Thermal Rearrangements, XX[1]

The Kinetics of Thermal Isomerisation of 4-Methyl-1,2,5-hexatriene in the Gas Phase

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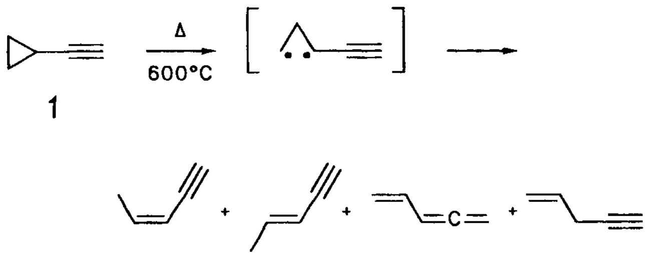
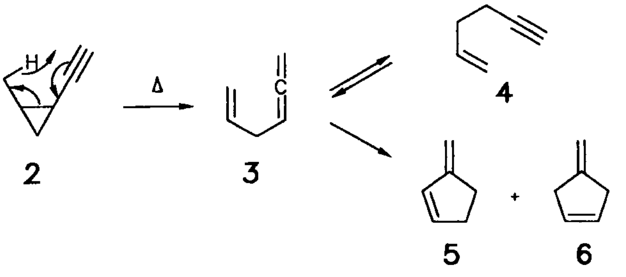
4-Methyl-1,2,5-hexatriene (**13**) has been prepared and subjected to gas-phase pyrolysis. Above 220°C, **13** rearranges reversibly to both *trans*-5-hepten-1-yne (**14**) and its *cis*-isomer **15**. Formation of **14** is faster than that of **15**. These isomerisations are accompanied by a slower irreversible rearrangement to 1-methyl-4-methylene-1-cyclopentene (**16**) and 1-methyl-3-methylene-1-cyclopentene (**17**). Rate constants and Arrhenius parameters have been obtained for all these reactions which were shown to be homogeneous and unimolecular. For the processes **13** ⇄ **14** and **13** ⇄ **15** the data are consistent with [3,3] Cope-type sigmatropic rearrangements. For the process **13** → **16** + **17**, a rate-determining formation of the 1-methyl-3-methylenecyclopentane-2,5-diyl diradical is proposed. The rearrangements form a consistent pattern with other known examples. – The equilibrium data are shown to be in good agreement with thermodynamic estimates based on Group Additivity. The additivity scheme of Benson required extension to provide values for two new group contributions.

Thermal rearrangements of hydrocarbons continue to attract considerable interest[2–4], and many examples of basic, unimolecular pericyclic processes[5] are known[2]. However, most of the well-studied examples of electrocyclic and sigmatropic reactions, requiring π-orbital participation in the underlying bond forming and breaking dynamics, have involved alkene or polyene systems. Rather few examples exist of comparable processes involving the π systems of alkynes or allenes, although there is a steadily increasing interest in such reactions[6,7]. It seems safe to predict that isomerisations of this latter kind will eventually also play a significant role in synthetic organic chemistry.

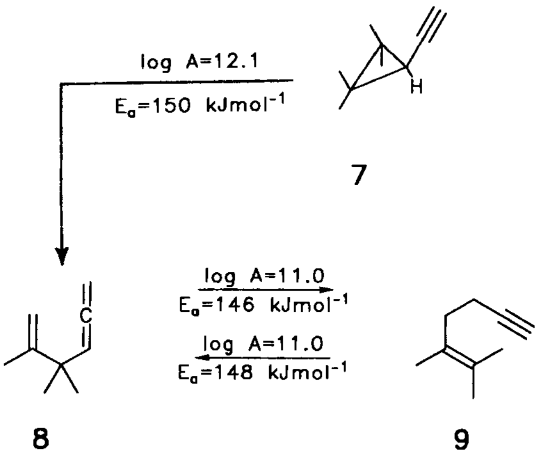
For some time we have been interested in the modification of the cyclopropane ring reactivity caused by introduction of an ethynyl substituent. The parent molecule, ethynylcyclopropane (**1**), which decomposes at temperatures of 600°C (flow system), is thought to rearrange by a mechanism involving ring-bond fission yielding a 1,3-diradical[8]. Although the ultimate products are a mixture of alkenynes and alkatrienes, the mechanism essentially resembles that of the parent cyclopropane itself, as well as its alkenyl derivative, vinylcyclopropane[2].



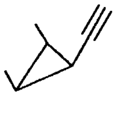
Prior to this, we have discovered an example of a homodienyl-1,5-hydrogen shift process in *cis*-1-ethynyl-2-methylcyclopropane (**2**), the first such example involving an alkyne substrate[9]. In this case ring opening is strongly facilitated by the hydrogen-shift process, and a concerted sigmatropic reaction with a relatively low energy barrier is observed. Once again, the mechanism has its analogue in the *cis*-1-vinyl-2-methylcyclopropane case[10].



In the decomposition of **2** the initial product, 1,2,5-hexatriene (**3**), is itself not stable and undergoes a reversible Cope rearrangement to 1-hexen-5-yne (**4**). There is a further, slower isomerisation to the methylenecyclopentene molecules **5** and **6**, and at higher temperatures aromatisation reactions set in. The kinetics of the processes **3** ⇄ **4** and **3** → **5**, **6** has been studied by Huntsman[11]. A more detailed gas-phase kinetic investigation[1] of the analogous rearrangement of 1-ethynyl-2,2,3,3-tetramethylcyclopropane (**7**) has provided Arrhenius parameters not only for the initial decomposition but also for the subsequent triene-to-enyne isomerisation (**8** ⇄ **9**).



As part of a continuing investigation of these isomerisations, we have recently undertaken a gas-phase study of the 1-ethynyl-2,3-dimethylcyclopropane rearrangement[12]; all possible isomers, viz. *syn*-1-ethynyl-*cis*-2,3-dimethyl- (**10**), *syn*-1-ethynyl-*trans*-2,3-dimethyl- (**11**), and *anti*-1-ethynyl-*cis*-2,3-dimethylcyclopropane (**12**) have been prepared and pyrolysed.


10


11


12

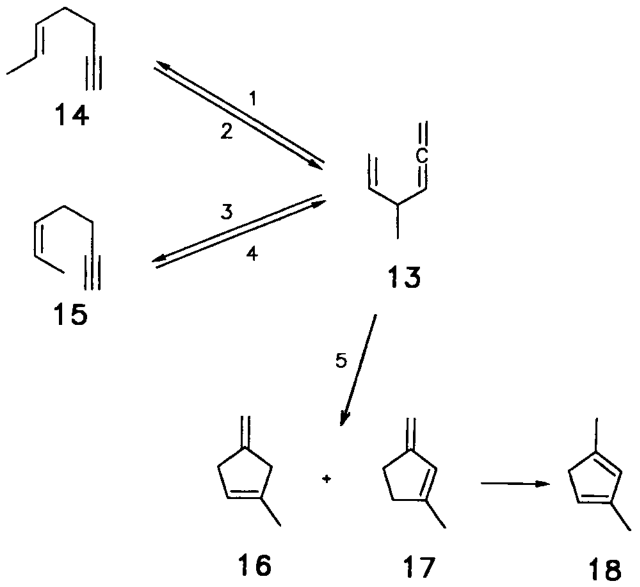
Each of these isomers has been found[12] initially to decompose to 4-methyl-1,2,5-hexatriene (**13**), with other product formation indicative of further isomerisation. The kinetics of rearrangement of a number of methyl-substituted 1,2,5-trienes, as well as those of the parent molecule **3**, has been investigated by Huntsman and coworkers[11]. The kinetics of **13** is not reported in ref.[11], although the involvement of **13** in the reversible acetylenic Cope rearrangements of **14** and **15**[13] is mentioned elsewhere by Huntsman[14,15]. We have decided, therefore, in order to assist our investigation of **10**–**12**, to study independently the gas-phase kinetics of the rearrangement of **13**. This study also offers the opportunity to provide detailed information of methyl-substituent effects on both the kinetics and thermodynamics of the 1,2,5-hexatriene rearrangement pathways. Recently, Owens and Berson[16] have shown by stereochemical labelling experiments that the interconversion **4** → **3** is unlikely to involve the intermediacy of the 1-cyclohexene-1,4-diyl diradical.

