Gas-Phase Kinetics of the Pyrolysis of Some 3,3-Dimethyl-1-(trimethylsilyl)cyclopropenes – Unexpected Product Distribution in the Cyclopropene Rearrangement

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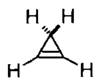
The gas-phase pyrolyses of 1,3,3-trimethyl-2-(trimethylsilyl)cyclopropene (**9**), 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene (**10**), and 3,3-dimethyl-1-(methylthio)-2-(trimethylsilyl)cyclopropene (**11**) have been studied, and the pressure-independent Arrhenius parameters listed in the table were obtained. All three rearrangements are homogeneous, first-order and unimolecular reactions. Rather surprisingly all reactions give the corresponding isomeric allenes as the main products. Amongst possible mechanisms discussed, **10** is proposed to react via a cyclopropylidene intermediate, whilst the results for **9** and **11** throw light on the relative importance of the diradical- and vinylcarbene-type intermediates produced by cyclopropene ring opening.

Reactant	$\log(A/s^{-1})$	E_a/kJ mol^{-1}	(kcal mol^{-1})
9	13.41 ± 0.22	192.1 ± 2.5	(45.9 ± 0.6)
10	13.54 ± 0.19	184.4 ± 2.1	(44.1 ± 0.5)
11	12.17 ± 0.38	124.6 ± 3.1	(29.8 ± 0.7)

The thermal rearrangements of small prototype strained-ring organic compounds continue to attract interest[1,2] as they contribute to a general mechanistic understanding of hydrocarbon rearrangements[3–5]. Cyclopropenes in particular have caught our attention[1,2,6–14] not only because they are particularly strained, but also because of continuing uncertainty and complexity in their rearrangement mechanisms. For instance, a major pathway for cyclopropene (**1**) isomerisation to acetylene (**2**) has long been thought[13,14] to be via intermediate **3**, whose structures may be represented either as diradical **3a** or vinylcarbene **3b**.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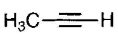
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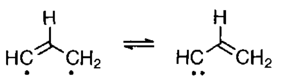
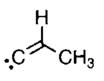

3a 3b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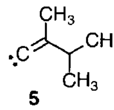
However, recent ab initio calculations by Yoshimine et al. suggested the possible involvement of 1-propylidene (**4**)[15]. Following this proposition we have recently shown[1] that the suggested vinylidene intermediate **5** offers a better understanding of the isomerisation of 1,3,3-trimethylcyclopropene (**6**) to 4-methyl-2-pentyne (**7**).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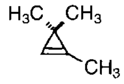
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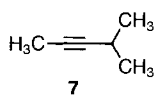
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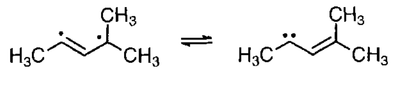
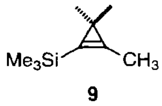

8a 8b

The remaining diene products from **6** can be rationalised as formed via diradical/carbene intermediates **8a**/**8b**. The involvement of diradicals as the precursors for the diene products of cyclopropene isomerisation is reinforced by the effects of specific trimethylsilyl substitution in selected examples studied in our laboratories[2].

However, the unexpected formation of allene-type products in the thermal rearrangements of 3,3-dimethyl-1-(methylthio)-2-(trimethylsilyl)cyclopropene (**11**) and 1-(*tert*-butoxycarbonyl)-3,3-dimethyl-2-(trimethylsilyl)cyclopropene[11] indicates that the mechanism of cyclopropene isomerisation is more complicated than so far supposed. We were therefore drawn to study the kinetics and product distribution of tetrasubstituted cyclopropenes including **11** in the hope of gaining further understanding. Because of our previous experience with trimethylsilyl substitution we selected the compounds **9**, **10**, and **11** for kinetic study.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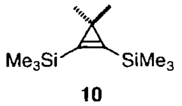
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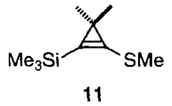
11

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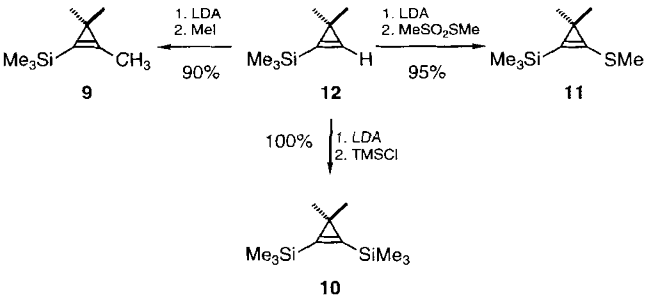
Preparation of Cyclopropenes and Kinetic Measurements

