Some Striking Rate and Migration Effects of Trimethylsilyl Substituents on Cyclopropene Isomerisation

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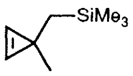
Kinetic studies of the gas-phase isomerisation of two trimethylsilyl substituted cyclopropenes reveal a novel 1,4 Me_3Si-shift and a rate enhancement of *ca.* 1200 corresponding to a 1,2 Me_3Si-shift, both explicable in terms of β-stabilisation of the biradical intermediate.

Activating groups are of great benefit in synthetic organic chemistry. Trimethylsilyl substituents, Me_3Si–, are known to produce a variety of effects on hydrocarbon thermal isomerisations. In trimethylsilylcyclopropane, the Me_3Si group exerts a modest acceleration relative to cyclopropane of *ca.* a factor of 5, which is product directing and seems to occur by preferential 1,2 Me_3Si-shift in the biradical intermediate.[1] The Me_3Si group can undergo concerted, sigmatropic 1,3-migration across an acyclic allylic carbon framework[2] where alkyl groups would require the driving force of built-in strain (*e.g.* in the bicyclo[2.1.1]- to bicyclo[3.1.0]-hexene rearrangement[3]). Perhaps the most dramatic example is the 1,5 Me_3Si-shift in 5-trimethylsilylcyclopentadiene which occurs some 10^6 times faster than the corresponding H-shift.[4] We recently studied the 1-trimethylsilyl-3,3-dimethylcyclopropene isomerisation and were surprised to find, rather than an acceleration, a *ca.* factor of 3 decrease in rate compared with 3,3-dimethylcyclopropene.[5] This communication describes some new rate effects induced by the Me_3Si group.

We have carried out gas-phase kinetic and product analytical studies on two more Me_3Si-substituted cyclopropenes. The compounds selected, shown below, were chosen in order to position the Me_3Si group in potentially activating sites of previously studied methyl substituted cyclopropenes.[5,6]

3-Methyl-3-(trimethylsilylmethyl)cyclopropene **1** was studied between 423 and 474 K. Five products were found, of which four (constituting >97% of the total) were positively identified (by ^1H and ^{13}C NMR spectroscopy) and quantitatively analysed by GC. The major product was (*E*)-1-trimethylsilyl-3-methylbuta-1,3-diene (48%), with the (*E*)- and (*Z*)-isomers of 1-trimethylsilyl-2-methylbuta-1,3-diene present at 36 and 7%, respectively and 3-(trimethylsilyl)-methylbut-1-yne at 6%. All products were formed by



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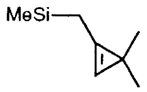

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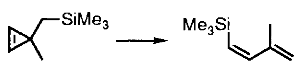
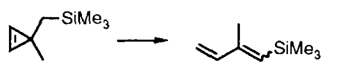
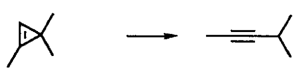
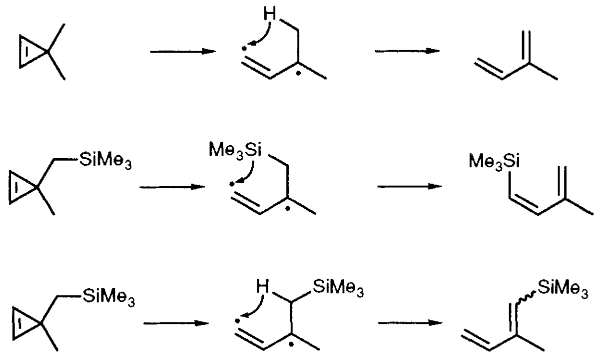
Table 1 Rate constants for selected product formation from some cyclopropenes at 500 K

Reaction	$k/10^{-4}\,s^{-1}$	$k_{rel}/\sigma^{a,b}$	Ref.
1,4-Shift			
	0.973	1	5
	43.0	265	This work
	40.6	125	This work
1,2-Shift			
	0.769	3.16	6
	306	3774	This work
-Yne formation			
	9.47	58.4	5
	0.520	6.41	6
	3.47	42.8	5

[a] k relative to the value for 3,3-dimethylcyclopropene. [b] σ is path degeneracy.



