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[14] IR peak of the reaction solution: $\tilde{\nu}_{CN} = 2229\ cm^{-1}$.

[15] Selected IR spectroscopic and MS data of **6**, **8**, **9**; **6**: MS (EI, 70 eV, ^{184}W): *m/z* 696 [M^+]; **8**: IR (KBr, $\nu_{C=O}$ region): $\tilde{\nu}$ = 2070.5 m, 1947.4 vs, 1921.6 s cm^{-1}; MS (EI, 70 eV, ^{184}W): *m/z* 696 [M^+]; *9*: IR (KBr, $\nu_{C=O}$ region): $\tilde{\nu}$ = 2073.8 m, 1988.0 w, 1953.7 vs, 1904.9 s cm^{-1} and $\tilde{\nu}$ = 1625.6 m ($\nu_{C=C}$); **9**: MS (EI, 70 eV, ^{184}W); *m/z* = 634 [M^+]; correct C,H elemental analyses for **6**, **8**, **9**.

[16] Crystal structure analysis of **8**: $C_{25}H_{29}O_6PSi_2W$, monoclinic, space group $P2_1/c$, $a = 1135.9(4)$, $b = 1174.4(3)$, $c = 2107.9(4)$ pm, $\beta = 100.87(2)^\circ$, $V = 2.7615(12)\ nm^3$, $Z = 4$, $\rho_{calcd} = 1.675\ Mg\,m^{-3}$, $\lambda = 0.71073$ pm, $T = 173$ K. The crystal ($0.44 \times 0.44 \times 0.38$ mm) was mounted in perfluoropolyether oil at $-100\,^\circ C$ on a Siemens P4 diffractometer. Intensities were collected by ω scans in the 2θ range 5–60°. Of 8860 reflections, 8026 were independent ($R_{int} = 0.0169$). After a semiempirical absorption correction (ψ scans) the structure was solved with the heavy atom method and refined with full-matrix least-squares methods against F^2 (SHELXL-93, G. M. Sheldrick, Universität Göttingen). Hydrogen positions were included by using a riding model or rigid methyl groups. Final $wR2 = 0.0692$ based on F^2 for all data, conventional $R(F)$ ($R1$) = 0.0309. 322 parameters and 165 restraints; max. Δp 1229 $e\,nm^{-3}$ [25].

[17] Crystal structure analysis of **9**: $C_{20}H_{27}O_6PSi_2W$, monoclinic, space group $P2_1/n$: $a = 1088.3(2)$, $b = 1264.4(2)$, $c = 1928.5(2)$ pm, $\beta = 102.807(8)^\circ$, $V = 2.5878(7)\ nm^3$, $Z = 4$, $\rho_{calcd} = 1.628\ Mg\,m^{-3}$, $\lambda = 0.71073$ pm, $T = 173$ K. Details as for ref. [16], except: crystal dimensions $0.64 \times 0.48 \times 0.32$ mm, 2θ range 6–50 , 7188 reflections, 4540 independent ($R_{int} = 0.0200$). The structure was solved with direct methods and refined as in ref. [16]. The hydrogen atom at phosphorus was refined freely. $wR2 = 0.0458$, $R1 = 0.0235$, 281 parameters and 9 restraints; max. Δp 1074 $e\,nm^{-3}$.

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[19] [$PhPW(CO)_5$] reacts with benzophenone in a sequence of intermolecular reactions, finally forming a six-membered ring compound: Y. Inubushi, N. H. Tran Huy, L. Ricard. F. Mathey, *J. Organomet. Chem.* in press.

[20] [$PhPW(CO)_5$] reacts with αC–H acidic ketones at 120 °C, forming comparable insertion products. The authors discuss a [2 + 1] cycloaddition of the C–C double bond of the enol to the phosphanediyl complex, followed by a ring-opening rearrangement: Y. Inubushi, N. H. Tran Huy, F. Mathey, *Chem. Commun.* **1996**, 1903.

[21] The by-product ($\delta^{31}P = -15.4$) could not be completely separated from compound **12** by chromatography or by crystallization. However, since this had no influence on the elemental analysis of **12**, the by-product could be a stereoisomer of **12**.