Synthesis, Qualitative Pyrolysis Study, and Product Analysis

4-Methyl-1,2,5-hexatriene (**13**) was prepared by known procedures[17,18] by reaction of allenylmagnesium bromide with 1-methylallyl chloride providing a mixture of C_7H_{10} hydrocarbons in 51% overall yield. This mixture was separated and analysed (see Experimental) to consist of **13** (20%), *trans*-1,2,5-heptatriene (51%), *cis*-1,2,5-heptatriene (19%), and *trans*-5-hepten-1-yne (**14**) and *cis*-5-hepten-1-yne (**15**) (combined yield 10%). In view of the rather low yield of the desired **13**, an alternative route was tried, in which *trans*-crotyl chloride was employed instead of 1-methylallyl chloride. The overall yields improved slightly to 55% of which 25% was the desired **13**. No further refinements or improvements of the preparation were pursued, and the hydrocarbon **13** was purified by preparative chromatography.

For the product study a sample of **13** was pyrolysed at 320°C for 20 minutes (evacuated ampoule), and the products were separated by gas chromatography and identified by the usual spectroscopic methods (see Experimental). The observed products were **14**, **15**, 1-methyl-4-methylene-1-cyclopentene (**16**), and 1-methyl-3-methylene-1-cyclopentene (**17**), with small amounts of a further product, 1,3-dimethyl-1,3-cyclopentadiene (**18**), produced at longer pyrolysis times (repeat pyrolysis for 90 minutes at 310°C, Scheme 1).

Scheme 1. The mechanism of the thermal isomerisation of 4-methyl-1,2,5-hexatriene (**13**)



Kinetic Measurements

These were carried out in a similar manner to previous studies[1,19]. Gaseous samples were prepared containing 2.1 ± 0.2% of **13** diluted in nitrogen (initially at 700 Torr). These mixtures were used as the supply for all kinetic runs. No internal standard was employed since our earlier investigation[1] of a similar system had shown complete mass recovery. The most plausible side reaction, viz. allene dimerisation, was made unlikely by use of initial total pressures between 6 and 10 Torr, meaning that the *reactant* partial pressure never exceeded 0.2 Torr. There was certainly no GC evidence for dimer formation or gross mass loss. A complete reactant/product separation was achieved on an OPN column (concerning details see Experimental), and therefore the product distribution could be obtained without difficulty.

The reaction was studied as a function of time and temperature. Initial pressures (see above) were sufficiently high

Table 1. Time dependence of reactant and product percentages in the isomerisation of **13** at 260.0°C

Product	Time/min 5	7	10	15	20	25	30	40	50	65	80
13	87.06	80.78	74.59	62.19	57.97	51.77	44.06	42.90	39.63	36.80	36.54
14	10.53	15.52	20.61	29.25	32.16	36.56	40.78	41.60	42.05	42.33	41.29
15	1.22	2.44	2.51	4.80	5.30	6.25	7.81	7.52	8.97	9.42	9.92
16	1.19	1.66	1.00	1.59	2.12	2.44	3.24	3.61	4.24	5.14	5.81
17			1.29	2.17	2.45	2.98	4.41	4.37	5.10	6.31	6.44

Table 2. Time dependence of reactant and product percentages in the isomerisation of **13** at 290.0°C

Product	Time/min 2	4	10	20	30	40	60	100	140	180
13	70.60	54.26	38.51	31.81	29.80	25.24	21.53	15.15	11.57	7.87
14	22.84	34.16	41.47	38.09	33.34	30.42	25.71	18.55	13.57	10.11
15	3.68	6.26	10.16	12.84	12.93	13.64	11.86	8.51	5.75	3.88
16	1.26	2.42	4.67	7.95	11.13	13.51	18.06	25.39	31.09	35.08
17	1.62	2.90	5.18	9.31	12.80	17.19	22.84	32.40	38.02	43.06

to render unlikely any problems of unimolecular "fall-off"[20]. This reaction system turned out to be susceptible to investigation over an unusually wide temperature range, brought about by the reversible nature of some of the reactions involved. Times ranged from 3 to 310 minutes, conversions of **13** between 13 and 92%, and temperatures from 220 to 330°C. The temperature range could be divided, somewhat arbitrarily, into a low-temperature region (220–270°C) and a high-temperature region (290–330°C). Table 1 gives a typical set of data for the low- (260°C) and Table 2 for the high-temperature region (290°C). These sets of data are shown graphically in Figures 1 and 2, respectively. Similar sets were obtained for all temperatures between 220 and 330°C in 10-degree steps[21].

Examination of the tables and figures suggests the following conclusions: a) At all the temperatures the most rapidly formed product is **14**, and this approaches a maximum concentration in the low-temperature region. b) At all temper-

