perimental evidence from our laboratory on thioether oxidations establishes this fact. The following points can be made: (1) Although superoxide is undoubtedly generated via reduction of O_2 by $W_{10}O_{32}^{5-}$ or $W_{10}O_{32}^{6-}$,[2] its known rates of reaction with both thioethers and the principal initial product, sulfoxide, are sufficiently low that the latter processes are unlikely to contribute significantly to the chemistry.[34] Disproportionation or capture by electrophiles is a more likely fate of superoxide. (2) Both singlet oxygen, a species known to react with thioethers,[35] and thioether–dioxygen complexes also not likely to play a major role in the chemistry. There is no evidence that polyoxometalates upon excitation with the light used in these studies ($\lambda > 280$ nm) can photosensitize the production of significant quantities of singlet oxygen, and the known absorption spectrum of thioether–dioxygen complexes are such that direct excitation of such species would not compete with the strongly absorbing $W_{10}O_{32}^{4-}$ chromophore. (3) One main role of O_2 in $W_{10}O_{32}^{4-}$-catalyzed oxidative degradation of thioethers under aerobic conditions is doubtless its participation in radical-chain autoxidation at sulfur, a process whose catalysis by metal ions and basic kinetic features have been fairly well investigated.[11b,c]

(33) (a) Capozzi, G.; Modena, G. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974, Part 2, p 785 and references cited within. (b) Reference 7, Chapter 13 and references cited within.
(34) Oae, S.; Takata, T.; Kim, Y. H. *Tetrahedron* **1981**, *37*, 37.
(35) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

Conclusions

A unique catalytic redox system is presented that combines reduction of the excited state of the oxidized form of the catalyst by substrate with reoxidation of the resulting reduced form of the catalyst by another molecule of substrate. The catalyst is the isopolytungstate $W_{10}O_{32}^{4-}$, a complex that has fairly negative ground-state redox potentials (−1.3 and −1.8V vs Ag/Ag^+),[1e,14] yet whose oxidized form has a highly oxidized and kinetically competent charge-transfer excited state.

The principal oxidative process involves abstraction of the hydrogens α to the sulfur atoms of the thioether substrates, while the principal reductive process involves reduction of these substrates by the two-electron-reduced form of the catalyst, $W_{10}O_{32}^{6-}$, generating the thioether anion radical. The latter than undergoes principally C–S bond cleavage.

The unusual dual oxidation and reduction processes lead to products almost never seen in reactions of thioethers with stoichiometric oxidants. High yields of dimeric products resulting from coupling at the α-carbon atoms are seen in some systems, while high yields of hydrocarbons from complete desulfurization of the substrates are seen with the aromatic thioethers.

Acknowledgment. We thank the U.S. Army Research Office (Grant No. DAAL03-87-K-0131) for support of this work. We are indebted to David Bostwich of Georgia Institute of Technology for providing the mass spectral data.

Stereoselective Thermal Rearrangement of *syn*-7-(1,2-Butadienyl)-1-methylbicyclo[2.2.1]hept-2-ene [*syn*-7-(3-Methylallenyl)-1-methylnorbornene]†

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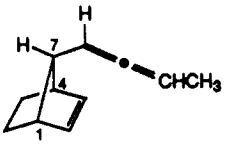
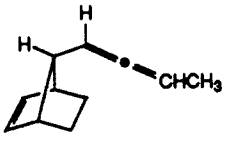
Abstract: The synthesis and separate thermal rearrangements of (±)-(1*R**,4*S**,7*S**)-7-[(*R**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**8a**) and (±)-(1*R**,4*S**,7*S**)-7-[(*S**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**8b**) are described. Both **8a** and **8b** are shown to rearrange to (±)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-6-methylindene (**9**) and (±)-*cis*-1-ethylindene-3a,4,5,7a-tetrahydro-3a-methylindene (**10**) with greater than 90% stereoselectivity. Epimer **8a** gives predominantly (*E*)-**9** and (*Z*)-**10**, whereas **8b** gives predominantly (*Z*)-**9** and (*E*)-**10**, results consistent with either a six-electron [σ2s + π2s + π2s] Cope or eight-electron [σ2s + π2s + (π2s + π2a)] augmented Cope process. Stereochemical assignments (**8a** vs **8b**, (*E*)-**9** vs (*Z*)-**9**, and (*E*)-**10** vs (*Z*)-**10**) are based upon experiments in nuclear Overhauser effect (NOE) difference spectroscopy.

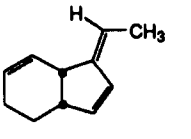
Earlier we reported[1] that (±)-*syn*-7-(1,2-butadienyl)bicyclo-[2.2.1]hept-2-ene (**1a**) undergoes a thermal rearrangement above 160 °C to give racemic trienes (*E*)-**2** and (*Z*)-**2** as the only products, whereas the anti epimer **1b** was found to be thermally stable. We contrasted our results with those obtained with similar vinyl compounds,[2] which tend to indicate that thermal reorganization of the 1,5-diene moiety in **1a** by an ordinary orbital symmetry controlled[3] [σ2s + π2s + π2s] concerted boat-like Cope rearrangement process might be sterically retarded. For example, it was reported[2b] that at 250 °C (±)-*syn*-7-ethenyl-*anti*-7-methoxynorbornane (**3a**) and its anti, syn epimer **3b** rearrange to the same formal Cope product, 1-methoxy-3a,6,7,7a-tetrahydroindene (**4**). 2-Methoxybicyclo[3.2.2]nona-2,6-diene (**5**), a formal [1,3] sigmatropic shift product, was also formed in each case. These results were interpreted in terms of biradical processes initiated by the cleavage of the 1,7-bond in **3a** or **3b**. The methoxy substituents, which are known to stabilize radical centers, undoubtably play a role in favoring the biradical process in these cases. In fact



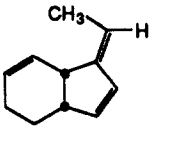
1a



1b



(*E*) · **2**



(*Z*) · **2**

† Taken in part from the 1986 Undergraduate Thesis of R.T.H. and the 1987 Undergraduate Thesis of K.S.K.

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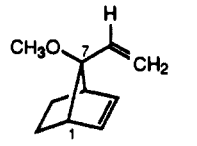
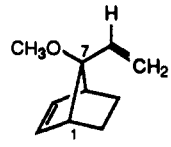
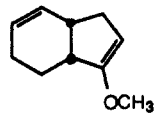
Berson[4] has found that the parent vinyl hydrocarbon *syn*-7-ethenylnorbornene (**6**) is stable at 250 °C and decomposes without rearrangement at 320 °C. The relatively facile **1a** → **2** rearrangement and the relative thermal stability of **1b** clearly show that the allenyl group affords an improved pathway for [3,3] sigmatropic rearrangement relative to a vinyl group in these systems. The fact that only *syn*-allene **1a** but not *anti*-allene **1b** rearrange under these conditions and that no formal [1,3] sigmatropic shift of carbon to give triene **7** is observed for either **1a** or **1b**, as is found for **3a** and **3b**, tends to point to a mechanism which does not involve formation of a biradical derived from initial cleavage of the 1,7-bond in **1a**.



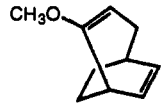
3a



3b



4



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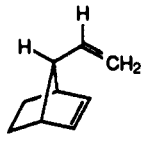

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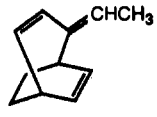
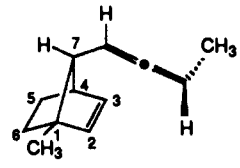


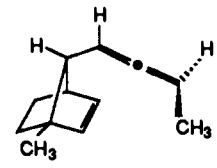
7

In order to learn more about the exact nature of the **1a** → **2** type of rearrangement process, we have now studied the thermal rearrangement of (±)-*syn*-(1,2-butadienyl)-1-methylbicyclo-[2.2.1]hept-2-enes (**8a** and **8b**). These 1-methyl-substituted derivatives of **1a** allow for a test of a concerted vs a nonconcerted process for the corresponding rearrangement of **8** to give trienes **9** and **10**. For example, **8a** would afford only (*E*)-**9** and (*Z*)-**10** if a concerted boat-type Cope process was followed. Likewise **8b** would afford only (*Z*)-**9** and (*E*)-**10** by the same process.

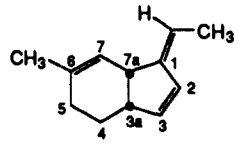
A nonstereoselective biradical process, on the other hand, should give significant amounts of all four trienes (*E*)-**10**, (*Z*)-**10**, (*E*)-**11**, and (*Z*)-**11**. For example, initial bond formation between a carbon of the norbornene double bond and the center allene carbon in either **8a** or **8b**, leading nonstereoselectively to tricyclic biradicals **11a** and **11b** might be feasible. Such a process would benefit from the relief of extra strain in the norbornene ring due to the double bond as well as relief of the strain that results from the cumulated π bonds in the allene group. In addition a biradical corresponding to **11** has been implicated as an intermediate in the photosensitized Cope rearrangement of **1a**, which affords (*E*)-**2** and (*Z*)-**2** as the only products.[5]



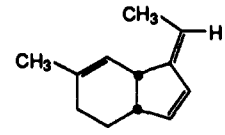
8a



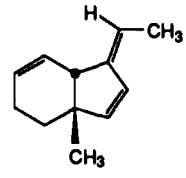
8b



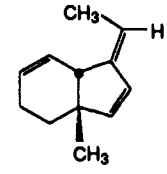
(E) · **9**



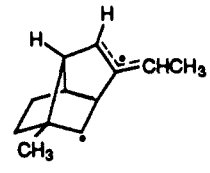
(Z) · **9**



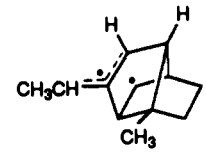
(E) · **10**



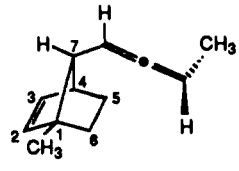
(Z) · **10**



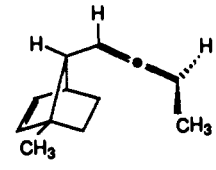
11a



11b



12a



12b

Herein we report on the synthesis, isolation, and stereochemistry of the separate thermolyses of syn epimers (±)-(1*R**,4*S**,7*S**)-7-[(*R**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]-hept-2-ene (**8a**) and (±)-(1*R**,4*S**,7*S**)-7-[(*S**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**8b**), which were first prepared as a mixture along with their corresponding anti epimers (±)-(1*R**,4*S**,7*R**)-7-[(*S**)-1,2-butadienyl]-1-methylbicyclo-[2.2.1]hept-2-ene (**12a**) and (±)-(1*R**,4*S**,7*R**)-7-[(*R**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**12b**).

Results and Discussion

Synthesis, Isolation, and Characterization of 8a, 8b, 12a, and 12b. We patterned our synthesis of a mixture of the *syn*- and *anti*-allenylnorbornenes **8a**, **8b**, **12a**, and **12b** after the synthesis we used to prepare a mixture of **1a** and **1b** from bicyclo[2.2.1]-hept-2-ene (2-norbornene) (**13**), as outlined in Scheme I (R = H).[1a] The 2-methylbicyclo[2.2.1]hept-2-ene (**14**) required in the present case was prepared by a scale up of similar procedures employed by Burgess et al.[6] 2-Norbornanone (norcamphor) (**20**) was converted into *endo*-2-methylbicyclo[2.2.1]heptan-2-ol (**21**) with CH_3MgBr in 96% yield. Then **21** was dehydrated with (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester ($Et_3N^+SO_2N^-CO_2Me$) to afford a 66% yield of a 1:1 mixture of **14** and **19**. This mixture was partially separated by spinning

(1) (a) Duncan, J. A.; Bohle, D. S.; Blanchard, C. A.; Bossé, M. L.; Noland, T. W.; Ford, C. M.; Powell, M. A.; Sutton, M. C.; Eggleston, A. C.; Klevit, R. E.; Krueger, S. M. *J. Am. Chem. Soc.* **1982**, *104*, 2837–2839. (b) Duncan, J. A.; Lee, B. A.; Teng, D. *J. Org. Chem.* **1983**, *48*, 1772–1774.

