On the Substituent Effects of the Thermal Ethenylcyclopropane-to-Cyclopentene Rearrangement: Gas-Phase Kinetics of Ethoxy-, Methylthio- and Trimethylsilyl-Substituted Ethenylcyclopropanes

Gregory McGaffin,[a] Bernd Grimm,[a] Ute Heinecke,[a] Holger Michaelsen,[a] Armin de Meijere,*[a] and Robin Walsh*[b]

Dedicated to Professor Siegfried Hünig on the occasion of his 80th birthday

Keywords: Isomerization / Cyclopropanes / Kinetics / Structure−reactivity relationships / Gas-phase reactions

A series of 1- and 2-substituted ethenylcyclopropanes were prepared in high yields and subjected to gas-phase pyrolytic kinetic investigations. All ethenylcyclopropanes rearranged cleanly to the correspondingly substituted cyclopentenes, although in the case of the 2-substituted compounds, *cis/trans* isomerization was additionally observed (both stereoisomers were investigated in these cases). All rearrangements obeyed first-order kinetics independent of pressure and surface-to-volume ratio. Reasonable Arrhenius parameters were obtained for these homogeneous, unimolecular reactions. 1-Trimethylsilyl and 1-methylthio substituents produced modest rate accelerations, consistent with biradical mechanisms. A previous finding of rate retardation by 1-trimethylsilyl substitution is attributed to steric hindrance. 2-Ethoxy and 2-methylthio substituents [in both (*E*)- and (*Z*)-configurations] produced greater rate accelerations, inconsistent with biradical mechanisms. The steric effects on the kinetics of the (*Z*)-isomer rearrangements appear relatively unimportant. The methylthio substituent effects are documented and analyzed for the first time.

Introduction

Ever since the discovery of the thermal ethenylcyclopropane-to-cyclopentene (ECP-CP) rearrangement independently by Neureiter and Vogel in 1959,[1] this $C_3 \rightarrow C_5$ ring expansion process has enjoyed the considerable attention of both organic and physical chemists. During the course of the following four decades the synthetic potential of this reaction as a powerful cyclopentene annelation scheme has been successfully exploited. Today's knowledge can, in terms of historical development, be roughly divided into the following stages of evolution: (i) fundamental gas-kinetic studies of the thermal rearrangement during the 1960s, establishing the mechanism of smaller non-heteroatom-substituted ECPs in static reactors;[2−12] (ii) similar studies of smaller heteroatom-substituted ECPs in static and flow reactors in the 1970s and early 1980s, documenting the rate-accelerating effects of alkoxy,[13a] dimethylamino,[13b] cyano[14] and silyloxy[15] groups; (iii) at almost the same time a parallel branch of qualitative thermal studies on larger heteroatom-substituted ECPs was performed;[16] (iv) the discovery of evidence for concerted effects in the thermal rearrangement, beginning in 1976 with Baldwin's[17a] legendary experiment with an enantiopure ECP which revived discussion and triggered off further intense research work[17b−17p] on the mechanism to the present day;[17e−17q] (v) the discoveries of the low-temperature oxy anion driven rearrangement by Danheiser et al.[18a−18e] in the early 1980s and the low-temperature cation-radical-accelerated rearrangement by Dinnocenzo et al.[18f] in the late 1980s. Both discoveries greatly simplified the reaction conditions for more feasible organic preparations.

Besides these milestones a myriad of new and interesting modifications have been devised by other researchers (e.g. the transition metal-, acid- and base-induced ECP-CP rearrangement), many of which have turned out to provide indispensable steps in natural product synthesis. The complete arsenal of today's known synthetic methodologies has been excellently reviewed by Hudlicky et al.[19]

Our motivation for the investigation of various heteroatom-substituted ECPs was to probe previously unknown substituent effects on the homogeneous thermal rearrangement, and in particular to dissect these effects in terms of activation parameters. Both 1- and 2-substituted ECPs were considered to see what differences might arise between substitution at the anchor point and at the migrating carbon atom in the ECP-CP process. The rearrangement of 1-substituted ECPs (**1-X**) is shown in Scheme 1. We extend our previous study of **1-OEt**[20] to **1-SiMe$_3$** and **1-SMe**. 1-Trimethylsilyl ring substitution is of interest since it has been reported to exert a retarding effect[16c,16d] on the ECP-CP process, in contrast to its rate-enhancing effect on the parent cyclopropane ring opening reaction.[21a] 1-Methylthio ring substitution will quantitatively reveal for

[a] Institut für Organische Chemie der Georg-August-Universität, Tammannstraße 2, 37077 Göttingen, Germany
Fax: (internat.) +49-551/39-9475
E-mail: Armin.deMeijere@chemie.uni-goettingen.de
[b] Department of Chemistry, University of Reading, Whiteknights, P. O. Box 224, Reading RG6 6AD, UK
E-mail: R.Walsh@reading.ac.uk

  1434−193X/01/0918−3559 $ 17.50+.50/0

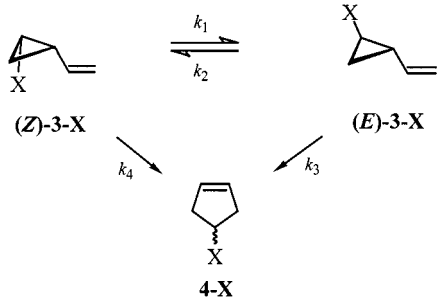
the first time the effect of a sulfur substituent on the rearrangement.

1-X **2-X**

X = $SiMe_3$: ΔT = 313.3– 363.1 °C; Δp = 15–25 Torr
X = SMe: ΔT = 241.0–289.9 °C; Δp = 12–15 Torr

Scheme 1

The rearrangement of 2-substituted ECPs (**3-X**) is shown in Scheme 2. We investigate here compounds **3-OEt** and **3-SMe** with 2-ethoxy and 2-methylthio substituents. Previous reports[13a] on the kinetics of 1-ethenyl-2-methoxycyclopropane suggested a negligible participation of the (*Z*)-isomer in the ring expansion. By careful analytical studies of the system time evolution starting with each pure stereoisomer, combined with computer modeling, we anticipated obtaining reliable values for all constants of this four-rate-constant scheme (for each substituent). This study will therefore permit us to document the effect of these substituents in either starting stereochemistry on the ECP-CP process, and additionally on the stereoisomerization process itself.



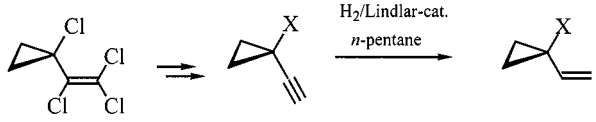
X = OEt: ΔT = 220.8–278.1 °C; Δp = 18–25 Torr
X = SMe: ΔT = 239.3–289.2 °C; Δp = 14–21 Torr

Scheme 2

Results and Evaluation of Data

Synthesis of Ethenylcyclopropanes

Both 1-substituted ethenylcyclopropanes **1-X** (X = $SiMe_3$, SMe) were prepared from their corresponding ethynylcyclopropane precursors **6-X** by high-yielding hydrogenation reactions in the presence of appropriately deactivated (quinoline) Lindlar catalyst (Scheme 3). The ethynylcyclopropane **6-SiMe$_3$** [22a] reacted extremely rapidly under (approx.) atmospheric hydrogen pressure, giving pure 1-ethenyl-1-trimethylsilylcyclopropane (**1-SiMe$_3$**) in 85% isolated yield. The ethynylcyclopropane **6-SiMe$_3$** was prepared from commercially available 1-chloro-1-(trichloroethenyl)-cyclopropane (**5**)[22b–22f] in only two steps, following standard literature procedures.[22a]



5 **6-X** X = $SiMe_3$: 85% **1-X**
X = SMe: 97%

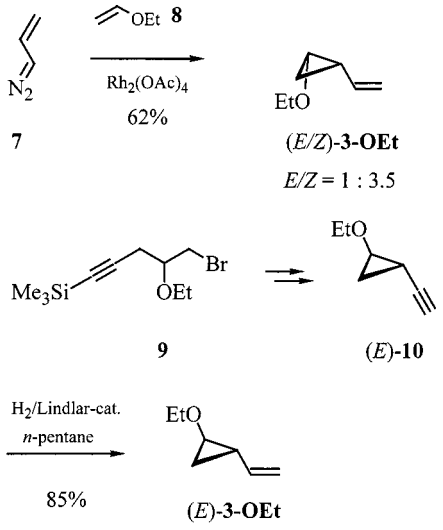
Scheme 3

The versatility of the ethenylcyclopropane **5**[22f] also made the 1-methylthio-substituted ethynylcyclopropane **6-SMe**, a precursor to **1-SMe**, easily accessible in three steps.[22g] Reaction of **5** with two equivalents of *n*-butyllithium and subsequent quenching with chlorotrimethylsilane afforded 1-chloro-1-(trimethylsilylethynyl)cyclopropane which, upon lithiation and reaction with *S*-methyl methanethiosulfonate gave 1-methylthio-1-(trimethylsilylethynyl)cyclopropane in high yield (90%). Subsequent protiodesilylation of the terminal acetylene with K_2CO_3 in methanol solution yielded **6-SMe** (79%). In contrast to **6-SiMe$_3$**, the ethynylcyclopropane **6-SMe** was hydrogenated extremely slowly to **1-SMe**. Obviously, the Lindlar catalyst was prone to poisoning by the sulfur-containing reactant itself or by other minor sulfide contaminants (in the absence of quinoline no reaction occurred). Nevertheless **6-SMe** was slowly (within 144 h), but steadily converted into 1-ethenyl-1-methylthiocyclopropane (**1-SMe**) without forming any by-products under a hydrogen pressure of 3.5 bar (97% yield).[23a]

For the preparation of the diastereopure ethenylcyclopropanes (*E*)- and (*Z*)-**3-OEt** two different and well-known procedures were chosen, each predominantly giving either the (*E*)- or the (*Z*)-ethenylcyclopropane. Thus, (*Z*)-2-ethoxy-1-ethenylcyclopropane [(*Z*)-**3-OEt**] was accessible by $Rh_2(OAc)_4$-catalyzed decomposition of ethenyldiazomethane (**7**)[24] in the presence of an excess amount of ethenyl ethyl ether (**8**) (Scheme 4). (*E*/*Z*)-**3-OEt** was obtained in 62% yield with an isomeric ratio *E*/*Z* = 1:3.5. The major (*Z*)-isomer was separated from the *E*/*Z* mixture by preparative GC (*de* = 98.0%).

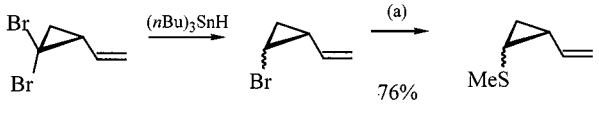
The recently published[25] efficient 1,3-dehydrobromination of 5-bromo-4-ethoxy-1-trimethylsilyl-1-pentyne (**9**) and subsequent base-induced $Z \rightarrow E$ isomerization of the resulting *E*/*Z* mixture of 2-ethoxy-1-(trimethylsilylethynyl)-cyclopropane gave the diastereopure (*E*)-isomer. Subsequent protiodesilylation as mentioned above afforded (*E*)-2-ethoxy-1-ethynylcyclopropane [(*E*)-**10**] which, upon facile catalytic hydrogenation, was converted into diastereopure (*E*)-**3-OEt** on a multigram scale (85% isolated yield).

Initial attempts to prepare (*E*/*Z*)-1-ethenyl-2-methylthiocyclopropane [(*E*/*Z*)-**3-SMe**] in one step in analogy to procedures for similar compounds by Schöllkopf et al.[26] and Rynbrandt et al.[27] were abandoned. The outcome of several experiments was that a base-induced (KO*t*Bu) generation of methylthiomethylenoid from chloromethyl methyl sulfide and its subsequent trapping with excess 1,3-butadi-



Scheme 4

ene did actually give (*E*/*Z*)-**3-SMe** in high yields, but always contaminated to a substantial extent with several other unidentified sulfide by-products (10−15%, GC). It proved to be an impossible task to obtain analytically pure (*E*)- and (*Z*)-**3-SMe** from these coeluting intractable mixtures by preparative GC methods. Therefore a three-step, and more selective, route to (*E*/*Z*)-**3-SMe** was undertaken (Scheme 5), starting from the available 2,2-dibromo-1-ethenylcyclopropane (**11**), first reported by Skattebøl.[28] According to the protocol of Marino et al.,[29] compound **11** was easily reduced to the monobromide (*E*/*Z*)-**12** [*E*/*Z* = 1.0:2.8] with tri-*n*-butyltin hydride. Subsequent lithiation of (*E*/*Z*)-**12** in THF/Et_2O (2:1) at −78 °C with 2 equiv. of *tert*-butyllithium and quenching with *S*-methyl methanethiosulfonate, smoothly gave (*E*/*Z*)-**3-SMe** in 76% yield [*E*/*Z* = 1.0:2.8]. Thus, the pure *E*/*Z* mixture was available in large quantities, and even the minor (*E*)-isomer was obtained in sufficient amounts for gas-phase kinetic studies after preparative GC separation. (*Z*)-**3-SMe** was obtained in 97.5% *de* and (*E*)-**3-SMe** in 98.6% *de*.