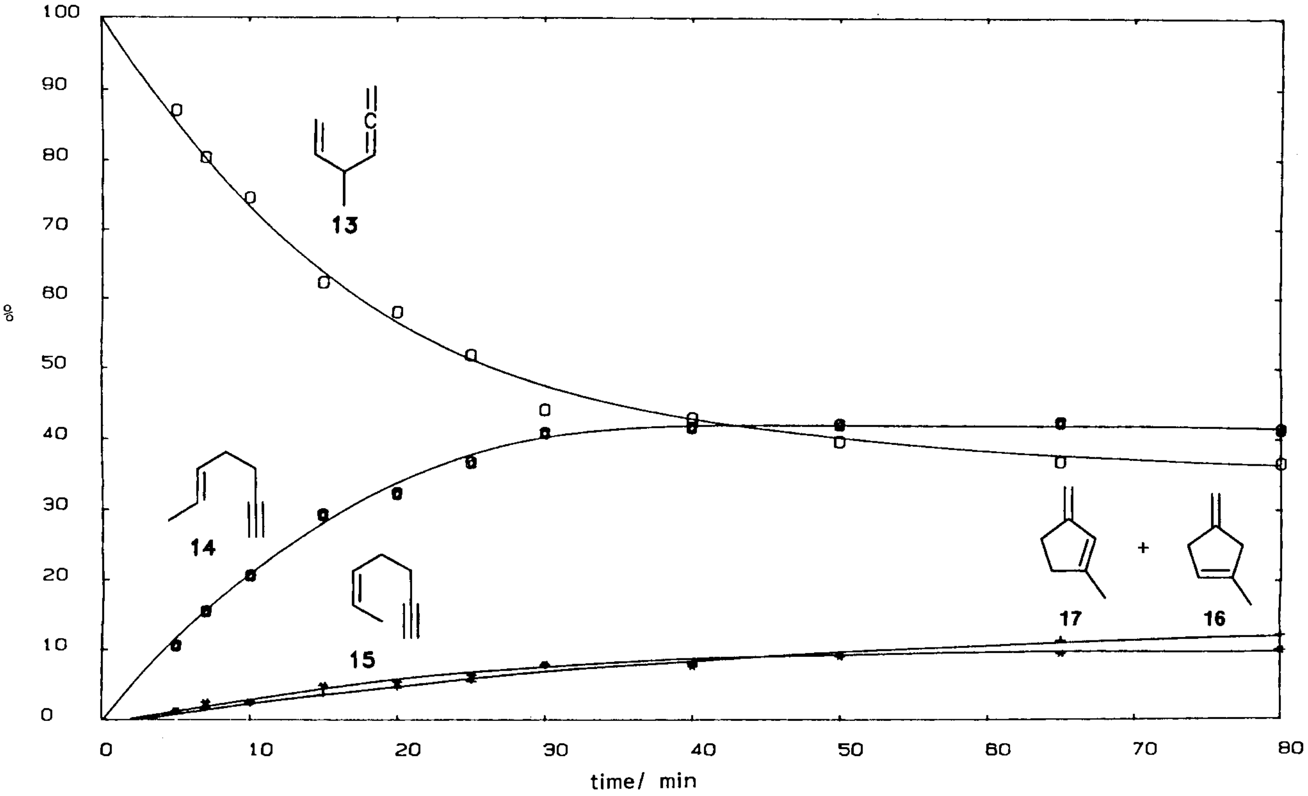


Figure 1. Product percentage time dependence at 260.0°C

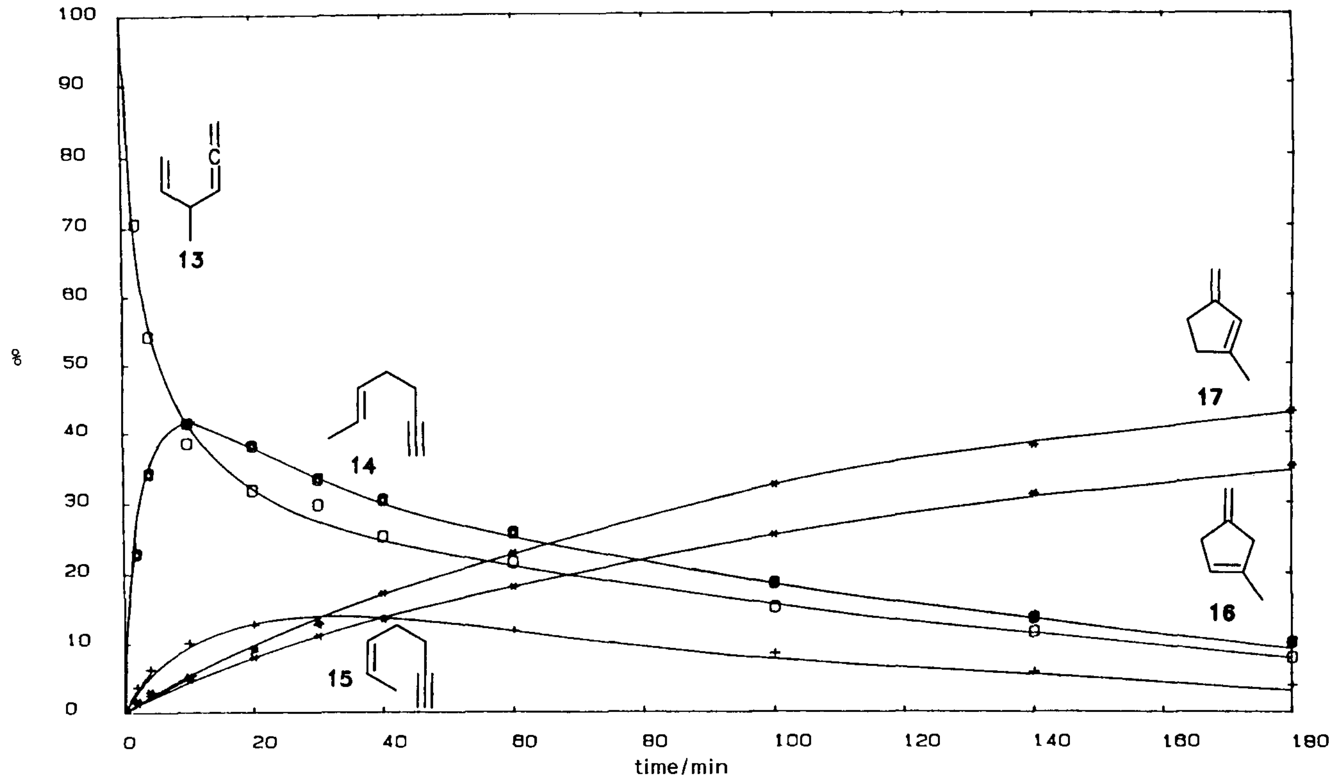


Figure 2. Product percentage time dependence at 290.0°C

atures **15** is also formed, much slower than **14**, but it also eventually reaches a maximum concentration at longer times (and higher temperatures) than **14**. c) The end products are **16** and **17**, but these are only produced at a significant rate at higher temperatures. These conclusions lead logically to the mechanism shown in Scheme 1, which is entirely consistent with expectations based on Huntsman's studies[11], i.e. the relatively facile and reversible [3,3] sigmatropic Cope-type rearrangements to 1-en-5-yne products and the slower irreversible cyclisation to 3- and 4-methylene-1-cyclopentenes. Further support for this comes from the high-temperature steady-state product ratios[21]. Table 3 gives some values of the ratios [**14**]/[**13**], [**15**]/[**13**], and [**17**]/[**16**] obtained at 330°C. As can be seen these ratios, corresponding to conversion of **13** between 70 and 92%, appear to remain constant, within a smaller scatter. This leads us to conclude that the reactions **13** ⇄ **14** and **13** ⇄ **15** have reached a steady state and are essentially at equilibrium. The ratio [**17**]/[**16**] is simply a product ratio reflecting parallel pathways of formation, **13** → **16** and **13** → **17**. This latter ratio is time invariant over the whole course of the reaction (from data at lower temperatures). It is also practically temperature independent.

Table 3. Some product ratios in the pyrolysis of **13** at 330°C

Ratio	Time/min					
	3	6	9	12	16	20
[**14**]/[**13**]	1.194	1.103	1.204	1.191	1.219	1.205
[**15**]/[**13**]	0.430	0.520	0.578	0.546	0.562	0.499
[**17**]/[**16**]	1.239	1.151	1.229	1.226	1.255	1.201

In order to exploit our measurements to the maximum extent, we have carried out a kinetic modelling exercise based on the scheme, and applied it to the analytical data at each temperature. The calculations are based on a variable-step integration program, employing the Gear algorithm[22]. In practice the program requires an initial set of estimates for the rate constants of the scheme. The program then calculates the species concentrations at specified times, which may be compared with the observed data. After successive adjustments of the rate constants, the calculations are repeated until the best fit to experiment is obtained (as judged by the minimum sum of squares of all deviations). In practice, with five adjustable rate constants this is a delicate operation since the data at different times and temperatures are not equally sensitive to each rate constant. Therefore, some constraints were applied. At each temperature the ratios k_1/k_2 ($= K_{1,2}$) and k_3/k_4 ($= K_{3,4}$) were kept fixed until k_1, k_3 and k_5 had been optimally adjusted. The values initially chosen for these ratios were obtained from the average steady-state values of [**14**]/[**13**] and [**15**]/[**13**] in the temperature range 290 to 330°C (data such as those of Table 3). For the lower temperature range where steady-state concentrations were not reached, extrapolation of the rate constant ratios was made by use of van't Hoff plots (see below). By this procedure we ensured that the most important rate constants, i.e. those to which the product distribution was most sensitive, could be adjusted quickly without introducing unreasonable values for rate constants to which the distribution was less sensitive. Although the final judgement of the best fit was based on the minimisation of total deviations, care was also taken to ensure that deviations for minor products were optimised in proportion to their quantities. For example, products **16** and **17** were minor at low temperatures, and the total fit was not especially sensitive to k_5, and thus this rate constant was adjusted separately to give the best fit for **16** and **17**. Optimisation of the complete fitting procedure could be achieved, with experience, after relatively few steps (10–20) but in practice to ensure that no remaining serious errors were present usually 25–30 steps were carried out for each data set (6–11 different times). From this procedure values for the rate constants were obtained at each temperature, and Table 4 summarizes these data.

