Thermal Isomerisations, Part 30[+]

Gas-Phase Kinetic and Mechanistic Studies of some Interconverting Alkylcyclopropene Pairs: Involvement of Dialkylvinylidene Intermediates and Their Quantitative Behaviour

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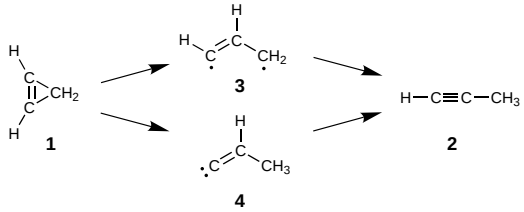
Dedicated to Professor Wolfgang Lüttke on the occasion of his 80th birthday

Abstract: The pyrolyses of two isomeric pairs of alkylcyclopropenes, namely 1,3-dimethyl- (**15**) and 1-ethyl-cyclopropene (**16**), and 1,3,3-trimethyl- (**5**) and 1-isopropyl-cyclopropene (**17**), have been studied in the gas phase. Complete product analyses at various conversions up to 95% were obtained for the decomposition of each compound at five temperatures over a 40 °C range. The time-evolution data showed that the isomerisation reactions **15** ⇌ **16** and **5** ⇌ **17** were occurring. Kinetic modelling of each system allowed the determination of rate constants for these and all other decomposition processes. Tests confirmed that all reactions were unimolecular and homogeneous. Arrhenius parameters are reported for overall reactions and individual product pathways. Further kinetic analysis allowed us to extract the propensities (at 500 K) for 1,3-C–H insertion of the dialkylvinylidene intermediates involved in the rearrangements as follows: k_{prim}:k_{sec}:k_{tert} = 1:16.5:46.4. Additional experiments with ^{13}C-labelled cyclopropenes yielded alkyl group migration aptitudes for the dialkylvinylidenes (from the pattern of ^{13}C in the alkyne products) as follows: Me:Et:*i*Pr = 1:3.1:1.5. Explanations for these trends are given. Another important finding is that of the dramatic rate enhancements for 1,3-diene product formation from the 1-alkylcyclopropenes; this can be explained by either hyperconjugative stabilisation of the vinylcarbene intermediates involved in this pathway, or their differing propensities to 1,2 H-shift. The observed large variations in product distribution amongst these four cyclopropenes is interpreted in terms of these specific effects on individual pathways.

Keywords: cyclopropenes · isomerizations · kinetics · reaction mechanisms · vinylidenes

Introduction

The study of thermal rearrangements of small prototype strained-ring organic compounds has contributed both to a theoretical understanding of unimolecular reactions,[2] and a general mechanistic understanding of hydrocarbon isomerisation reactions.[2–6] Early ideas of diradicals as intermediates developed from studies of cyclopropane and cyclobutane decomposition and rearrangement. When the more highly strained cyclopropenes were first investigated by Srinivasan,[7] 1,3-diradicals were naturally proposed as likely intermediates. Thus for conversion of cyclopropene (**1**) to propyne (**2**) the intermediacy of propene-1,3-diyl (**3**) formed by ring opening of **1** was suggested. A subsequent 2,3 H-shift converts **3** into **2** as shown in Scheme 1. Our own early studies of cyclopropene



Scheme 1.

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[+] For Part 29, see ref. [1].

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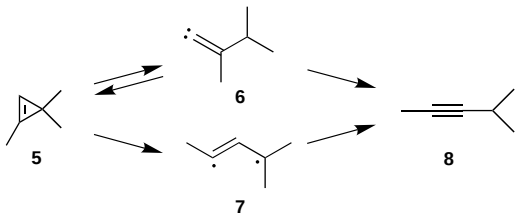
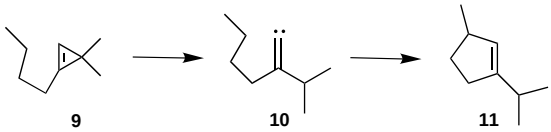
isomerisations[8–10] appeared consistent with this mechanism. The first indication that the mechanism might not be so simple was provided in 1989 by Yoshimine, Pacansky and Honjou,[11] who, on the basis of ab initio calculations, suggested that the key intermediate was not **3** but rather propylidene (**4**) formed from **1** by ring opening with synchronous 1,3 H-transfer, followed by a 2,1 H-shift to give **2** (Scheme 1). At that time existing experimental studies were unable to distinguish between these alternatives. However in 1992, Walsh et al.[12] found that alkyne formation was 18 times slower from 1,3,3-trimethylcyclopropene (**5**) than from 3,3-dimethylcyclopropene. They argued that this was because of the involvement of 2-methyl-2-isopropylvinylidene (**6**) as an intermediate (the analogue of **4** in Scheme 1) rather than trans-4-methylpent-2-ene-2,4-diyl (**7**) (the analogue of **3** in Scheme 1). The reason why the route via **6** can cause a rate reduction is because the second step of the isomerisation, **6** → **8**, involves an alkyl migration (methyl or isopropyl) rather than a hydrogen shift. This will slow down the overall reaction and implies reversibility of the first step, **5** → **6** (Scheme 2). We have obtained



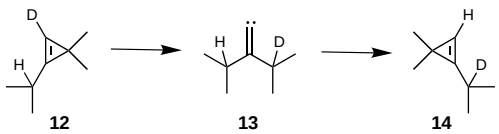
Scheme 2.

further evidence[13, 14] in favour of the involvement of vinylidenes in cyclopropene isomerisations by intramolecular trapping of the alkylvinylidene intermediate **10**, which is involved in the conversion of cyclopropene **9** to cyclopentene **11** (Scheme 3). Evidence for the reversibility of formation of



Scheme 3.

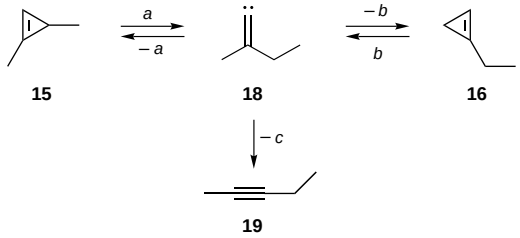
alkylvinylidenes was found in an elegant deuterium-labelling experiment by Likhotvorik, Brown and Jones.[15] They studied the exchange of label between ring and side chain in cyclopropene **12** (Scheme 4). Although the yield of 0.5% at



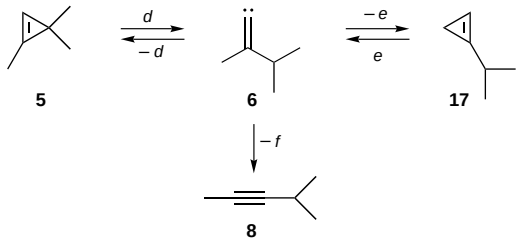
Scheme 4.

90% conversion was small, the evidence for the formation of **14** was unequivocal. We have found further suggestive evidence for this process in pyrolytic kinetic studies[14] of a series of 1-alkyl-3,3-dimethylcyclopropenes. These investigations revealed the formation of 2–3% yields of unstable isomers that, although not unequivocally identified, were consistent with their being isomeric cyclopropenes.

The objective of the work undertaken here was to provide more conclusive evidence for the reversibility of the cyclopropene ring-opening process and to obtain some quantitative information about the behaviour of the alkylvinylidene intermediates involved. To this end we have prepared four cyclopropenes, **15**–**17** and **5**, which fall potentially into two interconverting pairs involving methylethylvinylidene (**18**) and methyl-isopropylvinylidene (**6**), respectively (Schemes 5 and 6). A further target of this study was to determine which



Scheme 5.



Scheme 6.

alkyl groups preferentially migrate in the conversion of the dialkylvinylidenes to alkynes, namely **18** → **19** and **6** → **8**, and also their relative migration rates.

Preliminary accounts of this work have appeared.[1, 16] As well as the original study of Srinivasan,[7] there has been a previous kinetic study of the decomposition of **5**.[12]

Results

Preparation of cyclopropenes: 1-Ethylcyclopropene (**16**) was prepared by the method of Binger[17] using 2-(chloromethyl)-1-butene (**20**) treated with sodium amide. To prepare the 1,3-dimethylcyclopropene (**15**), 1,3,3-trimethylcyclopropene (**5**) and 1-isopropylcyclopropene (**17**) three two-step syntheses were carried out using the method of Baird.[18–20] Trihalogenocyclopropanes, **22**, were prepared in good yields from alkenyl halides **21** by a [1,2]-cycloaddition reaction of either dibromocarbene or dichlorocarbene (generated from bromoform or chloroform) under phase-transfer catalysis conditions with cetrimide (hexadecyltrimethylammoniumbromide) as catalyst. To improve the transparency of the organic and

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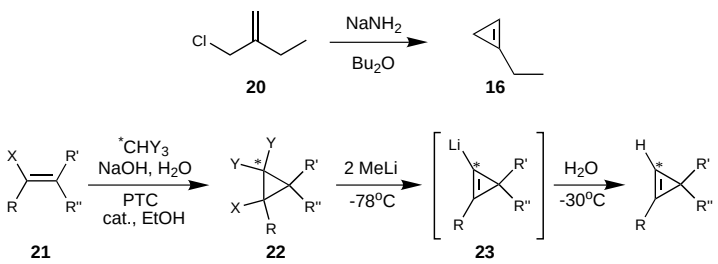
water phases (which thereby improves the yield), 2% ethanol was added to the reaction suspension.[21] Further reaction of the trihalogenocyclopropanes **22** with methyllithium at low temperature gave 1-lithiumcyclopropenes, **23**, which were carefully quenched with water to give the cyclopropenes **5**, **15** or **17**. This preparation is shown in Scheme 7. All cyclopropenes were purified by preparative gas chromatography. The cyclopropenes **15**, **16** and **17** (the non-3,3-disubstituted cyclopropenes) were very unstable at room temperature, tending to oligomerise by an ene reaction to form dimers and oligomers. Therefore, these cyclopropenes were stored below −26 °C prior to their use.



Y	X	R	R'	R"	21/22
Br	Br	Me	Me	H	**a**
Cl	Br	Me	Me	H	**b**
Cl	Br	Me	Me	Me	**c**
Br	Cl	*i*Pr	H	H	**d**

R	R'	R"	
Me	Me	H	**15**
Me	Me	Me	**5**
*i*Pr	H	H	**17**

Scheme 7.

Kinetic measurements

General considerations: For reasons discussed previously,[8–10, 14] kinetic studies with cyclopropenes were carried out using the "internal standard" method, in which the reactants were copyrolysed with a stable, nonreacting substance in a fixed ratio. For all the unlabelled cyclopropenes studied here the standard was *n*-pentane. Gaseous mixtures that contained 1–2% of reactant and 1–2% of internal standard diluted in N_2 were prepared. Pressures of about 50 Torr were used for kinetic runs. Reaction products were analysed by gas chromatography. Conventional columns with a polar liquid phase (oxydipropionitrile or cyanosilicone oil) were required to separate the complex product mixtures formed in these systems. To avoid the risk of condensation or adsorption losses, all gases and gaseous mixtures were handled in heated vacuum lines and analysed by using heated GC sampling valves (see Experimental Section). During kinetic runs, mass recoveries were close to 100% and never less than 95% for reaction systems **15** and **16**, or 93% for the reaction systems **5** and **17**. In order to minimize risks of surface reactions the reaction vessel was conditioned with HMDS [HMDS = 1,1,1,3,3,3-hexamethyldisilazane] as previously reported.[8–10, 14] A number of other checks were also carried out (see below).

The major products of the decompositions of **15**, **16**, **5** and **17** are dienes and alkynes, but the most significant findings of this work are that **16** is formed from **15** and vice versa, and that **17** is formed from **5** and vice versa; in other words **15** and **16**, and also **5** and **17** form interconverting pairs of cyclopropenes. Since, when starting from any individual cyclopropene, its isomer, after initial formation, is also unstable, a complex mechanism ensues in which both cyclopropenes (of a given isomeric pair) decompose together to give (largely) the same array of final products. The quantitative product distribution from each isomer of each pair is, however, different and this has the consequence that the product distribution from each starting cyclopropene is time dependent. The detailed time-evolution of each decomposition and the consequent inferred mechanisms are described in the next section. Although the decomposition of **5** was studied previously,[7, 12] **17** was not at the time detected amongst the products.

Time dependence and overall mechanism: For each of the compounds **15**–**17** and **5**, a set of runs (usually six or seven) was carried out for times corresponding to between 10 and 95% decomposition, at each of five temperatures spanning a 40 °C range. Hydrocarbons **5** and **15** were studied between approximately 210 and 250 °C, while **16** and **17** were studied between about 200 and 240 °C. For each isomeric pair, namely **15** and **16** or **5** and **17**, studies were arranged at four precisely matched temperatures in the overlap region of 210–240 °C. Initial pressures of reactant mixtures were kept at 51 ± 4 Torr for **15** and **16** and 52 ± 11 Torr for **5** and **17** (corresponding to actual reactant pressures of between 0.5 and 1.0 Torr) although the overall pressure dependence was briefly investigated down to about 7 Torr for **15** and **16** and 10 Torr for **5** and **17** (see below).

