Vinylidenes as Intermediates in Thermal Cyclopropene-to-Acetylene Rearrangements[1]

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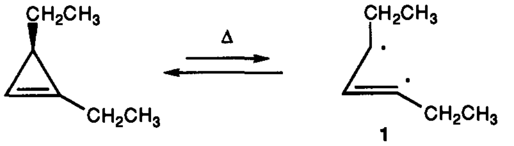
Abstract: Pyrolysis of labeled 1,3,3-trimethylcyclopropene shows that rearrangement to 4-methyl-2-pentyne is mediated by a reversible formation of a vinylidene, the rearrangement of which is rate determining in this case.

That cyclopropenes open thermally can be no surprise, given the substantial strain energy of these species, estimated at more than 50 kcal/mol.[2] In fact, when substituted cyclopropenes are heated or irradiated, complex mixtures of 1,3-dienes, allenes, and acetylenes are formed.[3] A classic experiment in the thermal chemistry of cyclopropenes is that of Bergman,[4] who used optically active 1,3-diethylcyclopropene to demonstrate the reversible ring opening to an intermediate, presumed at the time to be the diradical **1**.



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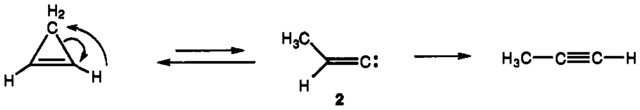
Until recent times, the products of cyclopropene thermal isomerizations were rationalized on the basis of hydrogen shifts in intermediate diradicals related to **1**.[3] In 1989, however, theoretical work by Yoshimine, Pacansky, and Honjou[5] raised the possibility that the acetylenic products issued not from the classical diradical intermediate but instead from a vinylidene (**2**) produced through simultaneous (?) bond breaking and hydrogen shift. The concerted version of this process is the reversal of a carbon-hydrogen insertion by the vinylidene. The acetylenes would then be produced through a 1,2-migration, a well-known process.[6]



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Alert experimentalists quickly tested Yoshimine's notion. In an investigation of the photochemical isomerization of cyclopropenes, Fahie and Leigh used ^{13}C-labeled 1,3,3-trimethylcyclopropene to show that when the cyclopropene was irradiated at 194 nm, as much as 40% of the 4-methyl-2-pentyne was formed from the vinylidene.[7] This result is not shocking, given the well-known transformations of alkenes to carbenes when irradiated with light of such high energy,[8] and it seems dangerous to extend the photochemical results to thermal reactions at ca. 250 °C. Indeed, Fahie and Leigh took care not to do this.[7] However, there are some related thermal reactions known. For example, thermal conversions of alkynes to vinylidenes do occur, but only under conditions of flash vacuum pyrolysis at temperatures much higher than 250 °C.[9a] Especially strained bridgehead alkenes occasionally can be induced to revert to carbenes.[9b] Of course, the diradical **1** is also a vinylcarbene if the proper rotational niceties are observed in its formation.

Three years after the photochemical experiments, Walsh, de Meijere, and their co-workers provided evidence "strongly ... suggestive" of the idea that even the thermal formations of acetylenes involved vinylidenes.[10] These authors built upon the earlier observation that a 1-methyl group actually deactivated cyclopropene toward product formation,[11] surely an odd occurrence if formation of a diradical such as **1** were involved in the rate-determining step. An earlier[12] pyrolysis of 1,3,3-trimethylcyclopropene (**3**) was reinvestigated, and new kinetic data were provided. Pyrolysis of **3** leads to 4-methyl-2-pentyne (**4**) in 22% yield along with a mixture of four dienes. Acetylene formation from **3** was slower than from 3,3-dimethylcyclopropene itself by a factor of 9.1 (Table 1). It was also suggested[10] that thermal ring opening might not be the rate-determining step in cyclopropenes that would rearrange to dialkylvinylidenes, such as 1,3,3-trimethylcyclopropene, **3**. Here, alkyl migration is required to produce the acetylene, and this process is surely much slower than hydrogen migration.[6,13] Perhaps in such reactions the alkyl shift becomes rate determining. The sensible observation was made that it was difficult to see a rate-retarding effect of an added methyl group at the 1-position of **3** if a diradical were the

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(1) Support for this work from ATM, Inc., Danbury, CT, and by the National Science Foundation through Grant CHE 9024996 is acknowledged with thanks.

