The cyclopropene pyrolysis story

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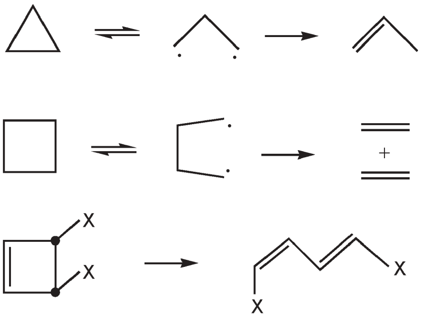
Cyclopropene is the last of the small strained ring hydrocarbons to have its thermal decomposition subjected to intensive investigation. This *critical review* describes the nearly 40 year history of this investigation largely by gas kinetic methods with chromatographic analysis. These studies have revealed that cyclopropenes can decompose by a variety of mechanisms involving diradicals, vinylcarbenes and vinylidenes. Much detailed information has been obtained about the reactivity of these intermediates which has wider implications for thermal hydrocarbon pyrolysis. Theory has also played a important role. Cyclopropene itself has been shown to be an intermediate in the allene → propyne rearrangement. The story itself illustrates how the evolution of mechanistic understanding has been anything but straightforward. (68 references.)

1 Introduction

Cyclopropene occupies a unique place amongst hydrocarbons. It is arguably the most strained single ring organic molecule.[1–3] Yet its thermal stability is such that it doesn't begin to decompose until temperatures approaching 200 °C. The factors which determine the thermal stability of strained ring hydrocarbons were the subject of intensive investigation during the period 1930 to 1980. During this time the pyrolyses of cyclopropane, cyclobutane and cyclobutene and many of their derivatives were studied both by gas kineticists and physical organic chemists.[4,5] In the gas phase these thermal processes are all unimolecular. Gas kineticists tended to concentrate on measurement of Arrhenius parameters and study of pressure dependencies as a means of understanding mechanism and developing unimolecular reaction theory.[6] Physical organic chemists usually focused on more stereochemical aspects of the rearrangement processes, which, as well as revealing crucial mechanistic details, also provided a significant input to the theory of orbital symmetry control, the Woodward–Hoffmann rules.[7] The conclusions which emerged were that cyclopropane and cyclobutane rearrange and decompose *via* diradical† intermediates (formed *via* C–C bond cleavage) and cyclobutene isomerises *via* a concerted electrocyclic ring opening (conrotatory) process under orbital symmetry control (Scheme 1).

While reaction mechanisms are always subject to conjecture, for these prototype ring systems our understanding of their thermal rearrangements has reached a maturity that little doubt remains about their mechanisms. The most recent advance has been the actual observation of the diradical intermediates by femtosecond laser spectroscopy.[8,9]

It is therefore somewhat surprising that for cyclopropene, such a close relative, understanding of its rearrangement mechanism has lagged significantly behind. No kinetic study was reported until 1969 (Srinivasan[10]), although it was known in 1965[11] that its rearrangement product was largely isomeric propyne (methylacetylene). Undoubtedly part of the reason for its lack of study lay in the difficulty of handling cyclopropene and in its tendency to polymerise rapidly both as a cold liquid



Scheme 1

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† Originally named 'biradicals', modern usage prefers the name diradicals.

and in the gas phase at pressures above *ca.* 10 Torr. However, if stored with inert gas in dilute mixtures, and studied in the presence of reference (thermally stable) hydrocarbons as a check against polymerisation losses, it is found to be perfectly amenable to quantitative study. This also applies to most of its higher homologues (alkyl- and other substituted cyclopropenes).

In this article I describe the gas phase kinetic and mechanistic studies of thermal isomerisation of cyclopropene and its alkyl homologues which have revealed a rich complexity unimagined at the time of Srinivasan's work. Much of this effort was carried out in our own laboratories as a result of a fruitful collaboration with the groups of Professors H. Hopf (Braunschweig) and De Meijere (Göttingen). The article attempts to trace the historical development of mechanistic ideas and contrasts with a recent review of the subject by Baird.[12]

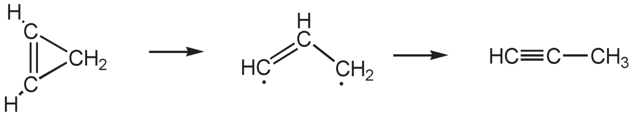
2 First kinetic studies

Srinivasan[10] studied the pyrolyses of both cyclopropene and 1-methylcyclopropene in the temperature range 470–500 K, using low pressures of cyclopropene (1–3 Torr) diluted in 50–60 Torr of CO_2. The kinetics were first order and the Arrhenius parameters were the following:

Cyclopropene: $\log(A/\mathrm{s}^{-1}) = 12.13$; $E_a = 147 \pm 5$ kJ mol^{-1}

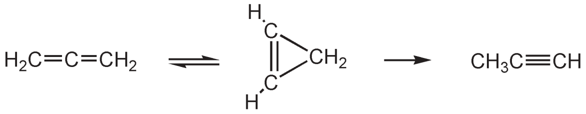
1-Methylcyclopropene: $\log(A/\mathrm{s}^{-1}) = 11.4$; $E_a = 145 \pm 5$ kJ mol^{-1}

While cyclopropene gave propyne as the unique (100%) product, 1-methylcyclopropene gave a mixture of products comprising 2-butyne (92%), 1,3-butadiene (5.5%) and 1,2-butadiene (2.5%). Drawing upon the parallel with cyclopropane isomerisation, Srinivasan proposed for cyclopropene the involvement of the 1,3-prop-1-ene diradical, *viz.*



The mechanism involves a simple ring opening followed by a 1,2 H-shift in the diradical. In the case of methylcyclopropene, an analogous diradical could lead to all three products by parallel (but differing) H-shift processes.

We developed our interest in cyclopropene pyrolysis by a somewhat roundabout route. Our early work was concerned with measurement of bond dissociation energies and in particular the C–H bond in propyne[13] was a target (the purpose being to obtain a value for the propargyl radical stabilisation energy). The method involved the kinetic investigation of the iodine catalysed interconversion of propyne and allene. This in turn led to an interest in the processes which caused thermal isomerisation between propyne and allene and in 1976 we showed[14] that the existing data on the thermal isomerisation of allene were closely consistent with a mechanism involving the intermediacy of cyclopropene, *viz.*



This interpretation contrasted with the mechanism of direct 1,3 H-migration previously suggested.[15,16] This naturally led us to an interest in the thermal rearrangement of cyclopropene itself.

In order to verify our hypothesis about the allene isomerisation mechanism, it was necessary to check whether allene was formed in cyclopropene pyrolysis, since Srinivasan had only reported formation of propyne. A reinvestigation of cyclopropene pyrolysis also seemed worthwhile because the Srinivasan's *A* factor seemed very low for a ring opening process (for cyclopropane isomerisation, $\log(A/\mathrm{s}^{-1}) = 15.5^{6}$). Our study of cyclopropene pyrolysis[17] was carried out with an internal standard (C_3H_8), with corrections for mass loss, and also with a radical scavenger (toluene) to eliminate a small H-atom catalysed pathway. We also verified that there was no surface component to the rates. The reaction was found to be pressure dependent and fall-off curves were obtained both in N_2 and SF_6, in the latter case over five orders of magnitude of pressure. The Arrhenius parameters, obtained in 70 Torr SF_6 (close to the high pressure limit), were: $\log(A/\mathrm{s}^{-1}) = 13.09 \pm 0.04$ and $E_a = 156.1 \pm 0.4$ kJ mol^{-1}. Adjusted, *via* RRKM theory,[17,18] to the high pressure limit, these correspond to: $\log(A^{\infty}/\mathrm{s}^{-1}) = 13.25$ and $E_a^{\infty} = 156.8$ kJ mol^{-1}.

The proportion of allene in the product was 0.26% (fully corrected for the atomic pathway). The allene yield corresponds to a free energy activation barrier, $\Delta G^{\ddagger}$, higher by 24.5 kJ mol^{-1} than that for propyne formation. By combining this value with the overall thermodynamics of the reaction,[17] we were able to obtain direct estimates for the Arrhenius parameters for the allene to propyne interconversion *via* cyclopropene which are compared below with those of the earlier studies.[15,16]

Us:[17] $\log(A/\mathrm{s}^{-1}) = 13.05$; $E_a = 266.5$ kJ mol^{-1}

Lifshitz *et al.*:[16] $\log(A/\mathrm{s}^{-1}) = 13.17$; $E_a = 253$ kJ mol^{-1}

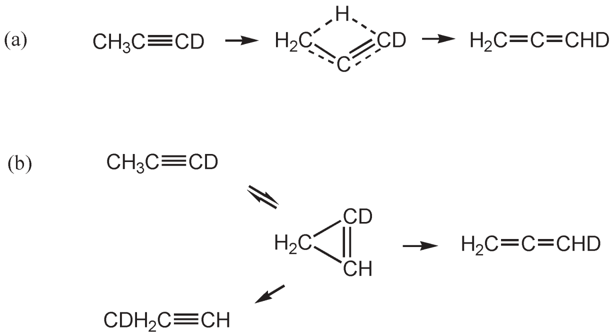
Bradley and West:[15] $\log(A/\mathrm{s}^{-1}) = 13.05$; $E_a = 388$ kJ mol^{-1}

Our rate constant estimate was close enough to that of Lifshitz *et al.*[16] at the temperature (1125 K) of study (*i.e.* within experimental and extrapolational error) to support the idea of the intermediacy of cyclopropene. The Bradley and West[15] data, with its $E_a = 388$ kJ mol^{-1}, cannot be correct because if so the reaction could not conceivably compete with a process with E_a in the range 250–270 kJ mol^{-1} as estimated and measured. This was pointed out by others[19] as well as ourselves.[17]

In the cyclopropene isomerisation itself we rationalised the small yield of allene relative to propyne by the relative strain involved in the H-shift transition state structures, *viz.*

Whereas in the propyne forming reaction, the migrating H-atom spans a formally single C–C bond, in the allene forming process a double bond is spanned. The diradical proposed by Srinivasan was shown by us to be consistent with the energetics of reaction using a thermochemical estimate, requiring allylic stabilisation, and implying that the actual intermediate was in reality a resonance hybrid of the 1,3 diradical form and the alternative vinylcarbene form. The structure of the diradical, more rigid than the trimethylene-1,3-diyl intermediate in cyclopropane isomerisation, was rationalised as consistent with the lower *A* factor. (Our value,[17] although higher than Srinivasan's,[10] is still more than two orders of magnitude lower than that for the cyclopropane reaction.) In addition there was stereochemical evidence supporting a diradical mechanism for alkyl substituted cyclopropenes. Bergman's group[20] had found that an optically active cyclopropene (1,3-diethyl-) underwent racemisation about 9 times faster than isomerisation to products, implying the involvement of a rapidly stereo-randomising intermediate. At this point it seemed to us that the mechanism of cyclopropene isomerisation was well understood. The only loose end seemed to be the question of fitting the pressure dependence to unimolecular reaction theory, which was not addressed by us in our paper.[17] Subsequently RRKM calculations[6] were carried out by us[18] which fitted the pressure dependence ("fall-off") of the rate constant (at 495 K) over the whole five orders of magnitude of pressure (10^3–10^{-2} Torr) between $\log(k/\mathrm{s}^{-1}) = -3.3$ (high pressure limit) and -5.4 (close to the low pressure limit) for SF_6, N_2, Ar and He as bath gases.

