# Thermal Electrocyclic Ring Closure of Alkenylhexa-1,3,5-trienes and the Question of Anchimeric π-Bond Participation [1]

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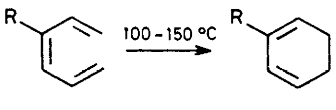
The anomalously fast electrocyclic ring closure of 3-vinylhexa-1,3,5-triene to yield 2-vinylcyclohexa-1,3-diene had previously been interpreted as involving anchimeric π-bond participation of the 3-vinyl group in the electrocyclization transition state. In order to determine whether this observation and interpretation was indeed characteristic of alkenyl side-chains, 3-allylhexa-1,3,5-triene and 3-propylhexa-1,3,5-trienes were synthesized and their electrocyclization rates and activation parameters compared both to each other and to the corresponding 3-ethyl and 3-vinyl trienes. The results conclusively show that the accelerative effect operative in 3-vinylhexa-1,3,5-triene ring closure does not extend to non-conjugated alkenyl side chains.

THE hexa-1,3,5-triene–cyclohexa-1,3-diene interconversion has been studied extensively during the past decade as the simplest example of electrocyclic ring closure involving $4n + 2\pi$ electrons. Although much of the earlier research was concerned with the stereochemistry of this reaction, more recently the energetics and structure/reactivity relationships have been of greater interest as a means of gaining insight into the nature of the electrocyclization transition state.

The first kinetic study of trienic ring closure was conducted by Lewis and Steiner [2] in 1964. Electrocyclization of (*Z*)-hexa-1,3,5-triene was studied from 120—190 °C and was found to be quantitative. Under the same conditions the *E*-isomer is unaffected. In general, thermal ring-closure of substituted hexa-1,3,5-trienes are also quantitative and show little or no tendency for thermal reversion.



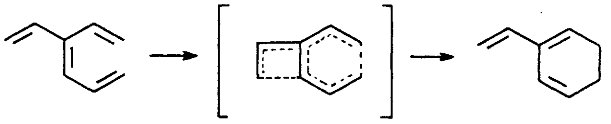
(1) (2)

a; R = Me
b; R = Et
c; R = Bu$^t$

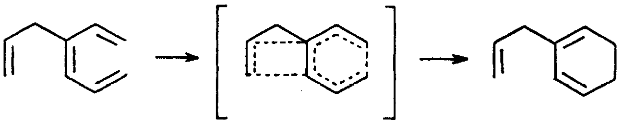
Spangler and his co-workers [3] have demonstrated that alkyl substitution in the 3-position accelerates the rate of ring closure and also lowers the activation enthalpy by *ca.* 3—5 kcal mol$^{-1}$. These results have been interpreted in terms of the donative abilities of the alkyl groups and differences in the ground-state energies and/or conformations.

More recently, Spangler has reported [4] the extremely ready thermal electrocyclization of 3-vinylhexa-1,3,5-triene to 2-vinylcyclohexa-1,3-diene. This appears to be the most thermally labile $4n + 2$ electrocyclization of an acyclic system yet studied. In comparison to the saturated ethyl substituent, the rate of ring closure of the 3-vinyltriene (3) is over 30 times faster. This acceleration has been interpreted in terms of an anchimeric participation of the vinyl group in the electrocyclization transition state.

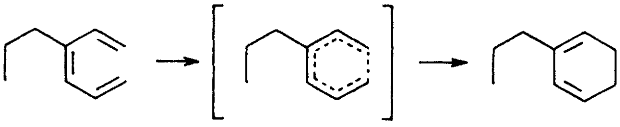
This speculation led us to question the possibility of generalized anchimeric participation of π-bonds, even when separated by methylene groups from the conjugated trienic system. Homoallylic effects in pericyclic processes, for example, are well known, particularly in sigmatropic migrations.[5] If anchimeric π-bond participation in electrocyclization is a general phenomenon in $4n + 2$ systems, then (*Z*)-3-allylhexa-1,3,5-triene should ring close considerably faster than the saturated 3-propyl analogue *via* a transition state such as (7).



