

Gas-Phase Kinetics of Pyrolysis of 3,3-Dimethylcyclopropene and Its 1-Trimethylsilyl Derivative

The Effect of Silyl Substitution on Cyclopropene Isomerisation

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The gas-phase pyrolysis of 3,3-dimethylcyclopropene (**1**) in the temperature range of 185–225°C gives 3-methyl-1-butyne (**2**) (91%) and isoprene (**3**) (9%). The gas-phase pyrolysis of 3,3-dimethyl-1-trimethylsilylcyclopropene (**4**) in the temperature range of 195–235°C gives 3-methyl-1-trimethylsilyl-1-butyne (**5**) (99%) and *trans*-3-methyl-1-trimethylsilyl-1,3-butadiene (**6**) (1%). Both rearrangements are homogeneous, first-order, unimolecular reactions with the following pressure-independent Arrhenius parameters.

Reactant	$\log(A/s^{-1})$	E_a [kJ mol ⁻¹ (kcal mol ⁻¹)]
1	13.34 ± 0.04	156.1 ± 0.3 (37.3 ± 0.1)
2	12.81 ± 0.16	155.7 ± 1.5 (37.2 ± 0.4)

Rather surprisingly, the trimethylsilyl group deactivates cyclopropene with respect to its isomerisation. Possible mechanisms are discussed.

Gas-Phasen-Kinetik der Pyrolyse von 3,3-Dimethylcyclopropen und seinem 1-Trimethylsilyl-Derivat. – Der Effekt der Silyl-Substitution auf die Cyclopropen-Isomerisierung

Die Gasphasen-Pyrolyse von 3,3-Dimethylcyclopropen (**1**) im Temperaturbereich 185–225°C ergibt 3-Methyl-1-butin (**2**) (91%) und Isopren (**3**) (9%). Die Gasphasen-Pyrolyse von 3,3-Dimethyl-1-trimethylsilylcyclopropen (**4**) führt zu 3-Methyl-1-trimethylsilyl-1-butin (**5**) (99%) und *trans*-3-Methyl-1-trimethylsilyl-1,3-butadien (**6**) (1%). Beide Umlagerungen sind homogene, unimolekulare Reaktionen erster Ordnung mit den folgenden druckunabhängigen Arrhenius-Parametern.

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Überraschenderweise desaktiviert die Trimethylsilyl-Gruppe das Cyclopropen in bezug auf seine Isomerisierung. Mögliche Mechanismen werden diskutiert.

The study of small prototype strained-ring organic compounds has contributed both to a theoretical understanding of unimolecular reactions¹¹ and to a mechanistic understanding of hydrocarbon isomerisations^{2,3}. As part of our continuing interest in cyclopropenes^{4–9} we wish to report details of a study of the thermal decompositions of 3,3-dimethylcyclopropene (**1**) and 3,3-dimethyl-1-trimethylsilylcyclopropene (**4**). Srinivasan^{10,11} has previously studied the pyrolysis of **1** but no study of the decomposition of **4** has been reported.

Apart from general interest in cyclopropenes, we were principally attracted to the study of **4** by the desire to investigate the effect of silyl group substitution on cyclopropene rearrangement. Thermal rearrangements of organosilicon compounds are a topic of great current interest¹². Part of the interest is centred on the migratory aptitude of a silyl (or trimethylsilyl) group¹³. Silyl group migrations have been effectively put to use in the preparation of reactive silicon-containing intermediates (for example in silene-to-silylene conversions¹⁴). As far as migration rates are concerned, a trimethylsilyl group is known to migrate ca. 10⁶ times faster than a hydrogen atom in the [1,5] sigmatropic rearrangements of cyclopentadiene¹⁵. On the other hand, a much more modest factor of ca. 5 (again

favouring Me₃Si over H migration) seems to operate for the [1,2] shift in the biradical intermediate implicated in the isomerisation of trimethylsilylcyclopropane¹⁶. A comparison of the rates and products of isomerisation of **4** and **1** should reveal whether silyl group migration occurs, and with what aptitude, during cyclopropene rearrangement.

