has not been determined, an estimate has been made that transoid conformation **25a** is approximately 4 kcal/mol more stable than the cis form (**25b**).[21b] The lesser stability of **25b** is presumably due to the nonbonded repulsions which develop on the interior of the structure because of the interpenetration of the two endo protons. Comparable repulsions are certain to play a significant role in controlling the equilibrium thermodynamics of the bis- and trishomocycloheptatrienes described herein.



25a 25b

As concerns the anti,anti trishomo derivative **7**, conformation **26a** is seemingly free of serious nonbonded interactions

26a 26b

since all three cyclopropyl substituents adopt an "equatorial" relationship relative to the central seven-membered ring. Because conformational inversion leading to **26b** generates a structure having closely proximate pairs of hydrogens on both of its surfaces (and particularly the underside as drawn), this conformer is forced at best to approach a more energy demanding planar form to decrease such interactions. Distortions of this type should decisively favor **26a**, a conclusion which is fully supported by the NMR spectra. Its inflexible conformational nature at room temperature is signaled not only by the widely separated chemical shifts of the two cycloheptyl methylene protons (δ 2.38 and ca. 1.0), but also by the appearance of two appreciably shielded cyclopropyl hydrogens (δ −0.05). This observation requires that long-range anisotropic shielding by one or more of the cyclopropane rings[22] operate on a pair of chemically equivalent protons. This criterion is uniquely satisfied by the "endo" methylene protons of the 1,2 and 5,6 bridges which find themselves mutually projected into positions above the plane of the opposite cyclopropyl group. The methylene protons on the central cyclopropane ring are oriented away from the inner core and consequently do not experience these effects. Additionally, not one of the three-membered rings in **26a** is aligned geometrically to be capable of shielding the sp^3-hybridized cycloheptyl carbon.[23] As a consequence, the ^{13}C chemical shift of this atom (32.47 ppm) is lowest of all three $C_{10}H_{14}$ isomers (Table I).

Table I. ^{13}C Chemical Shift Data of the Trishomocycloheptatrienes[a]

Compd	Cycloheptyl methylene	Methines	Cyclopropyl methylenes
7	32.47	17.23, 15.32, 12.19	14.82, 14.22
11	26.98	16.91, 15.54, 14.95, 13.54, 12.19, 11.60	14.65, 12.41, 5.26
24	29.46	18.29, 16.62, 10.36	12.63, 7.55

[a] In ppm vs. Me_4Si ($CDCl_3$ solutions).

Using similar lines of reasoning, the preferred conformations of **11** and **24** are deduced to be **27** and **28**, respectively. That

27 28

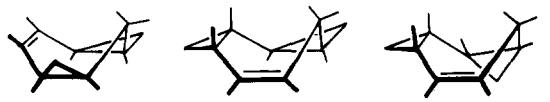
ring flipping is again inconsequential to these molecules on the NMR time scale at 30 °C is evident from the appearance of the "equatorial" H_7 proton at δ 2.37 (note constancy of this signal) and its "axial" counterpart above 1.55. In **27**, this particular cyclopropyl triad arrangement serves to orient the endo proton of the 3,4 and 5,6 bridges into the shielding region below the opposite three-membered ring. These protons are assumed to be the pair which gives rise to the high field multiplet at δ 0.1 to −0.01. In **28**, the severe nonbonded interaction generated between the cycloheptyl methylene group and the carbon of the 3,4 bridge is expected to be relieved by attainment of a more planar arrangement. Notwithstanding, at least four protons should be subject to effective anisotropic shielding. In agreement with this interpretation, two sets of resonances do appear above Me_4Si at δ −0.05 (2 H) and −0.38 (2 H).

Furthermore, the rigid three-dimensional features of **28** are such that C(7) can only experience moderate shielding by the somewhat remote central cyclopropane ring. For **27** one can discern that C(7) should experience an anisotropic effect from the more proximal axially disposed 1,2 bridge. The actual ^{13}C chemical shifts of these carbons are indeed shifted to higher field than that in **26**, and the ordering (29.46 and 26.98 ppm, respectively) is commensurate with the above estimate of long-range shielding.

