Competition Between [1,7] Hydrogen Migration and Electrocyclic Ring Closure in 6-Methylhepta-1,3,5-triene [1]

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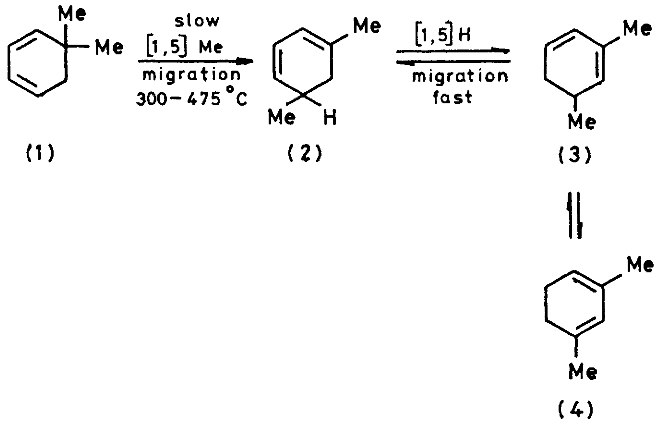
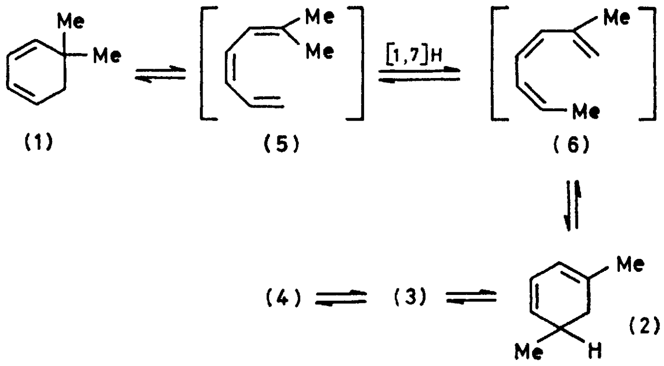
(*Z*)-6-Methylhepta-1,3,5-triene and (*Z*,*Z*)-2-methylhepta-1,3,5-triene have previously been proposed as intermediates in the thermolysis of 5,5-dimethylcyclohexa-1,3-diene, the latter compound derived from the former by fast [1,7] antarafacial hydrogen migration in the gas phase. (*Z*)-6-Methylhepta-1,3,5-triene has now been synthesized and its thermal behaviour in the gas phase studied in the range 481—533 K. The thermal behaviour of both (*Z*)-6-methylhepta-1,3,5-triene and (*Z*)-2,7-dimethylocta-2,4,6-triene indicates that [1,7] hydrogen migration in acyclic trienes is not nearly as ready as has been previously postulated in the literature.

THERMAL [1,5] sigmatropic hydrogen migration in cyclic dienes and trienes is well known and has been studied extensively.[2] However [1,5] alkyl group migrations, although well-documented [2] in cyclopenta-1,3-diene and indene systems, are rather uncommon in acyclic dienes and trienes, and in cyclohexa-1,3-diene. Spangler and Boles [3] reported an apparent [1,5] sigmatropic methyl migration in the flow thermolysis of 5,5-dimethylcyclohexa-1,3-diene occurring between 300 and 475 °C (Scheme 1), but their interpretation has been questioned by several workers including Kloosterziel,[4] Schiess,[5] and Dreiding.[6] These workers prefer an alternative reaction scheme initially proposed by Pines and his co-workers,[7,8] for the thermolysis of (1) at 500 °C, which involves an initial ring-opening of the 5,5-dialkylcyclohexa-1,3-diene to a dialkyltriene, followed by a [1,7] sigmatropic hydrogen shift to form a new dialkyl triene, and finally electrocyclic ring closure to the rearranged dimethylcyclohexa-1,3-diene. This latter process is illustrated in Scheme 2.