Table 4. Rate constants obtained by modelling the analytical data to Scheme 1

T/°C	$10^5\ k$/s^{-1} k_1	k_2	k_3	k_4	k_5
220.0	3.45	2.43	0.440	0.889	0.291[a]
230.0	6.90	4.95	0.899	1.79	0.636[a]
240.0	13.3	9.75	1.70	3.36	1.28[a]
250.0	24.9	18.7	3.63	7.10	2.63[a]
260.0	45.0	34.4	6.35	12.3	4.90[a]
270.0	81.0	63.0	12.1	23.3	8.85[a]
290.0	337[a,b]	293[a,b]	50.5[a,b]	110[a,b]	36.8
300.0	603[a,b]	518[a,b]	90.4[a,b]	188[a,b]	65.9
310.0	979[a,b]	890[a,b]	147[a,b]	317[a,b]	107
320.0	1690[a,b]	1490[a,b]	253[a,b]	527[a,b]	185
330.0	2880[a,b]	2550[a,b]	431[a,b]	912[a,b]	314

[a] Not used in the determination of Arrhenius parameters: see text. – [b] Only used to determine equilibrium constants, viz. either k_1/k_2 or k_3/k_4.

It is hard to estimate the uncertainties in these rate constants since in the fitting procedure they are mutually dependent, i.e. correlated to some extent. It is tempting to give them equal weight for the purpose of determining Arrhenius parameters. However, one other test was made to see whether a variation of rate constants, two at a time, could affect the fit. For instance, at 310.0°C, values of $k_1 = 866 \times 10^{-5}$, $k_2 = 793 \times 10^{-5}$, $k_3 = 130 \times 10^{-5}$, $k_4 = 283 \times 10^{-5}$, and $k_5 = 107 \times 10^{-5}$ (all in s^{-1}) produced an almost equally good fit as those shown in Table 4. This is because the fit is largely intensitive *in this temperature range* to the approach to equilibrium of **13** ⇄ **14** and **13** ⇄ **15**. The important parameters, apart from k_5, are the rate constant ratios k_1/k_2 and k_3/k_4, respectively. Thus, for the purpose of computing Arrhenius parameters only the more precisely determined rate constant values were used. This meant that only limited subsets of the rate constants of Table 4 could be employed. For reactions 1 to 4 (Scheme 1) only the lower-temperature and for step 5 only the higher-temperature rate constants were employed. However, for *equilibrium constants* higher-temperature ratios (k_1/k_2 and k_3/k_4) were used. The designated rate constants were fitted by least-squares analysis *to the Arrhenius equation*, and the resulting activation parameters are collected in Table 5.

Table 5. Arrhenius parameters for the isomerisation reactions of **13**, **14**, and **15**

Reaction	log(A/s^{-1})	E_a/kJ mol^{-1} (kcal mol^{-1})
13 → **14**	10.40 ± 0.04	140.3 ± 0.4 (33.5 ± 0.1)
14 → **13**	10.72 ± 0.04	144.8 ± 0.4 (34.6 ± 0.1)
13 → **15**	10.29 ± 0.20	148 ± 2 (35.3 ± 0.5)
15 → **13**	10.36 ± 0.20	145 ± 2 (34.8 ± 0.5)
13 → **16** + **17**	10.50 ± 0.21	150 ± 2 (35.9 ± 0.6)

Table 6. Thermodynamic quantities for the reversible isomerisation reactions of **13**

Reaction	ΔH^0 [kJ mol^{-1} (kcal mol^{-1})]	ΔS^0 [J K^{-1} mol^{-1} (cal K^{-1} mol^{-1})]
13 ⇄ **14**	−2.0 ± 2.5 (−0.5 ± 0.6)	−2.3 ± 4.3 (−0.6 ± 1.0)
13 ⇄ **15**	+1.9 ± 3.1 (+0.5 ± 0.8)	−3.1 ± 5.4 (−0.7 ± 1.3)

The error limits shown (single standard deviations) probably underestimate the true uncertainties. If all the rate constants shown in Table 4 were used for Arrhenius parameter determinations this would raise the A factor by between $10^{0.45}$ and $10^{1.65}$ s^{-1} and the activation energies by between 8 and 14 kJ/mol[21]. However, for the reasons given, we feel this is unreasonable. The realistic uncertainties are probably 2–3 times those of the standard deviations cited with an error likely to be the greatest in the reverse processes 2 and 4 and the least in the processes 1, 3, and 5.

In addition to Arrhenius parameter determination the specified rate constant ratios were used as equilibrium constants to evaluate thermodynamic quantities with the help of van't Hoff plots. These are shown in Table 6. The uncertainties are again hard to assess, although it should be noted that since the reactions approach close to equilibrium (see steady-state ratios of Table 3) errors should not be too serious. Nevertheless, using the parameters of Table 6 the rate constant ratios, k_1/k_2 and k_3/k_4 are underestimated in the lower temperature range (220–270°C) by between 10 and 20% compared with those obtained from Table 5[21]. There appears to be a small residual unassessed source of error.

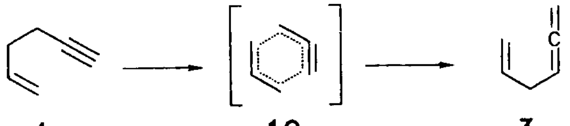
In addition to the measurements, one further test was carried out. A brief study of the reaction was made in a vessel packed with pyrex tubes (surface/volume ca. 13 cm^{-1}) and conditioned with hexamethyldisilazane (HMDS). The reaction was studied at six different times, at both 250.0 and 310.0°C[21]. When compared with the unpacked vessel the results at the lower temperature were very similar, e.g. at a time of 50 min: **13**, 50% (48.8% in the unpacked vessel); **14**, 36.3% (38.9% in the unpacked vessel). Other products were also similar although there was ca. 4% of a new and unidentified product. At 310°C yields for most products were again very similar in both vessels, except for **17**, which was significantly less in the packed vessel, e.g. 4.9% (after 50 min) and 39.8% in the empty reaction flask. The deficit in **17** appeared to be almost entirely made up of two other products, one identified as **18** (26.0% at 50 min) and the other, not identified as yet, but probably another isomeric dimethylcyclopentadiene (10.3% at 50 min). It thus appears that transformation of **17** to these products is selectively catalyzed in the packed vessel (although **16** remains unaffected). Catalytic conversion of **17** on metal surfaces was also noted in our study of **10, 11,** and **12**[12]. Apart from this problem in the packed vessel there appears to be no evidence to suggest any serious heterogeneous contribution to the reactions studied in the unpacked vessel.

Discussion

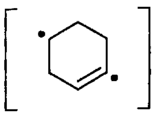
The consistency of the product time evolution studies carried out here with the mechanism presented above is fully in accord with the work of Huntsman on related systems[11]. The mechanism does not require, and would be inconsistent with, direct pathways for **15** → **14** or from **14** or **15** to **16** and **17**. Thus, direct *cis/trans*-isomerisation does not occur, nor does conversion of the enynes into the methylenecyclopentenes. The principal parts of the discussion are therefore the kinetic and equilibrium data obtained in this study. For convenience, the discussion is divided into three parts.

1) *Kinetics of the Reversible [3,3] Sigmatropic Cope-Type Rearrangements:* The kinetic data obtained in the present study are compared with selected data of Huntsman and our own earlier work[1] in Table 7. For ease of comparison, only Arrhenius parameters for the enyne → alkatriene process are presented. However, from published equilibrium constants[11] a comparison is also possible for the absolute rate constants in both forward and reverse directions at 500 K.