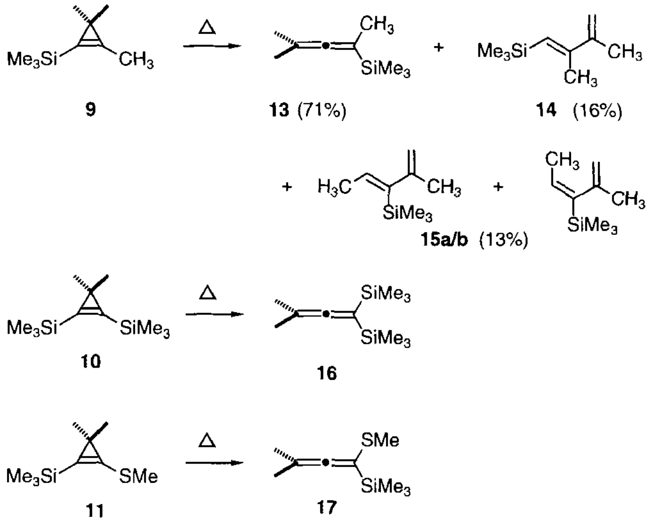
3,3-Dimethyl-1-(trimethylsilyl)cyclopropene (**12**) was prepared in two steps according to a procedure of Baird[16]. **12** could then be deprotonated with lithium diisopropylamide (LDA) and the resulting anion trapped with the necessary reagents to yield the desired cyclopropenes. The anion reacts with methyl iodide to give **9**, with chlorotrimethylsilane (TMSCl) to give **10** and with *S*-methyl methanethiosulfonate[11,17,18] to give **11**. All compounds were purified by preparative-scale gas chromatography.



(i) General Considerations and Reaction Stoichiometry

Because of problems previously encountered with cyclopropene (**1**) itself[7] we have usually attempted to carry out kinetic studies[1,2,7,10,12] using the "internal standard" method, in which the reactants were co-pyrolysed together with a stable, non-reacting substance in a fixed ratio. This was done here for **9**, but not in the case of **10** and **11**, because of practical difficulties arising from their low vapour pressures (100–200 mTorr). Gaseous mixtures, with or without internal standard, were prepared highly diluted in N_2 and handled in heated vacuum lines during thermolysis experiments (see experimental section). For **9**, in kinetic runs, the recovery was always within 100 ± 5%, thus indicating no mass loss. Although this test could not be carried out for **10** and **11**, our previous experience has shown no mass losses for any of the 3,3-dimethyl-substituted cyclopropenes[1,2,12]. However, it is possible that errors could have arisen by material absorption losses during gaseous handling. In this respect we note there was no systematic indication of changes in chromatographic peak count totals during analysis of reactant or pyrolysis product samples. Each reaction was studied over a temperature range of 50°C in a vessel conditioned with hexamethyldisilazane (HMDS). A number of other checks (see below) were also carried out.

The products of the decomposition of **9** were 2-methyl-4-(trimethylsilyl)-2,3-pentadiene (**13**) (71%), 2,3-dimethyl-1-(trimethylsilyl)-1,3-butadiene (**14**) (16%, one isomer, presumed *trans*), and 2-methyl-3-(trimethylsilyl)-1,3-pentadiene (**15**) (13%, *cis* and *trans* isomers in almost equal amounts). There was ca. 1% of another (unidentified) product. The only product of the decomposition of **10** was 3-methyl-1,1-bis(trimethylsilyl)-1,2-butadiene (**16**). The decomposition of the (methylthio)cyclopropene **11** gave 3-methyl-1-(methylthio)-1-(trimethylsilyl)-1,2-butadiene (**17**) as the only product. Products were identified by NMR and IR on isolated pyrolysis samples (see experimental section).



(ii) Time Dependence

For each of the compounds **9**, **10**, and **11** a set of runs was carried out at each temperature for times giving between 10 and 90% decomposition. The initial pressure of the reactant mixture was kept constant at 20 ± 2 Torr (corresponding to an actual reactant pressure of 0.2 Torr). In the case of compound **9** the product ratio shows only small scatter but no systematic tendency with time, indicating that the products are formed by parallel pathways. The product ratios are almost independent of temperature. For all three compounds, good linear first order plots [log (% reactant) versus time] were obtained at all temperatures. Rate constants were obtained by least-mean-squares fitting.

(iii) Temperature Dependence

Good first order rate constants (as judged by small standard deviations) were obtained for the decomposition of the cyclopropenes **9**, **10**, and **11** (see Tables 1–3). The data for each decomposition were fitted to the Arrhenius equation giving the parameters shown in the summary. For **9**, rate constants for individual pathways could be obtained from the product analysis. The rate constants for these are shown in Table 4 and the Arrhenius parameters in Table 5. The quality of the data may be judged by the Arrhenius plots for the overall decomposition shown in Figures 1 to 3. For **9** and **10** the fit is extremely good, while that for **11** shows

Table 1. Rate constant variation with temperature for **9**

Temperature/°C	10^4 k/s^{-1}
300.3	0.811 ± 0.003
311.8	1.80 ± 0.01
319.5	3.15 ± 0.02
329.8	6.22 ± 0.03
340.0	10.91 ± 0.04
350.9	21.40 ± 0.11

Table 2. Rate constant variation with temperature for **10**

Temperature/°C	10^4 k/s^{-1}
269.7	0.609 ± 0.002
280.2	1.45 ± 0.04
290.5	2.81 ± 0.07
302.0	6.34 ± 0.17
311.9	12.03 ± 0.13
322.9	22.93 ± 0.16

Table 3. Rate constant variation with temperature for **11**

Temperature/°C	10^4 k/s^{-1}
120.5	0.464 ± 0.005
129.8	0.961 ± 0.062
142.5	3.18 ± 0.07
149.8	6.94 ± 0.17
160.4	15.07 ± 0.49
167.8	24.60 ± 0.44

Table 4. Rate constants for specific products from **9** and their temperature dependences

Temperature/°C	10^4 k/s^{-1}			
	13	**14**	**15a**[a]	**15b**[a]
300.3	0.585	0.128	0.052	0.046
311.8	1.29	0.288	0.120	0.104
319.5	2.23	0.516	0.213	0.196
329.8	4.41	0.995	0.420	0.393
340.0	7.67	1.77	0.758	0.732
350.9	14.90	3.50	1.50	1.49

[a] These products are the *cis/trans* pair, **15a** and **15b**, but are not individually identified (see text).