The time evolution of each cyclopropene is illustrated in Figures 1 and 2. Similar figures were obtained at each of the five temperatures of study for each compound. Full details of product analytical percentages at each reaction time and temperature are contained in references [22] and [23]. However, all the important features are visible in the given diagrams. The formation (and intermediacy) of **15** from **16** can clearly be seen in Figure 1 (right), with a maximum of **15** of about 10%. Similarly a maximum of approximately 14% of **5** from **17** can be seen in Figure 2 (right). Formation in the reverse direction of **16** from **15** and **17** from **5** is less evidently visible, but the analytical sensitivity is such that they are nevertheless still clearly detected as intermediates. This is illustrated in Figure 3 which shows the minor products formed from **5**. Although the yield of **17** reaches only 0.6% the presence of a maximum is clearly seen. Similarly a maximum of about 1.2% was found for **16** formed from **15**. These maximum percentages are almost independent of temperature. In view of the low yield of **17** from **5** it is not surprising that this product was overlooked in the earlier kinetic study.[12]

Another noteworthy feature is the variability of alkyne yields from one cyclopropene to another. These range from approximately 80% of the total products from **15** through about 30% from **16** and 20% from **5**, down to 13% from **17**. Diene yields are similarly variable in the complementary sense to those of the alkynes. Similar product yield variability has been found previously in cyclopropene pyrolysis.[14] The main product distribution from **5** is closely similar to that found previously[12] in our laboratory, although it differs

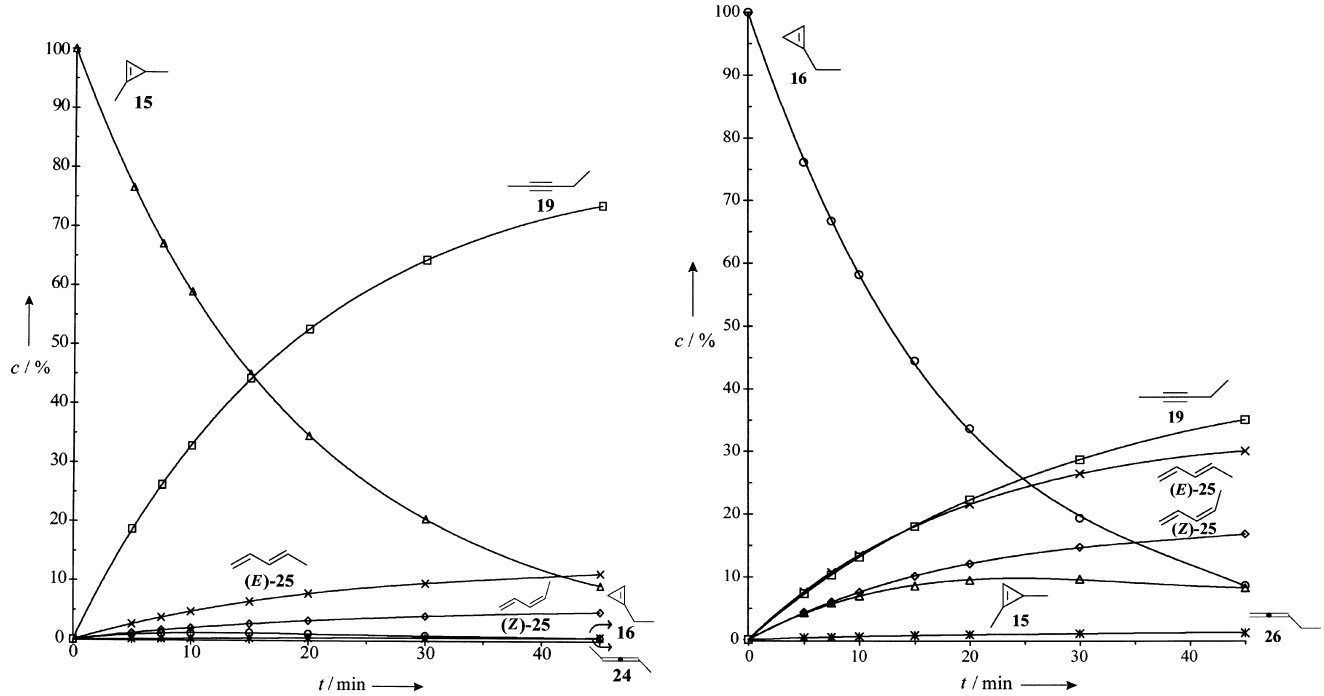


Figure 1. Time evolution of the decomposition of **15** at 248.4 °C (left) and of **16** at 238.6 °C (right).

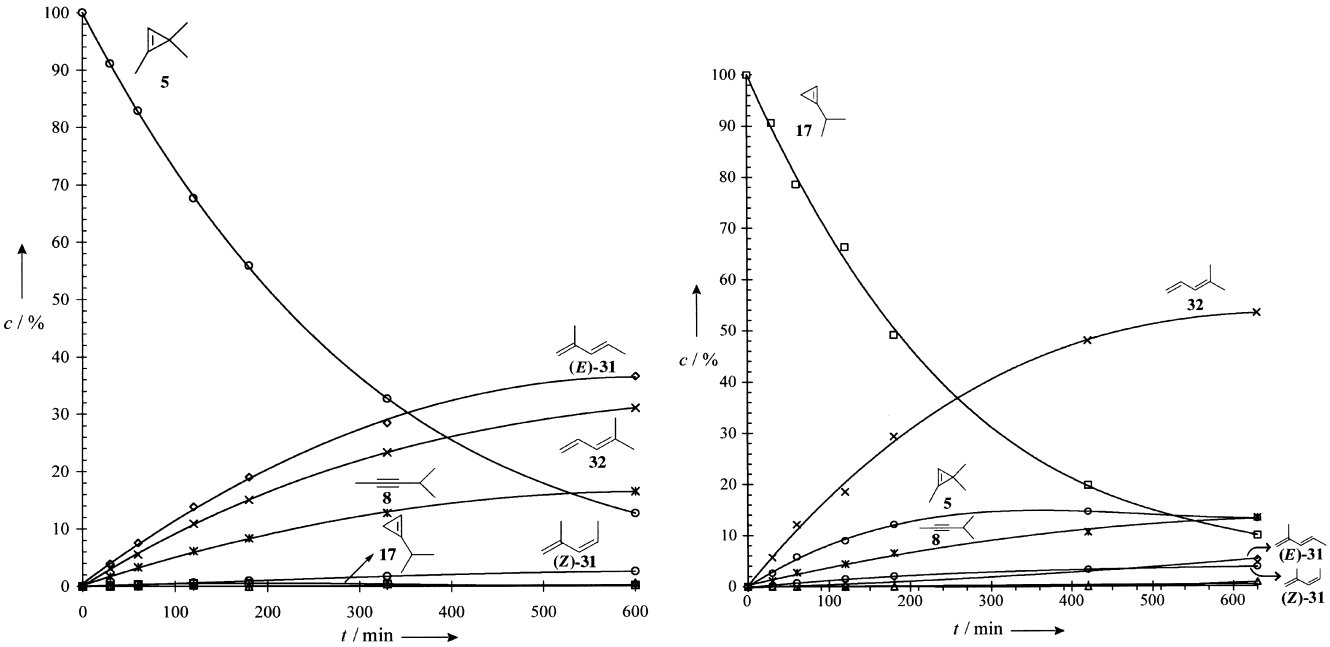


Figure 2. Time evolution of the decomposition of **5** at 210.6 °C (left) and of **17** at 200.9 °C (right).

somewhat from that reported by Srinivasan.[7] It should be added that there is no evidence of variation of product distributions at times beyond the consumption of cyclopropenes in any of the systems.

From these product time-variation data, overall mechanistic schemes of reaction for each of the two coupled reaction systems **15**/**16** and **5**/**17** were proposed. These are shown in Schemes 8 and 9. The schemes show the sources of every product identified, as indicated in Figures 1 and 2, as well as the minor products 4-methyl-1,2-pentadiene (**28**) and (*Z*)-1,4-hexadiene (**30**) coming from **17**. The origins of some products, namely **(*E*)-31** from **5** and **(*E*)-** and **(*Z*)-31** from **17**, were not evident at the outset, but Scheme 9 shows our final preferred mechanism, after the kinetic-modelling exercise described in the next-but-one section. Although the mechanisms are complex, overall decays of **5** and **15**–**17** closely approximate first-order behaviour (good linear fits to log[% reactant] versus time plots). Thus ahead of the modelling exercise, unimolecular behaviour can be anticipated.

Some additional kinetic tests: Unimolecular rate processes show characteristic pressure dependencies[2] and it is impor-

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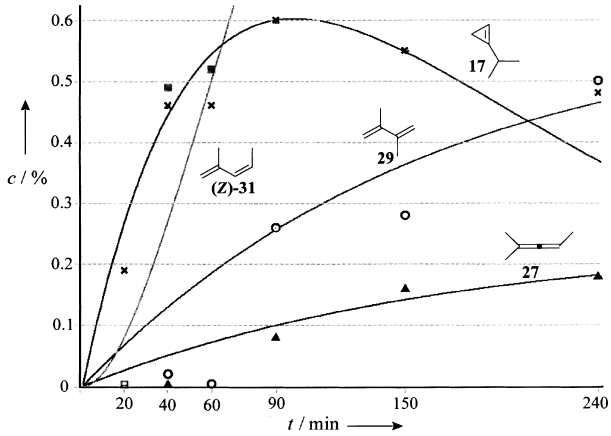
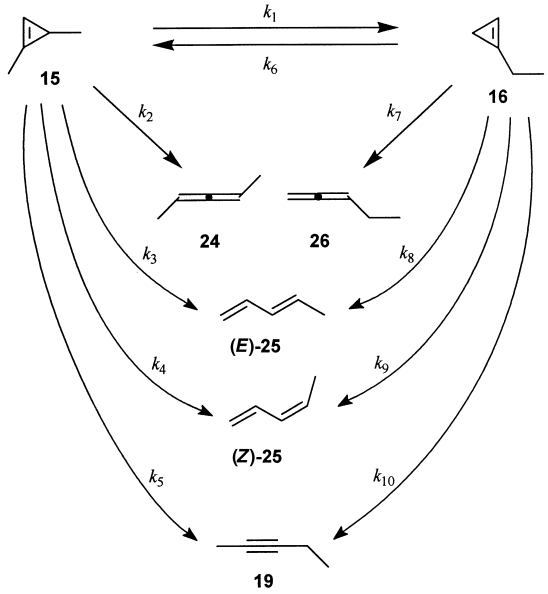
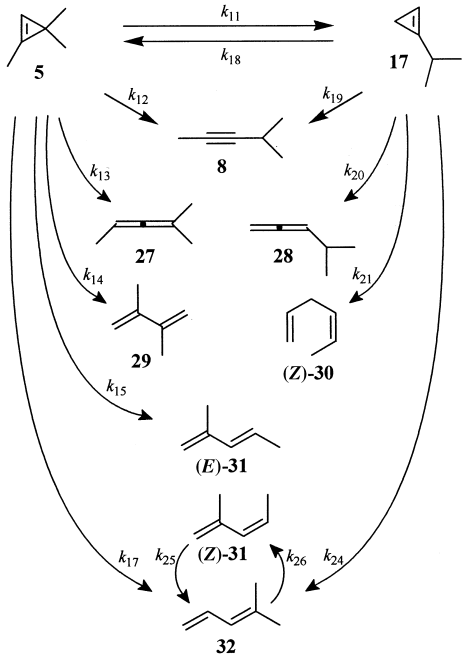


Figure 3. Time evolution of minor products of decomposition of **5** at 218.6 °C.



Scheme 8.



Scheme 9.

tant to know for the purposes of interpretation and comparison with other studies that the rate constants of these reactions are at or near their high-pressure limits under experimental conditions. For **15** a test was carried out at 227.5 °C, for 60 min (approximate half life) at four pressures from 53 down to 7.5 Torr. The conversions decreased slightly with decreasing pressure which corresponded to a 6.5% reduction in rate constant over this factor of about a sevenfold drop in pressure. At intervening pressures the change was even less. Very similar figures were obtained for the corresponding test with **16**. For **5** and **17**, for pressures from 50 down to 10 Torr, conversions were unchanged within experimental error. Thus under operating conditions for all four of these cyclopropenes the high-pressure criterion has been met.

Other potential problems include free-radical-chain contributions and heterogeneous (surface) catalysis. To test for free-radical-chain processes, a particular run for each compound was carried out in the presence of a free-radical inhibitor (isobutene for **15** and **16**, (*Z*)-2-butene for **5** and **17**) in about tenfold excess. In no case was there any change in conversion or product distribution within experimental error. Tests for heterogeneity were carried out in a special reaction vessel packed with glass tubes (with flame polished ends). This vessel had a surface-to-volume ratio, *S*/*V*, of $\approx$11.1 cm^{-1} compared with $\approx$1.0 cm^{-1} for the normal (unpacked) vessel. The vessel was conditioned with HMDS at reaction temperatures for several hours prior to use. Runs with **15** and **16** gave rate constants 4% and 12% faster than in the unpacked vessel at 227.5 °C. For **15** this was accompanied by formation of isoprene (**33**) in small yield (0.8%). Runs with **5** and **17** showed rate increases of 22% and 2%, respectively, relative to the unpacked vessel at 231.1 °C. In the case of **5** the rate increase was accompanied by formation (9.7%) of 2,3-dimethylbuta-1,3-diene (**29**) present at only 0.7% in the unpacked vessel. Interestingly after further conditioning of the packed vessel by HMDS, both the reaction rate and the yield of **29** decreased. These findings suggest that surface effects are negligible in the unpacked, HMDS-treated vessel and that where they do occur, in the packed vessel, they lead to the formation of new products, **33** or **29** through additional pathways.

Kinetic modelling and extraction of the rate constants: In order to obtain the desired values for the first-order rate constants for the processes shown in Schemes 8 and 9, the differential equations corresponding to formation of each product from each starting cyclopropene were first set up. These coupled differential equations were then solved by means of a variable-step integration program, employing the Gear Algorithm.[24] In practice the program required an initial set of estimates for the rate constants of each scheme. For each starting cyclopropene at each temperature the program then calculated the species concentrations at specified times; these were then compared with the observed data. After successive

adjustments of the rate constant values, the calculations were repeated until the best fit to experiment was obtained, as judged by a minimum value for the sum of squares of all deviations, $\Sigma\chi^2$. In practice, the complexity of both schemes, with ten or more adjustable rate constants, meant that this was a delicate operation since the data points are not all equally sensitive to each rate constant. Therefore some constraints were applied. At most temperatures, each scheme had to fit two sets of data, one from each cyclopropene. After an initial rough fit was obtained, the rate contants for decomposition of one cyclopropene were optimised as described by fitting the decomposition data from that cyclopropene, while the rate constants for decomposition of its isomer were kept fixed (e.g., starting from **15**, k_1-k_5 were refined with k_6-k_{10} fixed). The process was then continued for the isomeric cyclopropene by refining its decomposition rate constants with the new values of rate constants for the original cyclopropene now fixed (i.e., starting from **16**, k_6-k_{10} were refined, while the new values for k_1-k_5 were fixed). This cycle was repeated until the best values for all rate constants were obtained. For the temperatures for which only one set of data was available (for **15**, 248.4 °C; for **16**, 198.7 °C; for **5**, 249.6 °C; for **17**, 200.9 °C), the optimisation process was the same except that the rate constant set for the missing isomer (i.e., the fixed values) were obtained by extrapolation of their Arrhenius equations obtained from values at the other temperatures. For Scheme 9 some further constraints were applied. Because (*Z*)-2-methyl-1,3-pentadiene (**(*Z*)-31**) and 4-methyl-1,3-pentadiene (**32**) are known to interconvert by a rapid 1,5 H-shift process, the known rate constants for this process[25] were taken as fixed. While direct formation of **(*Z*)-31** from **5** and **17** could not be rigorously excluded, modelling with these pathways included gave only small and erratic rate constants for them. A similar argument applied to formation of **(*E*)-31** from **17**. We therefore decided to exclude them from the optimisation process. Speed of convergence to the optimum fit was increased by use of a program[26] based on algebraic functional solutions available from Maple.[27] Fuller details are given in references [22] and [23].