[22] Selected MS data of **12**: MS (EI, 70 eV, ^{184}W): *m/z* 633 [M^+]; correct C, H elemental analysis; see comment in ref. [21].

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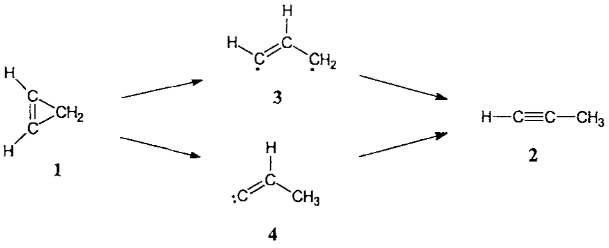
[25] Crystal structure analysis of **12**: $C_{20}H_{28}NO_5PSi_2W$, triclinic, space group $P\bar{1}$, $a = 929.81(12)$, $b = 984.9(2)$, $c = 1563.8(2)$ pm, $\alpha = 72.454(10)$, $\beta = 75.738(8)$, $\gamma = 76.715(10)^\circ$, $V = 1.3046(3)\ nm^3$, $Z = 2$, $\rho_{calcd} = 1.613\ Mg\,m^{-3}$, $\lambda = 0.71073$ pm, $T = 173$ K. Details as in ref. [16]: crystal dimensions $0.68 \times 0.56 \times 0.42$ mm, 2θ range 6–50°, 4826 reflections, 4538 independent ($R_{int} = 0.0120$), structure solution as in ref. [17], refinement as in ref. [16]. The hydrogen atom H6 bonded to C6 was refined freely. $wR2 = 0.0626$, $R1 = 0.0249$, 283 parameters; max. Δp 1265 $e\,nm^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-141. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

Direct Study of a Nondegenerate Cyclopropene-to-Cyclopropene Isomerization[**]

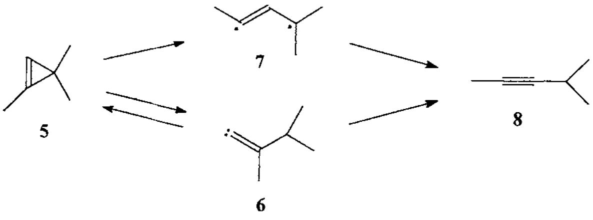
Henning Hopf,* Wilhelm Graf von der Schulenburg, and Robin Walsh*

Until 1989 the mechanism of the thermal isomerization of cyclopropene (**1**) to propyne (**2**) was thought to proceed via the propene-1,3-diyl (**3**) intermediate formed by ring opening of **1**. A subsequent 2,3 hydrogen-shift results in **2**.[1] In that year, Yoshimine et al.[2] proposed a different mechanism on the basis of ab initio calculations at the SDQCI(DZP) and MRCI*(DZP) levels. They suggested a propenylidene (**4**) intermediate, which is formed by ring opening with a synchronous 1,3 H-transfer. This is then followed by a 2,1 H-shift.



At that time, existing experimental studies were unable to distinguish between these alternatives. However, in 1992 Walsh et al.[3] found that alkyne formation was 18 times slower for 1,3,3-trimethylcyclopropene (**5**) than for 3,3-dimethylcyclopropene. They argued that this is due to the 2-methyl-2-isopropylvinylidene intermediate (**6**, formed from **5**), which is an analogue of **4** (formed from **1**).

The reason why **6**, rather than *trans*-4-methylpent-2-ene-2,4-diyl (**7**), can lead to a rate reduction is provided by the second step of the isomerization (**6** → **8**), which involves an alkyl (methyl or isopropyl) rather than an H-shift. The expected lower rate of the alkyl shift makes the second step rate-determining.[3] This slows the overall reaction and implies reversibility of the first step (**5** → **6**). We have recently confirmed[4] the generality of the mechanism of alkyne formation from cyclopropene via a