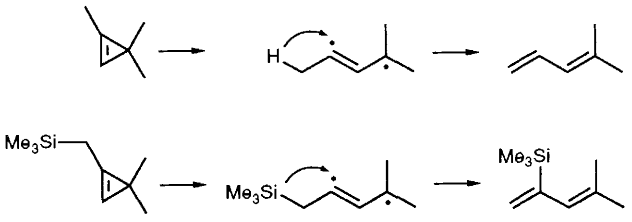
Scheme 1

homogeneous, unimolecular reactions (first-order kinetics up to 85% conversion; rate constants independent of reaction vessel surface-to-volume ratio) and their Arrhenius parameters were obtained. For the major product see eqn. (1).

$$\log(k/\mathrm{s}^{-1}) = (12.73 \pm 0.30) - (144.5 \pm 2.6\ \mathrm{kJ\ mol}^{-1})/RT\ln 10 \quad (1)$$

3,3-Dimethyl-1-(trimethylsilylmethyl)cyclopropene **2** was studied between 423 and 463 K. The major product (*ca.* 90% of the total) was 2-trimethylsilyl-4-methylpenta-1,3-diene (identified by ^{1}H and ^{13}C NMR spectroscopy). The remaining two products, as yet unidentified, appeared to be a slowly interconverting pair of further isomers. The reactions were again found to be unimolecular and homogeneous. The Arrhenius equation for the major product is shown in eqn. (2).

$$\log(k/\mathrm{s}^{-1}) = (13.95 \pm 0.16) - (148.0 \pm 3.0\ \mathrm{kJ\ mol}^{-1})/RT\ln 10 \quad (2)$$



Scheme 2

Comparison of the rate constants of some of these processes with earlier studied cyclopropene reference reactions are shown in Table 1. Rate accelerations in **1** and **2** are clearly dramatic and substantial. The processes by which the major products are formed are shown in Schemes 1 and 2. The mechanisms are most easily envisaged as proceeding *via* biradicals.[7]† The main findings are the following. (*i*) In **1** the major pathway involves a 1,4 Me_3Si-migration (to our knowledge, the first such example). (*ii*) In **1** the principal activating effect of Me_3Si is on the *ring-opening* step (shown by the accompanying large acceleration in the 1,4 H-migration). This is consistent with the known β-stabilising effect[8] of silicon on one of the radical centres. In the 1,4-shift itself, Me_3Si-migration is only favoured by a factor of 2.1 over H-migration. However, an indication of the high driving force of this rearrangement is the stereospecific formation of the highly hindered *cis* product. (*iii*) In **2**, the major pathway involves a 1,2 Me_3Si-migration. The rate acceleration here is

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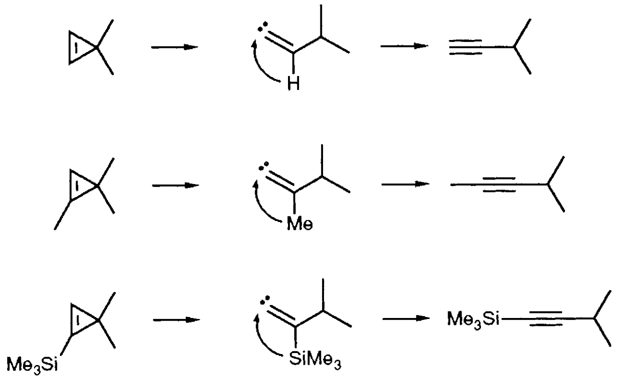
† The intermediate may be considered as either a biradical or a vinyl carbene. The possible electronic states of this intermediate have been considered in detail in a recent theoretical paper.[7] The distinctions are not critical for the interpretations presented here.



Scheme 3

ca. 1200 times compared with the model compound. (*iv*) In **2**, the activating effect is again largely associated with the *ring-opening* step (the minor products are not yet identified, but they arise almost certainly *via* either 1,2- or 1,4-H-shift processes in the biradical). The migratory aptitude of Me_3Si relative to that of H in the 1,2-shift must be at least 18-fold.

It is interesting to note the activating effects of Me_3Si- in **1** and **2** swing the mechanistic balance in favour of diene formation (*via* biradicals) against alkyne formation. This is further evidence in favour of our suggestion, in the previous communication,[6] that alkynes are formed by a different mechanism (*viz.* *via* alkylidene carbenes).

One further comparison supports the high migratory aptitude of Me_3Si in the cyclopropene system, although this one is less obvious. Table 1 shows that the 1-Me_3Si group is 6.7 times more activating than the 1-methyl, and almost as effective as 1-H, in the pathway leading to acetylene. We have argued[6] that the mechanism of this rearrangement involves alkylidene carbene intermediates as shown in Scheme 3. Theory[9] has suggested that a 1,2 silyl-shift is comparable to, if not faster than, the 1,2 H-shift in alkylidene carbenes, which has a very low energy barrier. Thus in the 1-Me_3Si–, and 1-H–compounds ring opening should be rate determining, and the overall rates should be of similar magnitude (as observed), whereas, as argued previously,[6] the 1-Me– compound is slow because of the low migratory aptitude of the Me group, making the second step rate determining.

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