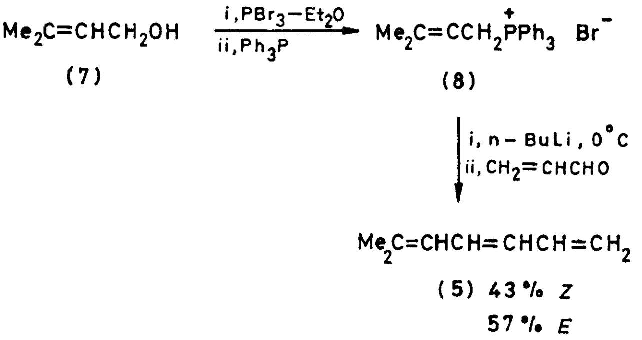


SCHEME 1



SCHEME 2

Spangler and Boles were unable to detect the presence of either (5) or (6) in their flow reaction products, even though the percent conversions were in the range 0.1—80%, and they were able to demonstrate that the lower triene detection limit was 0.01%. The key step in Scheme 2 is the [1,7] hydrogen migration conversion of (5) into (6). Although [1,7] hydrogen migrations of this type are known,[2] the kinetics and activation parameters for this reaction type are not well established, particularly for parent systems. For this reason, and in order to determine the feasibility of the (5) ⟶ (6) conversion, these compounds were synthesized, and their thermolysis kinetics in a flow system determined.



$$\underset{(7)}{\mathrm{Me_2C{=}CHCH_2OH}} \xrightarrow[\text{ii, Ph}_3\text{P}]{\text{i, PBr}_3\text{–Et}_2\text{O}} \underset{(8)}{\mathrm{Me_2C{=}CCH_2\overset{+}{P}Ph_3\ Br^-}}$$

$$\Big\downarrow \text{i, } n\text{-BuLi, 0 °C; ii, CH}_2\text{=CHCHO}$$

$$\underset{(5)\ 43\%\ Z,\ 57\%\ E}{\mathrm{Me_2C{=}CHCH{=}CHCH{=}CH_2}}$$

SCHEME 3

6-Methylhepta-1,3,5-triene (5) was obtained by Wittig condensation as outlined in Scheme 3, while 2-methylhepta-1,3,5-triene was prepared as previously described by Spangler *et al.*[9] These trienes may be easily separated by g.l.p.c. and have characteristic ^{1}H n.m.r. and u.v. spectra. Pure *Z*-(5) or a mixture of *Z*-(5) and *E*-(5) were thermolysed in a flash-flow apparatus,† the

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† The flow system is essentially equivalent to that previously described [10] except that stainless-steel columns (0.25 in i.d.) were utilized. Helium was utilized as the carrier gas, and product analysis was performed directly on the thermolysis sample by g.l.p.c.

products separated and isolated by g.l.p.c. techniques, and identified by g.l.p.c., ^1H n.m.r., and u.v. spectrometry as well as comparison to known samples in our laboratory. Two products were formed and identified as 5,5-dimethylcyclohexa-1,3-diene (1) and 1,5-dimethylcyclohexa-1,3-diene (2). First-order kinetics were obtained for the disappearance of (5). Between 8 and 10 runs were utilized in the calculation of k_{obs} at each temperature with deviations of less than 1% between individual runs.

Two thermal reactions are probable for the *Z*-isomer of (5): electrocyclic ring closure to 5,5-dimethylcyclohexa-1,3-diene (1), and [1,7] sigmatropic hydrogen migration yielding 2-methylhepta-1,3,5-triene (6). However, under the conditions employed for the thermolysis of (5), (6) apparently undergoes ring closure to the observed product (2). This latter reaction should not be surprising since both (*Z*)-2-methylhexa-1,3,5-triene,[11] and (*Z*,*E*)-hepta-1,3,5-triene both ring close completely in this temperature range under similar flow conditions. Thus it is reasonably safe to assume * that *k* (observed) for the rearrangement of (5) may be approximated by $k_{obs} \approx k_1 + k_2$,[11] with k_1 and k_2 being obtained from the product ratios (1) : (2). These results are tabulated in Tables 1 and 2. Activation parameters for the formation of (1) and (6) were determined and are listed in Table 3, and compared to previously obtained parameters for both hexa-1,3,5- and a few methyl-substituted trienes.

