(imine), and 2.95 Å (sulfide). Thus, if the cyclic bromonium ion geometry resembles these analogous heterocycles, the cis methyl–methyl distance would either be expected to remain roughly the same as that in the olefin, or decrease. Because of the longer bond lengths to the heteroatom and greater distortion of the three-membered-ring system from the equilateral cyclopropane structure, the ethylene sulfide is probably the best model for the cyclic bromonium ion. Therefore, all three methods of estimating its geometry suggest that the steric interactions between *cis*-1,2-methyl groups in a cyclic bromonium ion would either be as severe or, more probably, be increased over those present in the parent olefin.

Kinetics of Thermal Electrocyclic Ring Closure. Alkyl-1,3,5-hexatrienes[1]

CHARLES W. SPANGLER,* THOR P. JONDAHL, AND BRENDA SPANGLER

The Michael Faraday Laboratories, Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

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Kinetic studies of thermal electrocyclization of a series of 1- and 3-alkyl-1,3,5-hexatrienes (R = Me, Et, *t*-Bu) yielded the following relative rates: 3-*t*-Bu > 3-Et, 3-Me > 1-Et > 1-Me, H. The activation enthalpies of the 3-alkyl series were, in general, 3 kcal/mol less than either the 1-alkyl counterparts or the parent hydrocarbon. These results can be interpreted in terms of the donative ability of alkyl groups, steric retardation at the reaction sites, and differences in ground-state energies and/or conformation.

Thermal electrocyclic ring closure of various systems containing $4n + 2\ \pi$ electrons has been studied extensively during the past few years.[2,3] However, although the kinetics of isolated examples have been reported,[4-8] no comprehensive study has yet been reported which evaluates the magnitude of substituent effects as a function of chain position.[9] The Woodward–Hoffmann description[2] of this reaction as a disrotatory, concerted process has been confirmed repeatedly in the literature, but primarily in terms of stereochemistry. Few predictions concerning the ability or inability of substituents to affect the course or energetics of this process have been forthcoming, even though an examination of the scattered published examples[3-8] indicates possible substituent participation in the reaction.

In order to demonstrate the existence or absence (and/or magnitude) of substituent effects in the $4n + 2\ \pi$ system, we have studied the thermal ring closure of a series of 1- and 3-alkyl-1,3,5-hexatrienes (alkyl = Me, Et, *i*-Pr, *t*-Bu) in the temperature range 348–423° K, resulting in the formation of 5-alkyl- and 2-alkyl-1,3-cyclohexadienes, respectively, as shown in Scheme I.

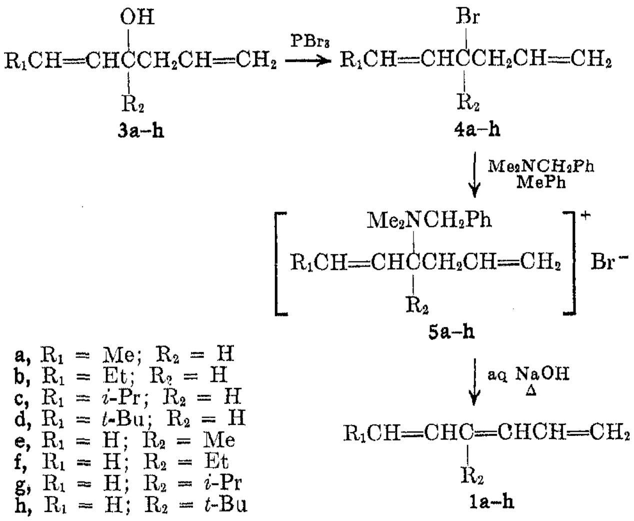
Pure substituted 1,3,5-hexatrienes were prepared from appropriately substituted hexadienols essentially by the method of Hwa, *et al.*,[10] which we have also used previously.[11,12] This is illustrated in Scheme II.

SCHEME I

1 **2**

1a, R_1 = Me; R_2 = H
b, R_1 = Et; R_2 = H
c, R_1 = *i*-Pr; R_2 = H
d, R_1 = *t*-Bu; R_2 = H
e, R_1 = H; R_2 = Me
f, R_1 = H; R_2 = Et
g, R_1 = H; R_2 = *i*-Pr
h, R_1 = H; R_2 = *t*-Bu

SCHEME II



$$R_1CH{=}CH\overset{OH}{\underset{R_2}{C}}CH_2CH{=}CH_2 \xrightarrow{PBr_3} R_1CH{=}CH\overset{Br}{\underset{R_2}{C}}CH_2CH{=}CH_2$$

3a–h **4a–h**

$$\Big\downarrow \begin{smallmatrix}Me_2NCH_2Ph\\MePh\end{smallmatrix}$$

$$\left[R_1CH{=}CH\overset{Me_2NCH_2Ph}{\underset{R_2}{C}}CH_2CH{=}CH_2\right]^+ Br^-$$

5a–h

$$\Big\downarrow \begin{smallmatrix}aq\ NaOH\\\Delta\end{smallmatrix}$$

$$R_1CH{=}CH\underset{R_2}{C}{=}CHCH{=}CH_2$$

1a–h

a, R_1 = Me; R_2 = H
b, R_1 = Et; R_2 = H
c, R_1 = *i*-Pr; R_2 = H
d, R_1 = *t*-Bu; R_2 = H
e, R_1 = H; R_2 = Me
f, R_1 = H; R_2 = Et
g, R_1 = H; R_2 = *i*-Pr
h, R_1 = H; R_2 = *t*-Bu

The trienes were obtained free of contamination from either the ring-closure products (**2a–h**) or the corresponding aromatized products. In general, a mixture of geometric isomers may be expected from the Hwa procedure; however, as can be seen in Table I, several trienes were obtained geometrically pure.

It is obvious that the 1-*i*-Pr and 1-*t*-Bu trienes thus could not be included in the kinetic analysis. We have not been able to synthesize these trienes with a cis configuration about the central double bond.

The trends evident in the two series can be rationalized from consideration of the most probable ground-

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[1] (a) Portions of this paper were presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. (b) Taken in part from the Ph.D. dissertation of Thor P. Jondahl, Northern Illinois University, Dec 1971.

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie-Academic Press, Weinheim/Bergstr., 1970.

[3] H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

[4] K. E. Lewis and H. Steiner, *J. Chem. Soc.*, 3080 (1964).

[5] E. N. Marvell, G. Caple, and B. Schatz, *Tetrahedron Lett.*, 385 (1965).

[6] K. W. Egger, *Helv. Chim. Acta*, **51**, 422 (1968).

[7] E. Vogel, W. Grimme, and E. Dinné, *Tetrahedron Lett.*, 391 (1965).

[8] C. J. Gaasbeek, H. Hogeueen, and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **91**, 821 (1972).

[9] The present discussion applies only to acyclic examples. The authors are aware of the many cyclic examples, but do not feel that their inclusion would be meaningful in that the complication of ring size and conformation obscures the presence or absence of steric and other secondary effects.

[10] J. C. H. Hwa, P. L. de Benneville, and H. J. Sims, *J. Amer. Chem. Soc.*, **82**, 2537 (1960).

[11] C. W. Spangler and G. F. Woods, *J. Org. Chem.*, **28**, 2245 (1963).

[12] C. W. Spangler and G. F. Woods, *ibid.*, **30**, 2218 (1965).