Table 5. Arrhenius parameters for the decomposition of **9** by individual pathways

Reaction product	log(A/s^{-1})	E_a/kJ mol^{-1}	(kcal mol^{-1})
13	13.09 ± 0.21	190.1 ± 2.5	(45.4 ± 0.6)
14	12.76 ± 0.24	193.7 ± 2.8	(46.3 ± 0.7)
15a	12.68 ± 0.22	197.1 ± 2.6	(47.1 ± 0.6)
15b	13.31 ± 0.24	204.6 ± 2.7	(48.9 ± 0.7)

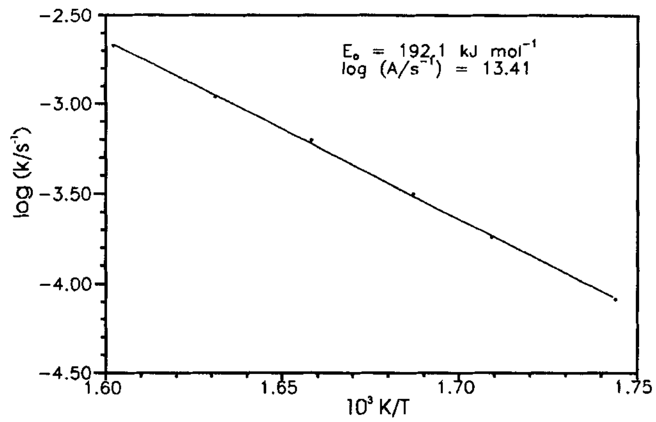


Figure 1. Arrhenius plot for the decomposition of 1,3,3-trimethyl-2-(trimethylsilyl)cyclopropene (**9**); line represents least squares fit

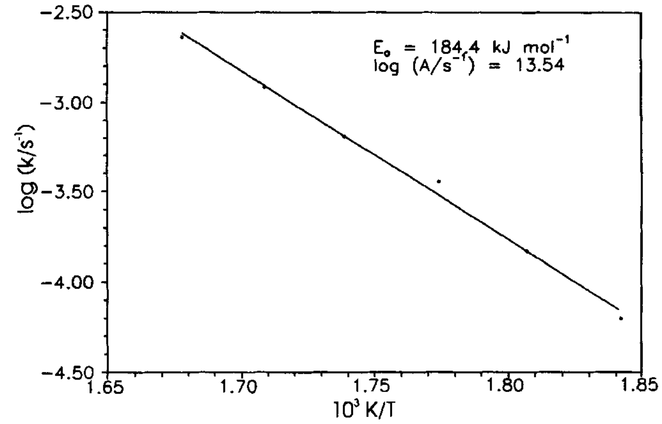


Figure 2. Arrhenius plot for the decomposition of 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene (**10**); line represents least squares fit

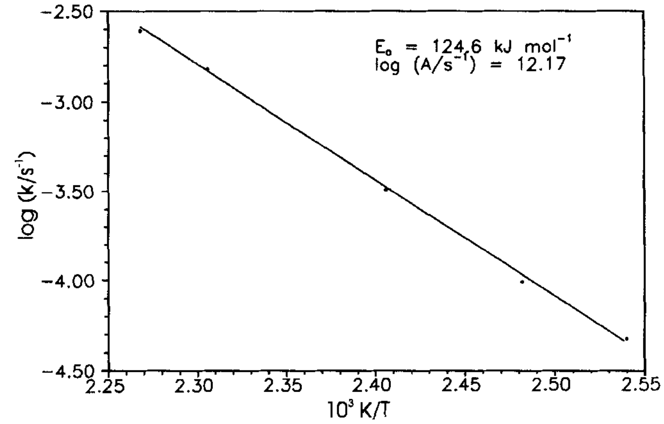


Figure 3. Arrhenius plot for the decomposition of 3,3-dimethyl-1-(methylthio)-2-(trimethylsilyl)cyclopropene (**11**); line represents least squares fit

slightly more scatter. The parameters for **11** are in reasonable agreement with those obtained in solution by Stohlmeier[18] [log(A/s^{-1}) = 11.97; E_a = 117.5 kJ mol^{-1}].

(iv) Further Kinetic Tests

Unimolecular rate processes can show characteristic pressure dependencies. Pyrolytic processes can be affected by free radical chain contributions and heterogeneous catalysis. Checks were carried out during the present studies to test whether any of these effects were occurring. For instance at 311.8°C in a 90-min run at a total pressure of 20 Torr the conversion of **9** was 57%. At a total pressure of 90 Torr the conversion was 59%. In the presence of a more than 20-fold excess of *cis*-butene (radical inhibitor) the conversion was 62%. These variations, within experimental error, indicate that the isomerisation of **9** is neither pressure-dependent nor involves a free radical process. Tests on **10** and **11** showed a similar lack of pressure dependence or radical chain contributions.