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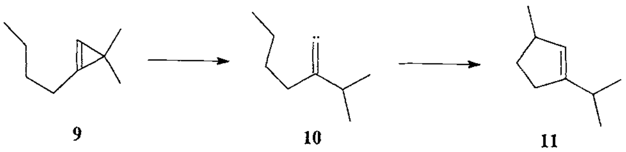
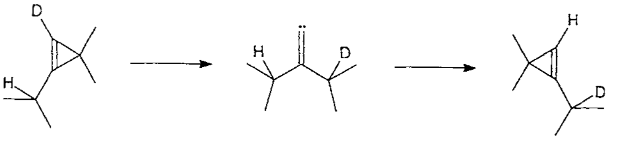
vinylidene intermediate by the intramolecular trapping of the alkyl vinylidene **10**, which is formed in the conversion of cyclopropene **9** into cyclopentene **11**.



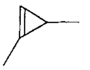
9 **10** **11**

Likhotvorik et al.[5] have found evidence for a vinylidene intermediate in an elegant deuterium-scrambling experiment. Although the product yields are very low (0.5% of **14** for 90% conversion of **12**), this result offers direct confirmation of the reversibility of cyclopropene ring opening. We have found further suggestive evidence for this process in a pyrolytic kinetic study of a series of 1-alkyl-3,3-dimethylcyclopropenes.[6] In this case, the probable isomeric cyclopropenes were formed in only 2–3% yields and were unstable under pyrolytic conditions.



12 **13** **14**

To provide more concrete evidence for the reversibility of the initial ring-opening step, we looked for a derivative of 1-alkylcyclopropene for which higher yields of an alternative, isomeric cyclopropene are formed during decomposition. 1,3-Dimethylcyclopropene (**15**) and 1-ethylcyclopropene (**16**) have been prepared by published procedures,[7, 8] and the kinetics of their pyrolyses investigated.



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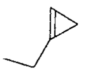


16

To avoid losses by oligomerization, both compounds were stored at low temperatures (– 26 °C) until shortly prior to the kinetic investigations. Gas phase kinetic studies were carried out in a pyrex vessel immersed in a stirred molten salt thermostat (static method). The temperature was controlled to ±0.1 K. The gaseous mixtures investigated contained 2.0±0.2% each of reactant (**15** or **16**) and pentane (internal standard) diluted in nitrogen. Six to eight runs were carried out at a total pressure of 50 Torr of reactant mixture for times that provided between 10 and 90% conversions at each of five temperatures (**15**: 482–522 K, **16**: 472–512 K). Products were quantitatively analyzed by GC (FID detector, electronic signal integration) on a packed β,β-oxydipropionitrile (ODPN) column at 40 °C. This resulted in a full separation of the products. Two examples of the chromatograms are shown in Figure 1. Pent-2-yne (**17**), (*E*)-penta-1,3-diene (**18**), (*Z*)-penta-1,3-diene (**19**), penta-2,3-diene (**20**), and penta-1,2-diene (**21**) were identified by NMR spectroscopy, and their column retention times compared with authentic samples. The C_5H_8 isomers were completely recovered (100±2% relative to *n*-pentane added). Figure 2 shows the time evolution curve for the decompositions of **16**; a similar graph was obtained for the pyrolysis of the isomer **15**.

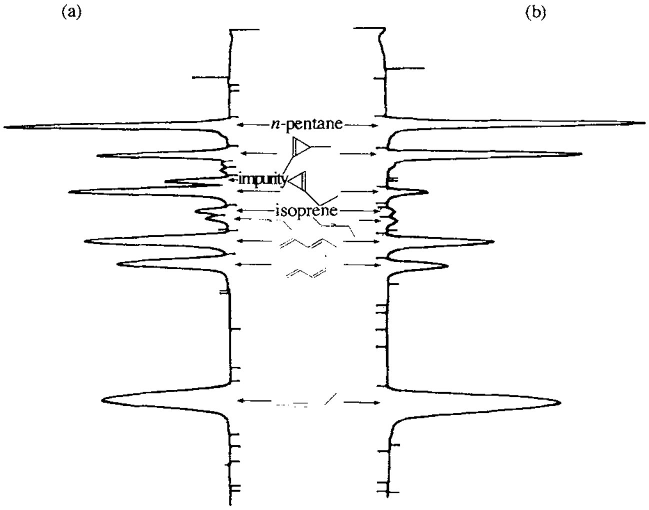


Figure 1. Gas chromatograms of cyclopropene pyrolysis product mixtures (ODPN column, 40°C): a) pyrolysis products of **16**, 198.7 °C, 600 min; b) pyrolysis products of **15**, 208.4 °C, 480 min.

