

Thermal Rearrangements, XIX¹⁾

The Kinetics of the Thermal Isomerization of 1-Ethynyl-2,2,3,3-tetramethylcyclopropane

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1-Ethynyl-2,2,3,3-tetramethylcyclopropane (**9**) has been prepared and subjected to gas phase pyrolysis. Above 200°C the hydrocarbon rearranges to 4,4,5-trimethyl-1,2,5-hexatriene (**10**) and 5,6-dimethyl-5-hepten-1-yne (**11**). Whereas the allene is produced directly from **9** by a 1,5-hydrogen shift, the alkyne is a secondary product formed from **10** by a [3,3] sigmatropic rearrangement. The activation parameters (E_a , $\lg A$) for both processes have been determined for the 210 to 250°C temperature range. The data are discussed and compared with those for other concerted reactions of alkynes and alkenes.

Thermische Umlagerungen, XIX¹⁾. — Kinetik der thermischen Isomerisierung von 1-Ethynyl-2,2,3,3-tetramethylcyclopropan

Die Darstellung und Gasphasenpyrolyse von 1-Ethynyl-2,2,3,3-tetramethylcyclopropan (**9**) werden beschrieben. Oberhalb 200°C lagert sich der Kohlenwasserstoff in 4,4,5-Trimethyl-1,2,5-hexatrien (**10**) und 5,6-Dimethyl-5-hepten-1-in (**11**) um. Während sich das Allen durch eine 1,5-Wasserstoffwanderung direkt aus **9** bildet, handelt es sich bei dem Alkin um ein Sekundärprodukt, das aus **10** durch eine [3,3]-sigmatrope Umlagerung entsteht. Die Aktivierungsparameter (E_a , $\lg A$) dieser beiden Prozesse wurden im Temperaturbereich von 210–250°C ermittelt. Die erhaltenen Zahlenwerte werden diskutiert und mit denjenigen anderer konzentrierter Reaktionen von Alkinen und Alkenen verglichen.

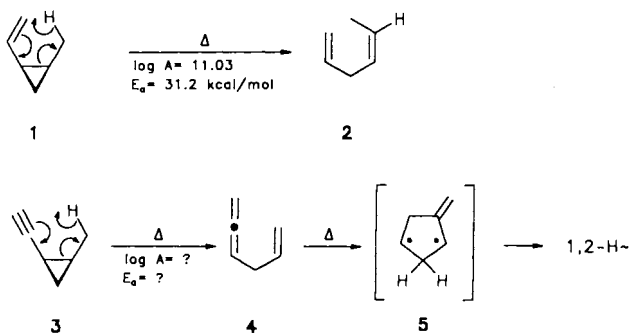
Thermal reactions of acetylenic hydrocarbons have received growing attention in recent years^{2–4}, and many studies have shown that these processes are chemically as varied and preparatively as useful as those of their olefinic counterparts^{4–6}. In contrast to these latter systems kinetic data for acetylenic molecules are conspicuously lacking⁷. A comparison between the two classes of hydrocarbons aimed at elucidating the effect caused by replacement of a double bond by the geometrically distinctly different triple bond group is thus hampered. A case in point is provided by *cis*-1-ethynyl-2-methylcyclopropane (**1**) and *cis*-1-ethynyl-2-methylcyclopropane (**3**), respectively.

Whereas the former molecule, which on heating undergoes a homodienyl-1,5-hydrogen shift — leading to *cis*-1,4-hexadiene (**2**) — has been investigated in great detail⁸, only qualitative results (i.e. a product study) are available for the thermal behavior of **3**. In our first experiments we found that the alkyne also suffers a 1,5-hydrogen shift providing 1,2,5-hexatriene (**4**) as the initial product. The allene undergoes subsequent isomerization reactions⁹, for example a ring closure that begins with the formation of diradical **5** which, in turn, may stabilize itself by 1,2-hydrogen shifts.

Since our initial work⁹ the parent molecule has been investigated (qualitative study of its high-temperature gas phase pyrolysis¹). In addition, the thermal isomerization of various acetylenic epoxides has been developed by Dreiding and co-workers into a valuable method for chain and ring extension¹⁰. Moreover, as part of an investigation of the trimethylene methane energy surface, Berson and his co-workers have studied briefly the pyrolysis of 1-ethynyl-2,2,3-trimethylcyclopropane¹¹. Once again there is good evidence for the occurrence of a 1,5-hydrogen shift.