(2) Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Wiley: New York, 1978; pp 91-94.

(3) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Wiley: New York, 1981; pp 22-25.

(4) York, E. J.; Dittmar, W.; Stevenson, J. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 2882; **1973**, *95*, 5680.

(5) Yoshimine, M.; Pacansky, J.; Honjou, N. *J. Am. Chem. Soc.* **1989**, *111*, 2785, 4198.

(6) Stang, P. J. In *Carbene(oide)*; Regitz, M., Ed.; Georg Thieme: Stuttgart, 1989; p 84ff.

(7) Fahie, B. J.; Leigh, W. J. *Can. J. Chem.* **1989**, *67*, 1859.

(8) Steinmetz, M. G. *Org. Photochem.* **1987**, *8*, 67. Kropp, P. J. *Org. Photochem.* **1979**, *4*, 1.

(9) (a) For a spectacular recent example of the use of this reaction see: Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. For an archival example by the discoverer of the reaction see: Brown, R. F. C.; Harrington, K. J.; McMullen, G. L. *J. Chem. Soc., Chem. Commun.* **1974**, 123. (b) Chan, T. H.; Massuda, D. *J. Am. Chem. Soc.* **1977**, *99*, 936. Conlin, R. T.; Huffaker, H. B.; Kwak, Y.-W. *J. Am. Chem. Soc.* **1985**, *107*, 731. Barton, T. J.; Yeh, M.-H. *Tetrahedron Lett.* **1987**, *28*, 6421. Eaton, P. E.; Hoffmann, K.-L. *J. Am. Chem. Soc.* **1987**, *109*, 5285. Chen, N.; Jones, M., Jr.; White, W. R.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 4981.

(10) Walsh, R.; Wolf, C.; Untiedt, S.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 421.

(11) Hopf, H.; Wachholz, G.; Walsh, R. *Chem. Ber.* **1985**, *118*, 3579.

(12) Srinivasan, R. *J. Chem. Soc., Chem. Commun.* **1971**, 1041.

(13) Stang, P. J. *Acc. Chem. Res.* **1978**, *11*, 107.

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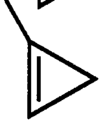
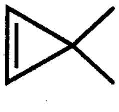
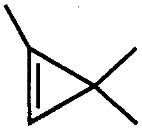
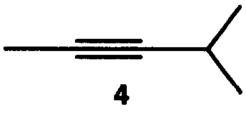
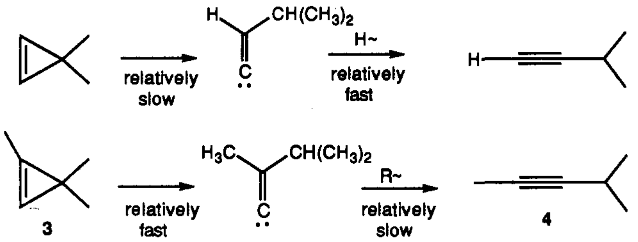
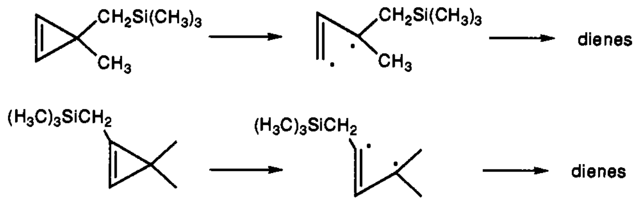
Table 1. Relative Rates of Acetylene Formation from Cyclopropenes[10]

cyclopropene	acetylene	k_{rel}
		1
		0.39
		1.31
3 	 4	0.144

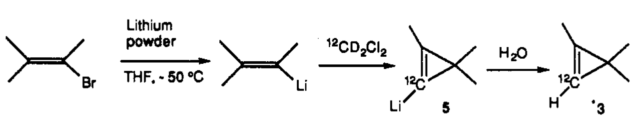
intermediate in formation of acetylene 4. Further evidence[14] appeared in the reactions of (trimethylsilyl)methyl-substituted cyclopropenes in which the β-stabilizing effect of silicon[15] favored ring opening to a diradical and hence skewed the product distribution toward dienes, not acetylenes. That the yield of acetylenes in these reactions was exceptionally low was taken as evidence that they are not formed from diradicals.



