Tetrahedron Vol 32, pp 2681 to 2684 Pergamon Press 1976 Printed in Great Britain

THE SYNTHESIS AND FACILE THERMAL ELECTROCYCLIZATION OF 3-VINYL-1,3,5-HEXATRIENE

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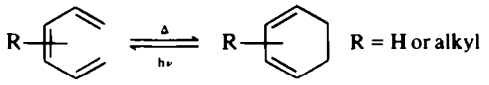
(*Received in USA* 6 *April* 1976; *Received in the UK for publication* 24 *June* 1976)

Abstract—3-Vinyl-1,3,5-hexatriene undergoes an extremely facile thermal electrocyclization to yield 2-vinyl-1,3-cyclohexadiene. Cyclization is at least thirty times faster than 3-ethyl-1,3,5-hexatriene, the saturated analog. Activation parameters indicate that this electrocyclization is one of the most facile yet observed for an acyclic 6π-electron system.

The 1,3,5-hexatriene-1,3-cyclohexadiene interconversion has been studied extensively during the past decade as a result of the interest generated by Woodward and Hoffman's treatment of this process as the simplest example of a disrotatory thermal 4n + 2 electrocyclization.[1] Much of the early research was concerned with the stereochemistry of this process, however recent interest has been directed towards energetics and structure-reactivity relationships as a means of gaining insight into the nature of the transition state. For simple alkylhexatrienes, electrocyclization proceeds at a reasonable rate (k *ca.* 10^{-4} to 10^{-5} sec^{-1}) only at temperatures above 100°, with activation enthalpies falling in the range 25–35 kcal per mole.[2-4] Ring closure, in most cases, is complete with little or no tendency for thermal reversion to the triene. The reaction, of course, may be reversed photochemically. The conversion of 3-vinyl-1,3,5-hexatriene to 2-vinyl-1,3-cyclohexadiene, however, is an extremely facile

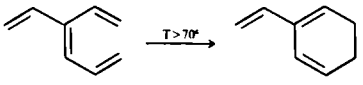


process and we wish to report our studies with this system, which appears to be the most thermally labile 4n + 2 acyclic electrocyclization yet studied.

RESULTS AND DISCUSSION

3-Vinyl-1,3,5-hexatriene (1) was prepared as outlined below:

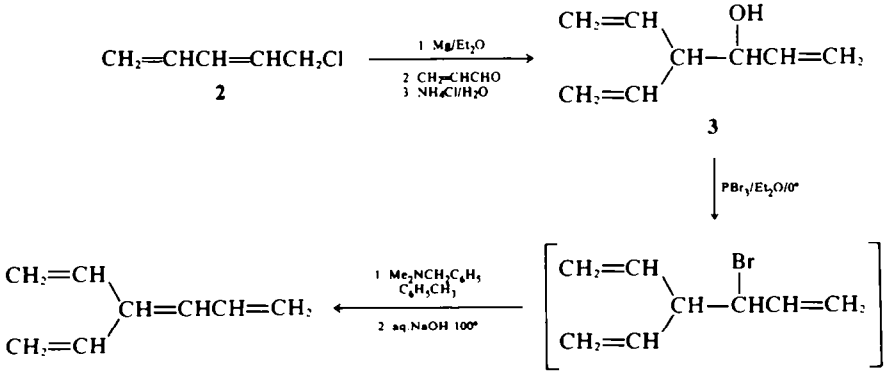
4-Vinyl-1,5-hexadien-3-ol (3) was obtained in 72% yield by reaction of pentadienylmagnesium chloride and acrolein, and reaction of 3 with phosphorus tribromide yielded crude 4, an unstable lachrymatory liquid which was not purified but reacted directly with N,N-dimethylbenzylamine to produce an ammonium salt in 72% yield. An aqueous solution of this salt was added directly to boiling aqueous sodium hydroxide and the triene (1) isolated by steam distillation in 33% yield. GLPC analysis on two different columns, with column temperatures kept below 60°, indicated a purity of at least 98% and IR, UV and PMR spectra were all consistent with the assigned structure. If GLPC analysis is carried out at temperatures above 70°, on column ring-closure occurs, with formation of a new product. Isolation of this product by trapping the effluent in a Dry Ice bath and subsequent analysis by UV and PMR spectroscopy demonstrated that the cyclization product was 2-vinyl-1,3-cyclohexadiene (5). Slow formation of 5 from samples of



1 5

pure 1 was also evident in samples stored at room temperature or 0° in the absence of light. However, pure 1 can be stored for extended periods of time at −78°.

