Thermal Isomerization of Cyclic *cis,trans,cis*-Trienes[1]

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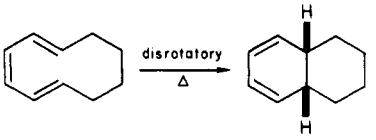
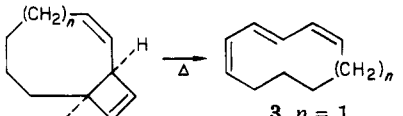
The thermal isomerization of a series of cyclic conjugated *cis,trans,cis*-trienes was examined. The results obtained show a structure–reactivity correlation between the size of the ring vs. the type of product observed. The eleven-membered-ring triene (4) yields a novel tricyclic isomer 8, whereas the nine-membered-ring triene (5) yields the bicyclic diene 9. The ten-membered analogue 3 yields a mixture of both types of observed products. Mechanistic possibilities are proposed to explain the formation of both types of products.

Conjugated trienes are known to undergo a number of thermally promoted rearrangements arising from both orbital symmetry allowed electrocyclic and nonorbital symmetry controlled processes.[2,3] When the triene system is restricted to a monocyclic ring, the most common isomerization pathway followed is simple disrotatory closure to yield a bicyclic cyclohexadiene in an orbital symmetry allowed manner.[3]



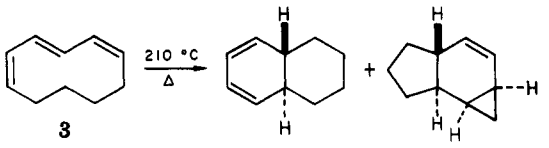
In an earlier report from this laboratory,[4] it was demonstrated that thermal isomerization of *cis*-bicyclo[6.2.0]deca-2,9-diene (1) and *cis*-bicyclo[7.2.0]undeca-2,10-dienes (2) yields monocyclic trienes 3 and 4, respectively, having a cis,trans,cis configuration of the conjugated double bonds. These cyclic trienes having this array of olefinic orbitals (e.g., trans central double bond) are members of a relatively new class of compounds for which there are no intuitively obvious routes for rearrangement. Thus, the thermal chemistry of *cis,trans,cis*-cyclodeca-1,3,5-triene (3) and *cis,trans,cis*-cycloundeca-1,3,5-triene (4) was explored in some detail. The thermal isomerization of the nine-membered-ring analogue 5, obtained by the irradiation of bicyclo[4.3.0]nona-2,4-diene, was also studied.



1, n = 1
2, n = 2

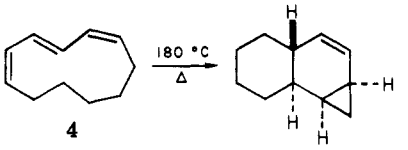
3, n = 1
4, n = 2
5, n = 0

Triene 3 displayed remarkable thermal stability; it was recovered virtually unchanged after heating for 2 h at 170 °C, a stability consistent with the trans configuration of the central double bond. However, upon heating at 210 °C for 1.5 h, 3 gave rise to compounds 6 and 7, in near equal amount. The structure of 6 was established by comparison with a sample of the known compound.[3,5] and the structure of 7 was elucidated as *trans*-tricyclo-[5.3.0.0^{4,6}]dec-2-ene from spectral data (see the experimental section). In particular, the magnitude of the vinyl hydrogen coupling constant ($J_{2,3}$ = 10.5 Hz) shows that the double bond is located within a six-membered ring[6] and the UV maximum at 213 nm is indicative of a vinyl cyclopropane moiety.[7] Confirmation of the cyclopropane ring came from both ^{1}H and ^{13}C NMR values (δ 0.4–1.0 and δ 16.31 (d), 12.23 (d), and 7.09 (t), respectively), while the mass spectrum required four degrees of unsaturation, supportive of the tricyclic nature of the molecule.[8]



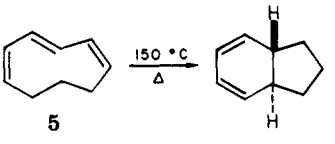
3 6 7

The larger, eleven-membered-ring *cis,trans,cis*-triene 4 was less thermally stable and readily rearranged at 180 °C. In contrast to 3, this triene 4 yielded mainly one product (8), accounting for greater than 95% of the products. This product 8 was identified as *trans*-tricyclo[5.4.0.0^{4,6}]undec-2-ene on the basis of its spectral similarity to 7.