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 ca. 13 cm^{-1} compared with ca. 0.7 cm^{-1} in the normal (unpacked) vessel. The packed vessel was conditioned with HMDS prior to use. The isomerisation of **10** and **11** showed negligible alterations in conversion under test conditions (e.g. for **10** at 280.2°C, reaction for 60 min gave 34% conversion in the unpacked vessel, 36% in the packed vessel). However, the reaction of **9** was affected in a more significant way. In the packed vessel at 311.8°C a run of 90 min gave 89% conversion (62% in the unpacked vessel). This corresponds to a factor of 2.6 increase in rate of product formation (mainly **13**). Even with repeated HMDS conditioning of the packed vessel this could not be reduced. Since this clearly indicated some heterogeneous contribution, its effect was further investigated by reducing the vessel packing to give a "half-packed" vessel of surface-to-volume ratio of ca. 4 cm^{-1}. The repeat test with **9** now gave a conversion of 73% (after HMDS conditioning), less than in the fully packed vessel but more than in the unpacked vessel. Although this still suggests some surface activity, the conversion now corresponds to only a factor of 1.4 faster rate of product formation. Thus the reduction in S/V by a factor of ca. 3 has reduced the product formation rate by nearly a factor of 2. If the reaction was mainly heterogeneous in all vessels then the further reduction of S/V by a factor of 6 from the half-packed to the unpacked vessel should reduce product formation by a further substantial factor (of greater than 2). Since the excess rate in the half-packed vessel is only 40% this suggests that in the unpacked vessel the reaction is mainly homogeneous. Whilst we cannot rule out a small surface contribution to the rate, we believe the effect to be minimal in the unpacked vessel.

Discussion

(i) General Comments

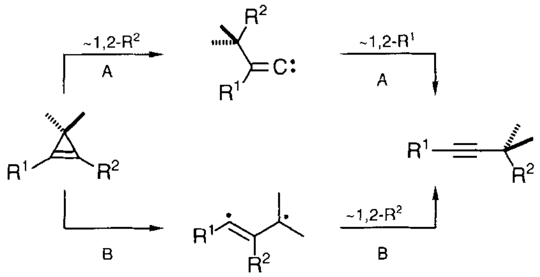
There are no previous kinetic studies of **9** and **10** and no previous gas-phase measurements of the rate constants of **11**. The A factors (see summary and Table 5) for these decompositions are generally consistent with those obtained previously[1,2,6–13] for other cyclopropenes. A_9 and A_{10}, corresponding to ca. zero entropies of activation, are in accord with fairly rigid transition states. A_{11} looks to be a little low, and although no evidence for a surface reaction was found, this still suggests a possible small contribution to the rate from such a source at low temperatures.

The rate pattern, largely determined by the magnitudes of the activation energies, is somewhat complex. Compared with other cyclopropenes, the isomerisations of **9** and **10** are very slow, whilst that of **11** is very fast. As a reference point, 1,2,3,3-tetramethylcyclopropene (**18**), the only other tetrasubstituted cyclopropene for which gas-phase rate data is available[13], decomposes significantly more slowly [$\log(A/s^{-1}) = 12.5$, $E_a = 167$ kJ mol^{-1}] than di- and trimethyl-substituted cyclopropenes.

The product pattern is even more confusing. The formation of allenes as sole or major products is highly unusual. Allenes are usually very minor products (for cyclopropene itself[7] or 1-methylcyclopropene[9]), and for many cyclopropene decompositions allenes are not formed at all.

We believe we can offer an explanation for these apparently surprising results (vide infra), but it should be born in mind that a satisfactory explanation must include an account of why other possible isomerisation products are *not* formed. This is most important for **9** and **10**, since these two cyclopropenes react more slowly than expected, but less serious for **11**, because the rate of its decomposition is fast enough to outstrip other pathways even if they could occur in principle. These other products include acetylenes and dienes, which are the common products of isomerisation of cyclopropenes. Most easy to understand is the lack of acetylenes. This is explained with the aid of Scheme 1, which shows the two possible mechanistic pathways for isomerisation of tetrasubstituted cyclopropenes to acetylenes, viz. via a vinylidene (route A) or via a diradical (vinylcarbene) (route B) intermediate.

Scheme 1



Along either route, at least one of the two groups R^1 or R^2 has to migrate, and along route A both R^1 and R^2 have to undergo 1,2-shifts in consecutive steps. It is already clear from existing studies that only H atoms have a high tendency to migrate. Methyl groups do not seem to migrate during any cyclopropene decomposition so far studied, and trimethylsilyl groups, whilst they can undergo 1,2-shifts in vinylidenes[2] (R^1 = Me_3Si, Scheme 1, second step along route A) apparently would have a very small tendency to undergo a 1,2-shift as in the first step along route A[2,12].

Dienes are formed from **9**, albeit as minor products, but not at all from **10**. Diene formation appears to require the intermediacy of diradicals[2,12], and therefore inhibition of diene formation or drastic slowing down of their rates of formation implies *either* that diradical formation is inhibited *or* that, if formed, diradical rearrangement to dienes is prevented. With these general points in mind, we now offer detailed suggestions for the mechanisms of each of the cyclopropenes studied.

(ii) 1,3,3-Trimethyl-2-(trimethylsilyl)cyclopropene (9)

The major product is 2-methyl-4-(trimethylsilyl)-2,3-pentadiene (**13**). For comparison purposes, relative rate constants for all the observed allene-forming reactions from cyclopropenes are shown in Table 6. It appears that allene formation from **9** is only a factor of ca. 6 slower than allene formation from cyclopropene (**1**) itself (this may seem surprising, but it should be recalled that allene itself is only a very minor product of ca. 0.27% in the parent case). Since allene is thought to arise from **1** by a 1,2-H shift in intermediate **3a/3b**[7,9,15], a similar process needs to be considered for **9**. The corresponding intermediates are the diradicals/vinylcarbenes **20a/20b** and/or **21a/21b**.