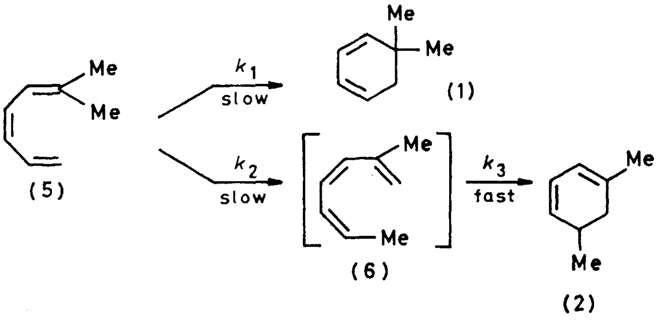


TABLE 1

Flow thermolysis of *Z*-6-methylhepta-1,3,5-triene

t/°C	τ/s	$-\ln C/C_0$	$k_{obs} \times 10^4$
208	537	0.091	1.7
225	346	0.246	7.1
238	339	0.508	15.0
249	329	1.019	31.0
260	329	2.120	64.5

The results shown in Tables 2 and 3 indicate that electrocyclic ring closure is preferred over [1,7] sigmatropic hydrogen migration in the thermolysis of *Z*-6-methylhepta-1,3,5-triene. Many previous workers have alluded to [1,7] hydrogen migrations in acyclic systems as ready reactions, although without any direct evidence,[15,16] and have claimed that in the absence of specific steric interference, this rearrangement is the dominant reaction. Our results would seem to contradict this supposition, although it is clear that [1,7] hydrogen migration does compete with electrocyclic ring closure. Considering the stringent steric requirements of the transition state for antarafacial [1,7] hydrogen migration compared to that of $6\pi \rightarrow 4\pi 2\sigma$ electrocyclic ring closure, this result should have been predictable.

TABLE 2

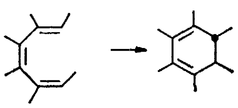
Product ratios and rate constants for *Z*-6-methylhepta-1,3,5-triene

t/°C	[(1)]/[(2)]	k_{obs} [a]	$k_2 \times 10^4$	$k_1 \times 10^4$
208	*b*			1.7
225	3.56	4.56 k_2	1.6	5.5
238	3.07	4.07 k_2	3.7	11.0
249	3.00	4.00 k_2	7.7	23.0
260	2.58	3.58 k_2	18.0	46.0

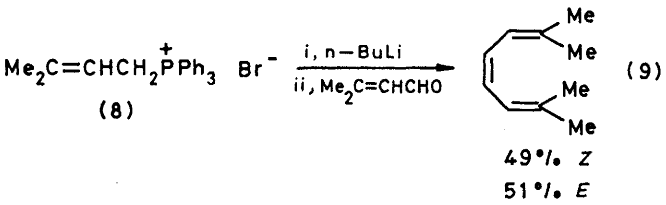
[a] k_3 Assumed to be large compared to k_2. [b] [(2)] too low to be measured accurately.

TABLE 3

Activation parameters for thermal rearrangement of *Z*-6-methylhepta-1,3,5-triene

Reaction	log *A*	$\Delta H^\ddagger$/kcal mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1} (*T*/K)	Ref.
(5)→(1)	10.8 ± 2.5	31 ± 1.2	−8.1 ± 2.4 (522)	
(5)→(6)	12.1 ± 2.1	35 ± 1.4	−6.9 ± 2.7 (522)	
	11.8	28.9	−4.9 (374)	12
	11.9	29.1	−5.2 (428)	13
		27.4	−19 (466)	14