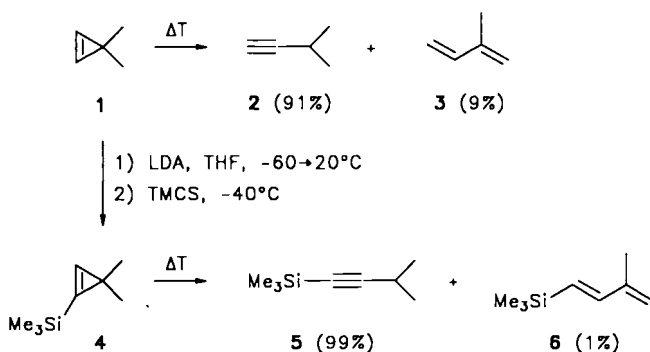
Preparation of Cyclopropenes and Kinetic Measurements

3,3-Dimethylcyclopropene (**1**) was prepared in three steps by the addition of dibromocarbene to isobutene¹⁷, reductive monodebromination of the adduct with lithium aluminum hydride in the presence of silver perchlorate¹⁸, and dehydrobromination with potassium *tert*-butoxide in dimethyl sulfoxide¹⁹.

1 was deprotonated with lithium diisopropylamide (LDA) in tetrahydrofuran²⁰, and the anion trapped with chlorotrimethylsilane (TMCS) to give 3,3-dimethyl-1-trimethylsilylcyclopropene (**4**) and 3,3-dimethyl-1,2-bis(trimethylsilyl)-

cyclopropene in a ratio of 10:7. The monosilyl derivative was purified by preparative scale gas chromatography.

(i) *General Considerations and Reaction Stoichiometry:* The kinetic studies were carried out using the "internal standard" method, in which reactants were copolyrised together with a stable nonreacting substance in a fixed ratio. This approach was adopted because of problems previously encountered with cyclopropene itself⁵. The mixtures were highly diluted with nitrogen and thermolysed (see experimental section). The products of decomposition of **1** were 3-methyl-1-butyne (**2**) (90.7 ± 0.4%) and isoprene (**3**) (9.3 ± 0.4%) in good agreement with Srinivasan¹⁰. The products of decomposition of **4** were 3-methyl-1-trimethylsilyl-1-butyne (**5**) (98.8%) and *trans*-3-methyl-1-trimethylsilyl-1,3-butadiene (**6**) (ca. 1.2%).



Yields of compound **6** were too small to monitor for kinetics. In kinetic runs the recovery of **1**, **2**, and **3** starting from **1**, and of **5** starting from **4**, was always within 100 ± 3% thus indicating no mass loss in these decompositions. This is consistent with earlier studies of methylated cyclopropenes^{7,10} although not cyclopropene itself⁵. Each reaction was studied as a function of time at five different temperatures in a reaction vessel conditioned with hexamethyldisilazane (HMDS). A number of other tests and checks (see below) were also carried out.

(ii) *Time Dependence:* For each reactant compound a set of runs was performed at each temperature at times corresponding to decomposition between 10 and 85%. Initial reactant mixture pressures were kept constant at 21 ± 2 Torr (corresponding to actual reactant pressures of ca. 0.2 Torr). Examples of the analytical results are shown in Tables 1 and 2. The product ratio **2/3** shows a small scatter but no systematic tendency with time. This was confirmed at other temperatures and indicates that both products were formed by parallel pathways. Good first-order plots (in % of **1** or **4** vs. time) were obtained at all temperatures. Rate constants were obtained from the slopes by least-mean-squares fitting. In the decomposition of **1** the rate constants were divided into contributions from individual pathways in accordance with product ratios.

(iii) *Temperature Dependence:* For the decomposition of **1** and **4** first-order rate constants were obtained (see Table 3 and 4, respectively) with a good quality of data fit, as judged by the small uncertainties. The data for each decomposition, including the individual pathways for **1**, were fitted to the

Table 1. Pyrolysis of 3,3-dimethylcyclopropene (**1**); product variation with time at 204.6 °C^{a)}

Time [min]	1	Total (%) 2	3	Ratio 2/3
10	89.33	9.67	0.99	9.74
20	79.82	18.28	1.90	9.65
40	63.98	32.64	3.38	9.66
60	51.41	44.03	4.57	9.64
80	41.05	53.40	5.55	9.63
120	26.52	66.62	6.86	9.71

^{a)} Initial pressure ca. 21 Torr (1% of **1** in N₂).

Table 2. Pyrolysis of 3,3-dimethyl-1-trimethylsilylcyclopropene (**4**); product variation with time at 203.8 °C^{a)}

Time [min]	30	55	120	180	240	300
4 (%)	89.5	81.9	65.7	52.3	42.8	35.3

^{a)} Initial pressure ca. 21 Torr (1.2% of **4** in N₂).