The most reasonable conformations of **8** and **23** are those (**29** and **30**) in which both cyclopropyl groups are positioned in extended "exo" fashion. Interestingly, although the H_7 protons in **8** are clearly anisochronous (δ 2.50 and 2.30), the magnitude of the chemical shift difference has been greatly

Table II. Kinetic and Thermodynamic Data for the Thermal Rearrangement of **9**

T, °C	$k \times 10^5$, s^{-1}	Activation parameters
151.0	2.44	$\Delta H^{\ddagger} = 32.7 \pm 0.2$ kcal/mol
	2.53	$\Delta S^{\ddagger} = -3.1 \pm 0.5$ eu
162.6	7.16	$\Delta G^{\ddagger}_{298} = 33.7$ kcal/mol
	7.20	$E_A = 33.6 \pm 0.2$ kcal/mol
173.8	18.9	
	19.1	

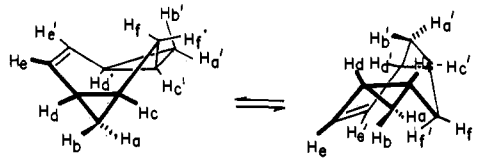


29 30 31

reduced by comparison to the $\Delta\delta$ values in related trishomocycloheptatrienes **7** and **24.** This dramatic trend is further accentuated in **23** where axial and equatorial H_7 now exhibit nearly identical resonances (ca. 2.13). This phenomenon is not attributable to a rapid conformational inversion process. Rather, this is a particularly good example of the differing spatial projections of π-olefinic and cyclopropyl anisotropic influences in rigid systems.

From a consideration of Dreiding models, the more thermodynamically favored conformation of **20** is deemed to be **31** where the 3,4 and 5,6 bridges reside in "equatorial" and "axial" environments, respectively. In the ring-flip form, considerable interpenetration of "axial" H_7 with the endo proton of the 3,4 bridge occurs with resultant energetic disfavor. Although the room-temperature ^1H NMR spectrum of **20** exhibits two well defined H_7 proton multiplets centered at δ 2.80 and 2.42, insufficient evidence is currently available to permit full consideration of the conformational mobility of this structure.

On the other hand, bishomocycloheptatriene **9** is seen to undergo rapid ring inversion at room temperature. The dynamic process is degenerate (**32a** $\rightleftarrows$ **32b**) and gives rise to an



32a 32b

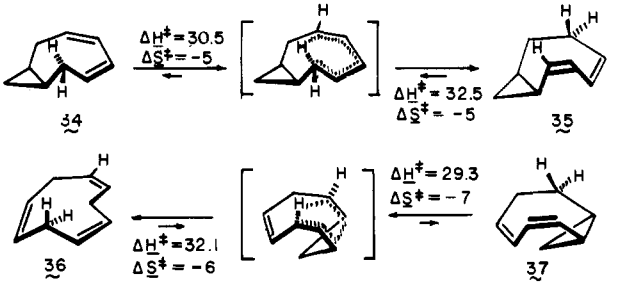
identical molecule in which the chemical environments of all six types of protons (labeled a-f) have been interchanged. Therefore, sufficiently rapid exchange of the environments of these six pairs of protons generates a spectrum determined by the time averaged environments of the exchanging nuclei. As the process is gradually slowed by external cooling, the spectrum passes through an intermediate stage showing broadened lines and ultimately appears as a superposition of the resonances of all individual nuclei.

Upon cooling chlorodifluoromethane solutions of **9,** the original cycloheptane methylene triplet first coalesced and then separated at −120 °C into two distinct signals due to $H_{f'}$ and H_f (partially hidden, see **32**) at δ 2.54 and 1.34 (J = 13.5 Hz), respectively. No further changes were noted below this temperature. Simutaneously, three protons originally centered at 1.00 were shifted upfield to 0.88 (H_c), 0.76 ($H_{c'}$), and −0.03. The experimental spectra were insufficiently resolved to provide all necessary coupling constants of the four protons in question. However, trishomocycloheptatriene **11** serves as a good model for conformationally frozen **9** since the only structural permutation involves replacement of the olefinic linkage by a cyclopropane ring, the effect of which is to lock the tetracyclic structure into the closely related conformation depicted by **27.** The following experimentally determined coupling constants were utilized in the computer simulation: $J_{H_c,H_f} = 9$, $J_{H_c,H_{f'}} = 0.5$, $J_{H_{c'},H_{f'}} = 6$, $J_{H_c,H_f} = 6$, and $J_{H_c,H_{c'}} = <0.1$ Hz. From data acquired at eight temperatures, the relevant thermodynamic and activation parameters were determined to be $E_a = 8.13 \pm 0.25$ kcal/mol, $\Delta H^{\ddagger} = 7.74 \pm 0.27$ kcal/mol, $\Delta S^{\ddagger} = -4.5 \pm 1.4$ eu, and $\Delta G^{\ddagger}_{298} = 9.07$ kcal/mol.