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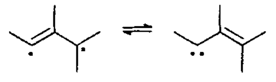
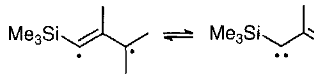
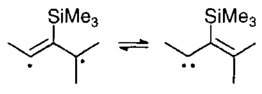


19a **19b**

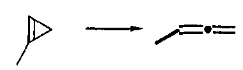
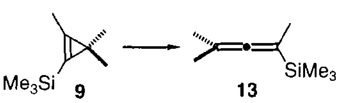
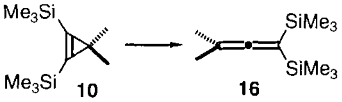
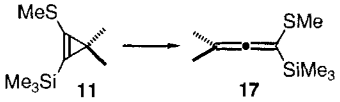


20a **20b**



21a **21b**

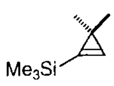
Table 6. Rate constants for allene formation from some cyclopropenes at 500 K

Reaction	10^6 k/s^{-1}	k_{rel}/σ[a,b]	Ref.
	2.04	1	7
	2.41	2.36	9
 **9** → **13**	0.17	0.17	This work
 **10** → **16**	1.88	0.92	This work
 **11** → **17**	1.42×10^5	1.39×10^5	This work

[a] *k* relative to the value for cyclopropene (**1**). – [b] σ is path degeneracy.

Although these pairs of intermediates are undoubtedly involved in diene formation (vide infra), their implication in formation of **13** is not so obvious. **20a/20b** can be ruled out because the formation of **13** would require a 1,2-Me shift. This process is known not to occur from intermediates **19a/19b** since tetramethylallene is not a product of the decomposition of **18**. However, **13** could be formed by a 1,2-Me_3Si shift in **21a/21b**. This has some plausibility, since it seems that a 1,2-Me_3Si shift does occur in the vinylidene intermediate **23** implicated[2] in the isomerisation of 3,3-dimethyl-1-(trimethylsilyl)cyclopropene (**22**)[12] to 3-methyl-1-(trimethylsilyl)-1-butyne (**24**). Our earlier study[12] of **22**, a trisubstituted cyclopropene, showed it to undergo a particularly clean reaction giving 99% of **24**.

There was no evidence for the formation of the diradical/vinylcarbene intermediates **26a/26b** which could lead to allene formation. If the rate constant for this from **22** had been comparable to that for **9** to **13**, shown in Table 6, then less than 0.1% of allene would be expected. Thus the results for **9** and **22** are not incompatible. It is merely that **22** has the much faster acetylene-forming channel available. In spite of this, there is an alternative mechanism for the **9**-to-**13** rearrangement, which is discussed in the next section concerning the **10**-to-**16** interconversion.



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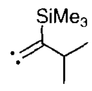

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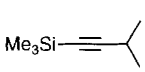

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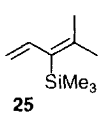

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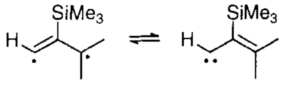
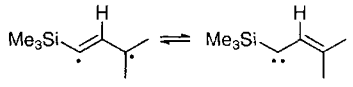


26a **26b**

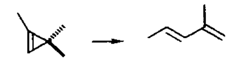
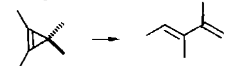
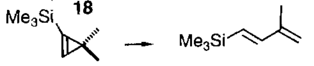
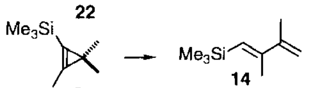
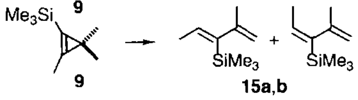


27a **27b**

We next consider the formation of the diene products **14** and **15**. For comparison purposes, relative rate constants for diene formation from a set of closely related cyclopropenes, including **9**, are shown in Table 7. It is clear that the formation of **14** and **15** from **9** is much slower than any other of the reactions listed. This appears to be the result of a combination of two effects. First the replacement of a 1-methyl with a 1-trimethylsilyl group lowers the rate by a factor of ca. 20 (cf. **22** and **6**) and secondly the addition of a fourth methyl (2-methyl) to a trisubstituted cyclopropene also lowers the rate by a factor of ca. 20 (cf. **18** and **6**). The fact that diene formation from **9** is even slower than the combination of these two factors is probably due to the extreme steric crowding in the diene products **14**, **15a** and **15b**, two of which contain vicinal methyl and trimethylsilyl groups in a *cis* arrangement. However, the underlying reasons for these effects are not fully clear. The diene products shown in Table 7 are best explained[2,12] as 1,4-H shift products from diradical intermediates. Then the reason for the rate reduction from **6** to **18** is probably the steric crowding in diradical **19a** (methyl group *cis* interaction) compared to **8a**. The reason for the rate reduction from **6** to **22** is not at all obvious. The diradical involved (from **22**) is **27a** which does not appear to possess any exceptional steric crowding. We can only presume that there is an electronic effect causing a small, but effective, bond strengthening in the cyclopropene ring, when a 1-methyl group is replaced by a 1-trimethylsilyl. Thus, although the reasons for the low rate constants for **9** are only partially apparent, the rate data are nevertheless fully consistent with other cyclopropenes studied[1,12,13].