All this work has been qualitative, and the determination of reliable kinetic data has hence become highly desirable.

We report here a detailed study of the gas phase pyrolysis of 1-ethynyl-2,2,3,3-tetramethylcyclopropane (**9**). This hy-



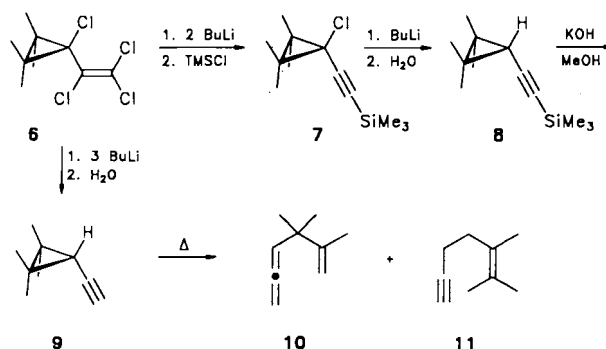
drocarbon was selected since it offers some distinct advantages over less methylated cyclopropylacetylenes. A fully methylated derivative may not prevent the occurrence of *cis*, *trans*-isomerization reactions – a well-known and thoroughly studied phenomenon in vinylcyclopropane pyrolysis¹² – but it makes it “invisible” because of its degenerate nature. A second simplification of the analysis, both kinetically and productwise, is expected to be caused by the methyl groups if the primary allene product of type **4** undergoes a cycloaddition to a diradical like **5**. With two methyl substituents in the 3-position 1,2-hydrogen shifts cannot take place, and the intermediate should re-open to its acyclic precursor¹³. The anticipated low pyrolysis temperatures for the 1,5-hydrogen shift in **9** should have the favorable effect of reducing the danger of side reactions like the well-known thermal oligomerization of allenes¹⁴.

Results

Qualitative Pyrolysis Study, Product Analysis

1-Ethynyl-2,2,3,3-tetramethylcyclopropane (**9**) was prepared from the adduct **6** of thermally ring-opened tetrachlorocyclopropene and tetramethylethylene¹⁵. Treatment of **6** with three equivalents of *n*-butyllithium and hydrolysis of the resulting dilithio derivative¹⁶ gave a mixture of compounds from which **9** could only be separated by tedious vapor-phase chromatography in poor yield (13%). Almost pure material was obtained in three steps by treating **6** with two equivalents of *n*-butyllithium and chlorotrimethylsilane (TMSCl), lithiating the resulting **7** again with *n*-butyllithium followed by hydrolytic workup¹⁶, and subsequent removal

of the trimethylsilyl group from **8** with potassium hydroxide in methanol.



For the product study and the kinetic analysis a sample of **9** was purified by preparative vapor-phase chromatography. When a sample of the hydrocarbon was pyrolyzed at 250°C for 1 h in a static system (evacuated ampoule), and the product mixture analyzed by capillary gas chromatography it was found that only two products in comparable relative amounts (3:2) had been formed, the material balance being quantitative: 4,4,5-trimethyl-1,2,5-hexatriene (**10**) and 5,6-dimethyl-5-hepten-1-yne (**11**). The hydrocarbons were separated by preparative gas chromatography and identified by their spectral data (cf. Experimental Section). Whereas **10** is the expected 1,5-hydrogen shift product, **11** is produced from it by a Cope-type rearrangement. [3,3] Sigmatropic rearrangements between allylallenes and 1,5-hexenyne have been investigated thoroughly by Huntsman and co-workers¹⁷, and the above equilibrium (see below) is just