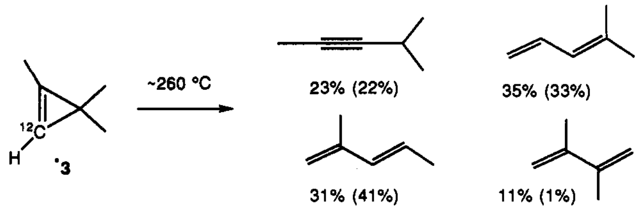


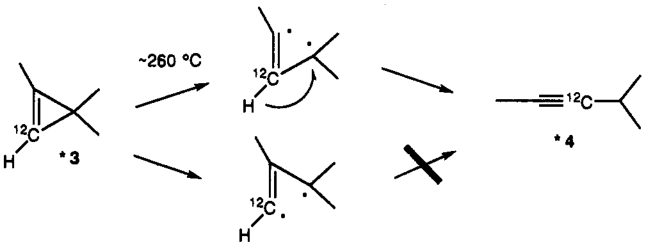
In sum, there is substantial suggestive evidence, both theoretical and experimental, that vinylidenes are the critical intermediates in the thermal rearrangements of cyclopropenes to acetylenes. They are firmly implicated in photochemical reactions. In addition, it appears that ring opening may not be rate determining when an alkyl migration is required to produce the acetylene. In this paper we present new experiments on labeled cyclopropenes that speak to both these ideas. Our work supports the intermediacy of vinylidenes in the thermal acetylene-forming process, as well as the notion that it is the alkyl migration in the carbene that is rate determining. In addition, we show that the thermal formation of a vinylidene is reversible.

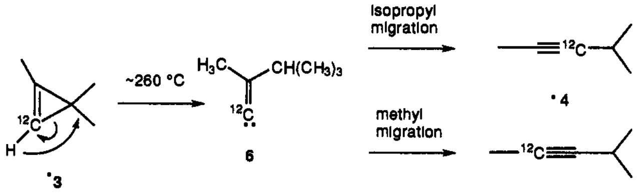
^{12}C-labeled 1,3,3-trimethylcyclopropene (*3) was prepared by the method of Closs and Closs.[16] Use of deuterated methylene chloride was dictated by availability and price. Almost all of the deuterium washes out in the synthesis, as the penultimate product is cyclopropenyllithium compound **5**.



Pyrolyses of *3 were carried out at 250–270 °C in evacuated and conditioned ampules. Analysis by gas chromatography and ^{1}H NMR spectroscopy showed that the acetylene 4 isolated earlier by Walsh, de Meijere, and their co-workers[10] was formed in our reactions in similar amounts (Walsh and de Meijere's results are shown in parentheses). The dienes described[10] were also formed, although we find substantially more of one of them, 2,3-dimethyl-1,3-butadiene.[17] Of critical importance is the position of the label in the acetylene *4. Diradical formation must lead to *4 labeled in only one position. Opening of *3 in the "wrong" direction does not lead to an intermediate capable of producing *4, although it might lead to 2,3-dimethylbutadiene. By contrast, formation of a vinylidene seemed likely to lead to *4 labeled in both the acetylenic positions. This idea rests on the assumption that there would be no great migratory preference of methyl or isopropyl in the vinylidene **6**. This idea has not been tested,[6,18] but the risk seemed worth taking. Clearly, were only one labeled acetylene to be found, mechanistic interpretation would be difficult in the absence of migratory aptitude data. But this is not the case. The two positions in *4 appear approximately equally labeled, as two signals of approximately equally lowered intensity relative to *4 containing ^{13}C at natural abundance appear at δ 74.45 and 85.02 ppm. The two positions can be assigned through synthesis of ^{13}C-labeled 4 by the following route, modeled on that of Corey and Fuchs.[19] The critical point is the absence of an intense signal for a single position in *4, unlabeled by ^{12}C. Although the two signals we observed for the acetylenic carbons of *4 appear equally diminished, it is not possible to quantify these data. However, the labeling results are clearly in accord