(a) 1) *t*BuLi, THF/Et_2O (2 : 1), –78 °C. – 2) $MeSSO_2Me$.

Scheme 5

Kinetics of 1-Trimethylsilyl- and 1-Methylthio-1-ethenylcyclopropane (1-$SiMe_3$ and 1-SMe)

The gas-phase kinetics of the two 1-substituted ethenylcyclopropanes **1-$SiMe_3$** and **1-SMe** were established in an identical manner to the previously reported kinetic studies on 1-alkoxy-1-ethenylcyclopropanes.[20] Both **1-$SiMe_3$** and **1-SMe** were investigated as nitrogen-diluted gaseous mixtures with cyclohexane (CH) as an internal standard. Depending on the reactant vapor pressures (see Table 11, Exp. Sect.) these master mixtures contained a maximum of 1.03% of **1-$SiMe_3$** (with 0.65% of CH) and 0.20% of **1-SMe** (0.50% of CH), respectively. Total reaction pressures were in the range of 12−25 Torr (Scheme 1 and Table 11). The thermolyses were performed over a temperature interval of 50 °C for both reactions, which allowed the determination of rates at six approximately equidistant reaction temperatures. **1-$SiMe_3$** was examined between 313.3 and 363.1 °C and **1-SMe** between 241.0 and 289.9 °C. After the recorded reaction times, the gaseous reaction mixtures of partially converted **1-X** (for ranges of conversion see Table 11) and **2-X** were pressurized and further diluted with nitrogen before analysis by GC. Integration of the individual reaction components allowed a quantitative determination and time tracking of the mixture composition.

Total mass recoveries were achieved for **1-$SiMe_3$** as both the reactant and the ring-expanded cyclopentenylsilane **2-$SiMe_3$** proved volatile enough for quantitative gas handling. However, in the pyrolysis of **1-SMe** the thioenol methyl ether product **2-SMe** was incompletely recovered due to its low volatility, with mass losses consistently increasing at higher reactant conversions. Several checks and careful product GC analyses verified, as was previously shown in kinetic studies of similar ethenylcyclopropanes,[20] that the generation of additional side-products can be excluded as possible sources of product mass loss. Because there was no mass loss of reactant, **1-SMe**, the kinetics were based on reactant disappearance. Excellent linear first-order plots (least mean-squares procedure) were found from the time evolution studies for both **1-SMe** and **1-$SiMe_3$**. The temperature dependence of rate constants derived from the slopes of the first-order plots is shown in Table 1. Again, applying least mean-squares procedures to the rate constants in Table 1 gave linear Arrhenius plots (Figure 1) for both reactions which obey Equation (1) and Equation (2).

$$\textbf{1-SMe}: \log(k/s^{-1}) = (13.94 \pm 0.35) - (197.5 \pm 4.0\ \text{kJ mol}^{-1})/RT\ln 10 \quad (1)$$

$$\textbf{1-SiMe}_3: \log(k/s^{-1}) = (13.59 \pm 0.23) - (201.4 \pm 2.7\ \text{kJ mol}^{-1})/RT\ln 10 \quad (2)$$

Table 1. Rate constant variation with temperature for ECP-CP rearrangements **1-X** → **2-X**

1-$SiMe_3$ → **2-$SiMe_3$** Temp. [°C]	$10^4\ k$ [s^{-1}][a]	**1-SMe** → **2-SMe** Temp. [°C]	$10^4\ k$ [s^{-1}][a]
313.3	0.47 ± 0.01	289.9	0.38 ± 0.01
323.1	0.88 ± 0.02	299.7	0.91 ± 0.05
333.3	1.72 ± 0.05	310.2	1.83 ± 0.04
343.5	3.48 ± 0.07	320.2	3.69 ± 0.12
352.9	6.48 ± 0.14	330.9	7.21 ± 0.29
363.1	11.24 ± 0.27	341.0	13.30 ± 0.49

[a] Error limits are standard deviations.

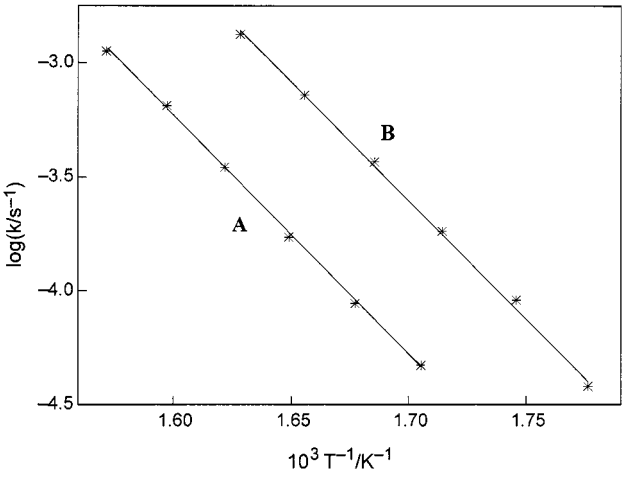


Figure 1. Arrhenius plots for thermal ECP-CP rearrangements of **1-X**: A: **1-SiMe$_3$**; B: **1-SMe**

Precautionary checks were also carried out at elevated pressures in order to evaluate the possibility of pressure-dependent first-order rate constants in the "fall-off" region, although molecules of the size of **1-X** are not usually affected in this way. Pyrolyses for 10 min of **1-SiMe$_3$** at 363.1 °C and 10, 20 and 75 Torr showed reproducible reactant conversions of 48.3, 48.1 and 48.3%. Similarly, 30-min. runs at 322.1 °C at 7, 14 and 57 Torr took **1-SMe** to consistent conversions of 48.3, 49.9 and 49.7%.

More detailed attention was given to checks on surface activity and possible radical chain processes. For this purpose the reaction vessel was removed from the vacuum line and replaced by an HMDS-conditioned, glass-tube-packed vessel with an approximate surface-to-volume ratio of 10 cm^{-1} (see Exp. Sect.). Pyrolyses were carried out at the same temperatures as for the unpacked vessel. In further experiments an olefin was added to serve as an inhibitor and therefore test for potential radical chain reactions. The results for these investigations are summarized in Table 2.

Table 2. Product variation in packed and unpacked vessels for ECP-CP rearrangements **1-X** → **2-X**

Reaction vessel	Reaction **1-SiMe$_3$** → **2-SiMe$_3$** Conversion **1-SiMe$_3$**[a] (%)	**1-SMe** → **2-SMe** Conversion **1-SMe**[b] (%)
Unpacked	48.1	49.0
Unpacked	48.7[c]	49.4[d]
Packed	48.6	48.2
Packed	49.2[c]	48.9[d]

[a] 10 min pyrolysis at 363.1 °C and 18 Torr. − [b] 30 min pyrolysis at 322.1 °C and 14 Torr. − [c] 15-fold excess of isobutene added. − [d] 10-fold excess of *cis*-2-butene added.

In addition to the above data a complete set of runs was performed for **1-SiMe$_3$** in the packed vessel at 343.5 °C, and from the first-order plot linear regression gave k(343.5 °C) = (3.42 ± 0.12) × 10^{-4} s^{-1}, in good agreement with the value for the unpacked vessel (Table 1). Thus, the experimental data show no variation in ethenylcyclopropane conversion other than from reasonable experimental scatter, and are therefore consistent with a homogeneous reaction, unperturbed by radical chain processes.

Kinetics of (*E*)-, (*Z*)-2-Ethoxy- and (*E*)-, (*Z*)-2-Methylthio-1-ethenylcyclopropane [(*E*)-, (*Z*)-3-OEt and (*E*)-, (*Z*)-3-SMe]

General

The complex reaction mechanism for the thermal reactions of 2-substituted ethenylcyclopropanes is indicated in Scheme 2.[13a,13b,14] The thermolysis of either (*E*)- or (*Z*)-isomers induces geometrical $E \rightarrow Z$ or $Z \rightarrow E$ isomerisation (k_1, k_2), accompanied by the simultaneous ring expansion with k_3 [(*E*)-isomer] and k_4 [(*Z*)-isomer]. Determination of the individual rate constants k_1 to k_4 is therefore a more sophisticated task than for the simple ECP-CP rearrangements **1-X** → **2-X**. We have applied computer-based kinetic modeling schemes, based on the Gear algorithm,[30] which employs a variable-step integration of the differential equations involved in Scheme 2, or least mean-squares fitting to the analytical solution[31] of Scheme 2.

On the basis of assumed first-order reactions the Gear algorithm required an initial set of estimated rate constants k_1 to k_4 for which the concentration/time data of each isomer at each reaction temperature were numerically calculated[32a] and compared with the experimental time evolution plots. Calculations were repeated with an appropriately altered set of values for k_1 to k_4 until the best fit between calculated and experimental data was achieved (as evaluated by the relative minimum in the sum of the squares of all deviations, Σx^2). The analytical data for the pyrolyses of both (*E*)- and (*Z*)-**3-OEt** were processed in this way.[32b]

The computational processing of the kinetic data of complex schemes invariably gives difficulties arising from the differing sensitivities of individual product channels towards the adjustment of specific k values. Thus, in the pyrolyses of neat (*Z*)-**3-X**, steps 1 and 4 are primary (Scheme 2) and therefore affect the decomposition rate directly, while steps 2 and 3 are secondary and therefore have a lesser affect. The situation is reversed when neat (*E*)-**3-X** is considered. However, the overall quality of fitting *does* depend on the absolute magnitude of all four of the rate constants k_1 to k_4. It follows from this that the pyrolysis of (*Z*)-**3-X** will give greater certainty for k_1 and k_4 (and less for k_2 and k_3), whereas the pyrolysis of (*E*)-**3-X** will give greater certainty for k_2 and k_3 (and less for k_1 and k_4). These considerations guided us in our procedure for refining the rate constants. For example, as k_4 proved to be the smallest rate constant for the scheme involving **3-OEt** the values were taken from the processed data for the (*Z*)-isomer and then incorporated (frozen) into the data matrix for the (*E*)-isomer. The data were then reprocessed for (*E*)-**3-OEt** and the resulting rate

constants taken to be the best extractable values. This is discussed in more detail below.

(E)- and (Z)-3-OEt

(*E*)-**3-OEt** was pyrolyzed between 18 and 22 Torr in a temperature range of 221.0−278.1 °C. Similarly, pyrolyses of (*Z*)-**3-OEt** were performed between 18 and 25 Torr and at 220.8−277.6 °C (for further information on conditions see Table 11, Exp. Sect.). (*E*)-**3-OE**t was 100.0% isomerically pure but (*Z*)-**3-OE**t was contaminated with 3.0% of the (*E*)-isomer (due to incomplete separation during isolation). This isomeric impurity was taken into account in the data processing. The collecting of analytical time evolution data was carried out similarly to the method described for ethenylcyclopropanes **1-X** (see also Exp. Sect.). In order to achieve optimal *k* values a greater amount of analytical data was collected for each temperature (10 runs at least), covering total (*E*)- and (*Z*)-reactant conversions between 7.6 and 94.3% (see Table 11). Table 3 gives an example of the product time evolution for the pyrolysis of (*E*)-**3-OEt** at 266.8 °C. This is shown graphically in Figure 2 together with that for (*Z*)-**3-OEt** at the same temperature.

Table 3. Product time evolution for the thermal reactions of (*E*)-**3-OEt** at 266.8 °C

Time [min]	(*E*)-**3-OEt**[a] (%)	(*Z*)-**3-OEt**[a] (%)	**4-OEt**[a] (%)
0.0	100.00	0.00	0.00
2.5	82.96	6.37	10.67
5.0	71.61	9.26	19.13
7.5	61.73	11.55	26.72
10.0	53.72	12.73	33.56
15.0	41.15	13.67	45.18
20.0	32.75	13.07	54.18
26.0	24.96	11.47	63.57
30.0	21.49	10.54	67.97
40.0	14.74	8.02	77.24
50.0	10.41	5.77	83.82
60.0	7.47	4.18	88.35

[a] Gas-phase composition at time *t*.

Data for (*E*)- and (*Z*)-**3-OEt** were individually processed by the Gear algorithm. Additionally, the k_4 values from the optimal (*Z*)-**3-OEt** product fit were incorporated as fixed parameters into the data matrix for the (*E*)-isomer product fitting and k_1 to k_4 values processed again. Table 4 contains the k_1 to k_4 values for these three fitting exercises.

The data fit to the (*E*)- and (*Z*)-**3-OEt** product distributions using the Gear algorithm shows tolerable consistency between the k_1 to k_3 values starting from either isomer. The values of k_4, however, appear to be about four times greater when starting from (*E*)- than from (*Z*)-**OEt**. We believe that this probably arises from a small (unidentified) systematic error. However, because k_4 is the smallest rate constant, the only data points showing sensitivity to its value will be those at early reaction times starting from the (*Z*)-isomer.