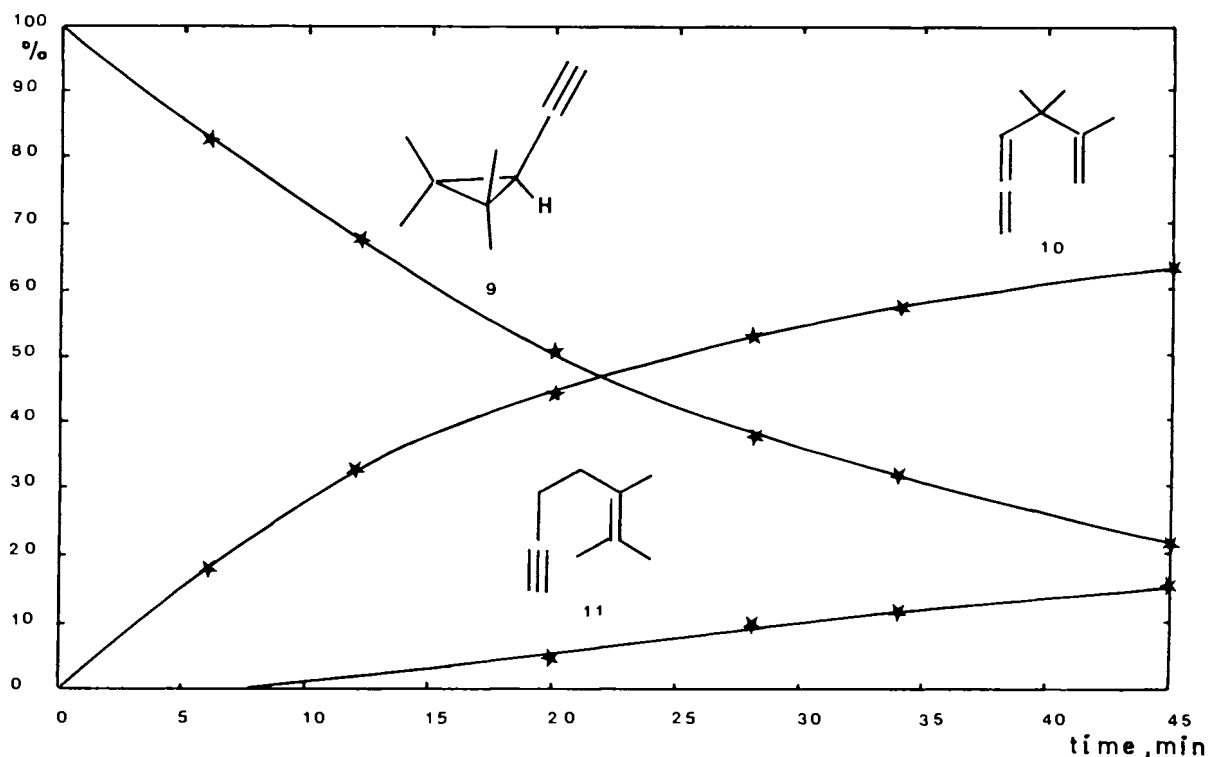


Figure 1. Time dependence of the product composition in the pyrolysis of **9** at 239.8°C

another example in a long row of cases. The NMR spectra of the raw pyrolysate did not contain any indications of the formation of dihydrofulvenes, clearly demonstrating that the methyl substituents had fulfilled their task of preventing 1,2-hydrogen shifts.

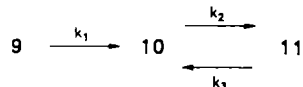
Kinetic Measurements: These were carried out in a similar manner to previous studies¹⁸. Gaseous samples of **9** were prepared highly diluted in SF₆ with the addition of a small amount of butane as an internal standard. These mixtures (master mixtures) were used as the supply for all kinetic runs. Under all conditions (temperatures up to 320°C) only products **10** and **11** were found, and the mass balance was complete.

Table 1. Time dependence of the product distribution in the pyrolysis of **9** at 239.8°C

Time [min]	Total [%]			Product [%]	
	9	10	11	10	11
6	82.28	17.72	—	100	0
12	67.69	32.31	—	100	0
20	50.59	44.38	5.02	89.8	10.2
28	37.16	53.05	9.79	84.4	15.6
34	31.38	57.09	11.53	83.2	16.8
45	21.23	63.17	15.60	80.2	19.8

The reaction was studied as a function of time and temperature. Initial pressures (20 Torr) were sufficiently high to avoid any problems of unimolecular "fall-off"¹⁹. A typical set of results for the time dependence of decomposition is shown in Table 1. It can be seen that there is a steady change in the product distribution with time as well as reactant disappearance. This indicates clearly a consecutive step reaction in which **9** is converted first to **10**, and then **10** isomerizes further to **11**. There is no indication of a direct pathway from **9** to **11**. A graphical presentation of these results is provided by Figure 1.

