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# Gas Phase Kinetics of Pyrolysis of 1-Methyl-1-cyclopropene[1)]

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The title study has been carried out in the temperature range 210–250 °C. The isomerisation products are 2-butyne (91–94%), 1,3-butadiene (5–8%), and 1,2-butadiene (1–2%). No other products were detected and material recovery was complete within experimental error (±5%). The reaction obeyed first-order kinetics, with the products formed by parallel pathways, and appeared to be both unimolecular and homogeneous although some surface sensitivity was detected in packed vessels. Studies of pressure dependence showed characteristic rate constant "fall-off" below 20 Torr ($SF_6$) and 100 Torr ($N_2$). Within at least 2% of the high pressure limit, the following Arrhenius equation for overall decomposition was found:

$$\log(k/\mathrm{s}^{-1}) = (12.91 \pm 0.15) - (160 \pm 1.5\ \mathrm{kJ\ mol^{-1}})/RT\ln 10$$

Arrhenius equations were similarly found for the individual pathways. The figures are discussed in the light of Transition State Theory and represent a significant improvement over a previous study. It is argued that all products arise via 1,2-H shifts in a diradical-like intermediate and the propensities for different H shifts are discussed. A 1-methyl substituent, rather surprisingly, *deactivates* cyclopropene in its isomerisation reactions.

## Die Gasphasenkinetik der Pyrolyse von 1-Methyl-1-cyclopropen[1)]

Die Pyrolyse von 1-Methyl-1-cyclopropen wurde im Temperaturbereich von 210–250 °C untersucht. Als Isomerisierungsprodukte wurden 2-Butin (91–94%), 1,3-Butadien (5–8%) und 1,2-Butadien (1–2%) nachgewiesen; andere Produkte entstehen bei vollständiger Materialbilanz (±5% Abweichung vom berechneten Wert) nicht. Die Reaktion verläuft nach einem Zeitgesetz 1. Ordnung, wobei die isomeren Produkte in parallelen Reaktionswegen gebildet werden. Die Umlagerungen erfolgen unimolekular und homogen, obwohl in gepackten Reaktionsgefäßen eine gewisse Oberflächenabhängigkeit beobachtet wurde. Charakteristisches "fall-off"-Verhalten tritt in Gegenwart von $SF_6$ unterhalb von 20 Torr, in Gegenwart von $N_2$ unterhalb von 100 Torr ein. Die Gesamtreaktion läßt sich innerhalb des Hochdruckbereichs durch die folgende Arrhenius-Gleichung beschreiben:

$$\log(k/\mathrm{s}^{-1}) = (12.91 \pm 0.15) - (160 \pm 1.5\ \mathrm{kJ\ mol^{-1}})/RT\ln 10$$

Auf ähnliche Weise wurden die Arrhenius-Gleichungen der konkurrierenden Reaktionswege ermittelt. Die Resultate werden im Rahmen der Theorie des Übergangszustands diskutiert und stellen eine beträchtliche Verbesserung früherer Untersuchungen dar. Es wird vorgeschlagen, daß alle Produkte durch 1,2-Wasserstoffwanderungen aus einem diradikalischen Intermediat entstehen; die Wanderungstendenz der verschiedenen Wasserstoffatome wird

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diskutiert. Überraschenderweise *desaktiviert* ein 1-Methylsubstituent die Isomerisierungsneigung des Cyclopropensystems.

The study of small prototype strained ring organic compounds has contributed both to a theoretical understanding of unimolecular reactions[2] and a mechanistic understanding of hydrocarbon isomerisations[3]. As part of our continuing interest in cyclopropenes[4-6] we wish to report details of a study of the thermal decomposition of 1-methyl-1-cyclopropene (**1**). This compound has been investigated previously by *Srinivasan*[7,8]. In the presence of $CO_2$ diluent (50–60 Torr) he observed a homogeneous first order reaction with 2-butyne (**3**) as the major product and 1,3-butadiene (**4**) and 1,2-butadiene (**5**) as minor products. Rate constants fitted the Arrhenius equation

$$\log(k/\mathrm{s}^{-1}) = 11.4 - 145\ \mathrm{kJ\ mol}^{-1}/RT\ln 10$$

We have reinvestigated these kinetics for three reasons. First the *A* factor appears to be too low for a ring opening reaction[2,9] and in any case out of line with data on other cyclopropenes[7]. Secondly in order to understand the results of chemical activation experiments involving methylene ($CH_2$, $^1A_1$ state) addition to propyne[10] it is necessary to have a reliable knowledge of the energy barrier to isomerisation. Thirdly the mechanism of formation of minor products is not clear because of scatter in the original data[8].