4 8

The thermal isomerization of the more highly strained nine-membered-ring triene 5 also yielded a single isomeric product which was identified as the known *trans*-bicyclo[4.3.0]nona-2,4-diene (9).[3,5]



5 9

(1) This work was supported by Grant No. AM 00709, National Institute of Arthritis, Metabolism, and Digestive Diseases.

(2) (a) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press, Inc.: New York, 1970; pp 52–61. (b) Marvell, E. N.; Caple, G.; Schatz, B.; Pippin, W. *Tetrahedron* **1973**, *29*, 3781. (c) Marvell, E. N. *Ibid.* **1973**, *29*, 3791. Marvell, E. N.; Caple, G.; Delphey, C.; Platt, J.; Polston, N.; Tashiro, J. *Ibid.* **1973**, *29*, 3797.

(3) (a) Dauben, W. G.; Rabinowitz, J.; Vietmeyer, N. D.; Wendschuh, P. *J. Am. Chem. Soc.* **1972**, *94*, 4285. (b) Dauben, W. G.; Kellogg, M. S. *Ibid.* **1972**, *94*, 8951. (c) Dauben, W. G.; Kellogg, M. S.; Seeman, J. I.; Vietmeyer, N. D.; Wendschuh, P. H. *Pure Appl. Chem.* **1973**, *33*, 197. (d) Dauben, W. G.; Williams, R. G.; McKelvey, R. D. *J. Am. Chem. Soc.* **1973**, *95*, 3932.

(4) Dauben, W. G.; Michno, D. M. *J. Am. Chem. Soc.*, in press.

(5) Dauben, W. G.; Kellogg, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 4456.

(6) Laszlo, P.; Stang, P. "Organic Spectroscopy: Principals and Applications", Harper and Row, Inc.: New York, 1971; p 26.

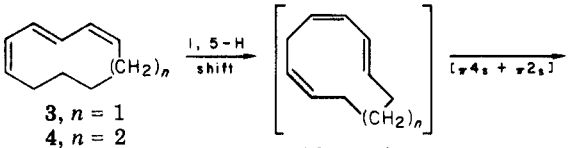
(7) Djerassi, C.; Donovan, F. W.; Burstein, S.; Mauli, R. *J. Am. Chem. Soc.* **1958**, *80*, 1972. Zürcher, A.; Jeger, O.; Ruzicka, L. *Helv. Chim. Acta* **1954**, *37*, 2145.

(8) After completion of this study, the preparation of 7 by a thermally promoted isomerization of *cis*-bicyclo[7.1.0]deca-2,3-diene was reported (Minter, D. E.; Fonken, G. J.; Cook, F. T. *Tetrahedron Lett.* **1979**, 711). The spectral properties of the material are identical with those reported in the present study.

0022-3263/81/1946-0687$01.00/0

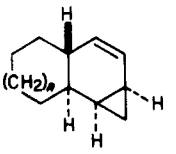
Discussion

The formation of the tricyclic olefins upon thermal activation of the trienes **3** and **4** is both an interesting and an unusual isomerization. Of the many possible explanations to account for this type of stereospecific transformation, one of the most credible would involve the generation of the transient, partially conjugated *trans,cis,cis*-cyclo-1,3,6-trienes **10** and **11**. These trienes could



3, $n = 1$
4, $n = 2$

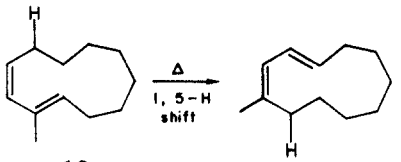
10, $n = 1$
11, $n = 2$



7, $n = 1$
8, $n = 2$

arise via one of the allowed sigmatropic 1,5-hydrogen shifts from the conjugated trienes and could undergo a second facile $[{}_{\pi}4_s + {}_{\pi}2_s]$ cycloaddition reaction to yield the observed products.