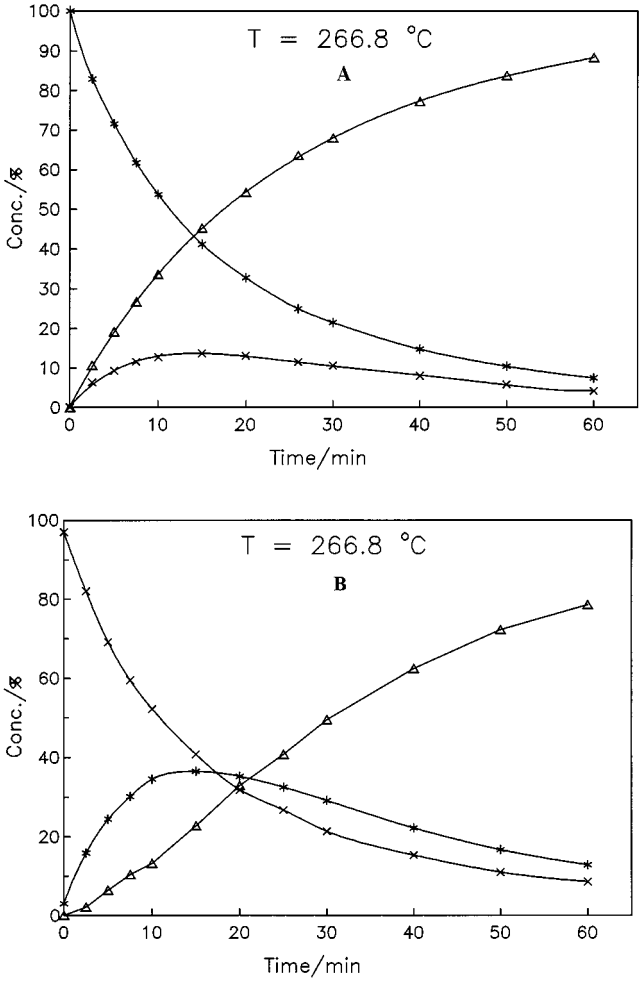


Figure 2. Product distribution for thermal rearrangements of (*E*)- and (*Z*)-**3-OEt** at 266.8 °C: A: (*E*)-**3-OEt**; B: (*Z*)-**3-OEt**; * = (*E*)-**3-OEt**; × = (*Z*)-**3-OEt**; Δ = **4-OEt**

Table 4. Individual variation of rate constants k_1 to k_4 with temperature for thermal isomerizations of both (*E*)- and (*Z*)-**3-OEt** determined by the Gear algorithm

Temp. [°C]		221.0	234.0	248.1	257.6	266.8	278.3
$10^5\ k_1$ [s^{-1}]	[a]	2.63	6.81	28.1	59.9	117	284
	[b]	2.76	8.28	27.3	54.8	112	260
	[c]	3.04	9.00	28.1	61.7	130	303
$10^5\ k_2$ [s^{-1}]	[a]	1.12	3.29	10.8	21.7	45.8	106
	[b]	1.38	3.54	12.3	19.1	44.3	101
	[c]	1.05	3.22	10.1	20.8	44.3	101
$10^5\ k_3$ [s^{-1}]	[a]	2.73	7.28	21.0	41.8	74.5	156
	[b]	2.81	7.58	21.3	43.6	78.7	166
	[c]	2.85	7.70	21.5	42.7	78.1	164
$10^5\ k_4$ [s^{-1}]	[a]	1.09	2.95	5.20	7.85	23.2	45.0
	[b]	0.26	0.83	2.61	3.47	7.50	10.8
	[c]	0.26	0.83	2.61	3.47	7.50	10.8
Σx^2	[a]	1.84	4.96	4.58	5.36	3.21	2.80
Σx^2	[b]	30.2	6.40	17.9	52.9	10.33	19.9
Σx^2	[c]	6.09	10.1	8.49	7.90	9.49	11.7

[a] (*E*) isomer product fit. − [b] (*Z*) isomer product fit. − [c] (*E*) isomer product fit with frozen k_4 values from (*Z*) isomer product fit.

Thus, we believe that a better data analysis is obtained from the (*E*)-isomer with the k_4 value fixed. An examination of the table shows that the k_1 to k_3 values thus derived are not substantially different and in most instances within a few percent of those from the unconstrained *Z* and *E* fits. The quality of fit (Σx^2) is not seriously worsened and the graphical plots show a good fit of experiment to the modeled product-time curves. A test (not shown) with $k_4 = 0$ produced significantly poorer fits, thus showing that, in spite of its small contribution, step 4 cannot be neglected. The Arrhenius equations for reaction steps 1−4 [Equation (3) to Equation (6)] were derived from the Gear-processed and -correlated data for the (*E*)-isomer (Figure 3). Minor sources of error are due to the slightly different temperatures (a few tenths of K at most) for (*E*)- and (*Z*)-**3-OEt**, but calculations show these to cause less than 5% deviation in determined *k* values, thus being well within experimental error.

$$\log(k_1/s^{-1}) = (14.80 \pm 0.18) - (182.9 \pm 1.8\ \text{kJ mol}^{-1})/RT\ln 10 \quad (3)$$

$$\log(k_2/s^{-1}) = (14.13 \pm 0.12) - (180.8 \pm 1.2\ \text{kJ mol}^{-1})/RT\ln 10 \quad (4)$$

$$\log(k_3/s^{-1}) = (12.44 \pm 0.04) - (160.7 \pm 0.4\ \text{kJ mol}^{-1})/RT\ln 10 \quad (5)$$

$$\log(k_4/s^{-1}) = (10.22 \pm 0.95) - (148.8 \pm 9.6\ \text{kJ mol}^{-1})/RT\ln 10 \quad (6)$$

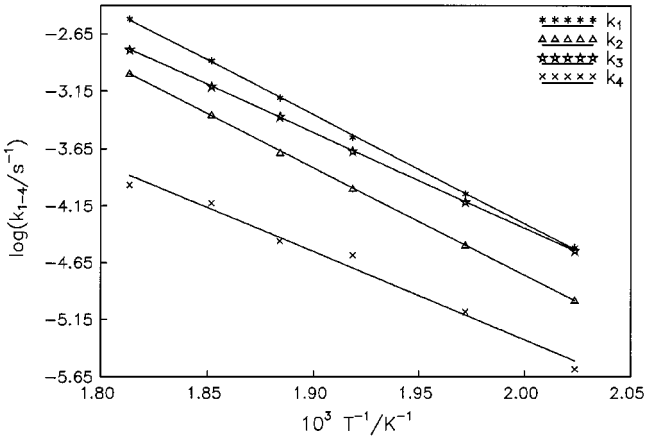


Figure 3. Arrhenius plots for thermal rearrangements of (*E*)-**3-OEt** (based on correlated data and the Gear algorithm).

(E)- and (Z)-3-SMe

The kinetic data for (*E*)- and (*Z*)-**3-SMe** were collected in an identical manner to the procedure described for (*E*)- and (*Z*)-**3-OEt**. Both ethenylcyclopropanes were pyrolyzed in a common pressure range between 14 and 21 Torr and a temperature interval of 238.3−289.2 °C [the upper range limit for (*E*)-**3-SMe** is insignificantly different at 289.1 °C, see Table 11]. Both isomers were chemically pure, although "stereochemically" marginally impure [the (*E*)-isomer sample contained 1.4% of the (*Z*)-isomer; the (*Z*)-isomer sample contained 2.5% of the (*E*)-isomer]. The stereoisomeric impurities were accounted for in the data fitting. Table 5 contains sample experimental data for the product time evolution from pyrolysis of (*Z*)-**3-SMe** at 259.0 °C and Figure 4 gives a graphical impression of the product distri-

Table 5. Product time evolution for the thermal reactions of (*Z*)-**3-SMe** at 259.0 °C

Time [min]	(*E*)-**3-SMe**[a] (%)	(*Z*)-**3-SMe**[a] (%)	**4-SMe**[a] (%)
0.0	2.46	97.54	0.00
4.0	41.51	56.37	2.11
10.0	62.94	32.54	4.52
15.0	66.31	25.52	8.17
20.0	68.60	22.33	9.08
30.0	67.53	19.78	12.68
40.0	64.87	18.99	16.14
60.0	59.51	17.30	23.19
80.0	53.95	16.19	29.86
100.0	50.15	14.31	34.26
120.0	45.94	13.56	40.50
150.0	40.51	11.61	47.87
180.0	36.30	10.85	52.85

[a] Gas-phase composition at time *t*.

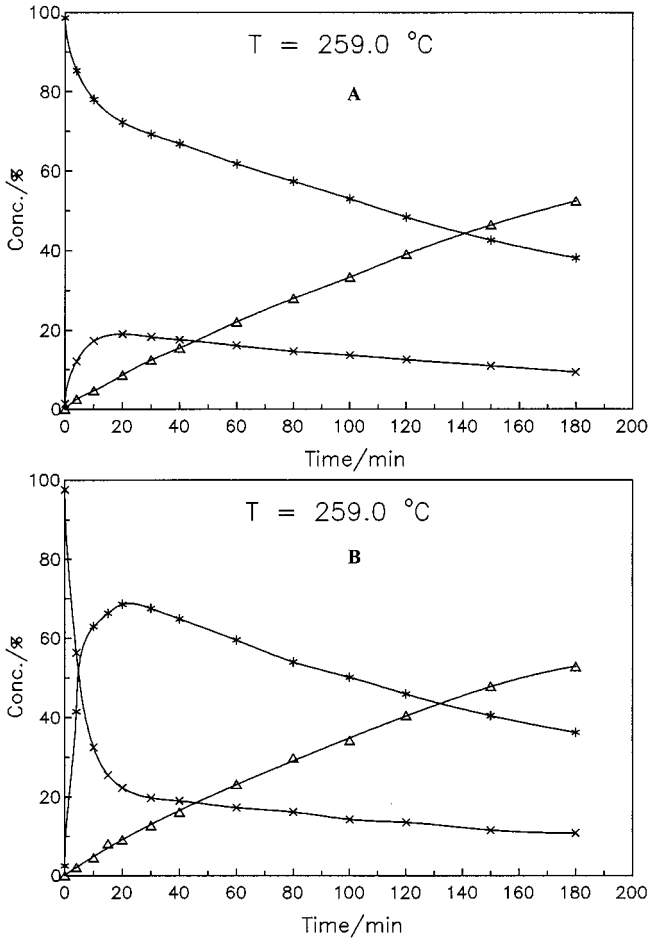


Figure 4. Product distribution for thermal rearrangements of (*E*)- and (*Z*)-**3-SMe** at 259.0 °C: A: (*E*)-**3-SMe**; B: (*Z*)-**3-SMe**; * = (*E*)-**3-SMe**; × = (*Z*)-**3-SMe**; Δ = **4-SMe**

butions during pyrolyses of the individual (*E*)- and (*Z*)-isomers at this temperature.

In view of the reasonable modeling outcome for (*E*)- and (*Z*)-**3-OEt** (Table 4) the analytical data for (*E*)- and (*Z*)-**3-SMe** were processed in a similar way. In this case we had available a program for minimization to an analytical fit.[31a] The problem with fitting the analytical data here was that for this reaction system both k_3 and k_4 were significantly smaller than k_1 and k_2. Thus, in this case, under the operating conditions, only at the lowest three temperatures (239−259 °C) was the equilibration between (*E*)- and (*Z*)-**3-SMe** slow enough to permit the determination of all four rate constants. At 269 °C the data fitting could only be achieved for the (*Z*)-isomer, whereas for the (*E*)-isomer at this temperature and both isomers at the higher temperatures, fitting was achieved only by keeping k_1/k_2 fixed with values taken by extrapolation from lower temperatures. In this way, the values for k_3 and k_4 could be obtained. Since the magnitudes of k_3 and k_4 were comparable there was no special problem with discrepancies between them arising from fitting to each isomer. Indeed the values derived (Table 6, Figure 5) show a good consistency of the data from each isomer at those temperatures where unique values were obtained.

Table 6. Individual variation of rate constants k_1 to k_4 with temperature for thermal isomerizations of both (*E*)- and (*Z*)-**3-SMe** determined by least-squares analytical fitting

Temp. [°C]		239.3	249.1	259.0	269.4[a]	279.0[a]	289.1[a]
$10^5\ k_1/s^{-1}$	[b]	54.4	123.5	246.8	(538)	(1062)	(2072)
	[c]	54.4	120.7	242.8	536.6	(1091)	(2035)
$10^5\ k_2/s^{-1}$	[b]	14.9	34.1	67.5	(150)	(282)	(565)
	[c]	14.9	35.9	71.0	168.8	(354)	(682)
$10^5\ k_3/s^{-1}$	[b]	1.57	3.34	6.73	15.0	28.8	57.5
	[c]	1.57	3.47	7.08	15.3	30.2	58.5
$10^5\ k_4/s^{-1}$	[b]	1.48	3.28	6.92	15.3	32.7	67.6
	[c]	1.48	3.08	6.90	15.3	30.9	60.7

[a] Figures in parentheses used for fitting purposes only (not Arrhenius parameters); see text. − [b] (*E*)-isomer fit. − [c] (*Z*)-isomer fit.