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(14) Walsh, R.; Wolf, C.; Untiedt, S.; de Meijere, A. *J. Chem. Soc., Chem. Commun.* **1992**, 422.

(15) Auner, N.; Walsh, R.; Westrup, C. *J. Chem. Soc., Chem. Commun.* **1986**, 207.

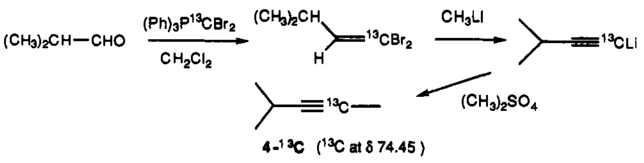
(16) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1963**, *85*, 99.

(17) Early reports[12] find much more of this compound, and we have found its yield to vary unpredictably from run to run. The value quoted comes from the run with labeled material.

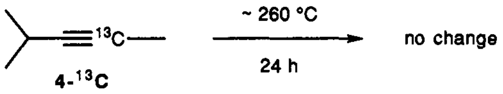
(18) Stang, P. J. Private communication, December, 1993.

(19) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

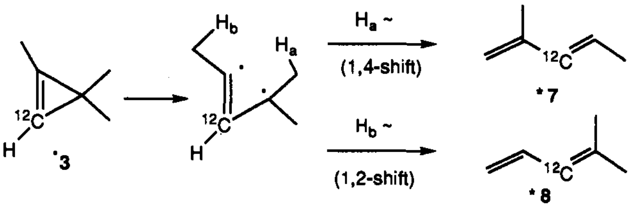
with a vinylidene-mediated reaction, but not with a hydrogen shift in a diradical, a process that can only give **4** labeled by ^{12}C in one position.



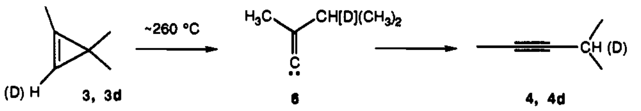
This synthesis also provided material for a necessary control experiment. Pyrolysis of ^{13}C-labeled **4** at 250–270 °C led to no detectable isomerization of the label.

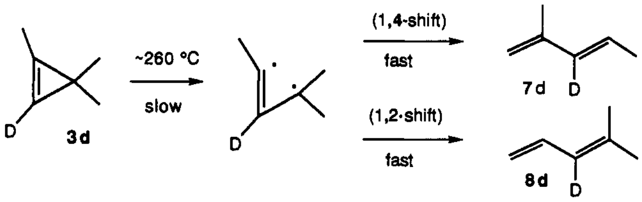


The labeling experiment also confirms that the dienes **7** and **8** are formed through hydrogen shifts in the diradical formed by opening of the more substituted ring bond in ***3**. The position of the label in ***7** and ***8** formed in our work was determined by comparison of the crude NMR spectrum of the products with freshly run spectra of the starting material and authentic products. In this way comparisons of chemical shifts could be made and temperature and concentration-induced differences between our data and earlier reports minimized. Our spectra were always consistent with those reported earlier (see the Experimental Section for details).[7,20,21]