(2) (a) Berson, J. A.; Jones, M., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5017–5018, 5019–5020. (b) Berson, J. A.; Walsh, E. J., Jr. *Ibid.* **1968**, *90*, 4732–4733. (c) Berson, J. A.; Miyashi, T.; Jones, G. II. *Ibid.* **1974**, *96*, 3468–3476.

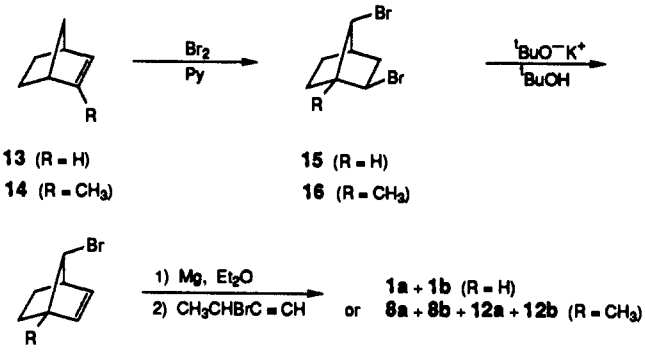
(3) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511–2513. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim/Bergst., 1970.

(4) Berson, J. A. Yale University, 1975; personal communication.

(5) Duncan, J. A.; Aki, L. Y.; Absalon, M. J.; Kwong, K. S.; Hendricks, R. T. *J. Org. Chem.* **1988**, *53*, 196–198.

(6) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26–31.

Scheme I[a]



13 (R = H)
14 (R = CH_3)

15 (R = H)
16 (R = CH_3)

1a + **1b** (R = H)
8a + **8b** + **12a** + **12b** (R = CH_3)

17 (R = H)
18 (R = CH_3)

[a] All compounds are racemic.

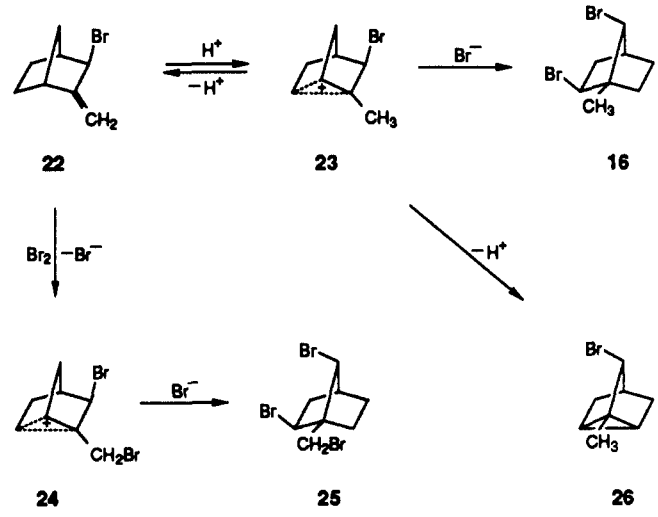
band distillation to give a 4:1 mixture of **14** and **19** which was used for the synthesis discussed below.

19 **20** **21**

The success of the synthesis of **8** and **12** outlined in Scheme I (R = CH_3) hinged upon whether the bromination of **14** would give **16** in a practical yield. It was reported by Werstiuk and Cappelli[7] that chlorination of **14** in pyridine gave 7-chloro-1-methylnortricyclene as the major component (35%) of a total of seven products. No report on the characterization of any of the other products was given. Full details on the results of the bromination[8] and chlorination[9] of 2-norbornene (**13**), however, provided the necessary encouragement to attempt to prepare **16** by bromination of **14** in pyridine. This proved to be very successful. To our surprise the expected 7-bromo-1-methylnortricyclene (**26**) was only a minor product, isolated in about 2% yield. The two major products turned out to be the known *exo*-3-bromo-2-methylenebicyclo[2.2.1]heptane[10] (**22**) and the desired *exo,syn*-2,7-dibromo-1-methylbicyclo[2.2.1]heptane (**16**), isolated by flash column chromatography in 37% and 17% yields, respectively. Only one other minor product, *exo,syn*-2,7-dibromo-1-(bromomethyl)bicyclo[2.2.1]heptane (**25**), was successfully isolated and characterized.

The formation of products **16**, **22**, and **26** can be explained if treatment of **14** with bromine results in bridged ion **23** as a common intermediate which may eliminate a proton to afford either **22** or **26** or add bromide ion to give **16** (Scheme II). The obtension of tribromide **25** can also be explained in a similar way. Reaction of **22** with bromine may afford bridged ion **24**, which may be trapped by bromide ion to give **25**. We recognized that protonation of **22** should lead to bridged ion **23**, hence we treated **22** with hydrogen bromide and obtained additional **16** in 48% yield, resulting in a combined yield of **16** from **14** of 34%. When we omitted the pyridine from the reaction of **14** with bromine, however, hoping that the hydrogen bromide formed in the reaction might convert much of **22** into **16**, capillary GC analysis of the reaction product mixture showed that it was much more complicated than when the pyridine was included. Finally when a small scale reaction using **14** of 99% purity (separated from **19** by preparative GC) was used in place of the preparative scale run, which employed a 4:1 mixture of **14** and **19**, the product distribution was almost identical, showing that all four products may be derived from **14**. In fact **19** was found to be quite unreactive to bromination relative to **14**, and successful reactions were performed on other mixtures of **14** and **19**, even some containing more **19** than **14**.

Scheme II[a]



22 **23** **16**

24 **25** **26**

[a] All compounds are racemic.

Products **16**, **22**, **25**, and **26** were characterized by mass spectrometry (MS), ^1H and ^{13}C NMR including DEPT[11] studies, and in the cases of **16**, **22**, and **25** by ^1H–^{13}C PSCSCM[12] experiments (cf. Experimental Section). The combination of DEPT and PSCSCM experiments made possible the assignment of all carbon and the majority of the proton resonances for dibromide **16**, mp 104–106 °C. The important byproduct **22**, although reported on before,[10] was also fully characterized by NMR spectroscopy, and to our knowledge no NMR data for it has been reported before. 7-Bromo-1-methylnortricyclene (**26**) was in part characterized by comparison of its ^1H NMR spectrum to that reported for 7-chloro-1-methylnortricyclene.[7]

Next in a manner similar to the dehydrobromination of **15** to give **17**,[8] dibromide **16** was successfully dehydrobrominated with $^tBuO^-K^+$ in ^{t}BuOH to afford *syn*-7-bromo-1-methylbicyclo[2.2.1]hept-2-ene (**18**) in 78% yield. Bromoalkene **18** was characterized by MS, ^1H and ^{13}C NMR including a DEPT study, and a ^1H–^{13}C PSCSCM experiment (cf. Experimental Section). Characteristically, the ^1H NMR spectrum of **18** exhibited a doublet of doublets at 6.02 ppm with ^3J = 5.7 and 2.9 Hz for H-3 and a doublet at 5.70 ppm, ^3J = 5.7 Hz, for H-2. The ^{13}C NMR spectrum exhibited corresponding vinyl carbon resonances at 133.12 (C-3) and 136.72 (C-2) ppm, respectively.

The final reaction in our synthesis of **8** and **12**, the coupling of the Grignard of **18** with 3-bromo-1-butyne (cf. Scheme I), proved more troublesome than we had anticipated, given the good results we obtained in coupling the Grignard of **17** with 3-bromo-1-butyne, which afforded **1** in about 25% isolated yield.[1] The reactivity of **18** was found to be considerably less than **17**, and as reflux could not be maintained during the slow dropwise addition of an ether solution of **18** to magnesium, the formation of the Grignard of **18** could not be satisfactorily monitored. This invariably resulted in the production of significant quantities of coupling products of **18**, the six possible $C_{16}H_{22}$ dimethyldinorbornenes, as evidenced by capillary GC and ^1H NMR analysis. The ratio of dimethyldinorbornenes to allenes **8** and **12** was always greater than 3:2.

(7) Werstiuk, N. H.; Cappelli, F. P. *Can. J. Chem.* **1980**, *58*, 1725–1737. Some typographical errors exist in the ^1H NMR data reported for 7-chloro-1-methylnortricyclene.
(8) Kwart, H.; Kaplan, L. *J. Am. Chem. Soc.* **1954**, *76*, 4072–4077.
(9) Roberts, J. D.; Johnson, F. O.; Carboni, R. A. *J. Am. Chem. Soc.* **1954**, *76*, 5692–5699.
(10) Jefford, C. W.; Wojnarowski, W. *Helv. Chim. Acta* **1970**, *53*, 1194–1202. Jefford, C. W.; Wojnarowski, W. *Ibid.* **1972**, *55*, 2244–2252. These reports provide no ^1H or ^{13}C NMR data for the characterization of **22**.
(11) Doddrell, D. M.; Pegg, D. T.; Bendall, M. R. *J. Magn. Reson.* **1982**, *48*, 323–327.
(12) Bax, A.; Sarkar, S. K. *J. Magn. Reson.* **1984**, *60*, 170–176.

We solved this problem by employing an entrainment procedure[13] whereby an equivalent of 1,2-dibromoethane was mixed with **18**, and the mixture was added slowly to 2.2 equiv of magnesium, during which reflux was readily maintained. Use of this procedure resulted in fewer side products, especially the dimethyldinorbornenes, which were formed in a 1:2 ratio along with **8** and **12**. The mixture of syn epimers **8** (37%) and anti epimers **12** (63%) were isolated by preparative GC in approximately 23% yield and partially separated on small scale by rotating disk chromatography by using a rotor coated with silica gel containing silver nitrate. Epimers **8a** and **8b** were cleanly separated from each other and from a mixture of **12a** and **12b** which could not be further separated by this method. The three samples were obtained free of solvent by preparative GC and individually characterized.

Allenes **8a** and **8b** were characterized by MS, ^{1}H NMR including COSY[14] and homonuclear proton decoupling studies, ^{13}C NMR including a DEPT study, and ^{1}H–^{13}C PSCSCM experiments. Full details on these as well as TIIR and nuclear Overhauser effect (NOE)[15] studies are summarized in the Experimental Section. Homonuclear proton decoupling produced the typical result in all cases. For example, irradiation of the overlapping allenyl H resonances in both **8a** and **8b** resulted in the collapse of both the H-7 and allenyl CH_3 resonances to singlets, whereas irradiation of the allenyl CH_3 resonance in each case resulted in a simplification of the allenyl H resonances to pairs of overlapping doublet of doublets. The allenyl CH_3 resonance of one of the epimers of **8** (later determined to be **8a**) was also irradiated at −80 °C in CD_3COCD_3 and the allenyl resonances, which were completely separated under these conditions, collapsed to two separated doublet of doublets (^4J = 6.6 Hz, ^5J = 0.7 Hz for =C=C*H*CH$_3$ and ^3J = 9.4 Hz, ^4J = 6.4 Hz for —C*H*=C=CHCH$_3$). Both **8a** and **8b** produced virtually identical COSY spectra with the expected number of cross peaks, and all the ^{13}C resonances of each could be assigned from the DEPT and PSCSCM studies. Both epimers exhibited the quaternary =C= resonance at 206.1 ppm, characteristic of the allene grouping. The *anti*-allene mixture, **12a** and **12b**, was also characterized by MS, ^{1}H NMR including a COSY experiment, and ^{13}C NMR including a DEPT study.[16]

The coupling constants between the H-7 and —C*H*=C=CHCH$_3$ protons were measured for both **8a** and **8b** at 20 °C and −50 °C in $CDCl_3$ and at −80 °C in CD_3COCD_3 and found to increase only slightly with decreasing temperature. Both **8a** and **8b** were observed at each temperature to have identical ^3J values of 8.0, 8.8, and 9.4 Hz. These large coupling constants suggest a large (~180°) or perhaps, though less likely, a small (~0°) dihedral angle for this vicinal proton coupling at all three temperatures, corresponding to preferred *extended* (cf. Figure 1) or *collapsed* conformations of **8**. Extended conformations would seem to be far less sterically hindered than collapsed ones.[17] Furthermore the ^{1}H NMR spectra of **8a** and **8b** are remarkably similar for both the norbornene ring and allenyl moieties (all corresponding resonances within ±0.02 ppm and nearly equivalent J values), presumably because preferred extended conformations keep the two moieties relatively far apart.