Arrhenius equation yielding the parameters shown in Table 5. The quality may be judged by the Arrhenius plots for overall decompositions of **1** and **4** shown in Figure 1. The data for **1** may be compared with Srinivasan's previous results^{10,11}. Although Srinivasan's quoted Arrhenius parameters [$\log(A/s^{-1}) = 13.0 \pm 0.4$, $E_a = 153 \pm 4$ kJ mol⁻¹] are not quite the same as those of Table 5, the absolute rate constants are in good agreement.

(iv) *Further Kinetic Tests:* Small molecules may show characteristic pressure dependencies of their first-order rate constants. Since the principle aim of this study was to obtain and compare rates under limiting high-pressure conditions, it was important to verify that the chosen pressures were sufficiently high. For **1**, a run carried out for 30 min at 214.4 °C with an initial pressure of 193 Torr gave 53.4%

Table 3. Rate constant variations with temperature for **1**^{a)}

Temperature [°C]	10 ⁴ k [s ⁻¹]	10 ⁴ k ₁ [s ⁻¹] ^{b)}	10 ⁵ k ₂ [s ⁻¹] ^{c)}
184.8	0.338 ± 0.001	0.308 ± 0.001	0.305 ± 0.005
194.0	0.77 ± 0.014	0.70 ± 0.014	0.73 ± 0.017
204.6	1.843 ± 0.004	1.670 ± 0.004	1.727 ± 0.005
214.4	4.09 ± 0.014	3.71 ± 0.014	3.79 ± 0.03
224.2	8.75 ± 0.031	7.91 ± 0.031	8.39 ± 0.06

^{a)} Error limits are one standard deviation. — ^{b)} Rate constant for formation of **2**. — ^{c)} Rate constant for formation of **3**.

Table 4. Rate constant variation with temperature for **4**^{a)}

Temperature [°C]	195.7	203.8	214.7	225.4	234.6
10 ⁴ k [s ⁻¹]	0.303 ± 0.003	0.582 ± 0.005	1.36 ± 0.012	3.24 ± 0.01	6.38 ± 0.09

Table 5. Arrhenius parameters for the decomposition of **1** and **4**^{a)}

Reaction	$\log(A/s^{-1})$	E_a [kJmol^{-1} (kcal mol^{-1})]
1 (overall decomp.)	13.34 ± 0.04	156.1 ± 0.3 (37.3 ± 0.1)
1 \rightarrow 2	13.28 ± 0.04	156.0 ± 0.3 (37.3 ± 0.1)
1 \rightarrow 3	12.5 ± 0.15	158 ± 1.4 (37.8 ± 0.3)
4 \rightarrow 5	12.8 ± 0.16	156 ± 1.5 (37.2 ± 0.4)

^{a)} The data for **4** \rightarrow **5** effectively are overall decomposition parameters as **5** constitutes 99% of products.

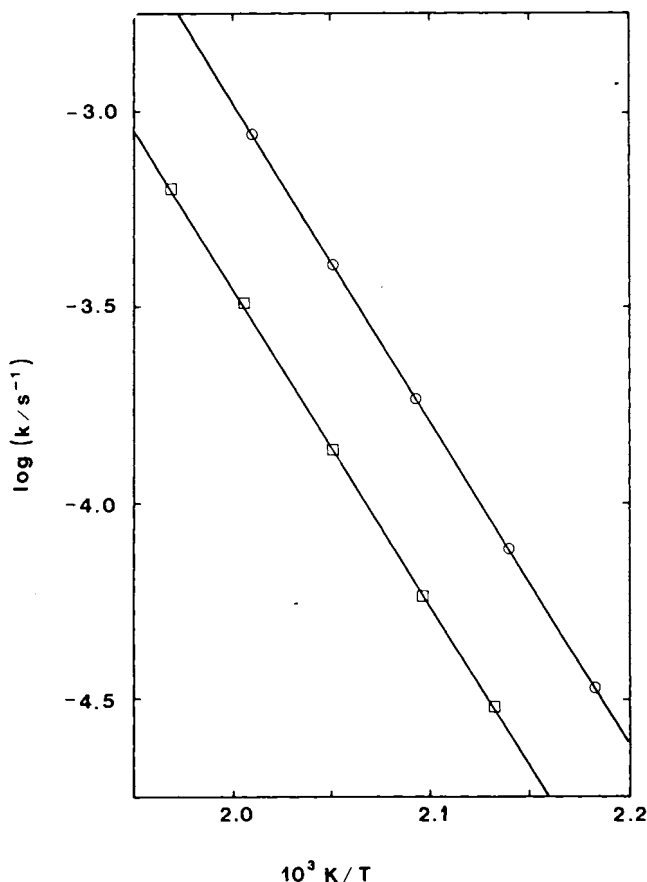


Figure 1. Arrhenius plots for the decompositions of **1** (○) and **4** (□); lines represent least squares fit