The particular distribution of the dienes is also worthy of comment. The excess of **14** over **15** indicates that passage of the reaction via **20a/20b** is slightly preferred over **21a/21b**. The substituent effects already discussed are in reasonable accord with this. The origin of the *cis* product **15b** is interesting. Dienes formed according to this mechanism are invariably formed in the *trans* configuration, because of the steric requirements of the transition state for the 1,4-H transfer[1,12,13]. We therefore think that **15b** is more likely to arise by a rapid secondary reaction. The reaction temperature is a little low for direct *trans*-to-*cis* isomerisation[19], and a more reasonable alternative would be via 4-

Table 7. Rate constants for diene formation from some cyclopropenes at 500 K

Reaction	10^4 k/s^{-1}	$k_{rel}/\sigma^{[a,b]}$	Ref.
 6	0.96	1	1
 6	0.026	0.027	1
 18	0.094	0.049	13
 22	0.046	0.048	12
 9 → 14	3.4 x 10^{-4}	3.5x10^{-4}	This work
 9 → 15a,b	2.1x10^{-4}	2.2x10^{-4}	This work

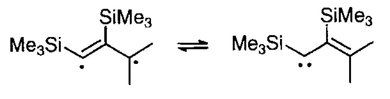
[a] k relative to value for 1,3,3-trimethylcyclopropene (6). – [b] σ is path degeneracy.

methyl-3-(trimethylsilyl)-1,3-pentadiene (**25**). This would be formed from **21b** by a 1,2-H shift and would indeed be expected in comparable yield to **15a** based on the product distribution found for the decomposition of 1,3,3-trimethylcyclopropene (**6**)[1]. **15b** then should be formed from **25** by a 1,5-H shift, a process which should occur rapidly at the temperatures of study[20]. Normally, these 1,5-H shift processes are highly reversible as well as rapid, but **25** looks to be an extremely sterically crowded compound, with four substituents on a double bond, one of which is a trimethylsilyl group. Therefore the equilibrium pressure of **25** is almost certainly small compared with that of **15b**. The diene product distribution from **9**, therefore, looks entirely reasonable.

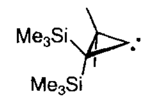
(iii) 3,3-Dimethyl-1,2-bis(trimethylsilyl)cyclopropene (10)

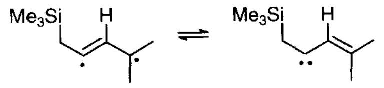
The sole product of isomerisation of **10** is the allene 3-methyl-1,1-bis(trimethylsilyl)-1,2-butadiene (**16**). Examination of Table 6 indicates that the rate constant for its formation is comparable to that for allene from cyclopropene (**1**). Thus, the obvious suggestion for the mechanism of formation of **16** is by a 1,2-Me$_3$Si shift in the diradical/vinylcarbene **28a/28b**. There are two reasons, however, to question this. In the first place, there are no diene products, which might be expected from diradical **28a**. Secondly, **28a** and to a lesser extent **28b** contain severe *cis* interactions. The starting material cyclopropene **10** itself has a *cis* interaction of the two trimethylsilyl groups, but because of the wider angle between 1,2-substituents on the cyclopropene ring, this is not so severe as that in the putative diradical **28a**. It is hard to estimate this effect, but it is known that the *cis* repulsion between two *tert*-butyl groups is about 40 kJ mol^{-1}[21,22]. Thus the involvement of **28a/28b** is open to serious doubt.

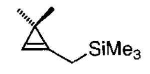
An alternative intermediate, not previously invoked in thermal cyclopropene isomerisations, is a substituted cyclopropylidene.


28a **28b**

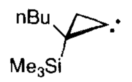

29

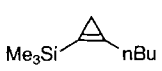

30


31a **31b**


32

Unsubstituted cyclopropylidene (**29**) lies 166 kJ mol^{-1} higher in energy than cyclopropene (**1**), according to most recent ab initio calculations[15]. However, the 1,2-H shift transition state necessary to reach it requires a further 62 kJ mol^{-1}. In the case of **10**, the intermediate would be the 2,2-bis(trimethylsilyl)cyclopropylidene **30**. To reach this requires a 1,2-Me$_3$Si shift and so, in view of apparent facility of this process, described here and elsewhere[2], **30** is a possible intermediate. Furthermore it seems likely that not only is the formation of **30** facilitated, but that **30** is actually stabilised by an effect of the β-trimethylsilyl groups, similar to that found for the diradical/vinylcarbene **31a/31b** implicated in the rearrangement of 3,3-dimethyl-1-[(trimethylsilyl)methyl]cyclopropene (**32**)[2]. These arguments are supported indirectly by a recent observation[23] of a reverse 1,2-Me$_3$Si shift in the rearrangement of the directly prepared cyclopropylidene **33** to cyclopropene **34**. One question remains. Could the energy barrier for the rearrangement of **30** to **16** be prohibitive? For the rearrangement of the parent cyclopropylidene (**29**) to allene the ab initio calculations[15] indicate an energy barrier of 43 kJ mol^{-1}, although it is the formation of **29** from **1** that is rate-determining in the overall cyclopropene (**1**)-to-allene process according to this route. For **30** we suspect rearrangement to **16** rather than formation from **10** should now be rate-determining, because of the silicon substitution effects. This is implicit in the rearrangement of **33** to **34**[23]. Since the allene **35** is not the observed product from **33**, its rate of formation must be slower.