TABLE I

GEOMETRIC COMPOSITION OF TRIENES

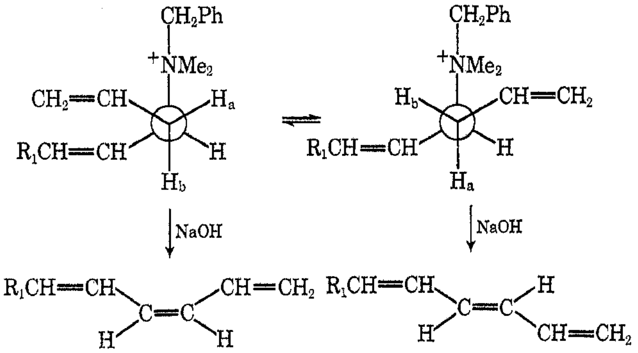
$R_1CH{=}CHCR_2{=}CHCH{=}CH_2$

Substituents	Composition
R_1 = H; R_2 = Me	55% trans; 45% cis
R_1 = H; R_2 = Et	35% trans; 65% cis
R_1 = H; R_2 = *i*-Pr	25% trans; 75% cis
R_1 = H; R_2 = *t*-Bu	100% cis
R_1 = Me; R_2 = H	56% trans,trans; 44% cis,trans
R_1 = Et; R_2 = H	68% trans,trans; 32% cis,trans
R_1 = *i*-Pr; R_2 = H	100% trans,trans
R_1 = *t*-Bu; R_2 = H	100% trans,trans

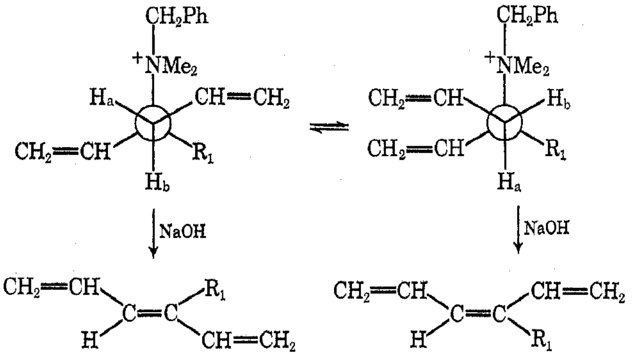
state conformations of the intermediary ammonium salts which result from minimization of electronic and steric interactions.

Thus, in Scheme III, as R_1 increases in bulk, the conformation leading to formation of a trans central double bond is preferred, while, in Scheme IV, the conformation yielding a cis configuration would predominate.

SCHEME III



SCHEME IV



The pure trienes, usually a geometric mixture containing the isomer with a central cis configuration, were sealed in Pyrex capillary ampoules and placed in thermostatically controlled baths at various temperatures. The progress of the reaction was followed by measuring the loss of cis isomer, as well as the appearance of the appropriate 1,3-cyclohexadiene, by quantitative gas-liquid partition chromatography (glpc).

Lewis and Steiner[4] indicated in their study of the thermal behavior of pure *cis*- and pure *trans*-1,3,5-hexatriene that no cis-trans isomerization occurs below 460° K. However, other workers[5,13] have found that isomerization does occur to some extent with substituted trienes. In our studies we found isomerization occurring in the following trienes as well as ring closure: 1-Me, 3-Me, 1-Et, and 3-Et. For the larger groups, no thermal isomerization occurs below 410° K. Ring closure of 3-isopropyl-1,3,5-hexatriene was complicated by other thermal processes, primarily double-bond migration into the isopropyl group. Similarly, the 1-isopropyl counterpart was severely contaminated with a nonconjugated triene formed during the Hwa process. Thus the isopropyl members of the series were not amenable to clean kinetic analysis.

Since some cis-trans isomerization in the unreacted trienes (**1a**,**b**,**e**,**f**,**h**) occurs simultaneously with thermal ring closure, loss of cis isomer is not a simple first-order process.[14] However, corrections of this type are easily handled by digital computer, utilizing a program DRATE,[14] developed by Butterfield,[15] and modified by us for use with an IBM 360-67 system. The program incorporates a minimization technique developed by Rosenbrock and Story,[16] which minimizes the summed squared error between the calculated and experimentally measured data until the rate constants are changing by less than 1% on successive calculations.[17] *cis*-3-*tert*-Butyl-1,3,5-hexatriene followed simple first-order kinetics as determined by the least squares program. Similarly, temperature dependence of the rate constants calculated by the above methods and the corresponding Arrhenius parameters were determined by least squares analysis. Rate constants for thermal ring closure are shown in Table II, while the activation parameters are shown in Table III.[18]

Examination of the results leads to several interesting conclusions. It appears that introduction of an electron-donating group in the 3 position, relatively remote from the reaction centers, increases the cyclization rate: 3-*t*-Bu > 3-Et ~ 3-Me > H. Similarly, introduction of the same group in the 1 position, a reaction site, has a much smaller effect on the overall rate: 1-Et > 1-Me ~ H. Activation enthalpies show a similar trend, the compounds having 3 substituents having lower activation enthalpies than the parent 1,3,5-hexatriene, while the 1-substituted compounds are essentially the same. Activation entropies are all negative, indicating similar transition states for all trienes in this study.

The results can be interpreted as indicating the operation of several possible effects: (1) an increase in the polyene π-electron density by introduction of a substituent electron-donating group remote from the reaction center will increase the rate of ring closure and lower the activation enthalpy; (2) introduction of a group in the 3 position will alter the relative amounts of s-trans and s-cis conformations, thereby allowing an increase in cyclization rate as the relative percentage of

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[13] P. Vander Burg, Ph.D. Dissertation, University of Leiden, 1970.

[14] The data may be fit to either of the following isomerization schemes: (a) trans $\rightleftharpoons$ cis $\rightarrow$ diene, or (b) trans $\rightarrow$ cis $\rightarrow$ diene. In either case, the rate constants for ring closure are identical. The mechanism for the isomerization process is obscure at present, but probably involves activation by the walls of the capillary tube. Cis-trans isomerization occurs only about the central 3,4 double bond; the configurations about the terminal double bonds remain fixed.

[15] R. O. Butterfield, *J. Amer. Oil Chem. Soc.*, **46**, 429 (1969).

[16] H. H. Rosenbrock and C. Story, "Computational Techniques for Chemical Engineers," Pergamon Press, Elmsford, N. Y., 1966, pp 64-68.

[17] A 360-67 source listing in Fortran IV and test data for a variety of first-order schemes will be sent to interested people on request.

[18] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 378-379.

TABLE II

RATE CONSTANTS[a] FOR ELECTROCYCLIZATION OF ALKYL-1,3,5-HEXATRIENES

Substituent	Temp, °C	$k \times 10^5$, sec^{-1}	Substituent	Temp, °C	$k_1 \times 10^5$, sec^{-1}
1-Me[b]	98.8	0.196	1-Et[d]	98.8	0.735
	109.8	0.815		115.0	2.03
	124.1	2.39		125.0	5.56
	140.0	11.9		135.0	15.5
	150.0	28.3		150.0	66.9
3-Me[c]	101.0	1.02	3-Et[e]	101.0	2.14
	109.9	3.03		115.7	6.74
	121.0	6.43		124.1	13.2
	131.2	21.9		135.0	42.4
	150.0	88.8		150.0	92.8
H[4]	150.0	24.1	3-*t*-Bu[f]	75.0	0.54
				85.0	1.68
				100.0	7.82
				115.0	31.9
				125.4	84.6

[a] All rate constants fitted to a minimum sum-squared error and change <1% on successive calculations. All temperatures maintained to within ±0.1°. [b] Thermolysis of mixture containing 56% trans,trans and 44% cis,trans. [c] 55% trans and 45% cis. [d] 68% trans,trans and 32% cis,trans. [e] 35% trans and 65% cis. [f] Cis isomer present initially in >99%.