We had previously determined that electrocyclic ring closure of 1-substituted hexa-1,3,5-trienes was influenced by steric factors.[12] It is apparent, now, that [1,7] hydrogen migration may also be affected in the same manner. In order to determine whether either electrocyclic ring closure or [1,7] H migration could be totally discriminated against in hexa-1,3,5-trienes, (*Z*)-2,7-dimethylocta-2,4,6-triene was prepared in a manner similar to *Z*-6-methylhepta-1,3,5-triene and thermolysed in both flow and static systems. Sealed samples of a pentane solution of (9) at 150 °C for 8 h resulted in no



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* It is true that a direct determination of k_3 by a kinetic study of the thermolysis of (6) would be desirable. However, the *ZZ*-isomer of this compound has not yet been synthesized in our laboratory nor has it been reported in the literature.

discernible reaction. Similarly, flow thermolysis of (9) in the range 200—300 °C produced neither ring closure nor sigmatropic migration products. Obviously, then, both these reactions become quite difficult when the potential reaction sites are sterically crowded. It seems quite clear that even simple pericyclic reactions in acyclic systems are more susceptible to steric influence than previously believed, and, in fact, that this system represents the first example wherein normally ready thermal pericyclic processes are prevented on steric grounds alone.

The question remains as to the viability of the ring-opening, [1,7] hydrogen migration, ring-closure mechanism proposed for the thermolysis of 5,5-dimethylcyclohexa-1,3-diene. Our results show, for the first time, that this route is indeed energetically feasible. However, the relative contributions of Schemes 1 and 2 cannot be estimated from currently available data.

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 20 M SS columns (column temperature 50—75 °C; He pressure 60 lb in^{-2}, 60 ml min^{-1} flow rate). U.v. spectra were recorded with a Perkin-Elmer 202 and i.r. spectra with a Beckman IR-8 spectrophotometer. N.m.r. spectra were determined for solutions in $CDCl_3$ (Me_4Si standard) with a Varian A-60A spectrometer. All triene spectra were recorded for mixtures of geometric isomers unless otherwise stated. C and H analyses were obtained for all compounds reported with a Perkin-Elmer model 240 elemental analyser and were satisfactory. All boiling points are uncorrected.

3-*Methylbut*-2-*enyltriphenylphosphonium Bromide*.—A solution of 3-methylbut-2-en-1-ol (19.2 g, 0.22 mol) in 100 ml anhydrous ether was added dropwise to phosphorus tribromide (19 g) at 0 °C. The resulting mixture was then allowed to warm to room temperature and stirred overnight. The product was poured into ice–water and the resulting mixture neutralized with sodium carbonate. The bromide was extracted with diethyl ether, and the ether solution was then washed with water and dried ($MgSO_4$). The bromide is an unstable lachrymatory liquid, and the ether solution of the crude product was not purified further. The drying agent was filtered off and the clear ether solution of the bromide added to a solution of triphenylphosphine (53 g, 0.20 mol) in dry benzene (300 ml). Precipitation of product occurred almost immediately, and the reaction mixture was set aside overnight at room temperature. The product was filtered off, washed with dry benzene, and then air-dried to yield 3-methylbut-2-enyltriphenylphosphonium bromide (8) as white crystals, m.p. 228—229 °C (80.3 g, 93% overall yield for two steps), $\tau(CDCl_3)$ 8.7 (3 H, d, J = 3 Hz), 8.3 (3 H, d, J = 6 Hz), 5.2—5.8 (2 H, m), 4.6—5.1 (1 H, m), and 2.2 (15 phenyl H).