Sigmatropic hydrogen transfer reactions have been shown to occur in medium-ring compounds of limited conformational mobility.[9] Since a conjugated diene unit with an accessible allylic hydrogen is all that is required for such a thermally promoted 1,5-hydrogen shift to occur, the thermal chemistry of 2-methyl-*trans,cis*-cycloundeca-1,3-diene (**12**)[4] was examined to determine if the requisite



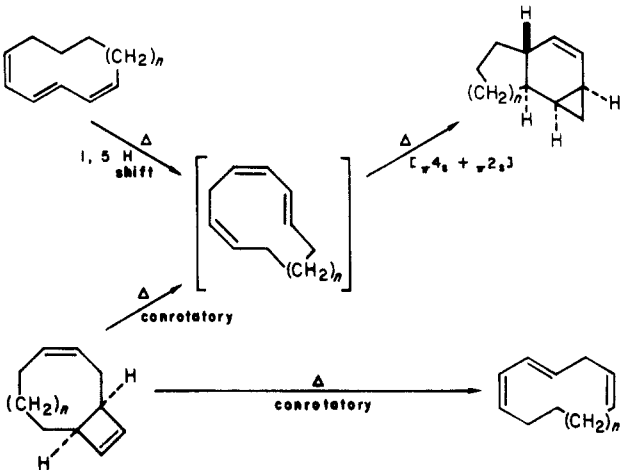
12 **13**

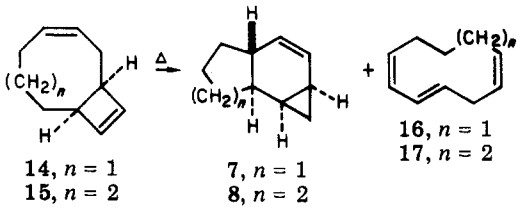
hydrogen transfer was feasible in the present ring systems. When a dilute benzene solution of **12** was heated at 205 °C, the sole product formed was 1-methyl-*cis,trans*-cycloundeca-1,3-diene (**13**). This finding of such a facile, stereospecific 1,5-hydrogen migration fully supports the previously proposed mechanistic scheme.

Further evidence, however, was desired to substantiate fully and to define the proposed mechanism of this unusual isomerization. This evidence was obtained by an independent synthesis or generation of the proposed thermally labile partially conjugated trienes **10** and **11**.

In the first approach, the dual nature of conrotatory ring opening of cis-fused bicyclic cyclobutenes was utilized to generate, in situ, the desired trienes **10** and **11** from *cis*-bicyclo[6.2.0]deca-3,9-diene (**14**) and *cis*-bicyclo[7.2.0]-undeca-3,10-diene (**15**), respectively. Based upon results reported earlier,[4] it was anticipated that thermal activation of each of these two dienes would lead to the initial formation of two monocyclic trienes, depending upon which conrotatory movement (clockwise or counterclockwise) was followed. Furthermore, since the conditions employed to isomerize the cyclobutene ring would be sufficient to further isomerize the expected thermally labile *trans,cis,cis*-1,3,6-trienes **10** and **11**, it was expected that the isomeric mixture obtained from the thermal activation of dienes **14** and **15** would consist of the thermally stable *cis,trans,cis*-1,3,6-trienes **16** and **17** and the tricyclic isomers **7** and **8**, respectively.

Scheme I





14, $n = 1$
15, $n = 2$

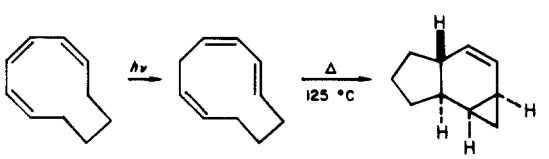
7, $n = 1$
8, $n = 2$

16, $n = 1$
17, $n = 2$

Thermal valence isomerization of **14** produced a two-component mixture which was separated by preparative VPC. The material with the longer retention was identified as *cis,trans,cis*-cyclodeca-1,3,6-triene (**16**) on the basis of spectral data and the material with the shorter retention time was shown to be **7**. Similar results were obtained when the higher homologue **15** was thermally isomerized, the products being the tricyclic olefin **8** and *cis,trans,cis*-cycloundeca-1,3,6-triene (**17**).

The interpretation of these results, in conjuction with those obtained from the valence isomerization of trienes **3** and **4** is presented in Scheme I. The key feature of this explanation is that the same intermediate *trans,cis,cis*-1,3,6-triene is obtained via a suprafacial 1,5-hydrogen shift from the fully conjugated *cis,trans,cis*-1,3,5-triene or via a conrotatory opening of a cis-fused allyl bicyclic cyclobutene. This 1,3,6-triene, thermally labile at the reaction conditions, then undergoes an intramolecular $[{}_{\pi}4_s + {}_{\pi}2_s]$ cycloaddition to yield the observed tricyclic compounds.