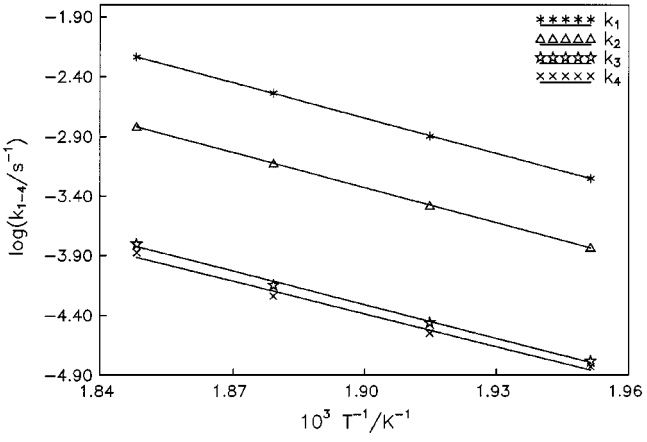


Figure 5. Arrhenius plots for thermal rearrangements of (*E*)-**3-SMe**

Because the data set from (*Z*)-**3-SMe** was marginally more extensive than for (*E*)-**3-SMe**, it was preferred as the basis for working out the Arrhenius equations [Equation (7) to Equation (10)]. Nevertheless, the alternative set from (*E*)-**3-SMe** is, within error limits (single standard deviations), the same.

$$\log(k_1/s^{-1}) = (14.54 \pm 0.32) - (174.6 \pm 3.2\ kJ\ mol^{-1})/RT\ln 10 \quad (7)$$

$$\log(k_2/s^{-1}) = (14.92 \pm 0.62) - (183.9 \pm 6.3\ kJ\ mol^{-1})/RT\ln 10 \quad (8)$$

$$\log(k_3/s^{-1}) = (12.91 \pm 0.11) - (173.8 \pm 1.1\ kJ\ mol^{-1})/RT\ln 10 \quad (9)$$

$$\log(k_4/s^{-1}) = (13.52 \pm 0.13) - (180.2 \pm 1.1\ kJ\ mol^{-1})/RT\ln 10 \quad (10)$$

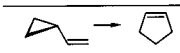
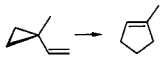
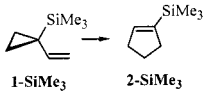
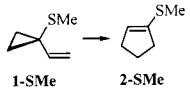
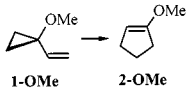
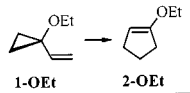
Additional experimental checks addressing possible pressure effects and surface catalysis were performed representatively for (*E*)-**3-OEt** and (*Z*)-**3-SMe**. Identical reactant conversions were found in all pressure checks. In the surface catalysis test, a 10-min. pyrolysis of (*E*)-**3-OEt** in a packed vessel at 266.9 °C gave 54.07% of (*E*)-**3-OEt**, 12.54% of (*Z*)-**3-OEt** and 33.39% of **4-OEt** in comparison with 53.72% of (*E*)-**3-OEt**, 12.73% of (*Z*)-**3-OEt** and 33.56% of **4-OEt** obtained from an identical run in the unpacked vessel. Similarly, a 15-min. pyrolysis of (*Z*)-**3-SMe** in the same packed vessel at 289.2 °C revealed a product distribution of 44.40% of (*E*)-**3-SMe**, 14.26% of (*Z*)-**3-SMe** and 41.34% of **4-SMe**, compared with a reaction mixture composition of 44.63% of (*E*)-**3-SMe**, 13.93% of (*Z*)-**3-SMe** and 41.45% of **4-SMe** in the unpacked vessel under otherwise identical conditions. Checks on radical chain components in the presence of excess amounts of *cis*-2-butene [(*E*)-**3-OEt**] and isobutene [(*Z*)-**3-SMe**] revealed no deviations in product distributions outside experimental scatter. Thus, these complex systems represent true homogeneous unimolecular processes.

Discussion

General

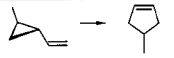
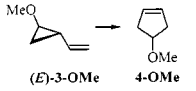
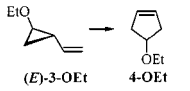
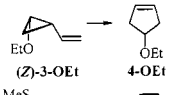
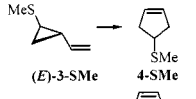
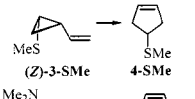
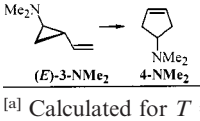
Table 7 and Table 8 contain the Arrhenius parameters [see Equations (1), (2), (5), (6), (9) and (10)] for the gas-phase ECP-CP reactions studied in the present work. Also included are the known values for other examples of 1-substituted (**1-X**) and 2-substituted [(*E*)- and (*Z*)-**3-X**] ethenylcyclopropanes. To facilitate discussion, the rate-accelerating factors due to substitution [given by the ratio of rate constants k_X/k_H at 300 °C for substituted (X) and unsubstituted (X = H) ethenylcyclopropanes] are also given.

Table 7. Arrhenius parameters for the thermal ECP-CP rearrangements of various 1-substituted ethenylcyclopropanes **1-X**

Reaction ECP → CP	log (A/s^{-1})	E_a	E_a	$10^4\,k$	Rel. rate[a]	Ref.
1-X → 2-X		[kJ mol^{-1}]	[kcal mol^{-1}]	[s^{-1}][a]	k_X/k_H	
 **1-H** **2-H**	13.50	207.7	49.6	0.04	1.0	[2a]
 **1-Me** **2-Me**	14.11	206.8	49.4	0.18	4.5	[2d]
 **1-SiMe$_3$** **2-SiMe$_3$**	13.59	201.4	48.1	0.17	4.3	this work
 **1-SMe** **2-SMe**	13.94	197.5	47.2	0.87	21.8	this work
 **1-OMe** **2-OMe**	(a) 13.43	187.2	44.7	2.30	57.5	[13a]
	(b) 13.89	191.3	45.7	2.80	70.0	[20]
 **1-OEt** **2-OEt**	13.77	188.8	45.1	3.60	90.0	[20]

[a] Calculated for T = 300 °C.

Table 8. Arrhenius parameters for the thermal ECP-CP rearrangements of various 2-substituted ethenylcyclopropanes (*E*)- or (*Z*)-**3-X**

Reaction ECP → CP	log (A/s^{-1})	E_a	E_a	$10^4\,k$	Rel. rate[a]	Ref.
(*E*)- or (*Z*)-**3-X → 4-X**		[kJ mol^{-1}]	[kcal mol^{-1}]	[s^{-1}][a]	k_X/k_H	
 (*E*)-**3-Me** **4-Me**	13.67	203.9	48.7	0.13	3.3	[2f]
 (*E*)-**3-OMe** **4-OMe**	12.52	162.0	38.7	56.20	1405	[13a]
 (*E*)-**3-OEt** **4-OEt**	12.44	160.7	38.4	62.06	1552	this work
 (*Z*)-**3-OEt** **4-OEt**	10.22	148.8	35.6	4.55	114	this work
 (*E*)-**3-SMe** **4-SMe**	12.91	173.8	41.5	11.8	295	this work
 (*Z*)-**3-SMe** **4-SMe**	13.52	180.2	43.1	12.5	313	this work
 (*E*)-**3-NMe$_2$** **4-NMe$_2$**	10.30	130.6	31.2	250	6250	[13b]

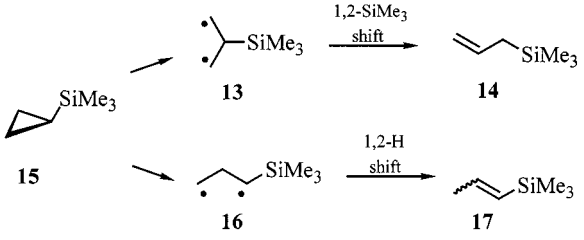
[a] Calculated for T = 300 °C.

The values for the Arrhenius A factors are generally reasonable, corresponding to small entropies of activation (either positive or negative). It is noteworthy that for the **1-X** series (Table 7), the values of A are about an order of magnitude greater than for the **3-X** series (Table 8). This signifies a general tightening of the transition state for the 2-substituted examples, suggesting a restriction of motion probably brought about by the more demanding environment of the bulky substituent. While this may be indicative of a greater degree of concert in the rearrangements of the ethenylcyclopropanes **3-X** compared with **1-X**, it could also arise from a biradical mechanism in which ring closure to the cyclopentene (i.e. the second step) was rate determining. In this latter case the bulky substituent would interfere sterically in the transition state for this step. We are aware of the vexed question of the mechanism of this reaction,[17] and these questions are addressed further in the discussion of the individual molecules. It should be noted that the very low A factor [log (A/s^{-1}) = 10.22] for (*Z*)**-3-OEt** is probably an error arising from the fact that the rate constants were small and hard to measure reliably.

1-Substituted Ethenylcyclopropanes (1-X)

Table 7 reveals that both 1-trimethylsilyl and 1-methylthio substitution cause modest rate acceleration factors, arising mainly from activation energy reductions of 6.3 and 10.2 kJ mol^{-1} relative to parent ethenylcyclopropane. These are not as large as the ca. 19 kJ mol^{-1} reduction caused by 1-methoxy and 1-ethoxy substitution.[20]

For **1-SiMe$_3$**, the result is consistent with the reported activating effect of trimethylsilyl substitution on the cyclopropane rearrangement although comparisons have to be made with care. Conlin and Kwak[21a] have studied the isomerization of trimethylsilylcyclopropane (**15**) for which the major product is allyltrimethylsilane (**14**). However, this is not the correct comparison since **14** is believed to form via a β-stabilized biradical **13** (Scheme 6). Only the minor products, (*Z*)- and (*E*)-1-trimethylsilylpropene [(*E*)- and (*Z*)-**17**] formed via the α-stabilized biradical **16**, provide the correct comparison. Nevertheless, from the reported rate constants for this latter pathway there is still a rate-accelerating factor of ca. 3 compared with cyclopropane itself.[21b] The α- and β-stabilizing effects of trimethylsilyl substitution have been nicely rationalized by bond dissociation energy measurements.[34]

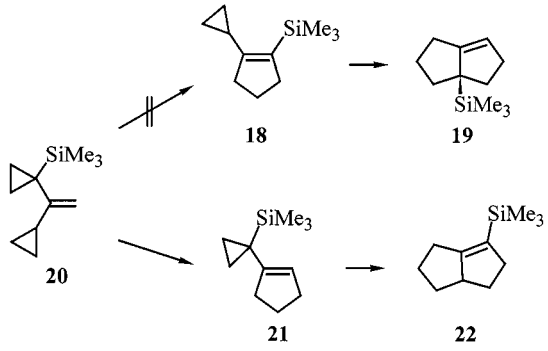


Scheme 6

In the case of **1-SiMe$_3$**, the stabilizing effect of the ethenyl group is so dominating that adjacent bond breaking of the cyclopropane ring overwhelms any tendency to remote bond breaking caused by the SiMe$_3$ β-stabilization effect.

Thus, only the modest α-stabilization effect is possible. The fact that the trimethylsilyl group activating effect is of the correct magnitude supports the idea that stabilizing effects are additive and provides further evidence that the energy considerations appropriate to biradical mechanisms apply in these ECP-CP rearrangements in spite of evidence of concerted effects[17e,17h] (in other cases).

A seemingly conflicting finding of rate retardation by a 1-trimethylsilyl group on the ECP-CP rearrangement has been reported by Paquette et al.[16c][16d] Upon pyrolysis, 1-cyclopropyl-1-(1′-trimethylsilylcyclopropyl)ethene (**20**) was quantitatively converted into 2-trimethylsilylbicyclo[3.3.0]oct-1-ene (**22**). It was proposed that in this intramolecular competition situation the ECP-CP rearrangement of the unsubstituted unit in **20** going to **21** wins over the one of the substituted side going to **18** which would have led to 5-trimethylsilylbicyclo[3.3.0]oct-1-ene (**19**) (Scheme 7). From this observation it was concluded that 1-trimethylsilyl substitution must exert a *retarding* effect on the ECP-CP rearrangement.

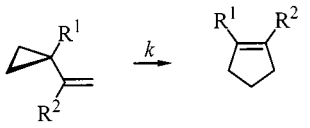


Scheme 7

Taking our kinetic results for **1-SiMe$_3$** into account, we believe that the likely explanation for the selective rearrangement of **20** to **22** lies in steric effects. Formation of **18** from **20** requires the incorporation of an extremely crowded substituent at the double bond, involving a *cis* interaction between trimethylsilyl and cyclopropyl groups; this sterically unfavorable situation already exists in the intermediate biradical precursor to **18**. Thus, the weak electronic effect of the trimethylsilyl group will be totally offset by the steric disadvantage of forming **18** rather than **21** (and hence the observed product **22**).

Some indication that such steric effects might be important can be gleaned from a comparison of methyl-substituted ethenylcyclopropanes, as shown in Table 9. The effects are not large but clearly the double methyl substitution ($R^1 = R^2 = Me$) produces less than half the rate enhancement of single methyl substitution ($R^1 = Me$). A more significant test would be to place the methyl group in the potentially sterically crowded site in **1-SiMe$_3$**. This test is planned.