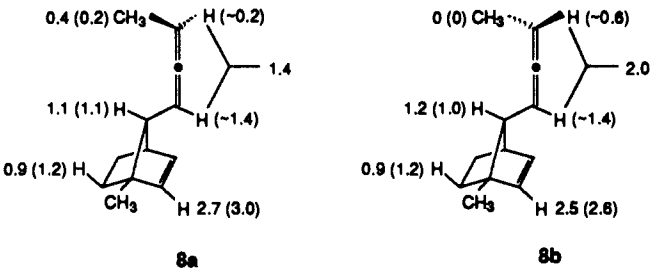


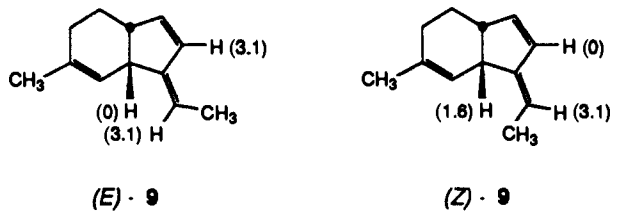
Figure 1. Percent NOE enhancements at 25 °C (no parentheses) and −50 °C (parentheses) for *syn*-allenes **8a** and **8b** in $CDCl_3$ with saturation of the bridgehead CH_3 resonance.

The critical assignment of stereochemistry to the two possible epimers of **8**, i.e., as **8a** or **8b**, was made on the basis of the NOE experiments. Longitudinal (T_1) relaxation times for each epimer were measured at 25 °C and −50 °C in $CDCl_3$. At 25 °C some of the resonances (e.g., allenyl hydrogens) had T_1s as long as 34.5 s. Even at −50 °C some T_1s were 10 s long, and hence 1D NOE experiments were performed instead of 2D NOESY[18] ones, which would have required very long times for data acquisition. For the experiments performed at 25 °C the presaturation time was 10 s and the total recycle time was 22.3 s, whereas at −50 °C the presaturation and total recycle times were 3.5 and 7.6 s, respectively. The results are summarized in Figure 1 which shows the percent NOE enhancements measured for various resonances upon saturation of the bridgehead CH_3 resonance in each epimer at 25 °C (no parentheses) and −50 °C (parentheses). At both 25 °C and −50 °C, consistent NOE enhancements to H-2, H-7, and H_{exo}-6, closest neighbors to the saturated bridgehead CH_3 in the rigid norbornene ring, were observed as expected for both epimers. Also as expected, no detectable enhancements were observed for the H-3, H-4, and H_{exo}-5 resonances. Possible NOE enhancement for either H_{endo} was obscured by off resonance effects.

Most importantly, we were able to assign structure **8a** to the compound that exhibited a nonzero NOE enhancement to the allenyl CH_3 at both 25 °C and −50 °C, i.e., the compound that has the CH_3 groups syn when in an extended or nearly extended conformation, as shown in Figure 1. As expected, the other epimer with the CH_3 groups anti in an extended conformation, and assigned structure **8b**, was shown to exhibit the larger NOE enhancement (2.0% vs 1.4%) for the allenyl hydrogens, the resonances of which are nearly completely overlapped at 25 °C. Furthermore at −50 °C, conditions under which the allenyl H resonances are partially separated and hence could be approximately integrated separately in the difference spectrum, the NOE enhancement for the =C=C*H*CH$_3$ nucleus of **8b** (0.6%) was, as expected, found to be greater than the enhancement for the same nucleus in **8a** (0.2%). The fact that an NOE enhancement of 1.4% (−50 °C) was measured for the —C*H*=C=CHCH$_3$ nucleus in both **8a** and **8b**, probably indicates a similar conformation for the two epimers.

Thermal Rearrangement of 8a and 8b (Preparative Scale). When a mixture containing 37% *syn*- and 63% *anti*-allenylnorbornenes **8a**, **8b**, **12a**, and **12b** was injected on a preparative GC with an oven temperature of 215 °C and an injector temperature of 310 °C, the *anti*-allenes **12a** and **12b** were recovered unchanged; however, four rearrangement products, trienes (*Z*)-**9**, (*E*)-**9**, (*Z*)-**10**, and (*E*)-**10**, were formed from **8a** and **8b**, which survived in only trace quantities themselves. The four trienes were partially separated by rotating disk chromatography on SiO_2/$AgNO_3$ into a mixture of the *E* and *Z* diastereomers of (±)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-6-methylindene (**9**) and a mixture of the *E* and *Z* diastereomers of (±)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-3a-methylindene (**10**). These two structurally isomeric mixtures of diastereomers were both characterized by MS, ^{1}H, NMR, including homonuclear proton decoupling, and 1D NOE

(13) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, pp 417–418.
(14) Morris, G. A. *Magn. Reson. Chem.* **1986**, *24*, 371–403.
(15) Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergomon: Oxford, 1987; Chapter 5.
(16) Although the differentiation between *syn*- and *anti*-allenes **8** and **12** was primarily based upon which pair could be thermally rearranged and which could not, the relatively short longitudinal (T_1) relaxation time of 15.6 s (25 °C) measured for the —C*H*=C=CHCH$_3$ resonance of the **12a** and **12b** mixture, compared to T_1s of 34.5 and 30.7 s for **8a** and **8b**, respectively, tends to support this conclusion. Presumably, preferred conformations of **12a** and **12b** would be extended ones, as opposed to the collapsed ones represented above, which allow a close enough approach of the —C*H*=C=CHCH$_3$ nucleus to the H_{exo} nuclei, in order to significantly shorten the T_1 for the —C*H*=C=CHCH$_3$ resonance in **12** relative to **8**.
(17) The long T_1s observed for the —C*H*=C=CHCH$_3$ resonance appear to support this contention since in a collapsed conformation the T_1 might be expected to be much shorter, given that the —C*H*=C=CHCH$_3$ and H-7 nuclei would be quite close to each other.
(18) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546–4553.



(*E*)-**9** (*Z*)-**9**

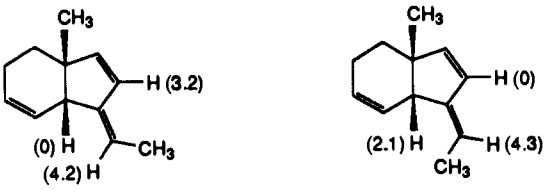
Figure 2. Percent NOE enhancements at 25 °C for trienes (*E*)-**9** and (*Z*)-**9** in C_6D_6 with saturation of the $=CHCH_3$ resonance.

studies (cf. Experimental Section). It was clear from the ^1H NMR spectrum of each mixture that two diastereomers were present in a 2:3 ratio. Furthermore it was shown that the diastereomer determined by NMR integration to be present in the greater quantity also gave the greater integrated response at the flame detector of a capillary GC. This was accomplished by analyzing mixtures of **9** or **10** with different ratios of *E* to *Z* diastereomers by both capillary GC and ^1H NMR integration. Hence once the *E* or *Z* stereochemical assignments were made by critical NOE experiments (see below), mixtures containing any or all of the trienes (*Z*)-**9**, (*E*)-**9**, (*Z*)-**10**, and (*E*)-**10** could be easily analyzed to determine the approximate percent of each component present. (See section on stereochemistry below.)

Trienes (*Z*)-**9** and (*E*)-**9** both exhibited complex multiplets for the H-3a, H-7a, H_{exo}-4, H_{exo}-5, H_{endo}-4, and H_{endo}-5 protons, broad doublets for H-3, and broad quartets for $=CHCH_3$. In addition the H-2 resonance in (*Z*)-**9** was a doublet of doublets with coupling both to H-3 (^3J = 5.5 Hz) and H-3a (^3J = 2.3 Hz), whereas in (*E*)-**9** it was a broad doublet with measurable coupling only to H-3 (^3J = 5.6 Hz). On the other hand, the $=CHCH_3$ resonance, which appeared only as a doublet (^3J = 7.0 Hz) in (*Z*)-**9**, due to coupling to $=CHCH_3$, appeared as a doublet of doublets in (*E*)-**9** due to additional long-range coupling to H-7a (^5J = 1.9 Hz). These assignments were confirmed by the homonuclear proton decoupling experiments. When the H-2 resonances of (*Z*)-**9** and (*E*)-**9** were separately irradiated, the corresponding H-3 resonances collapsed to broad singlets in each case. Furthermore, saturation of the quartet for $=CHCH_3$ in (*Z*)-**9** caused the collapse of the $=CHCH_3$ resonance to a singlet, whereas saturation of the quartet in (*E*)-**9** resulted in simplification of the $=CHCH_3$ resonance from a doublet of doublets to a doublet (^5J = 1.9 Hz). When the H-3a resonance in (*Z*)-**9** was irradiated, the H-2 resonance collapsed to a doublet (^3J = 5.5 Hz), and when the H-7a resonance in (*E*)-**9** was saturated, the $=CHCH_3$ resonance simplified to a doublet (^3J = 7.0 Hz). Finally, simultaneous irradiation of the $=CHCH_3$ resonances in the (*Z*)-**9** and (*E*)-**9** mixture caused the two $=CHCH_3$ quartets to collapse to singlets.

The assignment of *E* or *Z* stereochemistry to the epimers was readily made by using NOE difference spectroscopy. These experiments used a presaturation time of 20 s, and the total relaxation delay time was 11.6 s. The important results are summarized in Figure 2, which shows the percent NOE enhancements measured for three of the resonances upon saturation of the $=CHCH_3$ resonance in both (*Z*)-**9** and (*E*)-**9** at 25 °C. NOE enhancements for other resonances were either affected or obscured by the nonselective nature of the saturation of the $=CHCH_3$ resonance, which resulted in at least partial saturation of the H_{exo}-4, H_{exo}-5, H_{endo}-4, H_{endo}-5, and C6:CH_3 resonances as well. Nevertheless, the results are clear. The *Z* epimer is the one which shows an NOE enhancement (1.6%) of the H-7a resonance but no detectable enhancement of the H-2 resonance. Likewise the *E* epimer is the one which shows an enhancement of the H-2 resonance (3.1%) but no detectable NOE enhancement of the H-7a resonance. Good consistency is demonstrated by the observance of the same measured value of 3.1% for the NOE enhancement of the $=CHCH_3$ resonance in both cases.

Both trienes (*Z*)-**10** and (*E*)-**10** also exhibited complex multiplets for the H_{exo}-4, H_{exo}-5, H_{endo}-4, H_{endo}-5, and H_{endo}-7a protons. In addition the H-6 and H-7 resonances for both epimers, along with the H-3 resonance of (*E*)-**10**, were all overlapped together in the 300-MHz spectrum, obscuring their separate coupling



(*E*)-**10** (*Z*)-**10**

Figure 3. Percent NOE enhancements at 25 °C for trienes (*E*)-**10** and (*Z*)-**10** in C_6D_6 with saturation of the $=CHCH_3$ resonance.

patterns. Broad doublets were observed for the H-2 protons in each case and for the H-3 resonance in (*Z*)-**10** (^3J = 5.5 Hz). As was the case for (*Z*)-**9** and (*E*)-**9**, epimer (*Z*)-**10** exhibited only a doublet (^3J = 6.9 Hz) for $=CHCH_3$, whereas in (*E*)-**10** this resonance appeared as a doublet of doublets as a consequence of long-range coupling to H-7a (^5J = 1.5 Hz). These assignments were confirmed by homonuclear proton decoupling experiments. Irradiation of the doublet for H-3 in (*Z*)-**10** caused the H-2 doublet to collapse to a singlet and visa versa, and saturation of the multiplet containing the several overlapping resonances specified above caused, among other things, the H-2 resonance of (*E*)-**10** to collapse to a singlet. Furthermore, saturation of the quartet belonging to $=CHCH_3$ in (*Z*)-**10** caused the $=CHCH_3$ doublet resonance to simplify to a singlet, overlapped with the doublet of doublets for the corresponding resonance in (*E*)-**10**. Likewise, irradiation of the $=CHCH_3$ quartet resonance in (*E*)-**10** gave a doublet for the $=CHCH_3$ resonance, overlapped with the doublet for the corresponding resonance in (*Z*)-**10**. When the H-7a resonance in (*E*)-**10** was saturated, the $=CHCH_3$ resonance simplified to a doublet (^3J = 6.7 Hz). Finally, simultaneous irradiation of the $=CHCH_3$ resonances in the (*Z*)-**10** and (*E*)-**10** mixture caused the two $=CHCH_3$ quartets to collapse to singlets.