Temperature dependences: The optimised rate constants for the individual pathways of decomposition of each cyclopropene are listed in Tables 1–4. Uncertainties (single standard deviation) were about 1–2% for the overall decomposition where they were obtained from the linear regression analysis. For the Gear algorithm fitting process uncertainties are hard to specify. Since the general quality of the fits was good, with low values of $\Sigma\chi^2$, it seems reasonable to suppose that for the major product pathways errors were no greater than 5% and probably less. Only for the minor pathways (the allene forming steps 2, 7, 13, and 20 and also steps 14 and 21) were the errors larger. The rate constants for each compound and each pathway were fitted to the Arrhenius equation, which yielded the parameters shown in Tables 5–8. The quality of the data may be judged by the generally small uncertainties in these parameters. Apart from the minor product forming pathways mentioned above, A factors are uncertain by less than $10^{\pm0.36}$ and activation energies, E_a, by less than ±3.4 kJ mol^{-1}. The Arrhenius plots themselves are shown in Figures 4 and 5.

Table 1. Temperature dependence of rate constants k_1-k_5 for decomposition of **15** (Scheme 8).

T [°C]	overall [10^5 s^{-1}]	k_1 [10^5 s^{-1}]	k_2 [10^5 s^{-1}]	k_3 [10^5 s^{-1}]	k_4 [10^5 s^{-1}]	k_5 [10^5 s^{-1}]
208.4	3.82	0.180	0.0122	0.359	0.135	3.16
218.5	8.68	0.430	0.0282	0.839	0.322	7.14
227.5	17.94	0.895	0.0753	1.843	0.717	14.79
238.6	42.20	2.09	0.158	4.48	1.795	34.47
248.4	88.01	4.37	0.443	9.65	3.91	70.45

Table 2. Temperature dependence of rate constants k_6-k_{10} for decomposition of **16** (Scheme 8).

T [°C]	overall [10^5 s^{-1}]	k_6 [10^5 s^{-1}]	k_7 [10^5 s^{-1}]	k_8 [10^5 s^{-1}]	k_9 [10^5 s^{-1}]	k_{10} [10^5 s^{-1}]
198.7	3.74	0.769	0.0256	1.145	0.594	1.147
208.4	8.32	1.692	0.0624	2.57	1.35	2.52
218.5	19.12	3.85	0.168	6.04	3.27	5.82
227.5	38.61	7.59	0.324	12.29	6.74	11.69
238.6	90.96	17.35	1.09	28.99	16.3	27.09

Table 3. Temperature dependence of rate constants $k_{11}-k_{15}$ and k_{17} for decomposition of **5** (Scheme 9).

T [°C]	overall [10^5 s^{-1}]	k_{11} [10^5 s^{-1}]	k_{12} [10^5 s^{-1}]	k_{13} [10^5 s^{-1}]	k_{14} [10^5 s^{-1}]	k_{15} [10^5 s^{-1}]	k_{17} [10^5 s^{-1}]
210.1	5.77	0.13	1.03	0.0099	0.031	2.33	1.96
218.6	11.34	0.29	2.17	0.0239	0.062	4.77	3.69
231.1	33.0	0.74	6.30	0.0136	0.226	12.75	10.96
239.5	58.2	1.60	11.64	0.1260	0.322	23.88	19.56
249.6	118.6	3.30	24.99	0.2400	0.660	48.82	39.78

Table 4. Temperature dependence of rate constants $k_{18}-k_{21}$ and k_{24} for decomposition of **17** (Scheme 9).

T [°C]	overall [10^5 s^{-1}]	k_{18} [10^5 s^{-1}]	k_{19} [10^5 s^{-1}]	k_{20} [10^5 s^{-1}]	k_{21} [10^5 s^{-1}]	k_{24} [10^5 s^{-1}]
200.9	6.20	1.69	0.759	0.023	0.048	3.60
210.1	12.49	3.62	1.73	0.050	0.088	7.27
218.6	24.7	7.14	3.47	0.127	0.230	14.27
231.1	65.4	18.59	9.36	0.254	0.558	37.2
239.5	126.1	34.17	18.56	1.200	1.390	71.5

Table 5. Arrhenius parameters, rate constants at 500 K and entropies of activation for pyrolysis products of **15**.

Step	Product		log (A [s^{-1}])	E_a [kJ mol^{-1}]	$10^5\,k_{500}$ [s^{-1}]	$\Delta S^{\neq}_{500}$ [J K^{-1} mol^{-1}]
overall	-		13.36 ± 0.08	164.0 ± 0.8	17.1	-1.7
1		**16**	12.29 ± 0.07	166.2 ± 0.6	0.84	-22.3
2		**24**	13.20 ± 0.80	185.6 ± 7.7	0.0648	-4.8
3		(***E***)-**25**	13.25 ± 0.12	172.4 ± 1.2	1.73	-3.9
4		(***Z***)-**25**	13.26 ± 0.12	176.4 ± 1.1	0.676	-3.7
5		**19**	13.12 ± 0.07	162.5 ± 0.6	14.0	-6.4

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Table 6. Arrhenius parameters, rate constants at 500 K and entropies of activation for pyrolysis products of **16**.

Step	Product	log (A [s^{-1}])	E_a [$kJ\,mol^{-1}$]	$10^5\,k_{500}$ [s^{-1}]	$\Delta S^{\neq}_{500}$ [$J\,K^{-1}\,mol^{-1}$]
Overall	-	13.36 ± 0.09	160.7 ± 0.9	37.0	-1.8
6	**15**	12.26 ± 0.06	156.9 ± 0.5	7.26	-22.9
7	**26**	13.96 ± 0.72	185.8 ± 6.8	0.352	9.7
8	**(*E*)-25**	13.09 ± 0.08	162.9 ± 0.8	11.7	-7.0
9	**(*Z*)-25**	13.26 ± 0.11	167.1 ± 1.0	6.43	-3.7
10	**19**	12.71 ± 0.09	159.5 ± 0.9	11.1	-14.3

Table 7. Arrhenius parameters, rate constants at 500 K and entropies of activation for pyrolysis products of **5**.

Step	Product	log (A [s^{-1}])	E_a [$kJ\,mol^{-1}$]	$10^5\,k_{500}$ [s^{-1}]	$\Delta S^{\neq}_{500}$ [$J\,K^{-1}\,mol^{-1}$]
overall	-	13.25 ± 0.28	161.8 ± 2.7	22.36	-3.9
11	**17**	12.65 ± 0.36	171.4 ± 3.4	0.55	-15.4
12	**8**	13.35 ± 0.18	169.6 ± 1.7	4.30	-2.0
13	**27**	10.6 ± 5.4	163 ± 52	0.033	-55.0
14	**29**	11.27 ± 1.06	164.2 ± 10.2	0.128	-41.9
15	**(*E*)-31**	12.85 ± 0.09	161.7 ± 0.9	9.09	-11.5
17	**32**	12.79 ± 0.32	161.9 ± 3.1	7.46	-12.8

Table 8. Arrhenius parameters, rate constants at 500 K and entropies of activation for pyrolysis products of **17**.

Step	Product	log (A [s^{-1}])	E_a [$kJ\,mol^{-1}$]	$10^5\,k_{500}$ [s^{-1}]	$\Delta S^{\neq}_{500}$ [$J\,K^{-1}\,mol^{-1}$]
overall	-	13.20 ± 0.24	158.1 ± 2.3	47.94	-4.8
18	**5**	12.58 ± 0.02	157.5 ± 0.2	13.46	-16.7
19	**8**	13.20 ± 0.12	166.3 ± 1.2	6.82	-4.8
20	**28**	14.8 ± 3.2	194 ± 22	0.267	25.0
21	**(Z)-30**	12.99 ± 0.99	175.6 ± 9.3	0.441	-8.9
24	**32**	12.81 ± 0.21	156.7 ± 2.0	27.46	-12.3

The mechanism of alkyne formation and further kinetic analysis: The conclusive finding of the reversible interconversion of both **15** and **16**, and **5** and **17** offers substantive and concrete evidence in favour of our original argument[12] for the involvement of vinylidene intermediates in alkyne formation, which follow on the theoretical prediction of Yoshimine et al.[11] The present result follows on the isotopic-scrambling study of Likhotvorik et al.[15] and the earlier intramolecular vinylidene trapping experiment in our own laboratories.[13] It also fully confirms our earlier suspicions of cyclopropene-to-cyclopropene isomerisation.[14] We are now in a position to exploit the results beyond the qualitative conclusion. The rate data found here permit a deeper analysis. The rate constants of Schemes 8 and 9, specifically k_1, k_5, k_6, k_{10} and k_{11}, k_{12}, k_{18}, k_{19}, can be related to the elementary rate constants of Schemes 5 and 6, which involve the formation and rearrangement of the two vinylidenes, **18** and **6**, themselves. The algebraic relationships are given in the appendix. By use of these we have calculated absolute values of the rate constants (k_a, k_b for **18** and k_d, k_e for **6**) for formation of the two vinylidenes from their precursor cyclopropenes, as well as the relative rate constants for intramolecular rearrangement (C–H insertion or alkyl migration) of each vinylidene, namely

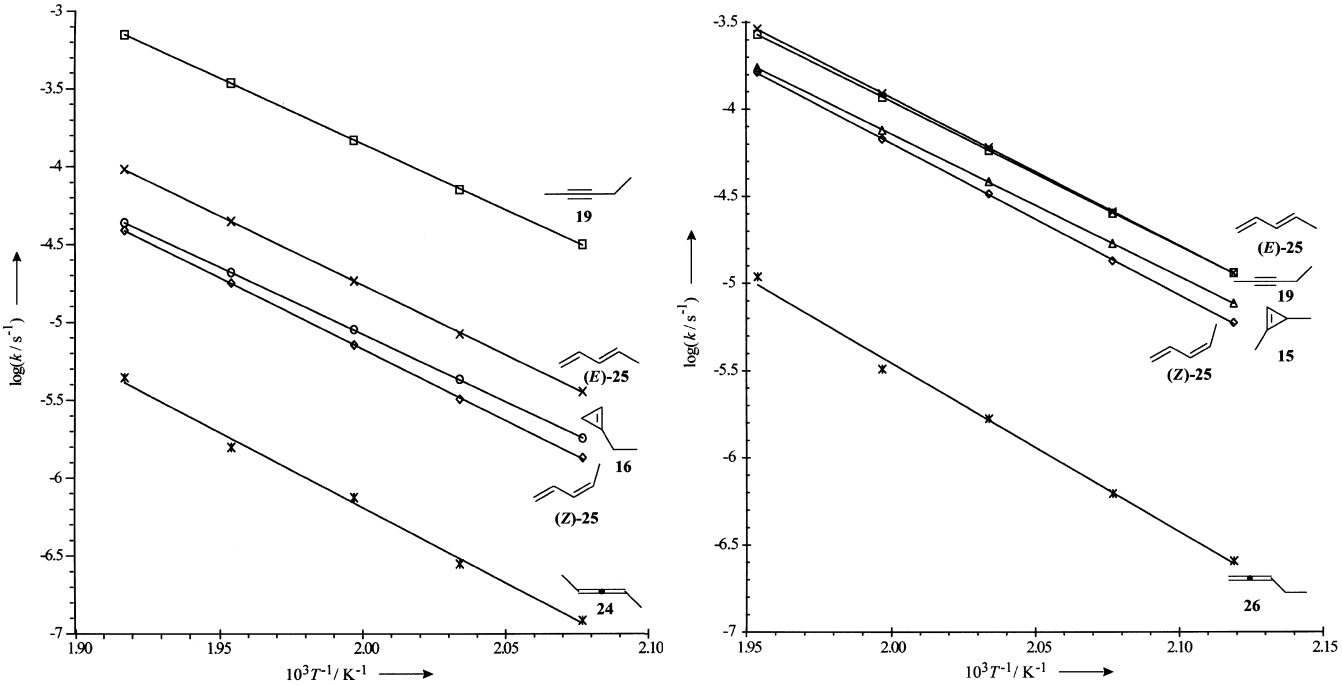
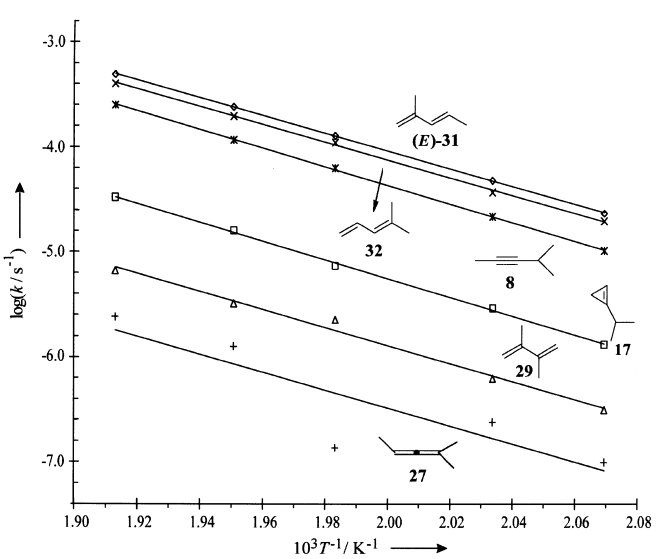


Figure 4. Arrhenius plots for pyrolysis products of **15** (left) and **16** (right).



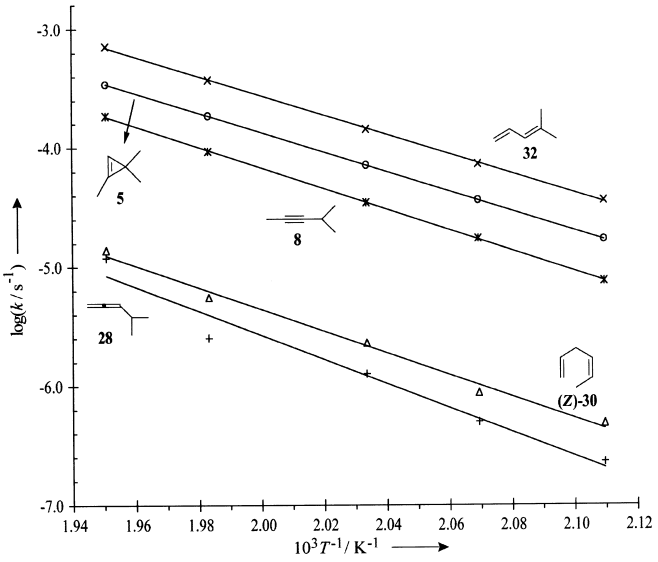


Figure 5. Arrhenius plots for pyrolysis products of **5** (left) and **17** (right).

k_{-a}:k_{-b}:k_{-c} for **18** and k_{-d}:k_{-e}:k_{-f} for **6**. Unfortunately it is not possible to obtain absolute values for these latter rate constants without an independent knowledge of the lifetimes of **18** and **6**.

The results of this analysis are shown in Tables 9 and 10, in which the relative rate constants are expressed as percentages.

Table 9. Elementary rate constants for ring opening of cyclopropenes **15** and **16** and relative rate constants of rearrangement of vinylidene **18** (Scheme 5) as a function of temperature.