TABLE III

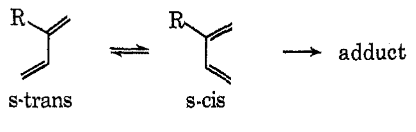
ACTIVATION PARAMETERS FOR ELECTROCYCLIZATION OF ALKYL-1,3,5-HEXATRIENES[a]

Substituent	Temp, °K	Log *A*, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu (temp, °K)
1-Me	372–423	11.8 (11.6)[b]	28.9 ± 0.2 (29.2)[b]	−4.9 ± 0.5 (374)
3-Me	374–423	11.7	26.1 ± 0.3	−12.4 ± 0.7 (374)
1-Et	372–423	11.2	27.8 ± 0.4	−6.2 ± 1.2 (372)
3-Et	374–423	9.9	26.0 ± 0.5	−11.3 ± 1.5 (374)
3-*t*-Bu	348–398	11.9	26.7 ± 0.1	−11.3 ± 0.3 (373)
H[4]	390–434	11.9	29.1 ± 0.5	−7.3

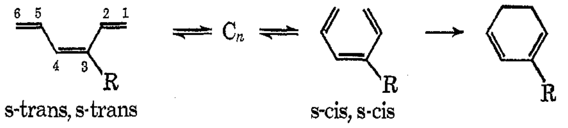
[a] Errors quoted are standard errors. See ref 18. [b] Reference 13.

s-cis conformations increase; (3) introduction of a group in the 1 position leads only to a very slight increase in rate, and no meaningful reduction in the enthalpy owing to a competing steric retardation at the reaction sites. That this retardation is not more dramatic supports our contention that alkyl groups are acting as electron donors in this reaction.

Craig and coworkers[19] have observed similar rate phenomena in their study of the reaction of 2-alkyl-1,3-butadienes with maleic anhydride (*t*-Bu > *i*-Pr > Et > Me > H). They attribute this rate increase to the increasing stability of the s-cis conformation relative to the s-trans. Thus as R increases in bulk, the s-cis conformation becomes more stable.



The situation with regard to this argument is more complicated. The most stable conformation of both *trans*- and *cis*-1,3,5-hexatriene is linearly extended.[20,21] Substitution of an alkyl group in the 3 position should produce effects similar to those observed by Craig,[19] since a group in the 3 position would destabilize the s-trans conformation as one goes from hydrogen to *tert*-butyl. However, two double bonds must achieve an s-cis conformation prior to ring closure, and only a partial enhancement of rate might be expected.[22,23] It is highly unlikely that the 3-alkyl group will affect the conformational equilibrium involving the 5,6-vinyl group. It is interesting to also note that Craig attributed partial rate enhancement in the 1- and 2-alkyl-1,3-butadienes to the electron-releasing character of the alkyl group (both 1-Me and 2-Me > H).



C_n = other intermediate conformations

Since the enthalpy and entropy differences for the trienes in this study are relatively small, it is quite possible that they merely represent differences in ground-state energies. It is not immediately obvious, however, how one can account for a difference of 3 kcal/mol by this line of reasoning for the 3-alkyl trienes.

Thus we feel that substituents remote from the reaction site *do* affect the rates of electrocyclization and, to a lesser extent, the activation enthalpy. Groups at the 1 position display similar behavior, although at a much reduced level, primarily owing to the added phenomenon of steric retardation. It would be extremely interesting to examine the electrocyclization of trienes containing either strong electron-donating or withdrawing groups (OR, NR_2, NO_2, CN, Cl, etc.). However, these compounds have either not been produced in a pure state, or they are not particularly stable.[11,13,24] We believe that our results indicate that much more attention should be paid to perturbations in either the electron density or steric requirements of the electrocyclization transition state, although the latter has been recognized previously by some workers.[5,8,25] It is quite probable that investigations with strong donating or withdrawing groups, or with much greater steric interference at the reaction centers, will reveal much greater deviations than we have observed.

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(19) D. Craig, J. Shipman, and R. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961).

(20) E. Lippincott, C. White, and J. Siblia, *ibid.*, **80**, 2926 (1958).

(21) E. Lippincott and T. Kenney, *ibid.*, **84**, 3641 (1962).

(22) An excellent discussion on diene reactivity in general, and the effect of conformation on the rate of Diels–Alder addition in particular, may be found in J. Sauer. *Angew. Chem., Int. Ed., Engl.*, **6**, 16 (1967), and references cited therein.

(23) A referee has suggested that these arguments violate the Curtin–Hammett principle. However, this principle is usually invoked for the situation in which two conformations, in equilibrium with each other, produce different transition states which, in turn, produce different products which are not easily interconvertible. The reaction sequence in the case of conformational equilibrium of 3-alkyl-1,3,5-hexatriene allows only one conformation (s-cis,s-cis) to produce one transition state and one product. Thus the rate of formation of the transition state and product is directly proportional to the relative percentage of triene having an s-cis,s-cis conformation and the Curtin–Hammett principle is not violated.

(24) C. W. Spangler and R. P. Hennis, *Org. Prep. Proced.*, **2**, 75 (1970).

(25) R. Huisgen, A. Dahmen, and H. Huber, *Tetrahedron Lett.*, 1461 (1969).

Experimental Section[26]

1,3,5-Heptatriene (1a).—1,3,5-Heptatriene was prepared and purified essentially by the method of Spangler and Woods,[12] bp 30–32° (25 mm), $n^{23}\text{D}$ 1.5231 [lit.[12] bp 115° (760 mm), $n^{24}\text{D}$ 1.5239]. The triene was subjected to glpc analysis, which revealed a mixture of two isomers. Subsequent analysis showed this to be a mixture of 56% trans,trans and 44% cis,trans isomers. The nmr spectrum revealed τ 8.25 (d, 3 methyl protons, J = 5.5 Hz), 4.6–5.2 (m, 2 vinyl protons), 3.0–4.6 (m, 5 vinyl protons). The ir spectrum was consistent with the assigned structure.

5-Methyl-1,3-cyclohexadiene (2a).—A kinetics sample tube containing 1,3,5-heptatriene (56% trans,trans and 44% cis,trans) was heated at a constant temperature of 150° for 2 hr and then submitted to glpc analysis, revealing one new peak (*ca.* 36% conversion). The new product was collected by preparative glpc and assigned the structure of 5-methyl-1,3-cyclohexadiene based on its uv and nmr spectra. The uv spectrum contained one broad absorption at λ_{max} 258 nm (ϵ_{max} 4200) [lit.[27] λ_{max} 259 nm (ϵ_{max} 3700)]. The nmr spectrum revealed τ 9.0 (d, 3 methyl protons, J = 7.0 Hz), 7.3–8.3 (m, 4 allylic protons), 3.8–4.6 (m, 4 vinyl protons).

1,5-Octadien-4-ol (3b).—*trans*-2-Pentenal (63.0 g, 0.72 mol) dissolved in 200 ml of dry ether was added dropwise to chilled allylmagnesium bromide prepared from allyl bromide (145.0 g, 1.2 mol) and magnesium turnings (73.0 g, 3.0 g-atoms) in 500 ml of dry ether. Hydrolysis and isolation of *trans*-1,5-octadien-4-ol (75.1 g, 83%) was accomplished in the usual manner, yielding a colorless liquid, bp 66–67° (10 mm), $n^{23}\text{D}$ 1.4523.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.52; H, 11.38.

The nmr spectrum revealed τ 9.0 (t, 3 methyl protons, J = 7.5 Hz), 8.12 (s, 1-OH proton), 7.5–8.2 (m, 4-allylic protons), 5.89 (q, 1 methine proton, J = 6.0 Hz), 3.75–5.15 (br m, 5 vinyl protons). The ir spectrum was consistent with the assigned structure.

Benzyldimethyl-4-(1,5-octadienyl)ammonium Bromide (5b).—1,5-Octadien-4-ol (75 g, 0.60 mol) in 200 ml of dry ether was added dropwise over a period of 2 hr with stirring to phosphorus tribromide (81 g, 0.3 mol). During the addition the reaction mixture was cooled in an ice bath. The work-up and isolation of the crude 4-bromo-1,5-octadiene (99 g, 87%) follows the procedure described by us previously[11,12] for allylic bromides.