Direct proof for the proposed mechanism, however, came from the finding that *cis,cis,cis*-cyclodeca-1,3,5-triene (**18**) upon direct irradiation afforded *trans,cis,cis*-cyclodeca-1,3,6-triene (**10**). When a dilute benzene solution of **10**



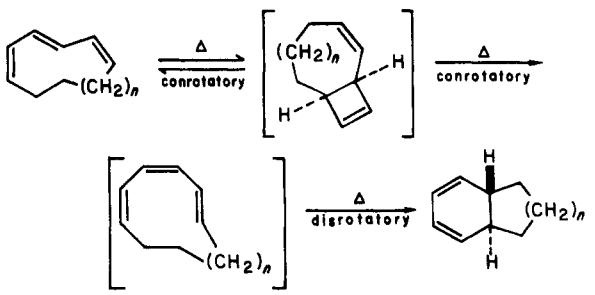
18 **10** **7**

was heated, the compound rearranged to a *sole* isomeric product, the predicted tricyclic isomer **7**. These results establish the mechanism proposed in Scheme I.

The formation of the 1,3-cyclohexadienes **6** and **9** upon thermal activation of trienes **3** and **5**, respectively, is also an unusual isomerization. As presented earlier, it was

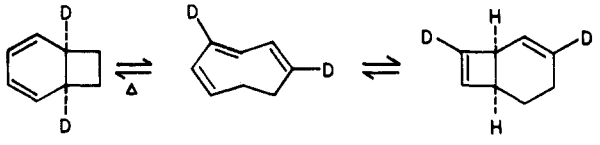
(9) Berson, J. A.; Willcott, M. R., III *J. Am. Chem. Soc.* **1966**, *88*, 2494 and references cited therein. Murray, R. W.; Kaplan, M. L. *Ibid.* **1966**, *88*, 3527.

Scheme II



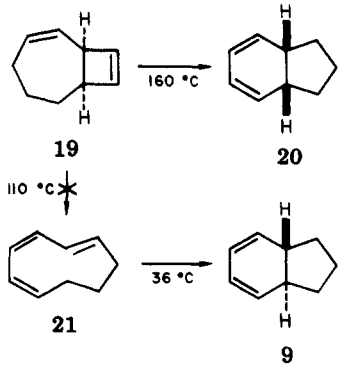
found that as the size of the ring containing the *cis,trans,cis*-triene increased, the amount of 1,3-cyclohexadiene formed decreased and the amount of tricyclic products increased. Such a result is indicative that these two distinct thermal products arise from different and competing mechanistic pathways. The pathway for the tricyclic product has been summarized in Scheme I. The 1,3-cyclohexadiene could be formed directly from the triene via a symmetry-allowed ring closure [$_\pi 2_s + {}_\pi 2_a + {}_\pi 2_a$]. However, the distance between the ends of the triene in this rigid system makes the mechanism unattractive.

A simplistic alternate pathway for the 1,3-cyclohexadiene formation is shown in Scheme II. In this scheme, the triene, under the more forcing conditions used in the isomerization could initially close to the cis-fused bicyclic vinylcyclobutene. Under the reaction conditions, the cyclobutene ring in this latter compound could ring open in both allowed conrotatory modes to yield the starting, more thermally stable, *cis,trans,cis*-triene and the thermally labile *trans,cis,cis*-triene. This latter type of triene is known to undergo a thermal disrotatory closure to the observed trans-fused 1,3-cyclohexadiene **6** and **9**.[3,5] Indeed, such a reversibility in a bicyclic cis-fused cyclobutene to a cyclic triene has been demonstrated in the bicyclo[4.2.0]octa-2,7-diene ring system.[10]



Reaction Scheme II fits well the known thermal chemistry of *cis*-bicyclo[6.2.0]deca-2,9-diene (**1**) which at 140 °C is known to yield both triene **3** and diene **6**.[4] The actual involvement of an intermediate vinylcyclobutene in the nine-membered-ring system, however, has been ruled out. In this present study, it has been found that the cis isomer **19** at 160 °C gave only the *cis*-diene **20**. The *trans,cis,cis*-triene **21**, made photochemically, readily ring closed at 36 °C to yield the *trans*-diene **9**.[5,11] Thus, the bicyclic diene **19** cannot be an intermediate in the thermal conversion of the *cis,trans,cis*-1,3,5-cyclononatriene **3** to *trans*-diene **9**.[12]

Other reaction pathways for the conversion of a cyclic *cis,trans,cis*-triene to a bicyclic *trans*-diene can be postulated,[13] but the finding of only the thermodynamically less stable diene in the nine-carbon system indicates a concerted process in that ring system. Further study is needed in order to develop the detailed steps in the thermal formation of the trans-fused dienes.