## Results

### General Considerations

Because of problems encountered previously with cyclopropene itself[5], neat reactant vapour was not used in these experiments. Instead mixtures containing **1** (ca. 1.5%) and *n*-butane (ca. 2%) highly diluted in either $N_2$ or $SF_6$ were prepared. This dilution reduced the risk of dimerisation (or other polymerisation) processes and the *n*-butane served as a nonreactive internal standard to enable checks to be made of the mass balance after a reaction run. In the majority of over 60 runs, recovery of $C_4H_6$ isomers totalled 100 ± 5% of the original **1**. Thus unlike for cyclopropene[5], there was no mass loss under these conditions. The reaction was studied as a function of time, pressure, and temperature.

### Time Dependence

Runs were performed at each of five temperatures at constant initial mixture pressures of 20.5 ± 1.5 Torr ($SF_6$ mixtures) at times corresponding to between 15 and 90% decomposition of **1**. An example of the analytical results is shown in Table 1 for $T$ = 230.2°C. The observed products confirm earlier findings[8], with 2-butyne (**3**) the major, 1,3-butadiene (**4**)[11] and 1,2-butadiene (**5**) the minor products.

From the distribution of products alone it looks as if there are no trends with time[9], only normal experimental scatter. This was confirmed at other temperatures and strongly suggests all products were formed by parallel pathways. Good fits were obtained to first order plots for the consumption of **1**. The data in Table 1 gave a rate constant $k = (4.41 \pm 0.05) \times 10^{-4}\ \mathrm{s}^{-1}$ by least-mean squares fitting.

Table 1. Pyrolysis of 1-methyl-1-cyclopropene (**1**): Product variation with time[a)]

| Time/min | Total % | | | | Product % | | |
|---|---|---|---|---|---|---|---|
| | **1** | **3** | **4** | **5** | **3** | **4** | **5** |
| 10 | 77.82 | 20.20 | (1.51)[b)] | 0.37 | 91.49 | (6.83)[b)] | 1.68 |
| 20 | 58.57 | 38.10 | (2.85)[b)] | 0.49 | 91.95 | (6.87)[b)] | 1.17 |
| 30 | 45.41 | 49.89 | (3.76)[b)] | 0.94 | 91.39 | (6.89)[b)] | 1.72 |
| 45 | 29.04 | 65.21 | 4.72 | 1.03 | 91.89 | 6.66 | 1.45 |
| 60 | 20.04 | 73.62 | 5.31 | 1.04 | 92.07 | 6.64 | 1.30 |
| 90 | 9.42 | 82.71 | 6.21 | 1.67 | 91.31 | 6.85 | 1.84 |

[a)] Temp. 230.2 °C; initial pressure ≃20.5 Torr (1.4% **1** in $SF_6$). — [b)] These are empirically corrected for small chromatographic peak overlap.

Thus overall rate constant can be divided amongst the products to obtain individual rate constants as follows: $CH_3C{\equiv}CCH_3$, 91.96%, $k_1 = 4.05 \times 10^{-4}\ s^{-1}$; $CH_2{=}CH{-}CH{=}CH_2$, 6.79%, $k_2 = 3.00 \times 10^{-5}\ s^{-1}$; $CH_3CH{=}C{=}CH_2$, 1.53%, $k_3 = 6.75 \times 10^{-6}\ s^{-1}$.