A solution of the crude 4-bromo-1,5-octadiene (99 g, 0.52 mol) and *N*,*N*-dimethylbenzylamine (94.5 g, 0.70 mol) in 800 ml of dry toluene was prepared and allowed to stand overnight. The solution was then heated on a steam cone for 2–3 hr to complete salt formation. The product separated as a mixture of crystalline and brown glassy material (126 g, 75%). A small portion was recrystallized from ethyl acetate–ethanol, mp 141–142°.

Anal. Calcd for $C_{17}H_{26}BrN$: C, 62.96; H, 8.08; N, 4.32. Found: C, 62.62; H, 7.95; N, 4.55.

The combined crystalline–amorphous product was dissolved in 600 ml of water and the resulting aqueous solution was extracted several times with ether to remove suspended organic material. The yellow aqueous solution was heated to boiling to remove dissolved ether and then cooled to room temperature.

1,3,5-Octatriene (1b).—The above aqueous solution of benzyldimethyl-4-(1,5-octadienyl)ammonium bromide was added dropwise to a solution of sodium hydroxide (128 g in 800 ml of water) which was undergoing distillation. The product was extracted from the distillate in *ca.* 200 ml of ether and washed twice with 3 *N* HCl and twice with water before drying with anhydrous magnesium sulfate. After removal of the solvent, distillation at reduced pressure yielded 1,3,5-octatriene (12 g, 29%), bp 52–53° (23 mm), $n^{23}\text{D}$ 1.5200 [lit.[28] bp 66–67° (60 mm), $n^{20}\text{D}$ 1.517].

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.78; H, 11.22.

Glpc analysis of the product indicated a mixture of two isomers. Subsequent analysis showed this to be a mixture of 68% *trans*,-*trans*- and 32% *cis*,*trans*-1,3,5-octatriene. The nmr spectrum showed τ 9.0 (t, 3 methyl protons, J = 7.5 Hz), 7.6–8.2 (q, 2 methylene protons, J = 7.0 Hz), 2.8–5.2 (br m, 7 vinyl protons).

5-Ethyl-1,3-cyclohexadiene (2b).—A kinetics sample tube containing 1,3,5-octatriene (68% trans,trans and 32% cis,trans) was heated at 150° for 2 hr and then submitted to glpc analysis, revealing one additional product (*ca.* 50% conversion), 5-ethyl-1,3-cyclohexadiene, based on the uv and nmr spectra: λ_{max} 259 nm (ϵ_{max} 4000) [lit.[29] λ_{max} 259 nm (ϵ_{max} 4300)]; τ 8.9–9.3 (m, 3 methyl protons), 8.35–8.8 (m, 2 methylene protons), 7.7–8.0 (m, 3 allylic protons), 3.9–4.4 (br m, 4 vinyl protons).

7-Methyl-1,5-octadien-4-ol (3c).—*trans*-4-Methyl-2-pentenal (66.3 g, 0.68 mol), dissolved in 250 ml of anhydrous ether, was added slowly to a chilled solution of allylmagnesium bromide prepared from allyl bromide (194 g, 1.6 mol) in 600 ml of anhydrous ether and magnesium turnings (97 g, 4.0 g-atoms). The product, *trans*-7-methyl-1,5-octadien-4-ol, was obtained in the usual manner, bp 68–70° (7 mm), $n^{22}\text{D}$ 1.4497 (72.7 g, 76%).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.55; H, 11.78.

The nmr revealed τ 9.02 (d, 6 methyl protons, J = 7.0 Hz), 8.11 (s, 1-hydroxyl proton), 7.5–8.1 (m, 3 allylic protons), 5.88 (q, 1 methine proton, J = 6.0 Hz), 3.8–5.13, (br m, 5 vinylic protons). The ir spectrum was consistent with the assigned structure.

Attempted Preparation of 7-Methyl-1,3,5-octatriene (1c).—7-Methyl-1,5-octadien-4-ol (72.5 g, 0.52 mol) in 200 ml of dry ether was added dropwise during a period of 2.5 hr to phosphorus tribromide (85.5 g, 0.32 mol) with cooling. The crude bromide (100 g, 94%) was isolated in the manner described previously.[11,12]

Crude 4-bromo-7-methyl-1,5-octadiene (100 g, 0.5 mol) and *N*,*N*-dimethylbenzylamine (81 g, 0.60 mol) were mixed in 800 ml of dry toluene. Heating on a steam cone for 3 days produced a a brown residue which proved to be *N*,*N*-dimethylbenzylammonium bromide, indicating dehydrohalogenation rather than salt formation.

The toluene solution was washed several times with 3 *N* HCl to remove amine, then with water, and finally dried with anhydrous-magnesium sulfate. The volume of the solution was reduced to 100 ml with a rotary evaporator. The toluene–triene mixture was then steam distilled from a solution of phosphoric acid (5 ml of 85% phosphoric acid in 500 ml of water). The organic product was extracted into pentane and the resulting pentane solution was dried with anhydrous magnesium sulfate. Distillation at reduced pressure yielded crude 7-methyl-1,3,5-octatriene, bp 52–54° (15 mm), $n^{21}\text{D}$ 1.4982 (10.4 g, 17% based on the bromo precursor), as a colorless liquid.

Glpc analysis of the crude product showed three peaks, the first of which (13%) proved to be toluene. The uv spectrum of the second product (25%) was that of a typical triene, λ_{max} 253.0, 262.5, 273.5 nm ($\epsilon_{max} \times 10^{-4}$ 2.93, 4.04, 3.27), and the nmr showed τ 8.9–9.0 (d, 6 methyl protons, J = 6.5 Hz), 7.0–7.4 (m, 1 allylic proton), 3.5–5.2 (br m, 7 vinyl protons). There was no ir absorption in the region 800–850 cm^{-1}. On the basis of these results, the structure was assigned as *trans*,*trans*-7-methyl-1,3,5-octatriene.

The ultraviolet spectrum of the third component (62%) revealed one absorption band, λ_{max} 238.5 nm ($\epsilon_{max} \times 10^{-4}$ 2.84), and the nmr showed τ 8.27 (s, 6 methyl protons), 7.14 (t, 2 allylic protons, J = 6.5 Hz), 3.4–5.2 (br m, 6 vinylic protons). On this basis the third component was assigned the *trans*-2-methyl-2,4,7-octatriene structure. The ir spectra of the two trienes were consistent with the assigned structures. An analytical sample was collected *via* glpc, and contained the two trienes.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.32; H, 11.68.

7,7-Dimethyl-1,5-octadien-4-ol (3d).—*trans*-4,4-Dimethyl-2-pentenal (56 g, 0.50 mol) in 200 ml of anhydrous ether was added to chilled allylmagnesium bromide, prepared from allyl

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[26] Gas–liquid partition chromatography (glpc) was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370A electronic integrator for peak area measurement. Glpc conditions for all runs: 0.25-in. SS columns, 15 ft, 15% 1,2,3-triscyanoethoxypropane (TCEP), column temperature 50–75°, He pressure 60 psig, flow rate 60 ml/min. Ultraviolet spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer using Spectrograde isooctane as the solvent (λ_{max} values are reported in nanometers), and infrared spectra with Beckman IR-8 or IR-12 spectrophotometers. Nmr spectra were determined as solutions in $CDCl_3$ (TMS) using a Varian A-60A spectrometer. All trienic spectra were recorded for mixtures of geometric isomers unless otherwise stated. All boiling and melting points are uncorrected. C, H, and N analyses were obtained using a Perkin-Elmer Model 240 elemental analyzer. Assignment of the hydroxyl proton in the nmr spectra of alcohols was accomplished by D_2O exchange.

