Alkyl Migration Aptitudes in the Vinylidene–Acetylene Rearrangement and Isotope Effect in the Vinylidene Formation Process from a Deuterium-Labeled Cyclopropene**

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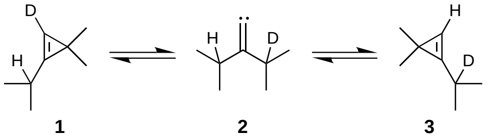
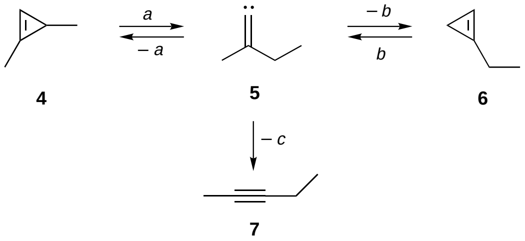
In memory of Wolfgang Roth

Investigation of vinylidenes and their rearrangement mechanisms are difficult because good sources of these highly reactive species do not exist. They are known to be involved in the high temperature thermal rearrangements of acetylenes,[1, 2] but the very high temperature required (about 600 °C) make acetylenes an unsuitable source. We and others[3–8] have recently shown the involvement of vinylidenes as crucial intermediates in the thermal isomerization of cyclopropene to acetylene under mild conditions. A key experimental study was that of Jones and colleagues[5] who provided evidence for the vinylidene carbene hypothesis by means of an elegant deuterium scrambling experiment.

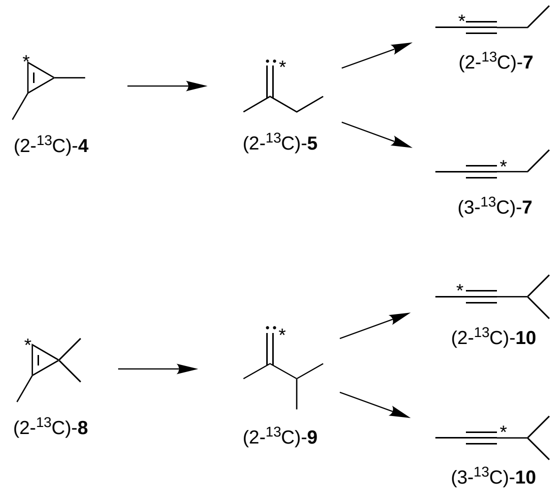
This experiment offered direct confirmation of the proposed reversibility[4] of the cyclopropene ring-opening process, although product yields were low (0.5 % of **3** at 90 % conversion of **1**). We have also found similar evidence by means of a kinetic study of a nondegenerate cyclopropene–cyclopropene isomerization,[8] namely the interconversion of 1,3-dimethylcyclopropene **4** and 1-ethylcyclopropene **6**, via 1-ethyl-1-methylvinylidene **5** (Scheme 1). Kinetic modeling of the analytical results of this study[8] enabled us to obtain, for the first time, a quantitative measure of the relative propensities of vinylidene **5** to form stable products by C–H insertion (to form cyclopropenes **4** and **6**), and alkyl migration (to produce 2-pentyne (**7**)). However **7** can be formed from **5** by either methyl or ethyl migration and what is not known from our earlier study, or indeed any other source, is which route is preferred, and to what extent. With our proven capability to generate specific vinylidenes from cyclopropenes, we have now carried out experiments to resolve the question of relative migratory aptitudes of alkyl groups in vinylidenes and we report the results here. Additionally we describe a deuterium scrambling experiment, which allows us to extract the kinetic isotope effect for the true cyclopropene ring-opening process that leads to a vinylidene.





Scheme 1. Thermal generation of 1-ethyl-1-methylvinylidene **5** from cyclopropenes **4** and **6**.

To address the first question we have prepared specifically ^{13}C-labeled cyclopropenes **4** and **8**, which are expected to yield mixtures of two differently ^{13}C-labeled 2-pentyne products **7** and two differently labeled ^{13}C-labeled 4-methyl-2-pentyne products **10**, respectively, on pyrolysis. Compounds (2-^{13}C)-**4** and (2-^{13}C)-**8** were prepared in two steps by adapting published labeling procedures[9–11] (use of 70 % ^{13}C-enriched chloroform). Two pyrolysis runs of both pure (2-^{13}C)-**4** and (2-^{13}C)-**8** were used for each ^{13}C NMR product sample at a pressure of 50–70 Torr and with a conversion over 95 %.[12, 13] Their ^{13}C NMR spectra were recorded using the inverse gated decoupling method to suppress NOE effects and with a pulse delay of 120 s to avoid any relaxation effects.[14] The ^{13}C shifts of the expected 2- and 3-positions of alkyne products **7** and **10** were identified by nondecoupling experiments of the pyrolyzed ^{13}C samples.[15] The distribution of the label in (^{13}C)-**7** and (^{13}C)-**10** was determined as the average of two to four independent runs (after correction for the only 70 % ^{13}C enrichment), and the error is quoted as a single standard deviation from the mean. Pyrolysis of (2-^{13}C)-**4** at 523 K gave a ratio of products $[(3\text{-}^{13}\mathrm{C})\text{-}\mathbf{7}]/[(2\text{-}^{13}\mathrm{C})\text{-}\mathbf{7}] = 3.0 \pm 0.1$ while pyrolysis of (2-^{13}C)-**8** at the same temperature gave the