**Pressure Dependence**

Small molecules show characteristic pressure dependences of their first order rate constants[2)]. Since a principal aim of this study was to obtain the limiting high pressure Arrhenius parameters, it was important to verify that the chosen pressure was sufficient to achieve this end. A series of runs was carried out at 239.2 °C, both with $SF_6$ and $N_2$ diluted reactant mixtures, in which initial pressures were varied from 4 to 250 Torr. Run times were kept fixed at 30 minutes, and overall rate constants calculated assuming first order behaviour. Table 2 shows the values obtained. The data in both $N_2$ and $SF_6$ at the highest pressures suggest the limiting value, $k_\infty \simeq 4.5 \times 10^{-4}\ s^{-1}$ and that "fall-off" is indicated at the lowest pressures in both diluent gases. As expected, "fall-off" is more marked for the weaker collider gas $N_2$, than for the stronger one, $SF_6$. Pressures greater than ca. 100 Torr $N_2$ or ca. 20 Torr $SF_6$ would appear sufficient to be at least within 2% of the high pressure limit (and probably closer). A more detailed investigation of the fall-off phenomenon (i.e. lower pressure studies) was not deemed worthwhile. It was noted, however, that the minor products decreased as a proportion of the total as the pressure decreased ($N_2$ diluent). This is in qualitative accord with findings in other unimolecular systems with competitive reaction channels[12)].

Table 2. Rate constant variation with pressure[a)]

| Initial pressure[b)] | $10^4\ k/s^{-1}$ | Initial pressure[c)] | $10^4\ k/s^{-1}$ |
|---|---|---|---|
| 250.3 | 4.52 | 77.0 | 4.46 |
| 135.2 | 4.48 | 30.7 | 4.43 |
| 36.9 | 4.33 | 22.0 | 4.39 |
| 11.4 | 3.87 | 12.0 | 4.37 |
| 5.2 | 3.69 | 4.2 | 3.80 |

[a)] Temp. = 239 °C; run time = 30 minutes. — [b)] Mixture 1.1% **1** in $N_2$. — [c)] Mixture ca. 2.4% **1** in $SF_6$.

## Temperature Dependence

First order rate constants were obtained for all products at each temperature of the study as described above. The data are shown in Table 3. The data for each pathway were fitted to the Arrhenius equation yielding the parameters shown in Table 4. Uncertainties are

Table 3. Rate constant variation with temperature[a)]

| Temperature/°C | $10^4 k/s^{-1}$ [b)] | $10^4 k_1/s^{-1}$ [b)] | $10^5 k_2/s^{-1}$ [c)] | $10^6 k_3/s^{-1}$ [d)] |
|---|---|---|---|---|
| 210.0 | 0.470 ± .012 | 0.440 ± .011 | 0.247 ± .025 | 0.48 ± .12 |
| 219.9 | 0.996 ± .012 | 0.926 ± .011 | 0.576 ± .058 | 1.2 ± .3 |
| 230.1 | 2.21 ± .04 | 2.05 ± .04 | 1.30 ± 0.13 | 2.5 ± .6 |
| 239.2 | 4.41 ± .05 | 4.05 ± .05 | 3.00 ± 0.30 | 6.8 ± 1.7 |
| 250.1 | 9.75 ± .14 | 8.88 ± .13 | 7.11 ± 0.71 | 16 ± .4 |

[a)] Initial pressure = 20.5 Torr ($SF_6$ mixture). — [b)] Errors based on the standard deviation of the slopes of linear fits to first order plots. — [c)] Errors based on assessment of overall scatter of **4** yields at ±10%. — [d)] Errors based on assessment of overall scatter of **5** yields at ±25%.