[27] C. W. Spangler and N. Johnson, *J. Org. Chem.*, **34**, 1444 (1969).

[28] K. Alder, H. von Brachel, and K. Kaiser, *Justus Liebigs Ann. Chem.*, **608**, 195 (1953).

[29] H. Pines and C. Chen, *J. Amer. Chem. Soc.*, **81**, 928 (1959).

bromide (135.5 g, 1.12 mol) and magnesium shavings (68 g, 2.8 mol) in 400 ml of dry ether. The product, *trans*-7,7-dimethyl-1,5-octadien-4-ol, bp 69–70° (5 mm), $n^{21.5}_{\mathrm{D}}$ 1.4492, was obtained in the usual manner (71 g, 92%).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.63; H, 12.02.

The nmr spectrum revealed τ 9.0 (s, 9 methyl protons), 8.18 (s, 1 hydroxyl proton), 7.7 (t, 2 allylic protons, J = 6.5 Hz), 5.88 (q, 1 methine proton, J = 6.0 Hz), 3.9–5.15 (br m, 5 vinylic protons). The ir spectrum was consistent with the assigned structure.

7,7-Dimethyl-1,3,5-octatriene (1d).—A solution of 7,7-dimethyl-1,5-octadien-4-ol (70.5 g, 0.46 mol) in 100 ml of dry ether was added dropwise to phosphorus tribromide (81 g, 0.3 mol) with cooling. The crude bromide, 4-bromo-7,7-dimethyl-1,5-octadiene (95 g, 95%), was isolated in the usual manner.

Reaction of the crude bromide (95 g, 0.44 mol) with *N*,*N*-dimethylbenzylamine (91.5 g, 0.68 mol) in 750 ml of dry toluene at room temperature for 1 week, followed by heating on a steam cone for 72 hr, yielded only *N*,*N*-dimethylbenzylammonium bromide. The toluene solution was thus treated as described above for 7-methyl-1,3,5-octatriene, and 7,7-dimethyl-1,5-octatriene was obtained (12.4 g, 21%) by vacuum distillation, bp 45–47° (6 mm), n^{23}_{D} 1.5052.

Glpc analysis showed only one peak, while the uv spectrum had $\lambda_{\max}$ 252.0, 261.5, 272.5 nm ($\epsilon_{\max} \times 10^{-4}$ 3.30, 4.54, 3.60). The nmr spectrum showed τ 8.98 (s, nine methyl protons), 4.6–5.15 (m, 2 vinyl protons), 3.7–4.3 (m, 5 vinyl protons). On the basis of the above, and subsequent thermal behavior, the product is assigned as *trans*,*trans*-7,7-dimethyl-1,3,5-octatriene.

Attempted Cyclization of 7,7-Dimethyl-1,3,5-octatriene (1d).—A sealed Pyrex ampoule containing *trans*,*trans*-7,7-dimethyl-1,3,5-octatriene was heated at 135° for 24 hr. Glpc analysis showed that no reaction had occurred.

7,7-Dimethyl-1,3,5-octatriene (5.0 g, 0.037 mol) was thermolyzed by dropwise addition through a 22-mm Pyrex tube packed to a depth of 27 cm with glass helices and externally heated to 350° with a Lindberg Hevi-duty split-tube electric furnace (0.5 ml/min). The thermolysis product was collected in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temperature. Glpc analysis of the crude product (4.7 g, 94% recovery) revealed at least 11 components. Seven of these minor constituents (3% of total product) were not identified. The four remaining constituents were identified by collecting the glpc effluent emanating from the chromatograph for each peak and analyzing by uv, ir, and nmr spectrometry. The mixture consisted of 5% 2-*tert*-butyl-1,3-cyclohexadiene, 16% 5-*tert*-butyl-1,3-cyclohexadiene, 72% *trans*,*trans*-7,7-dimethyl-1,3,5-octatriene, and 4% *tert*-butylbenzene. No *cis*,*trans*-7,7-dimethyl-1,3,5-octatriene could be detected. The ir, uv, and nmr spectra were all consistent with these assigned structures.

3-Methyl-1,3,5-hexatriene (1e).—3-Methyl-1,3,5-hexatriene was prepared and purified essentially by the method of Spangler and Woods,[12] bp 28–29° (25 mm), n^{24}_{D} 1.5189 [lit.[12] bp 74° (50 mm), n^{26}_{D} 1.5198]. Glpc analysis indicated a mixture of two isomers. Subsequent analysis showed this to be a mixture of 55% *trans*- and 45% *cis*-3-methyl-1,3,5-hexatriene. The nmr spectrum revealed τ 8.15 (s, three methyl protons), 4.5–5.2 (br m, 4 vinyl protons), 2.7–4.2 (br m, 3 vinyl protons). The ir spectrum was consistent with the assigned structure.

2-Methyl-1,3-cyclohexadiene (2e).—A sealed ampoule of 3-methyl-1,3,5-hexatriene (55% trans, 45% cis) was heated at 150° for 1 hr. Glpc analysis indicated one new product (*ca.* 80% conversion). This component was isolated by preparative glpc and had $\lambda_{\max}$ 260.5 nm ($\epsilon_{\max}$ 4200) (lit.[27] $\lambda_{\max}$ 261 nm). The nmr spectrum of the diene revealed τ 8.3 (d, 3 methyl protons, J = 1.5 Hz), 7.92 (narrow m, 4 allylic protons), 4.55 (br m, 1 vinyl proton), 4.22 (m, 2 vinyl protons); thus the structure was assigned as 2-methyl-1,3-cyclohexadiene.

3-Ethyl-1,5-hexadien-3-ol (3f).—1-Penten-3-one (100 g, 1.2 mol) in 250 ml of dry ether was added to chilled allylmagnesium bromide prepared from allyl bromide (218 g, 1.8 mol) and magnesium turnings (110 g, 4.5 g-atoms) in 900 ml of anhydrous ether. 3-Ethyl-1,5-hexadien-3-ol was obtained in the usual manner (74 g, 49%), bp 47–48° (25 mm), n^{25}_{D} 1.4500.

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.07; H, 11.22.

Benzyldimethyl-3-(3-ethyl-1,5-hexadienyl)ammonium Bromide (5f).—3-Ethyl-1,5-hexadien-3-ol (74 g, 0.59 mol) in 200 ml of anhydrous ether was added to phosphorus tribromide (80 g, 0.30 mol) cooled by an ice bath. The crude product, 3-bromo-3-ethyl-1,5-hexadiene, was obtained as described previously as an unstable lachrymatory liquid (87 g, 78%). The crude product was treated immediately with *N*,*N*-dimethylbenzylamine (85 g, 0.63 mol) in 800 ml of dry toluene. The reaction mixture was allowed to stand for several days at room temperature. The crystalline salt (90 g, 60%) was then dissolved in water (500 ml) and treated as described above. A small portion was recrystallized from ethyl acetate–ethanol, mp 112–113°.

Anal. Calcd for $C_{17}H_{26}BrN$: C, 62.96; H, 8.08; N, 4.32. Found: C, 62.75; H, 7.89; N, 4.23.

3-Ethyl-1,3,5-hexatriene (1f).—The above aqueous solution of benzyldimethyl-3-(3-ethyl-1,5-hexadienyl)ammonium bromide (90 g, 0.28 mol) in 500 ml of water was added dropwise to a solution of sodium hydroxide (96 g in 800 ml of water) undergoing distillation. The distillate was treated as has been described previously. 3-Ethyl-1,3,5-hexatriene (23 g, 78%) was obtained as a colorless liquid, bp 46–47° (25 mm), n^{24}_{D} 1.5175.

Anal. Calcd for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.67; H, 11.33.