The assignment of *E* or *Z* stereochemistry to **10** was made by NOE difference spectroscopy under the same conditions as described above for the NOE study of **9**. The essential results are summarized in Figure 3 which shows the percent NOE enhancements measured for three of the resonances upon saturation of the $=CHCH_3$ resonance in both (*Z*)-**10** and (*E*)-**10**. NOE enhancements for other resonances were either affected or obscured by the nonselectivity of the saturation or by being overlapped with other resonances. As was the case for **9**, the results are strikingly clear. The *Z* epimer is the one which shows an NOE enhancement (2.1%) of the H-7a resonance but no detectable enhancement of the H-2 resonance. Similarly the *E* epimer is the one which shows an enhancement of the H-2 resonance (3.2%) but no detectable NOE enhancement of the H-7a resonance. Good consistency is again demonstrated by the similar NOE enhancements measured for the $=CHCH_3$ resonance in each case (4.2% and 4.3%).

Stereochemistry of the Separate Thermal Rearrangements of 8a and 8b. When *syn*-allenylnorbornene **8a** was thermally rearranged by injecting it onto a preparative GC (injector temperature 310 °C, oven temperature 215 °C), it afforded 95% trienes (*E*)-**9** (64%) and (*Z*)-**10** (31%), as determined by capillary GC analysis. (Percentages represent percent of product mixture.) Minor quantities of trienes (*Z*)-**9** (3%) and (*E*)-**10** (2%) were obtained as the only other products detected by capillary GC, along with residual **8a** which did not rearrange to **8b**. Thermal rearrangement of *syn*-allenylnorbornene **8b** under the same conditions gave the essentially opposite result, affording 96% trienes (*Z*)-**9** (59%) and (*E*)-**10** (37%) as the major products. The only other products detected were (*E*)-**9** (3%) and (*Z*)-**10** (1%), along with residual **8b**. When a mixture of *anti*-allenylnorbornenes **12a** and **12b** in a 2:3 ratio was injected onto the preparative GC under the same conditions, they were recovered unrearranged in the original 2:3 ratio.

Conclusions

(±)-*syn*-7-(1,2-Butadienyl)-1-methylbicyclo[2.2.1]hept-2-enes (**8a** and **8b**) were synthesized and found to undergo Cope-type

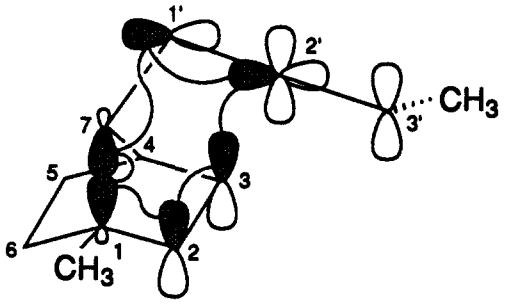


Figure 4. Six-electron [σ2s + π2s + π2s] Cope process for **8a**.

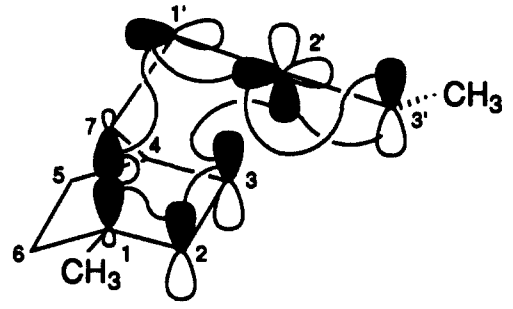


Figure 5. Eight-electron [σ2s + π2s + (π2s + π2a)] augmented Cope process for **8a**.

thermal rearrangements with greater than 90% stereoselectivity as explained above. These *syn*-allenylnorbornenes certainly behave differently than (1) their anti epimers **12a** and **12b**, which experience no rearrangement at least under the same conditions; (2) the *syn*- and *anti*-vinylnorbornenes **3a** and **3b**, which *both* rearrange under similar conditions,[2b] albeit almost certainly by a nonconcerted pathway; and (3) *syn*-vinylnorbornene **6**, which could not be made to rearrange in any manner whatsoever without first decomposing.[4] Rearrangements of **8a** and **8b** by a mechanism involving initial cleavage of their 1,7- or 4,7-bonds to form biradicals, which might account for the rearrangements of vinyl systems **3a** and **3b**,[2b,19] seem unlikely since presumably less stereoselectivity and a more equal product distribution from both **8a** and **8b** should be observed in that case. If such a biradical mechanism was involved in the **8a** and **8b** rearrangements, then **12a** and **12b** might also be expected to rearrange under the same conditions and **8** and/or **12** might be expected to afford formal [1,3] sigmatropic shift products (i.e., 1- and 4-methyl-substituted trienes **7**) as well, since **3a** and **3b** have been shown to thermally rearrange to **5**.[2b]

The high level of stereoselectivity observed in the rearrangements of **8a** and **8b** suggest that they are probably concerted. The demonstrated stereopreference [i.e., **8a** → (*E*)-**9** + (*Z*)-**10** and **8b** → (*Z*)-**9** + (*E*)-**10**][20] is consistent with an orbital symmetry controlled[3] six-electron [σ2s + π2s + π2s] boat-type Cope process as depicted in Figure 4 for **8a**. When the methyl-substituted bridgehead bond (1,7-bond) in **8a** is cleaved, it is easy to see from Figure 4 that triene (*E*)-**9** should be the product of such a concerted Cope process. Likewise when the other bridgehead bond (4,7-bond) in **8a** is cleaved, the expected product by this pathway should be triene (*Z*)-**10**, as is observed, and clearly **8b** would be expected to give trienes (*Z*)-**9** and (*E*)-**10** by this same pathway.

The increased reactivity and high stereoselectivity observed in the rearrangements of **8a** and **8b**, relative to the vinyl systems, might also be attributed in part to the excellent overlap of the norbornene ring C_2–C_3 π bond and the p AO on the central carbon atom of the 1,2-butadienyl moiety that is part of the $C_{2'}$–$C_{3'}$ π bond. This p AO can be oriented directly above the C_2–C_3 π bond of the norbornene ring in collapsed[21] conformations of **8a** and **8b**, and such orbital interaction would directly involve the $C_{2'}$–$C_{3'}$ π bond. This is in sharp contrast to the poor overlap of the C_2–C_3 π bond of the norbornene ring with the other p AO on the central carbon atom of the allenyl moiety (belonging to the $C_{1'}$–$C_{2'}$ π bond) that results from the limited conformational mobility associated with these systems (cf. Figure 4). Consequently the allenyl system might be considered to be utilized as a four-electron (π2s + π2a) component in an orbital symmetry controlled[3] overall eight-electron [σ2s + π2s + (π2s + π2a)] augmented Cope process as depicted in Figure 5 for **8a**. As can clearly be seen by comparing Figures 4 and 5, the symmetry allowed orbital topology for this eight-electron process is also consistent with the observed stereochemistry [e.g., formation of (*E*)-**9** from **8a** when the methyl-substituted bridgehead bond (1,7-bond) is cleaved]. In addition, the strain which results from the cumulated[22] π bonds present in **8a** and **8b**, that reduces the strength of the π bonds relative to a vinyl group, may be partially responsible for the increased reactivity observed in the allenyl vs vinyl systems.

The use of an allene as a four-electron component has been considered previously.[23] Second-order PMO calculations applied to a transition-state model involving an allene as a π2s + π2s component in [π2s + (π2s + π2s)] cycloadditions with alkenes have been compared to calculations applied to models which use the allene as only a π2a component in [π2s + π2a] cycloadditions, and only the augmented six-electron process correctly predicted experimentally observable regio- and stereoselectivities in many cases.[23] Nevertheless, there appears to be no clear experimental evidence in the literature for the participation of an allene as a four-electron component in a cycloaddition reaction. Such participation might be expected to be more common in an *intramolecular* cycloaddition process, involving a transition state of more restricted conformational mobility, however, than for an *intermolecular* cycloaddition process. In fact in a recent presentation, Danheiser[24] proposed a [π2s + (π2s + π2s)] transition state model for an intramolecular cycloaddition involving allene and alkene components. Thus, it is certainly plausible that an allene might be utilized as a four-electron [π2s + π2a] component in other intramolecular processes such as a Cope rearrangement, especially in molecules such as **8a** and **8b** which can take advantage of especially favorable orbital overlap.

In summary we have demonstrated that allenylnorbornenes **8a** and **8b** readily undergo thermal rearrangement in a highly stereoselective (~90%) fashion. The lack of 100% stereoselectivity can be attributed to a minor pathway involving the formation of the previously mentioned tricyclic biradical intermediates **11a** and **11b**. Cleavage of the 1,7-bond in **11a** would lead to (*E*)-**9** and (*Z*)-**9** and of the 1,4-bond in **11b** to (*E*)-**10** and (*Z*)-**10**.[25]

(19) In ref 2c, Berson proposes an alternative mechanism for the thermal rearrangement of 7-propenyl-7-methoxynorbornenes analogous to **3a** and **3b**, involving an initial [1,3] sigmatropic shift of unknown concert with the C_7 carbon acting as the migrating group. Such a rearrangement could lead to *exo*- or *endo*-7-propenylbicyclo[4.1.0]heptenes which could then afford a formal [1,3] sigmatropic shift product analogous to 4, via bridgehead carbon migration. Since neither **1b** nor **12** could be made to rearrange, and **1a** and **8** give only formal [3,3] sigmatropic shift products with no trace of [1,3] sigmatropic shift products of any kind, it seems unlikely that the mechanism proposed in ref 2c is followed by compounds **1** and **8**.

(20) The obtension of about twice as much vinyl methyl-substituted triene **9** as bridgehead methyl-substituted triene **10** amongst the two major rearrangement products of both **8a** and **8b** probably reflects an approximate 2:1 greater ease of cleavage of the 1,7-bonds (i.e., the methyl-substituted bridgehead bonds) relative to the 4,7-bonds in **8a** and **8b**.

(21) The relatively high temperatures required for these rearrangements may be due, as suggested previously,[1a] to a low incidence of the required collapsed conformations, as supported by the ^{1}H NMR data discussed above. In this regard it should be noted that **8a** and **8b** were successfully rearranged with the preparatory GC injector set to the lower temperature of 250 °C (oven temperature 210 °C) as well; however, the percent which rearranged was less. It has been reported[1b] that **1a** rearranges above 160 °C; however, the **8a** or **8b** rearrangements were not checked at temperatures between 150 °C, at which temperature (GC injector and oven) they were collected without any detectable rearrangement by preparatory GC, and 250 °C.

(22) For example, the observed standard heat of formation of 2,3-pentadiene (31.79 kcal mol^{-1}) is 6.4 kcal mol^{-1} higher than the observed standard heat of formation of 1,4-pentadiene (25.41 kcal mol^{-1}) [Fraser, F. M.; Prosen, E. J. *J. Res. Natl. Bur. Std.* **1955**, *54*, 143.]

(23) Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 37–46, and references therein.

(24) Danheiser, R. L. Presented at the 199th National Meeting of the American Chemical Society, Boston, MA, April 1990; paper ORGN 265.

Nevertheless, the major preferred pathway for the thermal rearrangement of **8a** and **8b** appears to be a concerted one. The observed stereopreference is equally consistent with a six-electron [σ2s + π2s + π2s] Cope (cf. Figure 4) or an eight-electron [σ2s + π2s + (π2s + π2a)] augmented Cope process (cf. Figure 5) as described above. Although our data does not fully distinguish between these two alternatives, we have presented supportive arguments in favor of the eight-electron process. It is probable that the **1a** → **2** rearrangement[1] then also follows the same pathway as does the **8** → **9** + **10** rearrangement.