decomposition, which may be compared with 52.6% decomposition for the run at 21 Torr. The product distributions were also the same (within experimental error) thus indicating no pressure dependence at or above 21 Torr. For a larger molecule such as **2**, a pressure dependence of the rate constant would be even less likely. Nevertheless, a similar test was carried out, which confirmed that no pressure dependence occurred in this case either.

Tests for homogeneity were carried out by a study of the reaction in an HMDS-conditioned packed vessel (surface-to-volume ratio $S/V \approx 13 \text{ cm}^{-1}$). For the decomposition of **1**, a run carried out for 4 h at 184.8°C gave 49.0% decomposition compared with 39.2% decomposition in the unpacked vessel ($S/V \approx 0.7 \text{ cm}^{-1}$). However, the increased conversion was entirely due to increased formation of isoprene (**5**) since the amount of 3-methyl-1-butyne (**4**) (35.5%)

was identical. Despite repeated conditioning, it proved impossible to reduce the amount of isoprene. Thus, the evidence on heterogeneity is not clear-cut. While the major product, **2**, is clearly produced by a homogeneous process, the minor product may be slightly affected by surfaces. However, the increase in isoprene yield in the packed vessel is by no means in proportion to the increase in S/V . This fact, taken together with the consistent product ratios and good first-order kinetics, suggests that, in the unpacked vessel, isoprene formation is also probably homogeneous.

For the decomposition of **4**, a run carried out for 4 h at 195.7°C, gave 35.5% decomposition in the packed vessel compared with 34.8% decomposition in the unpacked vessel. These are in essential agreement, and thus the decomposition of **4** is free of surface catalysis, although it should be noted that the minor formation of **6** increased to 1.13% (from 0.44%) in the packed vessel.

Further tests to probe for a possible radical component of the reaction were carried out by pyrolysis of each reactant mixture in the presence of a 10-fold excess of *cis*-2-butene. These tests were carried out in both packed and unpacked vessels. For **1**, the only observed effect was a reduction (by ca. 50%) of the formation of isoprene (**3**) in the packed vessel. The unpacked vessel product yields (and rate constants) were unaffected. For **4**, there were no significant changes in either packed or unpacked vessel. Thus, there appears to be no radical component to these decompositions except to the minor surface-catalysed isoprene (**3**) formation in the packed vessel.

Discussion

(i) *3,3-Dimethylcyclopropene* (**1**): The Arrhenius parameters for this decomposition are consistent with those obtained previously^{5,7,8,10,11} for other cyclopropenes and within error limits the same as Srinivasan determined previously for **1**¹⁰. The effects of methyl group substitution in the 3-position on cyclopropene are shown in Table 6. There is a slight effect of rate enhancement on 3-methyl substitution. This is in contrast to the previously found deactivating effect of a 1-methyl substituent^{7,8}, but more in line with methyl substitution effects in cyclopropane and cyclobutane pyrolyses. These findings, however, leave the question of mechanism ambiguous.

The magnitudes of the Arrhenius parameters previously obtained have been argued to be consistent with the involvement of an intermediate considered either as a biradical **7** or vinylcarbene **8** (Scheme 1). Recent ab initio calculations on the C_3H_4 potential energy surface²¹ suggest a possible alternative mechanism (for the acetylene-forming pathway) via a vinylidene-type intermediate **9**, which can undergo a facile [1,2-H] shift to yield **2**. The Arrhenius parameters measured here and previously^{5,7,8,10,11} do not permit a distinction between these possibilities. It should, however, be said that low A factors are probably more consistent with the concerted-type process involving transition state **10**, which is required to reach **9**, than with the more open structure of the rate-determining transition state **11** leading from biradical **7** to product **2**. On the other hand it is known