Table 4. Arrhenius parameters for the decomposition of **1**

| Product | $\log (A/s^{-1})$ | $E_a$/kJ mol$^{-1}$ (kcal mol$^{-1}$) |
|---|---|---|
| Overall | 12.91 ± 0.15 | 160 ± 1.5 (38.1 ± 0.4) |
| $CH_3-C{\equiv}C-CH_3$ (**3**) | 12.72 ± 0.15 | 158 ± 1.5 (37.8 ± 0.37 |
| $CH_2{=}CH-CH{=}CH_2$ (**4**) | 13.48 ± 0.31 | 177 ± 3 (42.2 ± 0.7) |
| $CH_2{=}C{=}CHCH_3$ (**5**) | 13.49 ± 0.66 | 183 ± 6 (43.8 ± 1.5) |

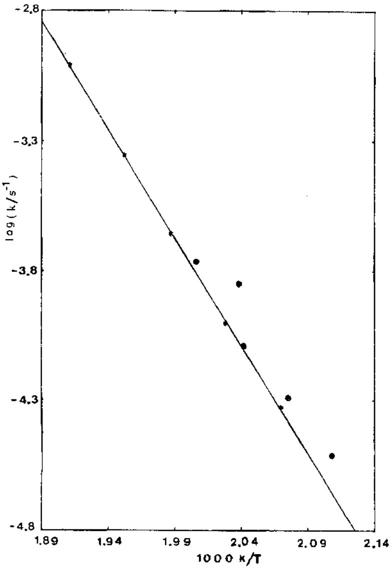


Figure 1. Arrhenius plot for the decomposition of **1**. *, experimental data this work; — least squares fit; ⊕, experimental data ref.[8)]

inevitably greater for the parameters associated with the minor products but in spite of this the fit to these data is reasonably good. The data for the overall reaction are shown in a plot in Figure 1 which demonstrates a reasonable fit. *Srinivasan*'s data[8] are also shown. Although the best line through his data is different from that through ours, the individual rate constants are in fairly close agreement.

### Further Tests

Test for both homogeneity and radical chain processes were carried out. The former involved rate measurements in packed vessels, whilst the latter consisted of a run in the presence of a large excess of olefin inhibitor (propene). The results for the packed vessels are shown in Table 5.

Table 5. Further checks on rate data at 220°C

| Pressure/Torr | $10^4 k/s^{-1}$ | Vessel |
|---|---|---|
| 19.7 | $0.996 \pm .012$ | Normal vessel (S/V = 0.71 $cm^{-1}$)[b] |
| 17.8 | $1.32 \pm .07$[a] | Packed vessel (S/V = 13.3 $cm^{-1}$) |
| 17.9 | $1.48 \pm .13$[a] | Packed vessel, HMDS treated |
| 19.8 | $1.28 \pm .23$[a] | Partially packed vessel (S/V = 4.9 $cm^{-1}$)<br>HMDS treated |

[a] Rate constants based on runs at 3 different times. — [b] S/V = surface to volume ratio.

As can be seen, the evidence on heterogeneity is not unequivocal. Runs were carried out in a packed vessel (untreated), a packed vessel treated with hexamethyldisilazane (HMDS), and a partially packed vessel (also HMDS treated). The data produced considerable scatter on the first order plots and the rate constants are all higher than in the normal vessel with a qualitative trend with S/V (all vessels were conditioned by long time pre-pyrolysis with **1**). Another feature of these runs was the higher than normal proportion of **4** (21 ± 6%) in the product. This suggests a surface component to the reaction producing mainly **4** in the packed vessels. Whether or not there is a surface component in the unpacked vessels remains unclear but in view of consistent product distribution and good fits to the first order plots we are inclined to doubt it. In any case in the packed vessel runs the enhancement of the major product (**3**) forming pathway is quite small (<10%). A run with an 11-fold excess of propene over **1**, at a total pressure of 21 Torr and temperature of 239.2°C gave a rate constant of $4.42 \times 10^{-4} s^{-1}$, which is identical with the run (Table 3) without added propene. Moreover, the product distribution was also similar to that without propene. This suggests that there is almost certainly no radical component to the reaction.