Since the free energy of activation at 298 °C for ring inversion in cycloheptatriene is on the order of 6.75 kcal/mol,[18] **9** exhibits a measurably greater hindrance (ca. 2.3 kcal/mol) to attainment of a presumably planar central seven-membered core. Interestingly, this decrease in conformational flexibility parallels closely in magnitude the barrier found for several 1,5-bishomocyclooctatetraenes relative to cyclooctatetraene.[24]

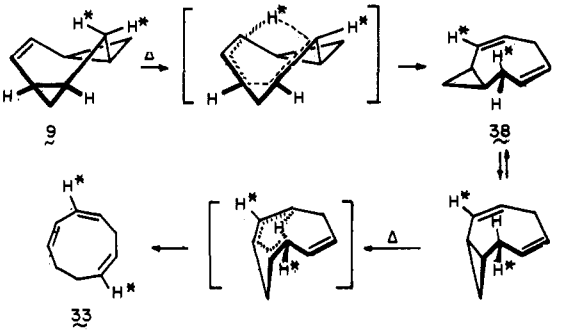
Thermochemical Studies

When a benzene solution of **9** was heated in a sealed tube at 180 °C for 5 h, essentially quantitative conversion to a single isomeric hydrocarbon (86% isolated) occurred. On the basis of direct spectral comparisons with an authentic sample, this product was identified as *cis*[3]-1,3,6-cyclononatriene (**33**). The kinetics of this rearrangement as monitored by VPC analysis of reaction mixtures obtained at 151-174 °C, and the resulting thermodynamic data are summarized in Table II. It was immediately evident that **9** undergoes reaction with an energy and enthalpy of activation very similar to those found previously by Winstein for the **34** $\rightleftarrows$ **35** and **36** $\rightleftarrows$ **37** interconversions.[25] Considering the geometry of **9** (as given by formula **32**), we



34 35 36 37

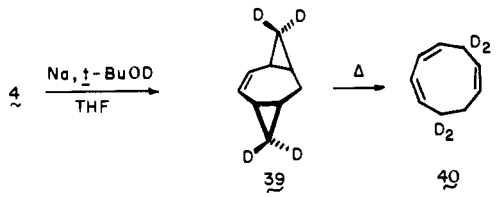
see that the endo cycloheptyl hydrogen is both ideally aligned with, and in adequate proximity to, the π bond for concerted homo-1,5-dienyl shift as illustrated in the scheme.[26] This process gives rise to bicyclo[6.1.0]nona-2,5-diene (**38**), the



9 38 33

conversion of which to **33** has previously been studied.[27] Since the homodienyl proton shift which transforms **38** to **33** is complete within 1 h at 130 °C, whereas the half-life for the conversion of **9** to **33** at 150 °C is approximately 10 h, the rate-determining step would have to be the first hydrogen migration. In accord with this analysis, the presence of **38** was not detected in the various reaction mixtures.

To gain further insight into this rearrangement, the d_4 de-



39 40

rivative **39** was prepared by reduction of **4** with sodium in *tert*-butyl alcohol-*O*-*d* and tetrahydrofuran. Thermolysis of **39** gave a tetradeuterio labeled *cis*[3]-1,3,6-cyclononatriene whose ^{1}H NMR spectrum shows a 3:1 ratio of olefinic to allylic protons. Accordingly, deuterium was present exclusively at allylic sites. The doubly allylic methylene triplet seen at δ 2.67 in **33** was now clearly absent, and the original four-proton allylic multiplet centered at 2.10 was now a somewhat broadened two-proton doublet. Importantly, the multiplicity of the 1,3-dienyl olefinic protons was greatly simplified while that of the isolated vinylics was appreciably less so. On this basis, the labeling scheme must be that given by **40**, indicating that the original cyclopropyl methylene groups retain their integrity.

These data do not rule out the possible operation of a radical process involving initial homolytic cleavage of an internal cyclopropane bond, followed by opening of the second three-membered ring and ultimate 1,2-hydrogen shift to deliver **40**. Ideally, this distinction could be made by specifically labeling **9** with two deuterium atoms at the cycloheptyl methylene group (the reader will recall that the ring inversion in **9** which is rapid and degenerate interconverts the exo and endo protons in question). Although such an experiment remains to be accomplished,[28] the above scheme outlines the fate of these isotopic labels (H*) if the twofold 1,5-homodienyl rearrangement is adhered to. In this particular pathway, the molecule makes recourse to "hydrogen rebounding"[29] to avoid otherwise nonconcerted reactions. The first rate-determining deuterium transfer which involves migration from C(7) to C(4) sets the stage (presumably because of exothermicity) for subsequent transfer from C(4) back to the original C(6) site. But because of the usual stereoselectivity demands on 1,5-homodienyl shifts,[25,30] conformational ring inversion to the "saddle" form must precede the "rebound". But this flexing of the ring simultaneously exchanges the relative positioning of hydrogen and deuterium such that only hydrogen is now stereodisposed for migration. The final diene is therefore predicted to be labeled as shown in **33**. The biradical mode would require instead that the nine-membered ring be isotopically substituted at vicinal carbon atoms.