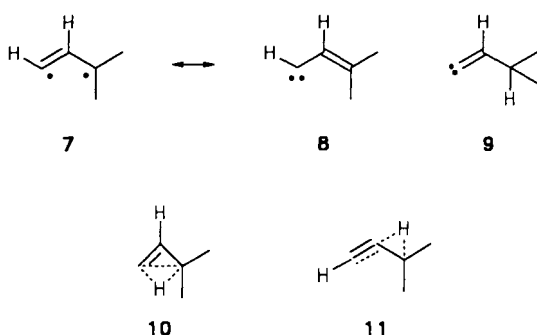
Table 6. Comparison of high-pressure rate constants

Reaction	$\log(A/s^{-1})$	ΔS^\ddagger [JK ⁻¹ mol ⁻¹] ^{a)}	E_a [kJmol ⁻¹] (kcalmol ⁻¹)	$10^4 k$ [s ⁻¹]	Ref.
Cyclopropene → Propyne	13.25	-4	157 (37.5)	7.4	⁵⁾
3-Methylcyclopropene → 1-Butyne + 1,3-Butadiene	13.5	+1	157 (37.6)	11.6	¹⁰⁾
1 → 2 + 3	13.34	-2	156 (37.3)	10.8	this work

^{a)} At 500 K.

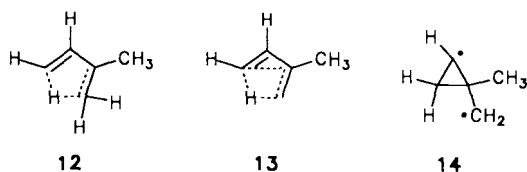
from thermochemical estimates⁵⁾ that the activation energy can accommodate biradical intermediate **7**, whereas it is impossible to estimate from thermochemical kinetics²⁾ the energetics of the pathway via **10**, which, with its bridging hydrogen and bicyclic structure, looks intrinsically more strained. The process, **10** → **9** corresponds to the reverse of a carbene insertion reaction. The choice between these alternative mechanisms remains a pressing problem for the cyclopropene isomerisation reaction.

Scheme 1



The formation of the minor product isoprene (**3**) is in our view best envisaged as a [1,4-H] shift process from biradical **7** occurring via transition state **12** (Scheme 2). The loss of internal rotation of the methyl group in **12** accounts for the low *A* factor (corresponding to $\Delta S^\ddagger = -18 \text{ JK}^{-1} \text{ mol}^{-1}$). Other possible mechanisms for the formation of **3** include a totally concerted process via transition state **13** suggested by Srinivasan¹⁰⁾ or prior H migration in **1** to give biradical **14**, which on ring-opening yields **3**. A thermochemical estimate²²⁾ suggests a minimum activation energy of 184 kJmol⁻¹ for the involvement of **14**, thus ruling it out. The concerted process cannot be completely ruled out, but **12** looks to be a less strained structure and therefore more likely a transition state than **13**. Lastly, the nonobservance of 3-methyl-1,2-butadiene (dimethylallene) (<0.5% of product) is consistent with the generally very low levels of allene

Scheme 2



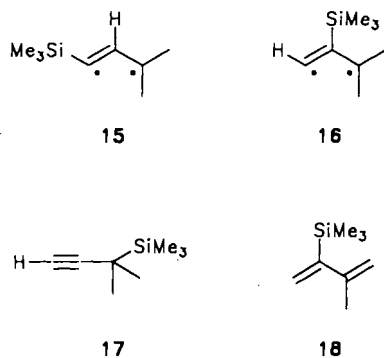
formation in cyclopropene⁵⁾ and 1-methylcyclopropene⁷⁾ pyrolyses.

(iii) *3,3-Dimethyl-1-trimethylsilylcyclopropene* (**4**): The Arrhenius parameters for this decomposition are consistent with those for the decomposition of **1** and other nonsilicon-containing cyclopropenes. It can be readily seen from the rate measurements (Tables 3 and 4) or calculated from the Arrhenius parameters (Table 5) that the 1-trimethylsilyl group exerts a deactivating effect on cyclopropene ring-opening. At 500 K the rate decrease of **4** compared with **1** is by a factor of 2.99. For the major-product-forming pathways (**1** → **2**, **4** → **5**) the rate decrease is by a factor of 2.70. In this respect the trimethylsilyl group behaves semiquantitatively like a methyl group in the 1-position⁷⁾. For the minor-product-forming pathway (**1** → **3**, **4** → **6**) the factor of rate decrease is ca. 22. These rate retardations indicate that the trimethylsilyl substituent is behaving here quite differently from its effect in other pericyclic reactions. In contrast to trimethylsilylcyclopropane isomerisation¹⁶⁾, where the trimethylsilyl group itself migrates in the rate-determining step, we can show that for the isomerisation of **4**, the trimethylsilyl group only migrates, *if at all*, after the rate-determining step.