At this point the pressing question seemed to be whether any more direct evidence for cyclopropene involvement in the allene → propyne rearrangement could be found. We therefore conceived and undertook an isotope labelling experiment, involving the pyrolysis of propyne-1-d in a flow tube over the temperature range 853–1033 K.[21] Scheme 2 shows the mechanistic possibilities.



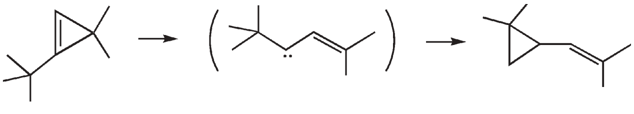
Scheme 2 (a) Direct mechanism, (b) mechanism *via* cyclopropene

The major finding was the formation of propyne-3-d as a primary product.[21] This was an immediate indication that the direct mechanism had at least a competitor. Our measurements gave a value for the primary product ratio, [propyne-3-d]/[allene-1-d], of 3.5 ± 0.5. The kinetic analysis (including allowance for experimental and isotope effect uncertainties) showed that the mechanism involving cyclopropene contributed at least 50% (and probably 100%) of the total pathway. Thus our original proposal[14] about how propyne and allene interconverted was confirmed. More recently Lifshitz's group[22] have carried out a detailed analysis of the product ratio, [allene]/[propyne], in the pyrolysis of cyclopropene in a shock tube study at 800–1200 K. Using RRKM theory combined with a theoretically derived transition state model they demonstrated[22] the consistency of their measured ratio with our earlier value,[17] and thus provided further confirmation for the intermediacy of cyclopropene in the allene ⇄ propyne isomerisation.

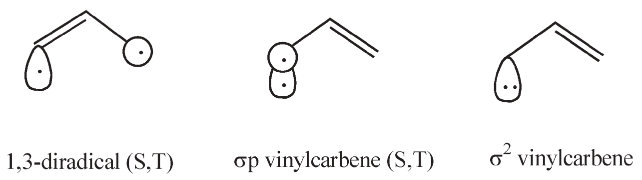
3 Early kinetic studies with alkyl substituted cyclopropenes

The effects of alkyl substituents on the kinetics of thermal isomerisation of small hydrocarbon rings have been a useful probe in unravelling mechanism[4–6] and so it was hardly surprising that Srinivasan extended his earlier studies[10] to include those of the pyrolyses of 3-methyl-, 3,3-dimethyl-, 1,3,3-trimethyl- and 1,2,3,3-tetramethylcyclopropene.[23] These results are not discussed in detail at this point, but they did reveal a number of unusual findings. Methyl substitution seemed to cause decreases in rate constants for these cyclopropenes in contrast the situation for cyclopropanes. This was a puzzle because methyl groups are generally thought of as stabilisers of radicals and biradicals, and therefore, should have produced increases in the values of the rate constants. Another curiosity was that the alkyne formation pathway (over 90% for 3-methyl- and 3,3-dimethylcyclopropene, not to mention 1-methylcyclopropene[10] and cyclopropene itself[10,17]) seemed to diminish rather abruptly with 1,3,3-trimethylcyclopropene (no alkyne product at all was identified, although it could have been an unidentified minor product of <5%). Although not considered as of significance when published two years later, alkyne formation from 1,3-diethylcyclopropene in Bergman's racemisation study[20] was only *ca.* 33%, another unexpectedly low yield.

Concerning the mechanism, Srinivasan[23] raised the issue of the possible importance of vinylcarbenes as intermediates in cyclopropene rearrangements, although he still favoured the 1,3-diradicals. Vinylcarbenes, produced from tosylhydrazones,[24] were known to ring close to form cyclopropenes; it was not known whether the reverse could happen. On the same question, Bergman,[20] however, preferred the vinylcarbene intermediate, arguing that it should be stabilised by allylic resonance, while assuming the diradical would not be so stabilised. Our belief at this point (see above) was that the biradical and vinylcarbene *were* resonance hybrids of the true intermediate and the distinction between them was not important. Around this time a more specific claim was made for the involvement of vinylcarbenes by the finding of the product 1-(2′,2′-dimethylethenyl)-2,2-dimethylcyclopropane as a product of the pyrolysis of 1-*tert*-butyl-3,3-dimethylcyclopropene in a study (in benzene solution, in the presence of solid $CaCO_3$) by Streeper and Gardner,[25] *viz.*

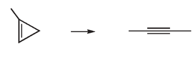
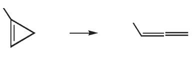


Such a product is indeed hard to explain in another way, but the kinetics of this reaction (very low Arrhenius parameters) give rise to the concern that, under the conditions of study, this may not have been a truly unimolecular process. At this time there were no theoretical calculations on these systems. Indeed



Scheme 3

Table 1 Arrhenius parameters and rate constants at 500 K for some cyclopropene pyrolyses

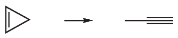
Reaction	$\log(A/s^{-1})$	E_a/kJ mol^{-1}	$10^4 k/s^{-1}$	ref
	13.25	157	7.41	17
	12.72	158	1.62	28
	13.48	177	0.106	28
	13.49	183	0.0218	28
	13.63	184	0.0275	29

the prevailing atmosphere of the time (certainly among experimentalists) was that theory had not advanced to the point where it could calculate reliably the energies of such complicated species as diradicals and carbenes. Notwithstanding this a theoretical *ab initio* GVB study (incorporating CI wavefunctions) soon appeared,[26] which reported calculations of the energies of the 1,3-diradical and two types of vinylcarbene. Both singlet (S) and triplet (T) states were included and these are shown in Scheme 3.

Although a triplet state (σp vinylcarbene, T) was the lowest energy species overall, on the singlet surface, the σ^2 vinylcarbene and the 1,3-diradical were the lowest energy states (only 10 kJ mol^{-1} apart), and the energy differences between them and reactant cyclopropene were close to those measured experimentally. Assuming intersystem crossing did not occur, the authors favoured the diradical (S) species as the intermediate. A few years after this a useful review of theory and experiment for both thermal and photochemical C_3H_4 interconversions was published.[27]

We started our work on alkylcyclopropene pyrolysis more as a refinement exercise than with the expectation of resolving the issue of which were the intermediates involved. Thus we wanted to eliminate the possibilities of surface reactions and material loss, as well as obtain precise product distributions and Arrhenius parameters. Our first two studies were of 1-methyl-[28] and 1,2-dimethyl-cyclopropene.[29] Experiments were carried out at high enough pressures not to be in the fall-off region of unimolecular processes. The results of these are shown in Table 1. Apart from revising upwards the overall Arrhenius parameters for 1-methylcyclopropene compared to Srinivasan[10] ($\log(A/s^{-1})$ from 11.4 to 12.91, E_a/kJ mol^{-1} from 145 to 160) the striking points were (i) the decrease in rate constants with methyl substitution, (ii) the still relatively low *A* factors and (iii) the elimination of the alkyne formation pathway for 1,2-dimethylcyclopropene. The products were all explained as arising from diradical intermediates *via* 1,2 H-shifts. The diradicals were still regarded as being in resonance with vinylcarbenes. The pattern of yields seemed to fit the ease or difficulty of H-bridging in the various transition states for product formation, implying that H-shift in the diradical was the rate determining step. In 1,2-dimethylcyclopropene, alkyne formation would have required a difficult methyl-group shift in the diradical, which explains the absence of this pathway.

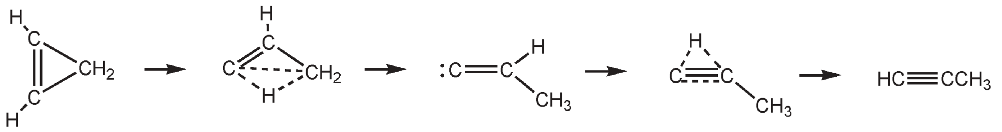
Table 2 Arrhenius parameters and rate constants at 500 K for some more cyclopropene pyrolyses

Reaction	$\log(A/s^{-1})$	E_a/kJ mol^{-1}	$10^4 k/s^{-1}$	ref
	13.25	157	7.41	17
	13.28	156	9.62	30
	12.5	158	0.986	30

Further studies of 3,3-dimethylcyclopropene by us[30] and others[31] largely confirmed the findings of Srinivasan.[23] The data are shown in Table 2 and confirm the fact that methyl substitution in the 3-position produces small enhancements in rate in contrast to the decreases of 1-methyl substitution.[28,29] This did not throw any further light on the issue of mechanism, *viz.* diradicals or vinylcarbenes as the key intermediates. However by this time a dramatic new suggestion had been made about the mechanism of cyclopropene isomerisation. This is discussed in the next section.

4 Later kinetic studies with alkyl substituted cyclopropenes

In 1984, a note was published by Honjou, Pacansky and Yoshimine[32] titled "The C_3H_4 surface", later expanded into a series of three papers,[33] suggesting, *inter alia*, that the propyne formation pathway from cyclopropene, came not *via* vinylmethylene (or even the 1,3-diradical), but *via* propenylidene, as shown in Scheme 4 below. This proposal was based on high



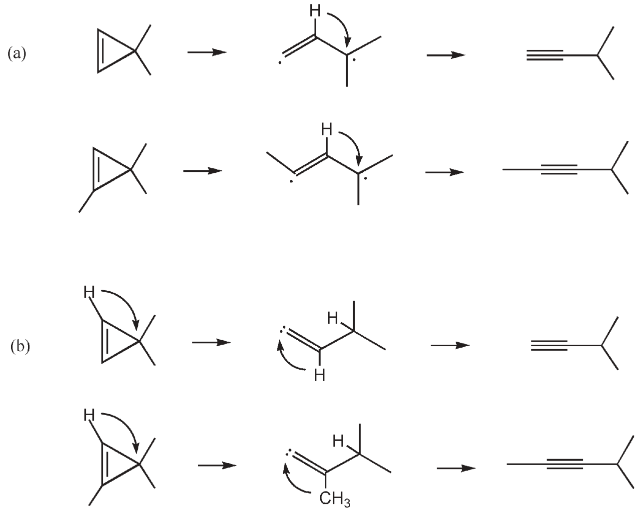
Scheme 4

level (SDCI/DZP and MRSDCI/DZP) theoretical calculations which, however, still implicated vinylmethylene in allene formation.

This paper came as somewhat of a shock (at least to the present author, not used to theory making mechanistic proposals ahead of experiment). The calculated activation energies for all the known processes (cyclopropene → propyne, cyclopropene → allene and allene → propyne) were only a few kcal mol^{-1} higher than the experimental values, and therefore did not seem unreasonable. The hardest aspect to swallow was the crowded and strained nature of the transition state for formation of propenylidene from cyclopropene, with its H atom migrating over the simultaneously breaking C–C bond. We have subsequently come to regard this as a retro C–H insertion by a carbene, which seems more acceptable as a description.