Glpc analysis showed the triene to be a mixture of two isomers of 3-ethyl-1,3,5-hexatriene and 3% 2-ethyl-1,3-cyclohexadiene. Subsequent analysis showed the triene fraction to be composed of 64% *cis*- and 33% *trans*-3-ethyl-1,3,5-hexatriene. The nmr revealed τ 8.7–9.2 (t of d, J_{ab} = 7.0, J_{ax} = 2.0 Hz, 3-methyl protons), 7.4–8.0 (quintet, 2 methylene protons, J = 7.0 Hz), 4.5–5.1 (br m, 4 vinyl protons), 2.8–4.2 (br m, 3 vinyl protons).

2-Ethyl-1,3-cyclohexadiene (2f).—An ampoule containing a mixture of geometric isomers of 3-ethyl-1,3,5-hexatriene (64% cis, 33% trans) was heated at 150° for 1 hr. Glpc analysis revealed the major product to be 2-ethyl-1,3-cyclohexadiene (*ca.* 86% conversion). The uv spectrum revealed one broad absorption, $\lambda_{\max}$ 259 nm ($\epsilon_{\max}$ 4400), while the nmr showed τ 8.8–9.2 (t, some narrow, long-range splitting superimposed on triplet splitting, 3 methyl protons, J = 7.0 Hz), 7.55–8.3 (br m, 6 allylic protons), 4.4–4.7 (br, m, 1 vinyl proton), 4.05–4.25 (m, 2 vinyl protons).

A Typical Oxidation of 4-Methyl-1-penten-3-ol (6).—4-Methyl-1-penten-3-ol (20 g, 0.20 mol)[30] dissolved in 400 ml of ether and 140 ml of water was oxidized essentially by the method of Vanstone and Johnson[31] with Jones reagent.[32] Glpc analysis (6 ft, 15% Carbowax 20M on 60–80 mesh Chromosorb W columns at 90°) of the ether solution showed the product composition to be 68.5% 4-methyl-1-penten-3-one and 31.5% unreacted alcohol. A sample of the pure ketone was collected and converted to the 2,4-dinitrophenylhydrazone. This derivative was recrystallized from ethanol–ethyl acetate, mp 126–128°.

Anal. Calcd for $C_{12}H_{14}N_4O_4$: C, 51.80; H, 5.07; N, 20.13. Found: C, 51.86; H, 5.40; N, 19.92.

Isolation of the pure ketone was not attempted on a large scale and the above crude product mixture was dried with anhydrous magnesium sulfate and utilized directly in the next step.

3-Isopropyl-1,5-hexadien-3-ol (3g). A Typical Preparation.—The crude reaction product from three oxidation runs of 4-methyl-1-penten-3-ol, reduced in volume to 200 ml, was added to chilled allylmagnesium bromide, prepared from allyl bromide (121 g, 1.0 mol) and magnesium turnings (73 g, 3 g-atoms). The product was isolated in the usual manner, yielding 3-isopropyl-1,5-hexadien-3-ol (20 g, 23% overall based on starting 4-methyl-1-penten-3-ol), bp 60° (25 mm), n^{25}_{D} 1.4517.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.88; H, 11.44.

The nmr spectrum revealed τ 9.1 (d, 6 methyl protons, J = 7.5 Hz), 8.09 (s, 1 hydroxyl proton), 7.9–8.6 (m, 1 methine proton), 7.7 (d, 2, allylic protons, J = 7.0 Hz), 3.8–5.17 (br m, 6 vinylic protons). The ir spectrum was consistent with this structure.

Benzyldimethyl-3-(3-isopropyl-1,5-hexadienyl)ammonium Bromide (5g).—3-Isopropyl-1,5-hexadien-3-ol (67.9 g, 0.48 mol) dissolved in 100 ml of anhydrous ether was added dropwise to phosphorus tribromide (70 g, 0.26 mol) with cooling. The crude product, 3-bromo-3-isopropyl-1,5-hexadiene, was obtained as described previously as an unstable lachrymatory liquid (82 g, 90%). The crude bromide (82 g, 0.40 mol) was added to *N*,*N*-dimethylbenzylamine (67.6 g, 0.50 mol) in 800 ml of dry toluene. This mixture was allowed to stand at room temperature for 1

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(30) K & K Laboratories, Plainview, N. Y.

(31) A. E. Vanstone and J. S. Whitehurst, *J. Chem. Soc. C*, 1972 (1966).

(32) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *ibid.*, 2548 (1953).

week and the crystalline product was collected (97 g, 72%). A small sample was recrystallized from ethyl acetate–ethanol, mp 124–126°.

Anal. Calcd for $C_{18}H_{28}NBr$: C, 63.71; H, 8.61; N, 4.13. Found: C, 63.77; H, 8.64; N, 4.23.

3-Isopropyl-1,3,5-hexatriene (1g).—A solution of benzyldimethyl-3-(3-isopropyl-1,5-hexadienyl)ammonium bromide (97 g, 0.27 mol in 500 ml of water) was added to a solution of sodium hydroxide (96 g in 800 ml of water) undergoing distillation. The distillate was treated as has been described previously. 3-Isopropyl-1,3,5-hexatriene, bp 51–53° (25 mm), n^{25}_{D} 1.5012, was obtained as a colorless liquid (10 g, 29%).

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.42.

Glpc analysis indicated that the product was a mixture of two isomers. Subsequent analysis showed this to be a mixture of 75% cis and 25% trans isomers. The nmr revealed τ 8.75–9.05 (d, 6 methyl protons, J = 7.0 Hz), 6.7–7.5 (septet, 1 methine proton, J = 6.5 Hz), 4.4–5.15 (br m, 4 vinyl protons), 2.9–4.2 (br m, 3 vinyl protons).

2-Isopropyl-1,3-cyclohexadiene (2g).—An ampoule containing 3-isopropyl-1,3,5-hexatriene (75% cis, 25% trans) was heated at 150° for 0.75 hr. Glpc analysis indicated *ca.* 90% conversion to 2-isopropyl-1,3-cyclohexadiene. The uv spectrum showed one broad absorption, λ_{max} 258 nm (ϵ_{max} 5200). The nmr spectrum revealed τ 8.80–9.15 (d, 6 methyl protons, J = 6.5 Hz), 7.50–8.0 (br m, 5 allylic protons, 4.4–4.7 (m, 1 vinyl proton), 4.0–4.2 (m, 2 vinyl protons).

3-*tert*-Butyl-1,5-hexadien-3-ol (3h).—4,4-Dimethyl-1-penten-3-one[33] (74 g, 0.66 mol) in 250 ml of anhydrous ether was added to chilled allylmagnesium bromide, prepared from allyl bromide (2.8 g, 1.8 mol) and magnesium turnings (110 g, 4.5 g-atoms). 3-*tert*-Butyl-1,5-hexadien-3-ol was obtained in the usual manner (35 g, 34%), bp 59–60° (1 mm), n^{24}_{D} 1.4521.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.92; H, 12.17.

The nmr spectrum showed τ 8.8–9.5 (m, 9 methyl protons), 8.5 (s, 1 hydroxyl proton), 7.5–8.1 (m, 2 allylic protons), 3.79–5.25 (br m, 6 vinyl protons). The *tert*-butyl signal appeared as three singlets whose peak heights were in the ratio 1:1.5:5.7 (total of 9 protons by integration) and this is interpreted as representing preferred but unknown conformations of the *tert*-butyl group. The ir spectrum was conistent with the assigned structure for this alcohol.