Just as in the case of **1**, two mechanisms must be considered as the Arrhenius parameters do not offer a distinction. In the biradical mechanism (for simplicity the vinylcarbene states are omitted) two possible biradicals **15** and **16** must be considered (Scheme 3). These correspond to the two alternative C–C bond-breaking processes from **4**. If the biradical mechanism is the correct one then **15** must be the intermediate since it can readily lead to **5** via [1,2-H] shift and to **6** via [1,4-H] shift. If **16** were the intermediate then products **17** (formed by [1,2-SiMe₃] shift) and **18** (formed by [1,4-H] shift) would have been expected; they were not observed. Trimethylsilyl groups are thought to stabilise β-radical centres^{23,24)} to a greater extent than α-radical centres, and this appears to offer an explanation for the rate and products of trimethylsilylcyclopropene isomerisation¹⁶⁾. This argument might appear to favour involvement of **16** rather than **15** and therefore be counted against the biradical mechanism. However, potential interactions of silicon with the radical centres in **15** and **16** are complicated by the presence of the π system and cannot be considered as straightforward.

These observations and arguments for **4** contrast with those for the thermal rearrangement of 3,3-dimethyl-1-methylthio-2-trimethylsilylcyclopropene⁹⁾, which yields 3-methyl-1-methylthio-1-trimethylsilyl-1,2-butadiene as the sole

Scheme 3



product apparently by a [1,2-SiMe₃] shift in a biradical/vinylcarbene intermediate corresponding to **16**.

The alternative mechanism involves one or the other of the two vinylidene homologues **19** and **20** (Scheme 4). In fact only **19**, reached from **4** by synchronous ring-opening and [H] shift, can be involved. Observed product **5** is formed from **19** by [1,2-SiMe₃] shift. If **20** were the intermediate (requiring an [SiMe₃] shift during its formation) then a subsequent [1,2-H] shift would lead to **17**, which was not observed.

Scheme 4



The distinction between the two mechanisms is not clear-cut even though the only intermediates that need consideration are **15** and **19**. Since there is no path degeneracy in forming either intermediate [compared with a path degeneracy of 2 for 3,3-dimethylcyclopropene (**1**) itself] the true rate retardation factor is only 1.35 for the acetylene-forming pathway. Thus the trimethylsilyl group plays a very small role in this rearrangement. A weak argument against the biradical mechanism for the major products is provided by the minor products. These *must* stem from biradicals, and, since the rate retardations are more substantial, this suggests that the biradical mechanism *should* be more prone to retardation than is observed. Indeed, if the biradical mechanism were important it is not obvious why **18** is not a product.

Lastly, it is worth noting that the observed *trans* configuration of diene **6** is demanded by the steric requirements of the formation of the transition state, either **21** or **22**

Scheme 5



(Scheme 5), which are the trimethylsilyl analogues of **12** and **13**, the possible transition states in the diene formation process from **1**. This point was first suggested by Stechl²⁵ and reiterated by Srinivasan¹⁰ for tri- and tetramethylcyclopropene pyrolyses.

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Experimental

¹H-NMR: Bruker WH 270 (270 MHz), Perkin-Elmer R34 (220 MHz); δ = 7.15 for [D₅]benzene, 7.26 for chloroform. — ¹³C-NMR: Bruker WH 270 (67.93 MHz), Jeol FX90Q (22.49 MHz), δ = 128.0 for [D₆]benzene. — IR: Perkin-Elmer 297, 399. — MS: Varian MAT 112 with Varian Aerograph 1400 (GC with 25-m fused silica capillary Oribond SE 54, carrier gas: He) and Varian MAT 311A (high resolution). — GC: analytical: Perkin-Elmer F 33; preparative: Varian Aerograph 920 (carrier gas H₂; 3/8" Teflon columns with Chromosorb W-AW-DMCS, 60–80 mesh). — Materials: Nitrogen (British Oxygen, White Spot Grade) contained no detectable impurity.

Preparation of Compounds

3,3-Dimethylcyclopropene (**1**) was prepared by dehydrobromination of 1-bromo-2,2-dimethylcyclopropene according to the procedure of Binger¹⁹.