The general magnitude of the measured Arrhenius parameters obtained in the present work is consistent with those of earlier studies (both in Table 7 and elsewhere[11]). More stringent tests may, however, be applied. The basic process (**4** → **3**), now thought to be fully concerted[16], is represented with its transition state **19** in the following diagram. A minimum entropy estimate for this transition state may be obtained if it is assumed to possess the tighest possible structure. This should correspond to the cyclohexene-1,4-diyl diradical (**20**).



4 19 3



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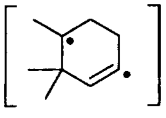

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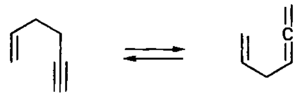
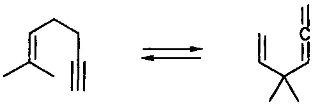
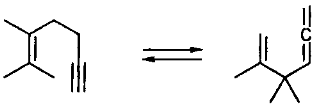
Table 7. Rate data for some reversible alkenyne-to-alkatriene isomerisations

Reaction	$\log(A/s^{-1})$	E_a /kJ mol^{-1}	K_{eq} (500K)	k_f / 10^{-4} s^{-1} [a]	k_r / 10^{-4} s^{-1} [a]	Ref.
 4 3	10.49	137	2.73	1.57 (1)	0.58 (1)	11
 14 13	10.72	145	0.71[b]	0.40 (0.25)	0.56 (0.97)	this work
 15 13	10.36	146	2.02[b]	0.14 (0.090)	0.070 (0.12)	this work
 23 22	10.25	148	0.14	0.060 (0.038)	0.43 (0.74)	11
 9 8	11.00	148	0.47	0.37 (0.24)	0.79 (1.36)	1

[a] Rate constants at 500 K; k_f and k_r are forward and reverse rate constants, resp. Figures in parentheses are relative values. — [b] Equilibrium constants from ratios of rate constants (220–270 °C).

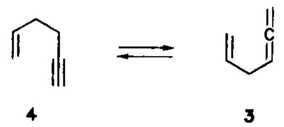
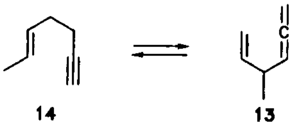
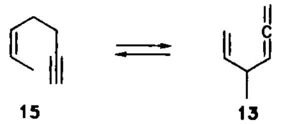
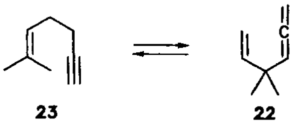
Entropy estimates for **20** and **4** are shown in the Appendix from which it is estimated by transition-state theory that a *minimum* A factor for the rearrangement **4** → **3** is ca. $10^{11.0}$ s^{-1}. Thus, it appears that some of the measured A factors in Table 7 may be slightly too low. With respect to the present work it was pointed out that realistic uncertainties were likely to be rather greater than those shown in Table 5. It should be added that from Owen and Berson's work[16] the diradical **20** is not thought to be involved and the transition state **19** *should* have a slightly looser structure then that of **20**. It is, however, also possible to make an independent judgement about the involvement of **20** by an estimate of the energy for the process **4** → **20**, details of which are also shown in the Appendix. The value of 155 kJ mol^{-1} contains uncertainties arising from radical heats of formation probably amounting to ca. ± 12 kJ mol^{-1}. It is apparent that the energy requirement for a diradical intermediate is not much greater than the observed activation energy. Thus, although the kinetic data are consistent with a concerted process[16], it is possible that with certain substituents the non-concerted process could become competitive.

The scatter in the Arrhenius parameters makes it difficult to pick out trends in the reactions of Table 7. However, from the absolute rate constants certain effects can be discerned. The reverse processes (i.e. alkatriene to alkenyne) show only small variations (provided the conversion of **13** into **14** and **15** is taken as a joint process proceeding via a common transition state). This reflects the fact that there are no methyl substituents at the positions of ring closure of the terminal vinyl and allenyl groups. In the forward direction (conversion of alkenyne to alkatriene) variations are larger. Methyl substitution at the terminal vinyl group alone substantially and consistently lowers the rate constant, viz. k_f(**23**) < k_f(**14**) < k_f(**4**). This is undoubtedly caused by steric interference at the point of ring closure of the terminal vinyl and ethynyl groups. However, k_f(**9**) is by a factor of ca. 6 larger than k_f(**23**). This is hard to understand on the basis of a concerted process alone, since the extra methyl group is in a non-interfering position. If, however, the process occurred via diradical **21**, then an extra stabilization of ca. 12 kJ mol^{-1} would be present in **21** – compared with **20** – because of the tertiary radical centre. This would make the involvement if **21** competitive and explain the high value for k_f(**9**).

Other methyl-substituted derivatives of **4**[11] show a pattern of variation of rate constants consistent with steric hindrance to bond formation or inductive weakening to bond breaking. The magnitude of these effects appears in accordance with concerted reactions in all cases[23].

2) *Equilibrium Between 1-Alken-5-ynes and 1,2,5-Alkatrienes:* These reversible reactions provide good examples with which to test the predictions of additivity rules such as

Table 8. Equilibrium data for some reversible alkenyne-to-alkatriene isomerisations

Reaction	ΔH° / kJ mol^{-1}	ΔS° / JK^{-1} mol^{-1}	ΔG° / kJ mol^{-1} a)	K_{eq} (calc)a)	K_{eq} (obs)a)	Ref.
 **4** **3**	-1.0	+2.6	-2.3	1.73	2.73	11
 **14** **13**	+1.8	+0.6	+1.5	0.70	0.82b)	this work
 **15** **13**	-2.4	+0.6	-2.7	1.92	2.27b)	this work
 **23** **22**	-0.8	-15.1	+6.8	0.20	0.14	11
 **9** **8**	-7.0	-15.1	+0.5	0.89	0.47	1

[a] Equilibrium constants and Gibbs energy changes at 500 K. – [b] Preferred values from high-temperature range (290–330 °C), calculated from Table 6.

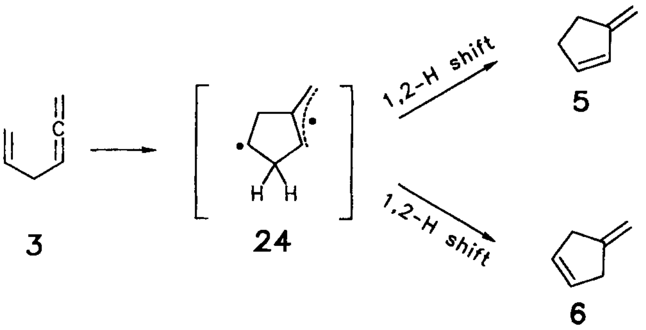
those of Benson and coworkers[24,25]. Enthalpies of formation and entropies have been calculated for each of the compounds participating in the reactions of Table 7. These quantities are tabulated in the Appendix. The derived standard enthalpy and entropy changes are compiled in Table 8, together with Gibbs energy changes and calculated equilibrium constants at 500 K. It should be noted that $-\Delta H^0$ and ΔS^0 were not corrected from 298 to 500 K, since the correction was found to be negligible for the reaction **4** → **3**.

A comparison of K_{eq} values shows that experiment is in good agreement with prediction, no case being worse then a factor of 2 in error, despite variations in K_{eq} of nearly an order of magnitude. In fact, the agreement[23] extends to other cases[11], where variations of K_{eq} cover a factor of 600. The factor of 2, corresponding to ± 2.9 kJ mol^{-1} for ΔG^0 is well within the stated uncertainties of the additivity rules[24,25]. It should also be noted that it was necessary to derive new values for two groups during this exercise (see Appendix).

As with the absolute values for K_{eq} (500 K), comparison can be made of the estimated ΔH^0 and ΔS^0 values for reactions **13** → **14** and **13** → **15** with those measured (Table 6). The agreement is reasonable and well within the claimed error limits. The equilibria of Table 8 and from other sources[11] thus provide a good verification and check on the basic reliability of hydrocarbon thermodynamic additivity schemes.