6-*Methylhepta*-1,3,5-*triene* (5).—A solution of n-butyllithium (354 ml; 1.6M-solution) in hexane was added dropwise to a stirred suspension of 3-methylbut-2-enyltriphenylphosphonium bromide (232.4 g, 0.565 mol) in ether at 0 °C. The resulting deep red mixture was stirred for an additional hour after the addition was complete, and then a solution of freshly distilled acrolein (31.6 g, 0.565 mol) in anhydrous diethyl ether (100 ml) was added dropwise, the reaction temperature being maintained at 0 °C. After the addition was complete, the mixture was allowed to warm to room temperature after which it was stirred for an additional ½ h. The product mixture was then filtered through Celite and the filtrate washed several times with water and then dried ($MgSO_4$). The solvent was removed and the product distilled at reduced pressure to yield 6-methylhepta-1,3,5-triene (5) as a colourless liquid, b.p. (20 mmHg) 43—45 °C, $n_D^{22.5}$ 1.5226 (20.1 g, 33%); $\lambda_{max.}$ (EtOH) 281 (ε 26 800), 271 (31 000), and 260 nm (24 800); $\nu_{max.}$ (film) 3 080—2 800, 1 785, 1 640, 1 620, 1 575, 1 440, 1 370, 1 340, 1 200, 1 140, 1 000, 935, 885, and 815 cm^{-1} (pure E-isomer). G.l.p.c. revealed the presence of two isomers of (5) (E and Z) in almost equal amounts with the E-isomer being eluted first. The E-isomer has three distinct peaks (281, 270, and 260 nm), while the Z-isomer shows only one major absorption (269 nm) with shoulders at 279 and 260 nm) in the u.v. region. Fast-flow thermolysis at 260 °C shows total disappearance of the peak assigned the Z-configuration, while the peak assigned to the E-isomer remains unaffected. The n.m.r. spectrum for the pure E-(5) showed 8.2 (s, 6H, $2CH_3$), 4.6—5.1 (m, 2H, CH_2=), and 3.0—4.3 (m, 4H, CH=CH).

2,7-*Dimethylocta*-2,4,6-*triene* (9).—A solution of n-butyllithium (400 ml, 0.64 mol) in hexane was added to a stirred solution of (8) (0.64 mol) as described above. 3-Methylbut-2-enal (0.64 mol) in anhydrous diethyl ether (700 ml) was then added to the Wittig reagent dropwise, during a 3 h period, the temperature being maintained at 10 °C. The reaction mixture was then allowed to warm to room temperature after which it was heated under reflux for 1 h. The mixture was cooled, filtered through Celite, washed with water, and then dried ($MgSO_4$). The solution was concentrated to a volume of *ca.* 100 ml under reduced pressure and then cooled in a solid CO_2–acetone bath. The product crystallized rapidly from solution and was isolated in several batches by rapid filtration to yield essentially pure 2,7-dimethylocta-2,4,6-triene, (9) (26.6 g, 30%), m.p. 45—47 °C. G.l.p.c. analysis revealed the presence of two isomers of (9) in approximately equal amounts: $\lambda_{max.}$ (EtOH) 291 (ε 27 900), 279 (35 700), and 269 nm (27 400); τ 8.25 (m, 12 H, $4CH_3$) and 3.5—4.3 (m, 4 H, –CH=CH–); $\nu_{max.}$ (film) 3 050—2 840, 1 720, 1 680, 1 620, 1 450, 1 370, 1 350, 1 220, 1 160, 980, 870, and 805 cm^{-1}.

Identification of Thermolysis Products.—5,5-Dimethyl- and 1,5-dimethyl-cyclohexa-1,3-dienes were prepared as previously described.[3] The thermolysis products were isolated by trapping the g.c. effluent and comparing the u.v., n.m.r., and g.c. retention times to those of authentic samples.

2-Methylhepta-1,3,5-triene was prepared as previously described,[9] to yield the EE- and EZ-isomers. Admixture with a sample of 6-methylhepta-1,3,5-triene (both E and Z isomers) followed by g.l.c. analysis demonstrated that all four isomers were readily separable. Attempts at photoisomerization (sensitized with fluorenone) of (6) failed to produce any ZZ-isomer. Several additional preparations of (6) (alumina dehydration, MTPI/HMPT dehydrations,[17,18] Hwa procedure,[12,19,20] *etc.*) commonly used as triene preparations similarly failed to yield any ZZ-isomer.

Thermolysis of 5,5-*Dimethylcyclohexa*-1,3-*diene*.—Pure compound (1) was thermolysed at 220, 230, 240, 250, and

260 °C in the flow-kinetics system under the same conditions as described for (5). No discernible reaction occurred.

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