T [°C]	$10^5\ k_a$ [s^{-1}]	$10^5\ k_b$ [s^{-1}]	k_{-a} :	k_{-b} :	k_{-c}
198.7	2.35	1.98	38.82 %	3.29 %	57.89 %
208.4	5.46	4.36	38.85 %	3.30 %	57.86 %
218.5	12.3	10.0	38.39 %	3.50 %	58.11 %
227.5	25.3	20.0	37.97 %	3.54 %	58.49 %
238.6	58.6	46.1	37.65 %	3.56 %	58.79 %
248.4	109.5	92.3	37.41 %	3.67 %	58.93 %

Table 10. Elementary rate constants for ring opening of cyclopropenes **5** and **17** and relative rate constants of rearrangement of vinylidene **6** (Scheme 6) as a function of temperature.

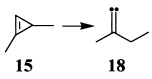
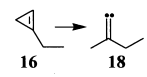
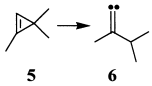
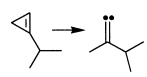
T [°C]	$10^5\ k_d$ [s^{-1}]	$10^5\ k_e$ [s^{-1}]	k_{-d} :	k_{-e} :	k_{-f}
200.9	1.54	2.55	66.42 %	3.75 %	29.82 %
210.1	3.30	5.57	64.93 %	3.95 %	31.12 %
218.6	6.93	11.08	64.48 %	4.19 %	31.33 %
231.1	19.55	29.04	64.01 %	3.77 %	32.23 %
239.5	34.67	55.28	61.81 %	4.61 %	33.57 %
249.6	73.28	114.00	61.39 %	4.51 %	34.10 %

Following this the rate constants k_a, k_b, k_d and k_e were fitted to the Arrhenius equation and the parameters obtained are shown in Table 11. Once again these rate constants and their associated Arrhenius parameters have the same high precision as the generic rate constants. The data for the relative rate constants indicate only very slight variations over the temperature range of study for both systems.

^{13}C labelling experiments

Alkyl group migratory aptitudes in vinylidene rearrangements: The analysis of the previous section leaves open the question

Table 11. Arrhenius parameters, rate constants at 500 K and entropies of activation for vinylidene formation from all four cyclopropenes.

Step		log (A [s^{-1}])	E_a [kJ mol^{-1}]	$10^5\ k_{500}$ [s^{-1}]	$\Delta S^{\neq}_{500}$ [J K^{-1} mol^{-1}]
a	 **15** **18**	13.27 ± 0.04	161.6 ± 0.4	24.0	-3.6
b	 **16** **18**	12.85 ± 0.05	158.6 ± 0.5	19.1	-11.5
d	 **5** **6**	13.26 ± 0.16	164.0 ± 1.6	13.3	-3.6
e	 **17** **6**	13.12 ± 0.03	160.7 ± 0.3	21.2	-6.4

of which alkyl group is migrating in the vinylidene-to-alkyne rearrangements of **18** and **6** (Schemes 5 and 6). Put more quantitatively the questions are what is the ratio of ethyl/methyl migration in **18** → **19** (step −c) and of isopropyl/methyl migration in **6** → **8** (step −f). To probe these questions we prepared the specifically ^{13}C-labelled cyclopropenes **15** and **5**, which are expected to yield, in each case, mixtures of two differently ^{13}C-labelled alkynes, either **19** or **8** upon pyrolysis, as shown in Scheme 10. The compounds **15**(2-^{13}C) and **5**(2-^{13}C) were prepared by the same procedures[18–20] as their unlabelled counterparts apart from the use of 70 % ^{13}C-enriched chloroform. Two pyrolysis runs of both pure **15**(2-^{13}C) and **5**(2-^{13}C) at a pressure of 50 – 70 Torr and with a conversion of over 95 % were used to obtain each product sample for ^{13}C NMR analysis. The product distributions were checked by GC analysis and confirmed to be the same as those obtained already from the unlabelled molecules. Product ^{13}C NMR spectra were recorded using the inverse-gated decoupling method to suppress NOE effects and with a pulse delay of 120 s to avoid any relaxation effects.[28] Tests showed very little effect of pulse delay time at times greater than 60 s. The ^{13}C shifts of the expected 2- and 3-positions of the alkyne

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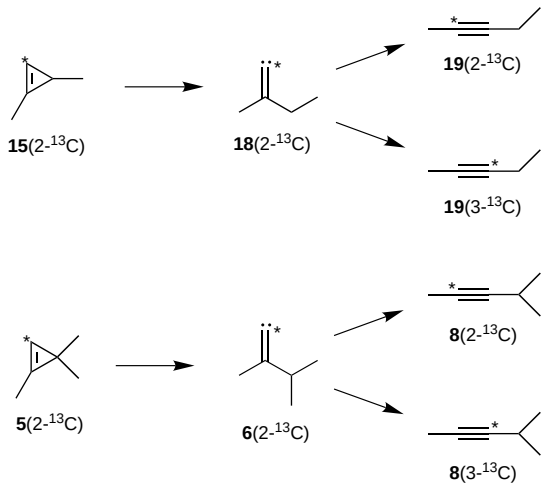

Scheme 10.

products **19** and **8** were identified by nondecoupling experiments with the pyrolysed ^{13}C samples. Their values are given in the Experimental Section. The distribution of the label in **19**(^{13}C) and **8**(^{13}C) was determined as the average of two – four independent runs (after correction for the only 70% ^{13}C enrichment) and the error is quoted as a single standard deviation from the mean. Pyrolysis of **15**(2-^{13}C) at 250 °C gave a ratio of products of [**19**(3-^{13}C)]/[**19**(2-^{13}C)] = 3.0 ± 0.1, while pyrolysis of **5**(2-^{13}C) at the same temperature gave the product ratio [**8**(3-^{13}C)]/[**8**(2-^{13}C)] = 1.40 ± 0.05. Further checks showed no significant pressure or conversion dependence of the label distribution. The lack of a conversion dependence demonstrates that there is no tendency for the alkynes **19** or **8** to undergo any degenerate scrambling processes under experimental conditions. A small temperature dependence was detected with the label distribution ratio (as before) of 3.2 ± 0.1 for **19**(^{13}C) and 1.60 ± 0.05 for **8**(^{13}C) at 209 °C.

These numbers correspond to ratios of migration rates of ethyl to methyl in **18** and isopropyl to methyl in **6** (Scheme 10). If we take the mid-range temperature as 500 K, and combine the averages of these figures with those of Tables 9 and 10, we obtain the relative rates of all the possible intramolecular processes of vinylidenes **18** and **6**. These are shown in Table 12.

Diene product analyses: The ^{13}C-product NMR spectra in the above experiments gave, in addition to the desired ^{13}C distribution in the alkyne products, the distribution for the other major products, which are the dienes. Pyrolysis of **15**(2-^{13}C) at 250 °C gave the ratio [**(*E*)-25**(3-^{13}C)]/[**(*E*)-25**(2-^{13}C)] = 13 ± 2 and also [**(*Z*)-25**(3-^{13}C)]/[**(*Z*)-25**(2-^{13}C)] = 5 ± 1. Pyrolysis of **5**(2-^{13}C) at the same temperature gave mainly **32**(3-^{13}C) although a small amount of **32**(2-^{13}C) was present, but could not be quantified because of overlapping NMR peaks. For **(*E*)-** and **(*Z*)-31** the ^{13}C label was found almost entirely at 3-C. These results are discussed later.

Table 12. Relative rate constants for all rearrangement processes of methylethyl vinylidene (**18**) and methylisopropyl vinylidene (**6**) at 500 K.

Reactant	Product			
step	-a	-b	-c (Me)	-c (Et)
relative *k* / [%]	38.2	3.5	14.2	44.1
step	-d	-e	-f (Me)	-f (*i*Pr)
relative *k* / [%]	63.8	4.1	12.8	19.2

Discussion

Apart from our preliminary communications[1, 16] there are no studies of the thermal decompositions of **15**, **16** or **17**. Cyclopropene **5** has been previously investigated by one of us with very similar final product distributions and Arrhenius parameters,[12] although without the detection of **17**. Likhotvorik, Brown and Jones[15] also studied **5** as part of their isotopic-labelling study of cyclopropenes and found a similar product distribution. On the substantive mechanistic question of the involvement of vinylidenes in cyclopropene decomposition, there can now be little room for doubt. The pattern of interconversion of cyclopropene isomers is very hard to explain in any other way. As to whether biradicals/vinyl carbenes are involved in alkyne formation, this can largely be ruled out by the ^{13}C-labelling results. Biradicals from **15** or **5** would have led to alkynes **19** and **8** uniquely labelled in the 3-position and not mixtures of the 3- and 2-labelled product as observed. This point was made previously by Likhotvorik et al.[15] in a ^{12}C-labelling experiment, but the low sensitivity of detection of ^{12}C in the product (**8**) meant that the ratio of 3- to 2-position labels was hard to quantify. It remains to ask whether biradicals can be rigorously excluded from even a minor contribution to the rate. This is more difficult to prove (at present), but ab initio theoretical studies of the energy surface[11, 29] suggest that the pathway via a biradical/vinylcarbene is too high in energy to contribute. There are several quantitative aspects of the findings of this work which are new and significant: the pattern of reactivity of the vinylidene intermediates, the specific rate constants for ring opening of cyclopropenes to vinylidenes and the pattern of substituent effects on the differing product distributions of the four cyclopropenes studied here. These are discussed in the following sections.

Intramolecular reactivity of dialkylvinylidenes: The relative rate constants and product distributions listed in Table 12 permit us to calculate three important ratios.

First the relative propensities for 1,3-C–H insertion (which lead from vinylidenes to cyclopropenes) may be obtained. For methylethylvinylidene (**18**), the proportion k_{-a}:k_{-b}, statistically corrected, provides the secondary/primary C–H insertion ratio of 16.5. For methylisopropylvinylidene (**6**), the proportion k_{-d}:k_{-e}, again statistically corrected, gives us the tertiary/primary C–H insertion ratio of 46.4. Assuming primary C–H insertion can be taken as a fixed reference the numbers may be combined and then these relative rates can be compared with those of other carbene insertion processes into all three types of C–H bond as shown in Table 13. Although the other processes in Table 13 involve 1,2-C–H

Table 13. Selectivities in various carbene C–H insertion processes.

Species	Insertion	k_{prim}	k_{sec}	k_{tert}	T [K]	Ref.
alkyl carbenes	1,2 C–H	1	40	90	400 – 450	[30]
vinyl carbenes	1,2 C–H[a]	1	18	45	500	[14]
vinylidenes	1,3 C–H	1	16.5	46.4	500	this work

[a] May include stabilisation effects.

insertions and the carbenes are all different, there is a remarkable similarity between these numbers. It demonstrates that all these carbenes are fairly discriminating amongst the different C–H bonds, which, after all, differ in strength only by about 20 kJ mol^{-1} overall.[31] It should be borne in mind that these numbers are, in principle, temperature dependent although variations are only very slight within the temperature range of study. Nevertheless in the present system the slight trend (see data in Tables 9 and 10) is towards higher selectivities at lower temperatures, as we might expect for activated processes. At the present time there are no absolute rates available for such processes, but given the generally undiscriminating nature of the parent carbene, methylene ($^1A_1$ state), in its intermolecular insertion reactions[32] combined with our current knowledge that it reacts virtually at every collision,[33] we suspect that these carbene intramolecular processes are considerably slower. In view of the strained nature of the transition-state structures of these processes, this would not be too surprising. A theoretical study of the vinylidene 1,3-C–H insertion processes[29] carried out in conjunction with the present study,[23] suggests energy barriers of approximately 30 – 60 kJ mol^{-1}, with values highest for primary and lowest for tertiary C–H insertion. Similar values have been found in theoretical studies of 1,2-C–H insertion reactions of dialkylcarbenes.[34]

Secondly the relative ratios for C–H insertion to total alkyl migration may be obtained. For methylethylvinylidene (**18**), the proportion $(k_{-a}+k_{-b}):k_{-c}$ furnishes a value of 0.71. For methylisopropylvinylidene (**6**), the proportion $(k_{-d}+k_{-e}):k_{-f}$ gives us a value of 2.12. These ratios are a measure of "reversibility" in the cyclopropene ring-opening reactions leading to alkynes. A low number ($\ll 1$) means that ring opening is rate-determining, whilst a high number ($\gg 1$) indicates that alkyl migration in the vinylidene ("step 2" of the overall process) is rate-determining. The numbers obtained indicate an in-between situation with neither stage completely rate-controlling. Nevertheless the high value for **6** does show that the second step for the isomerisation of **5** to **8** is more nearly the bottleneck as Walsh et al.[12] originally suggested.

Thirdly the relative propensities for alkyl migration in the vinylidene to alkyne rearrangement are obtained. These were of course directly measured in this study by the ^{13}C-labelling measurements. The preferences for the larger alkyl group migration (ethyl or isopropyl against methyl) are clear from the results. If we assume that the rate of methyl migration is not affected by the presence of the other alkyl substituent, this establishes a non-monotonic migration order with relative rates of Me:Et:*i*Pr of 1:3.1:1.5. These relativities are slightly temperature dependent in the sense of greater selectivity at lower temperatures. This is again indicative of an activated process as might have been expected. The non-monotonic reactivity order is reminiscent of the sequence Me:Et:*i*Pr of 1:1.40:0.47 obtained by Casanova, Werner and Schuster[35] in the isoelectronic isonitrile-nitrile (RN≡C → RC≡N) rearrangement, except that the rate for the isopropyl group is even slower than that for the methyl group. For the vinylidene rearrangement, as for the isonitrile isomerisation, two effects are needed to explain these sequences. A hyperconjugative effect will lead to increasing stabilisation of the positively charged migrating carbon atom in the transition state in the order methyl to ethyl to isopropyl; this would mean rate increases in this sequence. However, as the bulk of the alkyl group increases, steric or statistical factors may lead to congestion or restriction of the number of rotameric forms in the transition state; this would cause rate decelerations. Thus a combination of these effects offers a plausible explanation of these findings. This is supported by theoretical calculations.[29]

Lastly it is worth pointing out that the relative rates for the minor processes in these vinylidenes are very similar in magnitude. Thus for methylethylvinylidene (**18**), $k_{-b}:k_{-c}$ (Me) is 0.25 and for methylisopropylvinylidene (**6**), $k_{-e}:k_{-f}$ (Me) is 0.32. This provides a reassuring check that for different vinylidenes the same type of process (primary C–H insertion or methyl group shift) has approximately the same rate constant.