3) *Kinetics of the Irreversible Alkatriene Isomerisations to Dihydrofulvenes:* The kinetic data obtained in the present study are compared with selected data of Huntsman in Table 9. The general magnitude of the measured Arrhenius parameters obtained in this work is consistent with those obtained earlier (both in Table 9 and elsewhere[11]).

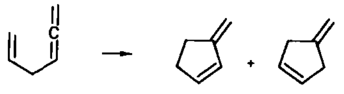
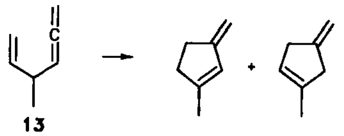
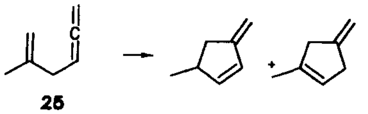
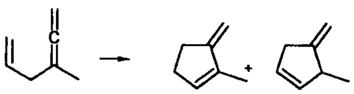
Scheme 2



Once again the *A* factors may be examined in the light of transition-state theoretical expectations. The basic process is thought to proceed via diradical **24** as shown in Scheme 2.

Diradical formation has been proposed to be rate-determining[11], rather than the second step, the 1,2-hydrogen shift process. The energy required to reach the diradical is ca. 84 kJ mol^{-1} (see Appendix), which is only just over half of the observed activation energy. This must indicate a transition-state structure with a fairly tight steric requirement imposed on the approach from the reactant. The geometry must resemble the diradical itself with perhaps its *exo*-methylene group not yet twisted to take advantage of the allylic stabilisation. Once again a minimum *A* factor may be estimated by a minimum entropy calculation. We have used the product **5** as a model structure in this case because

Table 9. Rate data for selected 1,2,5-alkatriene cyclisation reactions

Reaction	log (A/s^{-1})	E_a /kJ mol^{-1}	3-MCP / 4-MCP [a]	k / 10^{-4} s^{-1} [b]	Ref.
 **3**	10.85	156	1.27	1.17 (1)	11
 **13**	10.50	150	1.22	1.70 (1.45)	this work
 **25**	10.71	155	1.30	1.02 (0.87)	11
 **26**	10.60	157	1.28	0.46 (0.39)	11

[a] 3-MCP = 3-methylene-1-cyclopentene; 4-MCP = 4-methylene-1-cyclopentene. — [b] Rate constants at 550 K. Figures in parentheses are relative values.

it appears to represent the tightest possible structure. Entropy estimates for **3** and **5** are shown in the Appendix from which it is estimated that the minimum value for A is ca. $10^{10.3}$ s^{-1}. Thus the measured A factors of Table 9 seem just about reasonable.

The similarities of Arrhenius parameters make trends in the reactions of Table 9 hard to discern. From the absolute rate constants it can be seen that there is very little rate variation with methyl substitution. Potential stabilisation of the diradical by the methyl groups in reactions of **25** and **26** leads to rate retardations relative to **3**, while the methyl substituent in **13** enhances the rate yet substitutes a "neutral" position in the diradical intermediate. Small steric factors probably determine these rate effects. A larger rate retardation does result[11] when methyl groups substitute the vinyl group (position of ring closure) as expected. A more extensive discussion of substituent effects in these and other examples can be found in Huntsman's review[11]. It is remarkable how little variation there is in the product ratios. The 1,2-H shift processes leading to them are highly exothermic. This leads to early transitions states which therefore show only a marginal preference for the more stable, conjugated product isomer. 1,2-H shift reactions in sterically constrained or partially stabilised diradicals can sometimes be quite slow[26], but in the case of **24** there are no realistic alternatives.

An enthalpy surface which encompasses all the rearrangements observed in this study is shown in Figure 3.

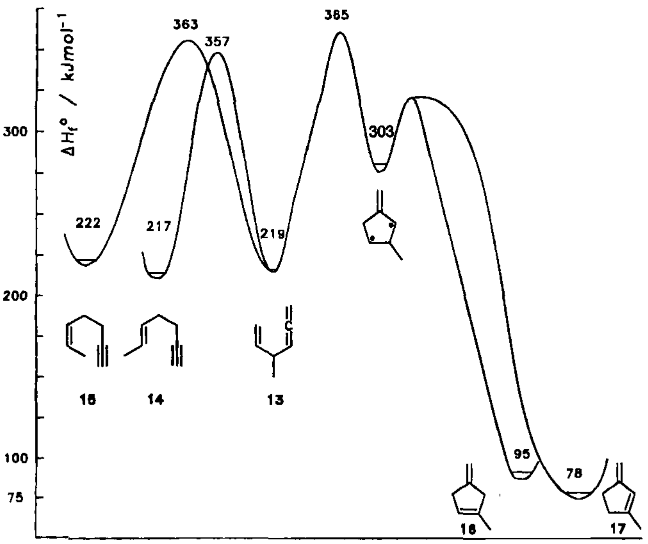


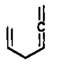
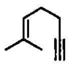
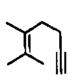
Figure 3. Enthalpy surface for the isomerisation reactions of **13**

Appendix

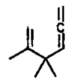
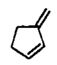
Thermodynamic estimates of stable molecules are obtained by using the group additivity method of Benson[24,25]. Minimum A factor estimates are derived from entropies of activation based on assumed activated complex structures corresponding to the stiffest imaginable transition state. Diradical enthalpies of formation are obtained from combining enthalpies of formation of a reference molecule with C–H dissociation energies. These latter were taken from the review by Macmillen and Golden[27], updated where necessary for recent remeasurement[28].

For ease of manipulation data are calculated in units of calories (entropies are given in cal K^{-1} mol^{-1}, enthalpies of formation in kcal mol^{-1}) and only converted to joules in the results and discussion sections.

(i) *Additivity estimates for ΔH_f^0 and S^0*

Compound	Groups	ΔH_f^0	S^0
 **4**	$C_d-(H)_2$	6.26	27.61
	$C_d-(C)(H)$	8.59	7.97
	$C-(C_d)(C)(H)_2$	−4.76	9.80
	$C-(C_t)(C)(H)_2$	−4.73	10.30
	$C_t-(C)$	27.55	6.35
	$C_t-(H)$	26.93	24.70
		59.84	86.73
 **3**	$2\ C_d-(H)_2$	2 × 6.26	2 × 27.61
	$2\ C_d-(C)(H)$	2 × 8.59	2 × 7.97
	$C-(C_d)_2(H)_2$	−4.29	10.20
	C_a	34.20	6.00
		59.61	87.36
 **14**	$C-(C_d)(H)_3$	−10.20	30.41
	$2\ C_d-(C)(H)$	2 × 8.59	2 × 7.97
	$C-(C_d)(C)(H)_2$	−4.76	9.80
	$C-(C_t)(C)(H)_2$	−4.73	10.30
	$C_t-(C)$	27.55	6.35
	$C_t-(H)$	26.93	24.70
	symmetry (= 3)		−2.18
		51.97	95.32
 **15**	As for compound **14** but with *cis*-correction:		
	14	51.97	95.32
	cis	1.00	
		52.97	95.32
 **13**	$2\ C_d-(H)_2$	2 × 6.26	2 × 27.61
	$2\ C_d-(C)(H)$	2 × 8.59	2 × 7.97
	$C-(C_d)_2(C)(H)$[a]	−1.31	−11.31
	C_a	34.20	6.00
	$C-(C)(H)_3$	−10.20	30.41
	symmetry (= 3)		−2.18
	chiral centre (1/2)		1.38
		52.39	95.46
 **23**	$2\ C-(C_d)(H)_3$	2 × −10.20	2 × 30.41
	$C_d-(C)_2$	10.34	−12.70
	$C_d-(C)(H)$	8.59	7.97
	$C-(C_d)(C)(H)_2$	−4.76	9.80
	$C-(C_t)(C)(H)_2$	−4.73	10.30
	$C_t-(C)$	27.55	6.35
	$C_t-(H)$	26.93	24.70
	symmetry (3^2)		2 × −2.18
	cis-correction	1.00	
		44.52	102.88
 **22**	$2\ C_d-(H)_2$	2 × 6.26	2 × 27.61
	$2\ C_d-(C)(H)$	2 × 8.59	2 × 7.97
	$C-(C_d)_2(C)_2$[b]	0.84	−34.34
	C_a	34.20	6.00
	$2\ C-(C)(H)_3$	2 × −10.20	2 × 30.41
	symmetry (3^2)		2 × −2.18
		44.34	99.28
 **9**	$3\ C-(C_d)(H)_3$	3 × −10.20	3 × 30.41
	$2\ C_d-(C)_2$	2 × 10.34	2 × −12.70
	$C-(C_d)(C)(H)_2$	−4.76	9.80
	$C-(C_t)(C)(H)_2$	−4.73	10.30
	$C_t-(C)$	27.55	6.35
	$C_t-(H)$	26.93	24.70
	symmetry (3^3)		3 × −2.18
	di-*cis*-correction	3.00	
		38.07	110.44