Experimental Section

The following columns were used in this study: (A) 10 ft × $^1/_8$ in. 5% Carbowax 20M, 5% KOH on 60/80 Chromosorb G; (B) 10 ft × 0.25 in. 10% Carbowax 6000 on 60/80 Chromosorb W; (C) 10 ft × 0.25 in. 5% SE-30 on 60/80 Chromosorb G; (D) 10 ft × $^1/_8$ in. 10% Carbowax 6000, 10% KOH on 60/80 Chromosorb W.

Infrared and NMR spectra were run in carbon tetrachloride as solvent unless otherwise noted. ^{13}C NMR spectra were run in deuteriochloroform unless otherwise noted and the chemical shifts are reported relative to tetramethylsilane as an internal standard, with multiplicity given for off-resonance proton decoupling.

Thermal Isomerization of 3. A solution of 134 mg of **3**[4] in 0.28 mL of benzene-d_6 in a thick-walled Pyrex tube sealed at one end was cooled to −78 °C, under N_2, and the tube sealed. The tube was warmed to room temperature and then heated at 210 °C for 1.5 h, cooled to −78 °C, and opened. The individual components of the reaction mixture were isolated by preparative VPC (column B, 120 °C) to yield, in the order of increasing retention time, **6** (39% relative yield) which was identical with an authentic sample[5] and **7** (43% relative yield): IR 1618, 1021, 700 cm^{-1}; UV max (hexane) 213 nm (ε 5000); NMR δ 0.4–1.0 (m, 2), 1.1–2.1 (m, 10), 5.62 (d, J = 10.5 Hz, 1), 5.99 (dd, J = 10.5, 4.5 Hz, 1); ^{13}C NMR δ 7.09 (t), 12.23 (d), 16.31 (d), 22.27 (t), 28.20 (d), 29.04 (d), 39.75 (d), 41.51 (d), 127.58 (d), 128.70 (d); mass spectrum (70 eV), m/e 134. The third fraction was 1,2,3,4-tetrahydronaphthalene.

A similar result was obtained when the neat triene was heated in the same way.

Thermal Isomerization of 4. In the manner described above, a solution of 25 mg of **4**[4] in 0.4 mL of benzene-d_6 was heated at 205 °C for 2 h. The major component of the reaction mixture (95% relative yield) was isolated by preparative VPC (column B, 120 °C) and identified as **8**: IR 3085, 3040, 3025, 1450, 1030, 1008, 818, 700 cm^{-1}; UV max (hexane) 214 nm (ε 3600); NMR δ 0.30–0.98 (m, 2), 1.0–2.7 (m, 12), 5.17 (d, J = 10.0 Hz, 1), 6.02 (d, J = 10.0 Hz, 1); ^{13}C NMR δ 8.49 (t), 11.07 (d), 19.99 (d), 26.69 (t), 27.28 (t), 33.35 (t), 34.44 (t), 37.09 (d), 37.52 (d), 128.16 (d), 128.60 (d); mass spectrum (70 eV), m/e 148, 133, 119, 105, 91; exact mass 148.1220.

Thermal Isomerization of 5. (a) Preparation of 5. A solution of 1.0 g of *trans*-bicyclo[4.3.0]nona-2,4-diene (**9**)[5] in 140 mL of spectroquality pentane was irradiated at 254 nm in a Rayonet reactor at 25 °C for 4 h. The reaction was followed by VPC (column A, 128 °C) and at the end of the irradiation period the mixture was shown (VPC) to consist of 65% starting *trans*-diene, 15% *cis,cis,cis*-cyclonona-1,3,5-triene, and 15% tricyclo[4.3.0.0^{2,9}]non-7-ene. The reaction mixture was concentrated at 0 °C and the NMR spectrum displayed vinyl proton bands in