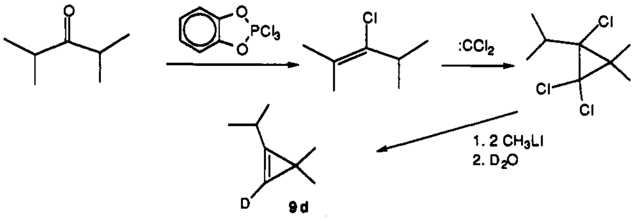


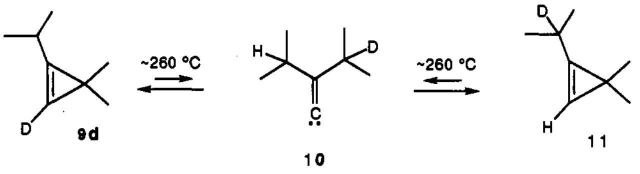
Walsh suggested that alkyl migration in the vinylidene might become the rate-determining step in the rearrangement of highly substituted cyclopropenes to acetylenes.[10] We probed this point by searching for an isotope effect in the rearrangement of the deuterated cyclopropene **3d** to acetylene **4**. If vinylidene formation were rate determining, **3d** would surely react more slowly than **3**. A mixture of approximately equal amounts of **3** and **3d** was heated. The rate of decline in the ratios of the peak for the vinyl hydrogen (or deuterium) at δ 6.68 to that for the isopropyl CH (or CD) in acetylene **4** (δ 2.45) was compared by following the reaction by both ^{1}H and ^{2}H NMR spectroscopy. Within experimental error there was no difference discernible between the protio and deuterio compounds. For example, after 3 h at 260 °C analysis of the ^{1}H NMR spectrum showed a ratio of 1:1.12 for the intensities of the peaks at δ 6.68 and 2.45. The ^{2}H NMR spectrum showed the same ratio of intensities: δ 6.68:2.45 = 1:1.11. There can be no important bond breaking of the C–H (or C–D) bond in the transition state of the rate-determining step. It appears that the alkyl migration in the dialkylvinylidene **6** is indeed the slow step. Similarly, no isotope effect could be detected in formation of dienes **7d** and **8d**, as expected for a reaction in which opening to a diradical is the rate-determining step.

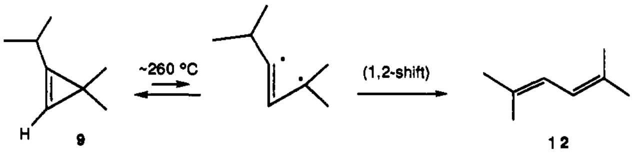




Now we turn to the question of the reversibility of vinylidene formation. We first synthesized 1-isopropyl-3,3-dimethylcyclopropene-d_1 (**9d**), from diisopropyl ketone, with a method adapted from published procedures for related materials.[22-24] Thermal rearrangement of **9d** must give vinylidene **10**, a species symmetrical but for the deuterium. If formation of **10** is reversible, recovered starting material should show protium in the vinyl position and, more important, deuterium in the isopropyl CH (D) position, as in **11**. This experiment is difficult, as **9** rearranges almost entirely (>90%) to 2,5-dimethyl-2,4-hexadiene (**12**) and other isomeric dienes, a reaction not involving a vinylidene and not able to scramble the label in **9d**. Vinylidene **10** is formed, however, as traces of diisopropylacetylene[25] are found in the products.







Nonetheless, we were able to detect the appearance of ^{1}H in the vinyl position of recovered **9d**. One can imagine many possible sources of this exchange in which environmental protium becomes incorporated into **9d**. However, in the ^{2}H NMR spectrum we also see deuterium appear at δ 2.75, the position of the isopropyl CH of **9**. For example, at 90% conversion of **9d** we see a reaction mixture containing ~73% deuterated **12**, 7–10% **9d**, 0.5% **11**, and 17–18% other dienes. Despite the small amount of **11**, the signal in the ^{2}H NMR spectrum is unmistakable and completely absent in the spectrum of starting material, **9d**.

To summarize, we have shown that the unsubstituted olefinic carbon of 1,3,3-trimethylcyclopropene appears in both acetylenic positions of 4-methyl-2-pentyne after pyrolysis. This is inconsistent with the conventional diradical mechanism and strongly implicates a vinylidene intermediate. Substitution of the vinyl hydrogen in 1,3,3-trimethylcyclopropene by deuterium leads to

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(20) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Specktroscopie*; George Thieme: Stuttgart, 1984.