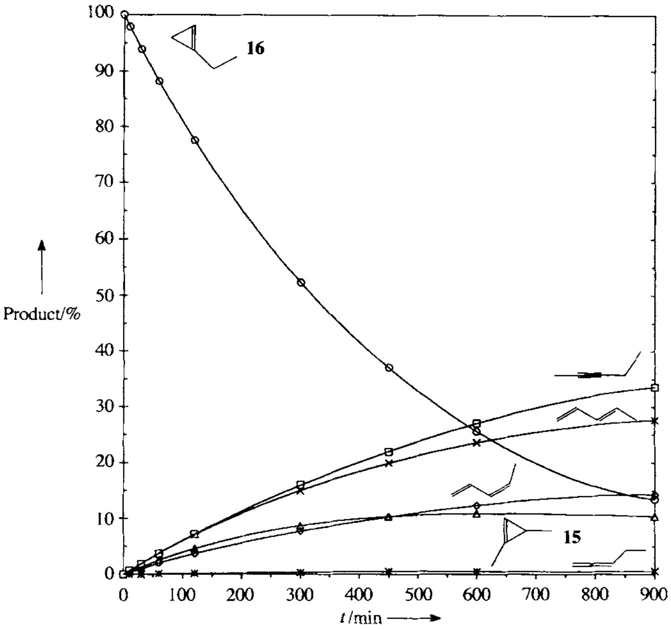


Figure 2. Product time evolution curves for the decomposition of **16** at 198.7 °C.

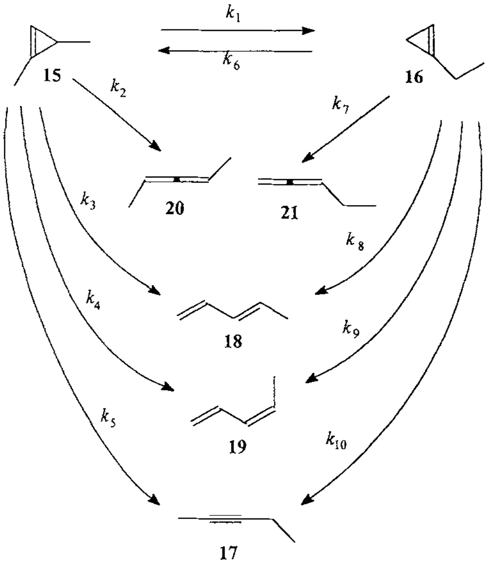
The chromatograms clearly show formation of **16** from **15** and vice versa. The product evolution curves indicate that each isomer has intermediate character when formed from the other. This is clearly seen in Figure 2 where yields of **15** formed from **16** approach 10% of the total mixture (at their maximum). Yields of **16** formed from **15** only reach about 1.1%, but a maximum is nevertheless also clearly visible. The formation of isomeric cyclopropenes and interconversion of **15** and **16** is unambiguously demonstrated by these data.

Rate constants for reactant disappearance were first obtained by a simplified procedure, which neglected reversibility and treated the reaction as first-order. This provided reasonably linear logarithm (% reactant) versus time plots. The temperature dependencies of the obtained rate constants gave the Arrhenius parameters shown in Table 1.

Subsequently, a more complex analysis with the Gear algorithm was undertaken to correlate the time evolution curves with the mechanism shown in Scheme 1. The rate constants were refined for an optimal fit to the analytical data at each temperature. Arrhenius parameters were obtained for all products, but, for reasons of space, only those for the direct transformation

Table 1. Arrhenius parameters for the overall decomposition and selected pathways of 1,3-dimethylcyclopropene (**15**) and 1-ethylcyclopropene (**16**).