33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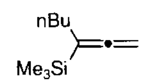

35

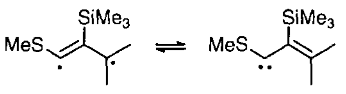
An increment of 43 kJ mol^{-1} for the rearrangement barrier of **30** would then give a maximum activation energy prediction for the isomerisation of **10** of 209 kJ mol^{-1}, without allowance for the β-stabilisation energy of the two trimethylsilyl groups. The 25 kJ mol^{-1} difference required to bring this figure into agreement with the experiment seems to us a very reasonable value for this stabilisation energy.

Thus, for this cyclopropene the trimethylsilyl substituents appear to dictate a mechanism via a cyclopropylidene rather than the more usual diradical/vinylcarbene intermediate. This is yet another example of the striking effects induced by trimethylsilyl groups on cyclopropene isomerisation[2]. It is possible, although not as likely, that the same mechanism could operate in the isomerisation of **9** to **13**, in which case the appropriate intermediate would be **36**.

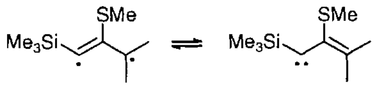
(iv) 3,3-Dimethyl-1-(methylthio)-2-(trimethylsilyl)-cyclopropene (11)

The sole product from **11** is 3-methyl-1-(methylthio)-1-(trimethylsilyl)-1,2-butadiene (**17**). Examination of Table 6 indicates that the rate for its formation is ca. 10^5 times faster than the isomerisation of **10** to **16**. The activation energy difference is some 60 kJ mol^{-1}. Since the only difference between **11** and **10** is the replacement of a Me_3Si by a MeS group, clearly the MeS substituent is responsible for this dramatic effect. Following the discussion of the rearrangement of **10**, the possible intermediates would appear to be the two diradical/vinylcarbene pairs **37a**/**37b** and **38a**/**38b**, and the cyclopropylidene **39**.

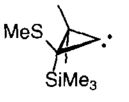
36



37a **37b**



38a **38b**



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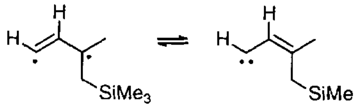
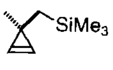
Whichever is involved will be determined by the magnitudes of the MeS interactions. Although to our knowledge these are quantitatively unknown, the required effect must be substantial. Diradicals **37a** and **38a** can probably be ruled out, because radical centre stabilisation by a MeS or a Me_3Si group are not of the required magnitude[24,25]. Of the carbenes, **37b** involves an α-interaction, whilst **38b** and **39** have β-interactions with the MeS group. α-Substituents in carbenes, particularly involving elements with lone pairs and/or empty d orbitals, are known to produce substantial stabilisations[26], and so **37b** seems a good candidate for the intermediate. The effects of β-substituents on carbenes are largely unknown[27], but we have evidence from further studies[28] that for MeO-substituted cyclopropenes, α-stabilisation of the vinylcarbene intermediates is greater than β-stabilisation. Furthermore, a variety of 1-chlorocyclopropenes undergo low-temperature ring opening to yield α-chlorovinylcarbenes which have been trapped[29,30]. These arguments seem to favour **37b** over **38b** and **39** as the likely intermediate in the isomerisation of **11**. To form the product **17** then requires a 1,2-Me_3Si shift in **37b**. We have seen this process already (vide supra) as a likely explanation of the formation of **13** from **9**. Because no dienes are formed from **11** this argues against the formation of intermediate **37a**.

This result seems to be the first in the gas phase, where the ambiguity of which valence isomer, diradical or vinylcarbene intermediate, is clearly removed. For the C_3H_4 system itself, described in detail by Yoshimine, Pakansky, and Honjou[15,31], these forms are very close in energy and interact resonantly at certain geometries, thus making the experimental distinction between their reactivities impossible. However, it now seems clear that, by suitable substitution, at least the vinylcarbene form can be stabilised at the expense of the diradical. The closest example of the opposite situation appears to be that of the intermediates **40a**/**40b** involved in the isomerisation of 3-methyl-3-[(trimethylsilyl)-methyl]cyclopropene (**41**)[2]. In this reaction 91% of the products can be explained by 1,4-shifts (of either H or Me_3Si) in the diradical **40a**. In that case the diradical is stabilised at the expense of the vinylcarbene by a β-silicon interaction. We intend to expand on these ideas in a future publication[32].



40a **40b**



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Experimental

^1H NMR: Bruker WM 250 (250 MHz), Perkin Elmer R 34 (220 MHz), Jeol JNM X 400 (400 MHz); δ = 7.15 for [D5]benzene, 7.26 for chloroform. – ^{13}C NMR: Bruker WM 250 (67.9 MHz), Jeol FX 90Q (22.5 MHz), Jeol JNM X 400 (100 MHz); δ = 128.0 for [D6]benzene, 77.0 for [D1]chloroform. – IR: Perkin Elmer 399. – GC: Analytical: Perkin Elmer 8410, Siemens Sichromat 3; preparative: Varian Aerograph 920 (carrier gas H_2, 3/8" Teflon columns with Chromosorb W-AW-DMCS, 60–80 mesh). – Materials: Nitrogen (British Oxygen, White Spot Grade) containing no detectable impurities.

Preparation of the Compounds: 3,3-Dimethyl-1-(trimethylsilyl)cyclopropene (**12**) was prepared according to a procedure of Baird[16]. 3,3-Dimethyl-1-(methylthio)-2-(trimethylsilyl)cyclopropene (**11**) and 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene (**10**) were prepared following a procedure of de Meijere et al.[11].