(21) Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*; Aldrich: Milwaukee, 1993; Vol. 1, p 38B.

(22) Gross, H.; Gloede, J. *Chem. Ber.* **1963**, *96*, 1387.

(23) Julia, S.; Ginebreda, A. *Synthesis* **1977**, 682.

(24) Baird, M. S.; Hussain, H. H.; Nethercroft, W. *J. Chem. Soc., Perkin Trans. I* **1986**, 1845.

(25) Nicholas, K. M.; Siegel, J. *J. Am. Chem. Soc.* **1985**, *107*, 4999.

no discernible isotope effect, thus showing that it is the alkyl shift in the dialkylvinylidene that is rate limiting in this reaction. Finally, another deuterium labeling experiment shows that vinylidene formation is reversible.

Experimental Section

1,3,3-Trimethyl[2-^{12}C]cyclopropene (*3). A solution of 2-bromo-3-methyl-2-butene (31.3 g, 0.21 mol) in 100 mL dry THF was added to a suspension of Li powder (7.2 g, 1.04 mol) in 50 mL of THF at −30 °C under an argon atmosphere. Upon completion of the addition, the reaction mixture was allowed to warm to −10 °C with stirring. The orange solution was transferred with a syringe from residual Li into another flask and cooled to −45 °C. A solution of $^{12}CD_2Cl_2$ (1.6 mL, 25 mmol, Matheson Isotopes, Inc.) in 10 mL of dry THF was added dropwise to the stirred mixture at −45 °C under argon. After this addition the reaction mixture was allowed to stir at −30 °C for 1 h and was then treated with 2.5 mL of water. All volatile products and solvents were then distilled at room temperature under ca. 1 Torr of pressure into a cold trap held at 77 K. A solution of 2.5 M butyllithium in hexanes (15 mL) was added to the distillate, the mixture was stirred for 4 h at room temperature, and the solvents were removed at ca. 1 Torr at room temperature. To the resulting dry residue was added 5 mL of THF. The mixture was cooled to 0 °C and 0.5 mL of water added. The volatile part of the mixture was transferred at room temperature and ca. 1 Torr into a trap cooled to 77 K. This solution was then separated by preparative gas chromatography (PGC) at 40 °C on a 7 ft × 0.25 in. 15% OV-101 column. First to elute was *3, a colorless liquid (0.30 g, 15% based on methylene chloride). Comparison was made with authentic unlabeled 3.[20] ^{13}C NMR ($CDCl_3$, 75.0 MHz): δ 9.94, 17.81, 26.97, 130.94 (note that the signal in unlabeled 3 at 112.53, reported[20] at 113.0, is absent). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.09 (s, 6H), 2.04 (s, 3H), 6.68 (s, 1H).

1,1-Dibromo-3-methyl[1-^{13}C]-1-butene. A suspension of $^{13}CBr_4$ (1.04 g, 3.1 mmol, Matheson Isotopes, Inc.), triphenylphosphine (0.89 g, 3.4 mmol), zinc dust (0.26 g, 4.0 mmol), and zinc–copper couple (Alfa Inorganics, Inc., 0.025 g) in 5 mL of CH_2Cl_2 was stirred at room temperature under a positive argon pressure for 30 h. A solution of freshly distilled isobutyraldehyde (0.30 g, 4.2 mmol) in 2 mL of CH_2Cl_2 was then added. The mixture was allowed to stir for 2 h at room temperature. Then 30 mL of pentane was added. The mixture was allowed to stir for an additional 10 min and the upper pentane layer separated with a syringe. The remaining gray viscous oil was dissolved in 3 mL of CH_2Cl_2 and 12 mL of pentane added. The mixture was stirred for 10 min and the pentane solution separated with a syringe from the residual gray liquid. The combined pentane extracts were filtered through alumina and evaporated to afford 1,1-dibromo-3-methyl[1-^{13}C]-1-butene as a colorless oil (0.55 g, 77% based on CBr_4). ^{13}C NMR ($CDCl_3$, 75.0 MHz): δ 20.70, 32.66, 86.53, 144.49. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (d, J = 6.7 Hz, 6H), 2.59 (m, J = 6.7 Hz, 9.1 Hz, 1H), 6.23 (d, J = 9.1 Hz, 1H).