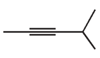
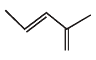
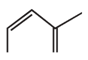
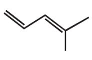
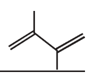
The publication of this paper was an enormous stimulation to try to find experimental evidence for propenylidene or one of its higher (vinylidene‡) homologues. To this end we decided to reinvestigate the pyrolysis kinetics of 1,3,3-trimethylcyclopropene.[34] This compound, already studied by Srinivasan,[23] anyway intrigued us because of the reported product distribution (lack of an alkyne) so controversially different from those of other methylcyclopropenes.[23,28,30] Product analyses by GC (with identification confirmed by NMR), immediately showed (Table 3) that Srinivasan's products were incomplete or misidentified. Specifically the alkyne (4-methyl-pent-2-yne) *was* formed, albeit only in 22% yield. Arrhenius parameters were determined for all products.[35] and those for the alkyne[34] allowed us to obtain $k = 5.27 \times 10^{-5}\ s^{-1}$ at 500 K. Comparison with Table 2 shows that this is a factor of *ca.* 18 slower than that for 3-methyl-but-1-yne formation from 3,3-dimethyl-cyclopropene. Apart from a factor of 2 (path degeneracy difference), this is still a 9-fold reduction in rate. We argued[34] that this could be accounted for by a mechanism involving a vinylidene as intermediate but not a diradical. The reasoning was based on Scheme 5, which compares the two mechanisms for each of the cyclopropenes, differing only by the 1-methyl substituent.

If the diradical mechanism were involved, it is hard to see how a rate difference could arise, except possibly an enhancement of the rate of diradical formation (by methyl stabilisation) from 1,1,3-trimethylcyclopropene in the first step. For the vinylidene mechanism, the second steps are quite different involving respectively an H-atom and methyl group migration in the vinylidenes generated from 3,3-dimethyl- and 1,3,3-trimethyl-cyclopropenes, respectively. The reasonable assumptions that the second step is rate determining, and that Me-migration is much more difficult than H-migration can then account for this dramatic rate difference. Thus the theoretical proposal of Honjou *et al.*[32,33] was supported by our rate studies[34] and indeed seemed to offer the prospect of explaining the hitherto strange variations in alkyne yields from cyclopropenes. It also provided a much better rationalisation of the low *A* factors for cyclopropene isomerisation (compared with cyclopropane), because of the tight transition states required by the vinylidene mechanism. This seemed like a breakthrough, although Fahie and Leigh[36] had already found evidence for vinylidene involvement in the *photochemical* rearrangement of 1,3,3-trimethylcyclopropene.



Scheme 5 (a) Diradical mechanism (b) vinylidene mechanism.

Table 3 Product distribution (%s) for pyrolysis of 1,3,3-trimethylcyclopropene at 500 K

Compound					
Us[a]	22.2	40.9	3.1	32.8	1.1
Srinivasan[b]	<5	71		<5	21

[a] Ref. 34. [b] Ref. 23.

We noted[34] that the involvement of vinylidenes, formed reversibly from cyclopropenes, provided another explanation for the racemisation observations of Bergman, some 18 years earlier.[20] The formation of dienes from cyclopropenes still however seemed to us to require the involvement of diradical/vinylcarbene intermediates. As a result of experiments carried out with various trimethylsilyl (Me_3Si-) substituted cyclopropenes,[30,37,38] (beyond the scope of this review§) we came to the view that the biradical *versus* vinylcarbene argument could be better understood if they were regarded as two independent species, but capable of rapid interconversion (*i.e.* potentially at equilibrium). Thus different substituents would alter rates and product pathways according to their different effects on the diradical–vinylcarbene interconversion and product formation rates. Substituent effects would also determine the relative importance of the vinylidene pathway leading to alkynes.

Our next foray into this increasingly complex subject was to conceive of, and carry out, an experiment which would demonstrate the vinylidene pathway, not just based on rates, but on an actual unique product formation pathway. Vinylidene itself, $H_2C{=}C{:}$, is an unstable isomer of acetylene

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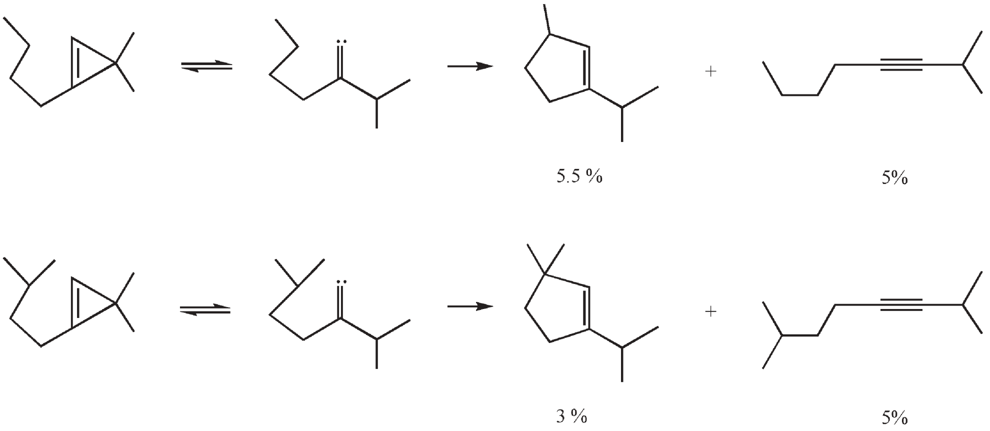
‡ "Vinylidene" is the name chosen here to refer to species $R_1(R_2)C{=}C{:}$, superseding the earlier used "alkylidene carbene".

§ Details of these results can be found in the review of Baird.[12]



Scheme 6

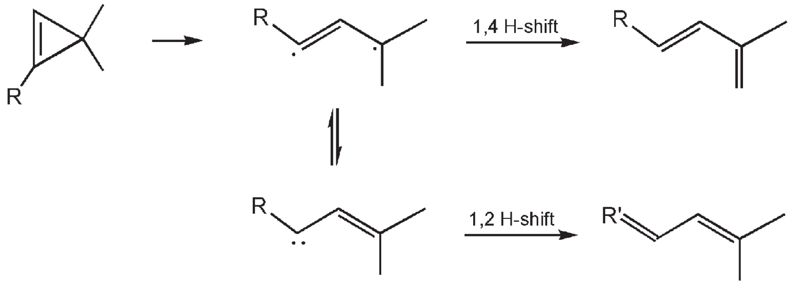
and had been proposed by Brown as an intermediate to explain the degenerate rearrangement of acetylene.[39] If formed, vinylidene reverts to acetylene *via* a rapid 1,2 H-shift (with almost no energy barrier)[40]. It therefore looks to be impossible to trap. Higher homologues such as isopropenylidene, $Me_2C=C$: appear to live long enough to be trapped *via* alkene addition,[41] implying that the 1,2 Me-shift process is much slower than 1,2 H-shift. Because of the known propensities of carbenes to undergo C–H insertion reactions and in particular the fact that certain substituted vinylidenes, independently generated, underwent intramolecular 1,5 C–H insertion,[42,43] we decided to try to divert the vinylidene intermediates formed from specifically tailored cyclopropenes *via* such a pathway. We therefore synthesised a series of 1-alkyl-3,3-dimethylcyclopropenes, including 1-butyl- and 1-isoamyl-, and carried out a full gas phase kinetic and product analytical study of their pyrolysis products in the range 463–513 K, separating products by GC and characterising them by NMR, IR, and GCMS.[44] The key products, which demonstrated the trapping of the vinylidene intermediates, are shown in Scheme 6.

The observations of the cyclopentene products, although formed in relatively small yields, provided very strong evidence for the intermediacy of vinylidenes. This was strengthened by checking for the absence of the 1,6 C–H insertion product, 1-isopropylcyclohexene (from 1-n-butyl-3,3-dimethylcyclopropene). The absence of a 1,6 C–H insertion product had been noted previously for similar alkyl substituted vinylidenes.[42,43] Additionally the measured ratios of cyclopentene/alkyne found by us were in reasonable agreement with those found for the earlier studied vinylidenes[42,43] at the same temperature.

In addition to providing definitive evidence for vinylidene intermediates, these studies provided a wealth of other information about the cyclopropene decomposition mechanism. Yields of alkynes for this series of 1-alkyl-3,3-dimethylcyclopropenes, fell to 5 ($\pm$1)% for 1-ethyl-, 1-butyl- and 1-isoamyl- and a minuscule 1% for 1-isopropyl-. Given the almost certain propensity for vinylidenes to revert to starting cyclopropenes, it was now clear that these figures and the rate constants for alkyne formation,[44] could not be fully understood without further experiments to assess the extent of reversibility in the first step of the mechanism. Some further comments on the implications of reversibility are made at the end of this section.

In this study[44] the major products were dienes, mainly 2,4- rather than 1,3-. As discussed earlier, these can be readily accounted for by H-shifts in the diradical/vinylcarbene intermediates. Our working hypothesis was that the 2,4-dienes came from vinylcarbene *via* a 1,2 H-shift, while the 1,3-dienes came from the diradical *via* a 1,4 H-shift. This is shown in Scheme 7.

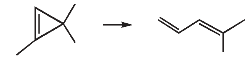
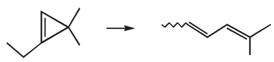
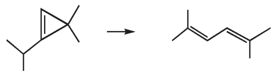
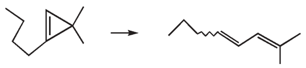
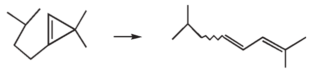
Arrhenius parameters and relative rate constants for the 2,4-diene products are shown in Table 4. The *A* factors are all close to one another, all typical values for cyclopropenes. The tightness of the transition states is caused not only by restricted rotation in the vinylcarbene part of the structure but also by



(R' is R less one H-atom)

Scheme 7

Table 4 Arrhenius parameters, rate constants and relative rates for 2,4-alkadiene formation from some 1-alkylcyclopropene pyrolyses at 500 K

Reaction	$\log(A/\mathrm{s}^{-1})$	E_a/kJ mol^{-1}	$10^4 k/\mathrm{s}^{-1}$	k_{rel}/σ [a,b]	ref
	13.19	165.6	0.770	1	34
	13.05[c]	153.8[c]	9.48	18.4	44*b*
	13.24	154.7	12.0	46.8	44*b*
	13.46[c]	158.1[c]	8.78	17.1	44*b*
	13.19[c]	153.7[c]	13.9	27.1	44*b*

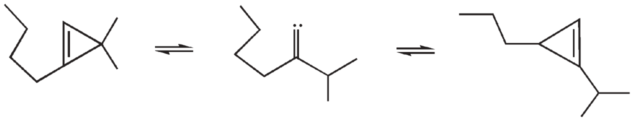
[a] σ is path degeneracy. [b] The figures given here are corrected for errors in the original paper (Table 10, ref. 44b). [c] Obtained by combining data for *cis*- and *trans*- products.

restricted rotation of the 1-alkyl group due to the bridging H-atom. There is no clear trend in the activation energies. In these situations comparisons of absolute rate constants at 500 K for specific pathways were instructive. These were corrected for path degeneracy (the number of migrating H-atoms). The numbers show clearly the significant rate increases resulting from replacement of methyl by ethyl and isopropyl in the 1-position. These groups must enhance the rate by selectively stabilising the intermediate or facilitating the necessary H-shift. This may be summarised in terms of per-H-atom migration, as the proportions 1:18:47 for primary:secondary:tertiary hydrogen atoms. These ratios indicate substantial selectivities. There is some spread in secondary H-atom migration rates between 1-ethyl-, 1-butyl- and 1-isoamyl-, but not enough to seriously distort the trend. From earlier studies of diazirine pyrolysis by Frey,[45] we were able to extract the H-atom migratory preferences for alkylcarbenes.[44b] These were in the proportions 1:40:97 for primary:secondary:tertiary hydrogen atoms, again very substantial selectivities. Although alkylcarbenes and vinylcarbenes are not necessarily expected to show identical patterns of reactivity, the similarity here is striking. Thus the intermediacy of vinylcarbenes offers a compelling explanation for the substantial relative rate effects in the 2,4-diene formation pathway, which are otherwise hard to understand.

