The Kinetics of Pyrolysis of 1,3,3-Trimethylcyclopropene. Evidence for the Involvement of Alkylidene Carbenes in the Thermal Isomerisation of Cyclopropenes

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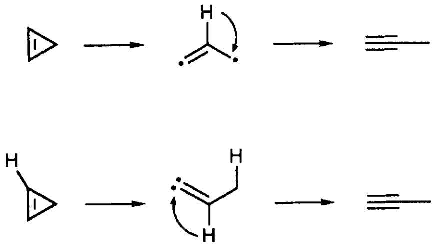
A low yield of 4-methylpent-2-yne in the gas-phase isomerisation of 1,3,3-trimethylcyclopropene is shown to be more consistent with an alkylidene carbene transient than with a 1,3-biradical intermediate.

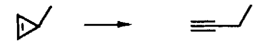
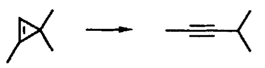
Vinylidene, $H_2C=C:$, is a thermodynamically unstable isomer of acetylene.[1] If it can be formed at all, it is almost certain that it reverts rapidly to acetylene by a 1,2 H-shift process, which is calculated to possess a very low (if not zero) activation barrier.[1] Its involvement as an intermediate in hydrocarbon chemistry may, therefore, be difficult to verify. It has, however, been proposed as a transient intermediate in the degenerate rearrangement[2a] and thermal oligomerisation chemistry of acetylene,[2b] in the high temperature decomposition of ethylene[3] and in the pyrolysis of methylenecyclopropane.[4] Higher homologues of vinylidene, such as isopropenylidene, $Me_2C=C:$, appear to have a long enough existence to be capable of intermolecular trapping,[5] presumably because the 1,2 methyl-shift required to form the acetylene isomer (in this case but-2-yne) is a much slower process than a 1,2 H-shift.[6]

Recent theoretical calculations[7] have implicated another alkylidene derivative, propenylidene, $MeCH=C:$, as an intermediate in the cyclopropene to propyne isomerisation. Prior to this proposal, this reaction was thought to proceed *via* the intermediacy of a 1,3 biradical.[8–10] The two possible mechanisms are shown in Scheme 1. Although a number of studies of this isomerisation have been carried out,[11] up to now no clear cut distinction has been possible between these alternatives. We present new evidence here which is strongly suggestive of the vinylidene type of intermediate in this rearrangement.



Scheme 1

Table 1 Rate constants for acetylene product formation from some cyclopropenes at 500 K

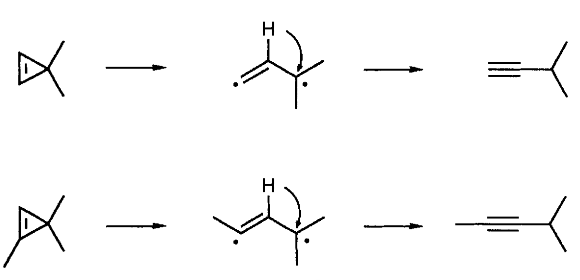
Reaction	$k/10^{-4}\,s^{-1}$	$k_{rel}/\sigma^{a,b}$	Ref.
	7.32	1	9
	1.44	0.39	10
	10.46	1.43	8
	9.47	1.31	11
	0.527	0.144	This work

[a] *k* relative to the value for cyclopropene. [b] σ is path degeneracy (*i.e.* = no. of migrating 1-hydrogens).

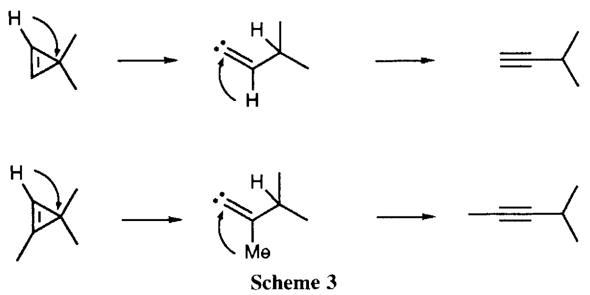
We have carried out a gas-phase kinetic and product analytical reinvestigation of the pyrolysis of 1,3,3-trimethylcyclopropene. In addition to our general interest in the cyclopropene rearrangement,[9–11] we were prompted to study this compound by the apparent finding in the earlier study by Srinivasan[8] that the acetylene derivative was less than 5% of the total products, in contrast to less substituted cyclopropenes where it is always greater than 90%. In the present study carried out between 483 and 523 K, six products were found, of which five (constituting >98% of the total) were positively identified (by ^1H and ^{13}C NMR spectroscopy) and quantitatively analysed by GC. The products are 4-methylpent-2-yne (22%), (*E*)-2-methylpenta-1,3-diene (41%), (*Z*)-2-methylpenta-1,3-diene (3%), 4-methylpenta-1,3-diene (33%), and 2,3-dimethylbuta-1,3-diene (1%). These products (and yields) contrast sharply with the earlier study,[8] which found only two major products not including 4-methylpent-2-yne. In our study the reaction was found to be homogeneous and unimolecular (first-order kinetics up to 90% conversion; rate constants independent of reaction vessel surface-to-volume ratio). Arrhenius parameters were obtained for the five observed products. In particular for the acetylene formation see eqn. (1).

$$\log(k/s^{-1}) = (12.78 \pm 0.28) - (163.3 \pm 2.7\ \text{kJ mol}^{-1})/RT\ln 10 \quad (1)$$

Thus for this particular cyclopropene, although the acetylene product is significant, there is no doubt that it is minor, in contrast to other cyclopropenes. Relative rate figures reinforce the unusually low rate of acetylene formation in this study. Table 1 shows a rate comparison for several methyl-substituted cyclopropenes. The comparison between 3,3-dimethylcyclopropene, **1**, and 1,3,3-trimethylcyclopropene, **2**, is most revealing. Schemes 2 and 3 show the two processes compared in terms of the two possible mechanisms. In Scheme 2, the obvious rate-discriminating step is ring opening, where



Scheme 2



Scheme 3

the 1-methyl substituent in **2** should enhance biradical formation. It is hard to see the 1,2 H-shift in the second step leading to any significant difference. Thus, this mechanism, if anything, suggests that **2** should react faster than **1**. In Scheme 3 the first step involves synchronous ring opening with H-transfer (the reverse of a carbene insertion process). This looks very similar for the two compounds. In the second step, however, the alkylidene carbene from **1** rearranges to the acetylene *via* a 1,2 H-shift, whereas that from **2** requires a 1,2 methyl-shift, a process known to be much slower. If this second step is sufficiently slow, the first step may cease to be rate determining and the overall rate will be slowed down. Thus Scheme 3, with this added postulate, offers an explanation of the rate retardation. There is, in fact, a study by Wolinsky *et al.*[12] of alkylidene carbenes which suggests that cyclopropene formation might be competitive with a 1,2-alkyl-group shift (although the particular cyclopropene, if formed, isomerised to a methylenecyclopropane derivative under experimental conditions).

It is worth adding that, in a study carried out some 18 years ago,[13] optically active 1,3-diethylcyclopropene was found to undergo racemization some 8 times faster than isomerisation. At the time, this was interpreted as indicating that ring opening was followed by rapid bond rotation and reclosure in excess over the second stage H-shift. However, ring opening to an alkylidene carbene with reinsertion also explains the loss of optical activity. In this example the acetylene product is also minor (33% of the total products) and its formation *via* this route requires a 1,2-ethyl shift in the second step.

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