Table 9. Methyl substituent effects on the ECP-CP rearrangement



R^1	R^2	log (A/s^{-1})	E_a [kJ mol^{-1}]	10^4 k [s^{-1}]	Rel. rate	Ref.
H	H	13.50	207.7	0.04	1.0	[2a]
Me	H	14.11	206.8	0.18	4.5	[2d]
H	Me	13.89	213.0	0.03	0.8	[2b]
Me	Me	14.14	211.3	0.08	2.0	[2h]

For **1-SMe**, the modest activating effect of the methylthio group is consistent with unpublished findings[35] for the pyrolysis of methylthiocyclopropane, which show a rate acceleration of a factor of ca. 30 compared with cyclopropane itself, but not as much as the factor of ca. 75 for methoxycyclopropane.[36] We have previously discussed[20] the magnitude of the methoxy stabilizing effect at a radical center of ca. 20 kJ mol^{-1}. The equivalent figure for the methylthio group may be represented by the bond dissociation energy difference, $D(CH_3CH_2CH_2-H) - D(CH_3SCH_2-H)$ which has the magnitude of ca. 8 kJ mol^{-1}.[37] The substituent effects on the parent cyclopropane suggest a slightly larger figure (ca. 12 kJ mol^{-1}), which is well within the margin of error. Thus, as Table 7 shows for **1-SMe**, just as for **1-SiMe$_3$**, the energetic effect of the SMe substituent is consistent with the additivity of the SMe and ethenyl stabilizing effects. It is worth noting that the methylthio substituent effect lies between those of methyl and methoxy.

2-Substituted Ethenylcyclopropanes (3-X)

Table 8 reveals that 2-methoxy, 2-ethoxy and 2-methylthio substitution cause quite large rate-acceleration factors, significantly greater than those for their 1-substituted counterparts. The effects are variable dependent on the (*E*) or (*Z*) starting configuration. For the (*E*)-isomers, the rate enhancements correspond to activation energy reductions of 47 kJ mol^{-1} (**3-OEt**) and 34 kJ mol^{-1} (**3-SMe**) relative to the parent ethenylcyclopropane. If the 1-substituted ethenylcyclopropane kinetics can be rationalized with the energetic arguments for biradical-type mechanisms, these figures are much more difficult to accommodate within this mechanistic framework. However, rate measurements do reveal some clear-cut features.

For (*Z*)-**3-OEt** we have established from the modeling calculations the unequivocal existence of the direct pathway (k_4) to **4-OEt**, even though the rate constants are small and have significant uncertainties. Since the 2-ethoxy substituent is certainly larger than the 2-methoxy group, this study improves on the study of **3-OMe** by Simpson and Richey,[13a] who could not detect this pathway and assumed that it was negligible. They rationalized this by pointing out that the (*Z*)-1-ethenyl-2-methoxycyclopropane could not reach

the transition state for formation of the necessary *cisoid* intermediate due to steric interactions between the methoxy and ethenyl groups.[38] Whether or not this is an important consideration, our findings show that the pathway exists. In our view the striking finding for the **3-OEt** system is not the low value for k_4 but rather the high value for k_3, the rate constant for the (*E*)-isomer. For all other substituents in these systems, viz. Me,[2f] SMe, and NMe_2,[13b] the (*E*) → (*Z*) isomerization is faster than ring expansion (i.e. $k_2 > k_3$) by at least an order of magnitude. The same is true for the nearly equivalent systems with slightly more encumbered alkenyl substitution.[14,17a,17b,17d] Only in the 2-methoxy[13a] and the 2-ethoxy cases is this not so. This argues strongly that step 3 has a large degree of concertedness. This is perhaps not altogether surprising since some of the earliest examples of concerted 1,3-sigmatropic shifts involved an alkoxy substituent at the migrating carbon atom.[39] The remaining rate constants in the **3-OEt** system, k_1, k_2 and k_4 are also quite high, and for them to be accommodated within a biradical energetic framework would require the ethoxy group to stabilize a radical center by at least a further 10 kJ mol^{-1} more than we have already suggested (i.e. 30 versus 20 kJ mol^{-1}).[40]

For **3-SMe**, there are some noteworthy features although a complete mechanistic understanding remains elusive. The values for k_3 and k_4 are much more nearly comparable than those for **3-OEt** and both are significantly smaller than k_1 and k_2. This makes the argument about the importance of the *synclinal* conformation of the ethenyl group as a critical rate-determining influence on the ECP-CP rearrangement highly questionable, since the steric bulk of the methylthio group ought thereby to render the rate for the (*Z*)-isomer even more marginal in this case. Indeed it seems that this argument can have very little force since in their study of (*E*)- and (*Z*)-2-cyano-1-isopropenylcyclopropanes, Doering and Sachdev[14] found that ring expansion to the cyclopentene product proceeded, remarkably, three times faster for the (*Z*)- than the (*E*)-isomer.

If the steric effects of the 2-substituents are not very important for the ECP-CP rearrangement it is tempting to suggest that initial cyclopropane ring-opening is not rate-determining and the mechanism is two-step, i.e. biradical in nature.[41] This idea would indeed fit in with the generally rapid (*Z*) → (*E*) isomerization compared with ring expansion. However, in view of the well-documented evidence for concertedness in the ECP-CP process[17] this would be a rash proposition. In this case, additionally, there are the arguments about the energy criterion. The lowering of the methylthio activation energy for **3-SMe** of ca. 34 kJ mol^{-1} is very significantly larger than that already indicated in this paper (vide supra) of ca. 8−12 kJ mol^{-1} for the stabilizing effect of the methylthio group at a radical center. Even if this quantity is regarded as still subject to further confirmation, there remains the contrast between the **3-X** examples (Table 8) in which X = SMe has a higher rate constant than X = OEt [(*Z*)-isomers] and the **1-X** examples (Table 7) where X = SMe has a lower rate constant than X = OEt.

Acknowledging that our values for k_4 are subject to some error, a perhaps better illustration of the reversal of substituent effects from 1- to 2-substitution is in the (*E*) → (*Z*) isomerization process. Table 10 shows some rate and equilibrium information on this.

It can be seen that for X = SMe compared with X = OEt the rate constants are greater in both directions showing clearly the greater activating effect of the methylthio substituent. These data also indicate how marginal is the steric effect in the reactant ethenylcyclopropanes **3-X**. Although the (*Z*)-compound is disfavored in both cases, the differences between them are very small. Thus, the steric bulk of SMe does not appear to be significantly larger than that of OEt. In summary, to explain the rate enhancements of the methylthio group and to a lesser extent the ethoxy group, on the 2-substituted ethenylcyclopropanes we are forced to invoke concerted processes with differing degrees of transition-state stabilization. These must be to some extent concertedness, based on the energy criterion. It may be that sulfur, with its greater capacity for expansion of its coordination (increase of its valency), is more capable of such stabilization than oxygen.

Experimental Section

Preparation of Compounds

General: IR: Perkin−Elmer 399 spectrophotometer. Abbreviations for signal assignments: Cp-H = cyclopropyl. − ^{1}H NMR: Bruker AM-250 (250 MHz), AW-250 (250 MHz), WH-270 (270 MHz) and Varian VXR 200 (200 MHz), VXR 500 S (500 MHz) spectrometers at ambient temperature. Chemical shifts are referenced to internal tetramethylsilane or to the solvent resonance employed as the internal standard (chloroform at δ = 7.24), multiplicity [d = doublet, *n*d = *n*-fold doublet (*n* = 2, 3, 4, 5), t = triplet, dt = double triplet, pt = pseudo triplet, q = quadruplet, dq = double quadruplet, pt = pseudo triplet, m = multiplet, m_c = symmetrical multiplet, s = singlet], coupling constant(s) [Hz], integration and assignment. All coupling constants were determined according to the rules for first-order spectra. − ^{13}C NMR: Bruker WP-80 (20.17 MHz), AM-250

Table 10. Kinetic and thermodynamic data for *cis*/*trans* isomerizations of (*E*/*Z*)-**3-OEt** and (*E*/*Z*)-**3-SMe** at 300 °C

ECP	$10^4\ k_1$	$10^4\ k_2$	$K = k_1/k_2$	$\Delta_R H^{\circ}$[a] [kJ mol^{-1}]	$\Delta_R S^{\circ}$[a] [J K^{-1} mol^{-1}]	$\Delta_R G^{\circ}$ [kJ mol^{-1}]
(*E*/*Z*)-**3-SMe**	506	133	3.82	−0.24	10.72	−6.39
(*E*/*Z*)-**3-OEt**	136	45	3.10	2.03	12.83	−5.39

[a] Temperature dependence was assumed to be negligible.[42]

(62.9 MHz), AW-250 (62.9 MHz) and Varian VXR 200 (50.3 MHz) spectrometers at ambient temperature; δ = 77.0 for $CDCl_3$. Signal multiplicity was determined by the DEPT method and is given as follows: + = primary or tertiary, − = secondary and C_{quat} = quaternary carbon atoms; * designates interchangeable assignments. − MS: Varian MAT CH-7 and MAT 311 A (high resolution) spectrometer. − Analytical GC: Siemens Sichromat 4 (25 m capillary column with CP-Sil-5-CB, carrier gas H_2). Preparative GC: Varian Aerograph 920 with 3/8" Teflon columns [1.5 m, 10 (15) % DC-710 on Chromosorb W-AW-DMCS (60−80 mesh), carrier gas H_2]. Retention times (R_t) [min]. − Combustion analyses: Beller Microanalytical Laboratory, Universität Göttingen. Starting materials 1-ethenyl-1-trimethylsilylcyclopropane (**1-SiMe$_3$**),[22a] 1-ethynyl-1-methylthiocyclopropane (**6-SMe**),[22g] (*E*)-2-ethoxy-1-ethynylcyclopropane (*E*)-**10**,[25] 3-diazopropene (**7**)[41] and (*E*/*Z*)-2-bromo-1-ethenylcyclopropane [(*E*/*Z*)-**12**][29] were prepared according to known literature procedures and were freshly distilled prior to use (except for **7**). All reactions were performed in anhydrous solvents and under nitrogen.

1-Chloro-1-(trimethylsilylethynyl)cyclopropane:[42] To a solution of 1-chloro-1-(trichloroethenyl)cyclopropane (**5**)[22f] (45.0 g, 0.22 mol) in 300 mL of dry diethyl ether was added dropwise with stirring at −78 °C a 1.3 M methyllithium solution in diethyl ether (390 mL, 0.5 mol) at such a rate that the temperature did not exceed −60 °C. After 1 h, the dark mixture was warmed to room temp. and stirred for an additional 1 h, then cooled to 0 °C, and trimethylsilyl chloride (freshly distilled from calcium hydride; 70 g, 0.65 mol) was added slowly. After the mixture had been stirred for an additional 12 h at room temp., the light brown suspension was cooled to 0 °C and hydrolyzed with 250 mL of saturated NH_4Cl solution. The organic phase was separated, and the aqueous phase extracted with three portions of diethyl ether (100 mL each). The combined organic phases were dried with $MgSO_4$. The solvent was removed by distillation through a 40-cm column packed with glass helices, and the black residue was bulb-to-bulb-distilled at 0.1 Torr. The colorless liquid was redistilled under reduced pressure through a 20-cm Vigreux column to yield 28 g (74%) of 1-chloro-1-(trimethylsilylethynyl)cyclopropane; bp 64 °C/20 Torr. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.45 (s, 9 H), 1.32 (m, 4 H). − ^{13}C NMR (20.15 MHz, $CDCl_3$): δ = 0.2, 20.4, 29.3, 86.5, 105.6. − IR (film): $\tilde{\nu}$ = 3090 cm^{-1}, 3010, 2170, 1240, 860, 840. − EIMS (70 eV): *m*/*z* (%) = 174/172 (1.2/4.5) [M^+], 159/157 (76) [$M^+ - CH_3$], 136 (1.2) [M^+ − HCl], 119/117 (100), 95/93 (82), 81/79 (27).

1-Methylthio-1-(trimethylsilylethynyl)cyclopropane:[22g] A 1.4 N *n*-butyllithium solution in *n*-hexane (22 mL, 31 mmol) in 70 mL of dry diethyl ether was added with stirring at −78 °C to a solution of 1-chloro-1-(trimethylsilylethynyl)cyclopropane (5.0 g, 29 mmol). The mixture was kept at −78 °C for 45 min, then warmed to room temp., and after another 45 min cooled to −78 °C again, whereupon methyl methanethiosulfonate (3.6 mL, 35 mmol) was added. The reaction mixture was stirred at room temp. for an additional 1 h, then hydrolyzed with 100 mL of saturated NH_4Cl solution. The organic phase was separated, the aqueous layer extracted with three portions of diethyl ether (50 mL each) and the combined organic phases were dried with $MgSO_4$. The solvents were removed by distillation through a 40-cm column packed with glass helices and the crude product was distilled under reduced pressure to yield 4.8 g (90%) of 1-methylthio-1-(trimethylsilylethynyl)cyclopropane as a colorless liquid; bp 90−92 °C/12 Torr. − IR (film): $\tilde{\nu}$ = 3080 cm^{-1}, 2160 (C≡C), 1440 ($SiCH_3$), 1270, 1250, 1160, 935, 870, 840, 760, 655. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.13 (s, 9 H), 1.02−1.08 (m, 2 H), 1.24−1.30 (m, 2 H), 2.28 (s, 3 H). − ^{13}C NMR (20.17 MHz, $CDCl_3$): δ = 0.1 (q), 15.2 (t), 16.0 (s), 19.4 (m), 82.1 (s), 108.2 (s). − GC/EIMS (70 eV): *m*/*z* (%) = 184 (100) [M^+], 169 [$M^+ - CH_3$], 141 [$M^+ - SiCH_3$], 129.