(3) (5) (4)



(6) (7) (8)



(9) (10) (11)

Syntheses of 3-allylhexa-1,3,5-triene and 3-propylhexa-1,3,5-triene followed standard synthetic routes previously shown to yield pure substituted hexa-1,3,5-trienes.[3,6,7] Both 3-allyl- and 3-propyl-hexa-1,3,5-trienes were sealed in degassed ampoules, and the kinetics of ring closure determined in the temperature range 125—150 °C. First-order rate constants were obtained, as shown in Table 1. As can readily be seen from the electrocyclization rates, there is little, if any, difference between the saturated and unsaturated substituent effects on the ring-closure transition state. This also can readily be seen from a comparison of activation parameters for the two trienes (Table 2). For comparison, the values for 3-ethyl- and 3-vinyl-hexa-1,3,5-triene are included.

TABLE 1

Electrocyclization rates for 3-alkylhexa-1,3,5-trienes

| $t$/°C [a] | 3-Subst. | $10^4k_{elec}$ [b] |
|---|---|---|
| 125.0 | Pr | 1.79 |
| | Al | 1.82 |
| 135.0 | Pr | 3.69 |
| | Al | 3.72 |
| 150.0 | Pr | 11.0 |
| | Al | 12.0 |

[a] All temperatures maintained to within ±0.1 °C. [b] All rate constants fitted to a minimum sum-squared error and change <1% on successive calculations. Some *cis–trans* isomerization occurs, and is corrected for in the rate-constant calculations as previously described.[3]

TABLE 2

Activation parameters for electrocyclization of 3-alkylhexa-1,3,5-trienes

| Subst. | $T$/K | log $A$/ $s^{-1}$ | $\Delta H^{\ddagger}$/ kcal $mol^{-1}$ | $\Delta S^{\ddagger}$/ J $K^{-1}$ $mol^{-1}$ | Ref. |
|---|---|---|---|---|---|
| 3-Vinyl | 357—395 | 10.3 | 22.0 | −13.8 | 4 |
| 3-Ethyl | 374—423 | 9.9 | 24.2 | −11.3 | 3 |
| 3-Allyl | 398—423 | 10.2 | 24.5<br>±0.3 [a] | −14.7<br>±0.9 [a] | This work |
| 3-Propyl | 398—423 | 9.6 | 23.5<br>±0.1 | −17.1<br>±0.4 | This work |

[a] Errors quoted are standard errors. $\Delta S^{\ddagger}$ Calculated for $T_m$.

The activation enthalpies and entropies for 3-allyl- and 3-n-propyl-hexa-1,3,5-trienes are not only quite similar to each other, but also are similar to 3-ethylhexa-1,3,5-triene. The 3-vinylhexa-1,3,5-triene to 2-vinylcyclohexa-1,3-diene conversion still remains as an anomolously fast reaction. Whatever effect is operative in the 3-vinyl participation does not extend to the homoallylic participation of an allyl group. We may conclude that if $\pi$-bond anchimeric participation is the main source of the enhanced reactivity of the 3-vinyltriene, it is a relatively short-range effect.

## EXPERIMENTAL

G.l.p.c. was performed with an Aerograph 202-1B dual-column instrument equipped with a Hewlett–Packard 3370A electronic integrator for peak-area measurement, and 20 ft, 15% Carbowax 20M SS columns. U.v. spectra were recorded with a Perkin-Elmer 202 and i.r. spectra with a Beckman IR-8 or Acculab 4 spectrophotometer. N.m.r. spectra were determined for solutions in $CDCl_3$ ($SiMe_4$ standard) with a Varian A-60A spectrometer. All triene spectra were recorded for mixtures of geometric isomers unless otherwise stated. C, H analyses were obtained for all new compounds with a Perkin-Elmer Model 240 elemental analyser and were satisfactory.*