(10) Baldwin, J. E.; Kaplan, M. S. *J. Am. Chem. Soc.* **1971**, *93*, 3969.
(11) Vogel, E.; Grimme, W.; Dinne, E. *Tetrahedron Lett.* **1965**, 391.
(12) The thermal conversion of *cis*-bicyclo[5.2.0]nona-2,8-diene to *cis*-bicyclo[4.3.0]nona-2,4-diene does not fit the behavior pattern reported for the homologous ten- and eleven-carbon analogues. However, the thermal behavior is consistent with that reported for other bicyclo[5.2.0]nonene derivatives (see: Jones, M., Jr.; Reich, S. D.; Scott, L. T. *J. Am. Chem. soc.* **1970**, *92*, 3118; Radlick, P.; Fenical, W. *Ibid.* **1969**, 1560). Clearly the mechanism operating in these examples must be different from the mechanism governing cis-fused bicyclic cyclobutenes with larger methyl chains which are known to give rise to trans-fused bicyclic dienes.

(13) Two such possible mechanisms are (a) thermally induced isomerization of two double bonds and (b) a 1,7-H sigmatropic shift.

addition to those related to the above mentioned irradiation products.

The concentrate was chromatographed on a 16% silver nitrate impregnated alumina column. Elution with pentane through ether yielded the above three compounds in pure form. The column packing was removed and treated with excess concentrated NH_4OH solution, and the mixture extracted with pentane. The solvent was removed by rotary evaporation to yield 50 mg of a new compound which possessed the same retention time on column B as did the *trans*-diene and readily polymerized. The compound was identified as *cis,trans,cis*-cyclonona-1,3,5-triene (**5**) on the basis of the spectral properties: IR (CCl_4) 2985, 1626, 978, 917, 678 cm^{-1}; UV max (EtOH) 246 nm (ϵ 2400); NMR δ 2.24–2.60 (br q, J = 5 Hz, 4), 5.10–5.30 (m, 4), 6.40 (s, $w_{1/2}$ = 2 Hz, 2).

(b) Thermal Isomerization. A solution of 150 mg of *trans*-bicyclo[4.3.0]nona-2,4-diene in 35 mL of pentane was irradiated as above for 45 min. The reaction product was separated by preparative VPC on a 10 ft × $^3/_8$ in. Carbowax 6000, 10% KOH column, using a column temperature of 100 °C and a detector temperature of 150 °C. Under these conditions the peak corresponding to the diene/triene was collected and NMR analysis showed the sample to have approximately equal amounts of the diene and triene. When a detector temperature of 250 °C was used, this same fraction consisted of only *trans*-bicyclo[4.3.0]-nona-2,4-diene (**19**).

Thermal Isomerization of 12. In a manner similar to that described for **3**, a solution of 30 mg of **12**[4] in 0.12 mL of benzene was heated at 205 °C for 3.0 h. The reaction mixture was analyzed by VPC (column A) and found to contain >95% of the isomeric **13**: IR 2873, 2832, 2666, 980, 842 cm^{-1}; UV max (methylcyclohexane) 236 nm (ϵ 8800); NMR δ 1.49 (m, 10), 1.78 (s, $w_{1/2}$ = 3.0 Hz, 3), 2.11 (m, 4), 5.37 (td, J = 16.0, 7.0 Hz, 1), 5.86 (d, J = 6.5 Hz, 1), 6.15 (dd, J = 16.0, 6.5 Hz, 1); ^{13}C NMR δ 24.46 (q), 24.56 (t), 25.29 (t), 25.44 (t), 26.94 (t), 27.14 (t), 29.13 (t), 31.89 (t), 123.11 (d, 130.00 (d), 131.36 (d), 140.44 (s).

***cis*-Bicyclo[6.2.0]deca-3,9-diene (14).** By use of the standard procedure for the synthesis of these bicyclic systems,[4] *cis,cis*-cycloocta-1,4-diene was converted to **14**: IR 3150, 3030, 1660, 900, 835, 770, 750, 710 cm^{-1}; NMR δ 1.1–1.8 (m, 4), 2.11 (m, 4), 2.88 (m, 2), 5.69 (m, 2), 6.08 (s, $w_{1/2}$ = 1.5 Hz, 2); ^{13}C NMR δ 27.29 (t), 29.37 (t), 30.24 (t), 30.73 (t), 48.45 (d), 48.98 (d), 129.96 (d), 130.06 (d), 138.89 (d), 140.11 (d).