Rate constants for cyclopropene ring opening to vinylidenes: We have pointed out previously the rather striking decline in the relative proportions of alkyne product with 1-alkyl substitution.[12, 14] It is now clear that part of the reason for this is the reversibility of the cyclopropene ring opening to vinylidenes. With the analysis of this work we can now focus specifically on the ring-opening process. Arrhenius parameters for k_a, k_b, k_d and k_e (Table 11) are reasonably self-consistent. Activation energies are comparable and entropies of activation are all small and negative consistent with a fairly tight transition state; this is to be expected for a process involving ring opening synchronous with H-migration across the opening bond. For comparison purposes we have calculated rate constants at 500 K. These are shown in Table 14, which also includes rate constants for some other cyclopropenes. For three of these (cyclopropene itself, 3-methyl- and 3,3-dimethyl-cyclopropenes) we may reasonably presume that ring opening is synonymous with alkyne formation, because in these cases the alkyne-forming step from the vinylidene intermediates involve only H-atom shifts and these are known to be very fast.[36] For 1-methylcyclopropene, we have estimated, with the aid of our intramolecular relative rates determined in the previous section, that ring opening should be about 25% faster than alkyne formation. We have therefore increased the published rate constant[9] by this amount.

The figures for relative rate constants show a pleasing self-consistency. In the first place the variation is very small for a process in which strong substituent effects are not anticipated. Methyl groups at the 3-position tend to increase the rate slightly. This is perhaps not too surprising, since it is the site of the breaking bond and arriving H atom, and is expected to be

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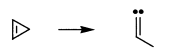
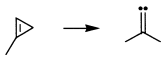
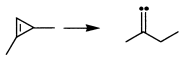
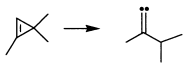
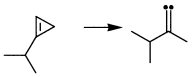
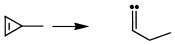
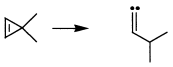
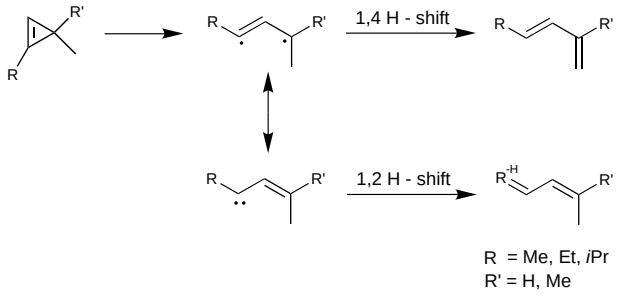
Table 14. Comparison of rate constants (500 K) for formation of vinylidenes from cyclopropenes.

Reaction	$10^4\ k\ [s^{-1}]$	$k_{rel}\ \sigma$[a]	Ref.
	7.32[b]	1	[8]
	1.80[c]	0.49	[9]
	2.40	0.66	this work
	1.91	0.52	this work
	1.33	0.36	this work
	2.12	0.58	this work
	10.46[b]	1.43	[7]
	9.62[b]	1.31	[37]

[a] σ is path degeneracy. [b] Values assumed equal to those for alkyne formation (see text). [c] Value increased from alkyne formation to allow for reversibility of formation (see text).

positively charged in the transition state. Less evident is that alkyl groups in the 1-position, which is remote from the reaction site, tend to exert a retarding effect. The only example that appears slightly anomalous is that of 1,3,3-trimethylcyclopropene (**5**) for which the retarding effect seems a bit large. Since **5** is the subject of the present work, we feel it is amongst the least likely to be in error. However, because we are discussing factors of somewhat less than two, it is worth remembering that a factor of two corresponds in energy terms to less than 3 kJ mol^{-1} at 500 K. Thus very small conformational effects in a specific case can easily account for such anomalies.

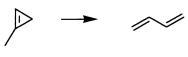
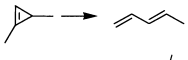
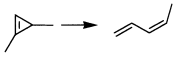
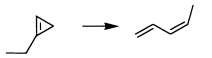
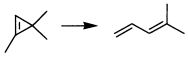
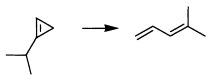
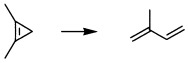
Rate constants for diene-forming pathways: As was shown previously[14, 37] there are two distinct pathways to dienes that can be explained as arising from H-shifts in the 1,3-diradical or vinylcarbene forms of the intermediate[38] still thought to be the species involved in their formation. Scheme 11 shows the



Scheme 11.

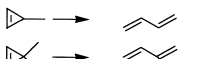
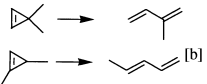
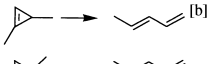
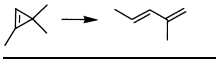
general mechanism for the formation of 1-alkyl-3-methyl-substituted cyclopropenes. The 1,2 H-shift, proceeding from the vinylcarbene form of the intermediate requires a 1-alkyl substituent, while the 1,4 H-shift proceeding from the diradical form of the intermediate requires a 3-alkyl substituent. The Arrhenius parameters for these pathways (Tables 5–8) are comparable and generally reasonable (small negative entropies of activation are consistent with restricted rotation in the transitions states arising from the H-atom migration). Once again we have found that for deeper understanding, the best approach is to compare rate constants at 500 K. The comparison for dienes formed by the 1,2 H-shift process is shown in Table 15, while for those formed through the 1,4 H-shift process is shown in Table 16. In most cases

Table 15. Comparison of rate constants (500 K) for formation of 1,3-dienes by 1,2 H-shift (vinylcarbene intermediate) from cyclopropenes.

Reaction	$10^4\ k\ [s^{-1}]$	$k_{rel}\ \sigma$[a]	Ref.
	1.07	1	[9]
	1.73[b]	1.62[c]	this work
	0.676	0.63[c]	this work
	11.7	16.4[d]	this work
	6.43	9.02[d]	this work
	7.46	6.97	this work
	27.5	77.0	this work
	0.137	0.064	[10]

[a] σ is path degeneracy. [b] Maximum value: assumes product comes *only* by this pathway. [c] Total diene rate constant (from **15**) = 2.25. [d] Total diene rate constant (from **16**) = 25.42.

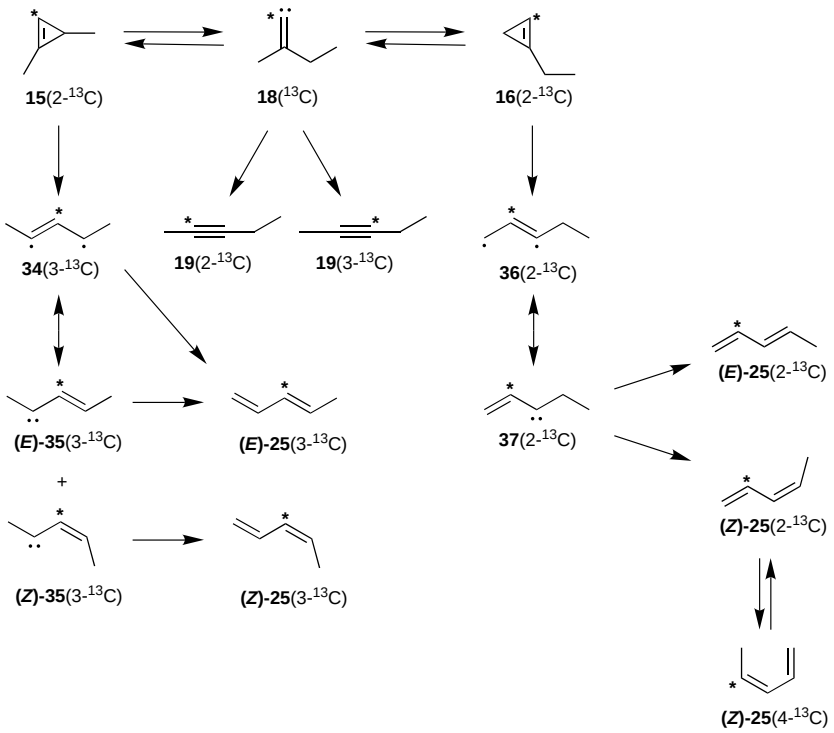
Table 16. Comparison of rate constants (500 K) for formation of 1,3-dienes by 1,4 H-shift (diradical intermediate) from cyclopropenes.

Reaction	$10^4\ k\ [s^{-1}]$	$k_{rel}\ \sigma$[a]	Ref.
	11.7	1	[7]
	9.87	0.42	[37]
 [b]	1.73[b]	0.30	this work
	9.09	0.78	this work

[a] σ is path degeneracy. [b] Maximum value: assumes product comes *only* by this pathway.

there is no ambiguity, but for *trans*-1,3-pentadiene [**(*E*)-25**] formed from **15** we cannot unambiguously assign it to either process. The comparisons shown here are extended to compare the data found in the present work with those from other simple cyclopropenes. We do not, however, include the larger 1-alkyl-3,3-dimethylcyclopropenes, which have been discussed earlier.[14] An examination of the relative rate constants in Table 15 reveals some quite striking variations. The largest of these arises amongst the 1-alkylcyclopropenes themselves, between 1-methyl-, 1-ethyl- (**16**) and 1-isopropyl-cyclopropene (**17**) for which the numbers, already statistically corrected for the number of migrating H atoms, give rate

ratios of 1:25:77. Since these figures correspond to insertion into primary:secondary:tertiary C–H bonds of the vinylcarbene form of the intermediate, they may be compared directly with those of Table 13. They are similar to, but actually larger than, those found earlier from analysis of 2,4-diene formation from the 1-alkyl-3,3-dimethylcyclopropenes.[14] Thus the pathways via the vinylcarbene intermediates without the added dimethyl substituents, as studied here, are even more selective than those with them. What is not clear is whether these rate effects are due to different stabilisations of the vinylcarbenes, such as by hyperconjugation,[34] or different propensities for H migration (or a combination of both). It is worth pointing out that unlike for the vinylidene pathway, we are not yet able to separate the substituent effects on ring opening (step 1) from those of rearrangement of the intermediate (step 2) for the vinylcarbene/diradical pathways. However it is known from the elegant racemisation experiment of Bergman's group[39] more than 25 years ago that ring closure of these intermediates is significantly faster than rearrangement (and the data cannot be explained by the reversible involvement of vinylidene intermediates, although their involvement was unknown at that time). This means that step 2 is probably rate-determining in these processes.



Scheme 12.

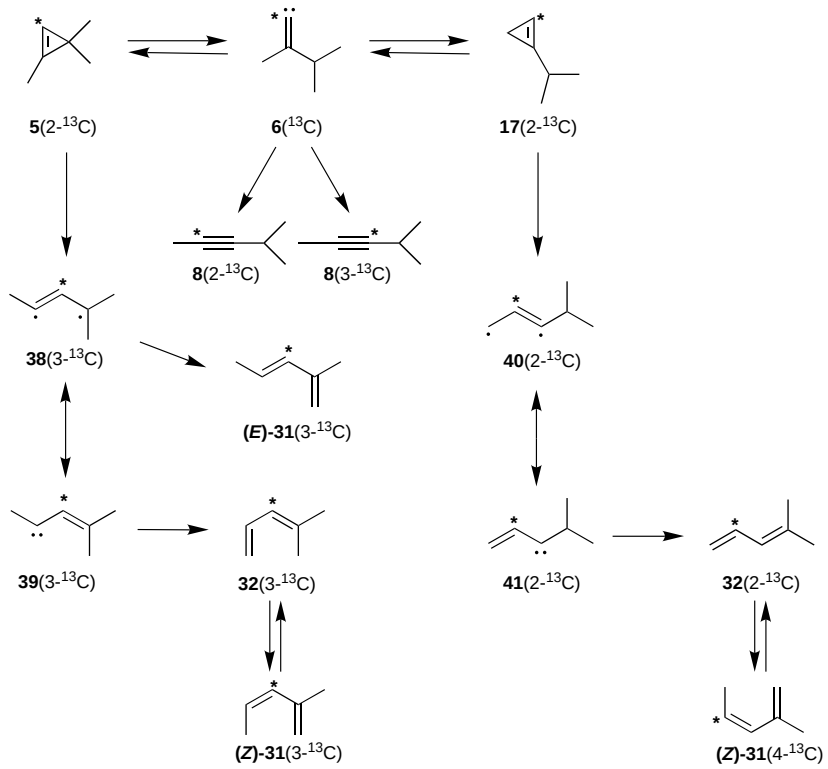
Another quite large variation involves the 1-methylcyclopropenes with increasing 3-methyl substitution. The sequence 1-methyl-, 1,3-dimethyl- (**15**) and 1,3,3-trimethyl-cyclopropene (**5**) give ratios 1:2.2:7.0, which correspond to a remote substituent effect on the same primary 1,2 H-atom migration assuming all diene formation from **15** comes from this route. It is hard to imagine a direct kinetic effect here, but it is easier to believe that the rates are indirectly enhanced by a methyl group stabilisation effect on the intermediate itself that assists the cyclopropene bond-breaking process. The case of 1,2-dimethylcyclopropene shows up another, different, remote substituent effect in which the non-participating methyl group exerts a strong retardation effect on diene formation. This is similar to, but stronger than the effect found on the ring-opening pathway to vinylidene (see previous section).

Examination of the relative rates in Table 16 shows that for the 1,4 H-shifts, rate constant variation is much less than for the 1,2 H-shifts. As we commented before[14] there is no obvious factor that should lead to much variation and therefore we conclude that small strain or conformational effects will account for the actual variation. It should be added that because of the ambiguity of the mechanism of **15** → ***(E)*-25** the value represents an upper limit and therefore this process appears to be a little on the slow side.

The ^{13}C-labelling pattern in the diene products: The labelling pattern found amongst the diene products of these cyclopropene isomerisations provides further general support for the overall mechanisms of their rearrangements. Schemes 12 and 13 show the detailed pathways of their formation starting from **15**(2-^{13}C) and **5**(2-^{13}C), respectively. The key point in these mechanisms is that *direct* formation of dienes leads in all cases to 3-^{13}C-labelled products, whereas *indirect* formation of dienes [via **16**(2-^{13}C) in the case of **15**(2-^{13}C) and **17**(2-^{13}C) in the case of **5**(2-^{13}C)] leads to 2-^{13}C-labelled products. Thus, since the isomerisations **15** → **16** and **5** → **17** are relatively minor pathways, the majority of the dienes formed have 3-^{13}C labels. Nevertheless the observation of 2-^{13}C-labelled products in small amounts is an important added support for the overall mechanism proposed.

The minor products: All the cyclopropenes studied here produce allenes in minor quantities. They are formed in $< 1\,\%$ amounts in all cases. The scatter in data at these low levels means that Arrhenius parameters (Tables 5–8) have very large uncertainties and this makes a quantitative discussion not very useful. From our own earlier studies[8, 9] and other investigations in which allenes are more prominent products,[37, 40, 41] it is thought most likely that allene formation occurs through a 1,2 H-shift (or other 1,2 group-shift) in the vinylcarbene intermediate. Since this shift involves a more strained transition state than the H shifts that lead to the

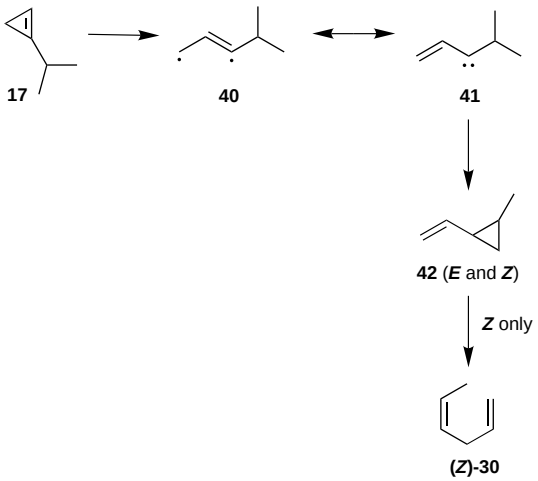
0947-6539/00/0611-1974 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 11



Scheme 13.

conjugated dienes, this rationalizes the small yields found in present systems.