4-Methyl[2-^{13}C]-2-pentyne (4-^{13}C). To a stirred solution of 1,1-dibromo-3-methyl[1-^{13}C]-1-butene (0.44 g, 1.9 mmol) in 1 mL of ether cooled to −78 °C with a dry-ice/ethanol mixture was added dropwise 3.2 mL of a 1.4 M solution of methyllithium in ether under an argon atmosphere. Upon completion of the addition the reaction mixture was allowed to warm to room temperature. It was then cooled to −40 °C, and dimethyl sulfate (0.33 g, 2.6 mmol) was added. The mixture was then stirred at −20 °C for 1 h. All volatile products and solvents were distilled at room temperature and ca. 1 Torr into a cold trap held at 77 K. This mixture was then separated by PGC at 45 °C on a 7 ft × 0.25 in. 15% OV-101 column. First to elute was ether. Second was 4-^{13}C (0.093 g, 58%). Comparison was made to authentic 4 purchased from Farchan Chemical Co. ^{13}C NMR ($CDCl_3$, 75.0 MHz): δ 74.45. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (d, J = 6 Hz, 6H), 1.79 (d, J = 11 Hz, 3H), 2.52 (m, 1H).

3-Chloro-2,4-dimethyl-2-pentene. To a solution of PCl_5 (143.5 g, 0.69 mol) in 1.2 L of dry benzene was added catechol (60 g, 0.54 mol) in small portions with intensive stirring at room temperature. After evolution of HCl ceased, the mixture was concentrated under reduced pressure at the water pump. The residue was then heated to 120 °C, and diisopropyl ketone (30 g, 0.26 mol) was added dropwise over 1 h with stirring. The mixture was then allowed to stir at 120 °C for an additional 1 h. The volatile products were then removed at 20–30 Torr. The distillate was washed with 50 mL of 10% NaOH solution and water and then dried over $MgSO_4$. Distillation at atmospheric pressure through a 15-cm Vigreaux column gave pure material as a colorless oil (11 g, 32%, bp 119.5–120 °C, lit.[26] 118–120 °C).

1,1,2-Trichloro-3,3-dimethyl-2-isopropylcyclopropane. A solution of 3-chloro-2,4-dimethyl-2-pentene (8.3 g, 63 mmol), powdered NaOH (8.5 g, 0.21 mol), and triethylbenzylammonium chloride (0.14 g, 0.63 mmol) in 100 mL of $CHCl_3$ was stirred at room temperature until an exothermic reaction began. The mixture was then allowed to stir at reflux for an additional 30 min. The mixture was cooled to room temperature and filtered through alumina, and the solvents were removed at the water pump. Distillation of the residue at 0.5 Torr gave a colorless oil, bp 50–51 °C (5.24 g, 39%). ^{13}C NMR ($CDCl_3$, 75.0 MHz): δ 18.55, 19.25, 21.73, 31.90. 33.52, 64.80, 73.29. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (d, J = 6 Hz, 3H), 1.14 (d, J = 6 Hz, 3H), 1.37 (d, J = 9 Hz, 6H), 2.16 (septet, J = 9 Hz, 1H). Precise mass calcd for $C_8H_{13}{}^{35}Cl^{37}Cl_2$: 218.0024. Found: 218.0005.