The remaining six bis- and trishomocycloheptatrienes do not undergo thermal rearrangement with facility. At temperatures up to 500 °C, flash vacuum pyrolysis conditions produced no structural changes. At 550 °C, carbonization was observed in all cases. Under these conditions, only **8** afforded recoverable volatile materials (<20%), but the complexity of these reaction mixtures (VPC analysis) discouraged more detailed examination. Based upon the conformational considerations presented earlier, we conclude that the cyclopropyl groups and olefinic bonds in these hydrocarbons are not suitably oriented for interaction. That **8** still does not experience transformation to *cis*[3]-1,3,6-cyclononatriene at these elevated temperatures could be construed as reasonable evidence against the incursion of biradical intermediates during the isomerization of **9**.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian A-60A and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C spectra were also run on the Bruker spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Preparative scale VPC separations were performed on a Varian Aerograph Model A-90-P3 instrument equipped with thermal conductivity detectors. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

Dichlorocarbene Addition to Cycloheptatriene. Into a 1-l. three-necked flask equipped with a mechanical stirrer was placed 16 g (0.17 mol) of cycloheptatriene, benzene (30 ml), 50% aqueous sodium hydroxide solution (300 ml), and triethylbenzylammonium chloride (0.5 g). With efficient stirring of this mixture, 70 ml of chloroform (104 g, 0.87 mol) was introduced dropwise during 10 h. After completion of the addition, the mixture was poured onto 1 l. of ice water, and the products were extracted into chloroform (3 × 200 ml). The combined organic layers were washed with water, dried, and evaporated to leave a residue which was purified by chromatography on silica gel. Elution with hexane followed by recrystallization of the properly combined fractions from methanol afforded 8.35 g (14.3%) of **2**, mp 134–135 °C (lit.[7] mp 139–142 °C); 6.47 g (14.5%) of **3**, mp 100–104 °C; and 10.2 g (22.9%) of **4**, mp 53–56 °C (lit.[7] mp 48–51 °C).

For **2**: ^{1}H NMR ($CDCl_3$) δ 2.36 (m, 1 H), 1.80 (m, 6 H), and 1.18 (m, 1 H); ν_{max} ($CHCl_3$) 2935, 1448, 1303, 1220, 1135, 1042, 1020, 898, and 770 cm^{-1}; *m/e* 338.

For **3**: ^{1}H NMR ($CDCl_3$) δ 5.67 (s, 2 H), 2.58 (m, 1 H), 2.44 (m, 1 H), and 2.3–2.0 (m, 4 H); ν_{max} ($CHCl_3$) 2995, 2940, 2875, 1650, 1448, 1210, 1130, 1086, 1025, 897, 840, 608, and 633 cm^{-1}; *m/e* 256.

For **4**: ^{1}H NMR ($CDCl_3$) δ 5.85 (m, 2 H), 2.58 (t, J = 5 Hz, 2 H), and 2.25–2.05 (m, 4 H); ν_{max} ($CHCl_3$) 2925, 1720, 1090, 1023, 851, and 750 cm^{-1}; *m/e* 256.

***anti,anti*-Trishomocycloheptatriene (7).** To a stirred solution of 4.6 g (0.20 g-atom) of sodium in 150 ml of anhydrous liquid ammonia cooled to −78 °C was slowly added 5.20 g (15.4 mmol) of **2** and 7.40 g (0.10 mol) of *tert*-butyl alcohol in 150 ml of ether. After 2 h at this temperature, solid ammonium chloride was introduced in small portions until the blue color faded. The ammonia was allowed to evaporate overnight, water (100 ml) was added, and the organic phase was dried and evaporated. Distillation afforded 1.33 g (65%) of **7** as a colorless oil, bp 85–90 °C (30 mm); ^{1}H NMR ($CDCl_3$) δ 2.38 (m, 1 H), 1.0–0.3 (m, 10 H), 0.10 (m, 1 H), and −0.05 (m, 2 H); ^{13}C NMR ($CDCl_3$) 32.47, 17.23, 15.32, 14.82, 14.22, and 12.19 ppm; ν_{max} (neat) 3050, 2980, 2900, 1450, 1060, 846, 818, and 790 cm^{-1}; *m/e* 134.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.32; H, 10.56.

***syn*-1,5-Bishomocycloheptatriene (8).** A 384-mg (1.50 mmol) sample of **3** and 444 mg (6.0 mmol) of *tert*-butyl alcohol in 150 ml of dry ether was added dropwise to 345 mg (15.0 mg-atom) of sodium in 15 ml of ammonia as described above. Molecular distillation [100 °C, (38 mm)] afforded 115 mg (64%) of **8** as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 5.55 (s, 2 H), 2.50 (m, 1 H), 2.30 (m, 1 H), 1.53–1.03 (m, 4 H), 0.78 (m, 2 H), and 0.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) 128.9, 33.6, 17.4, 14.9, and 13.0 ppm; ν_{max} (neat) 3045, 2920, 2860, 1730, 1643, 1451, 1440, 1022, and 708 cm^{-1}; *m/e* 120.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.71; H, 10.19.