1-Ethynyl-1-methylthiocyclopropane (6-SMe): Potassium carbonate 5.0 g (36 mmol) was added to a solution of 1-methylthio-1-(trimethylsilylethynyl)cyclopropane (3.5 g, 19 mmol) in 30 mL of methanol, and the mixture stirred at room temp. for 4 days. The progress of the reaction was monitored by gas chromatography. The mixture was diluted with 20 mL of water and then extracted with five portions of pentane (10 mL each), the combined extracts were washed with saturated NaCl solution (20 mL), and dried with $MgSO_4$. The solvent was removed by distillation through a 40-cm column packed with glass helices and the residue distilled through a 20-cm Vigreux column to yield 1.7 g (79%) of 1-ethynyl-1-methylthiocyclopropane as a colorless liquid; bp 86−88 °C. − ^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.05−1.12 (m, 2 H), 1.27−1.33 (m, 2 H), 2.10 (s, 1 H), 2.31 (s, 3 H). − ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 15.2 (s and q), 19.0 (m), 65.8 (d), 86.4 (s).

1-Ethenyl-1-methylthiocyclopropane (1-SMe): A solution of 1-ethynyl-1-methylthiocyclopropane (**6-SMe**) (3.00 g, 26.7 mmol) in 200 mL of *n*-pentane was placed in a Parr hydrogenator (volume 0.5 L) and a slow flow of nitrogen passed through the solution for 5 min. Lindlar catalyst (444 mg, 0.77 mol-% Pd) and quinoline (104 μL, 3 mol-%) were then added, the hydrogenator flushed several times with H_2 and the H_2 pressure raised to 3.5 bar at 20 °C (continuous H_2 feed). Several checks on the slow conversion were carried out during the reaction (GC). After complete conversion (144 h), the reaction was immediately stopped and the mixture filtered through a short Celite pad. The solvent was distilled through a 50-cm packed column and the residue trap-to-trap-distilled in vacuo yielding 2.99 g (97%) of **1-SMe** as a colorless liquid. A small sample was separated from solvent traces by preparative GC for analytical characterization. − IR (film): $\tilde{\nu}$ = 3084 cm^{-1} (C=CH), 3003, 2918 (CH), 1633 (C=C), 1419, 1250, 1171, 1024, 987, 909, 860. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 [m_c, AA′ part of an AA′BB′ system, 2 H, 2(3)-H_A], 1.05 [m_c, BB′ part of an AA′BB′ system, 2 H, 2(3)-H_B], 2.07 (s, 3 H, SCH_3), 5.04 (dd, ^2J = 1.6, $^3J_{2'(E),1'}$ = 10.0 Hz, 1 H, 2′-H_E), 5.25 (dd, ^2J = 1.6, $^3J_{1',2'(Z)}$ = 16.8 Hz, 1 H, 2′-H_Z), 5.57 (dd, $^3J_{1',2'(E)}$ = 10.0, $^3J_{1',2'(Z)}$ = 16.8 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.5 (+, SCH_3), 17.1 [−, C-2(3)], 27.9 (C_{quat}, C-1), 113.4 (−, C-2′), 140.3 (+, C-1′). − MS (EI, 70 eV): *m*/*z* (%) = 114 (23) [M^+], 99 (22) [M^+ − Me], 71 (38), 67 (100) [M^+ − SMe], 65 (41), 61 (15), 53 (10), 47 (8) [SMe^+], 45 (31), 41 (39). − $C_6H_{10}S$ (114.21): calcd. C 63.10, H 8.83, S 28.08; found C 63.25, H 8.92, S 27.96.

General Procedure for the Hydrogenation of Ethynylcyclopropanes 6-SiMe$_3$ and 10:[23a] In a hydrogenator (equipped with a burette for the determination of hydrogen consumption) a mixture of 1 mmol of ethynylcyclopropane in 10 mL of *n*-pentane, the specified amount of Lindlar catalyst and quinoline was first flushed with nitrogen and subsequently with hydrogen (continuous H_2 feed). Initiation of the reaction was performed by vigorous agitation at 20 °C and immediately stopped after total ethynylcyclopropane conversion (consumption of the equivalent volume-measured amount of H_2). The mixture was filtered through a short Celite pad and the solvent distilled through a 50-cm packed column. Trap-to-trap distillation of the residue in vacuo yielded the products as colorless liquids. A small sample was separated from solvent traces by preparative GC for analytical characterization.

1-Ethenyl-1-trimethylsilylcyclopropane (1-SiMe$_3$): 1-Ethynyl-1-trimethylsilylcyclopropane (**6-SiMe$_3$**; 2.33 g, 16.8 mmol),[22a] Lindlar

catalyst (233 mg, 0.65 mol-% Pd) and quinoline (15 μL, 0.70 mol-%) were allowed to react according to the General Procedure for 20 min, yielding 2.00 g (85%) of **1-SiMe$_3$** (consumption of 377 mL of H_2). − IR (film): $\tilde{\nu}$ = 3069 cm^{-1} (C=CH), 2995, 2957 (CH), 1626 (C=C), 1249, 1189, 1022, 991, 836, 748, 689, 663, 637. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = −0.04 [s, 9 H, $Si(CH_3)_3$], 0.55 [s, A_4 system, 4 H, 2(3)-H], 4.87 (m, 1 H, 2′-H$_E$), 4.92 (m, 1 H, 2′-H$_Z$), 5.91 (m, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = −3.3 [+, $Si(CH_3)_3$], 9.6 [−, C-2(3)], 11.4 (C_{quat}, C-1), 112.9 (−, C-2′), 142.9 (+, C-1′). − MS (EI, 70 eV): *m*/*z* (%) = 140 (2) [M$^+$], 125 (3) [M$^+$ − Me], 73 (100) [$SiMe_3^+$], 59 (18), 45 (17), 43 (18). − $C_8H_{16}Si$ (140.30): calcd. C 68.49, H 11.50; found C 68.44, H 11.44.

(*E*)-1-Ethenyl-2-ethoxycyclopropane [(*E*)-3-OEt]: Diastereomerically pure (*E*)-2-ethoxy-1-ethynylcyclopropane[25] [(*E*)-**10**] (5.46 g, 49.5 mmol), Lindlar catalyst (300 mg, 0.28 mol-% Pd) and quinoline (32 μL, 0.50 mol-%) were allowed to react according to the General Procedure for 1 h, yielding 4.72 g (85%) of pure (*E*)-**3-OEt**, *de* 100.0% (consumption of 1109 mL of H_2). − IR (film): $\tilde{\nu}$ = 3084 cm^{-1} (Cp-H), 2977, 2931, 2872 (CH), 1637 (C=C), 1446, 1374, 1351, 1300, 1257, 1190, 1121, 1087, 898, 818. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (3d, ^2J = 5.8, $^3J_{3(E),1}$ = 6.2, $^3J_{2(E),2}$ = 6.2 Hz, 1 H, 3-H$_E$), 1.01 (3d, ^2J = 5.8, $^3J_{3(Z),1}$ = 9.9, $^3J_{3(Z),2}$ = 3.5 Hz, 1 H, 3-H$_Z$), 1.20 (t, 3 H, OCH_2CH_3), 1.58 (6d, $^3J_{1,2}$ = 2.4, $^3J_{1,3(E)}$ = 6.2, $^3J_{1,3(Z)}$ = 9.9, $^3J_{1,1'}$ = 8.1, $^4J_{1,2'(E)}$ = 0.4, $^4J_{1,2'(Z)}$ = 0.8 Hz, 1 H, 1-H), 3.15 (3d, $^3J_{2,1}$ = 2.4, $^3J_{2,3(E)}$ = 6.2, $^3J_{2,3(Z)}$ = 3.5 Hz, 1 H, 2-H), 3.55 (q, 2 H, OCH_2CH_3), 4.88 (dd, ^2J = 1.6, $^3J_{2'(E),1'}$ = 10.3 Hz, 1 H, 2′-H$_E$), 4.99 (dd, ^2J = 1.6, $^3J_{2'(Z),1'}$ = 17.1 Hz, 1 H, 2′-H$_Z$), 5.51 (3d, $^3J_{1',1}$ = 8.1, $^3J_{1',2'(E)}$ = 10.3, $^3J_{1',2'(Z)}$ = 17.1 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 14.1 (−, C-3), 15.2 (+, OCH_2CH_3), 22.5 (+, C-1), 60.4 (+, C-2), 66.0 (−, OCH_2CH_3), 112.5 (−, C-2′), 138.4 (+, C-1′). − MS (EI, 70 eV): *m*/*z* (%) = 85 (5) [M$^+$ − C_2H_3], 84 (22), 83 (18) [M$^+$ − Et], 67 (10) [M$^+$ − OEt], 55 (100) [M$^+$ + 1 − CHOEt], 41 (50).

(*Z*)-1-Ethenyl-2-ethoxycyclopropane [(*Z*)-3-OEt]:[24] A precooled (−30 °C) 0.4 M solution of 3-diazopropene (**7**; 37.8 mL, 15.1 mmol)[41] in ether at 0 °C was slowly added (7 h) to a vigorously stirred suspension of $Rh_2(OAc)_4$ (6.7 mg, 0.1 mol-%) in ethenyl ethyl ether (**8**; 33.50 g, 465 mmol). The mixture was stirred for 8 h. The excess alkene was trap-to-trap-distilled in vacuo at 0 °C and 100 mL of *n*-pentane was added to the residue. After filtration of the mixture through a short Celite pad, the solvent was distilled through a 50-cm packed column and the residue slowly trap-to-trap-distilled in vacuo yielding 1.05 g (62%) of (*E*/*Z*)-**3-OEt** [*E*/*Z* = 1:3.5, NMR, GC] as a colorless liquid. A sample of the diastereomeric mixture was separated by preparative GC (25 °C) to yield pure (*Z*)-**3-OEt**, *de* 98.0% (t_R = 15). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (3d, ^2J = 6.2, $^3J_{3(Z),2}$ = 3.7, $^3J_{3(Z),1}$ = 6.2 Hz, 1 H, 3-H$_Z$), 0.94 (3d, ^2J = 6.2, $^3J_{3(E),2}$ = 6.3, $^3J_{3(E),1}$ = 9.2 Hz, 1 H, 3-H$_E$), 1.20 (t, 3 H, OCH_2CH_3), 1.49 (4d, $^3J_{1,2}$ = 6.2, $^3J_{1,3(Z)}$ = 6.2, $^3J_{1,3(E)}$ = 9.2, $^3J_{1,1'}$ = 9.4 Hz, 1 H, 1-H), 3.40 (3d, $^3J_{2,3(Z)}$ = 3.7, $^3J_{2,3(E)}$ = 6.3, $^3J_{2,1}$ = 6.2 Hz, 1 H, 2-H), 3.52 (q, 2 H, OCH_2CH_3), 5.00 (dd, ^2J = 2.0, $^3J_{2'(E),1'}$ = 10.4 Hz, 1 H, 2′-H$_E$), 5.18 (dd, ^2J = 2.0, $^3J_{2(Z),1'}$ = 17.2 Hz, 1 H, 2′-H$_Z$), 5.62 (3d, $^3J_{1',2'(Z)}$ = 17.2, $^3J_{1',1}$ = 9.4, $^3J_{1',2'(E)}$ = 10.4 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.6 (−, C-3), 15.1 (+, OCH_2CH_3), 21.9 (+, C-1), 57.8 (+, C-2), 66.2 (−, OCH_2CH_3), 113.8 (−, C-2′), 136.6 (+, C-1′).

(*E*)- and (*Z*)-1-Ethenyl-2-methylthiocyclopropane [(*E*)-, (*Z*)-3-SMe]: A 1.5 M solution of *t*BuLi in pentane (91.3 mL, 137 mmol) was added to a stirred and cooled (−78 °C) solution of (*E*/*Z*)-2-bromo-1-ethenylcyclopropane [(*E*/*Z*)-**12**][29] [10.0 g, 68 mmol; (*E*)/(*Z*) = 1.0:2.8, NMR, GC] in 100 mL of THF and 50 mL of ether. After 15 min, *S*-methyl methanethiosulfonate (8.6 g, 68 mmol) was added and the mixture left to warm to room temp. The mixture was then poured into 300 mL of satd. NH_4Cl solution, diluted with 100 mL of ether and the phases were separated. The organic phase was washed twice with 80 mL of satd. NaCl solution and dried with $MgSO_4$. The solvent was distilled through a 50-cm packed column and the residue trap-to-trap-distilled to yield 5.9 g (76%) of pure (*E*/*Z*)-**3-SMe** [*E*/*Z* = 1.0:2.8, NMR, GC] as a colorless liquid. A sample of the diastereomeric mixture was separated by preparative GC (80 °C) to give pure (*E*)-**3-SMe**, *de* 98.6% and pure (*Z*)-**3-SMe**, *de* 97.5%.