1-Isopropyl-3,3-dimethylcyclopropene-*1-d* (9). To a stirred solution of 1,1,2-trichloro-3,3-dimethyl-2-isopropylcyclopropane (2.94 g, 13.6 mmol) in 30 mL of anhydrous ether cooled in a dry-ice/ethanol bath was added 30 mL of a solution of 1.5 M methyllithium in ether. The reaction mixture was allowed to stir at 0 °C for an additional 15 min, then warmed to room temperature, and stirred for another 1 h. Most of the ether was removed at room temperature and ca. 1 Torr and D_2O (1.5 g, 75 mmol) added with stirring at 0 °C. All volatile products and ether were distilled at reduced pressure into a cold trap maintained at 77 K. This distillate was separated by PGC at 70 °C on a 7 ft × 0.25 in. 15% OV-101 column. First to elute was ether. Next came **9d** as a colorless liquid (1.22 g, 80%). ^{13}C NMR ($CDCl_3$, 75.0 MHz): δ 18.97, 20.93, 26.67, 27.90, 110.20, 140.27. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (m, 12H), 2.75 (septet, J = 6 Hz, 1H) 6.67 (s, 1H, present only in the protio compound (**9**) made in an exactly analogous fashion from unlabeled material).

General Procedure for Hydrocarbon Pyrolysis. The Pyrex pyrolysis tubes were conditioned by running test cyclopropene pyrolysis two to three times. The hydrocarbon (9–1200 mg) was placed in a conditioned 25-mL Pyrex tube, degassed by the freeze–thaw method, evacuated to 0.5 Torr, and sealed. The ampule was heated to 250–270 °C by immersion in a sand bath for 0.5–24 h. The resulting products were analyzed by GC/MS, ^{1}H, ^{2}H, and/or ^{13}C NMR spectroscopy.

Pyrolysis of *3. Pyrolysis of 300 mg of *3 was carried out at 250–270 °C for 15 h. Analysis of starting material and diene and acetylene products was done by comparison of GC/MS and NMR spectra with those of authentic compounds. The intensities of signals in the ^{1}H NMR spectra from authentic **4** or commerical **7**, **8**, and 2,3-dimethyl-1,3-butadiene were used to determine the composition of the mixture: **4** (δ 2.52), **7** (δ 5.69, 6.17), **8** (δ 4.85, 5.85), 2,3-dimethyl-1,3-butadiene (δ 4.9–5.15). ^{13}C NMR ($CDCl_3$, δ) ***4**: 3.32 ($\mathit{C}H_3C$), 20.46 (C_4), 23.27 ($\mathit{C}H_3CH$), 74.45 (C_2, weak), 85.02 (C_3, weak); lit.[20] 3.29, 20.34, 23.19, 74.37, 84.97. ***7**: 18.02 (C_2CH_3), 18.56 (C_4CH_3), 113.75 (C_1), 125.30 (C_4), 142.05 (C_2); lit.[21] 18.11, 18.66, 113.82, 125.35, 134.14, 142.10; lit.[20] 18.3, 18.8, 114.5, 125.1, 135.5, 142.2; lit.[7] 17.98, 18.56, 113.69, 125.27, 134.07, 142.05. ***8**: 18.14 (CH_3), 25.82 (CH_3), 114.03 (C_1), 133.35 (C_2), 135.77 (C_4); lit.[7] 18.09, 25.74, 113.98, 125.84, 133.35, 135.64.

Pyrolysis of Labeled 4. Pyrolysis of 9 mg of **4** labeled at C_2 with ^{13}C at 250–270 °C for 24 h led to no discernible change in starting **4**.

Pyrolysis of Deuterated 3. Pyrolysis of 300 mg of a 1:1 mixture of deuterated (at C_2) and undeuterated **3** was carried out at 250–270 °C for 4 h. The products were analyzed by ^{1}H and ^{2}H NMR spectroscopy.

Pyrolysis of 1-Isopropyl-2-deuterio-3,3-dimethylcyclopropene (9d). Pyrolysis of 1.2 g of **9d** at 250–270 °C was carried out for 0.5 h. The reaction mixture contained 73% **12**, 10% **9d**, 0.5% **11**, and 17% other dienes. Analysis of the reaction mixture by ^{1}H and ^{2}H NMR spectroscopy revealed the presence of protium in the vinyl position at δ 6.67 and deuterium in the isopropyl CH position at δ 2.75 of **9**.

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(26) Henry, L. *Ber. Dtsch. Chem. Ges.* **1875**, *8*, 398.