Experimental Section

General Procedures and Materials. All 75.5-MHz ^{13}C and 300-MHz ^1H NMR spectra, including COSY[14] (correlation spectroscopy), DEPT[11] (distortionless enhancement by polarization transfer), ^1H–^{13}C PSCSCM[12] (phase sensitive chemical shift correlation method), and ^1H NOE[15] (nuclear Overhauser effect) difference spectra, were recorded on a G.E. QE-300 spectrometer. Unless otherwise noted, ^1H NMR spectra were obtained at 20 ± 1 °C in $CDCl_3$ with $(CH_3)_4Si$ (δ = 0.0 ppm) or $CHCl_3$ (δ = 7.26 ppm) as internal standard. ^1H NMR spectra obtained in CD_3COCD_3 were referenced to the center multiplet of CD_3COCD_2H (δ = 2.04 ppm) and in C_6D_6 to C_6D_5H (δ = 7.15 ppm). All ^{13}C spectra were obtained at 20 ± 1 °C and referenced to the center multiplet of the $CDCl_3$ solvent (δ = 77.00 ppm).

2D COSY data sets for *syn*-allenes **8a** and **8b** consisted of 200 blocks of 1 K FIDs (free induction decays), with zero filling in the second FT such that the resulting 2D contour plot had 512 × 512 points. Sixteen acquisitions were collected per block with a delay time of 1 s, and a full cycle was used with compensation for quadrature error peaks in F2. ^1H–^{13}C PSCSCM spectra consisted of 128 blocks of 4 K FIDs obtained by the TPPI (time proportional phase incrementation) technique. T_1s (longitudinal relaxation times) were measured on the QE-300 by the inversion-recovery method (T1IR) and make use of the T1I3R fitting function.[26] Ten points were plotted for each separate resonance of **8a** and **8b** (25 °C and −50 °C) and **12** (25 °C) corresponding to acquisition delay times of 5 × 10^{-6}, 0.1, 0.5, 1.0, 3.0, 7.0, 15, 20, 30, and 45 s (recycle delay time 3 min).

^1H NOE difference spectroscopy of *syn*-allenes **8a** and **8b** as well as measurements of their T_1s, was performed on samples prepared in 99.96% $CDCl_3$ (Aldrich), which had been degassed by being subjected to five freeze–pump–thaw cycles before sealing under N_2 and vacuum. The NOE experiments were run in double precision at both 25 °C and −50 °C without spinning the samples. Eight scans were acquired with the irradiation on resonance followed by eight scans off resonance, and the process was repeated 128 times for the experiments done at 25 °C and 94 times at −50 °C. The difference spectra were obtained from subtraction of the FIDs collected for the resonance saturated and the off resonance nonsaturated experiments, prior to Fourier transformation. For the experiments conducted at 25 °C, the recycle delay, presaturation, acquisition, and total recycle times were 10.0, 10.0, 2.3, and 44.5 s, respectively (data size 16 K). At −50 °C the corresponding times were 3.5, 3.5, 1.1, and 16.3 s, respectively (data size 8 K). Percent NOE enhancements were obtained by integrating the affected resonance relative to the irradiated bridgehead CH_3 resonance (80% saturated) in the difference spectrum in each case. ^1H NOE difference spectroscopy of pairs of trienes (*Z*)-**9**/(*E*)-**9** and (*Z*)-**10**/(*E*)-**10** was performed on spinning (22 rpm) samples in 99.96% C_6D_6 (Aldrich), which had been degassed by bubbling with argon for 15 min. Eight scans were acquired with the irradiation on resonance followed by eight scans off resonance, and the process was repeated 20 times. The difference spectra were obtained from subtraction of the FIDs collected for the on resonance saturated and the off resonance nonsaturated experiments, prior to Fourier transformation. The recycle delay, presaturation, acquisition, and total recycle times were 0.1, 20, 11.5, and 63.0 s, respectively (data size 64 K). Percent NOE enhancements were obtained by integrating the affected resonance relative to the irradiated $=CHCH_3$ resonance (>90% saturated) in the difference spectrum in each case.

All melting points were determined with a Mel-Temp melting point apparatus and are uncorrected. IR spectra were recorded on an IBM Model 32 FT-IR. Mass spectra (EI) were obtained at 70 eV with a Finnigan Model 4000 mass spectrometer, equipped with an INCOS data system, or on a VG 77E-HF mass spectrometer. Capillary gas chromatographic analyses were performed at a flow rate of 1 mL/min (measured at 100 °C), by using a Hewlett-Packard Ultra no. 2 5% phenylmethylsilicone cross-linked column (25 M × 0.20 mm i.d.; 0.33 μM film thickness) or a Supelcowax 10 bonded phase fused silica Carbowax column (30 M × 0.25 mm i.d.; 0.25 μM film thickness) with a Hewlett-Packard Model 5790 gas chromatograph equipped with a flame ionization detector. Both columns gave similar results. Integrations and retention times were obtained with Hewlett Packard Model 3390A or 3396A integrators. Preparative GC was performed with a Varian Model 1520 gas chromatograph equipped with a thermal conductivity detector and a 10 ft 3 in. × $^3/_8$ in. column of 25% Carbowax 20M on 80/100-mesh Chromosorb W-NAW. Helium was used as the carrier gas, and liquid N_2 was used to condense the samples in collectors protected from moisture with $CaSO_4$. Rotating disk chromatography was performed with a Harrison Research Model 7924T "Chromatotron" by using a 1-mm rotor coated with silica gel 60, PF-254 (EM Reagents 7749) and containing 3.85% silver nitrate. The coating of the rotor with silica gel/$AgNO_3$ followed the recipe provided by Harrison Research. Spinning band distillation was performed on a B/R 36T apparatus. Flash column chromatography was performed under N_2 by using silica gel 60, 200–400 mesh (EM Reagents 9385). Most new compounds (**8a**, **9**, **10**, **12**, **16**, and **18**) were shown to be greater than 98% pure by capillary GC and ^1H NMR spectroscopy. Compounds **8b**, **25**, and **26** were shown to be 93, 96, and, 84% pure, respectively.

All glassware was cleaned in a KOH/2-propanol bath and then rinsed with dilute acetic acid, followed by dilute ammonium hydroxide, and finally distilled water before drying in an oven. Unless otherwise noted, all reactions and distillations were carried out under nitrogen in glassware which was flame-dried under vacuum and cooled under nitrogen before use.

Norbornanone (**20**), methylmagnesium bromide, chlorosulfonyl isocyanate, triethylamine (Gold label), potassium *tert*-butoxide, 3-butyn-2-ol, and phosphorous tribromide (Gold label) were purchased from Aldrich and used without further purification. Ether was distilled from lithium aluminum hydride, acetonitrile and *tert*-butyl alcohol from calcium hydride, benzene from the sodium benzophenone ketyl, and methanol from magnesium methoxide. Solvents (benzene, hexane, pentane, methanol, acetone, methylene chloride, and acetonitrile) were all EM Reagents "Omnisolv" grade.

***endo*-2-Methylbicyclo[2.2.1]heptan-2-ol (21).** A procedure similar to that used by Burgess et al.[6] was employed. A 3 M solution of 350 mL of methylmagnesium bromide in ether (1.05 mol) was cooled to 0 °C, and to it with stirring was added 110 g (1.00 mol) of norbornanone (**20**) over a 1.5-h period. The reaction mixture was stirred for an additional 30 min as it was warmed to room temperature, and then it was hydrolyzed with 160 mL of a solution of saturated ammonium chloride. The resulting ether solution was decanted from the granular magnesium salts, and the salts were extracted with ether (3 × 30 mL). The combined ether solution was concentrated in vacuo to yield 120.6 g (96%) of **21** as a light yellow oil which solidified on standing to give near white crystals, mp 31–32 °C (lit.[6] 30–31 °C). No further purification was necessary: ^1H NMR δ 2.19 (m, 1 H), 2.01 (m, 1 H), 1.94 (m, 1 H), 1.7–1.1 (m, 8 H), 1.30 (s, 3 H, CH_3); IR (CCl_4) 3623 (free OH), 3494 (H-bonded OH), 2955, 2872, 1458, 1449, 1373, 1308, 1186, 997, 951, 938, 926 cm^{-1}.

(Carboxysulfamoyl)triethylammonium Hydroxide Inner Salt Methyl Ester ($Et_3N^+SO_2N^-CO_2Me$). A procedure similar to that used by Burgess et al.,[6] but performed on much larger scale, was employed. Chlorosulfonyl isocyanate (202.5 g, 1.43 mol) was transferred via cannula to a flask containing 420 mL of benzene. A solution of 47.3 g (1.48 mol) of methanol in 60 mL of benzene was added with stirring over a 30-min period, with cooling in a water bath. The benzene and excess methanol were removed in vacuo to yield 248 g (99%) of *N*-carbomethoxysulfamoyl chloride as a white crystalline solid, mp 68–71 °C (lit.[6] mp 70–71 °C): ^1H NMR δ 8.64 (br s, 1 H, NH), 3.95 (s, 3 H, CH_3).

A solution of 297.5 g (2.9 mol) of triethylamine in 500 mL of benzene was cooled to 17 °C, and to it with stirring was added 248 g (1.42 mol) of the *N*-carbomethoxysulfamoyl chloride, dissolved in 200 mL of ether and 1000 mL of benzene, over a 2-h period. The internal temperature was never allowed to exceed 30 °C. The resulting dark amber mixture was filtered and the residue, which contained both $Et_3N^+SO_2N^-CO_2Me$ and $Et_3NH^+Cl^-$, was extracted with acetone. Removal of the acetone in vacuo yielded 315 g (92%) of $Et_3N^+SO_2N^-CO_2Me$, as yellow crystals containing approximately 10 mol percent of $Et_3NH^+Cl^-$ as determined

(25) As can be seen from the data, the vinyl methyl-substituted trienes **9** are slightly preferred over the bridgehead methyl-substituted trienes **10** in each case. Perhaps in the formation of biradical intermediates **11a** and **11b**, the sterically less encumbered **11a**, which leads to trienes **9**, is more readily formed in the initial step.

(26) Levy, G.; Peat, I. *J. Magn. Reson.* **1975**, *18*, 500–521.

(27) Sondheimer, F.; Ben-Efraim, D. A. *J. Am. Chem. Soc.* **1963**, *85*, 52–56.

(28) One of the unsymmetrical $C_{16}H_{22}$ dimethyldinorbornenes was isolated from the mixture by rotating disk chromatography on $SiO_2/AgNO_3$ and gave ^1H NMR (CD_2Cl_2) δ 6.02 (dd, 1 H, ^3J = 5.7, 3.3 Hz, H-3), 5.84 (dd, 1 H, ^3J = 5.5, 3.1 Hz, H-3′), 5.72 (d, 1 H, ^3J = 5.7 Hz, H-2), 5.56 (d, 1 H, ^3J = 5.5 Hz, H-2′), 2.84 (m, 1 H, H-4 or H-4′), 2.58 (m, 1 H, H-4 or H-4′), 1.8–0.9 (m, 10 H, H-5, H-5′, H-6, H-6′, H-7, and H-7′ protons), 1.25 (s, 3 H, CH_3), 1.22 (s, 3 H, CH_3).

by ^{1}H NMR: ^{1}H NMR of $Et_3N^+SO_2N^-CO_2Me$ δ 3.70 (s, 3 H, CO_2CH_3), 3.44 (q, ^3J = 7.3 Hz, 6 H, CH_2), 1.42 (t, ^3J = 7.3 Hz, 9 H, CH_3CH_2).

2-Methylbicyclo[2.2.1]hept-2-ene (14). A modification of the procedure used by Burgess et al.[6] was employed. To 310 g (1.3 mol) of $Et_3N^+SO_2N^-CO_2Me$ in 600 mL of acetonitrile was added 120.6 g (0.96 mol) of alcohol **21** in acetonitrile over a 40-min period, and the resulting dark amber solution heated to 51 °C for 2.5 days. The reaction mixture was cooled, and the yellow upper layer was decanted from the lower layer which was extracted with pentane (4 × 50 mL). The yellow oil obtained after removing the pentane by distillation through a Vigreux column was combined with the original yellow layer to give 68.9 g (66%) of a 1:1 mixture of alkenes **14** and **19**. Spinning band distillation of this mixture afforded 12.8 g (12.3%) of a 4:1 mixture of **14** and **19**, bp 122 °C (760 mm): ^{1}H NMR of **14** δ 5.50 (m, 1 H, =CH), 2.75 (br s, 1 H, CH), 2.59 (br s, 1 H, CH), 1.72 (d, ^3J = 1.63 Hz, 3 H, CH_3), 1.69–1.52 (m, 2 H), 1.38–1.32 (m, 1 H), 1.10–0.90 (m, 3 H).