***anti*-1,5-Bishomocycloheptatriene (9).** Reduction of 2.56 g (0.010 mol) of **4** with 3.00 g (40.6 mmol) of *tert*-butyl alcohol in ether (60 ml) and liquid ammonia (60 ml) containing 2.30 g (0.10 g-at) of sodium metal provided after distillation 830 mg (69%) of **9** as a colorless oil; bp 86–88 °C (38 mm); ^{1}H NMR ($CDCl_3$) 5.56 (m, 2 H), 1.92 (t, J = 4.5 Hz, 2 H), and 1.40–0.50 (m, 8 H); ^{13}C NMR ($CDCl_3$) 127.1, 27.5, 14.3, and 12.7 ppm; ν_{max} (neat) 3050, 2990, 2820, 1650, 1450, 1440, 1020, 782, 708, and 696 cm^{-1}; *m/e* 120.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.23.

Dibromocarbene Addition to 9. To a magnetically stirred slurry composed of **9** (800 mg, 6.7 mmol), potassium *tert*-butoxide (2.0 g, 19.2 mmol), and 15 ml of pentane cooled in an ice bath was added dropwise a solution of bromoform (2.0 g, 7.91 mmol) in pentane (5 ml). Upon completion of the addition, the mixture was stirred at room temperature for 4 h before pouring into water (50 ml) and extraction into pentane (3 × 25 ml). The combined organic layers were washed with water, dried, and concentrated to leave after filtration through silica gel 1.68 g (83%) of **10** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.47 (m, 1 H), 1.86 (narrow m, 2 H), 1.5–0.3 (m, 7 H), and 0.16 (m, 1 H); ^{13}C NMR ($CDCl_3$) 38.6, 33.9, 29.4, 26.5, 16.6, 14.7, 13.1, 10.9, 9.9, and 8.0 ppm; ν_{max} (neat) 3000, 2916, 2848, 1448, 1030, 981, 940, 875, 852, 831, 789, and 727 cm^{-1}; *m/e* 290.

***anti,syn*-Trishomocycloheptatriene (11).** A 1.60-g (5.48 mmol) sample of **9** was treated with sodium shot (2.3 g, 0.10 g-atom), *tert*-butyl alcohol (2.0 g, 27 mmol) in tetrahydrofuran (25 ml) at reflux for 2.0 h. The excess sodium was quenched with methanol. The mixture was poured into water and extracted with pentane (3 × 25 ml). The combined organic layers were washed with water, dried, and concentrated. Preparative VPC purification (105 °C, 15 ft × 0.37 in. 5% SE-30 on Chromosorb G) afforded 412 mg (56%) of **11** as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.37 (d of t, J = 14 and 6 Hz, 1 H), 1.55 (d of d, J = 14 and 9 Hz, 1 H), 1.3–0.1 (m, 10 H), and 0.1 to −0.1 (m, 2 H); ^{13}C NMR ($CDCl_3$) 26.98, 16.91, 15.54, 14.95, 13.54, 12.41, 12.19, 11.60, and 5.26 ppm; ν_{max} (neat) 3068, 2999, 2913, 2855, 1451, 1021, 846, 832, 819, and 805 cm^{-1}; *m/e* 134.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.30; H, 10.62.

Cyclopropanation of 8. Into a 15-ml flask equipped with a condenser, rubber septum, and magnetic stirring bar was placed 5 ml of a 1 M solution of ethylzinc iodide in ether (5.0 mmol). Methylene iodide (1.33 g, 4.96 mmol) was introduced via syringe, and the resulting solution was refluxed for 0.5 h. A solution of **8** (120 mg, 1.0 mmol) in 2 ml of ether was added in a comparable manner, and the mixture was heated at reflux for 12 h before being poured into 20 ml of cold saturated ammonium chloride solution. The ether layer and the single extract (10 ml) of the organic phase were combined, washed with saturated ammonium chloride solution, dried, and carefully concentrated. Final purification was achieved by VPC methods (140 °C, 12 ft × 0.25 in. 10% XF-1150 on Chromosorb P). There was isolated 63 mg (47%) of **7** and 15 mg (13%) of unreacted **8**.

***syn,syn*- and *syn,anti*-3,5-Bishomocycloheptadienol (14 and 15).** Methylene iodide (67 g, 0.25 mol) was added dropwise to 250 ml of 1 M ethylzinc iodide under nitrogen. The resulting solution was heated to reflux for 1 h whereupon 6.0 g (54 mmol) of **12** dissolved in 10 ml of ether was added dropwise. After a 23 h reflux period, the predescribed workup was employed to give a colorless oil which was analyzed by VPC methods (10 ft × 0.35 in. 10% SF-96 on Chromosorb G). Present was 6% of *anti*-bicyclo[5.1.0]oct-5-en-3-ol, 74% of **13**, 8% of **15**, and 14% of **14**. The entire procedure was repeated to give 5.06 g (67%) of a colorless oil, bp 70–84 °C (0.75 mm). The isomeric alcohols were separated by chromatography on silica gel using pentane–ether (20:1) elution.