The remaining dienes (classified as 1,3- as opposed to 2,4-) are relatively minor products. Except in the case of 1,3,3-trimethylcyclopropene, studied earlier,[34] the relative yields were less than 10%. Comparisons of relative rates (see original paper,[44b] Table 11) showed that, for these products, values spanned a range of a factor of *ca.* 2.5 (again on a per-H-atom basis), a much smaller variation than for the 2,4-dienes. All these cyclopropenes contain dimethyl substitution in the 3-position and formation of these dienes is explained by the 1,4 H-shift process in the biradical intermediate of Scheme 7. Small stabilisation and/or steric effects at the H-atom receiving radical centre may be expected to cause these small rate variations. The diradical mechanism is also supported by the lower *A* factors ($\log(A/\mathrm{s}^{-1}) = 12.8 \pm 0.3$)[44b] corresponding to a tighter transition state for a 1,4 H-shift (a 5-membered ring involving greater loss of internal rotational freedom) than for a 1,2 H-shift. All the 1,3-diene products are formed only as *trans* isomers which is consistent with the steric requirements of these transition states (as suggested previously by Srinivasan[23] and Stechl[46]).

In this work,[44b] the proven intermediacy of the vinylidene intermediates and their likely reversions to precursor cyclopropenes (the reversibility argument) gave rise to the further intriguing possibility that *isomeric* cyclopropenes might be formed. This could occur if the intermediate vinylidenes were unsymmetrical and would give rise, *via* 1,3 C–H insertion, to two different cyclopropenes. This is illustrated in Scheme 8.

Our experimental studies of the 1-alkylcyclopropene pyrolyses,[44b] showed strong evidence for formation of isomeric cyclopropenes, although yields were too low for unambiguous characterisation. Transient products, of similar stabilities to starting 3,3-dimethyl-cyclopropenes, were found for the 1-ethyl-, 1-butyl- and 1-isoamyl- compounds but (tellingly) not the 1-isopropyl. In this latter case, the relevant intermediate is the symmetrical di-isopropylvinylidene, not capable of forming an isomeric cyclopropene. By this time others had become interested in the intriguing mechanistic challenges offered by cyclopropene isomerisation and an elegant proof of the intermediacy of vinylidenes had been published[47] using an isotopic labelling experiment to demonstrate a cyclopropene

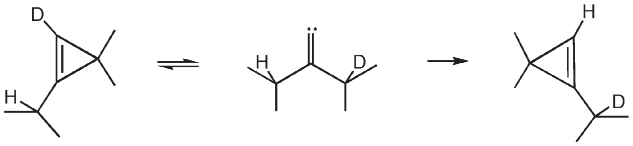


Scheme 8

degenerate rearrangement. This is described in the next section.

5 Cyclopropene-to-cyclopropene interconversions

In 1994, at the time we were undertaking our vinylidene intramolecular trapping study, Jones and coworkers[47] obtained evidence for vinylidene intermediates by observing a deuterium migration from the ring into the alkyl sidechain, during pyrolysis of 1-deutero-2-isopropyl-3,3-dimethylcyclopropene. The mechanism is shown in Scheme 9.

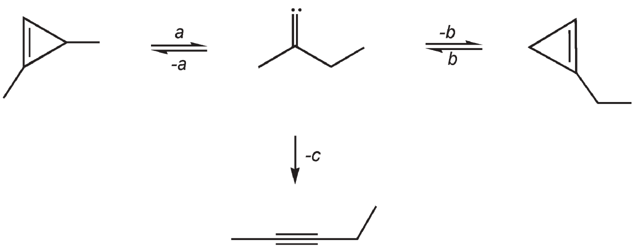


Scheme 9

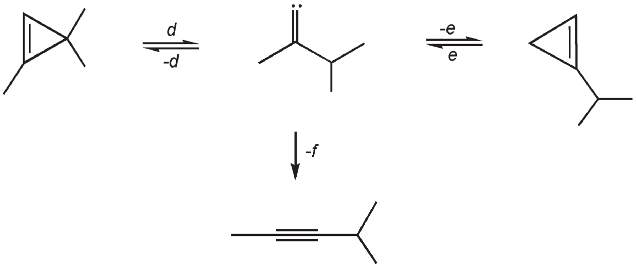
This is the first unequivocal example of the cyclopropene-to-cyclopropene rearrangement implicit in the vinylidene hypothesis, although the yields were small (0.5% of rearranged product at 90% conversion). Another significant result of this work[47] was the finding of a scrambled carbon label in the 4-methylpent-2-yne product from a labelled 1,3,3-trimethyl cyclopropene. The mechanism for this is shown in Scheme 10.

The rationale of this result was that only the vinylidene intermediate could explain the two differently labelled products. If the diradical mechanism had been operative, the label would have been uniquely in the 3-position of the alkyne. The sensitivity of detection of labelled products was not sufficient to determine the relative rates of migration of Me *versus* iPr in the vinylidene.

These experiments and our own earlier studies[34,44] stimulated our desire to try to measure precisely the extent of reversibility in the vinylidene pathway as well as to obtain a more quantitative picture of the reactivity of vinylidenes themselves. To this end we prepared and studied[48a,48c] the pyrolysis kinetics of four cyclopropenes, 1,3-dimethyl-, 1-ethyl-, 1,3,3-trimethyl- and 1-isopropyl-, which potentially comprised two interconverting pairs involving methylethylvinylidene and methylisopropylvinylidene, as shown in Schemes 11 and 12.

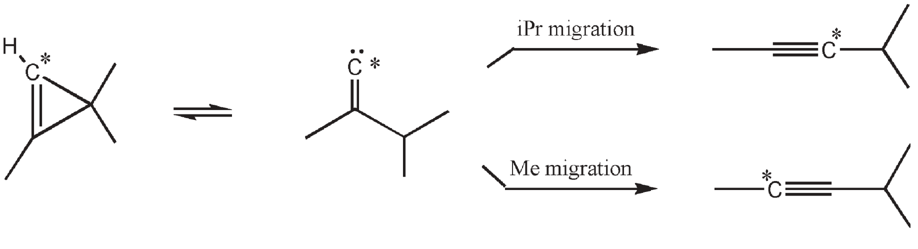


Scheme 11



Scheme 12

We were able to make a complete and quantitative analysis of products and their time evolution down to levels of *ca.* 0.1% for these four cyclopropenes¶. Fig. 1 illustrates one such concentration-time sequence. This shows the formation (up to 10%) of isomeric 1,3-dimethylcyclopropene starting from 1-ethylcyclopropene. It also shows clearly the unstable nature of the isomeric cyclopropene. Similar diagrams were obtained for each cyclopropene at each temperature of study. For each pair of interconverting cyclopropenes at each temperature a mechanistic scheme was fitted to the data (using well established kinetic modelling algorithms) to yield sets of mutually consistent rate constants for each product forming pathway. This yielded not only rate constants for pathways of previous expectation (*i.e.* to alkynes and dienes) but also for formation of the partner cyclopropene. These latter were fitted in turn to the mechanisms of Schemes 11 and 12, to yield absolute values for the ring opening processes ($k_{\rm a}$, $k_{\rm b}$, $k_{\rm d}$ and $k_{\rm e}$) as well as relative values for individual pathways of reaction of the two intermediate vinylidenes ($k_{-{\rm a}}$:$k_{-{\rm b}}$:$k_{-{\rm c}}$ and $k_{-{\rm d}}$:$k_{-{\rm e}}$:$k_{-{\rm f}}$) at each of six temperatures. The first set of rate constants allowed us at last to examine the elementary process of a cyclopropene ring opening to form a vinylidene, *i.e.* the



Scheme 10 (The C* atoms are ^{13}C depleted.)

¶ It should be noted that one of these studies, *viz.* for 1,3,3-trimethylcyclopropene was a repeat of an earlier investigation.[34,35] The analytical data (apart from those for the isomeric cyclopropene) were in good agreement with those obtained previously.

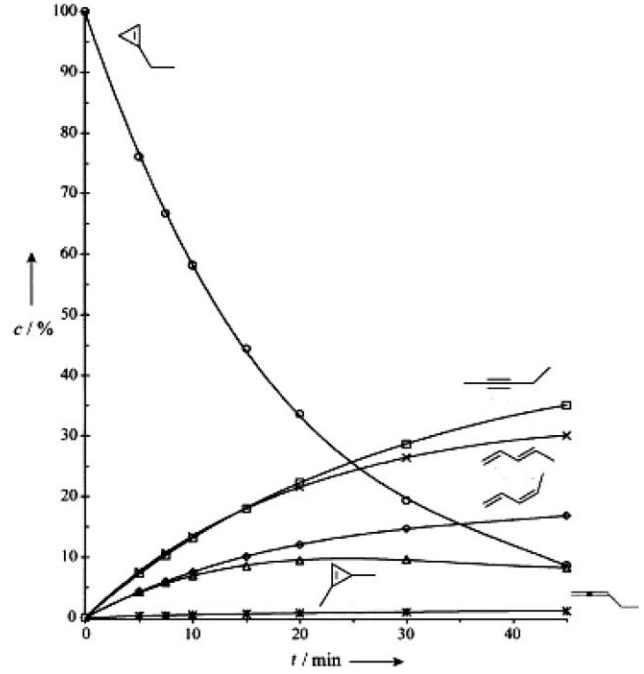
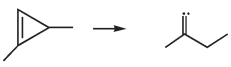
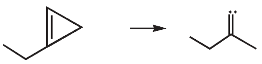
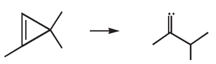
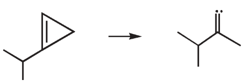


Fig. 1 Time evolution of the decomposition of 1-ethylcyclopropene at 511.8 K.

issue of reversibility having been factored out! *A* factors are fairly low ($\log(A/s^{-1} = 13.1 \pm 0.2)$ reflecting the tight structure of the transition state, and activation energies are all fairly similar (spanning the rather narrow range 159–164 kJ mol^{-1}).[48c] A more extensive evaluation can be made, based on the rate constants at 500 K shown in Table 5. This table includes not only the cyclopropenes of this work but others studied previously. It was reasonably assumed in the case of cyclopropene rings without 1-alkyl substituents that ring opening is synonymous with vinylidene formation since the second step for the vinylidenes in these cases involves an H-shift, known to be fast. The figures for k_{rel}, show a satisfying self-consistency. In the first place variations are very small for a process in which strong substituent effects are not expected. Me groups in the 3-position seem to increase the rate slightly while alkyl groups in the 1-position seem to retard it a bit. It is worth remembering that the small factors involved here, *ca.* 2, correspond to less than 3 kJ mol^{-1} in energy terms at 500 K. Very small conformational effects in any specific case could easily account for such effects.