***exo,syn*-2,7-Dibromo-1-methylbicyclo[2.2.1]heptane (16).** A solution of 12.8 g (0.118 mol) of a 4:1 mixture of alkenes **14** and **19** in 50 mL of CH_2Cl_2 containing 11.7 g (0.148 mol) of pyridine was cooled to −5 °C, and a solution of 18.8 g (0.117 mol) of bromine in 50 mL of CH_2Cl_2 was added over a 2-h period. No anhydrous precautions were taken. The mixture was filtered to remove the precipitated pyridinium bromide, and the filtrate was washed consecutively with 10% aqueous HCl (2 × 20 mL), saturated $NaHCO_3$ (30 mL), and brine (50 mL). The resulting organic solution was dried over $MgSO_4$ and concentrated in vacuo to give 21.6 g of oil. Capillary GC and ^{1}H NMR (integrated) analyses of the oil revealed four major components in an approximate 1:10:6:3 ratio (increasing retention times of 5.3, 5.9, 9.8, and 12.8 min, respectively; temperature program: 90 °C for 3 min and then heated to 225 °C at 15 °C/min). (Approximately the same ratio of products was obtained when an analytical sample of **14** (separated from **19** by preparatory GC) was brominated in the same manner.)

The four components were isolated by flash column chromatography of the oil in approximately three equal portions on three 25 mm × 54 cm columns of silica gel (265 cc) using hexane as eluent. First to be eluted was approximately 0.5 g of 7-bromonortricyclene (**26**) as a colorless oil: ^{1}H NMR δ 3.85 (br s, 1 H, H-7), 2.15 (br s, 1 H, H-4), 2.13 (br d, ^2J = 10.8 Hz, 1 H, H_{exo}-3), 1.52 (br d, ^2J = 11.5 Hz, 1 H, H_{exo}-5), 1.37 (overlapped br d, ^2J = 11.5 Hz, 1 H, H_{endo}-5), 1.34 (overlapped br d, ^2J = 10.8 Hz, 1 H, H_{endo}-3), 1.10 (br s, 2 H, H-2 and H-6); ^{13}C/DEPT δ 64.12 (CH), 39.37 (CH), 32.25 (CH_2), 31.45 (CH_2), 23.37 (C), 19.98 (CH), 18.84 (CH), 13.14 (CH_3); MS, *m/z* (rel intensity) 188 (M^+, 15), 186 (M^+, 18), 107 (100), 91 (75), 79 (100), 65 (20).

Next to be eluted was 8.3 g (37.3%) of *exo*-3-bromo-2-methylenebicyclo[2.2.1]heptane[7] (**22**) as a colorless oil, requiring no further purification: ^{1}H NMR (analysis assisted by a ^{1}H–^{13}C PSCSCM experiment) δ 5.16 (d, ^2J = 0.7 Hz, 1 H, =CH), 5.14 (d, ^2J = 0.7 Hz, 1 H, =CH), 4.46 (br d, 1 H, ^3J = 1.6 Hz, H_{endo}-3), 2.80 (m, 1 H, H-1 or H-4), 2.59 (m, 1 H, H-1 or H-4), 2.01 (m, 1 H), 1.8–1.4 (m, 2 H), 1.35 (m, 1 H), 1.3–1.2 (m, 2 H); ^{13}C/DEPT/PSCSCM δ 156.34 (C-2), 110.61 (=CH_2), 54.73 (C-3), 46.69 (C-1 or C-4), 45.03 (C-1 or C-4), 36.57 (C-7), 28.94 (C-5 or C-6), 26.52 (C-5 or C-6); MS, *m/z* (rel intensity) 188 (M^+, 9), 186 (M^+, 12), 160 (21), 158 (18), 107 (100), 91 (57), 79 (100), 65 (20).

Third to be eluted was 5.2 g (16.5%) of dibromide **16** as a white crystalline solid, mp 104–106 °C, requiring no further purification: ^{1}H NMR (analysis assisted by a ^{1}H–^{13}C PSCSCM experiment) δ 4.02 (m, 1 H, H-2), 3.81 (m, 1 H, H-7), 2.78 (m, 1 H, H_{exo}-3), 2.43 (m, 1 H, H-4), 2.38 (m, 1 H, H_{endo}-3), 1.73 (m, 1 H, H_{exo}-5 or H_{exo}-6), 1.69 (m, 1 H, H_{exo}-5 or H_{exo}-6), 1.44–1.38 (m, 2 H, H_{endo}-5 and H_{endo}-6), 1.33 (s, 3 H, CH_3); ^{13}C/DEPT/PSCSCM δ 61.04 (C-7), 55.80 (C-2), 49.27 (C-1), 44.50 (C-4), 43.53 (C-3), 34.84 (C-5 or C-6), 25.85 (C-5 or C-6), 18.50 (CH_3); MS, *m/z* (rel intensity) 189 (83), 187 (77), 147 (8), 145 (9), 107 (100), 91 (24), 79 (96), 67 (30).

The fourth and final product isolated by flash column chromatography was a solid (mp 37–39 °C) identified as *exo,syn*-2,7-dibromo-1-(bromomethyl)bicyclo[2.2.1]heptane (**25**): ^{1}H NMR (analysis assisted by a ^{1}H–^{13}C PSCSCM experiment) δ 4.12 (m, 1 H, H-2), 3.96 (m, 1 H, H-7), 3.77 (AB, 2 H, CH_2Br), 2.83 (m, 1 H, H_{exo}-3), 2.54 (m, 1 H, H-4), 2.51 (m, 1 H, H_{endo}-3), 2.03 (m, 1 H, H_{exo}-6), 1.78 (m, 1 H, H_{exo}-5), 1.6–1.4 (m, 2 H, H_{endo}-5 and H_{endo}-6); ^{13}C/DEPT/PSCSCM δ 57.44 (C-7), 52.70 (C-1), 52.25 (C-2), 44.60 (C-4), 43.51 (C-3), 35.95 (C-H_2Br), 32.13 (C-6), 25.42 (C-5); MS, *m/z* (rel intensity) 270 (50), 268 (100), 266 (52), 187 (54), 185 (56), 157 (17), 155 (13), 105 (95), 79 (71), 65 (21).

Additional dibromide **16** was secured through hydrobromination of bromide **22**: using no anhydrous precautions, hydrogen bromide gas was bubbled (dispersion tube) through a solution of 8.2 g (0.043 mol) of bromide **22** in 50 mL of CH_2Cl_2 for 1 h. Removal of the excess HBr and solvent in vacuo afforded 10.9 g of oil which was shown by TLC to contain five components. Flash column chromatography of this oil on a 25 mm × 54 cm column of silica gel (265 cc) using hexane as eluent gave a contaminated product which was rechromatographed on 265 cc of silica gel to give 5.56 g (47.5%) of dibromide **16** requiring no further purification: ^{1}H NMR and capillary GC analysis showed that this sample was indistinguishable from that obtained above from the bromination of **14**.

***syn*-7-Bromo-1-methylbicyclo[2.2.1]hept-2-ene (18).** Potassium *tert*-butoxide (5.1 g, 0.045 mol) was added all at once to a solution of 10.7 g (0.040 mol) of dibromide **16** in 40 mL of *tert*-butyl alcohol, and the mixture was heated at 80 °C for 2.5 days, during which another 2.0 g of potassium *tert*-butoxide was added. Capillary GC analysis showed about 7% starting material remained. The mixture was treated with 50 mL of water, and the resulting solution was extracted with ether (2 × 25 mL) followed by pentane (2 × 25 mL). The combined extract was first distilled at atmospheric pressure through a Vigreux column, and the concentrate was vacuum distilled to give 5.8 g (78%) of bromoalkene **18** as a clear colorless liquid, bp 76 °C (38 mm). Capillary GC analysis showed only one component (retention time 2.4 min; 175 °C): ^{1}H NMR (analysis assisted by a ^{1}H–^{13}C PSCSCM experiment) δ 6.02 (dd, ^3J = 5.7, 2.9 Hz, 1 H, H-3), 5.70 (d, ^3J = 5.7 Hz, 1 H, H-2), 3.74 (br s, 1 H, H-7), 3.02 (m, 1 H, H-4), 1.84 (m, 1 H, H_{exo}), 1.54 (m, 1 H, H_{exo}), 1.32 (s, 3 H, CH_3), 1.3–1.1 (m, 2 H, H_{endo} protons); ^{13}C/DEPT/PSCSCM δ 136.72 (C-2), 133.12 (C-3), 72.93 (C-7), 53.50 (C-1), 50.27 (C-4), 29.21 (C-5 or C-6), 24.15 (C-5 or C-6), 16.84 (CH_3); MS, *m/z* (rel intensity) 188 (M^+, 3), 186 (M^+, 4), 160 (48), 158 (51), 107 (100), 91 (26), 79 (83), 76 (27).

3-Bromo-1-butyne. A modification of the procedure used by Sondheimer and Ben-Efraim[27] was employed. To a solution of 39.2 μL of pyridine in 34.0 g (0.14 mol) of PBr_3, between −18 and −9 °C, was added a solution prepared from 25.0 g (0.36 mol) of 3-butyn-2-ol and 1.3 mL of pyridine over a 2.5-h period with stirring. The cold solution was stirred for 1 h more, and 40 mL of water was added cautiously. The mixture was extracted with ether (3 × 35 mL), and the combined ether extract was washed consecutively with water (3 × 30 mL), saturated $NaHCO_3$ (3 × 35 mL), and brine (2 × 50 mL). The ether solution was dried with $MgSO_4$ and filtered, and the ether was removed with a Vigreux column (760 mm). The residue was distilled (Vigreux column) at ~60–70 °C (~145 mm) to afford 15.2 g (29%) of $CH_3CHBrC{\equiv}CH$ containing 3% 3-butyn-2-ol and 2% ether by weight: ^{1}H NMR δ 4.58 (dq, ^3J = 6.9 Hz, ^4J = 2.3 Hz, 1 H, CHBr), 2.65 (d, ^4J = 2.3 Hz, 1 H, ≡CH), 1.92 (d, ^3J = 6.9 Hz, 3 H, CH_3).

(±)-(1*R*,4S*,7S*)-7-[(*R)-1,2-Butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (8a), (±)-(1*R*,4S*,7S*)-7-[(*S**)-1,2-Butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (8b), (±)-(1*R*,4S*,7*R**)-7-[(*S**)-1,2-Butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (12a), (±)-(1*R*,4S*,7*R**)-7-[(*R**)-1,2-Butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (12b).** A typical 6-mmol scale run is described. To 0.335 g (13.7 mmol) of Mg turnings and 2 mL of ether was added dropwise with stirring a solution of 1.16 g (6.20 mmol) of bromoalkene **18** and 1.17 g (6.20 mmol) of freshly distilled $BrCH_2CH_2Br$ in 8 mL of ether over a 75-min period. The solution began to boil when the first 0.5 mL of the **18**/$BrCH_2CH_2Br$/ether solution was added. After the addition, the mixture was heated at reflux for an additional 2.5 h, whereupon it was cooled to −55 °C in a dry ice/2-propanol bath. A solution of 0.88 g of 3-bromo-1-butyne (containing approximately 3% 3-butyn-2-ol and 2% of ether; bromide content 6.20 mmol) in 4 mL of ether was then added dropwise to the Grignard reagent with stirring over a 45-min period, and the resulting mixture was allowed to warm to room temperature overnight. Following careful hydrolysis of the reaction mixture with 7 mL of water, the ether layer was separated from the aqueous layer which was extracted with ether (3 × 7 mL). The combined ether extract was washed with brine, dried over $MgSO_4$, and concentrated below a Vigreux column to a 2-mL volume, which was injected on the preparatory GC in 500-μL portions (injector temperature 150 °C, detector temperature 175 °C, oven temperature 150 °C for 30 min, then heated to 220 °C). Approximately 200 mg (23%) of the **8a/8b/12a/12b** crude allene mixture (nonseparable; retention time 24 min) was collected between 20 and 28 min and coupling products (all six possible $C_{16}H_{22}$ dimethyldinorbornenes by capillary GC and ^{1}H NMR)[28] between 39 and 54 min after injection: IR of the **8a/8b/12a/12b** mixture ($CDCl_3$) 3057, 2959, 2928, 2903, 2870, 1964 (C=C=C), 1572, 1455, 1379, 1373, 1335, 1103, 1090 cm^{-1}. Integration of the H-4 protons in the **8a/8b/12a/12b** mixture showed the presence of 37% syn isomers (**8a/8b**) and 63% anti (**12a/12b**).