(*E*)-3-SMe: Fraction I, t_R = 9. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 (m, 2 H, 3-H$_Z$ and 3-H$_E$), 1.60 (m, 1 H, 2-H), 1.89 (m, $^3J_{1,1'}$ = 7.9, $^4J_{1,2'(E)}$ = 0.4, $^4J_{1,2'(Z)}$ = 0.6 Hz, 1 H, 1-H), 2.15 (s, 3 H, SCH_3), 4.91 (3d, $^3J_{2'(E),1'}$ = 10.2, ^2J = 2.0, $^4J_{2'(E),1}$ = 0.4 Hz, 1 H, 2′-H$_E$), 5.09 (3d, $^3J_{2'(Z),1'}$ = 17.5, ^2J = 2.0, $^4J_{2'(Z),1}$ = 0.6 Hz, 1 H, 2′-H$_Z$), 5.43 (3d, $^3J_{1',2'(Z)}$ = 17.5, $^3J_{1',2'(E)}$ = 10.2, $^3J_{1',1}$ = 7.9 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.4 (+, C-2), 16.5 (−, C-3), 23.1 (+, C-1), 26.2 (+, SCH_3), 113.3 (−, C-2′), 139.4 (+, C-1′).

(*Z*)-3-SMe: Fraction II, t_R = 12. − IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (Cp-H), 2999, 2917 (CH), 1634 (C=C), 1435, 1280, 1211, 1038, 992, 942, 895. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.66 (3d, $^3J_{3(Z),1}$ = 5.8, $^3J_{3(Z),2}$ = 5.6, ^2J = 5.2 Hz, 1 H, 3-H$_Z$), 1.22 (3d, $^3J_{3(E),2}$ = 8.2, $^3J_{3(E),1}$ = 8.2, ^2J = 5.2, 1 H, 3-H$_E$), 1.77 (5d, $^3J_{1,1'}$ = 8.9, $^3J_{1,3(E)}$ = 8.2, $^3J_{1,2}$ = 7.0, $^3J_{1,3(Z)}$ = 5.8, $^4J_{1,2'(Z)}$ = 0.4 Hz, 1 H, 1-H), 2.11 (s, 3 H, SCH_3), 2.17 (3d, $^3J_{2,3(E)}$ = 8.2, $^3J_{2,1}$ = 7.0, $^3J_{2,3(Z)}$ = 5.6 Hz, 1 H, 2-H), 5.07 (dd, $^3J_{2'(E),1'}$ = 10.3, ^2J = 1.9 Hz, 1 H, 2′-H$_E$), 5.21 (3d, $^3J_{2'(Z),1'}$ = 17.1, ^2J = 1.9, $^4J_{2'(Z),1}$ = 0.4 Hz, 1 H, 2′-H$_Z$), 5.81 (3d, $^3J_{1',2'(Z)}$ = 17.1, $^3J_{1',2'(E)}$ = 10.3, $^3J_{1',1}$ = 8.9 Hz, 1 H, 1′-H). − ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.1 (−, C-3), 18.2 (+, C-2), 22.3 (+, C-1), 22.6 (+, SCH_3), 115.1 (−, C-2′), 137.4 (+, C-1′). − MS (EI, 70 eV): *m*/*z* (%) = 114 (6) [M$^+$], 99 (37) [M$^+$ − Me], 75 (44), 67 (78) [M$^+$ − SMe], 66 (100), 65 (49), 47 (11) [SMe^+], 45 (42), 41 (59). − HRMS: calcd. for $C_6H_{10}S$ [M$^+$] 114.0503, found 114.0503.

Kinetic Measurements

General: Gas-phase thermolyses were performed in a hexamethyldisilazane (HMDS)-conditioned (24 h) static reaction vessel connected to a vacuum line similar to the previously described apparatus.[20] Conditioning was repeated after approx. 70−100 thermolytic runs. Prior to all GC runs with the thermolyzed reaction mixtures, reactant composition stability checks and mass recovery GC checks were carried out by injecting and analyzing a sample of the reactant mixture [= master mixture, containing defined amounts of the reactant, cyclohexane (CH) as an internal standard and diluted with nitrogen, see Table 11]. For checks on possible surface catalysis and on radical chain components the reaction vessel was exchanged for a spherical glass-tube-packed reaction vessel with an approximate surface (*S*) to volume (*V*) ratio *S*/*V* of 10 cm^{-1}. All reactant and reaction mixture samples were pressurized to 100−340 Torr with nitrogen before GC analysis.

Time, temperature and pressure dependencies were investigated for all ethenylcyclopropanes. Up to sixteen individual pyrolyses were performed for each measured temperature and approximately equidistant temperatures were selected over a range of 50 °C (ca. 10 °C intervals). Kinetics were based on reactant disappearance and good linear first-order graphs (least mean-squares procedure) were obtained for all ethenylcyclopropanes. For the straightforward decomposition reactions of **1-X** (X = $SiMe_3$, SMe) individual *k* values were derived from the slopes of the first-order graphs. From these,

Table 11. Physical properties, operational parameters and gas-handling conditions in the ECP-CP rearrangements of ethenylcyclopropanes **1-X** and (*E*)-, (*Z*)-**3-X**

ECP	Initial conc. of ECP (CH) (%)[a]	Vapor pressure [Torr][b]	Reaction pressure [Torr][c]	Conversion of ECP (%)[c]	Temp. [°C]
1-SMe	0.20 (0.50)	7	12−15	7.4−92.8	289.9−341.0
1-SiMe$_3$	1.03 (0.65)	12	15−25	6.5−89.9	313.3−363.1
(*E*)-**3-OEt**	0.66 (0.80)	15	18−22	16.3−94.0	221.0−278.1
(*Z*)-**3-OEt**	0.80 (0.80)[d]	10	18−25	7.6−94.3	220.8−277.6
(*E*)-**3-SMe**	0.58 (0.19)[d]	4	14−21	7.6−84.7	239.3−289.1
(*Z*)-**3-SMe**	0.53 (0.16)[d]	3	14−21	24.4−94.0	239.3−289.2

[a] Averaged over all master mixtures. − [b] At room temp. − [c] Maximum and minimum limits given over all measured time and temperature intervals. − [d] Diastereomeric impurities neglected.

Arrhenius plots (Figure 1) were then produced and the activation parameters determined. For (*E*)- and (*Z*)-**3-X** (X = OEt, SMe) a more sophisticated computer-based refinement proved to be necessary in terms of determining *k* values, employing Gear[30,32] and Marquardt[31,33] algorithms. Each temperature-dependent set of analytical data for the two individually pyrolyzed isomers of both compounds was examined and the four *k* values (k_1 to k_4) varied until a minimum of least-squares differences (Σx^2, see Table 4) between observed and calculated data were achieved. The Arrhenius parameters for all four steps of each reaction were obtained as mentioned above. All reactions proved to be pressure- and surface-independent. Table 11 contains practical conditions of operation for each individually investigated compound.

Analysis: GC analyses were performed with Perkin−Elmer 8310 [**1-SMe**, (*E*)- and (*Z*)-**3-OEt**] and Perkin−Elmer F 33 [**1-SiMe$_3$**, (*E*)- and (*Z*)-**3-SMe**] gas chromatographs with FID, and separations were carried out on 4 m × 3 mm [(*E*)-**3-OEt**, **1-SMe**] and 7 m × 3 mm [(*Z*)-**3-OEt**, **1-SiMe$_3$**, (*E*)- and (*Z*)-**3-SMe**] silicon oil columns (15% MS 550 on 60/80 Chromosorb P). In all cases well-defined peaks and excellent baseline separations were achieved. Retention times (t_R) [min]. Column temperatures were 50 °C for analyses of (*E*)-**3-OEt** [t_R = 4.35, CH; 15.06, (*E*)-**3-OEt**; 17.88, (*Z*)-**3-OEt**; 21.37, **4-OEt**], 95 °C for **1-SMe** (t_R = 1.73, CH; 5.32, **1-SMe**; 14.73, **2-SMe**), 80 °C for (*Z*)-**3-OEt** [t_R = 6.10, CH; 15.21, (*E*)-**3-OEt**; 17.40, (*Z*)-**3-OEt**; 20.53, **4-OEt**], 110 °C for **1-SiMe$_3$** (t_R = 4.39, CH; 7.64, **1-SiMe$_3$**; 10.83, **2-SiMe$_3$**) and 120 °C for (*E*)- and (*Z*)-**3-SMe** [t_R = 4.37, CH; 11.31, (*E*)-**3-SMe**; 13.76, (*Z*)-**3-SMe**; 16.44, **4-SMe**]. Constant gas pressures were 123 kPa (nitrogen carrier gas), 133 kPa (hydrogen) and 81 kPa (air) for studies of **1-SiMe$_3$**, (*Z*)-**3-OEt**, (*E*)- and (*Z*)-**3-SMe** and 166 kPa (nitrogen), 174 kPa (hydrogen) and 152 kPa (air) for **1-SMe** and (*E*)-**3-OEt**.

The columns described above were conditioned with HMDS (10 h, 150 °C) approximately after every 20 h of performance. All isomeric compounds were assumed to possess identical FID response factors. The characterization of all products under reaction conditions was achieved by freezing thermolyzed and totally converted reactant samples (without internal standard) from the line and recording the corresponding NMR spectra.

1-Methylthiocyclo-1-pentene (2-SMe): Seven independent quantitative pyrolyses were performed with **1-SMe** (30-min runs at 350.4 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90 (pt, 2 H, 4-H), 2.31 (s, 3 H, SCH_3), 2.40 [m, 4 H, 3(5)-H], 5.27 (m, 1 H, 2-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.1 (+, SCH_3), 23.9 (−, C-4), 32.7 (−, C-3*), 35.9 (−, C-5*), 120.4 (+, C-2), 138.4 (C_{quat}, C-1).

1-Trimethylsilylcyclo-1-pentene (2-SiMe$_3$): Three independent quantitative pyrolyses were performed with **1-SiMe$_3$** (30-min runs at 395.8 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.57 [s, 9 H, $Si(CH_3)_3$], 1.80 (m, 2 H, 4-H), 2.38 [m, 4 H, 3(5)-H], 5.97 (m, 1 H, 1-H). − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = −0.3 [+, $Si(CH_3)_3$], 25.4 (−, C-4), 37.2 (−, C-5*), 38.4 (−, C-3*), 141.7 (+, C-2), 145.9 (C_{quat}, C-1).

4-Ethoxycyclo-1-pentene (4-OEt): Four independent quantitative pyrolyses were performed with (*Z*)-**3-OEt** (20-min runs at 298.4 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.20 (t, 3 H, OCH_2CH_3), 2.48 [m, ^2J = 17.0 Hz, 4 H, 3(5)-H], 3.47 (q, 2 H, OCH_2CH_3), 4.20 (m_c, 1 H, 4-H), 5.68 [s, 2 H, 1(2)-H]. − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.5 (+, OCH_2CH_3), 39.3 [−, C-3(5)], 64.1 (−, OCH_2CH_3), 79.0 (+, C-4), 128.4 [+, C-1(2)].

4-Methylthiocyclo-1-pentene (4-SMe): Five independent quantitative pyrolyses were performed with (*Z*)-**3-SMe** (30-min runs at 315.3 °C). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, SCH_3), 2.36 [m_c, 2 H, 3(5)-H], 2.79 [m_c, 2 H, 3(5)-H], 3.39 (m_c, 1 H, 4-H), 5.71 [s, 2 H, 1(2)-H)]. − ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 14.3 (+, SCH_3), 40.2 [−, C-3(5)], 42.4 (+, C-4), 129.2 [+, C-1(2)].

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 357, Project A14), the Fonds der Chemischen Industrie and by a grant within the Academic Research Collaboration (ARC) Programme administered by the British Council and the Deutscher Akademischer Austauschdienst (DAAD). The authors are indebted to Dr. B. Knieriem, Göttingen, for his careful reading of the final manuscript.

[1] [1a] N. P. Neureiter, *J. Org. Chem.* **1959**, *24*, 2044−2046. − [1b] E. Vogel, *Angew. Chem.* **1960**, *72*, 4−26; see footnote [162] therein.