## Discussion

### Kinetic Aspects of the Overall Process

The results obtained in this work strongly support previous conclusions[7,8] that the isomerisation of **1** is a unimolecular reaction. The data obtained, however, represent a considerable improvement over those of *Srinivasan*[8]. We have checked that the Arrhenius parameters correspond to rate constants *at* or *close to* the high pressure limit. We have verified that no unobserved side reactions leading to mass imbalance are occurring (in contrast to cyclopropene itself[5]). The overall $A$ factor of $10^{12.91}$ $s^{-1}$ is both higher, and much more reasonable in magnitude than *Srinivasan*'s value[8] of $10^{11.4}$ $s^{-1}$. In terms of a comparison with the Transition State Theory expression[13] of $e\ kT/h\ e^{\Delta S^{+}/R}$, the activation entropy (500 K) corresponding to our data has a value of $-10$ $JK^{-1}$ $mol^{-1}$. A negative value is somewhat unusual for a ring opening process, however, as we have pointed out previously[5], the major pathway (i.e. 2-butyne formation, in this case) releases very little entropy *overall* and so a large positive value for $\Delta S^{+}$ is not expected. A comparison of **1** with cyclopropene shown in Table 6 shows that $A$ factors, entropies of activation, and activation energies are quite similar. Relative rates disfavour **1** by about a factor of four, but part of this is a path degeneracy difference of two (reflected in the $A$ factor and $\Delta S^{+}$). The remaining factor of 2 must be due to the deactivating effect of methyl substitution. This stands in contrast to isomerisations in the cyclopropane family where methyl substitution accelerates decomposition. The Arrhenius parameters shown in Table 6 also form a more consistent set with other, more highly methylated cyclopropenes (see ref.[7], Chart 1). While this adds confidence to the results, suggesting no great errors, it is still possible, in view of the negative activation entropy, that these parameters are slightly too low. Some support for the individual Arrhenius parameters contained in Table 4 comes from chemical activation experiments[10] in which **1** is prepared via $CH_2(^1A_1)$ addition to propyne with an internal vibrational energy of ca. 330 kJ $mol^{-1}$. In these experiments relative yields of isomerisation products are 2-butyne ca. 30%, 1,3-butadiene ca. 30%, 1,2-butadiene ca. 40%. The large increase in proportion of the minor thermal isomers at these high energies suggests they are produced by pathways of higher entropy (i.e. looser transition states) as the experimental $A$ factors indicate.

Table 6. Comparison of high pressure rate constants for thermal cyclopropene isomerisations

| Reactant | $\log A/s^{-1}$ | $\Delta S/JK^{-1}\ mol^{-1}$ [a] | $E_a/kJ\ mol^{-1}$ ($kcal\ mol^{-1}$) | $10^4k/s^{-1}$ [a] | Ref. |
|---|---|---|---|---|---|
| Cyclopropene[b] | 13.25 | $-3.9$ | 157<br>(37.5) | 7.41 | [5] |
| 1-Methyl-1-cyclopropene (**1**) | 12.91 | $-10.3$ | 160<br>(38.1) | 1.75 | This work |

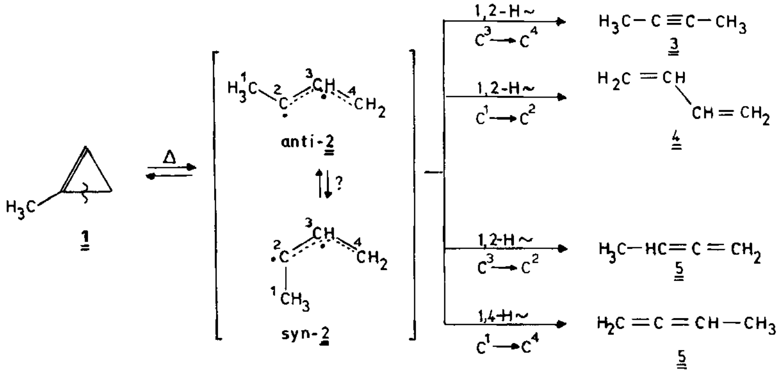
[a] Temp. 500 K. — [b] The parameter for cyclopropene have been adjusted to allow for unimolecular fall-off.