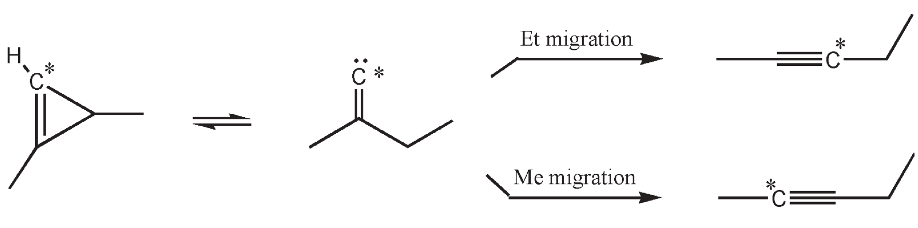
As part of this study[48b,48c] we also carried out ^{13}C labelling experiments to determine the relative migratory aptitudes of the differing alkyl groups in the alkyne formation step from the different vinylidenes. One of these, viz that for 1,3-dimethylcyclopropene, followed the logic of Scheme 13 shown below and the other, *viz.* that for 1,3,3-trimethylcyclopropene was the same as the experiment carried out by Jones,[47] shown in Scheme 10, except that we used ^{13}C enrichment rather than depletion.

Table 5 Comparison of rate constants and relative rates for formation of vinylidenes from cyclopropenes at 500 K

Reaction	$10^4k/s^{-1}$	k_{rel}/σ [a]	ref
	7.32[b]	1	17
	1.80[c]	0.49	28
	2.40	0.66	48*c*
	1.91	0.52	48*c*
	1.33	0.36	48*c*
	2.12	0.58	48*c*
	10.46[b]	1.43	23
	9.62[b]	1.31	30

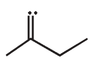
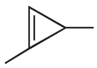
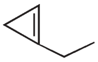
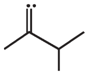
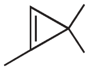
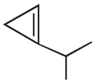
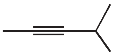
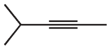
[a] σ is path degeneracy. [b] Values assumed equal to those for alkyne formation (see text). [c] Value for alkyne formation increased by factor of 1.25 to correct for reversibility in the first step.[48c]

These results gave relative rates of 3.1 ± 0.1 for Et:Me migration and 1.5 ± 0.1 for iPr:Me migration at 500 K, almost independent of temperature (482–523 K). When combined with the results for k_{-a}, k_{-b}.....k_{-f} obtained *via* kinetic modelling these provided the relative rates for the complete set of intramolecular processes undertaken by both vinylidenes (methyl, ethyl and methyl, isopropyl). These are shown in Table 6. The data reveal a number of interesting features. The ring closure and alkyl group shift processes are competitive, but whereas for methylethylvinylidene, alkyl group shift predominates, for methylisopropylvinylidene, ring closure is favoured. The latter case proves, as we suggested 8 years previously,[34] that in the isomerisation of 1,3,3-trimethylcyclopropene to 4-methylpent-2-yne, it is the



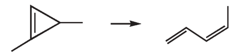
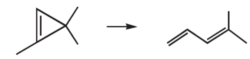
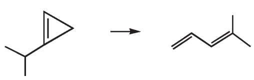
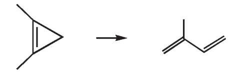
Scheme 13

Table 6 Relative rate constants for all rearrangement processes of methylethylvinylidene and methylisopropylvinylidene at 500 K

Reactant	Product[a]			
				
step	−*a*	−*b*	−*c*(Me)	−*c*(Et)
k_{rel}/%	38.2	3.5	14.2	44.1
				
step	−*d*	−*e*	−*f* (Me)	−*f* (iPr)
k_{rel}/%	63.8	4.1	12.8	19.2

[a] In the alkyl migration pathways (−*c*, −*f*) the migrating group is indicated.

Table 7 Comparison of rate constants and relative rates for formation of 1,3-dienes from cyclopropenes at 500 K

Reaction	10^5k/s^{-1}	$k_{\mathrm{rel}}/\sigma^{a}$	ref
	1.07	1	28
	1.73	1.62	48*c*
	0.68	0.63	48*c*
	11.7	16.4	48*c*
	6.43	9.02	48*c*
	7.46	6.97	48*c*
	27.5	77.0	48*c*
	0.274[b]	0.128[b]	29

[a] σ is path degeneracy. [b] These figures are corrected for errors in the original paper (Table 15, 48*c*).

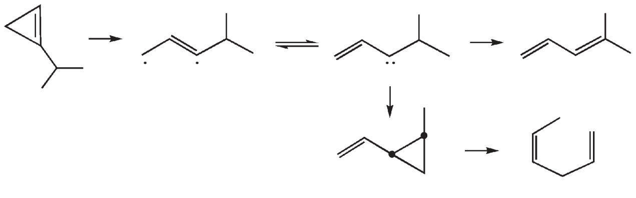
second step in the process which is rate determining. A more detailed discussion of these numbers is provided in the next section.

As with the earlier studied 1-alkyl cyclopropenes,[44] dienes are substantial products in these systems[48] as well. Yields were somewhat variable but the diene formation mechanisms can again be explained by H-shifts in the diradical/vinylcarbene intermediates. Using a scheme similar to that of Scheme 7, the dienes from each cyclopropene were separated into 1,2 H-shift products and 1,4 H-shift products with the exception of *trans*-1,3-pentadiene which comes from 1,3-dimethylcyclopropene *via* both processes. The *A* factors are all close to one another (log(A/s^{-1}) range; 12.79–13.26) but the activation energies spread from 157 to 176 kJ mol^{-1}. Once again it is instructive to compare relative rate constants at 500 K (corrected for path degeneracy). This is done in Table 7, for the dienes coming *via* 1,2 H-shift processes (vinylcarbene intermediates). The comparison is extended to include other cyclopropenes. Some striking rate relativities are again apparent, particularly for the 1-methyl-, 1-ethyl- and 1-isopropyl- cyclopropenes. These correspond to per-H propensities of 1:25:77 for insertion into primary:secondary:tertiary C–H bonds by the vinylcarbene. These are similar to, but larger than, those found earlier (Table 4) for the vinylcarbenes formed from the 1-alkyl-3,3-dimethylcyclopropenes.[44b] Again the 1-alkyl substituents must be operating either by selective stabilisation of the vinylcarbene or selective enhancement of the 1,2 H-shift process. Another quite large variation involves the 1-methylcyclopropenes with increasing 3-methyl substitution. The sequence 1-methyl-, 1,3-dimethyl- and 1,3,3-trimethyl-cyclopropene 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 the diene formation in the case of 1,3-dimethylcyclopropene comes *via* this route. It is hard to imagine a direct kinetic effect here, but easier to believe that the rates are enhanced by methyl group stabilisation of the intermediate itself which assists the cyclopropene bond breaking process. Interesting also is the case of 1,2-dimethylcyclopropene which demonstrates a different remote substituent effect in which the non-participating Me group exerts a strong retardation on diene formation.

For the dienes formed *via* the 1,4 H-shift process, comparisons of relative rate constants (see original paper,[48c] Table 16) showed that rate variations were relatively small, although it has to be borne in mind that the uncertainty of mechanism for formation of *trans*-1,3-pentadiene, means that the rate constant for this route represents only an upper limit. These are consistent with the diradical route. As mentioned earlier, small steric effects can account for these variations.

The pattern of ^{13}C labelling in the dienes formed from the ^{13}C labelled cyclopropenes (see original paper[48c]) did not reveal any new mechanisms but provided further support for cyclopropene-to-cyclopropene isomerisation mechanism. In the case of isopropylcyclopropene a minor pathway led to formation of *cis*-1,4-hexadiene (*ca.* 0.9% of total products). The proposed mechanism for this is shown in Scheme 14.

Because *cis*-1,4-hexadiene is known to result from rapid isomerisation of *cis*-1-methyl-2-vinyl-cyclopropane,[49,50] it is effectively a marker for the latter, which is hard to understand as other than coming from the 1,3 C–H insertion process from the vinylcarbene intermediate. This recalls the report of the

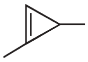
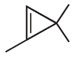


Scheme 14

detection of a vinylcyclopropane product in a 1-*tert*-butyl substituted cyclopropene pyrolysis study 27 years earlier.[25] This solution study would be worth repeating in the gas-phase under unambiguous unimolecular conditions, to see whether this unusual pathway really is important, and if so, to help understand why it is not more prominent for other cyclopropenes.

Up to this point the discussion of these systems has focused on the mechanism of formation and variations of rate constants for each particular reaction type (isomeric cyclopropenes, alkynes and dienes) one at a time. We are now in a position to return to the overall product distribution patterns for these four cyclopropenes in order to understand their wide variation. From the kinetic analysis at 500 K the initial product distributions have been calculated and are shown in Table 8. It can be seen that alkyne yields vary from 14.1 to 80.9%, dienes yields from 13.9 to 76.8% and isomeric cyclopropene yields from 2.6 to 27.8%. These variations can now largely be understood. For example 1,3-dimethylcyclopropene ring opens to form a vinylidene with a low degree of reversibility which leads on predominantly to alkyne. Its alternative ring opening to diradical/vinylcarbene produces an intermediate with no special stability or high propensity to undergo H-shifts to dienes. Thus for this cyclopropene, the isomer yield is very low, the alkyne yield is high and the diene yield low. By contrast isopropylcyclopropene ring opens to form a vinylidene with a high propensity to ring close to its isomeric cyclopropene, rather than shift an alkyl group to make an alkyne. The alternative ring opening to diradical/vinylcarbene gives an intermediate with a very high propensity to undergo a 1,2 H-shift. Thus for this cyclopropene, the isomer yield is substantial, the alkyne yield is low and the diene yield is high. Of course at high conversions of these cyclopropenes, actual product yields will change somewhat, because direct product yields will become diluted with those from the isomeric cyclopropene which is also decomposing.

Table 8 Comparison of patterns of primary product formation for four cyclopropenes at 500 K

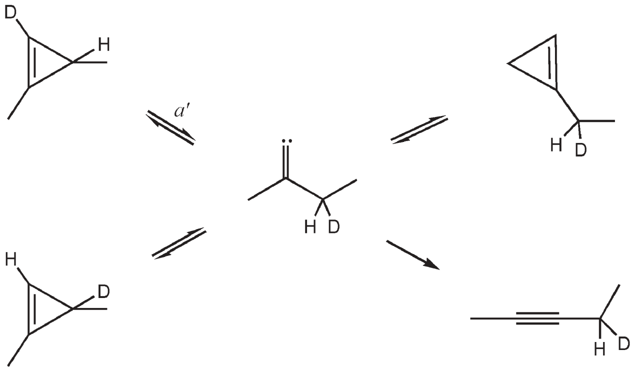
		Product %			
Reactant	10^5k/s^{-1}	Alkyne	Dienes	Cyclopropene	Other
	17.3	80.9	13.9	4.9	0.4
	36.8	30.1	49.2	19.7	1.0
	21.6	19.9	76.8	2.6	0.7
	48.4	14.1	56.7	27.8	1.5

6 Degenerate cyclopropene rearrangements and deuterium isotope effects

Although the studies described in the previous two sections look to have established beyond reasonable doubt that the route to alkyne formation from cyclopropene is *via* vinylidene, the involvement of this intermediate still carries unexplored implications which are open to further mechanistic investigation. We decided to look into two of these by preparation and pyrolysis of specifically deuterium labelled cyclopropenes.[48b,51]

(a) Interconversion of 1,3-dimethylcyclopropene-2-d and -3-d

NMR analysis of the pyrolysis products of 1,3-dimethylcyclopropene-2-d (as a function of time at 504 and 524 K) indicated formation of up to 8% of the -3-d isomer.[48b,51] This can be readily explained by the mechanism shown in Scheme 15.