Benzyldimethyl-3-(3-*tert*-butyl-1,5-hexadienyl)ammonium Bromide (5h).—3-*tert*-Butyl-1,5-hexadien-3-ol (68 g, 0.44 mol) in 100 ml of anhydrous ether was added dropwise to phosphorus tribromide (85.5 g, 0.32 mol) with cooling. The crude product, 3-bromo-3-*tert*-butyl-1,5-hexadiene, was obtained as described previously as an unstable, lachrymatory liquid (88 g, 92%). The crude bromide (88 g, 0.40 mol) was treated with *N*,*N*-dimethylbenzylamine (67.5 g, 0.50 mol) in 800 ml of dry toluene overnight, after which the white, crystalline product was obtained (96 g, 68%). A small sample was recrystallized from ethyl acetate–ethanol, mp 165–166°.

Anal. Calcd for $C_{19}H_{30}NBr$: C, 64.76; H, 8.58; N, 3.98. Found: C, 64.33; H, 8.52; N, 4.02.

3-*tert*-Butyl-1,3,5-hexatriene (1h).—A solution of benzyldimethyl-3-(3-*tert*-butyl-1,5-hexadienyl)ammonium bromide (96 g, 0.27 mol) in 800 ml of water was added to a solution of sodium hydroxide (96 g in 600 ml of water) undergoing distillation. The distillate was treated as has been described previously. 3-*tert*-Butyl-1,3,5-hexatriene, bp 57–58° (25 mm), n^{25}_{D} 1.4813, was obtained as a colorless liquid (18 g, 48%).

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.49; H, 11.57.

Glpc analysis revealed two peaks, of which the first peak (61% of the total) was subsequently shown to be 3-*tert*-butyl-1,3,5-hexatriene, and the second peak (39%) 2-*tert*-butyl-1,3-cyclohexadiene. Lowering both the column and detector temperatures shifted this ratio to 79:21. The nmr spectrum of the distilled sample revealed the *tert*-butyl group at τ 8.83 (9 methyl protons); however, this signal was split into very closely spaced singlets whose ratio was temperature dependent. The vinylic portion, τ 4.45–5.25 (m, 4 protons) and 2.8–4.1 (m, 3 protons), was the only other absorption. Inspection of models of *cis*-3-*tert*-butyl-1,3,5-hexatriene indicates that there are preferred orientations of the methyl groups, suggesting a possible magnetic nonequivalence (theoretical limit 2:1). At 31° the observed ratio is 4.3:1, while at −60° this ratio is lowered to 2.3:1, which supports this interpretation. The uv spectrum of the distilled triene shows a single absorption with no fine structure, λ_{max} 241.0 nm ($\epsilon_{max} \times 10^{-4}$ 1.46). On the basis of the spectral characteristics and glpc behavior, the product is assigned the *cis*-3-*tert*-butyl-1,3,5-hexatriene structure, which undergoes partial conversion to the diene when submitted to glpc analysis.

2-*tert*-Butyl-1,3-cyclohexadiene (2h).—An ampoule containing 100% *cis*-3-*tert*-butyl-1,3,5-hexatriene was heated at 150° for 1 hr. Glpc analysis of the product revealed only one product, λ_{max} 258 nm (ϵ_{max} 4100), nmr τ 8.95 (s, 9 methyl protons), 7.8–8.0 (m, 4 allylic protons), 4.34–4.65 (m, 1 vinyl proton), τ 3.7–4.2 (m, 2 vinyl protons). The structure was assigned as 2-*tert*-butyl-1,3-cyclohexadiene based on these properties.

Kinetic Studies.—The rates of electrocyclic ring closure of the substituted hexatrienes were determined using appropriate mixtures of geometric isomers, as neat liquids, at five different temperatures for each substrate. Ampoules (Pyrex glass, 12 cm × 2 mm i.d.) containing *ca.* 60 μl of neat liquid were degassed and sealed under 20 mm pressure and placed in a paraffin oil bath whose temperature was controlled by a CRC Circu-Temp temperature controller equipped with a CRC Temp-Tact Thermoregulator Model E. Bath temperatures were maintained to within ±0.1°. The disappearance of triene and appearance of the corresponding diene were followed by glpc analysis of the contents of a series of ampoules as a function of time. Ampoules were removed from the bath and quenched by plunging into an ice bath prior to analysis. Pretreatment of the ampoules by acid or base washing or by passage of steam through the capillary tubing was found to have little effect upon the rate of ring closure. Rates were followed generally for >50% conversion to the diene except for the lowest temperatures. In most cases, some trans–cis conversion also occurred. Thus rate constants were calculated using a modified DRATE[15] program which was able to correct the concentration of *cis* isomer as a function of time. Activation parameters were obtained from a standard least squares plot of ln k *vs.* $1/T$. All errors quoted are standard errors.

Assignments of Geometric Configuration. Alkyl-1,3,5-hexatrienes.—In the generation of the 1-alkyl series (alkyl = Me, Et, *i*-Pr, *t*-Bu), the configuration about one double bond (5–6) is fixed by starting with the trans aldehyde. Thus conversion of dienols **3a–d** *via* the reaction sequence outlines in Scheme II to trienes **1a–d** could produce either 3-trans,5-trans or 3-cis,5-trans (or both). For **1a** and **1b** (1-Me and 1-Et trienes), two isomers are indeed obtained, while only one is obtained for **1c** and **1d** (1-*i*-Pr and 1-*t*-Bu). The assignments of geometric isomerism is based on the following basis.

A. Flash Thermolysis.—All four samples (synthetic **1a**, **1b**, **1c**, and **1d**) were passed over Pyrex helices at 250° in a previously described[22] flow system (contact time 1 sec). For **1a** and **1b** glpc revealed that one of the isomers had been converted to a new compound. Isolation of the new substance followed by uv, nmr, and ir analysis showed them to be 5-alkyl-1,3-cyclohexadienes (5-Me and 5-Et, respectively). Area integration of the glpc trace showed that the decrease in area of the one triene peak was directly proportional to the area corresponding to the newly formed 5-alkyl-1,3-cyclohexadiene. Since only isomers with a cis configuration about the 3,4 double bond can undergo ring closure under these conditions,[4] the two isomers of **1a** and **1b** were assigned 3-trans,5-trans and 3-cis,5-trans configurations, respectively. The single geometric isomers obtained for the 1-*i*-Pr and 1-*t*-Bu trienes (**1c** and **1d**) were inert to thermolysis, indicating a 3-trans,5-trans configuration. Details of this technique have previously been described.[27] Thermolyses in sealed tubes, described above, follow the same pattern as flash thermolysis, except that a small amount of trans–cis isomerization occurs. Isolation and structure assignment of the 5-alkyl-1,3-cyclohexadienes, however, is identical in all respects.

The syntheses of **1e–g** (3-Me, Et, and *i*-Pr) produced both cis and trans isomers, while only one isomer of 3-*t*-Bu (**1h**) was obtained. Flash thermolysis of all four trienes were conducted as described above, yielding 2-alkyl-1,3-cyclohexadienes from the isomer having a 3-cis configuration, the 3-trans isomer being totally inert. These results agree with the predicted thermal behavior of 3-cis- *vs.* 3-trans configurations based on the results of Lewis and Steiner.[4]

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(33) S. Archer, W. B. Dickinson, and M. J. Unser, *J. Org. Chem.*, **22**, 92 (1957).

B. Comparison to Alkyl-1,3,5-hexatrienes Generated by Photochemical Ring Opening of Alkyl-1,3-cyclohexadienes.—Irradiation (2537 Å) of 5-alkyl-1,3-cyclohexadienes (**2a–d**) in pentane solution yields mixtures of 3-*cis*,5-*cis*- and 3-*cis*,5-*trans*-**1a–h**, as has been reported previously.[34,35] Similarly, irradiation of **2e–h** yields *cis*-**1e–h**. Prolonged irradiation produces mixtures containing all possible isomers, which are resolvable under the glpc conditions described herein.[26] Comparison of retention times and admixture of the synthetic samples with those generated photochemically confirmed the assignments based on the flash thermoylsis results.