For **14**: ^{1}H NMR ($CDCl_3$) δ 4.05 (m, 1 H), 2.36 (m, 2 H), 1.97 (s, 1 H), 1.50 (m, 2 H), 1.08 (m, 2 H), 0.73 (m, 4 H), and 0.13 (m, 2 H); ^{13}C NMR ($CDCl_3$) 71.4, 35.2, 13.5, 12.0, and 11.2 ppm; ν_{max} (neat) 3340, 3065, 1450, 1067, 1032, and 942 cm^{-1}; *m/e* 138.1047.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.92; H, 10.46.

For **15**: ^{1}H NMR ($CDCl_3$) δ 4.10 (m, 1 H), 2.13 (m, 2 H), 1.08 (s, 1 H), 1.27 (m, 2 H), 0.72 (m, 4 H), 0.00 (m, 2 H); ^{13}C NMR ($CDCl_3$) 70.4, 37.3, 37.2, 14.9, 13.9, 13.5, 13.1, 12.8, and 9.0 ppm; ν_{max} (neat) 3340, 3064, 2995, 2920, 1449, 1070, 1039, 1025, 994, and 730 cm^{-1}; *m/e* 138.1047.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.04; H, 10.25.

***syn*-3-Benzyloxybicyclo[5.1.0]oct-5-ene (16).** To a suspension of sodium hydride (750 mg of a 57% mineral oil dispersion freshly washed with pentane and tetrahydrofuran, 18 mmol) in 30 ml of anhydrous tetrahydrofuran was slowly added 2.00 g (16 mmol) of **13** dissolved in 8 ml of the same solvent. This mixture was heated at reflux for 6 h before dropwise addition of benzyl bromide (2.8 g, 16 mmol) dissolved in 5 ml of tetrahydrofuran. Heating was continued overnight before addition of methanol (5 ml) and water (100 ml). The product was extracted with ether (3 × 30 ml), and the combined organic layers were washed with water, dried, and evaporated. Distillation yielded 3.36 g (97.5%) of **16** as a colorless oil: bp 98–100 °C (0.10 mm); ^{1}H NMR (CCl_4) δ 7.32 (s, 5 H), 5.76 (m, 1 H), 5.42 (m, 1 H), 4.52 (s, 2 H), 3.72 (m, 1 H), 2.32 (m, 1 H), 1.67 (m, 1 H), 1.4–0.5 (m, 4 H), and 0.20 (m, 2 H); ν_{max} (neat) 3062, 2998, 2920, 2858, 1660, 1496, 1455, 1360, 1091, 1070, 1028, 732, and 695 cm^{-1}; *m/e* 214.

Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.21; H, 8.69.

Dichlorocarbene Addition to 16. Chloroform (8.1 ml, 0.10 mol) was added dropwise to a stirred slurry of **16** (3.36 g, 15 mmol), benzyltriethylammonium chloride (0.10 g), benzene (5 ml), and 50% aqueous sodium hydroxide solution (30 ml). After being stirred overnight, the reaction mixture was added to water (100 ml), and the product was extracted with chloroform (2 × 30 ml). The combined organic layers were washed with brine, dried, and evaporated. Chromatography on silica gel (elution with 15% ether in pentane) afforded 4.05 g (87.5%) of **17** as a pale-yellow viscous oil: ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 5 H), 4.52 (s, 2 H), 3.70 (m, 1 H), 2.34 (m, 2 H), 1.60 (m, 2 H), 1.26 (m, 2 H), 0.84 (m, 3 H), and 0.18 (m, 1 H); ν_{max} (neat) 3070, 3000, 2930, 2860, 1450, 1343, 1070, 1027, 732, and 695 cm^{-1}; *m/e* 296.

***syn,anti*-3,5-Bishomocycloheptadienol (15).** A solution of **17** (4.05 g, 13.6 mmol) dissolved in anhydrous ether (25 ml) was added dropwise to a magnetically stirred solution of sodium (2.6 g, 0.11 g-atom) in liquid ammonia (25 ml) cooled to −78 °C. After 1 h, the mixture was allowed to warm to room temperature. After 4 h, methanol (25 ml) was added followed by water (100 ml). Ether extraction (3 × 30 ml), washing and drying of the combined organic layers, solvent removal in vacuo, and distillation gave 1.73 g (92%) of **15**, bp 56–60 °C (0.3 mm). The spectral properties of this colorless liquid were identical with those of the material isolated earlier.