Thermolysis of 1 at various temperatures and flow rates, in a fast flow system,[5] yielded various mixtures of 1 and 5, with the extent of reaction ranging from 20 to 80%.

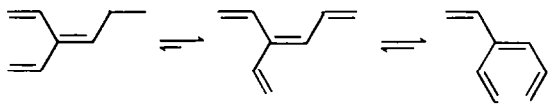


Rate constants were calculated as has been described previously[5] and are shown in Table 1 and compared to previously reported[2] values for 3-ethyl-1,3,5-hexatriene. Activation parameters were obtained by least squares analysis and are compared to both 3-ethyl-1,3,5-hexatriene and the parent 1,3,5-hexatriene in Table 2. Pure **5**, isolated by GLPC, was submitted to flow conditions at various temperatures and showed no tendency for thermal reversion to **1**, however **5** does have a tendency to undergo polymerization at elevated temperatures (>120°) in a flow system, or at lower temperatures in static experiments. Samples stored in solution exposed to light, however, do revert to **1** in a few days.

The rate of electrocyclization of **1** is considerably faster than analogous 3-alkyl-1,3,5-hexatriene cyclizations.[2] 3-Ethyl-1,3,5-hexatriene, for example, cyclizes at least 30 times slower. Similarly, the activation enthalpy for closure of **1** is 4 kcal lower than 3-ethyl-1,3,5-hexatriene and at least 7 kcal lower than the parent 1,3,5-hexatriene. We had previously suggested[2] that either electronic or steric factors could account for the increased cyclization

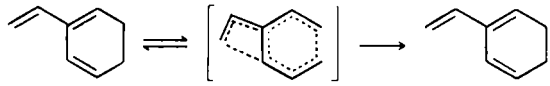
rel. rate: $CH_2{=}CH > CH_3CH_2 > H$
$\Delta H^{\ddagger}$: $H > CH_3CH_2 > CH_2{=}CH$

rates for 3-alkyl trienes over the parent. The most stable conformations of *cis*- and *trans*-1,3,5-hexatriene are linearly extended in both liquid and gas phase.[8,9] However **1** may be considered to be both a *trans* and *cis* triene simultaneously, and the *s-trans, s-trans* conformation would place all double bonds in a coplanar relationship. Although interaction between vinyl groups may be relieved by internal rotations to some degree, it is probable that conformational equilibrium is shifted more towards the *s-cis, s-cis* conformation necessary for ring closure, thus providing an increased driving force for cyclization. An alternative explanation for the extreme



s-trans,s-trans *s-trans,s-cis* *s-cis,s-cis*

ease of ring closure is the possibility of vinyl participation in the electrocyclization transition state. If this indeed is occurring, the system can be considered to be related to



1 **5**

an $8\pi \rightarrow 6\pi 2\sigma$ electrocyclization. In fact the reactivity of 3-vinyl-1,3,5-hexatriene towards thermal ring closure does seem to be more comparable to that reported for the octatetraene-1,3,5-cyclooctatriene conversion reported by Huisgen and coworkers.[10,11] It is probable that both effects contribute to the overall ease of the cyclization.

Attempts to prepare 2-vinyl-1,3-cyclohexadiene (**5**) by alternate means proved to be quite difficult. 1-Vinyl-2-cyclohexen-1-ol (**6**) was prepared by reaction of vinylmag-

Table 1. Rate constants for electrocyclization of 3-vinyl-1,3,5-hexatriene

Compound	Temp, °C[a]	Residence time, sec	C/Co[b]	k(sec^{-1}) x 10^3
3-Vinyl: (1)	83.9	998	0.7980	0.226[c]
	90.9	1171	0.6548	0.442
	109.0	486	0.3920	2.47
	122.1	309	0.3434	4.59
3-Et:	115.7	—	—	0.0674[d]
	124.1	—	—	0.1320[d]

[a]All temperatures maintained to within ± 0.1°. [b]Initial mol fraction of 1 was 1.000. [c]Estimated error in k (averaged over several runs) is ± 5%.
[d]See Ref. 2.