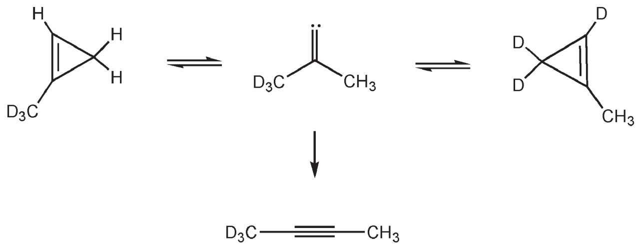


Scheme 15

Small amounts of 1-(ethyl-2-d)-cyclopropene as well as 2-pentyne-4-d (the main product) and the monodeutero-1,3-pentadienes were also detected. Kinetic modelling of the concentration time curves provided values for the elementary rate constants of the system.[51] As described in the previous section these were used to extract elementary rate constants for vinylidene formation, in particular $k_{a'}$. This enabled the isotope effect k_H/k_D ($=k_a/k_{a'}$) to be obtained and yielded values of 1.32 ± 0.07 (504 K) and 1.30 ± 0.06 (524 K). Although these numbers are relatively small for primary isotope effects, comparisons with other isotope effects for small ring isomerisation reactions show that these values are too large to be secondary in nature.[48b] Thus, additional to the shear fact of observation of this degenerate process, the measured isotope effect shows that 1-H(D) must be involved in the transition state for it.

(b) Interconversion of 1-methylcyclopropene-4,4,4-d_3 and -2,3,3-d_3

NMR analysis of the pyrolysis products of 1-methylcyclopropene-4,4,4-d_3 (as a function of time at 493 and 503 K) indicated formation of up to 5% of the -2,3,3-d_3 isomer.[51] This can be readily explained by the mechanism shown in Scheme 16.



Scheme 16

Small amounts of 1,3-butadiene-1,1,2-d_3 and 1,2-butadiene-4-d_3 were also detected.[51] Kinetic data could only be obtained for the 4,4,4-d_3 isomer of 1-methylcyclopropene, since a pure sample of the 2,3,3-d_3 isomer was not available. Nevertheless an approximate treatment of the data showed that it was consistent with an isotope effect, k_H/k_D, of *ca.* 1.3 between the ring opening rate constants of the two isomers.[52] These results are again consistent with a rate controlling process involving H(D) migration. This result was also used to calculate that in unlabelled 1-methylcyclopropene, vinylidene formation was between 19 and 24% reversible. Apart from these quantitative considerations, the really remarkable thing about this isotopic scrambling process is the way all three ring hydrogens exchange with those of the methyl substituent simultaneously!

7 Some quantitative aspects of vinylidene behaviour

Although this is not a review of reactive intermediates, our studies of cyclopropenes have revealed a considerable amount of new information about the behaviour of the intermediates involved, particularly the vinylidenes. It is my suspicion that vinylidenes play a larger role in high temperature hydrocarbon chemistry than is currently realised and therefore feel that it is worth collecting together what has emerged in these studies.

The vinylidenes produced thermally from cyclopropenes (at *ca.* 500 K), seem to react solely by intramolecular processes in these systems. There is no evidence for external trapping. The intramolecular processes identified consist of C–H insertion and alkyl group shift reactions. Most of the data we have obtained is shown in Table 6. These sets of relative rates for each of the two vinylidenes can be combined to make two interesting comparisons.

(a) Alkyl group shift propensities

Assuming that the Me group shift, which is common to both vinylidenes has a fixed migration rate, then the combined relative migration propensities for Me:Et:iPr are 1:3.1:1.5. These may be compared with the same set of propensities for the isoelectronic isonitrile to nitrile (RNC → RCN) rearrangement of Me:Et:iPr of 1:1.4:0.47 (at T = 473 K) obtained by Schuster and colleagues.[53] These non-monotonic sequences show that *two* effects must be operative. Following the discussion of the isonitrile/nitrile case, we suggested[48c] that the transition state is stabilised by a hyperconjugative effect which increases with alkyl group size, but which is partially offset by an increasing steric effect which particularly restricts rotation of the methyl groups in the larger isopropyl group.

(b) 1,3 C–H insertion propensities

Assuming that the primary C–H insertion rate for both vinylidenes is constant, the combined relative insertion propensites, the processes leading from vinylidene to cyclopropene, for $k_{\mathrm{prim}}:k_{\mathrm{sec}}:k_{\mathrm{tert}}$ are 1:16.5:46.4 on a per C–H bond basis. These numbers are compared with insertion propensities for other carbenes in Table 9. Although the other processes in this table involve 1,2 C–H insertions and the carbenes are all different there is a striking parallel in the trends of these numbers. It demonstrates that all these carbenes are quite discriminating between the different C–H bonds. A factor of 50 at 500 K corresponds to an activation free energy difference of 16 kJ mol^{-1} which is not much less than the overall difference in strengths of a primary and tertiary C–H bond (*ca.* 20 kJ mol^{-1}[54]). Of course these numbers are in principle temperature dependent, but the slightness of the observed variation within the temperature range of study does not permit an analysis of activation energies. At the present time there are no absolute rates available for such processes, but given the generally undiscriminating behaviour of the parent carbene, methylene ($^1A_1$ state), in its intermolecular insertion reactions,[55] combined with current knowledge that it reacts at virtually every collision,[56] it seems reasonable to infer that these carbene intramolecular processes are considerably slower. In view of the strained nature of their transition state structures this would not be too surprising.

It is worth pointing out that the assumptions of this analysis of the constancy of Me group migration rate and primary C–H insertion rate are confirmed (approximately) by the data of Table 6 which gives, for $k_{\mathrm{Me}}:k_{\mathrm{prim}}$, values of 4.1 for methylethylvinylidene and 3.1 for methylisopropylvinylidene. This interpretation of the experimental behaviour of these vinylidenes has received strong support from theoretical calculations by Goldberg and Graf von der Schulenburg[57] building on and extending the earlier work of Honjou *et al.*,[33] discussed in section 4. Using both *ab initio* and density functional theory (DFT), the authors have calculated[57] the energy surfaces for decomposition of 1-methyl-, 1,3-dimethyl- and 1,3,3-trimethyl-cyclopropenes. The DFT results relating to the vinylidenes are shown in Fig. 2. The portions of the surfaces shown have been selected to emphasise the varying energy barriers to rearrangement of the vinylidenes. The drop in values for the 1,3 C–H insertion process from primary to secondary to tertiary can clearly be seen as well as the drop in value from methyl to ethyl and slight rise from ethyl to isopropyl for the alkyl migration process. Also evident are the near constancy of the energy barriers for primary 1,3 C–H insertion and methyl migration processes for the three vinylidenes. The calculated energy differences match very well the experimental reactivity trends and show that theory and

Table 9 Selectivities for various C–H insertion processes

Species	Insertion	k_{prim}	k_{sec}	k_{tert}	T/K	Ref
Alkylcarbenes	1,2 C–H	1	40	97	400–450	45
Vinylcarbenes[a]	1,2 C–H[a]	1	18	47	500	44*b*
Vinylidenes	1,3 C–H	1	17	46	500	48*c*

[a] These figures may include carbene stabilisation effects.

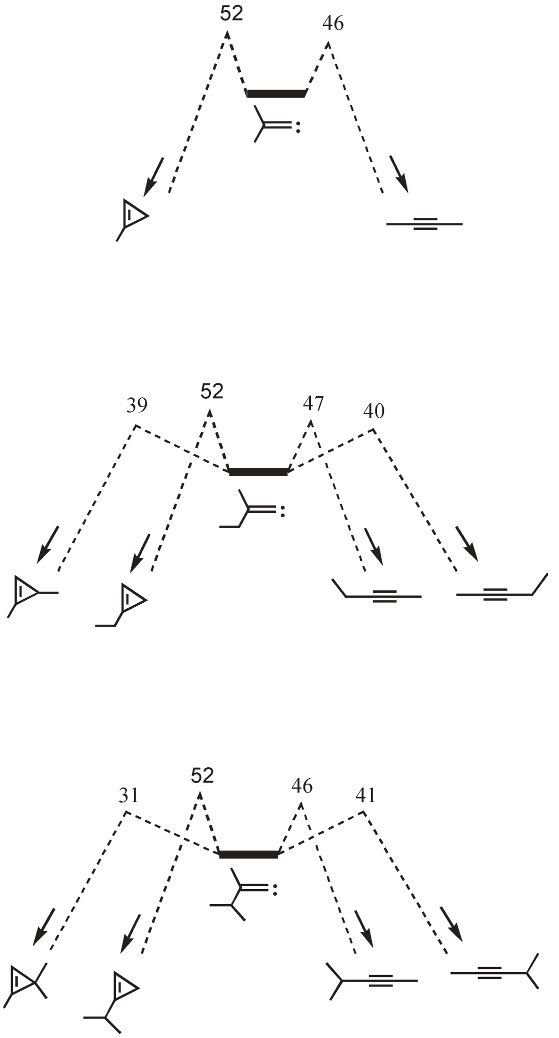


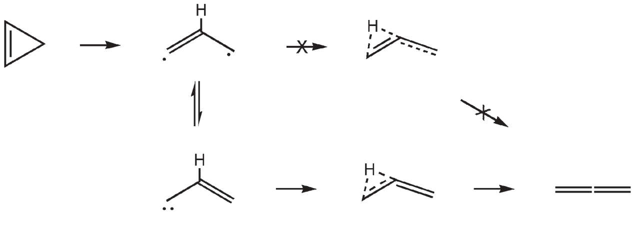
Fig. 2 Energy barriers (kJ mol^{-1}) calculated for vinylidene rearrangement processes at the B3LYP/6-31+G(2d,p) level (including ZPE corrections) in ref 57.

experiment are now in harmony at a detailed level on this aspect of the cyclopropene isomerisation mechanism. Further, more recent, DFT calculations[58] are also consistent with these findings.

8 Unfavourable products and processes

(a) Allene formation

Despite the large variations in distribution of the products of alkylcyclopropene pyrolysis, the allenes remain consistently minor, rarely rising above 1% of the total for any cyclopropene. In some cases (3-methyl- and 3,3-dimethyl-cyclopropene) they have not been detected at all. In these circumstances it is not surprising that there has been little change in our understanding of the mechanism of allene formation since the original suggestions by Srinivasan[10] and ourselves.[17] We both proposed a 1,2 H-shift in the diradical intermediate. The theoreticians[32,33] prefer to describe it as a 1,2 H-shift in the vinylcarbene intermediate, but it is the same mechanism. We accept that it is probably better envisaged as proceeding from the vinylcarbene, because the migrating H-atom formally bridges only a C–C single bond (rather than a double bond). The mechanism is summarised in Scheme 17.