(i) *Additivity estimates for ΔH_f^0 and S^0* (Continued)

Compound	Groups	ΔH_f^0	S^0
 **8**	2 $C_d-(H)_2$	2 × 6.26	2 × 27.61
	$C_d-(C)(H)$	8.59	7.97
	$C_d-(C)_2$	10.34	−12.70
	$C-(C_d)_2(C)_2$[b]	0.84	−34.34
	C_a	34.20	6.00
	3 $C-(C_d)(H)_3$	3 × −10.20	3 × 30.41
	symmetry (3^3)		3 × −2.18
	gauche	0.50	
		36.39	106.84
 **5**	$C_d-(H)_2$	6.26	27.61
	$C_d-(C_d)(C)$	8.88	−14.60
	$C_d-(C_d)(H)$	6.78	6.38
	$C_d-(C)(H)$	8.59	7.97
	2 $C-(C_d)(C)(H)_2$	2 × −4.76	2 × 9.80
	ring strain	6.00	25.80
		26.99	72.76

[a] Group values derived from $C-(C_d)_2(C)(H) = C-(C_d)(C)_2(H) + [C-(C_d)(C)(H)_2 - C-(C)_2(H)_2]$. – [b] Group values derived from $C-(C_d)_2(C)_2 = C-(C)_4 + 2\,[C-(C_d)(C)(H)_2 - C-(C)_2(H)_2]$.

(ii) *Estimates for the Process* **4** → **3**

The transition state is assumed to resemble **20**. Quantities obtained by adjustment from those of cyclohexene (Cy)[25]:

a) S^0(Cy) = 74.43 (300 K); loss of symmetry (1.38) and six vibration frequencies (0.20) give S^0(**20**) = 75.61 (**20** is assumed to be in its singlet state).

$$\Delta S^{+} \geq S^0(\mathbf{20}) - S^0(\mathbf{4}) = 75.61 - 86.73 = -11.12$$

$$A \geq \frac{ekT}{h} e^{\Delta S^{+}/R} = \underline{\underline{10^{11.02}\ \mathrm{s^{-1}}}}\ (500\ \mathrm{K})$$

(ΔS^{+} is assumed to be independent of temperature)

b) ΔH_f^0(Cy) = −0.84 (300 K); splitting of secondary C−H bond (97) and vinylic C−H bond (105) gives

$$\Delta H_f^0(\mathbf{20}) = -0.84 + 97 + 105 - 2 \times 52 = 97$$

$$\Delta H^0(\mathbf{4} \rightarrow \mathbf{20}) = \Delta H_f^0(\mathbf{20}) - \Delta H_f^0(\mathbf{4}) = 97 - 59.8 = \underline{\underline{37}}$$

(ΔH^0 is assumed to be independent of temperature)

(iii) *Estimates for the Process* **3** → **5**

The transition state is assumed to lie between **3** and **24** (Scheme 2):

a) The entropy of the transition state is assumed to be similar to that for **5**.

$$\Delta S^{+} \geq S^0(\mathbf{5}) - S^0(\mathbf{3}) = 72.76 - 87.36 = -14.6$$

$$A \geq \frac{ekT}{h} e^{\Delta S^{+}/R} = \underline{\underline{10^{10.26}\ \mathrm{s^{-1}}}}\ (500\ \mathrm{K})$$

(ΔS^{+} is assumed to be independent of temperature)

b) Diradical **24** is derived from methylenecyclopentane (MC): ΔH_f^0(MC) = 3.5 (300 K); cleavage of two ring secondary C−H bonds with one allylic stabilisation gives

$$\Delta H_f^0(\mathbf{24}) = 3.5 + 2 \times 96 - 12 - 2 \times 52 = 79.5$$

$$\Delta H^0(\mathbf{3} \rightarrow \mathbf{24}) = 79.5 - 59.6 = \underline{\underline{19.9}}$$

(ΔH^0 is assumed to be independent of temperature)

We thank the *Fonds der Chemischen Industrie* as well as the *Land Niedersachsen* (graduate stipend for G. W.) for the support of our work and the *BASF Aktiengesellschaft* for the generous gift of chemicals.

Experimental

^{1}H-NMR: Bruker AM 300 (300 MHz), Bruker WM 400 (400 MHz), in $CDCl_3$, if not stated otherwise with TMS (δ = 0) as internal standard. – ^{13}C-NMR: Bruker AM 300 (75.5 MHz), in $CDCl_3$ which also served as int. standard ($\delta^{13}C$ = 77.05). – IR: Perkin-Elmer 1420. – GC/MS: Carlo-Erba HRGC 5160 (15-m quartz capillary column, SE-30)/MS 30. – GC: analytical: Dani, model 3800 (15-m quartz capillary column, SPB 1); preparative: Varian 920 and Intersmat IGC 131 M, columns: see below.

4-Methyl-1,2,5-hexatriene (**13**) was prepared according to well-established literature procedures[17,18] by the cuprous chloride-catalyzed Grignard coupling of allenylmagnesium bromide with a) 1-methylallyl chloride and b) *trans*-crotyl chloride. The yields of the hydrocarbon mixtures obtained after distillative workup were 51% in the case of a) and 55% for b). As shown by analytical GC and the following spectroscopic data the product mixtures consisted of **13** (a: 20.6, b: 25%), *trans*-1,2,5-heptatriene (a: 51, b: 43%), *cis*-1,2,5-heptatriene (a: 19, b: 8%) as well as *trans*- (**14**) and *cis*-5-hepten-1-yne (**15**) (combined yield a: 9.5, b: 24%). The mixture was purified by preparative GC (2 m 25% OPN on Chromosorb W, 30°C) to give analytically pure samples of **13** and of *trans*- and *cis*-1,2,4-heptatriene as colourless liquids which rapidly polymerized on standing in the presence of air.