***syn*-3,5-Bishomocycloheptadienone (18).** Chromium trioxide (3.48 g, 34.8 mmol) was added in three portions to 5.50 g (69.6 mmol) of pyridine in 35 ml of distilled methylene chloride. After 30 min, 480 mg (3.48 mmol) of **14** in 5 ml of methylene chloride was added and stirring was continued for 0.5 h. The solution was decanted and evaporated. The insoluble inorganic solids were washed with ether (2 × 25 ml), and these washings were added to the methylene chloride residue. A chalky precipitate was filtered, and the filtrate was washed with 10% hydrochloric acid (2 × 50 ml) and saturated sodium bicarbonate solutions, dried, and evaporated. Molecular distillation afforded 450 mg (95%) of **18** as a colorless oil: ^{1}H NMR ($CDCl_3$) 2.93 (dd, J = 16 and 5 Hz, 2 H), 2.23 (dd, J = 17 and 7 Hz, 7 H), 1.60–0.4 (m, 6 H), and −0.10 (dd, J = 10 and 4.5 Hz, 2 H); ν_{max} (neat) 3070, 3000, 2920, 1695, 1440, 1415, 1350, 1290, 1258, 1163, 1028, 830, and 810 cm^{-1}; *m/e* 136.0890.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.38; H, 8.96.

***syn*-3,5-Bishomocycloheptadienone Enol Phosphate (19).** To a lithium diisopropylamide solution [prepared from 0.42 ml (1.0 mmol) of *n*-butyllithium in hexane and 101 mg (1.0 mmol) of diisopropylamine in 5 ml of dry tetrahydrofuran] cooled to −78 °C was added dropwise a solution of **18** (136 mg, 1.0 mmol) in 1 ml of tetrahydrofuran. After 10 min, 173 mg (1 mmol) of diethyl chlorophosphate and 0.1 ml of TMEDA were slowly introduced. The cooling bath was removed, and stirring at room temperature was maintained for 2 h. One ml of saturated ammonium chloride was added, and the reaction mixture was poured into 25 ml of water. The product was extracted with methylene chloride (3 × 8 ml), and the combined organic layers were washed with 10% hydrochloric acid (2 × 20 ml) and saturated sodium bicarbonate solution before drying and solvent removed. The residual pale-yellow oil was filtered through a short silica gel column (elution with 40% ether in hexane) to give 240 mg (88%) of **19**: ^{1}H NMR ($CDCl_3$) δ 5.50 (br s, 1 H), 4.13 (overlapping q, J = 7 Hz, 4 H), 2.57 (m, 1 H), 2.35 (m, 1 H), 1.35 (t, J = 7 Hz, 6 H), 1.6–0.6 (m, 6 H), and 0.2 (m, 2 H); *m/e* 272.

***syn*-3,5-Bishomocycloheptatriene (20).** To a solution of lithium metal (235 mg, 35 mg-atom) in 20 ml of liquid ammonia cooled to −78 °C was added dropwise a solution of **20** (1.09 g, 4.0 mmol) in 20 ml of ether. After 2 h at this temperature, solid ammonium chloride was added in portions until the blue color faded, and the ammonia was left to evaporate overnight. Ether (20 ml) was added and this mixture was poured into water (50 ml). The ether layer was dried and carefully concentrated. The residue was subjected to molecular distillation thereby yielding 410 mg (85%) of **20** as a colorless oil; ^{1}H NMR ($CDCl_3$) 5.70 (br d, J = 10 Hz, 1 H), 5.32 (m, 1 H), 2.80 (m, 1 H), 2.42 (m, 1 H), 1.6–0.5 (m, 6 H), and −0.2–0.5 (m, 2 H); ν_{max} (neat) 3070, 3000, 2920, 2850, 1657, 1450, 1260, 1026, and 830 cm^{-1}; *m/e* 120.0941.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.91; H, 10.26.

***anti*-3,5-Bishomocycloheptadienone (21).** Oxidation of **15** according to the procedure described above produced **21** in yields of 90%; ^{1}H NMR ($CDCl_3$) 2.50 (m, 2 H), 1.98 (m, 2 H), 0.82 (m, 6 H), and 0.08 (m, 2 H); ν_{max} (neat) 3060, 2970, 2950, 2900, 1708, 1448, 1410, 1282, 1182, 1029, 840, and 803 cm^{-1}; *m/e* 136.0890.

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.27; H, 9.01.

***anti*-3,5-Bishomocycloheptatriene (23).** Conversion of 338 mg (2.5 mmol) of **21** to its enol phosphate in the predescribed manner afforded 540 mg (80%) of **22** as a pale-yellow oil. Reduction of a 540-mg sample

(2.0 mmol) of **22** as outlined above furnished 220 mg (92%) of **23** as a colorless oil after molecular distillation: ^{1}H NMR ($CDCl_3$) 5.72 (m, 2 H), 2.13 (m, 2 H), 1.4–0.6 (m, 6 H), 0.42 (m, 1 H), and 0.17 (m, 1 H); ν_{max} (neat) 3070, 3000, 2930, 2860, 1645, 1450, 1025, 830, 804, and 693 cm^{-1}; *m/e* 120.0941.