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product ratio $[(3\text{-}^{13}C)\text{-}\mathbf{10}]/[(2\text{-}^{13}C)\text{-}\mathbf{10}] = 1.40 \pm 0.05$. Figure 1 shows the distribution of the quaternary carbon atoms of these alkynes in the ^{13}C NMR spectra. It should be noted that **7** and **10** are major products of reaction. Compound **7** represents 81 % of the products from **4**, while **10** represents 22 % of the products from **8**.

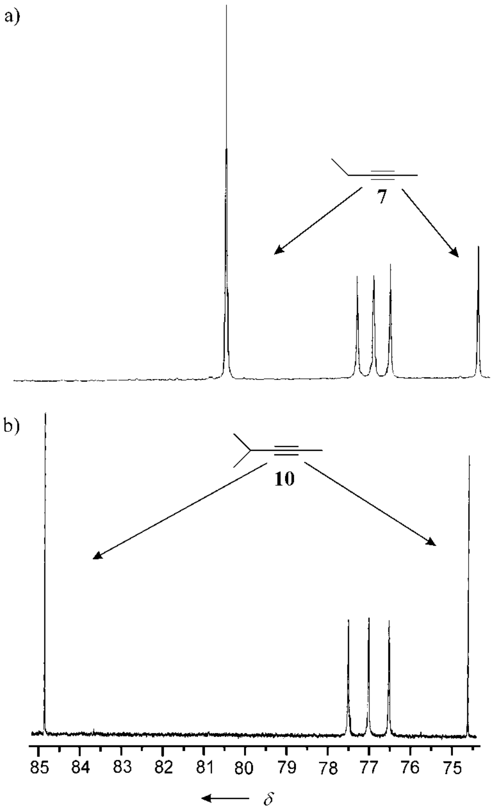
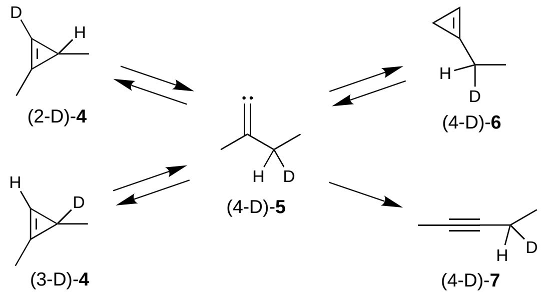


Figure 1. Distribution of the ^{13}C NMR signals ($CDCl_3$, 100 MHz) for the quaternary carbon atoms in alkyne products of pyrolysis at 523 K: a) **7** from ($2\text{-}^{13}C$)-**4**; b) **10** from ($2\text{-}^{13}C$)-**8**.

Further checks showed no significant pressure or conversion dependence of the label distribution. The lack of a conversion dependence demonstrates that there is no tendency for the alkyne products **7** and **10** to undergo any degenerate scrambling processes. A small temperature dependence was detected with a label distribution ratio of 3.2 ± 0.1 for (^{13}C)-**7** and 1.60 ± 0.05 for (^{13}C)-**10** at $T = 482$ K, which indicates a slightly stronger selectivity for the alkyl shift (ethyl or isopropyl against methyl) at lower temperature. The preference of an ethyl or an isopropyl migration over a methyl migration in the vinylidene–alkyne reaction is unambiguously shown by these data. If we reasonably assume that the rate of methyl migration is not affected by the presence of the other alkyl substituent, this establishes a non-monotonic migration order with relative rates of Me:Et:*i*Pr of 1:3.0:1.4. This is the first report of this migration sequence. Likhotvorik et al.[5] attempted this measurement for vinylidene **9** with ^{12}C enrichment, but the small size of the difference signals meant that the authors could only report that both methyl and isopropyl groups migrated, but not their relative rates. The non-monotonic reactivity order is reminiscent of the sequence Me:Et:*i*Pr of 1:1.40:0.47 obtained by Casanova et al.[17] in the isoelectronic isonitrile–nitrile ($RN{\equiv}C \rightarrow RC{\equiv}N$) rearrangement, except that the rate for the isopropyl group is even slower than that for the methyl group.

For the vinylidene rearrangement, as for the isonitrile isomerization, hyperconjugative effects that lead to a positively charged migrating carbon atom in the transition state will mean stabilization of the transition state by larger alkyl groups, and an expected rate acceleration. However, for the more bulky groups (isopropyl, or larger), statistical and steric effects may well play a role that lead to rate decelerations. A combination of these two effects offers a plausible explanation of the present findings. It is also consistent with the (admittedly small) temperature dependencies of these relative migratory aptitudes.