The components of the crude allene mixture were partially separated by rotating disk chromatography. Approximately 15-μL samples of the mixture in 150 μL of hexane were separated at a time on a 1-mm silica gel/$AgNO_3$ rotor in a darkened room. The rotor was developed first with 75 mL of hexane and then successively with 75 mL each of 5, 10, and

20% ethyl acetate/hexane. Sixty ~5-mL fractions were collected and analyzed by capillary GC (110 °C). Fractions 28–30 contained a 1:1 mixture of **12a** and **12b**, 33–34 contained **8b**, and **8a** was found in fractions 37–39. Samples of **8a**, **8b**, and the **12a**/**12b** mixture (usually from several combined runs) were obtained free of solvent by injecting concentrated samples onto the preparatory GC (150 °C; flow rate 40 mL/min; retention time 24 min) after removing most of the solvent by distillation through a Vigreux column. Each 15 μL (13.6 mg) sample of the crude reaction mixture afforded approximately 4 mg of **8a**, 1 mg of **8b**, and 8 mg of mixture **12** with retention times (capillary GC) of 5.37, 5.20, and 5.32/5.36 min, respectively. *syn*-Allene **8a** was obtained pure (>99%), and **8b** in 93% purity and without any contamination by **8a**. The **12a**/**12b** mixture was also obtained free from impurities. Trace impurities (uncharacterized) were detected in fractions 26 and 27 (retention times 4.86 and 5.10 min).

8a: ^{1}H NMR (analysis assisted by COSY and ^{1}H–^{13}C PSCSCM experiments, and some coupling constants and chemical shifts uncovered by homonuclear proton decoupling) δ 5.90 (dd, ^3J = 5.6, 3.0 Hz, 1 H, H-3), 5.61 (d, ^3J = 5.6 Hz, 1 H, H-2), 4.98 (ddq, ^3J = 6.5 Hz, ^4J = 6.4 Hz, ^5J = 1.6 Hz, 1 H, =C=C*H*CH$_3$), 4.96 (ddq, ^3J = 8.0 Hz, ^4J = 6.4 Hz, ^5J = 3.5 Hz, 1 H, —C*H*=C=CHCH$_3$) [allenyl resonances overlapped], 2.71 (overlapped dd, ^3J = 3.5, 3.0 Hz, 1 H, H-4), 1.96 (br d, ^3J = 8.0 Hz, 1 H, H-7), 1.8–1.7 (m, 1 H, H$_{exo}$-5), 1.62 (dd, ^3J = 6.5 Hz, ^5J = 3.5 Hz, 3 H, allenyl CH$_3$), 1.5–1.4 (m, 1 H, H$_{exo}$-6), 1.22 (s, 3 H, bridgehead CH$_3$), 1.1–1.0 (m, 2 H, H$_{endo}$ protons); ^{1}H NMR (CDCl$_3$, −50 °C) δ 1.94 (d, ^3J = 8.8 Hz, H-7); ^{1}H NMR (CD$_3$COCD$_3$, −80 °C) δ 5.89 (dd, ^3J = 5.6, 3.0 Hz, 1 H, H-3), 5.61 (d, ^3J = 5.6 Hz, 1 H, H-2), 4.97 (ddq, ^3J = 6.9 Hz, ^4J = 6.6 Hz, ^5J = 0.7 Hz, 1 H, =C=C*H*CH$_3$), 4.83 (ddq, ^3J = 9.4 Hz, ^4J = 6.6 Hz, ^5J = 3.2 Hz, 1 H, —C*H*=C=CHCH$_3$) [allenyl resonances completely resolved in CD$_3$COCD$_3$ at −80 °C], 2.61 (overlapped dd, 1 H, H-4), 1.88 (br d, ^3J = 9.4 Hz, 1 H, H-7), 1.8–1.7 (m, 1 H, H$_{exo}$-5), 1.53 (dd, ^3J = 6.9 Hz, ^5J = 3.2 Hz, 3 H, allenyl CH$_3$), 1.5–1.4 (m, 1 H, H$_{exo}$-6), 1.13 (s, 3 H, bridgehead CH$_3$), 1.05–0.9 (m, 2 H, H$_{endo}$ protons); ^{13}C/DEPT/PSCSCM δ 206.06 (=C=), 136.53 (C-2), 132.86 (C-3), 88.54 (—*C*H=C=CHCH$_3$), 84.25 (—CH=C=*C*HCH$_3$), 64.54 (C-7), 52.43 (C-1), 48.09 (C-4), 33.13 (C-6), 26.41 (C-5), 16.58 (bridgehead CH$_3$), 14.82 (allenyl CH$_3$); COSY (25 °C) cross peaks for H-2/H-3, H-3/H-4, allenyl hydrogens (overlapped)/H-7, allenyl hydrogens (overlapped)/allenyl CH$_3$, H-4/H$_{exo}$-5, H$_{exo}$-5/H$_{exo}$-6, H$_{exo}$-5/H$_{endo}$ protons (overlapped), H$_{exo}$-6/H$_{endo}$ protons (overlapped); T_1s (seconds) at 25 °C (−50 °C) 23.3 (6.5), 24.2 (6.9), 34.5 (9.9), 14.8 (3.8), 11.2 (2.8), 3.4 (0.96), 6.8 (2.0), 4.1 (0.81), 3.5 (0.90), 3.7 (0.92) for H-3, H-2, allenyl hydrogens, H-4, H-7, H$_{exo}$-5, allenyl CH$_3$, H$_{exo}$-6, bridgehead CH$_3$, and H$_{endo}$ protons, respectively; 1D NOE (25 °C) irradiation of bridgehead CH$_3$ generated NOEs (%) to H-2 (2.7) H$_{exo}$-6 (0.9), H-7 (1.1), overlapped allenyl hydrogens (1.4), and allenyl CH$_3$ (0.4); 1D NOE (−50 °C), irradiation of bridgehead CH$_3$ generated NOEs (%) to H-2 (3.0), H$_{exo}$-6 (1.2), H-7 (1.1), —C*H*=C=CHCH$_3$ (~1.4), —CH=C=C*H*CH$_3$ (~0.2) [allenyl hydrogens partially resolved in CDCl$_3$ at −50 °C], and allenyl CH$_3$ (0.2); MS, *m*/*z* (rel intensity) 160 (M$^+$, 12), 159 (7), 145 (100), 131 (42), 117 (58), 105 (57), 91 (78), 79 (38), 77 (33), 65 (21).

8b: ^{1}H NMR (analysis assisted by COSY and ^{1}H–^{13}C PSCSCM experiments, and some coupling constants and chemical shifts uncovered by homonuclear proton decoupling) δ 5.90 (dd, ^3J = 5.6, 3.0 Hz, 1 H, H-3), 5.60 (d, ^3J = 5.6 Hz, 1 H, H-2), 4.97 (ddq, ^3J = 6.6 Hz, ^4J = 6.7 Hz, ^5J = 1.8 Hz, 1 H, =C=C*H*CH$_3$), 4.94 (ddq, ^3J = 8.0 Hz, ^4J = 6.6 Hz, ^5J = 3.5 Hz, 1 H, —C*H*=C=CHCH$_3$) [allenyl resonances overlapped], 2.71 (overlapped dd, ^3J = 3.5, 3.0 Hz, 1 H, H-4), 1.97 (br d, ^3J = 8.0 Hz, 1 H, H-7), 1.8–1.7 (m, 1 H, H$_{exo}$-5), 1.61 (dd, ^3J = 6.6 Hz, ^5J = 3.5 Hz, 3 H, allenyl CH$_3$), 1.5–1.4 (m, 1 H, H$_{exo}$-6), 1.20 (s, 3 H, bridgehead CH$_3$), 1.1–1.0 (m, 2 H, H$_{endo}$ protons); ^{1}H NMR (CDCl$_3$, −50 °C) δ 1.94 (d, ^3J = 8.8 Hz, H-7); ^{1}H NMR (CD$_3$COCD$_3$, −80 °C) δ 1.89 (d, ^3J = 9.4 Hz, H-7); ^{13}C/DEPT/PSCSCM δ 206.07 (=C=), 136.43 (C-2), 132.89 (C-3), 88.52 (—*C*H=C=CHCH$_3$), 84.31 (—CH=C=*C*HCH$_3$), 64.25 (C-7), 52.65 (C-1), 48.34 (C-4), 33.24 (C-6), 26.37 (C-5), 16.64 (bridgehead CH$_3$), 14.53 (allenyl CH$_3$); COSY (same as for compound **8a** above); T_1s (seconds) at 25 °C (−50 °C) 23.3 (6.7), 24.2 (7.0), 30.7 (9.7), 13.9 (3.6), 10.8 (2.7), 3.6 (1.2), 6.6 (1.9), 4.0 (0.81), 3.3 (0.87), 3.6 (0.90) for H-3, H-2, allenyl hydrogens, H-4, H-7, H$_{exo}$-5, allenyl CH$_3$, H$_{exo}$-6, bridgehead CH$_3$, and H$_{endo}$ protons, respectively; 1D NOE (25 °C), irradiation of bridgehead CH$_3$ generated NOEs (%) to H-2 (2.5), H$_{exo}$-6 (0.9), H-7 (1.2), overlapped allenyl hydrogens (2.0), but not to allenyl CH$_3$; 1D NOE (−50 °C), irradiation of bridgehead CH$_3$ generated NOEs (%) to H-2 (2.6), H$_{exo}$-6 (1.2), H-7, (1.0), —C*H*=C=CHCH$_3$ (~1.4), —CH=C=C*H*CH$_3$ (~0.6), but not to allenyl CH$_3$; MS, *m*/*z* (rel intensity) 160 (M$^+$, 14), 159 (7), 145 (100), 131 (38), 117 (48), 105 (47), 91 (54), 79 (23), 77 (20), 65 (11).

12a/**12b mixture**: ^{1}H NMR (analysis assisted by a COSY experiment) δ 6.09–6.06 (overlapping dd, 1 H each, H-3), 5.89, 5.87 (two resolved d, 1 H each, H-2), 5.09–4.99 (two overlapping ddq, 1 H each, —CH=C=C*H*CH$_3$), 4.85–4.72 (two overlapping ddq, 1 H each, —C*H*=C=CHCH$_3$), 2.65–2.55 (two overlapping dd, 1 H each, H-4), 1.94–1.87 (two overlapping d, 1 H each, H-7), 1.87–1.78 (two m, 1 H each, H$_{exo}$-5 protons), 1.69–1.62 (two overlapping dd, 3 H each, allenyl CH$_3$), 1.48–1.36 (two overlapping m, 1 H each, H$_{exo}$-6 protons), 1.21, 1.20 (two resolved s, 3 H, bridgehead CH$_3$), 1.12–0.88 (overlapping m, 2 H each, two sets of H$_{endo}$ protons); ^{13}C/DEPT δ 205.77 (C), 141.54/141.44 (CH), 135.85/135.76 (CH), 88.41 (CH), 85.02/84.88 (CH), 61.56/61.30 (CH), 51.38/51.29 (C), 46.31/46.22 (CH), 29.04/29.01 (CH$_2$), 24.99/24.96 (CH$_2$), 16.20/16.15 (CH$_3$), 14.61/14.30 (CH$_3$); COSY (25 °C) cross peaks for H-3/H-2, H-3/H-4, —CH=C=C*H*CH$_3$/—C*H*=C=CHCH$_3$, —CH=C=C*H*CH$_3$/allenyl CH$_3$, —C*H*=C=CHCH$_3$/H-7, H$_{exo}$-5/H$_{exo}$-6, H$_{exo}$-5/H$_{endo}$ protons, H$_{exo}$-6/H$_{endo}$ protons; T_1s (seconds) at 25 °C 19.6, 21.2, 34.7, 15.6, 13.9, 12.4, 3.3, 7.4, 3.1, 3.5, and 3.2 for H-3, H-2, —CH=C=C*H*CH$_3$, —C*H*=C=CHCH$_3$, H-4, H-7, H$_{exo}$-5, allenyl CH$_3$, H$_{exo}$-6, bridgehead CH$_3$, and H$_{endo}$ protons, respectively; MS, *m*/*z* (rel intensity) 160 (M$^+$, 7), 159 (8), 145 (100), 131 (45), 117 (70), 105 (73), 91 (99), 79 (60), 77 (47), 68 (34), 65 (32).