C. Uv Spectra.—Uv analysis yields a great deal of pertinent information. Two observations seem to be of general[10,28,36,37] use in assigning geometric configuration. (1) Isomers having a cis arrangement of hydrogens display a red shift compared to those with trans configurations. In the case of 3-alkyl-1,3,5-hexatrienes, the isomers having a cis arrangement of the two most bulky groups display a red shift compared to those with trans configurations. (2) Isomers having all-trans configurations display much greater extinction than the corresponding isomers wiht all-cis configurations. Along with this observation, the two minima associated with the three maxima in the triene spectrum are *much* more pronounced for the isomers having a 3-trans configuration *vis-à-vis* a 3-cis configuration. This latter correlation, however, is most useful if one has spectra for all possible isomers.

The following spectra were obtained for samples collected by glpc and analyzed immediately. For the 1-alkyl series, the 3-cis,5-trans and 3-trans,5-trans spectra were obtained for both the synthetic and photochemically produced samples, while the 3-trans,5-cis and 3-cis,5-cis spectra were obtained from the photochemical sample *only*. The data are arranged as follows (Table IV).

TABLE IV

Triene	Isomer	$\lambda_{max}^{isooctane}$	$\epsilon_{max} \times 10^4$
1a	3-*t*,5-*t*	271.5, 260.0, 250.5, 242	3.82, 4.60, 3.43 sh
	lit.[31]	271.5, 261.0, 251.0, 242.5 sh	
1a	3-*t*,5-*c*	274.0, 263.5, 254.5	3.04, 3.67, 2.67
	lit.[36]	274.0, 263.5, 254.5	
1a	3-*c*,5-*t*	273.5, 263.0, 255.0	2.83, 3.60, 2.86
	lit.[36]	272.6, 262.2, 252.8	
1a	3-*c*,5-*c*	275.0, 265.0, 256.5	1.05, 1.34, 1.08
	lit.[36]	275.0, 265.0, 256.5	
1b	3-*t*,5-*t*	272.5, 261.5, 252.0, 241	3.15, 4.39, 3.48 sh
1b	3-*c*,5-*t*	274.0, 264.0, 254.0	2.68, 3.50, 2.86
1b	3-*t*,5-*c*	275.0, 264.5, 254.5	2.75, 3.60, 2.60
1b	3-*c*,5-*c*	276.0, 266.0, 256.5	1.10, 1.45, 1.15
1c	3-*t*,5-*t*	273.5, 262.5, 253.0, 242	3.27, 4.04, 2.93 sh
1c	3-*c*,5-*t*	274.0, 263.0, 253.5	2.83, 3.60, 3.08
1c	3-*t*,5-*c*	276.5, 266.0, 257.0	3.01, 3.70, 2.87
1c	3-*c*,5-*c*	277.0, 266.5, 257.0	1.17, 1.50, 1.29
1d	3-*t*,5-*t*	272.5, 261.5, 252.0, 241	3.60, 4.54, 3.30 sh
1d	3-*c*,5-*t*	274.0, 263.0, 253.5	2.77, 3.47, 2.79
1d	3-*t*,5-*c*	276.0, 264.5, 255.0	2.89, 3.53, 2.78
1d	3-*c*,5-*c*	278.0, 267.0, 257.5	1.07, 1.40, 1.19
1e	3-*c*	272.0, 261.5, 252.0	2.22, 2.86, 2.22
1e	3-*t*	273.5, 263.0, 253.0, 244	3.48, 4.39, 3.27 sh
1f	3-*c*	275.0, 265.5, 256.0	1.85, 2.46, 1.67
1f	3-*t*	277.0, 266.0, 257.0, 248.0	2.22, 2.97, 2.18 sh
1g	3-*c*	276.5, 266.0, 257.5	1.58, 2.12, 1.87
1g	3-*t*	279.0, 268.0, 259.0	2.20, 2.70, 2.37
1h	3-*c*	241.0	1.46

D. Ir Spectra.—1-Alkyl-1,3,5-hexatrienes with a cis configuration about the central double bond display ir absorption in the region 818–825 cm^{-1} which Lippincott, *et al.*,[20,21] have assigned to the cis out-of-plane CH deformation. The corresponding trans out-of-plane absorption occurs at *ca.* 940 cm^{-1}. Thus the 3-trans,5-trans and 3-cis,5-trans isomers can be distinguished. The single isomers obtained in the 1-*t*-Bu and 1-*i*-Pr cases do not absorb in the region 800–850 cm^{-1}, indicating a 3-trans,5-trans configuration, which agrees with our assignment based on the flash thermolysis results as well as the uv assignments.

Registry No.—3-*trans*,5-*trans*-**1a**, 17679-93-5; 3-*trans*,5-*cis*-**1a**, 30915-43-6; 3-*cis*,5-*trans*-**1a**, 24587-25-5; 3-*cis*,5-*cis*-**1a**, 30915-44-7; 3-*trans*,5-*trans*-**1b**, 33580-04-0; 3-*trans*,5-*cis*-**1b**, 33580-05-1; 3-*cis*,5-*trans*-**1b**, 40087-61-4; 3-*cis*,5-*cis*-**1b**, 40087-62-5; 3-*trans*,5-*trans*-**1c**, 40087-63-6; 3-*trans*,5-*cis*-**1c**, 40087-64-7; 3-*cis*,5-*trans*-**1c**, 40087-65-8; 3-*cis*,5-*cis*-**1c**, 40087-66-9; 3-*trans*,5-*trans*-**1d**, 40087-67-0; 3-*trans*,5-*cis*-**1d**, 40087-68-1; 3-*cis*,5-*trans*-**1d**, 40037-06-7; 3-*cis*,5-*cis*-**1d**, 40087-69-2; *cis*-**1e**, 24587-27-7; *trans*-**1e**, 24587-26-6; *cis*-**1f**, 40087-72-7; *trans*-**1f**, 40087-73-8; *cis*-**1g**, 40087-74-9; *trans*-**1g**, 40087-75-0; *cis*-**1h**, 40087-76-1; **2a**, 19656-98-5; **2b**, 40085-08-3; **2e**, 1489-57-2; **2f**, 40085-10-7; **2g**, 40085-11-8; **2h**, 40085-12-9; *trans*-**3b**, 40087-77-2; *trans*-**3c**, 40087-78-3; *trans*-**3d**, 40087-79-4; **3f**, 40085-13-0; **3g**, 40085-14-1; **3h**, 40085-15-2; *trans*-**4b**, 40087-80-7; *trans*-**4c**, 40087-81-8; *trans*-**4d**, 40087-82-9; **4f**, 40085-16-3; **4g**, 40085-17-4; **4h**, 40085-18-5; *trans*-**5b**, 40087-83-0; **5f**, 40087-84-1; **5g**, 40087-85-2; **5h**, 40087-86-3; *trans*-2-pentenal, 1576-87-0; *N*,*N*-dimethylbenzylamine, 103-83-3; *trans*-4-methyl-2-pentenal, 24502-08-7; *trans*-4,4-dimethyl-2-pentenal, 22597-46-2; 1-penten-3-one, 1629-58-9; 4-methyl-1-penten-3-ol, 4798-45-2; 4-methyl-1-penten-3-one dinitrophenylhydrazone, 40087-88-5; 4,4-dimethyl-1-penten-3-one, 2177-30-2.

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(34) C. Spangler and R. Hennis, *J. Chem. Soc., Chem. Commun.*, 24 (1972).

(35) R. Hennis, Ph.D. Thesis, Northern Illinois University, 1972.

(36) K. Egger and M. Jola, *Int. J. Chem. Kinet.*, 265 (1970).

(37) T. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).