To address the second question we have prepared deuterium-labeled 1,3-dimethylcyclopropene (2-D)-**4**, which because of our previous kinetic analysis of the pyrolysis of unlabeled **4**[8, 13] we expect to generate significant yields of (3-D)-**4** upon pyrolysis (Scheme 2). Compound (2-D)-**4** was prepared in two steps by adapting published labeling procedures.[9–11] The gas-phase kinetics of (2-D)-**4** were investigated using quantitative GC analysis, followed by ^1H NMR analysis to obtain the ratio of (2-D)-**4** and (3-D)-**4**. The kinetic studies of (2-D)-**4** were performed at two temperatures (504 and 524 K) at times covering conversions (to all products) between 20 and 80 %.[12] Five to six runs were carried out at each temperature under the same reaction conditions with undiluted cyclopropene at a total pressure of 50 Torr for ^1H NMR analysis. The proportion of (3-D)-**4** was obtained by comparing the integrated signal of the hydrogen atom at position 2 ($\delta = 6.62$[10, 13]) with that of the hydrogen atom at position 3 ($\delta = 1.42$[10, 13]) of **4** (total of (2-D)-**4** and (3-D)-**4**) in the ^1H NMR spectrum. This procedure provides an estimate of the proportion of (3-D)-**4** in the total mixture reliable to ±5 %.



Scheme 2. Formation of isotopomeric cyclopropene (3-D)-**4** from (2-D)-**4** via vinylidene (4-D)-**5**.

The product–time evolution curves (Figure 2) show the formation of the isotopomeric cyclopropene (3-D)-**4** as a transient product with a maximal yield of about 8 %. This demonstrates clearly the thermal interconversion of the two isotopomers (2-D)-**4** and (3-D)-**4**. It is worth noting that a small amount of the deuterium-labeled 1-ethylcyclopropene (4-D)-**6** is also present. The data of Figure 2 were fitted to a kinetic model[18] (based on an extended version of the mechanism of Scheme 2 that included all products) and optimum values of the rate constants were obtained. These were

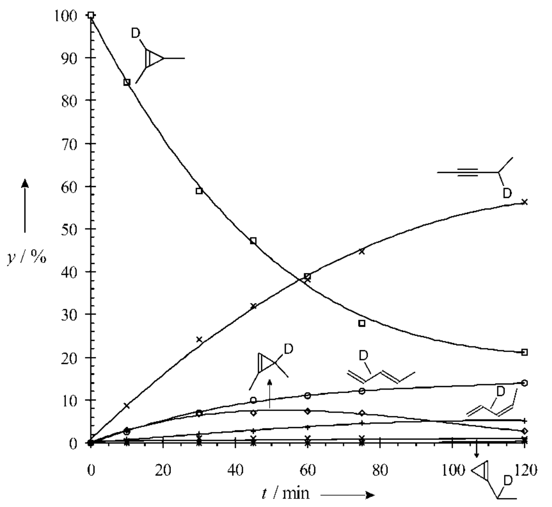
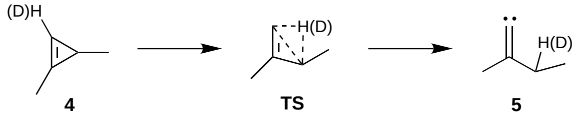


Figure 2. Product – time evolution curves for the decomposition of (2-D)-**4** at 504 K (y: percentage composition of the reactants).

compared with values for the unlabeled system (extended version of Scheme 1[8]) calculated from the appropriate Arrhenius equations at 504 K. From a steady-state analysis of the kinetic scheme[18] these values yielded, inter alia, the isotope effect for the specific rate constant for formation of the vinylidene involved, namely for (2-D)-**4**→(4-D)-**5**. The value of $k_H/k_D = 1.32 \pm 0.07$ obtained corresponds to the isotope effect for the ring-opening process of cyclopropene. A similar value of 1.30 ± 0.06 was obtained at 524 K.

The values of intermolecular kinetic isotope effects for unimolecular gas phase reactions are dependent not only on the reaction involved but also the conditions (temperature and pressure).[19] For example, for the [D$_6$]cyclopropane case, the overall intermolecular isotope effect at 783 K and high pressures is 2.0.[20, 21] Since this value is for the process that leads to [D$_6$]propene, and involves a rate-determining 1,2 H(D)-shift, this is clearly a primary isotope effect, although augmented by secondary effects. For the more specific ring-opening process of 1,2-dideuteriocyclopropane, not involving H(D)-transfer, calculations give values in the region of 1.13 – 1.18 at 696 K[22, 23] for the specific secondary isotope effect per deuterium atom. Thus the value for the isotope effect found here, based on these analogues, looks to be too large to be secondary. This suggests strongly that the 1-H(D) atom is involved in the transition state (**TS**) in the ring-opening process of **4**.



4 **TS** **5**

This result then is entirely consistent with the cyclopropene – vinylidene proposition. A theoretical calculation of the isotope effect has not yet been carried out but is planned. While a contribution of 1,3-biradicals to the formation of acetylenes from cyclopropenes cannot be entirely ruled out, the findings of this paper make this possibility rather unlikely.

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