4-*Vinylhepta*-1,6-*dien*-4-*ol*.—Allylmagnesium chloride was prepared from allyl chloride (234 g, 3 mol) in anhydrous diethyl ether (1.5 l) and magnesium (150 g) in the usual manner at 0 °C. After the reaction was complete, methyl acrylate (96.4 g, 1.1 mol) in anhydrous diethyl ether (100 ml) was added dropwise at 0 °C, and the resulting mixture stirred overnight at room temperature. The product mixture was hydrolysed by pouring it into a mixture of ammonium chloride, ice, and water, and worked up in the usual manner. After removal of solvent at reduced pressure, 4-vinylhepta-1,6-dien-4-ol was obtained as a clear, colourless liquid, b.p. 32—34 °C at 20 mmHg, $n_D^{25}$ 1.4605 (72 g, 47%); $\tau$ 8.1 (s, 1 H, OH), 7.8—8.0br (m, 4 H, $CH_2$), 5.5—5.8 (m, 6 H, $CH_2$=), and 4.9—5.3 (m, 3 H, CH=); $\nu_{max.}$ 3 460, 3 080, 3 010, 2 980, 2 915, 1 855, 1 725, 1 645, 1 440, 1 415, 1 345, 1 300, 1 225, 1 175, 1 140, 995, 920, 760, 720, and 625 $cm^{-1}$.

3-*Allylhexa*-1,3,5-*triene*.—4-Vinylhepta-1,6-dien-4-ol (90 g, 0.65 mol) in anhydrous diethyl ether (100 ml) was converted into crude 4-bromo-4-vinylhepta-1,6-diene by reaction with $PBr_3$ (90 g) at 0°C. The crude bromide was treated with an excess of *NN*-dimethylbenzylamine (150 g) in toluene (600 ml) and the resulting crude ammonium salt (206 g, 94%) dissolved in water. A small portion of the crude salt was recrystallized from EtOAc–EtOH, m.p. 72—74 °C. The ammonium salt was converted into 3-allylhexa-1,3,5-triene in a manner similar to that described by Spangler and Woods[7] for the preparation of methyltrienes. Distillation at reduced pressure yielded pure 3-allylhexa-1,3,5-triene (15) as a colourless liquid (30 g, 40%), b.p. 40—45 °C at 20 mmHg, $n_D^{25.5}$ 1.5290; u.v. (EtOH): $\lambda_{max.}$ ($\varepsilon_{max.} \times 10^{-4}$) 254 (3.29), 264 (41.9), 275 nm (35.3); i.r. (film): $\nu_{max.}$ 3 095, 3 015, 2 980, 2 930, 1 970, 1 820, 1 645, 1 625, 1 455, 1 430, 1 365, 1 300, 1 240, 1 135, 1 110, 990, 910, 825, 730, 660, and 625 $cm^{-1}$; $^1H$ n.m.r. $\tau$ 7.3—8.0 (m, 2 H, $CH_2$), 4.6—5.2 (m, 6 H, $CH_2$=), and 2.8—4.5 (m, 3 H, =CH). G.l.p.c. analysis revealed the presence of two isomers which subsequent analysis showed to be 68% *Z*, 32% *E*.

4-*Vinylhept*-1-*en*-4-*ol*.—Hex-1-en-3-one was prepared from hex-1-en-3-ol essentially by the method of Rao and Filler.[8] The alcohol (50 g, 0.5 mol) was added to a solution of sodium dichromate dihydrate (100 g, 0.33 mol) in $Me_2SO$ (1 100 ml). Sulphuric acid (72 ml, 1.33 mol) was then added to the mixture with stirring at room temperature (occasional cooling). After the addition was complete, the mixture was stirred for an additional 0.5 h and then poured onto ice and extracted three times with ether (200—300 ml). The ether solution was washed with sodium carbonate solution, then with water, and finally dried ($MgSO_4$). After filtration, the solution volume was reduced to *ca*. 200 ml at reduced pressure.