***cis*-Bicyclo[7.1.0]dec-3-ene-10-carboxylic Acid.** By use of the standard procedure,[4] a 3:1 mixture of *cis,cis*-1,3- and -1,4-cyclononadiene was converted to the cyclopropylcarboxylic ester derivatives (2-ene to 3-ene, 5:3) and the esters were saponified. The solid acids were fractionally crystallized from petroleum ether to yield the desired acid: mp 150–155 °C; NMR δ 0.7–2.8 (m, 13), 5.59 (m, 2), 11.84 (s, 1); mass spectrum (70 eV), m/e 180, 162, 135, 67.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: 73.18; 8.91.

***cis*-Bicyclo[7.2.0]undeca-3,10-diene (15).** By use of the standard procedure for the synthesis of these bicyclic systems,[4] *cis*-bicyclo[7.1.0]dec-3-ene-10-carboxylic acid was converted into **15**: IR 3052, 3027, 1572, 737, 720 cm^{-1}; NMR (benzene-d_6) δ 0.9–3.1 (m, 6), 5.0–5.8 (m, 2), 5.95 (s, $w_{1/2}$ = 1.0 Hz, 2); ^{13}C NMR δ 22.39 (t), 23.07 (t), 23.87 (t), 23.88 (t), 28.02 (t), 48.51 (d), 49.48 (d), 127.59 (d), 131.33 (d), 138.95 (d), 139.92 (d); mass spectrum (70 eV), m/e 148, 133, 119, 105, 91, 79; exact mass 148.1287.

Thermal Isomerization of 14. In a manner similar to that described for isomerization of **3**, a solution of 225 mg of **14** in 0.5 mL of benzene-d_6 was heated at 150 °C for 1.5 h. An approximate 65% conversion to two isomeric products was detected by NMR spectroscopy and VPC (column B, 110 °C). The products were separated by preparative VPC (column B, 110 °C), in order of increasing retention time, to give **7** (42% of product) and **16**: IR 3020, 2925, 2860, 1660, 1640, 979, 832, 815, 715 cm^{-1}; NMR δ 1.63 (m, 2), 2.19 (m, 4), 2.86 (m, 2), 5.18–6.33 (m, 6); ^{13}C NMR δ 23.59 (t), 27.27 (t), 30.34 (t), 32.43 (t), 127.18 (d), 129.18 (d), 129.90 (d), 130.00 (d), 132.48 (d), 133.69 (d); mass spectrum (70 eV), m/e 134, 119, 106, 105, 95; exact mass 134.111.

Thermal Isomerization of 15. In a manner similar to that described for isomerization of **3**, a solution of 148 mg of **15** in 0.4 mL of benzene-d_6 was heated at 155 °C for 1.75 h. The products were isolated by preparative VPC (column B, 120 °C) to yield, with increasing retention time, **8** (41%) and **17** (49%): IR 3030, 2914, 2841, 1660, 1639, 967, 956, 844, 824, 750, 737, 700 cm^{-1}; UV max (methanol) 234 nm (ϵ 4900); NMR δ 1.38 (m, 4), 2.09 (m, 4), 2.78 (m, 2), 5.02–5.83 (m, 4), 6.05–6.58 (m, 2); ^{13}C NMR δ 24.08 (t), 25.54 (t, 2 C), 27.67 (t), 31.61 (t), 124.72 (d), 129.38 (d), 129.43 (d), 129.53 (d), 131.04 (d), 135.21 (d); mass spectrum (70 eV), m/e 148, 135, 120, 119, 105, 91, 79; exact mass 148.1228.

***cis,cis,cis*-Cyclodeca-1,3,5-triene (18).** A solution of 400 mg of **3**[4] in 200 mL of pentane was irradiated, under N_2, at 254 nm in a Rayonet reactor at room temperature. The course of the reaction was monitored by VPC (column A, 70 to 140 °C at 4 °C/min) and the irradiation halted at 105 min. VPC analysis showed that 75% of starting triene had been isomerized. Most of the pentane was removed by distillation through a 10-cm Vigreux column. The remaining yellow oil was purified by preparative VPC (column B, 100 °C) to afford 165 mg of pure *cis,cis,cis*-triene: IR 1669, 1648, 817, 727, 695 cm^{-1}; UV max (hexane) 216 nm (ϵ 4200); NMR δ 1.54 (m, 4), 2.17 (m, 4), 5.53 (m, 2), 5.68 (d, J = 9.0 Hz, 2), 5.95 (s, $w_{1/2}$ = 2.0 Hz, 2); ^{13}C NMR δ 24.47 (t), 25.86 (t), 126.17 (d), 128.99 (d), 133.50 (d); mass spectrum (70 eV), m/e 134.