Table 2. Activation parameters for electrocyclization of 3-vinyl-1,3,5-hextriene[a]

Compound	Temp. Range °K	log A sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu (Temp, °K)	Ref.
3-Vinyl (1)	356 - 395	10.3	22.0 ± 0.3	-13.8 ± 0.9 (364)	This work
3-Ethyl	374 - 423	9.9	26.0 ± 0.5	-11.3 ± 1.5 (374)	2
H	390 - 434	11.9	29.1 ± 0.5	-7.3	6

[a]Errors quoted are standard errors[7].

nesium bromide with 2-cyclohexenone in 60% yield. Although Nazarov *et al.*[12] had previously reported that **6** was extremely unstable, we encountered no difficulty in isolation and purification and the product could be stored for at least a month at 0° before spontaneous dehydration became evident. Alumina catalyzed dehydration under mild conditions (250°) yielded ethylbenzene as the major reaction product. Although aromatization is normally observed as a minor pathway[13,14] (< 5%) in dienol or cyclohexenol dehydration, the extent of this reaction is quite surprising, more so in that styrene is *not* an observed product. Mild dehydration with methyltriphenoxy-phosphonium iodide (MTPI) in hexamethylphosphoric triamide (HMPT)[15] produced a mixture of both 5- and 1-vinyl-1,3-cyclohexadiene (**7**). Similarly, thermolysis of **6** over Pyrex helices in the vapor phase also produced a mixture of **5** and **7**. Presumably **7** is generated either from an intermediary dienyl carbonium ion or by a facile[1, 5] sigmatropic hydrogen migration yielding **7** directly from **5** in the vapor phase, a process not normally observed at temperatures below 300° in a fast flow system in alkyl-1,3-cyclohexadienes.[14] This latter explanation can probably be ruled out on the basis that no 1-vinyl-1,3-cyclohexadiene is formed during the thermolysis of **1**, even at 122°.

In summary, it appears that electrocyclic ring closure of 3-vinyl-1,3,5-hexatriene is more facile than any previously reported acyclic hexatriene-cyclohexadiene pair. Similarly, isomerization of 2-vinyl-1,3-cyclohexadiene to 1-vinyl-1,3-cyclohexadiene also appears to be more facile than saturated analogs. In fact, the reactivity of this system seems to be more comparable to that reported for the octatetraene-1,3,5-cyclooctatriene conversion[10,11] than to the electrocyclizations of alkyl-1,3,5-hexatrienes.

EXPERIMENTAL

IR spectra were obtained with either Beckman IR-8 or IR-12 spectrophotometers. UV spectra were recorded with a Perkin-Elmer Model 202 spectrophotometer and PMR spectra were determined as solns in $CDCl_3$ (TMS) using a Varian A-60A spectrometer. All b.ps are uncorrected. C, H and N analyses were obtained for all compounds reported in this work using a Perkin-Elmer Model 240 elemental analyzer and were consistent with the assigned structures.

4-*Vinyl*-1,5-*hexadien*-3-*ol* (3)

Pentadienylmagnesium chloride was prepared from 5-chloro-1,3-pentadiene[16] (94 g, 0.92 mol) in 700 ml anhyd ether and 75 g Mg in the usual manner at 0°. After Grignard formation was complete, the creamy mixture was stirred at room temp. for an additional hr. Acrolein (45 g, 0.8 mol) in 200 ml anhyd ether was then added dropwise, with cooling, over a 2-hr period and the resulting mixture stirred for 1 hr at room temp. The product was hydrolyzed by pouring into a mixture of ammonium chloride, ice and water, the ether layer separated and the aqueous layer extracted twice with ether. The combined ether solns were washed once with water, dried with $MgSO_4$, filtered and distilled at reduced pressure yielding **3** as a colorless liquid (71 g, 72%), $b_{1.5}$ 53–55°; n_D^{23} 1.4724; PMR: τ 7.65 (s, 1, OH), 6.90–7.32 (bd. q, 1, J = 6 Hz), 5.75–6.05 (bd. t, 1, J = 5.5 Hz), 4.55–5.20 (m, 6, CH_2=C), 3.50–4.45 (m, 3, =CH–); IR (film): ν_{max} = 3420, 3090, 2990, 2885, 1855, 1650, 1430, 1300, 1130, 1000, 925, 775, 700 cm^{-1}. GLPC analysis indicated a purity of at least 98%.