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.92; H, 10.17.

***syn,syn*-Trishomocycloheptatriene (24).** Methylene iodide (6.0 g, 22 mmol) was added to 3.0 g (46 mmol) of zinc–silver couple in 20 ml of anhydrous ether. This mixture was heated at reflux for 30 min, cooled, and treated dropwise with 200 mg (1.67 mol) of **20** in 5 ml of the same solvent. After 24 h at the reflux temperature, the ether solution was decanted into 40 ml of cold, saturated ammonium chloride solution. The organic layer was washed with brine, dried, and carefully concentrated. Preparative VPC purification (108 °C, 12 ft × 0.25 in. 10% XF-1150 on Chromosorb P) gave 50 mg (25%) of unreacted **20**, 24 mg (11%) of **11**, and 12 mg (6%) of **24**: ^{1}H NMR ($CDCl_3$) 2.37 (d of m, J = 14 Hz, 1 H), 1.33 (m, 2 H), 1.03 (m, 4 H), 0.63 (m, 2 H), 0.28 (m, 2 H), −0.05 (m, 2 H), and −0.38 (q, J = 4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) 29.46, 18.29, 16.62, 12.63, 10.36, and 7.55 ppm; ν_{max} (neat) 3065, 3000, 2920, 1475, 1020, 840, and 690 cm^{-1}; *m/e* 134.1099.

Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.43; H, 10.51.

Kinetics Procedure. A standard solution of **9** in benzene was prepared by dissolving 45 mg of the hydrocarbon and 25 mg of cyclooctane (internal standard) in 6.0 ml of benzene (distilled from calcium hydride). Aliquots (15 μl) were sealed in each of nine ampules (constructed from 2-mm glass tubing and washed with hydrochloric acid and ammonium hydroxide before use) under a slight vacuum for individual runs. The sealed ampules were introduced simultaneously into a constant temperature oil bath. After 5 min, the first ampule was removed and immediately cooled while a timer was started. The kinetic data were determined by monitoring the disappearance of **9** with respect to the internal standard by electronic integration of VPC traces (Hewlett-Packard Model 5750 instrument fitted with a flame ionization detector; ⅛ in. × 8 ft column packed with 15% SE-30 on Chromosorb G, 50°).

Preparative Scale Thermolysis of 9. A 120-mg (1.00 mmol) sample of **9** in 1.0 ml of benzene was sealed in a thick-walled ampule and heated at 180 °C for 5 h. Solvent was removed by distillation. Analysis of the residual oil by VPC showed greater than 99% of a single component. Molecular distillation yielded 103 mg (86%) of a colorless oil whose spectral properties (IR, NMR) were identical with those of authentic *cis*[3]-1,3,6-cyclononatriene (**33**).

***anti*-1,5-Bishomocycloheptadiene-d_4 (39).** Sodium sand was prepared by shaking 2.30 g (0.10 g-atom) of molten sodium in 20 ml of hot xylene. The sand was allowed to cool and was subsequently washed with dry ether (3 × 25 ml) and dry tetrahydrofuran (2 × 20 ml). Tetrachloro compound **4** (768 mg, 3.0 mmol) and *tert*-butyl alcohol-*O*-*d* (1.00 g, 13.3 mmol) were dissolved in 20 ml of dry tetrahydrofuran and added to the sodium sand. The resulting mixture was stirred for 0.5 h (exotherm) and filtered through a pad of glass wool into 100 ml of water. The inorganic solids were washed with 20 ml of hexane, and the aqueous solution was extracted with hexane (3 × 25 ml). The combined organic extracts were dried and concentrated, and the residual oil was subjected to molecular distillation (80 °C, 30 Torr). There was isolated 205 mg (55%) of **39**, ^{1}H NMR analysis of which indicated 80% d_4 incorporation: ^{1}H NMR (CCl_4) δ 5.50 (br m, 2 H), 1.93 (t, J = 5 Hz, 2 H), and 1.43–0.70 (m, 4 H); *m/e* 124.1192.

Thermolysis of 39. A 30-mg sample of **39** was vaporized into a quartz tube packed with quartz chips maintained at 330 °C and 50 mm (slow nitrogen entrainment). The volatile components were collected in a trap cooled in a dry ice–acetone bath. ^{1}H NMR analysis denoted complete conversion to **40**: (CCl_4) δ 6.0–5.2 (m, 6 H) and 2.42–1.92 (br d, 2 H); *m/e* 124.1192.

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