Thermal Rearrangement of (±)-*syn*-7-(1,2-Butadienyl)-1-methylbicyclo[2.2.1]hept-2-enes (8a and 8b). (A) Preparative Scale Using a Mixture of Allenes 8a, 8b, 12a, and 12b. Five 20-μL samples of a mixture of 37% *syn*-allenes **8a**/**8b** and 63% *anti*-allenes **12a**/**12b** were injected on the preparatory GC (oven temperature 215 °C, injector temperature 310 °C, detector temperature 175 °C, flow rate 20 mL/min), giving in each case three peaks of retention times 15.6, 20.6, and 26.2 min, with the last two peaks being significantly overlapped. The material represented by the first peak was collected and shown by capillary GC and ^{1}H NMR analysis to consist of *anti*-allenes **12a** and **12b**, containing only trace amounts of *syn*-allenes **8a** and **8b** and trace amounts of rearrangement products.

The material represented by the overlapping second and third peaks (retention times 20.6 and 26.2 min) was collected together in each of the five runs, and the combined material (15.3 mg) was shown by capillary GC to consist of four components, which was partially separated by rotating disk chromatography. An 85-μL solution of 10.0 mg of this material in hexane was applied to a 1-mm silica gel/AgNO$_3$ rotor in a darkened room. The rotor was first developed with 75 mL of hexane and then successively with 75 mL each of 5, 20, 35, and 50% ethyl acetate/hexane. One hundred ~4-mL fractions were collected and analyzed by capillary GC (oven temperature 140 °C). Fractions 35–38 were found to contain traces of *anti*-allenes **12a** and **12b**. Combined fractions 26 and 27 were found to be a 2:3 mixture of only two compounds with retention times of 4.06 and 4.17 min, respectively. The compounds were obtained free of solvent by first concentrating the solution to 400 μL (<120 °C) below a Vigreux column and then injecting the concentrated sample in one portion on the preparatory GC (oven and injector temperature 150 °C, flow rate 40 mL/min, retention time 48 min with shoulder at 44 min). Fraction 28 was found to be a 2:3 mixture of the other two compounds with retention times (capillary GC, oven temperature 140 °C) of 3.19 and 3.33 min, respectively, that were isolated together free of solvent on the preparatory GC as described above (retention time 70 min with no shoulder). The four compounds with capillary GC retention times of 4.06, 4.17, 3.19, and 3.33 min were identified respectively by ^{1}H NMR, including NOE experiments, as (±)-(*Z*)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-6-methylindene ((*Z*)-**9**), (±)-(*E*)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-6-methylindene ((*E*)-**9**), (±)-(*Z*)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-3a-methylindene ((*Z*)-**10**), and (±)-(*E*)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-3a-methylindene ((*E*)-**10**).

(*Z*)-**9**: ^{1}H NMR (obtained on a 2:3 mixture of (*Z*)-**9** and (*E*)-**9** in C$_6$D$_6$; some coupling constants uncovered by homonuclear proton decoupling) δ 6.11 (dd, ^3J = 5.5 Hz, $^4J_{2,3a}$ = 2.3 Hz, 1 H, H-2), 5.60 (br d, ^3J = 5.5 Hz, 1 H, H-3), 5.44 (br s, 1 H, H-7), 5.38 (q, ^3J = 7.0 Hz, 1 H, =C*H*CH$_3$), 3.42 (m, 1 H, H-7a), 3.01 (m, 1 H, H-3a), 2.0–1.2 (m, 4 H, H-4, H-5), 1.70 (d, ^3J = 7.0 Hz, 3 H, =CHC*H*$_3$), 1.58 (br s, 3 H, C-6:CH$_3$); 1D NOE (C$_6$D$_6$, 25 °C), simultaneous irradiation of vinyl CH$_3$ resonances and H-4, H-5 protons, all of similar chemical shift, afforded NOEs (%) to H-7a (1.6), =C*H*CH$_3$ (3.1), H-7 (4.5), H-3 (2.1), and H-3a (5.4); MS, *m*/*z* (rel intensity) 160 (M$^+$, 58), 145 (100), 131 (42), 117 (66), 105 (69), 91 (83), 77 (49), 65 (35).

(*E*)-**9**: ^{1}H NMR (obtained on a 2:3 mixture of (*Z*)-**9** and (*E*)-**9** in C$_6$D$_6$; some coupling constants uncovered by homonuclear proton decoupling) δ 6.40 (d, ^3J = 5.6 Hz, 1 H, H-2), 5.85 (br d, ^3J = 5.6 Hz, 1 H, H-3), 5.52 (br s, 1 H, H-7), 5.17 (q, ^3J = 7.0 Hz, 1 H, =C*H*CH$_3$), 3.19 (m, 1 H, H-7a), 2.72 (m, 1 H, H-3a), 2.0–1.2 (m, 4 H, H-4, H-5), 1.66 (dd, ^3J = 7.0 Hz, $^5J_{CH_3,7a}$ = 1.9 Hz, 3 H, =CHC*H*$_3$), 1.62 (br s, 3 H, C-6:CH$_3$); 1D NOE (C$_6$D$_6$, 25 °C), simultaneous irradiation of vinyl CH$_3$ resonances and H-4, H-5 protons, all of similar chemical shift, afforded NOEs (%) to H-2 (3.1), =C*H*CH$_3$ (3.1), H-7 (2.4), H-3 (0.5),

and H-3a (2.8); MS, m/z (rel intensity) 160 (M^+, 58), 145 (100), 131 (42), 117 (66), 105 (69), 91 (83), 77 (49), 65 (35).

(*Z*)-**10**: ^{1}H NMR (obtained on a 2:3 mixture of (*Z*)-**10** and (*E*)-**10** in C_6D_6; some coupling constants uncovered by homonuclear proton decoupling) δ 5.99 (d, ^3J = 5.5 Hz, 1 H, H-2), 5.8–5.6 (m, 2 H, H-6, H-7), 5.48 (d, ^3J = 5.5 Hz, 1 H, H-3), 5.33 (q, ^3J = 6.9 Hz, 1 H, =C*H*CH$_3$), 3.01 (m, 1 H, H-7a), 2.0–1.2 (m, 4 H, H-4, H-5), 1.65 (d, ^3J = 6.9 Hz, 3 H, =CHC*H*$_3$), 1.03 (s, 3 H, bridgehead CH$_3$); 1D NOE (C_6D_6, 25 °C), simultaneous irradiation of vinyl CH$_3$ and the H-4, H-5 protons, all of similar chemical shift, afforded NOEs (%) to H-7a (2.1), =C*H*CH$_3$ (4.3), H-3 (2.4), bridgehead CH$_3$ (2.4), and to overlapping resonances for H-6, H-7 of (*Z*)-**11** and to H-3, H-6, H-7 of (*E*)-**11** (total of 4.2% as referenced to the vinyl CH$_3$ resonances in both (*Z*)-**10** and (*E*)-**10**); MS, m/z (rel intensity) 160 (M^+, 40), 145 (100), 131 (33), 117 (50), 105 (30), 91 (67), 77 (35), 65 (28).

(*E*)-**10**: ^{1}H NMR (obtained on a mixture of (*Z*)-**10** and (*E*)-**10** in C_6D_6; some coupling constants uncovered by homonuclear proton decoupling) δ 6.30 (d, ^3J = 5.7 Hz, 1 H, H-2), 5.8–5.6 (m, 3 H, H-3, H-6, H-7), 5.12 (q, ^3J = 6.7 Hz, 1 H, =C*H*CH$_3$), 2.74 (m, 1 H, H-7a), 2.0–1.2 (m, 4 H, H-4, H-5), 1.64 (dd, ^3J = 6.7 Hz, $^5J_{CH_3,7a}$ = 1.5 Hz, 3 H, =CHC*H*$_3$), 1.02 (s, 3 H, bridgehead CH$_3$); 1D NOE (C_6D_6, 25 °C), simultaneous irradiation of vinyl CH$_3$ and H-4, H-5 protons, all of similar chemical shift, afforded NOEs (%) to H-2 (3.2), =C*H*CH$_3$ (4.2), bridgehead CH$_3$ (1.4), and to overlapping resonances for H-3, H-6, H-7 of (*E*)-**11**, and to H-6, H-7 of (*Z*)-**11** (total of 4.2% as referenced to the vinyl CH$_3$ resonances in both (*Z*)-**11** and (*E*)-**11**); MS, m/z (rel intensity) 160 (M^+, 40), 145 (100), 131 (33), 117 (50), 105 (30), 91 (67), 77 (35), 65 (28).

(B) **Analytical Scale on Separated Allenes 8a and 8b.** Approximately 1.5 μL (1.4 mg) of *syn*-allene **8a** was injected neat on the preparatory GC (oven temperature 215 °C, injector temperature 310 °C, detector temperature 175 °C, flow rate 20 mL/min), and all the eluted material (retention time 15–36 min following injection) was collected and analyzed by capillary GC. The analysis showed 5.4% of **8a** remaining, and trienes (*Z*)-**9**, (*E*)-**9**, (*Z*)-**10**, and (*E*)-**10** in a percentage ratio of 2.7, 61.1, 29.2, and 1.6, respectively. (Approximate product percentage ratio 3:64:31:2.) When a solution of approximately 0.5 mg of *syn*-allene **8b** in 150 μL of acetone-d_6 was injected under the same conditions, capillary GC analysis of the collected material (retention time 15–36 min following injection) showed 22.5% of **8b** remaining, and trienes (*Z*)-**9**, (*E*)-**9**, (*Z*)-**10**, and (*E*)-**10** in a percentage ratio of 49.5, 2.5, 0.8, and 28.3, respectively. (Approximate product percentage ratio 59:3:1:37.) Similar results were obtained when **8a** was injected as a solution in hexane and **8b** as solution in $CDCl_3$; only the percent of **8a** and **8b** remaining changed; however, the stereoselectivity of the rearrangement remained approximately the same. Approximately 0.75 μL of a 2:3 mixture of *anti*-allenes **12a** and **12b** was also injected neat on the preparatory GC under the conditions described above. Capillary GC analysis of all eluted material showed only starting material (**12a**/**12b**) in approximately the original 2:3 ratio.

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Host Properties of Cyclodextrins toward Anion Constituents of Antigenic Determinants. A Thermodynamic Study in Water and in *N*,*N*-Dimethylformamide

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Abstract: Thermodynamic data for the transfer of α, β-, and γ-cyclodextrins from water to *N*,*N*-dimethylformamide derived from solution data in the two solvents are reported. Transfer data are characterized by rather small free energy values as a result of enthalpy (large and favorable) being largely compensated by entropy (large and negative) data. Data for cyclodextrins are not characteristic of those observed for the transfer of nonelectrolytes from water to the same reaction media and suggest a strong cyclodextrin–*N*,*N*-dimethylformamide interaction. Thermodynamic parameters for the complexation process involving *p*-hydroxyphenyl and substituted (*p*-hydroxyphenylazo)benzoate (hapten) anions and cyclodextrins in water and in *N*,*N*-dimethylformamide have been determined. The data suggest that two different types of complexation occurs as a result of a change in the reaction medium. In water, inclusion or axial type complexes are formed. In *N*,*N*-dimethylformamide, these anions interact with the hydroxyl groups of the cyclodextrin molecule and equatorial or lid type complexes are formed. A detailed explanation of the complexation process in water and *N*,*N*-dimethylformamide is given. Single ion free energy values for the transfer of the complexed anions from water to *N*,*N*-dimethylformamide show that no significant changes in solvation occurs, in both the anion and the ligand upon complexation. The free energy values are the result of a compensation effect between enthalpy and entropy data. These are the first data ever reported on the transfer of cyclodextrins and their adducts from water to a nonaqueous medium.

Several articles dealing with the properties of cyclodextrins can be found in the literature.[1-9] An enormous amount of effort has been devoted to explore their applications based on the ability of cyclodextrins to form complexes with a large number of substrates. An account on the uses of cyclodextrins in research and industry has been given by Saenger.[5] The pharmaceutical applications of

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