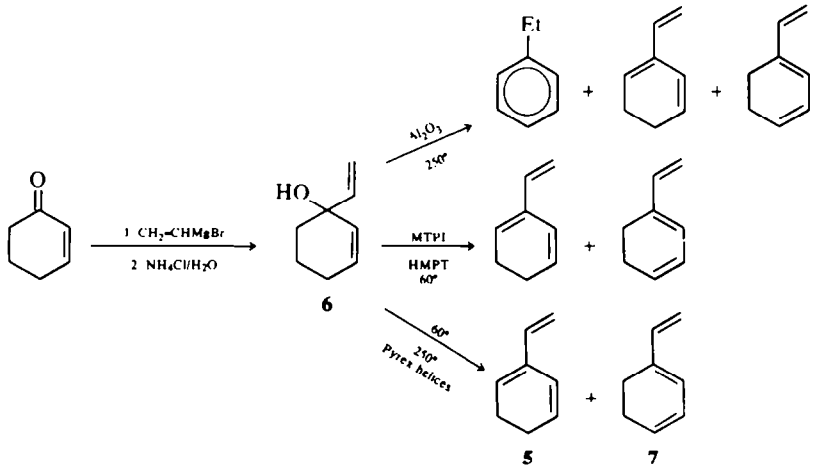
3-*Vinyl*-1,3,5-*hexatriene* (1)

3 (71 g, 0.57 mol) in 200 ml of dry ether was added dropwise over a period of 2 hr with stirring to PBr_3 (70 g, 0.26 mol). During the addition the reaction was cooled in an ice bath. After addition was complete, the resulting mixture was allowed to come to room temp. and stand overnight. The product was then poured into ice water and neutralized by adding Na_2CO_3. The ether soln was separated and the aqueous portion extracted with a further quantity of ether. The combined either soln was then dried with $MgSO_4$ and filtered.

N,N-dimethylbenzylamine (135 g, 1.0 mol) in 500 ml dry benzene was added to the ether soln of the crude **4**. After *ca.* 5 min the ammonium salt began to separate as a glass. After 24 hr slow crystallization of the salt was observed, and the solvent was decanted from the semi-crystalline mass yielding 132 g (72%) crude ammonium salt. This product was dissolved in water and the yellow soln was extracted with ether to remove suspended organic impurities, and then heated to remove dissolved ether.

The aqueous soln of the crude N,N-dimethylbenzylammonium salt of 3-bromo-4-vinyl-1,5-hexadiene was added dropwise to aq NaOH (50 g in 900 ml water) which was undergoing distillation. The product was extracted from the distillate in *ca.* 200 ml pentane and washed twice with 3N HCl and twice with water before drying with $MgSO_4$. After removal of pentane under reduced pressure and distillation at reduced pressure, 3-vinyl-1,3,5-hexatriene was obtained (14.5 g, 33%) b_{15} 50–52°, n_D^{22} 1.5460; UV λ_{max} (ϵ_{max}) 275, 227, 220, 214 (sh) nm, (31,600; 13,000; 14,000; 12,100); IR (film) ν_{max} 3050, 2090, 1780, 1580, 1405, 1265, 975 (bd), 885 (bd), 790, 742, 668 cm^{-1}; PMR: τ 4.70–5.0 (m, 4, CH_2=), 4.40–4.60 (m, 2, CH_2=), 2.80–4.0 (m, 4, =CH–). GLPC analysis on two different columns (col. T < 60°) indicated a purity of at least 98%.