Similar results were found at all temperatures of this study. For the disappearance of **9** good first-order kinetics were obtained [linear plots of ln (% **9**) versus time]. The rate constants derived from these plots are given in Table 3. In order to obtain a more complete picture of these isomerizations, the reaction was studied at higher temperatures, in the range 280 to 320°C. Under these conditions **9** was completely decomposed, and only **10** and **11** remained. The results of these experiments are shown in Table 2. It is clear that at temperatures above 290°C the product ratio has reached a steady value, and at 280°C it is very close to steady on the time scale employed. This is strongly supportive of the establishment of the Cope-type equilibrium previously found in many similar systems¹⁷. These findings therefore support the following mechanistic scheme:



In order to exploit our measurements to the full extent, we have carried out a kinetic modelling exercise based on

the above scheme for the analytical data obtained in the lower temperature range (210–250°C). The corresponding calculations are based on a variable-step integration program, employing the Gear algorithm²⁰. In practice the program requires an initial set of estimates for the rate constants of the scheme. The program then calculates the time evolution of the system, which is compared with the observed data. By successive adjustments of the rate constants the calculations are repeated until the best fit is obtained (as judged by the minimum sum of squares of all deviations). In practice, k_1 values were kept fixed at those already determined, and only k_2 and k_3 were varied; the resulting values are shown in Table 3.

Table 2. Product distribution in the pyrolysis of **9** at higher temperatures

Time [min]	$T = 280.0^\circ\text{C}$			$T = 290.0^\circ\text{C}$		
	10	11	11/10	10	11	11/10
20	37.46	62.04	1.66	32.53	67.47	2.07
30	36.29	63.71	1.76	32.47	67.53	2.08
40	34.76	65.24	1.88	32.95	67.05	2.03
	$T = 300.0^\circ\text{C}$			$T = 320.0^\circ\text{C}$		
	10	11	11/10	10	11	11/10
20	35.24	64.66	1.83	33.45	66.65	1.99
30	—	—	—	35.21	64.79	1.84
40	33.77	66.23	1.96	35.29	64.71	1.83

Table 3. Rate constants for the interconversion of **9**, **10**, and **11**

Temp. [°C]	k_1	$10^4 k [\text{s}^{-1}]$	
		k_2	k_3
210.0	0.653 ± 0.007	0.218	0.10
220.0	1.425 ± 0.024	0.496	0.23
230.0	2.904 ± 0.036	0.968	0.46
239.8	5.784 ± 0.068	1.54	0.74
250.0	11.48 ± 0.13	3.83	1.87

The uncertainties in k_1 are the standard deviations of the gradients of least-squares fit to the first-order decay plots. The uncertainties in k_2 and k_3 are harder to estimate; k_2 is quite well determined by the fitting procedure, and errors are probably less than $\pm 2\%$. However, the results are rather insensitive to k_3 , and this rate constant is probably only obtained to within $\pm 10\%$.

In addition to the above measurements, a brief study of the reaction was carried in a reaction vessel packed with pyrex tubes (surface/volume ca. 13 cm⁻¹) and previously conditioned with hexamethyldisilazane (HMDS). The study (at 239.8°C) compared favorably with that in the unpacked vessel. For example, after 20 min the product mixture contained 53.8% **9**, 40.7% **10**, and 5.6% **11**. The analyses suggest a slightly slower rate for **9** → **10** and a slightly higher one for **10** → **11**, but were well within the $\pm 10\%$ variation typically found in such comparisons. There is no substantial

evidence for a heterogeneous contribution to the reaction in the unpacked vessel.

For the temperature dependence of this reacting system the rate constants of Table 3 were fitted by least-squares analysis to the Arrhenius equation, and the resulting Arrhenius activation parameters are shown in Table 4.