The only other minor product detected was *cis*-1,4-hexadiene [**(*Z*)-30**] formed in the isomerisation of **17** at levels of up to 1%. The likely formation route for this is shown in Scheme 14; this route involves the intermediacy of *cis*-1-



Scheme 14.

methyl-2-vinylcyclopropane [**(*Z*)-42**], which is known to rearrange rapidly to **(*Z*)-30** at the temperatures of study.[42, 43] The formation of **(*Z*)-42** can be understood as a 1,3-C–H insertion product of the vinylcarbene intermediate. A similar vinylcyclopropane has actually been found as a major product (26%) in the pyrolysis of 1-*tert*-butyl-3,3-dimethylcyclopropene by Streeper and Gardner.[44] In this latter case presumably the extra methyl groups act as an effective inhibitor of the secondary rearrangement to the *cis*-1,4-diene product. The formation of vinylcyclopropanes or their rearrangement products has not been observed in our earlier studies[14] and we presume that the low levels found here reflect the basic difficulty of the process. We suspect that the presence of the *tert*-butyl group is crucial to its observation in higher yields, since the *tert*-butyl group has no H atom available for the more favourable 1,2 H-shift pathway characteristic of the vinylcarbene behaviour in the systems we have studied here and earlier.[14] Interestingly a similar situation exists in the dialkylcarbenes.[4, 34] Despite a search by GC and NMR spectroscopy for it, we could find no evidence of the *trans*-isomer **(*E*)-42** nor its higher temperature rearrangement product, 4-methylcyclopentene (**43**). Presumably if formed, the levels were below detection.

The overall product distribution pattern: The analysis up to now has focussed on mechanisms of formation and variations of rate of particular product types (alkynes and dienes). It is worth re-examining the product distributions for the four cyclopropenes studied here, in order to see the consequences of these considerations. From the kinetic analysis at 500 K, the initial product distributions have been calculated and are shown in Table 17. It can be seen that alkyne yields vary from a high of 80.9% from **15** to a low of 14.1% from **17**. 1,3-dienes on the other hand vary from a low of 13.9% from **15** to a high of 76.8% from **5**. These variations can now be largely understood. 1,3-Dimethylcyclopropene (**15**) ring-opens to form a vinylidene, **18**, with a low degree of reversibility, that

Table 17. Comparison of patterns of product distribution for the four cyclopropenes under investigation at 500 K.

Reactant		10^5 k [s^{-1}]	Product [%] alkyne	dienes	cyclopropene	other
	**15**	17.3	80.9	13.9	4.9	0.4
	**16**	36.8	30.1	49.2	19.7	1.0
	**5**	21.6	19.9	76.8	2.6	0.7
	**17**	48.4	14.1	56.7	27.8	1.5

leads on to alkyne. Ring opening of **15** to vinylcarbene/diradical, produces an intermediate with no special stability or high propensity to undergo H shifts to dienes. Thus for **15** the alkyne yield is high and diene yields are low. 1-Isopropylcyclopropene (**17**), on the other hand, ring-opens to form a vinylidene, **6**, with a high propensity to ring-close to give an isomer rather than shift an alkyl group to make alkyne. Ring opening of **17** to a vinylcarbene/diradical gives an intermediate with a very high propensity to undergo a 1,2 H-shift. Thus for **17** the alkyne yield is low, the isomer yield is substantial and the diene yield is high. A similar explanation of the product patterns of **16** and **5** may be given. Through these studies we are thus beginning to understand the underlying factors that give rise to the considerable and apparently bewildering variation in product distribution amongst seemingly similar cyclopropenes.

Experimental Section

General Remarks: IR: Nicolet DX320 FT-IR spectrophotometer. UV: Hewlett Packard HP8452A diode array spectrophotometer. ^{1}H NMR and ^{13}C NMR: Bruker AM400, JEOL JNM EX400, Bruker DPX250, Bruker AC200F; solvent $CDCl_3$; ^{1}H NMR: $\delta = 0$ for tetramethylsilane; ^{13}C NMR: $\delta = 77.05$ for $CDCl_3$. Substitution level of C atoms was obtained by DEPT-135 technique. If necessary selective ^{1}H decoupling or ^{13}C,^{1}H-COSY were performed to obtain the correct C–H assignment. Integration of ^{13}C NMR signals were performed by using the inverse-gated decoupling method to suppress NOE effects with a pulse delay of 120 s to avoid any relaxation effects.[28] If possible, the ^{13}C,^{13}C- and ^{13}C,^{1}H-coupling were additionally extracted from ^{13}C-enriched compounds. MS: Finnigan MAT8430 (EI, 70 eV); GC-MS: Carlo Erba HRGC5160, 30 m DB1 fused silica capillary column/Finnigan MAT4515 (EI, 40 eV). Analytical GC: DANI 86.10HT gas chromatograph, 50 m SE-54-DF-0.35 mm fused silica capillary column; preparative GC: Shimadzu GC-8A, 3 and 6 m packed steel columns. Solvents were purified prior to their use.

Preparation of the compounds: The following compounds were obtained by literature methods: 4-methyl-2-pentyne (**8**),[45] 2-(chloromethyl)-1-butene (**20**),[46, 47] 2,3-pentadiene (**24**),[48] 2-methyl-2,3-pentadiene (**27**)[49, 50] and 4-methyl-1,2-pentadiene (**28**).[49, 50]

General procedure for preparation of trihalogenocyclopropanes (A): Sodium hydroxide (4.2 equiv) in water (7–18 mL, 60 °C) was added to a rapidly stirred solution of halogenoalkene (1 equiv), chloroform or bromoform (1.5–5 equiv), cetrimide (1 mmol) and ethanol (1 mL). The reaction was stirred vigorously for 2 h at 50 °C and then stirred overnight at room temperature. The reaction mixture was worked-up by diluting with water (250 mL) and extracting with dichloromethane (3×100 mL). The combined organic extracts were washed with water (2×50 mL), dried with sodium sulfate and filtered, and the solvent was removed. Liquids were obtained by fractional distillation in vacuo to give the trihalogenocyclopropane as a thick colorless oil; solids were obtained by Kugelrohr distillation to give the trihalogenocyclopropane as a white crystalline solid.

General procedure for preparation of substituted cyclopropenes (B): Methyllithium (2.8 equiv, 1.5 M in diethyl ether) was carefully added to a solution of trihalogenocyclopropane (1 equiv) in diethyl ether (20–80 mL) at −78 °C over a period of 1 h. The reaction mixture was slowly warmed up to room temperature and stirred for 0.5 h. The solvent was removed in vacuo (0.1 mbar) at −20 °C. The residue, a slightly yellow solid, was cooled to −30 °C and quenched carefully with water (10 mL). Distillation of the reaction mixture in vacuo (20 mbar) was carried out at room temperature and the crude product was obtained in a −80 °C cooled tube. Purification by preparative gas chromatography (ODPN, 6 m, 30 °C) gave the cyclopropene as a colorless, volatile liquid.

1,1,2-Tribromo-(*E*)/(*Z*)-2,3-dimethylcyclopropane ((*E*)/(*Z*)-22a): General procedure A: Sodium hydroxide (16.3 g, 406 mmol) in water (18 mL), **(*E*)/(*Z*)-21a** (13.2 g, 98 mmol, *E* isomer: 33%, *Z* isomer: 67%), bromoform (49.4 g, 196 mmol), cetrimide (0.4 g, 1 mmol) and ethanol (1 mL) yielded **(*E*)/(*Z*)-22a** (19.6 g, 64 mmol, 65%). *E* isomer: 33%, *Z* isomer: 67% (^{1}H NMR); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.22$ (d, $^3J_{4,3} = 6.6$ Hz, 3H; 4-H, *E* isomer), 1.32 (ps d, $^3J_{4,3} = 6.6$ Hz, 3H; 4-H, *Z* isomer), 1.40 (m, 1H; 3-H, *Z* isomer), 1.87 (s, 3H; 5-H, *E* isomer), 1.96 (q, $^3J_{3,4} = 6.6$ Hz, 1H; 3-H, *E* isomer), 2.11 (s, 3H; 5-H, *Z* isomer); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta =$ 11.93 (q, C-4, *E* isomer), 16.15 (q, C-4, *Z* isomer), 23.98 (q, C-5, *E* isomer), 31.11 (q, C-5, *Z* isomer), 36.36 (d, C-3, *Z* isomer), 38.70 (d, C-3, *E* isomer), 42.55, 42.63, 42.73, 47.66 (s, C-1, C-2, *E*/*Z* isomers); IR (film): $\tilde{\nu} = 2981$ (m), 2930 (s, C–H-ν), 2866 (w), 1446 (s, C–H-δ), 1379 (m, C–H-δ), 1245 (w), 1121 (m), 1074 (m), 987 (s), 952 (w), 825 (m), 808 (w), 791 (w), 764 (vs, C–Br-ν), 753 cm^{-1} (s); UV (hexane): λ_{max} (lg ε) = 202 nm (3.45); MS (EI, 40 eV): *m*/*z* (%): 310 (0.02) $[M]^+$ ($3\,^{81}$Br), 308 (0.1) $[M]^+$ (^{79}Br, $2\,^{81}$Br), 306 (0.1) $[M]^+$($2\,^{79}$Br, ^{81}Br), 304 (0.02) $[M]^+$ ($3\,^{79}$Br), 228 (45), 227 (95), 226 (50), 147 (15), 145 (17), 66 (61), 65 (100), 51 (16).

1,3-Dimethylcyclopropene (15): General procedure B: Methyllithium in diethyl ether (140 mL, 160 mmol, 1.14 M) and **(*E*)/(*Z*)-22a** (17.4 g, 57 mmol) in diethyl ether (80 mL) yielded **15** (1.47 g, 21.6 mmol, 38%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.01$ (ps d, $^3J_{4,3} = 4.6$ Hz, 3H; 4-H), 1.42 (qd, $^3J_{3,4} =$ 4.6, $^3J_{3,2} = 1.8$ Hz, 1H; 3-H), 2.09 (d, $^4J_{5,2} = 1.0$ Hz, 3H; 5-H), 6.62 (m, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.09$ (q, C-5), 12.51 (d, C-3), 21.59 (q, C-4), 106.52 (d, C-2), 124.84 (s, C-1); IR (CCl_4): $\tilde{\nu} = 3121$ (vw), 3084 (vw), 2954 (vs, C–H-ν), 2915 (vs, C–H-ν), 2858 (s, C–H-ν), 2713 (w), 2686 (w), 1772 (s, C=C-ν), 1439 (s, C–H-δ), 1372 (m, C–H-δ), 1352 (s), 1087 (s), 1022 (w), 969 (s), 955 (s), 698 cm^{-1} (vs, C–H-ν); UV (hexane): $\lambda_{max} =$ 194 nm (Due to the high volatility of **15** the extinction coefficient ε could not be determined); MS (EI, 40 eV, headspace): *m*/*z* (%): 68 (21) $[M]^+$, 67 (100), 65 (14), 53 (75), 51 (18), 41 (57), 39 (85), 38 (15), 27 (72).

1-Bromo-2,2-dichloro-1,3,3-trimethylcyclopropane (22c): General procedure A: Sodium hydroxide (8.2 g, 204 mmol) in water (9 mL), **21c** (7.4 g, 50 mmol), chloroform (7.2 g, 60 mmol), cetrimide (0.3 g, 0.8 mmol) and ethanol (1 mL) yielded **22c** (6.91 g, 29.8 mmol, 59.6%) as a white crystalline solid (subl. temp.: 90 °C, 0.1 mbar). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.33$, 1.46 (s, 2×3H; 4-H), 1.95 (s, 3H; 5-H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 18.42$ (q, C-5) 24.05, 24.49 (q, C-4), 33.02 (s, C-3), 50.30 (s, C-1), 73.21 (s, C-2); IR (KBr): $\tilde{\nu} = 3007$ (s, C–H-ν), 2967 (vs, C–H-ν), 2934 (vs, C–H-ν), 2865 (s), 1632 (m), 1606 (m), 1459 (s, C–H-δ), 1447 (s), 1439 (s), 1377 (vs), 1217 (m), 1168 (m), 1111 (m), 1087 (vs), 1071 (s), 1018 (vs), 992 (m), 933 (s), 890 (m), 867 (vs, C–Cl-ν), 812 (vs, C–Cl-ν), 791 (w), 709 (vs, C–Br-ν), 592 cm^{-1} (vs, C–Br-ν); UV (hexane): λ_{max} (lg ε) = 192 nm (3.20); MS (EI, 40 eV): *m*/*z* (%): 219 (0.1) $[M-15]^+$ (^{81}Br, ^{35}Cl, ^{37}Cl/^{79}Br, $2\,^{37}$Cl), 217 (0.4) $[M-15]^+$ (^{81}Br, $2\,^{35}$Cl/^{79}Br, ^{35}Cl, ^{37}Cl), 215 (0.02) $[M-15]^+$ (^{79}Br, $2\,^{35}$Cl), 199 (2) $[M-Cl]^+$ (^{81}Br, ^{37}Cl), 197 (11) $[M-Cl]^+$ (^{79}Br, ^{37}Cl/^{81}Br, ^{35}Cl), 195 (9) $[M-Cl]^+$ (^{79}Br, ^{35}Cl), 155 (10) $[M-Br]^+$ ($2\,^{37}$Cl), 153 (64) $[M-Br]^+$ (^{35}Cl, ^{37}Cl), 151 (100) $[M-Br]^+$ ($2\,^{35}$Cl), 127 (3) $[M-Br-C_2H_4]^+$ ($2\,^{37}$Cl), 125 (13) $[M-Br-C_2H_4]^+$ (^{35}Cl, ^{37}Cl), 123 (20) $[M-Br-C_2H_4]^+$ ($2\,^{35}$Cl), 117 (10) $[M-Br-Cl-H]^+$ (^{37}Cl), 115 (26) $[M-Br-Cl-H]^+$ (^{35}Cl), 79 (65), 77 (45), 53 (12), 51 (10).