After standing for several days at 0° in a dark cold room, GLPC analysis indicated slow formation of a new product, subsequently shown to be **5**. In order to prevent this occurence, **1** should be stored in sealed ampoules over hydroquinone (as a polymerization inhibitor) in an inert atmosphere at Dry Ice/acetone temp. (−78°).



2-Vinyl-1,3-cyclohexadiene (**5**)

3-Vinyl-1,3,5-hexatriene (5 g) was added dropwise through a 22 mm Pyrex tube packed to a depth of 12 in with 1/16 in Pyrex helices and externally heated at 175° with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 Torr was maintained in the system to facilitate rapid removal of the product from the column. Contact time was estimated to be between 30 and 45 sec. The product was trapped in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temp. and analyzed immediately by GLPC (3.7 g, 74% recovery). Polymer formation and decomposition was evident throughout the column. GLPC indicated a 65% conversion to a new product, which was isolated in a pure state by trapping the GC effluent in a V-tube immersed in a Dry Ice bath. Reinjection of this sample in the GC indicated a purity of better than 99% and on the basis of the following spectral data the structure was assigned as 2-vinyl-1,3-cyclohexadiene: UV (λ_{max}) 267 nm; PMR τ 7.90 (bd. s, 4, $-CH_2-$), 5.32, 5.17, 4.85 (3 apparent singlets, 2H) 3.70–4.60 (m, 4H), n_D^{20} 1.5390. The product undergoes polymerization readily, even when stored at 0° over hydroquinone. Syringes utilized for GC injection should be cleaned *immediately* to prevent clogging of the needle.

1-Vinyl-2-cyclohexen-1-ol (**6**)

Vinyl magnesium bromide was prepared in the usual manner from 1 mol vinyl bromide and Mg (26 g) in 600 ml of anhyd THF. 2-Cyclohexenone (72 g, 0.75 mol) in 100 ml THF was then added dropwise to the cooled Grignard over a 2 hr period after which the resulting soln was stirred for 1 additional hr at room temp. The Grignard product was hydrolyzed by pouring into a mixture of NH_4Cl/ice/water and the product isolated in the usual manner. Distillation at reduced pressure yielded 1-vinyl-2-cyclohexen-1-ol as a colorless liquid (56.5 g, 61%), b_1 49–50°; n_D^{27} 1.4940; IR (film) ν_{max} 3400, 3085, 3015, 2940, 2870, 2840, 1710, 1645, 1450, 1440, 1410, 1320, 1260, 1230, 1190, 1125, 1080, 1020, 990, 960, 920, 870, 850, 740 cm^{-1}; PMR τ 7.65–8.65 (m, 6H, $-CH_2-$), 7.34 (s, 1H, OH), 4.1–5.35 (m, 5H, vinylic). [lit.[10] b_{15} 86–88°, n_D^{20} 1.4990]. Although **6** is reported to be very unstable in the lit.,[12] we found that the product can be stored for at least 1 month at 0° with little apparent decomposition, however at room temp., spontaneous dehydration and polymerization begins in a few days.

Attempted dehydrations of 1-vinyl-2-cyclohexen-1-ol (**6**)

(a) Compound **6** (5 g) was added dropwise through a 22 mm Pyrex tube packed to a depth of 12 in with activated γ-alumina and externally heated at 250° with a Lindberg Hevi-Duty split-tube furnace at a rate of 0.5 ml/min. The alumina had previously been dried by heating under vacuum at 300° for 1 hr. A pressure of 20–25 Torr was maintained in the system to facilitate rapid removal of the dehydration products which were trapped in a flask immersed in a Dry Ice–acetone bath. The product was warmed to room temp. and separated from a small quantity of water by filtration through anhyd $MgSO_4$. The product (2 g) was analyzed immediately by GLPC and 14 products were detected in the chromatogram, of which 3 were major products and were identified on the basis of their UV spectra and comparison to authentic samples as ethylbenzene (71%), 1-vinyl-1,3-cyclohexadiene (9.5%) and 2-vinyl-1,3-cyclohexadiene (10.1%).