The magnitude of the activation barrier throws no further light on the state of the intermediates involved. It appears probable[5,7] that the key intermediate is a state of either the diradical, $CH_3\dot{C}=CH-\dot{C}H_2$, or methyl vinyl carbene, $CH_3\ddot{C}CH=CH_2$. It is possible that more than one state is involved[7]. Theoretical calculations[7] all set a $^3\sigma p$ planar carbene ($^3A''$) as the lowest state of the non-methylated intermediate, but unless double intersystem crossing occurs, this state is unlikely to be involved in the *thermal* rearrangements of cyclopropene. Singlet states of both intermediate species lie higher in energy than the $^3A''$ and theoretical calculations[7] of the energy for cyclopropene ring opening (not the rate-determining step in the overall isomerisation process) produces values (178 – 289 kJ mol$^{-1}$) well in excess of the isomerisation activation energies measured here and previously[5]. Theoretical calculations thus need further refinement before they can provide a reliable guide to the mechanism of cyclopropene rearrangement. A thermochemical estimate[5], however, places the intermediate species only 128 kJ mol$^{-1}$ above the energy of cyclopropene, provided it is allylically stabilised (i.e. the true species is regarded as a resonance hybrid of diradical and carbene structures). Thus this satisfies the energy criterion but appears to conflict with theoretical descriptions of the states involved.

## H Shifts and Further Mechanistic Aspects of Product Formation

Scheme 1 shows the four possible 1,2- and 1,4-H shifts which can lead to products from the likely ring opened intermediate (*syn*- or *anti*-**2**). From the distribution of products, the $C^3 \rightarrow C^4$ 1,2-H shift is the most favoured process, followed by the $C^1 \rightarrow C^2$ 1,2-H shift.

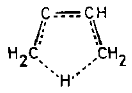
Scheme 1. Pyrolysis of 1-methyl-1-cyclopropene (**1**): Mechanism



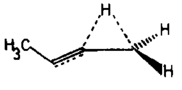
Two possibilities exist for 1,2-butadiene (**5**) formation, the $C^3 \rightarrow C^2$ 1,2-H shift and the $C^1 \rightarrow C^4$ 1,4-H shift. We favour the former process for two reasons. Firstly, the $A$ factor is larger than that for the principal 1,2-H shift whereas the transition state requirement for a 1,4-H shift is the 5-membered ring structure **6**, which should have a tighter structure and therefore lower $A$ factor. Secondly, the activation energy (Table 4) associated with this pathway is very comparable to that for allene formation (181 kJ mol$^{-1}$) from cyclopropene, which *can only* occur via a 1,2-H shift.

Since all products are therefore likely to arise via 1,2-H shifts, the $A$ factors should be fairly similar. 1,3-Butadiene formation has a path degeneracy of three compared with 2-butyne formation and the $A$ factors reflect this difference. If path degeneracy factors were the main difference, the $A$ factor for 1,2-butadiene formation would be the same as that for 2-butyne. This is not exactly the case but the uncertainties in the figure are large.

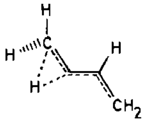
Transition state structures provide a possible clue to the migratory aptitudes of these hydrogen atoms, as shown below.



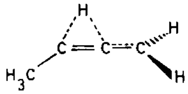
**6**



**7**



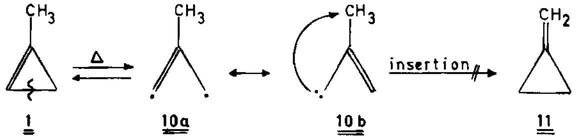
**8**



**9**

In the respective structures **7**–**9** the migrating H-atoms span C–C single, $C\overset{\cdots}{-}C$ one and a half and C=C double bonds, respectively. This corresponds to the order of increasing strain and therefore correlates with the increasing difficulty of forming the transition state. This is an extension of an idea previously proposed[5] for cyclopropene alone.

The alternative ring opening pathway available to **1** does not lead to any observed product. This suggests that compared with the observed processes intramolecular C–H insertion via the carbene form of the intermediate (**10b**) competes unfavourably.



This indicates that, as methylenecyclopropane (**11**) is not formed, either the intermediate **10** (which probably *is* formed) does not behave like a carbene or, despite the generally high reactivity of carbenes a 1,3-CH insertion is not a particularly favoured process.

We thank the *Fonds der Chemischen Industrie* and the *Riedel-de Haën AG* for financial support of this work.