Fraction I: **13**. IR (CCl_4): $\tilde{\nu}$ = 3085 cm^{-1} (w), 2975 (s), 2930 (m), 2875 (m), 1958 (s), 1640 (m), 1455 (m), 1375 (w), 992 (m), 917 (vs), 870 (m), 848 (vs). – ^{1}H NMR (300 MHz): δ = 1.17 (d, J = 6.9 Hz, 3H, CH_3), 2.86 (m, 1H, −CH), 4.73 (dd, J_1 = 3.1, J_2 = 6.6 Hz, 1H, −CH=C=), 4.95−5.12 ("dt", J_1 = 10.2, J_2 = 17.2, J_3 = 1.5 Hz, 2H, $=CH_2$), 5.15 (dd, J_1 = 6.5, J_2 = 3.1 Hz, 2H, $=C=CH_2$), 5.75−5.86 (ddd, J_1 = 10.2, J_2 = 17.2, J_3 = 3.3 Hz, 1H, −CH=). – ^{13}C-NMR: δ = 19.8 (CH_3), 36.6 (C-4), 75.9 (C-1), 94.6 (C-3), 112.9 (C-6), 142.6 (C-5), 207.8 (C-2). – MS (70 eV): m/z (%) = 94 (0.5), 93 (8) [M^+], 91 (11), 79 (100), 77 (57), 65 (9), 55 (45), 53 (10), 41 (16).

Fraction II: trans-1,2,5-Heptatriene. IR (CCl_4): $\tilde{\nu}$ = 3025 cm^{-1} (m), 2990 (m), 2970 (m), 2940 (m), 2920 (s), 1957 (s), 1452 (m), 1440 (m), 1378 (w), 968 (vs), 846 (vs). – ^{1}H NMR (300 MHz): δ = 1.66 (m, J = 6.9 Hz, 3H, CH_3), 2.68 (m, 2H, $-CH_2-$), 4.66 (dt, J_1 = 3.1, J_2 = 6.8 Hz, 2H, $=C=CH_2$), 5.09 (tt, J_1 = 6.8, J_2 = 7.8 Hz, 1H, −CH=C=), 5.47 (m, J_{trans} = 15.0 Hz, 2H, −CH=CH−). – ^{13}C NMR (75.5 MHz): δ = 17.7 (CH_3), 31.6 (C-4), 74.7 (C-1), 89.0 (C-3), 125.9 (C-6), 128.9 (C-5), 208.8 (C-2). – MS (70 eV): m/z (%) = 94 (1), 93 (12) [M^+], 79 (100), 77 (18), 65 (6), 55 (89), 53 (16), 41 (5).

Fraction III: cis-1,2,5-Heptatriene. IR (CCl_4): $\tilde{\nu}$ = 3028 cm^{-1} (m), 2990 (m), 1960 (s), 1795 (w), 1445 (m), 1405 (w), 1375 (w), 1100 (m), 855 (vs). – ^{1}H NMR (300 MHz): δ = 1.60 (m, J = 5.0 Hz, 3H, CH_3), 2.72 (m, 2H, $-CH_2-$), 4.67 (dt, J_1 = 3.0, J_2 = 6.4 Hz, 2H, $=C=CH_2$), 5.11 (tt, J_1 = 6.4, J_2 = 7.5 Hz, 1H, −CH=C=), 5.45 (m, 2H, −CH=CH−). – MS (70 eV): m/z (%) = 94 (1), 93 (11) [M^+], 91 (9), 79 (100), 77 (20), 65 (6), 55 (94), 53 (21), 51 (14), 44 (20).

Pyrolysis of **13**: For product identification, samples of **13** were pyrolysed, and the products separated by GC. Typically, a sample of 0.30 g (3.2 mmol) of **13** was admitted to a 400-ml ampoule and the latter sealed under high vacuum after several freeze-pump-thaw cycles. After 20 min at 320°C the pyrolysate was dissolved in cyclohexane and the product mixture separated by preparative GC (2 m, 25% OPN on Chromosorb W, 50°C). The observed products were the enynes **14** and **15**, the methylenecyclopentenes **16** and **17** and the cyclopentadiene **18**.

trans-5-Hepten-1-yne (**14**): Colourless liquid. – IR (CCl_4): $\tilde{\nu}$ = 3325 cm^{-1} (vs), 3030 (w), 2970 (m), 2922 (s), 2855 (m), 2115 (w), 1452 (m), 1440 (m), 1433 (m), 1245 (w), 966 (s), 633 (s). – ^{1}H NMR (400 MHz): δ = 1.67 (d, J = 4.8 Hz, 3H, CH_3), 1.96 (t, J = 2.5 Hz, 1H, $\equiv$CH), 2.21 (m, 4H, $-CH_2CH_2-$), 5.51 (m, J_{trans} = 15.0 Hz, 2H, $-CH{=}CH-$). – ^{13}C NMR (100.6 MHz): δ = 17.8 (CH_3), 18.9 (C-3), 31.6 (C-4), 68.4 (C-1), 84.2 (C-2), 126.4 (C-6), 129.3 (C-5). – MS (70 eV): m/z (%) = 94 (1), 93 (13) [M$^+$], 91 (8), 79 (100), 77 (18), 65 (6), 55 (92), 53 (15), 51 (10), 41 (6).

cis-5-Hepten-1-yne (**15**): Colourless liquid. – IR (CCl_4): $\tilde{\nu}$ = 3320 cm^{-1} (vs), 3035 (s), 2930 (s), 2870 (w), 2130 (w), 1410 (m), 1255 (w), 870 (m), 650 (vs). – ^{1}H NMR (300 MHz): δ = 1.64 (d, J = 5.6 Hz, 3H, CH_3), 1.96 (t, J = 2.3 Hz, 1H, CH), 2.26 (m, 4H, $-CH_2CH_2-$), 5.52 (m, J_{cis} = 11.0 Hz, 2H, $-CH{=}CH-$). – MS (70 eV): m/z (%) = 93 (6) [M$^+$], 91 (12), 79 (100), 77 (45), 65 (8), 55 (38), 53 (17), 51 (12), 41 (7).

The spectroscopic data of 1-methyl-4-methylene-1-cyclopentene (**16**)[11], 1-methyl-3-methylene-1-cyclopentene (**17**)[29] and 1,3-dimethyl-1,3-cyclopentadiene (**18**)[30,31] were consistent with those reported in the literature.

Apparatus: This was similar to that used in earlier studies[19]. A conventional grease-free static system constructed of Pyrex with rotaflo HP3 (Quickfit) stopcocks was used. The stirred salt-bath thermostat was controlled by a Systag TCU-2 controller, the temperatures were measured with a calibrated digital Lauda (MGW R 46 with PT-72) thermometer. The reaction vessel used for most runs was spherical (volume ca. 310 ml), but a second vessel for the experiments to test for surface effects was made by packing a cylindrical bulb with pyrex tubes (S/V ca. 13 cm^{-1}). Products were analysed by gas chromatography (Perkin Elmer F11) with FID detection and electronic peak integration (Shimadzu C-R1B). Pressures were measured with a conventional Hg manometer.

Experimental Procedure: The measurements were carried out in a manner similar to previous studies[1,19]. The reaction was studied by using gaseous samples containing 2.1 ± 0.2% of **13** diluted in N_2 to a pressure of initially ca. 700 Torr in a 500-ml reservoir. No internal standard was used. To minimise surface effects the reaction vessel was conditioned between the kinetic runs with HMDS.

Analysis: Chromatographic analyses were carried out on a 4 m × 3 mm diameter β,β′-oxydipropionitrile column (25% on infusional earth 60/80) operated at 50°C. With nitrogen as carrier gas (ca. 1.5 atm) the following reproducible retention times (min) were recorded: **13**: 9.4, **16**: 12.6, **17**: 22.4, **14**: 24.3, and **15**: 29.7. Product identities were confirmed by retention time comparison with authentic samples.

CAS Registry Numbers

13: 137670-03-2 / **14**: 127130-69-2 / **15**: 127130-70-5 / **16**: 14548-37-9 / **17**: 26345-99-3 / allenylmagnesium bromide: 18295-60-8 / 1-methylallyl chloride: 563-52-0 / *trans-* crotyl chloride: 4894-61-5 / *cis*-1,2,5-heptatriene: 137670-04-3 / *trans*-1,2,5-heptatriene: 137670-05-4

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