(b) Compound **6** (12.4 g, 0.10 mol) was reacted with methyltriphenoxy phosphonium iodide[17] (65.5 g, 0.15 mol) in hexamethylphosphoric triamide (250 cm^3) at 60° for 2 hr according to the procedure of Spangler and Hartford.[14] The mixture was then distilled at aspirator pressure (15–20 Torr) and the product trapped in a flask, cooled in a Dry Ice–acetone bath. The product (3.5 g) was warmed to room temp. and analyzed immediately by GLPC which showed the product to be a mixture of 1-vinyl-1,3-cyclohexadiene (40%) and 2-vinyl-1,3-cyclohexadiene (60%).

(c) Compound **6** (15 g, 0.12 mol) was thermolyzed at 200° as previously described for the conversion of 3-vinyl-1,3,5-hexatriene into **5**. The product (6.5 g) was warmed to room temp. and dried by filtering through anhyd $MgSO_4$ and then distilled, $b_{1.5}$ 44–45°. GLPC analysis showed the product to be a mixture of 1-vinyl-1,3-cyclohexadiene (36%) and 2-vinyl-1,3-cyclohexadiene (64%).

In all of the above, 1-vinyl-1,3-cyclohexadiene was identified by its characteristic UV spectrum: λ_{max} (ϵ_{max}) 312, 298, 288 [lit.[18,19] (cyclohexane) 313, 300, 290; (isooctane) 310, 298, 288]. 1-Vinyl-1,3-cyclohexadiene polymerizes very readily, even when stored at 0° over hydroquinone.

REFERENCES

[1] R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*, pp. 38–64 and refs therein. Verlag Chemie Gmbh/Academic Press, Weinheim/Bergstr. (1970).

[2] C. W. Spangler, T. P. Jondahl and B. Spangler, *J. Org. Chem.* **38**, 2478 (1973).

[3] E. N. Marvell, G. Caple, B. Schatz and W. Pippin, *Tetrahedron* **29**, 378 (1973).

[4] E. N. Marvell, G. Caple, C. Delphey, J. Platt, N. Polston and J. Tashiro, *Ibid.* **29**, 3797 (1973).

[5] The flow system is essentially equivalent to that previously described by H. Kwart, S. F. Sarner and J. H. Olson, *J. Phys. Chem.* **73**, 4056 (1969), except that stainless steel columns (0.25 in i.d.) were utilized. Behavior of **1** was essentially identical to that on packed columns. Helium was utilized as the carrier gas in all cases. Analysis of thermolysis products were carried out by GLPC on an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370A electronic integrator for peak area measurement: 15' SS columns packed with 15% *tris*-1,2,3-cyanoethoxy propane (TCEP) on 60–80 mesh Chromosorb W; column temp. 50°, He flow rate 60 ml/min.

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

[7] K. B. Wiberg, *Physical Organic Chemistry*, pp. 378–379. Wiley, New York (1964).

[8] E. Lippincott, C. White and J. Siblia, *J. Am. Chem. Soc.* **80**, 2926 (1958).

[9] E. Lippincott and T. Kenney, *Ibid.* **84**, 3641 (1962).

[10] W. Ziegenbein, *Chem. Ber.* **98**, 1427 (1965).

[11] R. Huisgen, A. Dahmen and H. Huber, *J. Am. Chem. Soc.* **89**, 7130 (1967).

[12] I. N. Nazarov, S. N. Ananchenko and I. V. Torgov, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim Nauk* 103 (1959); *Chem. Abstr.* **53**, 16089f.

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

[14] C. W. Spangler and R. P. Hennis, *Ibid.* **36**, 917 (1971).

[15] C. W. Spangler and T. W. Hartford, *Synthesis* 108 (1976).

[16] Prepared in the usual manner by stirring divinyl carbinol with excess conc. HCl.

[17] J. Verheyden and J. Moffat, *J. Org. Chem.* **35**, 2319 (1970).

[18] W. Ziegenbein, *Angew. Chem. I.E.*, **4**, 70 (1965).

[19a] W. von E. Doering and W. R. Roth, *Tetrahedron* **19**, 715 (1963); [b] W. R. Roth and B. Peltzer, *Liebigs Ann.* **685**, 56 (1965).