## Experimental Part

*Apparatus for Kinetic Measurements:* This consisted of a conventional grease-free static system constructed of Pyrex with rotaflo (Quickfit) stopcocks. The reaction vessel used for most experiments was spherical (volume, ca. 310 ml) and was placed in a stirred salt thermostat[14] controlled by a GEC RT5 controller. Other vessels, packed with Pyrex tubes, were used in experiments to test for surface effects. Temperatures were measured with a calibrated Pt/Pt-13% Rh thermocouple. Product analyses were made by gas chromatography (Perkin Elmer F 11) with FID detection and electronic peak integration (Hewlett Packard, HP 3380). Pressures were measured with a conventional Hg manometer.

*Experimental Procedure:* The reaction was studied using *n*-butane as an internal standard. 450-ml reservoirs containing ca. 1–2% of **1** and 2–3% of *n*-butane diluted in either $SF_6$ or $N_2$ to a pressure of ca. 1 atm, were made up and premixed to serve as the reactant mixture. Runs were carried out by admitting a known pressure of this mixture to the reaction vessel for a known time (between 10 min and 10 hours according to temperature and desired conversion). The reaction was quenched by sharing the reaction vessel contents with a preevacuated sample bulb, from which smaller samples could be taken and injected into the chromatograph. Every run was accompanied by a blank analysis of unused reaction mixture, in order to check the ratio [1]/[*n*-butane] prior to any run (for the mass balance check). Also checked was the proportion of impurity methylenecyclopropane (**11**) (see below) to verify that it was unaffected under reaction conditions and there was no interference with the reaction under study.

*Analysis:* Chromatographic analyses were carried out routinely on a 5-m × 3-mm diameter β,β′-oxydipropiononitrile-bonded Porasil C column (Waters Associates) operated at 30°C with nitrogen carrier gas (20 p.s.i.). Part way through the analysis the temperature was raised to 70°C to facilitate more rapid elution of the late peak (2-butyne). Typical retention times were: *n*-butane, 8 min; **1**, 12.5 min; methylenecyclopropane, 15 min; 1,3-butadiene, 17 min; 1,2-butadiene, 19.5 min; Temp. → 70°C at 24 min: 2-butyne, 40 min. Product identities were confirmed by retention time comparison with authentic samples. A check was made to verify that the detector response to 2-butyne was identical (within ±3%) to that for **1** under analytical conditions. It was assumed that the other $C_4H_6$ isomers had the same response factors.

*Materials: 1-Methyl-1-cyclopropene* (**1**) was prepared by the reaction of sodium amide with 3-chloro-2-methyl-1-propene according to established literature procedures[15]. Good yields (40%) were obtained provided freshly prepared $NaNH_2$ was used. **1** was purified by low pressure distillation and characterised by $^1H$ NMR ($\delta$ = 0.84 (d, 2H); 2.15 (d, 3H) and 6.41 (m, 1H)). The NMR revealed a small impurity of methylenecyclopropane (**11**), which was found to be 15% by GC. Since this interfered with neither reaction nor analysis, further purification of **1** was not deemed wortwhile. To avoid polymerisation the neat sample was stored at −196°C (liq. $N_2$). When made up into dilute mixtures (as described above) which contained partial pressures of **1** up to ca. 10 Torr, it remained stable indefinitely (several months) at room temperature.

*n-Butane* and *sulphur hexafluoride* (Matheson Instrument Grade), both ≥ 99% pure, were degassed before use.

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1) Thermal Rearrangements, part XIV. Part XIII: *H. Hopf, D. Gottschild* and *W. Lenk*, Israel J. Chem., in press.

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9) This was similarly the case for cyclopropene itself[8] prior to our earlier investigations[5].

10) *M. J. Ellis* and *R. Walsh*, unpublished studies.

11) Analyses for 1,3-butadiene are a little unreliable at low conversions (< 30%), due to small impurity peak overlap.

12) For example, *I. M. Bailey* and *H. M. Frey*, J. Chem. Soc., Faraday Trans. 1 77, 709 (1981).

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