Allylmagnesium chloride was prepared in the usual manner from allyl chloride (69 g, 0.9 mol) at 0 °C as described previously. The above ether solution of crude hex-1-en-3-one was then added dropwise to the cooled Grignard reagent, and worked up in the usual manner. The dried diethyl ether solution was distilled at reduced pressure and pure 4-vinylhept-1-en-4-ol (17) was obtained as a colourless liquid (23 g, 33%), b.p. 55—60 °C at 20 mmHg, $n_D^{25}$ 1.4253; i.r. (film) $\nu_{max.}$ 3 480, 3 090, 3 005, 2 960, 2 940, 2 880, 1 850, 1 645, 1 450, 1 380, 1 345, 1 150, 1 000, 920, and 730 $cm^{-1}$; $^1H$ n.m.r.: $\tau$ 9.0—9.2 (m, 3 H, $CH_3$), 8.4—8.8 (m, 4 H, aliphatic $CH_2$), 7.8—8.0 (d, 2 H, $J$ = 7 Hz, allylic $CH_2$), 7.7 (s, 1 H, OH), and 3.8—5.2 (m, 6 H, $CH_2$=CH).

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* Details are available as Supplementary Publication No. SUP 22553 (2 pp.). See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

3-*Propylhexa*-1,3,5-*triene*.—4-Vinylhept-1-en-4-ol (58 g, 0.40 mol) was treated with $PBr_3$ (58 g) and the crude bromide isolated and treated in *NN*-dimethylbenzylamine (100 g) in toluene (600 ml). An aqueous solution of the resulting crude ammonium salt was then converted into 3-propylhexa-1,3,5-triene as described previously [7] (15.7 g, 31%), b.p. 52—55 °C at 20 mmHg, $n_D^{22}$ 1.5162; u.v. (EtOH): $\lambda_{max.}$ ($\varepsilon_{max.} \times 10^{-4}$) 255 (2.72), 265 (3.44), and 276 nm (2.68); i.r. (film): $\nu_{max.}$ 3 100, 3 020, 2 970, 2 880, 1 815, 1 625, 1 470, 1 430, 1 380, 1 105, 990, and 905 cm$^{-1}$; $^1$H n.m.r.: $\tau$ 8.9—9.1 (t, 3 H, $J$ = 7 Hz, $CH_3$), 8.2—8.8 (m, 2 H, $CH_2$), 7.4—8.0 (q, 2 H, $J$ = 7 Hz, $CH_2$), 4.5—5.1 (m, 4 H, $CH_2$=), and 2.8—4.2 (m, 3 H, CH=). G.l.p.c. analysis revealed the presence of two isomers which subsequent analysis showed to be 73% *Z*, 27% *E*.

*Kinetic Studies*.—The rates of electrocyclic ring closure of the allyl and propyl trienes were determined by sealing neat liquids (60 μl) in Pyrex ampoules (12 cm × 2 mm i.d.). The samples were degassed and sealed under 15 mmHg pressure and placed in a paraffin oil-bath whose temperature was controlled by a CRC Temp-Tact Thermoregulator model E. Bath temperatures were maintained to within ±0.1 °C. The disappearance of triene and appearance of the corresponding diene were followed by g.l.p.c. analysis of the contents of a series of ampoules as a function of time. The ampoules were removed from the bath and quenched by plunging into an ice-bath prior to analysis. Some *cis–trans* isomerization occurs, and thus rate constants were calculated using a modified DRATE [9] program which was able to correct the concentration of *Z*-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.

*Assignment of Geometric Configuration*.—Both *Z*- and *E*-isomers were obtained for 3-allyl- and 3-propyl-hexa-1,3,5-trienes. Flash thermolysis of either triene at 250 °C over Pyrex helices yields one new compound and a concomitant decrease in the concentration of one of the geometric isomers as evidenced in the g.l.p.c. analyses. This isomer may thus be assigned the 3*Z*-configuration as the 3*E*-isomer is incapable of ring closure. 2-Alkylcyclohexa-1,3-dienes are characterized by both u.v. in EtOH (250—262 nm) and $^1$H n.m.r. spectra in the vinyl region ($\tau$ 4.4—4.7) (m, 1 vinyl-H), 4.0—4.2 (m, 2 vinyl-H) for samples trapped from the g.l.p.c. effluent.

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