1,3,3-Trimethylcyclopropene (5): General procedure B: Methyllithium in diethyl ether (53.5 mL, 80 mmol, 1.5 M) and **22c** (6.5 g, 28 mmol) in diethyl ether (30 mL) gave **5** (0.85 g, 10.3 mmol, 36.9%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.09$ (d, $^4J_{4,2} = 0.7$ Hz, 6H; 4-H), 2.03 (d, $^4J_{5,2} = 1.0$ Hz, 3H; 5-H), 6.74 (m, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 10.05$ (q, C-5), 17.90 (s, C-3), 27.07 (q, C-4), 112.62 (d, C-2), 131.05 (s, C-1); IR (film): $\tilde{\nu} =$ 3107 (vw, cyclo-C–H-ν), 2961 (vs, C–H-ν), 2932 (vs, C–H-ν), 2918 (vs, C–H-ν), 2858 (vs, C–H-ν), 2713 (w), 1762 (s, C=C-ν), 1439 (vs, C–H-δ), 1364 (vs, C–H-δ), 1262 (m, C–H-δ), 1189 (m), 1174 (m), 1118 (m), 1089 (w), 1019 (m), 936 (m), 698 cm^{-1} (w); MS (EI, 70 eV): *m*/*z* (%): 82 (6) $[M]^+$, 81 (8) $[M-H]$, 67 (100) $[M-CH_3]$, 65 (15), 53 (12), 51 (10), 41 (72), 39 (53).

1,1-Dibromo-2-chloro-2-isopropylcyclopropane (22d): General procedure A: Sodium hydroxide (16.3 g, 408 mmol) in water (18 mL), **21d** (10.2 g, 98 mmol), bromoform (64.1 g, 254 mmol), cetrimide (0.4 g, 1 mmol) and ethanol (1 mL) yielded **22d** (16.4 g, 59.4 mmol, 60.8%). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.15$, 1.18 ($2 \times$ d, $^3J_{CH_3,H\text{-isopropyl}} = 6.6$ Hz, $2 \times CH_3$, 4-CH_3-isopropyl), 1.79, 1.93 (m, 2×1H; 3-H), 1.98 (sept, $^3J_{H\text{-isopropyl},CH_3} =$ 6.6 Hz, 1H; H-isopropyl); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 17.89$, 19.62 ($2 \times$ q, $2 \times CH_3$-isopropyl) 33.90 (s, CBr_2), 37.15 (t, C-3), 37.50 (d, CH-isopropyl), 58.14 (s, C-2); IR (KBr): $\tilde{\nu} = 3078$ (w, C–H-ν-cyclopropane), 2972 (vs, C–H-ν), 2933 (s, C–H-ν), 2873 (m), 1459 (m, C–H-δ), 1368 (m), 1193 (m), 1056 (m), 1010 (vs), 953 (m), 805 (s, C–Cl-ν), 695 cm^{-1} (vs, C–Br-ν); UV (hexane): λ_{max} (lg ε) = 204 nm (3.39); MS (EI, 40 eV): *m*/*z* (%): 278

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(0.01) $[M]^+$ (^{79}Br, ^{81}Br, ^{37}Cl/2 ^{79}Br, ^{35}Cl), 276 (0.01) $[M]^+$ (^{79}Br, ^{81}Br, ^{35}Cl/2 ^{79}Br, ^{37}Cl), 274 (0.003) $[M]^+$ (2 ^{79}Br, ^{35}Cl), 243 (0.3) $[M-Cl]^+$ (2 ^{81}Br), 241 (0.5) $[M-Cl]^+$ (^{79}Br, ^{81}Br), 239 (0.3) $[M-Cl]^+$ (2 ^{79}Br), 237 (0.05) $[M-$ isopropyl$]^+$ (2 ^{81}Br, ^{37}Cl), 235 (0.7) $[M-$ isopropyl$]^+$ (^{79}Br, ^{81}Br, ^{37}Cl/2 ^{81}Br, ^{35}Cl), 233 (0.85) $[M-$ isopropyl$]^+$ (2 ^{79}Br, ^{37}Cl/^{79}Br, ^{81}Br, ^{35}Cl), 231 (0.44) $[M-$ isopropyl$]^+$ (2 ^{79}Br, ^{35}Cl), 199 (1.3) $[M-Br]^+$ (^{81}Br, ^{37}Cl), 197 (2.7) $[M-Br]^+$ (^{79}Br, ^{37}Cl/^{81}Br, ^{35}Cl), 195 (1.9) $[M-Br]^+$ (^{79}Br, ^{35}Cl), 118 (1.0) $[M-2Br]^+$ (^{37}Cl), 116 (2.7) $[M-2Br]^+$ (^{35}Cl), 107 (1.9), 105 (1.8), 92 (31), 90 (100).

1-Isopropylcyclopropene (17): General procedure B: Methyllithium in diethyl ether (107 mL, 160 mmol, 1.5 M) and **22d** (15.7 g, 56.8 mmol) in diethyl ether (80 mL) gave **17** (1.47 g, 17.9 mmol, 31.5 %). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.90$ (d, $^3J_{3,2} = 1.8$ Hz, 2H; 3-H), 1.15 (d, $^3J_{5,4} = 6.9$ Hz, 6H; 5-H), 2.73 (d sept, $^3J_{4,5} = 6.9$, $^4J_{4,2} = 1.24$ Hz, 1H; 4-H), 6.37 (m, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 4.87$ (t, C-3), 20.15 (q, C-5), 26.43 (d, C-4), 96.01 (d, C-2), 125.92 (s, C-1); IR (film): $\tilde{\nu} = 3151$ (vw, cyclo-C–H-ν), 2966 (vs, C–H-ν), 2935 (m, C–H-ν), 2880 (vs, C–H-ν), 1774 (w, C=C-ν), 1467 (m, C–H-δ), 1459 (m, C–H-δ), 1382 (w), 1364 (w), 1310 (w), 1103 (w), 1023 (vs), 989 (m), 958 (w), 929 (m), 846 (w), 713 cm^{-1} (s); UV (hexane): λ_{max} (lg ε) = 192 nm (3.2); MS (EI, 40 eV, headspace): m/z (%): 82 (0.5) $[M]^+$, 81 (8) $[M-H]^+$, 67 (82) $[M-CH_3]^+$, 65 (20), 53 (20), 41 (100), 39 (90), 27 (55).

1-Bromo-2,2-dichloro-(*E*)/(*Z*)-1,3-dimethyl-[2-^{13}C]cyclopropane ((2-^{13}C)-(*E*)/(*Z*)-22b): General procedure A: Sodium hydroxide (5.7 g, 141 mmol) in H_2O (7 mL), **(*E*)/(*Z*)-21a** (4.6 g, 33.9 mmol), 69 % enriched [^{13}C]chloroform (5.0 g, 41.6 mmol), cetrimide (0.4 g, 1 mmol), ethanol (1 mL) and with dibromomethane instead of dichloromethane for work up gave (2-^{13}C)-**(*E*)/(*Z*)-22b** (3.09 g, 14.1 mmol, 34 %). 69 % ^{13}C-enriched (MS analysis); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.22$ (d, $^3J_{4,3} = 6.6$ Hz, 3H; 4-H, *E* isomer), 1.31 (m, 3H; 4-H, *Z* isomer), 1.41 (m, 1H; 3-H, *Z* isomer), 1.82 (s, 3H; 5-H, *E*/^{12}C isomer), 1.82 (d, $^3J_{5,13C} = 5.6$ Hz, 3H; 5-H, *E*/^{13}C isomer), 1.96 (m, 1H; 3-H, *E* isomer), 2.04 (s, 3H; 5-H, *Z*/^{12}C isomer), 2.04 (d, $^3J_{5,13C} = 3.0$ Hz, 3H; 5-H, *Z*/^{13}C isomer); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 9.56$ (q, C-4, *E* isomer), 13.66 (q, C-4, *Z*/^{12}C isomer), 13.66 (qd, $^2J_{4,13C} = 5.1$ Hz, C-4, *Z*/^{13}C isomer), 21.75 (q, C-5, *E* isomer), 28.61 (q, C-5, *Z* isomer), 35.34 (d, C-3, *Z*/^{12}C isomer), 35.34 (dd, $^1J_{3,13C} = 14.8$ Hz, C-3, *Z*/^{13}C isomer), 37.60 (d, C-3, *E*/^{12}C isomer), 37.60 (dd, $^1J_{3,13C} = 14.1$ Hz, C-3, *E*/^{13}C isomer), 42.35, 47.40 (s, C-1, *E*/*Z*/^{12}C isomers), 42.35, 47.40 (d, $^1J_{3,13C} = 14.5$ Hz, C-1, *E*/*Z*/^{13}C isomers), 68.34 (s, C-2); MS (EI, 70 eV): m/z (%): 221 (0.5) $[M]^+$ (^{79}Br, ^{13}C, 2 ^{37}Cl/^{81}Br, ^{13}C, ^{35}Cl, ^{37}Cl), 219 (0.4) $[M]^+$ (^{79}Br, ^{13}C, ^{35}Cl, ^{37}Cl/^{81}Br, ^{13}C, 2 ^{35}Cl), 218 (0.1) $[M]^+$ (^{79}Br, ^{12}C, ^{35}Cl, ^{37}Cl/^{81}Br, ^{12}C, 2 ^{35}Cl), 217 (0.2) $[M]^+$ (^{79}Br, ^{13}C, 2 ^{35}Cl), 216 (0.05) $[M]^+$ (^{79}Br, ^{12}C, 2 ^{35}Cl), 208 (0.1) $[M-CH_3]^+$ (^{81}Br, ^{13}C, 2 ^{37}Cl), 207 (0.1) $[M-CH_3]^+$ (^{81}Br, ^{12}C, 2 ^{37}Cl), 206 (0.6) $[M-CH_3]^+$ (^{81}Br, ^{13}C, ^{35}Cl, ^{37}Cl/^{79}Br, ^{13}C, 2 ^{37}Cl), 205 (0.4) $[M-CH_3]^+$ (^{81}Br, ^{12}C, ^{35}Cl, ^{37}Cl/^{79}Br, ^{12}C, 2 ^{37}Cl], 204 (1.4) $[M-CH_3]^+$ (^{79}Br, ^{13}C, ^{35}Cl, ^{37}Cl/^{81}Br, ^{13}C, 2 ^{35}Cl), 203 (0.7) $[M-CH_3]^+$ (^{79}Br, ^{12}C, ^{35}Cl, ^{37}Cl/^{81}Br, ^{12}C, 2 ^{35}Cl), 202 (0.9) $[M-CH_3]^+$ (^{79}Br, ^{13}C, 2 ^{35}Cl), 201 (0.4) $[M-CH_3]^+$ (^{79}Br, ^{12}C, 2 ^{35}Cl), 186 (1.7) $[M-Cl]^+$ (^{81}Br, ^{13}C, ^{37}Cl), 185 (1.1) $[M-Cl]^+$ (^{81}Br, ^{12}C, ^{37}Cl), 184 (7.0) $[M-Cl]^+$ (^{79}Br, ^{13}C, ^{37}Cl/^{81}Br, ^{13}C, ^{35}Cl), 183 (3.9) $[M-Cl]^+$ (^{79}Br, ^{12}C, ^{37}Cl/^{81}Br, ^{12}C, ^{35}Cl), 182 (5.3) $[M-Cl]^+$ (^{79}Br, ^{13}C, ^{35}Cl), 181 (3.0) $[M-Cl]^+$ (^{79}Br, ^{12}C, ^{35}Cl), 142 (14) $[M-Br]^+$ (^{13}C, 2 ^{37}Cl), 141 (11) $[M-Br]^+$ (^{12}C, 2 ^{37}Cl), 140 (80) $[M-Br]^+$ (^{13}C, ^{37}Cl, ^{35}Cl), 139 (50) $[M-Br]^+$ (^{12}C, ^{37}Cl, ^{35}Cl), 138 (88) $[M-Br]^+$ (^{13}C, 2 ^{35}Cl), 137 (72) $[M-Br]^+$ (^{12}C, 2 ^{35}Cl), 112 (13), 111(10), 110 (19), 109 (15), 104 (10), 102 (30), 101 (16), 66 (100) $[M-Br-Cl_2-H_2]^+$ (^{13}C), 65 (88) $[M^+-Br-Cl_2-H_2]^+$ (^{12}C).

1,3-Dimethyl-[2-^{13}C]cyclopropene ((2-^{13}C)-15): General procedure B: Methyllithium in diethyl ether (27 mL, 40 mmol, 1.5 M) and (2-^{13}C)-**(*E*)/(*Z*)-22b** (3.09 g, 14.1 mmol) in diethyl ether (20 mL) gave crude (2-^{13}C)-**15** (0.4 g, 5.8 mmol, 41 %). 69 % ^{13}C-enriched (MS and ^{13}C NMR analysis); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.01$ (dd, $^3J_{4,3} = 4.5$, $^4J_{4,2} = 0.8$ Hz, 3H; 4-H, ^{12}C isotopomer), 1.01 (ddd, $^3J_{4,13C} = 4.9$, $^3J_{4,3} = 4.5$, $^4J_{4,2} = 0.8$ Hz, 3H; 4-H, ^{13}C isotopomer), 1.42 (m, 1H; 3-H), 2.09 (d, $^4J_{5,2} = 1.1$ Hz, 3H; 5-H, ^{12}C isotopomer), 2.09 (dd, $^3J_{5,13C} = 6.1$, $^4J_{5,2} = 1.1$ Hz, 3H; 5-H, ^{13}C isotopomer), 6.62 (m, 1H; 2-H, ^{12}C isotopomer), 6.62 (dm, $^1J_{2,13C} = 220.4$ Hz, 1H; 2-H, ^{13}C isotopomer); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 11.21$ (q, C-5), 12.62 (d, C-3, ^{12}C isotopomer), 12.62 (dd, $^1J_{3,13C} = 9.4$ Hz, C-3, ^{13}C isotopomer), 21.70 (q, C-4), 106.63 (dd, $^1J_{C,H} = 220.4$ Hz, C-2), 124.50 (s, C-1); MS (EI, 40 eV, headspace): m/z (%): 69 (18) $[M]+$ (^{13}C), 68 (100) $[M]^+$ (^{12}C) or $[M-H]$ (^{13}C), 67 (45) $[M-H]^+$ (^{12}C), 54 (48) $[M-CH_3]^+$ (^{13}C), 53 (29) $[M-CH_3]^+$ (^{12}C), 42 (25), 41 (28), 40 (38), 39 (32).