1-Bromo-2,2-dimethylcyclopropane: To a well-stirred suspension of 8.0 g (0.21 mol) of lithium aluminum hydride in 400 ml of anhydrous diethyl ether, kept at 0°C, was added against a flow of nitrogen 0.4 g (1.9 mmol) of silver perchlorate (**Caution**: without a reasonable flow of nitrogen the mixture has ignited occasionally upon addition of AgClO₄). The mixture was kept at 0°C under an atmosphere of nitrogen and 100 g (0.44 mol) of 1,1-dibromo-2,2-dimethylcyclopropane¹⁷ was added dropwise with stirring over a period of 4 h. The mixture was stirred for an additional 4 h at 0°C, then 8 ml of water, 8 ml of 15% aqueous sodium hydroxide, and again 24 ml of water were added dropwise in this sequence. The solution was filtered and the residue continuously extracted for 15 h with diethyl ether. The combined organic solutions were dried with CaCl₂, the ether distilled over a 30-cm packed column, and the residue over a 30-cm Vigreux column, yield 44 g (67%) of 1-bromo-2,2-dimethylcyclopropane¹⁷, b.p. 112°C.

3,3-Dimethyl-1-trimethylsilylcyclopropene (**4**): To a solution of 1.0 g (14 mmol) of **1** in 8 ml of anhydrous tetrahydrofuran (THF) was added at 60°C 9.8 ml of a 1.5 M solution of lithium diisopropylamide (LDA, 14.7 mmol) in THF/hexane. The mixture was stirred for 3 h, during which it warmed up to room temp. After cooling to –40°C, 1.6 g (14.7 mmol) of chlorotrimethylsilane in 10 ml of anhydrous THF was added dropwise, the mixture stirred for an additional 15 h at room temp. and then hydrolysed with 5 ml of satd. NH₄Cl solution. After separation, the organic phase was washed with three portions of water (5 ml each) and dried with CaCl₂. The solution was concentrated by distillation of the solvents through a 50-cm concentric tube column up to a head temperature of 60°C. According to its ¹H-NMR spectrum the residue consisted of THF (10%), **4** (53%) and 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropene (37%). This corresponds to a yield of 1.23 g (60%) of **2**. Upon preparative scale separation (2 m 10% SE 30, 25°C), **4** was collected as the second fraction [retention time 4.3 relative to THF (1.0)], yield 1.0 g (52%), colourless liquid. — IR (film): 2920 cm⁻¹ (C=CH), 2850, 1660 (C=C), 1450, 1355, 1240 (Si–CH₃) 1170, 1090,

1030, 860. — $^1\text{H-NMR}$ (270 MHz, C_6D_6): $\delta = 0.14$ [s, 9H, $\text{Si}(\text{CH}_3)_3$], 1.26 (s, 6H, $2 \times \text{CH}_3$), 7.79 (s, 1H, 2-H). — $^{13}\text{C-NMR}$ (67.93 MHz, C_6D_6 , DEPT): $\delta = 137.0$ (–, C-2), 134.2 (0, C-1), 29.0 [+, $\text{C}(\text{CH}_3)_2$], 17.3 (0, C-3), -0.86 [+, $\text{Si}(\text{CH}_3)_3$]. — MS (70 eV): m/z (%) = 140 (8) [M^+], 125 (16) [$\text{M}^+ - \text{CH}_3$], 83 (28), 73 (100) [$\text{Si}(\text{CH}_3)_3^+$].

$\text{C}_8\text{H}_{16}^{28}\text{Si}$ Calcd. 140.10213 Found 140.1021 (MS)

The third fraction (relative retention time 7.9) was pure 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropane, yield 0.80 g (27%), colourless oil. — IR (film): 2950 cm^{-1} , 2920, 2900, 2850, 1695, (C=C), 1360, 1240 (Si–CH₃), 930, 830. — $^1\text{H-NMR}$ (270 MHz, CDCl_3): $\delta = 0.15$ [s, 18H, $2 \times \text{Si}(\text{CH}_3)_3$], 1.11 (s, 6H, $2 \times \text{CH}_3$). — MS (70 eV): m/z (%) = 213 (3) [$\text{M}^+ + 1$], 212 (11) [M^+], 197 (4) [$\text{M}^+ - \text{CH}_3$], 155 (9) [$\text{M}^+ - (\text{CH}_3)_2\text{SiCH}_2$], 124 (78) [$\text{M}^+ - \text{SiC}_4\text{H}_{12}$], 73 (100) [$\text{Si}(\text{CH}_3)_3^+$].