Table 4. Arrhenius parameters for the isomerization reactions of **9**, **10**, and **11**

Reaction	lg <i>A</i> [s ⁻¹]	<i>E</i> _a [kJ mol ⁻¹ (kcal mol ⁻¹)]
9 → 10	12.07 ± 0.07	150.3 ± 0.6 (35.9 ± 0.2)
10 → 11	10.98 ± 0.81	146 ± 8 (34.6 ± 1.9)
11 → 10	11.00 ± 0.80	148 ± 8 (35.3 ± 1.8)

In addition to these figures the data of Table 3 and of the higher temperature equilibrium studies may be combined to yield the following thermodynamic quantities:

$$\Delta H_{2,3}^0 = -3.2 \pm 0.6 \text{ kJ mol}^{-1} (-0.8 \pm 0.2 \text{ kcal mol}^{-1})$$

$$\Delta S_{2,3}^0 = -0.1 \pm 1.9 \text{ J K}^{-1} \text{ mol}^{-1} (0.0 \pm 0.5 \text{ cal K}^{-1} \text{ mol}^{-1})$$

The error limits may be an underestimate owing to the greater uncertainties in *k*₃ values at the lower temperatures.

Discussion


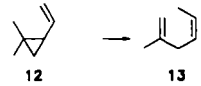
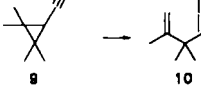
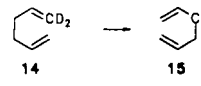

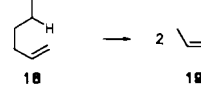
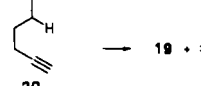

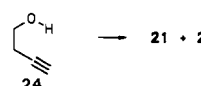
The study presented here reports for the first time kinetic data for a thermal 1,5-hydrogen shift of an alkyne. It is hence interesting to compare the activation parameters with those of structurally related olefins as well as those of other pericyclic alkyne and alkene isomerizations.

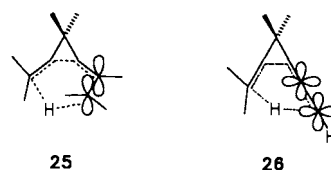
As already pointed out in the introduction, the thermal rearrangement of vinylcyclopropanes has been studied very extensively. There is possibly at present no thermal process of an organic compound that has been investigated with more care^{4,12}. Nevertheless, the rearrangement of the tetramethyl derivative corresponding to **9** is unknown. For a comparison of the kinetic parameters we therefore selected 1,1-dimethyl-2-vinylcyclopropane (**12**) which has been pyrolyzed by Solly and Frey²¹. The data in Table 5 show no significant difference between **9** and **12**. The slightly higher activation energy for **9** is offset by a larger *A* factor, although this arises, in part, from the higher path degeneracy for **9**. In terms of relative rates (corrected for path degeneracy) *k*(**12**)/*k*(**9**) = 4.9 at 500 K.

As can be seen from Table 5, other structurally and mechanistically related thermal reactions of alkenes and alkynes have also very similar parameters. This is shown by Cope rearrangements **14** → **15**²² and **16** → **17**²³, respectively, as well as various fragmentations of the retro-ene type, viz. **18** → **19**^{24,25} and **20** → **19/21**^{26,27}, and **22** → **19/23**^{7,28} compared to **24** → **21/23**^{7,28}. Such small differences as exist in these other cases tend to favor the alkynes over the alkenes.

The reasons for these similarities have been discussed very thoroughly and extensively by Viola⁷. We agree with him that it is the planarity of the acetylenic transition states that offsets the additional energetic requirement to allow the lin-

Table 5. Arrhenius activation parameters for selected alkene and alkyne thermal isomerizations and fragmentations