The compound upon taking up 3 mol of hydrogen gave cyclodecane as the sole product.

***trans,cis,cis*-Cyclodeca-1,3,6-triene (10).** A solution of 276 mg of **18** in 80 mL of pentane at −70 °C under N_2 was irradiated at 300 nm through Pyrex in a Rayonet reactor for 14.5 h. The solution was allowed to warm to 0 °C and extracted with two 15-mL portions of 50% aqueous silver nitrate solution and two 25-mL portions of water. The combined aqueous solution was washed with two 25-mL portions of pentane. The pentane extracts were united and dried ($MgSO_4$), and the solvent was removed, using a rotary evaporator, to yield 103 mg (37%) of **10**: IR 1665, 970, 958, 814, 796, 700 cm^{-1}; UV max (cyclohexane) 218 nm (ϵ 2000); NMR δ 1.59 (m, 2), 2.14 (m, 2), 2.66 (m, 2), 4.80–6.26 (m, 6); ^{13}C NMR δ 25.23 (t), 25.82 (t), 27.13 (t), 33.83 (t), 124.76 (d), 126.65 (d), 129.42 (d), 130.05 (d), 132.68 (d), 135.25 (d); mass spectrum (70 eV), m/e 134.

Thermal Isomerization of 10. In a manner similar to that described for the isomerization of **3**, a solution of 30 mg of **10** in 0.5 mL of benzene-d_6 was placed in a 5-mm od NMR tube which under N_2 at −78 °C, was sealed. The tube was heated at 125 °C for 1 h, cooled to room temperature, and opened. The contents were analyzed by NMR and by VPC (column D) and showed a quantitative conversion of **10** to **7**.

***cis*-Bicyclo[5.2.0]nona-2,8-diene (19).** By use of the standard procedure for the synthesis of these bicyclic systems,[4] *cis,cis*-cyclohepta-1,3-diene was converted to **19**: IR 1643, 1570, 850, 783, 691 cm^{-1}; NMR δ 1.10–1.93 (m, 1), 2.15 (m, 1), 2.95 (m, 1), 3.78 (m, 1), 5.38 (dd, J = 10.0, 3.0 Hz, 1), 5.58 (d, J = 10.0 Hz, 1), 6.04 (d, J = 2.2 Hz, 1), 6.09 (d, J = 2.2 Hz, 1); ^{13}C NMR δ 21.50 (t), 27.04 (t), 28.64 (t), 47.04 (d, 2C), 124.86 (d), 128.80 (d), 137.82 (d), 140.16 (d); mass spectrum (70 eV), m/e 120; exact mass 120.0933.

Thermal Isomerization of 19. In a manner similar to that described for the isomerization of **10**, a solution of 20 mg of **19** in 0.04 mL of benzene-d_6 contained in a sealed NMR tube was heated at 150 °C for 3 h. NMR spectroscopy and VPC (column A) revealed >90% conversion of **19** to **20** which was isolated by preparative VPC (column C, 100 °C); the spectral properties of the product were identical with those shown by an authentic sample.[5]

Registry No. 3, 75993-26-9; **4**, 75993-27-0; **5**, 75993-28-1; **6**, 7360-96-5; **7**, 71055-05-5; **8**, 75993-29-2; **9**, 2144-23-2; **10**, 75993-30-5; **12**, 75993-31-6; **13**, 75993-32-7; **14**, 19043-20-0; **15**, 75993-33-8; **16**, 75993-34-9; **17**, 75993-35-0; **18**, 75993-36-1; **19**, 75993-37-2; **20**, 3054-91-9; *cis*-bicyclo[7.1.0]dec-3-ene-10-carboxylic acid, 75993-38-3; *cis,cis*-1,3-cyclononadiene, 3726-88-3; *cis,cis*-1,4-cyclononadiene, 6731-21-1; *cis,cis*-cyclohepta-1,3-diene, 4054-38-0.