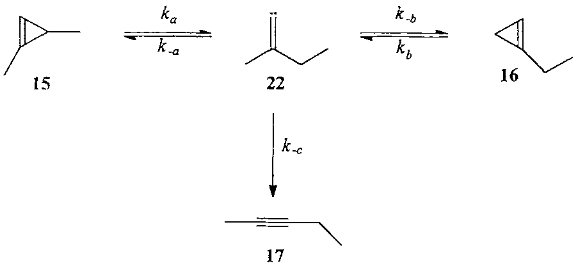
Reaction	lg (A/s^{-1})	E_a/kJ mol^{-1}
 overall decomp.	13.36 ± 0.08	164.0 ± 0.8
	12.29 ± 0.07	166.2 ± 0.6
 overall decomp.	13.36 ± 0.09	160.7 ± 0.9
	12.26 ± 0.06	156.9 ± 0.5
	13.27 ± 0.04	161.6 ± 0.4
	12.85 ± 0.05	158.6 ± 0.5



Scheme 1. Mechanism of the thermal isomerization of **15** and **16**.

15 → **16** are shown in Table 1. Variation of total pressure, alteration of reaction vessel surface-to-volume ratio, and addition of radical inhibitors show that these reactions are truly homogeneous and unimolecular at their high pressure limits.

Apart from providing dramatic support for the importance of vinylidene intermediates in the cyclopropene decomposition process, these results permit a deeper analysis. Scheme 2 shows the mechanistic pathways involving ethylmethylvinylidene (**22**). The elementary constants presented are related to the experimental rate constants[9] and can be analyzed to provide, firstly, the rate constants for the actual ring-opening steps (a) and (b) and, secondly, the relative rate constants for the ring-closing steps (− a) and (− b) as well as the alkyl migration step (− c) for **22**. Arrhenius parameters for (a) and (b) are given in Table 1.



Scheme 2. Ethylmethylvinylidene (**22**) as an intermediate in the **15** → **16** interconversion.

This analysis shows that ring opening of both **15** and **16** via **22** occurs nearly twice as rapidly as formation of pent-2-yne (**17**). Thus $k_a/k_5 = k_b/k_{10} = 1.712 \pm 0.015$ (values only very slightly temperature-dependent). This helps explain why alkyne formation from 1-alkyl-substituted cyclopropenes is so much slower than for cyclopropenes without 1- or 2- substitution.[3, 6] Furthermore, the relative values of k_{-a}:k_{-b}:k_{-c} are 0.380:0.035:0.585 (almost independent of temperature). Somewhat contrary to our expectations, this result shows that the alkyl migration step (methyl or ethyl) is the most favored for **22**. It also indicates that of the two other steps, by which the vinylidene reverts to cyclopropenes (formally 1,3 H-insertion processes), formation of **15** is favored over that of **16** by a factor of about 11. This outcome is understandable, since it indicates the reasonable preference for secondary over primary C–H insertion. Despite the preference of **22** for alkyl group migration (− c), this study shows that this step must be relatively slow (as proposed[3]). Furthermore, it must have a significant energy barrier to rearrangement, since it is competitive with the C–H insertion processes (− a) and (− b). Yoshimine et al.[2] have calculated that the energy of methylvinylidene (**4**) is approximately 86 kJ mol^{-1} lower than the transition state for rearrangement of cyclopropene **1** → **2**. This value corresponds to the energy barrier for C–H insertion; a thermochemical estimate is about 50 kJ mol^{-1}.[10] Thus, the alkyl migration barrier must be of comparable energy for step (− c) to be competitive. This contrasts with the almost zero energy barrier calculated for the migration of an H atom for **4** → **2** (and for the parent vinylidene[11]).

These findings open the way for obtaining considerable information on the behavior of vinylidenes. These species are of importance in high-temperature pyrolytic processes of unsaturated hydrocarbons,[12–14] including the oligomerization of acetylene leading to polyaromatics.[15] Complete details of these results and a thorough discussion will appear in a full paper.

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