$\text{C}_{11}\text{H}_{24}\text{Si}_2$ (212.5) Calcd. C 62.18 H 11.38
Found C 62.12 H 11.28

Kinetic Measurements

Apparatus: This was similar to that used in earlier studies^{7,8}. Gases were handled in a conventional grease-free vacuum system made from Pyrex with rotaflo (Quickfit) stopcocks. The reaction vessel used for most experiments was spherical (volume ca. 250 cm^3), it was placed in a stirred salt ($\text{NaNO}_2/\text{KNO}_3$ eutectic) thermostat controlled by an AEI (GEC) RT5 controller. A second vessel, packed with Pyrex tubes [surface-to-volume ratio (S/V) ca. 13 cm^{-1}] was used in experiments to test for surface effects. Temperatures were measured with a Pt/Pt-13%Rh thermocouple calibrated against an NPL precalibrated Pt resistance thermometer (Tinsley, Type 5187SA). Product analyses were made by gas chromatography (Perkin-Elmer F33) with FID detection and electronic peak integration (Hewlett-Packard, HP3380S). Pressures were measured with a conventional Hg manometer.

Experimental Procedure: The reactions were studied using internal standards chosen for stability and analytical convenience. For the study of **1**, the reactant master mixture consisted of 1.0% of **1** and 1.5% of isobutane (*i*BuH) diluted in N_2 to a pressure of ca. 700 Torr in a 500- cm^3 reservoir. For the study of **4** the reactant master mixture consisted of 1.2% of **4** and 0.8% of hexamethyldisiloxane (HMDSO) diluted in N_2 to a pressure of ca. 700 Torr in a 500- cm^3 reservoir. Runs were carried out by admitting a known pressure of the appropriate mixture to the reaction vessel for a known time (between 2.5 min and 10 h according to the desired conversion and temp.). The reaction was quenched by sharing the reaction vessel contents with a pre-evacuated sample bulb, from which smaller samples could be taken and injected into the gas chromatograph. Each sixth run was accompanied by a blank analysis of unused reaction mixture in order to check the ratio [**1**]/[*i*BuH] or [**2**]/[HMDSO] for mass balance purposes. Also checked were the proportions of any minor impurities to verify that they were unaffected, and therefore noninterfering, under reaction conditions.

Analysis: Chromatographic analyses were carried out routinely on a 4-m \times 3-mm diisodecylphthalate column (20% w/w on 60/80 Chromosorb P) operated at 0°C for the study of **1** or at 60°C for the study of **4**. The carrier gas was nitrogen (20 psi). The usual product retention times for the study of **1** at 0°C were: *i*BuH, 3.5 min; **2**, 10.7 min; **3**, 13.4 min. The product retention times for the

study of **2** at 60°C were: HMDSO, 9.5 min; **4**, 13.3 min; **5**, 22.7 min, unconfirmed product **6**, 25.6 min. Product identities were confirmed by retention time comparison with authentic samples where possible (**2** and **3**) and by $^1\text{H-NMR}$ spectroscopy (**5** and **6**) on isolated samples after pyrolysis to >95% conversion (see below). It should be added that the GC peak eluting at 25.6 min was assumed to be **6** in the absence of an authentic sample on the basis that **6** was the only other compound observed in the $^1\text{H-NMR}$ and was present at <5% of **5** in the NMR-analysed sample. For the GC analyses it was assumed that in each study all isomeric products had the same detector response factors. — $^1\text{H NMR}$ (220 MHz, CDCl_3): **5**: $\delta = 0.13$ (s, 9H), 1.16 (d, 6H), 2.58 (sept, 1H); **6**: $\delta = 1.85$ (s, 3H), 5.03 (s, 1H), 5.07 (s, 1H), 5.85 (d, 1H), 6.64 (d, 1H). The signal of the $\text{Si}(\text{CH}_3)_3$ protons is obscured by the more intense one of **5**. The *trans* configuration is based on the coupling constant between protons at $\delta = 5.85, 6.64$ ($^3J = 18.7$ Hz).

CAS Registry Numbers

1: 3907-06-0 / **4**: 107742-28-9 / TMCS: 75-77-4 / 1,1-dibromo-2,2-dimethylcyclopropane: 32264-50-9 / 1-bromo-2,2-dimethylcyclopropane: 3815-09-6 / 3,3-dimethyl-1,2-bis(trimethylsilyl)cyclopropane: 107736-03-8

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