1,3,3-Trimethyl-2-(trimethylsilyl)cyclopropene (**9**): To a solution of 6.9 ml (39 mmol) of diisopropylamine and 17.2 ml (36 mmol) of a 2.07 M solution of *n*-butyllithium in hexane in 30 ml of dry THF was added at –78°C 4.55 g (32.4 mmol) of the cyclopropene **12**. The mixture was stirred for 30 min at room temp., cooled again to –78°C and quenched with 6.1 ml (37 mmol) of dry methyl iodide. After 4 h at room temp. the mixture was added to 250 ml of water. The aqueous phase was extracted with three portions of diethyl ether (50 ml each), and the combined organic phases were dried with $MgSO_4$. The ether was distilled over a 25-cm packed column and the residue purified by bulb-to-bulb distillation under reduced pressure yielding 4.5 g (90%) of **9**. Samples for the kinetic studies were further purified by preparative-scale gas chromatography (2 m 10% SE 30, 40°C). – IR (film): $\tilde{\nu}$ = 2958 cm^{-1}, 2853, 1794, 1635 (C=C), 1437, 1363, 1249 (Si–CH_3), 1125, 1027, 839. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.10 (s, 3H, CH_3), 1.10 (s, 6H, CH_3), 0.15 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 144.8 (C-1), 121.5 (C-2), 27.2 (CH_3), 19.6 (C-3), 11.6 (CH_3), –0.5 [$Si(CH_3)_3$]. – $C_9H_{18}Si$ (154.3): calcd. C 70.05, H 11.76; found C 70.00, H 11.62.

Kinetic Measurements: Apparatus: This was similar to that used in earlier studies[9,10]. Gases were handled in conventional grease-free vacuum systems made from pyrex with Rotaflo (Quickfit) stopcocks. The reaction vessel used for most experiments was spherical (volume ca. 250 ml), it was placed in a stirred salt ($NaNO_2/KNO_3$ eutectic) thermostat controlled by an AEI (GEC) RT 5 controller for compounds **9** and **10**. For compound **11** an Ultrathermostat from the Meßgerätewerke Lauda filled with oil was used. Temperatures were measured with a Pt/Pt-13% Rh thermocouple calibrated against a precalibrated Pt resistance thermometer (Tinsley, Type 5187 SA). For the oil thermostat, a set of calibrated conventional Hg thermometers was used. Product analyses were made by gas chromatography (Perkin Elmer F 33 and 8410) with FID detection and electronic peak integration (Hewlett-Packard HP 3380 S). For compound **9** a 1.8 m × 1/8″ cyanosilicone column (15% on Chromosorb W) operated at 70°C was used for the quantitative analyses. The products from the pyrolyses of **10** and **11** were analysed on a 1.5 m × 1/8″ SE-30 column (5% on Chromosorb W) operated at 50°C. Pressures were measured with a conventional Hg manometer.

Experimental Procedure: The reaction of **9** was studied using an internal standard chosen for stability and analytical convenience. The reactant master mixture consisted of about 0.5% of **9** and 0.5% of *n*-hexane diluted to about 500 Torr with N_2 in a 500-ml reservoir. Runs were carried out by admitting a known pressure of the mixture into the reaction vessel for a certain time (2.5 min to 16 h). The reaction was quenched by sharing the reaction vessel contents with a pre-evacuated sample bulb, from which samples could be injected into the gaschromatograph. After five to six runs, a blank analysis was made of the unused master mixture to check the mass balance of the reaction. For compounds **10** and **11** this method was not convenient, as the vapour pressure of the substances was too low. In these cases the full vapour pressure was admitted into the line, diluted with 70 Torr of N_2, and the resulting mixture was shared with the pre-evacuated reaction vessel. Afterwards the resulting mixture was analysed as described above.

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 ^1H- and ^{13}C-NMR spectroscopy on isolated samples after pyrolysis. In the case of product **16** the amount of sample was not sufficient to detect the central carbon C-2 in the ^{13}C-NMR spectrum, so an additional IR spectrum confirmed its structure.

Spectroscopic Data of the Products

13: ^1H NMR (250 MHz, $CDCl_3$): δ = 1.63 (s, 6H, CH_3), 1.62 (s, 3H, CH_3), 0.05 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 204.8 (C-4), 112.6 (C-3), 88.0 (C-5), 20.1 (CH_3), 15.7 (CH_3), –1.6 [$Si(CH_3)_3$].

14: ^1H NMR (250 MHz, $CDCl_3$): δ = 5.66 (bs, 1H, 1-H), 5.12 (bs, 1H, 4-H), 5.01 (bs, 1H, 4-H), 2.00 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 0.18 [s, 9H, $Si(CH_3)_3$].

15: The concentration of **15a**/**15b** was too small for verifying the structure. At δ = 5.24 the quartet for the proton at C-4 was clearly visible. The formation of the possible products 2-methyl-3-(trimethylsilyl)-1,3-pentadiene and 4-methyl-4-(trimethylsilyl)-2-pentyne can be ruled out.

16: IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2900, 2840, 1933 (C=C=C), 1440, 1360, 1250 (Si–CH_3), 860, 840, 760, 695. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.58 (s, 6H, CH_3), 0.05 [s, 18H, $Si(CH_3)_3$].

17: ^1H NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 3H, SCH_3), 1.72 (s, 6H, CH_3), 0.15 [s, 9H, $Si(CH_3)_3$]. – ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 199.5 (C-2), 98.0 (C-1), 95.3 (C-3), 15.4 (SCH_3), –1.0 [$Si(CH_3)_3$].

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