Scheme 17

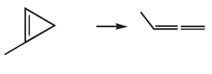
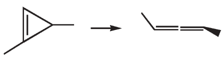
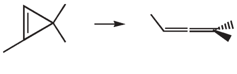
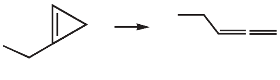
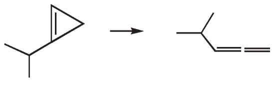
The observed rate constants at 500 K are shown in Table 10 together with their statistically corrected relative values. The data indicate slight variations between different cyclopropenes with 1-alkyl substituents producing increases and 3-alkyl substituents producing decreases (at 500 K). However given the low yields and therefore the high uncertainties of these numbers not too much significance should be attached to these trends. It is worth mentioning that for certain trimethylsilyl substituted cyclopropenes[38] (see also the review by Baird[12]) allene yields can be 100%! This is because the alkyne and diene pathways are essentially blocked in these cases. Another pathway which has been discussed in the cyclopropene-to-allene rearrangement is that *via* cyclopropenylidene shown in Scheme 18.

The theoretical calculations of Honjou *et al.*[33c] showed some time ago that this was unlikely (energy barrier too high). Even with silyl substituents, thought to favour the pathway, it also proved too high in energy.[59,12]

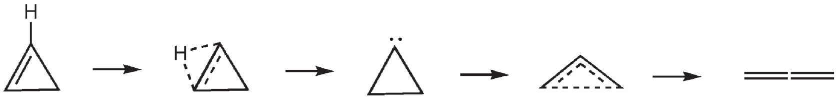
(b) Dienes formed by breaking the "wrong" C–C bond

The ring opening of 1-alkylcyclopropenes to form dienes shows a strong bias in favour of breaking the most substituted

Table 10 Comparison of rate constants and relative rates for allene formation from various cyclopropenes at 500 K

Reaction	$10^6 k/s^{-1}$	k_{rel}/σ^a	ref
	2.04	1	17
	2.41	2.41	28
	0.65	0.64	48*c*
	0.33	0.33	48*c*
	3.52	3.45	48*c*
	2.67	2.62	48*c*

^{a} σ is path degeneracy.



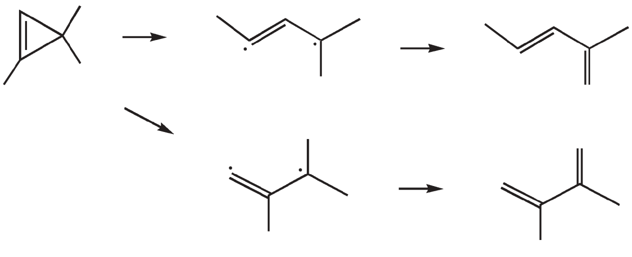
Scheme 18

C–C bond. In the pyrolyses of 1,3-dimethyl- and 1,3,3-trimethylcyclopropenes the dienes formed by breaking the least substituted C–C bond (isoprene and 2,3-dimethylbuta-1,3-diene) represent only 2.5 and 0.8% of the total dienes respectively.[48c] Indeed the yields may be even lower, because these products show the most susceptibility to catalysis by reaction vessel surfaces. The alternative bond breaking processes are shown in Scheme 19 for the case of 1,3,3-trimethylcyclopropene.

Only the diradical forms of the intermediate are shown, both for simplicity and because the diene products compared here are formed by 1,4 H-shifts (best envisaged as coming *via* this form of the intermediate as discussed earlier). The ratio of the product yields in this case is 71. A possible explanation for this lies in the structural differences between the two diradical intermediates. The diradical for the less favoured pathway suffers from disadvantages that the methyl group, instead of stabilising the vinylic radical position, is destabilising the structure by steric interference (gauche methyl interactions). Some support for the steric interference argument comes from the observation of the slow rates of pyrolysis of 1,2-dimethyl-[29] and tetramethyl-cyclopropenes,[23] where the C–C ring opening process cannot avoid placing a methyl group in the sterically unfavourable configuration. The effects found here contrast with the methylcyclopropane pyrolyses, where bond breaking preferences are much less marked and increasing methyl substitution leads to rate increases and not decreases.[11]

9 Some energetic considerations and a summary of current mechanisms

With the enormous improvements in computational power, theoretical calculations once thought difficult and unreliable are becoming commonplace. Their impact on this story has been significant. As a way of encapsulating the essence of a reaction mechanism and presenting it pictorially, a potential energy surface has few rivals. For the cyclopropene systems most recently investigated by us,[48c] *viz.* 1,3-dimethyl-, 1-ethyl-, 1,3,3-trimethyl- and 1-isopropyl-, Goldberg and Graf von der Schulenburg[51,57,60] have carried out a comprehensive set of calculations of the energy surfaces (at two levels of theory each with two basis sets). They have also done this for cyclopropene itself and 1-methylcyclopropene. Part of these results have been shown already in Fig. 2. Fig. 3 shows another illustration, this time for cyclopropene itself. The data for this surface are shown in Table 11 where they can be seen to be in reasonable agreement with the original calculations of Honjou *et al.*.[33c] This diagram effectively summarises all the essential features of the mechanism discussed in this review. The lowest energy pathway from cyclopropene to propyne is *via* propenylidene. This pathway contains three transition states of which the ring-opening TS1 is the highest in energy and therefore rate determining. TS2a corresponds to the 1,2 H-shift process for propenylidene to propyne and is barrierless. The 1,2 Me-shift *via* TS2b has a higher barrier and this route is therefore not competitive for propyne formation. The minor product allene comes through a higher (but not too high) energy pathway *via* vinylcarbene. Here the ring opening transition state TS3, is lower than the 1,2 H-shift transition state TS4 and so the latter is rate determining. Concerning the intermediates, although propenylidene is lower in energy than vinylmethylene, the lowest energy transition state is TS3. This means that racemisation of an optically active cyclopropene *via* ring opening and reclosure will occur *via* a vinylcarbene rather than a vinylidene. The originally postulated pathway from cyclopropene to propyne *via* a 1,2 H-shift process in vinylmethylene (or 1,3-propendiyl) requires passage *via* TS5, which is too high in energy to be competitive. This shows how intuitive arguments about transition states[17,28] can sometimes be wrong! The overall isomerisation from allene to propyne occurs *via* cyclopropene as postulated originally[14] with the highest transition state along this pathway being the first, *viz.* TS4.



Scheme 19

One further example is given here to illustrate the effects of methyl substituents. Fig. 4 shows the energy surface for 1,3-dimethylcyclopropene and the energy values are listed in Table 12. This surface is of necessity more complicated than that for cyclopropene itself because of the extra pathways. There is no clearcut lowest energy pathway. The calculations suggest that the rate limiting barriers to pent-2-yne (TS7b) *via* methylethylvinylidene, and to 1,3-pentadiene (TS9a) *via* pent-2-en-4-ylidene are almost equal (although experiment[48c] shows pent-2-yne formation has the lower activation energy). TS6a is the rate controlling transition state for the 1,3-dimethyl- to 1-ethyl-cyclopropene interconversion and its high energy reasonably reflects the low yield of this pathway.[48c] The relative heights of the barriers for TS6 and TS6a help explain why yields are greater for the 1-ethyl- to 1,3-dimethyl-cyclopropene isomerisation (*i.e.* the reverse reaction). The relatively high barrier to penta-2,3-diene formation (TS9b) is consistent with the low yield for this allene-forming pathway although the experimental activation energy[48c] is *ca.* 20 kJ mol^{-1} higher than calculated. The diagram shows that

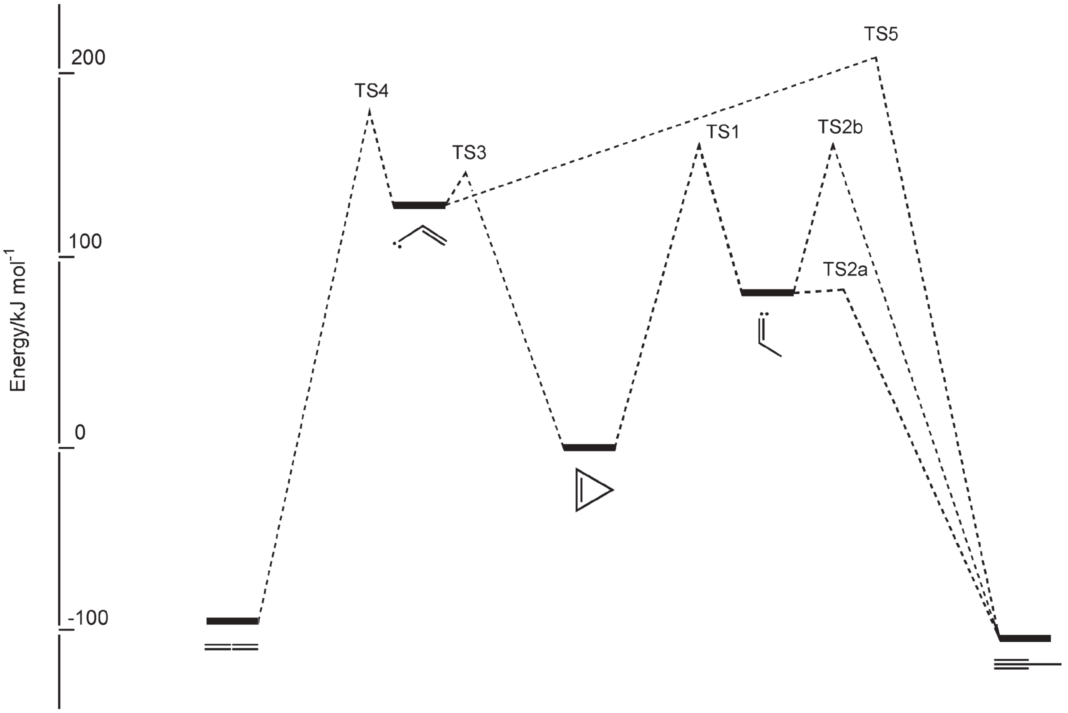
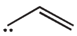


Fig. 3 Potential energy surface for cyclopropene rearrangement based on *ab initio* calculations of refs 33*c* (MRCI*/DZP) and 51 (B3LYP/6-31+G(2d,p)).

the vinylcarbene (pent-2-en-4-ylidene) is the lowest energy intermediate, accessed by the lowest barrier (TS8), which confirms that a chiral 1,3-dimethylcyclopropene will racemize faster than any of the observed isomerisation processes. The H-shift transition state (TS10) from pent-2-en-4-ylidene to pent-2-yne (analogue of TS5 in Fig. 3) is not shown but it is too high for the process to occur. The transition state TS9a leading to 1,3-pentadiene corresponds to the 1,2 H-shift process from pent-2-en-4-ylidene. The barrier for the alternative 1,4 H-shift pathway has not been calculated.‖ The potential energy surface of Fig. 4 is not a complete one for the C_5H_8 (cyclopropene) system since it does not include the 1-ethylcyclopropene decomposition pathways *via* pent-1-en-3-ylidene (vinylcarbene pathways).

‖ At the B3LYP/6-31G(d) level the barrier for the 1,4 H-shift in the *cis* carbene is *ca.* 7.7 kJ mol^{-1} lower than for the 1,2 H-shift in the *trans* carbene. Personal communication from Graf von der Schulenburg.