[2] [2a] M. C. Flowers, H. M. Frey, *J. Chem. Soc.* **1961**, 3547−3548. − [2b] H. M. Frey, D. C. Marshall, *J. Chem. Soc.* **1962**, 3981−3983. − [2c] R. J. Ellis, H. M. Frey, *Proc. Chem. Soc.* **1964**, 221. − [2d] R. J. Ellis, H. M. Frey, *J. Chem. Soc.* **1964**, 959−960. − [2e] R. J. Ellis, H. M. Frey, *J. Chem. Soc.* **1964**, 5578−5583. − [2f] C. S. Elliot, H. M. Frey, *J. Chem. Soc.* **1965**, 345−350. − [2g] C. S. Elliot, H. M. Frey, *J. Chem. Soc.* **1965**, 4289−4293. − [2h] H. M. Frey, *Adv. Phys. Org. Chem.* **1966**, *4*, 147−193. − [2i] H. M. Frey, R. K. Solly, *Int. J. Chem. Kinet.* **1969**, *1*, 473−477.

[3] C. G. Overberger, A. E. Borchert, *J. Am. Chem. Soc.* **1960**, *82*, 1007−1008, 4896−4899.

[4] C. A. Wellington, *J. Phys. Chem.* **1962**, *66*, 1671−1674.
[5] [5a] W. von E. Doering, W. R. Roth, *Angew. Chem.* **1963**, *75*, 27; *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 115. − [5b] W. von E. Doering, W. R. Roth, *Tetrahedron* **1963**, *19*, 715−737.
[6] G. S. Hammond, C. D. de Boer, *J. Am. Chem. Soc.* **1964**, *86*, 899.
[7] J. König, W. R. Roth, *Justus Liebigs Ann. Chem.* **1965**, *688*, 28−39.
[8] W. Grimme, *Chem. Ber.* **1965**, *98*, 756−763.
[9] A. J. Berlin, L. P. Fisher, A. D. Ketley, *Chem. Ind. (London)* **1965**, 509.
[10] A. D. Ketley, J. L. McClanahan, *J. Org. Chem.* **1965**, *30*, 940−943.
[11] [11a] M. R. Willcott, V. H. Cargle, *J. Am. Chem. Soc.* **1967**, *89*, 723−724. − [11b] V. H. Cargle, M. R. Willcott, *J. Am. Chem. Soc.* **1969**, *91*, 4310−4311.
[12] J. L. Brauman, D. M. Golden, *J. Am. Chem. Soc.* **1968**, *90*, 1920−1921.
[13] [13a] J. M. Simpson, H. G. Richey, Jr., *Tetrahedron Lett.* **1973**, 2545−2548. − [13b] H. G. Richey, Jr., D. W. Shull, *Tetrahedron Lett.* **1976**, 575−576.
[14] W. von E. Doering, K. Sachdev, *J. Am. Chem. Soc.* **1975**, *97*, 5512−5520.
[15] [15a] B. M. Trost, P. H. Scudder, *J. Org. Chem.* **1981**, *46*, 506−509. − [15b] J. Salaün, J. Ollivier, *Nouv. J. Chim.* **1981**, *5*, 587−594. − [15c] J. Salaün, in *The Chemistry of the Cyclopropyl Group* (Ed.: Z. Rappoport), Wiley, New York, **1987**, chapter 17.
[16] [16a] E. J. Corey, S. W. Walinsky, *J. Am. Chem. Soc.* **1972**, *94*, 8932−8933. − [16b] B. M. Trost, D. E. Keeley, H. C. Arndt, J. H. Rigby, M. J. Bogdanowicz, *J. Am. Chem. Soc.* **1977**, *99*, 3080−3087; B. M. Trost, D. E. Keeley, H. C. Arndt, M. J. Bogdanowicz, *J. Am. Chem. Soc.* **1977**, *99*, 3088−3100. − [16c] L. A. Paquette, G. J. Wells, K. A. Horn, T.-H. Yan, *Tetrahedron Lett.* **1982**, *23*, 263−266. − [16d] L. A. Paquette, G. J. Wells, K. A. Horn, T.-H. Yan, *Tetrahedron* **1983**, *39*, 913−924. − [16e] S. Keyaniyan, M. Apel, J. P. Richmond, A. de Meijere, *Angew. Chem.* **1985**, *97*, 763−764; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 770.
[17] [17a] G. D. Andrews, J. E. Baldwin, *J. Am. Chem. Soc.* **1976**, *98*, 6705−6706. − [17b] J. J. Gajewski, M. P. Squicciarini, *J. Am. Chem. Soc.* **1989**, *111*, 6717−6728. − [17c] R. H. Newman-Evans, R. J. Simon, B. K. Carpenter, *J. Org. Chem.* **1990**, *55*, 695−711. − [17d] J. E. Baldwin, N. D. Ghatlia, *J. Am. Chem. Soc.* **1991**, *113*, 6273−6274. − [17e] J. J. Gajewski, L. P. Olson, *J. Am. Chem. Soc.* **1991**, *113*, 7432−7433. − [17f] K. N. Houk, Y. Li, J. D. Evanseck, *Angew. Chem.* **1992**, *104*, 711−739; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 682. − [17g] J. E. Baldwin, K. A. Villacria, D. L. Freedberg, F. A. L. Anet, *J. Am. Chem. Soc.* **1994**, *116*, 10845. − [17h] J. J. Gajewski, L. P. Olson, M. R. Willcott III, *J. Am. Chem. Soc.* **1996**, *118*, 299−306. − [17i] E. R. Davidson, J. J. Gajewski, *J. Am. Chem. Soc.* **1997**, *119*, 10543−10544. − [17j] K. N. Houk, M. Nendel, O. Wiest, J. W. Storer, *J. Am. Chem. Soc.* **1997**, *119*, 10545−10546. − [17k] J. E. Baldwin, S. J. Bonacorsi, R. C. Burrell, *J. Org. Chem.* **1998**, *63*, 4721−4725. − [17l] C. Doubleday, M. Nendel, K. N. Houk, D. Thweatt, M. Page, *J. Am. Chem. Soc.* **1999**, *121*, 4720−4721. − [17m] J. E. Baldwin, R. C. Burrell, *J. Org. Chem.* **1999**, *64*, 3567−3571. − [17n] D. Sperling, J. Fabian, *Eur. J. Org. Chem.* **1999**, 215−220. − [17o] J. E. Baldwin, R. Shukla, *J. Am. Chem. Soc.* **1999**, *121*, 11018−11019. − [17p] M. Nendel, D. Sperling, O. Wiest, K. N. Houk, *J. Org. Chem.* **2000**, *65*, 3259−3268. − [17q] For a synopsis of work on the mechanistic aspects of the vinylcyclopropane-to-cyclopentene rearrangement, see: J. E. Baldwin, *J. Comput. Chem.* **1998**, *19*, 222−231.
[18] [18a] R. L. Danheiser, C. Martinez-Davila, J. M. Morin, Jr., *J. Org. Chem.* **1980**, *45*, 1340−1341. − [18b] R. L. Danheiser, C. Martinez-Davila, R. J. Auchus, J. T. Kadonaga, *J. Am. Chem. Soc.* **1981**, *103*, 2443−2446. − [18c] R. L. Danheiser, J. J. Bronson, K. Okano, *J. Am. Chem. Soc.* **1985**, *107*, 4579−4581. − [18d] R. L. Danheiser, J. J. Bronson, in *Comprehensive Organic Synthesis*, vol. 5 (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, chapter 8.3. − [18e] C. K. Murray, D. C. Yang, W. D. Wulff, *J. Am. Chem. Soc.* **1990**, *112*, 5660−5662. − [18f] J. P. Dinnocenzo, D. A. Conlon, *J. Am. Chem. Soc.* **1988**, *110*, 2324−2326.
[19] [19a] T. Hudlicky, D. A. Becker, R. L. Fan, S. I. Kozhushkov, *Methods Org. Chem. (Houben-Weyl)* (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**, vol. E17c, pp. 2538−2565. − [19b] T. Hudlicky, J. W. Reed, in *Comprehensive Organic Synthesis*, vol. 5. (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, chapter 8.1.
[20] G. McGaffin, A. de Meijere, R. Walsh, *Chem. Ber.* **1991**, *124*, 939−945.
[21] [21a] R. T. Conlin, Y.-W. Kwak, *Organometallics* **1986**, *5*, 1205−1207. − [21b] T. S. Chambers, G. B. Kistiakowsky, *J. Am. Chem. Soc.* **1934**, *56*, 399−405.
[22] [22a] T. Liese, A. de Meijere, *Chem. Ber.* **1986**, *119*, 2995−3026. − [22b] W. Weber, A. de Mejere, *Angew. Chem.* **1980**, *92*, 135−136; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 138−144. − [22c] T. Liese, A. de Meijere, *Angew. Chem.* **1982**, *94*, 65−66; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 34−40; *Angew. Chem. Suppl.* **1982**, 34−40. − [22d] T. Liese, G. Splettstösser, A. de Meijere, *Tetrahedron Lett.* **1982**, *23*, 3341−3344. − [22e] W. Weber, A. de Meijere, *Chem. Ber.* **1985**, *118*, 2450−2471. − [22f] T. Liese F. Jaekel, A. de Meijere, *Org. Synth.* **1990**, *69*, 144−147. − [22g] G. Bengtson, Dissertation, Universität Hamburg, **1985**.
[23] [23a] For hydrogenations of other 1-substituted ethynylcyclopropanes see: G. McGaffin, S. Michalski, A. Stolle, S. Bräse, J. Salaün, A. de Meijere, *Synlett* **1992**, 558−560. − [23b] For hydrogenations of further 2-substituted ethynylcyclopropanes see: G. McGaffin, A. de Meijere, *Synthesis* **1994**, 583−591.
[24] A. de Meijere, T.-J. Schulz, R. R. Kostikov, F. Graupner, T. Murr, T. Bielfeldt, *Synthesis* **1991**, 547−560.
[25] H.-C. Militzer, S. Schömenauer, C. Otte, C. Puls, J. Hain, S. Bräse, A. de Meijere, *Synthesis* **1993**, 998−1012.
[26] U. Schöllkopf, G. J. Lehmann, J. Paust, H.-D. Härtl, *Chem. Ber.* **1964**, *97*, 1527−1541.
[27] R. H. Rynbrandt, F. E. Dutton, *J. Org. Chem.* **1975**, *40*, 2282−2288.
[28] L. Skattebøl, *J. Org. Chem.* **1964**, *29*, 2951−2956.
[29] J. P. Marino, L. J. Browne, *Tetrahedron Lett.* **1976**, 3245−3248.
[30] [30a] C. W. Gear, in *Information Processing*, vol. 1 (Ed.: A. Morell), North Holland, Amsterdam, **1968**, p. 187. − [30b] C. W. Gear, *Numerical Initial Value Problems in Ordinary Differential Equations*, Prentice Hall, Englewood Cliffs, **1971**. − [30c] A. Jones, *Recent Advances in the Analysis of Kinetic Data* in *Reaction Kinetics*, vol. 1 (Ed.: P. G. Ashmore), The Chemical Society, Specialist Periodical Report, London, **1974**, p. 291.
[31] [31a] P. R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences*, McGraw Hill, New York, **1969**, pp. 235. − [31b] W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, *Numerical Recipes*, Cambridge University Press, Cambridge, **1986**, pp. 563.
[32] [32a] Calculations involving Gear algorithms were carried out with an Amdahl V7 A mainframe of the University of Reading, England. − [32b] For further recent applications of the Gear algorithm to thermal hydrocarbon rearrangements see: H. Hopf, G. Wachholz, R. Walsh, A. de Meijere, S. Teichmann, *Chem. Ber.* **1989**, *122*, 377−382; H. Hopf, G. Wachholz, R. Walsh, *Chem. Ber.* **1992**, *125*, 711−721.
[33] Calculations concerning Marquardt algorithms were performed with a Sun workstation at the University of Reading, England.
[34] R. Walsh, *Pure Appl. Chem.* **1987**, *59*, 69−72.
[35] J. Chickos, unpublished experiments carried out in Reading.

[36] I. A. Awan, M. C. Flowers, *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 1413−1420.

[37] L. G. S. Shum, S. W. Benson, *Int. J. Chem. Kinet.* **1985**, *17*, 277−292.

[38] [38a] A. de Meijere, W. Lüttke, *Tetrahedron* **1969**, *25*, 2047−2058. − [38b] M. Trætteberg, P. Bakken, A. Almenningen, W. Lüttke, *J. Mol. Struct.* **1988**, *189*, 357−371.

[39] F. Scheidt, W. Kirmse, *J. Chem. Soc., Chem. Commun.* **1972**, 716.

[40] This is not in line with a recent conclusion by Fabian et al. that the substituent effect on the activation enthalpy of the vinylcyclopropane was about the same as that on the stabilization of the corresponding radical (see ref.[17n]).

[41] This has, in fact, been concluded from all of the most recent computational and experimental studies of the ECP-CP rearrangement, at least for the parent compound (see ref.[17i−17q]).

[42] E. Wicke, *Physikalische Chemie* (Ed.: W. Walter), Akademische Verlagsgesellschaft, Wiesbaden, **1980**, pp. 250.

[43] J. Hooz, H. Kono, *Org. Prep. Proced. Int.* **1971**, *3*, 47−50.

[44] Procedure in close analogy to the previously published one for substituted 1-chloro-1-(trimethylsilylethynyl)cyclopropanes (see ref.[22a]): F. Jaekel, Dissertation, Universität Hamburg, **1988**.

Received March 12, 2001
[O01120]