1-Bromo-2,2-dichloro-1,3,3-trimethyl-[2-^{13}C]cyclopropane ((2-^{13}C)-22c): General procedure A: Sodium hydroxide (10 g, 250 mmol) in H_2O (20 mL), **21c** (6.7 g, 45 mmol), 69 % enriched [^{13}C]chloroform (5.0 g, 41.6 mmol), cetrimide (0.3 g, 0.8 mmol) and ethanol (1 mL) gave (2-^{13}C)-**22c** (6.19 g, 26.7 mmol, 64 %). 69 % ^{13}C-enriched (MS analysis); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.33$ (s, 3H; 4-H, ^{12}C isotopomer), 1.33 (d, $^3J_{4,13C} = 6.1$ Hz, 3H; 4-H, ^{13}C isotopomer), 1.46 (s, 3H; 4-H, ^{12}C isotopomer), 1.46 (d, $^3J_{4,13C} = 6.1$ Hz, 3H; 4-H, ^{13}C isotopomer), 1.95 (s, 3H; 5-H, ^{12}C isotopomer), 1.95 (d, $^3J_{5,13C} = 5.8$ Hz, 3H; 5-H, ^{13}C isotopomer); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 18.48$ (qd, $^2J_{5,13C} = 2.3$ Hz, C-5, ^{13}C isotopomer), 18.49 (q, C-5, ^{12}C isotopomer), 24.10 (qd, $^2J_{4,13C} = 2.2$ Hz, C-4, ^{13}C isotopomer), 24.11 (q, C-4, ^{12}C isotopomer), 24.55 (qd, $^2J_{4,13C} = 2.3$ Hz, C-4, ^{13}C isotopomer), 24.56 (q, C-4, ^{12}C isotopomer), 33.11 (d, $^1J_{3,13C} = 14.5$ Hz, C-3, ^{13}C isotopomer), 33.13 (s, C-3, ^{12}C isotopomer), 50.40 (d, $^1J_{3,13C} = 12.9$ Hz, C-1, ^{13}C isotopomer), 50.41 (s, C-1, ^{12}C isotopomer), 73.29 (s, C-2, [^{13}C,^{37}Cl,^{37}Cl] isotopomer), 73.30 (s, C-2, [^{13}C,^{35}Cl,^{37}Cl] isotopomer), 73.31 (s, C-2, [^{13}C,^{35}Cl,^{35}Cl] isotopomer); UV (hexane): λ_{max} (lg ε) = 192 nm (2.72); MS (EI, 40 eV): m/z (%): 200 (2) $[M-Cl]^+$ (^{81}Br, ^{13}C, ^{37}Cl], 199 (1) $[M-Cl]^+$ (^{81}Br, ^{12}C, ^{37}Cl), 198 (7) $[M-Cl]^+$ (^{79}Br, ^{13}C, ^{37}Cl/^{81}Br, ^{13}C, ^{35}Cl), 197 (3.5) $[M-Cl]^+$ (^{79}Br, ^{12}C, ^{37}Cl/^{81}Br, ^{12}C, ^{35}Cl), 196 (6) $[M-Cl]^+$ (^{79}Br, ^{13}C, ^{35}Cl), 195 (2.5) $[M-Cl]^+$ (^{79}Br, ^{12}C, ^{35}Cl), 156 (10) $[M-Br]^+$ (^{13}C, 2 ^{37}Cl), 155 (7) $[M-Br]^+$ (^{12}C, 2 ^{37}Cl), 154 (55) $[M-Br]^+$ (^{13}C, ^{37}Cl, ^{35}Cl), 153 (28) $[M-Br]^+$ (^{12}C, ^{37}Cl, ^{35}Cl), 152 (86) $[M-Br]^+$ (^{13}C, 2 ^{35}Cl), 151 (37) $[M^+-Br]^+$ (^{12}C, 2 ^{35}Cl), 128 (2.4) $[M-Br-C_2H_4]^+$ (^{13}C, 2 ^{37}Cl), 127 (2) $[M-Br-C_2H_4]^+$ (^{12}C, 2 ^{37}Cl), 126 (13) $[M-Br-C_2H_4]^+$ (^{13}C, ^{37}Cl, ^{35}Cl), 125 (7.5) $[M-Br-C_2H_4]^+$ (^{12}C, ^{37}Cl, ^{35}Cl), 124 (21) $[M-Br]^+$ (^{13}C, 2 ^{35}Cl), 123 (11) $[M-Br-C_2H_4]^+$ (^{12}C, 2 ^{35}Cl), 118 (4) $[M-Br-Cl-H]^+$ (^{13}C,^{37}Cl), 117 (6) $[M-Br-Cl-H]^+$ (^{12}C, ^{37}Cl), 116 (12) $[M-Br-Cl-H]^+$ (^{13}C, ^{35}Cl), 115 (4) $[M-Br-Cl-H]^+$ (^{12}C, ^{35}Cl), 81 (21), 80 (100), 79 (48), 78 (69), 77 (43), 66 (15), 54 (19), 53 (22), 52 (15), 51 (15).

1,3,3-Trimethyl-[2-^{13}C]cyclopropene ((2-^{13}C)-5): General procedure B: Methyllithium in diethyl ether (54.5 mL, 76 mmol, 1.4 M) and (2-^{13}C)-**22c** (6.19 g, 26.7 mmol) in diethyl ether (30 mL) gave (2-^{13}C)-**5** (0.68 g, 8.3 mmol, 31 %). 69 % ^{13}C-enriched (MS and ^{13}C NMR analysis); ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.09$ (s, 6H; 4-H, ^{12}C isotopomer), 1.09 (d, $^3J_{4,13C} = 4.9$ Hz, 6H; 4-H, ^{13}C isotopomer), 2.03 (d, $^4J_{5,2} = 1.0$ Hz, 3H; 5-H, ^{12}C isotopomer), 2.03 (dd, $^3J_{5,13C} = 6.0$, $^4J_{5,2} = 1.0$ Hz, 3H; 5-H, ^{13}C isotopomer), 6.74 (s, 1H; 2-H, ^{12}C isotopomer), 6.74 (d, $^1J_{2,13C} = 217$ Hz, 1H; 2-H, ^{13}C isotopomer); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 9.98$ (q, C-5, ^{12}C isotopomer), 9.98 (qd, $^2J_{5,13C} = 2.9$ Hz, C-5, ^{13}C isotopomer), 17.91 (d, $^1J_{3,13C} = 10.8$ Hz, C-3, ^{13}C isotopomer), 17.93 (s, C-3, ^{12}C isotopomer), 27.05 (qd, $^2J_{4,13C} = 0.6$ Hz, C-4, ^{13}C isotopomer), 27.05 (q, C-4, ^{12}C isotopomer), 112.65 (d, $^1J_{C,H} = 217$ Hz, C-2), 131.01 (d, $^1J_{1,13C} = 58.6$ Hz, C-1, ^{13}C isotopomer), 131.04 (s, C-1, ^{12}C isotopomer); MS (EI, 40 eV, headspace): m/z (%): 83 (3) $[M]^+$ (^{13}C), 82 (10) $[M]^+$ (^{12}C) or $[M-H]$ (^{13}C), 81 (3) $[M-H]^+$ (^{12}C), 68 (100) $[M-CH_3]^+$ (^{13}C), 67 (49) $[M-CH_3]$ (^{12}C), 65 (18), 55 (7), 54 (13), 53 (9), 52 (6), 42 (29), 41 (47).

1-Ethylcyclopropene (16): 2-(Chloromethyl)-1-butene **20** (9.18 g, 88 mmol) was added, over a period of 1 h to a suspension of sodium amide (freshly prepared[51], 6.0 g, 154 mmol) in dibutyl ether (20 mL) in a 100 mL three-neck flask equipped with dropping funnel and condenser ($T = 40\,^\circ$C). The suspension was refluxed for 2 h. The cyclopropene was removed from the reaction vessel by a slow nitrogen stream to a wash-flask that contained sulfuric acid (1 M), then it was passed into a drying tube that contained calcium chloride and finally to a cooled tube (methanol/nitrogen: $-80\,^\circ$C). The crude product was redistilled at low temperature and purified by preparative gas chromatography (ODPN, 6 m, 30 °C) to give the cyclopropene **16** as a very volatile liquid (0.74 g, 10.9 mmol, 12 %). ^{1}H NMR (400.1 MHz, $CDCl_3$): $\delta = 0.90$ (d, $^3J_{3,2} = 1.9$ Hz, 2H; 3-H), 1.16 (t, $^3J_{5,4} = 7.5$ Hz, 3H; 5-H), 2.49 (qd, $^3J_{4,5} = 7.5$, $^4J_{4,2} = 1.4$ Hz, 2H; 4-H), 6.43 (m, 1H; 2-H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 5.28$ (t, C-3), 11.42 (q, C-5), 20.35 (t, C-4), 97.26 (d, C-2), 122.02 (s, C-1); IR (film): $\tilde{\nu} = 3053$ cm^{-1} (w, C–H-ν), 2971 (vs), 2879 (vs, C–H-ν), 1778 (s, C=C-ν), 1459 (s, C–H-δ), 1378 (m, C–H-δ), 1312 (m), 1027 (vs), 944 (s), 899 (m), 700 (s), 678 (s, C–H-ν); UV (hexane): λ_{max} (lg ε) = 194 nm (3.42); MS (EI, 40 eV, headspace): m/z (%): 68 (12) $[M]^+$, 67 (100), 65 (15), 53 (60), 51 (15), 42 (15), 41 (47), 40 (32), 39 (75), 27 (58).

Kinetic measurements

Apparatus: The apparatus was similar to that used in earlier studies.[9, 14, 37] Gases were handled in conventional grease-free vacuum systems made from pyrex and with Youngs stopcocks. To avoid mass losses during

handling of the compounds, the whole vacuum system was wrapped with heating tape and kept at about 50 °C. The reaction vessel used for most experiments was spherical (volume ca. 250 mL). It was placed in a stirred salt ($NaNO_2/KNO_3$ eutetic, temperature range: 150 °C – 550 °C) thermostatically controlled by an AEI (GEC) RT5 controller. Temperatures were measured with a Pt/Pt-13 % Rh thermocouple calibrated against a precalibrated Pt resistance thermometer (Tinsley, Type 5187 SA). Product analyses were performed by gas chromatography (Perkin Elmer 8310 Gas Chromatograph with FID detection) and electronic peak integration (Hewlett – Packard HP 3380S). For compound **15** and **16**, a 6 m 15 % β,β'-ODPN, 60/80 Chromosorb W-packed steel column operated at 40 °C was used for the quantitative analyses. The products from the pyrolyses of **5** and **17** were analyzed on a 4 m cyanosilicon-oil-packed steel column connected to a 6 m 15 % OPN, Chromosorb P-packed steel column operated at 50 °C. Pressures were measured with a conventional Hg manometer.

The reactions were studied by using *n*-pentane as internal standard chosen for stability and analytical convenience. The reactant master mixture consisted of about 2 % of cyclopropene and 2 % of the standard diluted to about 500 Torr with N_2 in a 500 mL reservoir. Runs were carried out by admitting the mixture to the reaction vessel at a given pressure for a certain time (between 2.5 min and 15 h covering a conversion between 5 % and 95 %). The reaction was quenched by transferring the reaction vessel contents to a pre-evacuated sample bulb, from which samples could be injected into the gas chromatograph. To avoid mass losses during injection, the injector sample valve was wrapped with heating tape and kept at about 50 °C. Before each run, a blank analysis was made of the unused master mixture to check the mass balance of the reaction.

Analysis: The quantitative analyses were carried out as described before. It was assumed that in each study all isomeric products had the same detector response factors. Product identities were confirmed by mass spectrometry and ^{1}H NMR and, if possible, ^{13}C NMR spectroscopy on isolated samples after pyrolysis. Additionally certain products, which were only formed in small amounts, were identified by comparing their GC retention times with those of authentic samples of potential pyrolysis products. Determination of the ^{13}C isotopomeric distribution was carried out by ^{13}C NMR spectroscopy and MS analysis. For this purpose two pyrolysis runs of both pure **15**(2-^{13}C) and **5**(2-^{13}C) were used for each ^{13}C NMR product sample at a pressure of 50 – 70 Torr and a conversion over 95 %. Tertiary ^{13}C signals were identified as follows: 2-pentyne, **19**: $\delta = 74.64$(C-2), 80.68(C-3), in agreement with ref. [22]; 4-methyl-2-pentyne, **8**: $\delta = 74.53$(C-2), 85.03(C-3), in agreement with refs. [15, 52].

Spectroscopic data of the pyrolysis products

Pyrolysis of 15: Products identified by NMR spectroscopy and MS. **19**: published spectrum,[53] **(*E*)-25**: published spectrum,[54, 55] **(*Z*)-25**: published spectrum,[54, 55] and **24**: published spectrum.[22, 54, 56]

Pyrolysis of 16: Products identified by NMR spectroscopy and MS. **15:** see above, **19:** published spectrum,[53] **(*E*)-25**: published spectrum,[54, 55] **(*Z*)-25**: published spectrum,[54, 55] **26:** published spectrum.[22, 54]

Pyrolysis of 5: Products identified by NMR spectroscopy. **17:** see above, **8:** published spectrum,[15, 23, 52, 57] **32:** published spectrum,[15, 23, 52, 57] **(*E*)-31:** published spectrum,[15, 23, 57] **(*Z*)-31:** published spectrum,[15, 23, 52, 57] **27:** published spectrum,[23, 50] **29:** published spectrum.[23, 57]

Pyrolysis of 17: Products identified by NMR spectroscopy. **5:** see above, **32:** published spectrum,[15, 23, 52, 57] **(*E*)-31:** published spectrum,[15, 23, 57] **(*Z*)-31:** published spectrum.[15, 23, 52, 57]

Pyrolysis of 15(2-^{13}C): Products identified by NMR spectroscopy. **16**(2-^{13}C): see above, **19**(^{13}C): published spectrum,[23, 53] **(*E*)-25**(^{13}C): published spectrum,[23, 53] **(*Z*)-25**(^{13}C): published spectrum,[23, 54, 55] **24**(3-^{13}C): published spectrum.[22, 23, 54, 56]

Pyrolysis of 5(2-^{13}C): Products identified by NMR spectroscopy. **17**(2-^{13}C): see above, **8**(^{13}C): published spectrum,[15, 23, 52, 57] **32**(^{13}C): published spectrum,[15, 23, 52, 57] **(*E*)-31**(^{13}C): published spectrum,[15, 23, 57] **(*Z*)-31**(^{13}C): published spectrum,[15, 23, 52, 57] **27**(3-^{13}C): published spectrum.[23, 50]

Appendix

The elementary rate constants in Schemes 5 and 6, which show the proposed mechanisms involving the vinylidenes **18** and **6** as intermediates, respectively, are related to the phenomenological rate constants in Schemes 8 and 9. The relationships obtained by stationary state treatments of [**18**][22] and [**6**][23] are given in Equations (1) – (6) below.

$$k_a = k_1 + k_5 + k_5k_6/k_{10} \quad (1)$$

$$k_b = k_6 + k_{10} + k_{10}k_1/k_5 \quad (2)$$

$$k_{-a}:k_{-b}:k_{-c} = (k_6/k_{10}):(k_1/k_5):1 \quad (3)$$

$$k_d = k_{11} + k_{12} + k_{12}k_{18}/k_{19} \quad (4)$$

$$k_e = k_{18} + k_{19} + k_{19}k_{11}/k_{12} \quad (5)$$

$$k_{-d}:k_{-e}:k_{-f} = (k_{18}/k_{19}):(k_{11}/k_{12}):1 \quad (6)$$

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