Table 11 Comparison of energies (kJ mol^{-1}) from various quantum chemical calculations and experiment for the C_3H_4 molecular system[a]

Molecular species	B3LYP/6-31G(d)[b]	B3LYP/6-311+G(2d,p)[b]	CCSD(T)/6-31G(d)[b]	CCSD(T)/6-311+G(2d,p)[b]	MRCI*/DZP[c]	Expt
	0	0	0	0	0	0
TS1	168	158	174	151	159	157[d]
	100	90	100	80	82	—
TS2a	98	88	101	79	72	—
TS2b	—	158	—	—	162	—
	−91	−103	−92	−108	−95.0	−91[e]
TS3	157	144	172	148	150	—
	157	144	169	145	131	—
TS4	179	162	204	174	182	181[d]
	−103	−112	−91	−103	−94	−84[e]
TS5	251	228	274	241	210	—

[a] Calculations include ZPE corrections. [b] ref. 51. [c] ref. 33c. [d] ref. 17. [e] ref. 68.

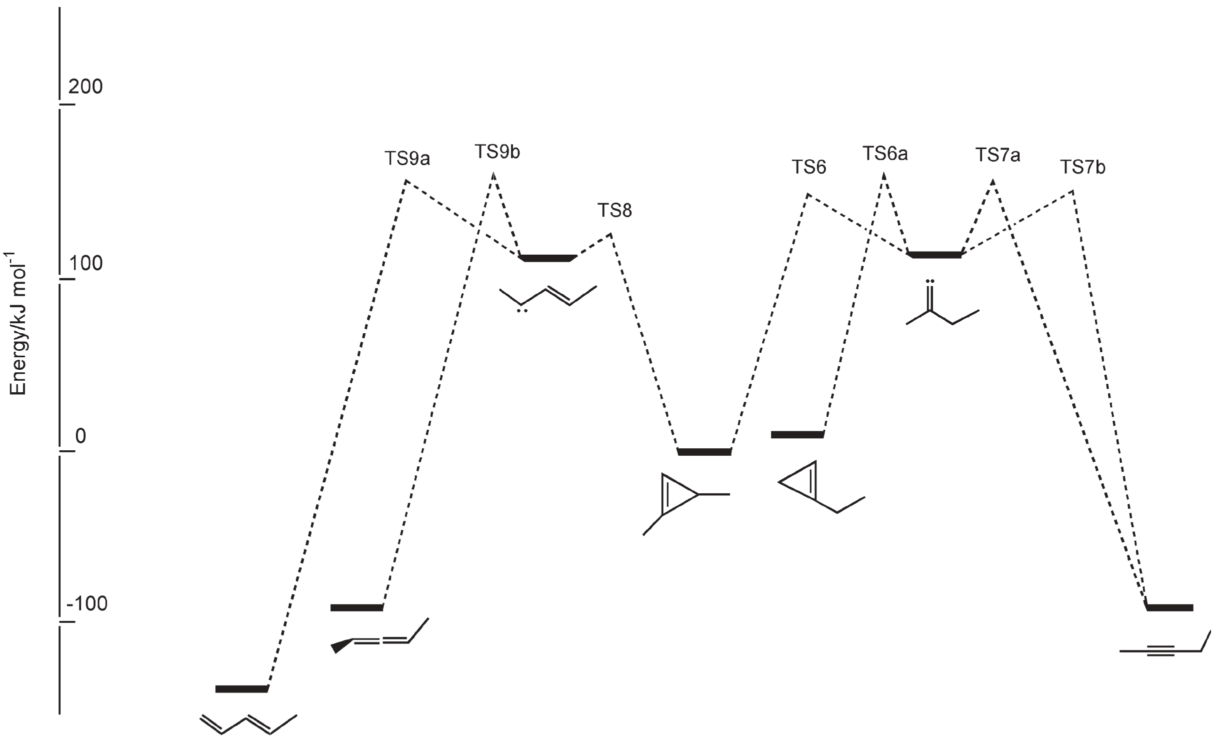


Fig. 4 Potential energy surface for 1,3-dimethylcyclopropene rearrangement based on *ab initio* calculations of ref 51 (B3LYP/6-31+G(2d,p)).

They have been calculated[51] but are omitted here for simplicity.

Thus Figs. 3 and 4 summarise virtually all of the essential mechanistic features of the cyclopropene and methycyclopropene isomerisation systems. Similar diagrams for the remaining alkyl cyclopropenes mentioned above are to be found in the pages of Graf von der Schulenburg's thesis.[51] The differences between the experimental and calculated values for activation energies or the stable species enthalpy differences are *ca.* 1 kcal mol^{-1} (4 kJ mol^{-1}) on average and not worse than 5 kcal mol^{-1} (20 kJ mol^{-1}) maximum but are dependent on the level of calculation. The differences are small enough that, for the major pathways, theory and experiment are now in pretty good agreement. However since small energy differences can have a significant effect on relative product yields there is still room for refinement of the theoretical calculations. It should also be remembered that energy surfaces do not quite capture the whole story of these mechanisms. Molecular structure will also affect entropy and thereby the *A* factor for each pathway. Experimental *A* factor variations amongst the various cyclopropene pathways are fortunately not very large. The best general summary of alkyl substituent effects on cyclopropene isomerisation, which covers the larger alkyl groups as well as methyl, is that contained in the last paragraph of section 5 and table 8.

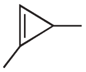
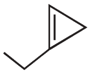
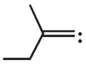
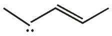
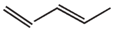
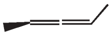
Apart from refinement of the energetics, the question to ponder at this point is... how well understood is cyclopropene decomposition? It is tempting to answer... pretty well. This would be premature. There remain questions. Some of these are addressed in the last section.

10 Conclusions and subjects for further study

It is clear that our understanding of the mechanism of cyclopropene rearrangement and indeed of all the thermal interconversions of the C_3H_4 reaction system, have significantly advanced over the past 40 years. I have tried to document the important milestones in this article as a committed participant rather than a detached observer. I hope this has not diminished the objectivity too much. As in any aspect of scientific advance one may reflect on what lessons have been learned and ponder what remains to be done.

One of the seismic shocks of this saga was the discovery of the vinylidene mechanism for propyne formation. Until that point it had seemed as if all small ring and related thermolysis processes involved either diradical intermediates or were concerted in nature. We (and Srinivasan) did not consider at the beginning of our studies of cyclopropenes, that vinylidenes might be important. Apart from lack of imagination, this was partly due to the feeling that all carbenes were high energy species and therefore inherently less likely to be involved in thermal processes. Indeed, even in 1989, Benson[61] was arguing that theoretical calculations of $\Delta H_f^o(H_2C{=}C:)$ must be wrong because they predicted values *ca.* 134 kJ mol^{-1} (32 kcal mol^{-1}) lower than his own thermochemical estimate, and because of this vinylidene could not be an intermediate in acetylene polymerisation.[62] What was missing by Benson (and others in the gas kinetics community, including ourselves) at that time was an understanding of the factors which stabilise carbenes. Some of these, such as angle bending and π-donor/acceptor substituent effects, had already been known

Table 12 Comparison of energies (kJ mol^{-1}) from quantum chemical calculations and experiment for species in the 1,3-dimethylcyclopropene rearrangement system[a]

Molecular species	B3LYP/6-31G(d)[b]	B3LYP/6-311+G(2d,p)[b]	CCSD(T)/6-31G(d)[b]	Expt[c]
	0	0	0	0
TS6	169	159	173	167[d]
	10	10	10	—
TS6a	182	171	186	166
	130	119	122	—
TS7a	177	166	179	—
TS7b	169	159	172	163[e]
	−79	−89	−76	—
TS8	145	131	160	—
	127	111	145	—
TS9a	180	159	198	172[f]
	−131	−142	−126	—
TS9b	186	166	197	186
	−84	−92	−73	—
TS10	238	217	256	—

[a] Calculations include ZPE corrections. [b] Ref. 51. [c] Ref. 48c. [d] Value from E_a for 1-ethyl-cyclopropene + 10 kJ mol^{-1} (enthalpy difference). [e] Average for pathways *via* TS7a and TS7b. [f] Value for combined 1,2 and 1,4 H-shift pathways.

for some years[63] but at that time theoretical calculations were not (or were not felt to be) reliable enough to quantify these factors. Moreover there were no experimental data on this. For us the shock of recognition that vinylidene could be regarded as a stabilised carbene was lessened by the fact that related group 14 species, the so called "heavy carbenes", were all subject to divalent state stabilisation. Indeed we had first estimated the divalent state stabilisation energies for silylenes in 1981.[64] By now it seems clear that vinylidenes, being stabilised carbenes, have to be taken seriously, not only as intermediates in cyclopropene isomerisations, but also as potential intermediates in other high temperature hydrocarbon pyrolysis systems, such as those where alkynes and aromatics are involved. This is already recognised by a number of researchers,[62,65] but by no means everyone in the world of high temperature hydrocarbon chemistry. It may be that vinylidenes also play a role in fullerene and soot formation.

Interestingly the establishment of the vinylidene mechanism for propyne formation from cyclopropene may have been responsible for stimulating a recent re-examination of the cyclopropane pyrolysis (specifically 1,1-dimethylcyclopropane-2,2-d_2[66]) to see whether there might have been a contribution to alkene formation *via* alkylcarbene involvement. The findings were negative and supported by the fact that the 1-propylidene intermediate (for cyclopropane → propene) was calculated[67] to be too high in energy to compete with the diradical (although only by *ca.* 10 kJ mol^{-1}). 1-Propylidene is less stabilised than propenylidene.

Theory has also helped to clarify the role of the vinylcarbene/1,3-diradical intermediates in the pathway by which cyclopropene converts to allene. On the prototype C_3H_4 surface (singlet surface) the lowest energy species of this type is the σ^2 vinylmethylene (in both *cis*- and *trans*- forms) with 1,3-propendiyl lying slightly higher in energy (although not a local minimum) according to Honjou *et al.*[32,33] Since the orbital occupancies of these two species are different, they have to be considered as separate electronic states and are therefore not resonant**. They lie, however, very close in energy according to the calculations, and conversion between them is easy. This is the reason that we have come to consider them to be in equilibrium (rather than in resonance as originally thought[17]). This seems to account both for the pattern of diene products formed and their observed rates of formation in the pyrolyses of alkyl substituted

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** 1,3-propendiyl is, however, resonant with σp vinylmethylene (see Scheme 3).

cyclopropenes††. It also accounts for the racemisation of optically active cyclopropenes. There is still quite a lot more to learn about these intermediates, however. For example the extent to which, when formed, they revert to cyclopropenes relative to the various possible H-shift processes open to them. This can only be discovered by further racemisation studies of the type carried out by Bergman's group[20] in 1973 and unfortunately not subsequently repeated. Another question still to be answered is whether the substituent accelerating effects on diene formation (such as that of 1-ethyl- ; see Tables 4 & 7), are due to stabilisation of the vinylcarbenes involved or merely lowering of the barriers to the H-transfer process.

A third question not yet clearly answered is why the cyclopropene ring opening processes (again to the vinylcarbene/diradical intermediates in the diene forming pathways) are so selective against the least substituted bond. Although a steric effect seems the likely cause of the higher energy barrier for the disfavoured pathway, this topic could do with further study (both experimental and theoretical) of, for example, 1,2-dialkyl substituted cyclopropenes.

The cyclopropene pyrolysis story is not yet at an end.

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†† A referee has raised the question whether the 1,3-diradical form of the intermediate needs to be considered at all if it is not a local minimum. Our argument is not based on theory alone (which may anyway be further refined in future) but rather that the 1,4 H-shifts are more characteristic of radical reactions (disproportionation analogy) than reactions of carbenes which should undergo C–H insertion. The latter process would lead to cyclobutenes, which have never been detected (even as transients).

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