Reaction	log <i>A</i> , s ⁻¹	<i>E</i> _a , kJ·mol ⁻¹ (kcal·mol ⁻¹)	Ref.
	11.03	130.5 (31.2)	8)
	11.41	140.2 (33.5)	21)
	12.07	150.3 (35.9)	this work
	11.1	148.5 (35.5)	22)
	11.4	143.9 (34.4)	23)
	12.6	240.2 (57.4)	24, 25)
	12.7	235.6 (56.3)	26, 27)
	170.3 (40.7)	28)	
	11.2	166.9 (39.9)	28)



ear acetylenic unit to conform to a cyclic transition state. In a planar arrangement *all* participating bond orbitals are centered in that plane thus providing maximum orbital overlap. In other words, the "aromaticity" of the acetylenic transition state is more pronounced than that of its olefinic counterpart. This is illustrated in **25** for a 1-ethynyl-2-methyl- and in **26** for a 1-ethynyl-2-methylcyclopropane system. In the former case the six atoms participating in the bond breaking and forming steps almost form a chair-like arrangement. The migrating hydrogen atom can approach the terminal olefinic carbon atom only from a direction nearly orthogonal to the plane of the double bond.

In **26** with its axially symmetric acetylenic unit, a π -lobe is available for bond formation with the rearranging hydro-

gen atom in any direction, thus allowing the formation of the planar transition state shown.

The surprise really is that these complex and subtle factors should virtually balance one another and cause such a close correspondence in rates. If there is an extra factor in the comparison between **9** and **12** it is the presence of the three-membered ring. Perhaps the small extra rigidity imposed on the transition states makes planarity in **26** slightly more difficult to achieve than in the corresponding transition states for **16**, **20**, and **24**. This would account for the small differential rate effects.

It is clear, however, that the rigidity of the triple bond is once again no hindrance to reaction. There need be no rigidity in the chemist's conception of the geometric properties and possibilities of this highly useful and reactive functional group.

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Experimental

General Remarks: NMR (CDCl₃, int. TMS): Varian T-60, Bruker AM 300, Perkin-Elmer R 32 (90 MHz). — IR (CCl₄): Perkin-Elmer 1420. — MS: MAT CH-7 and MAT 8430. — GC, analytical: Dani, model 3800, 15-m quartz capillary SPB-1; preparative: Carlo Erba Fractovap 2400 V, Varian 920, Intersmat IGC 131 M. — The experimental procedure for carrying out the kinetic experiments has been described in detail in this journal¹⁸.

1-Ethynyl-2,2,3,3-tetramethylcyclopropane (9)

a) To a solution of 5.0 g (19.2 mmol) of 1-chloro-2,2,3,3-tetramethyl-1-(trichlorovinyl)cyclopropane (**6**)¹⁵ in 50 ml of dry diethyl ether was added dropwise with stirring at -78°C 40 ml (60 mmol) of a 1.5 N solution of *n*-butyllithium in *n*-hexane. After 10 min the mixture was slowly warmed to ambient temp., stirred for 45 min, and cooled to -78°C again. After addition of 20 ml of water the mixture was warmed to 0°C and further diluted with 50 ml water. The organic phase was separated and washed with two 20-ml portions of water. The combined aqueous phases were extracted with 20 ml of diethyl ether and the combined organic phases dried with magnesium sulfate. The solvents were distilled over a 30-cm column packed with glass helices, the residue was condensed (0.05 Torr, 30 $^{\circ}\text{C}$) into a cold (-78°C) flask and the condensate analyzed by GC/MS and GC (Carlo Erba 6 m 10% SE 30 on Chromosorb W-AW-DMCS 60/80 mesh, 70 $^{\circ}\text{C}$). The crude product weighed 1.79 g and contained 53% **9** corresponding to a 43% yield. Preparative scale GC gave 336 mg (13%) of pure **9**.

b) To a solution of 650 mg (2.85 mmol) of 1-chloro-2,2,3,3-tetramethyl-1-[(trimethylsilyl)ethynyl]cyclopropane (**7**)¹⁶ in 10 ml of dry diethyl ether was added dropwise with stirring at -78°C 3.4 ml (3.4 mmol) of 1 N *n*-butyllithium solution in *n*-hexane. After 15 min at -78°C the mixture was stirred an additional 60 min at ambient temp. then cooled to -78°C and quenched with 188 mg (5.9 mmol) of methanol. The mixture was stirred at room temp. for 1 h, then poured into 50 ml of water, and the aqueous phase extracted with two portions of 50 ml of ether. The combined organic phases were washed with two 20-ml portions of saturated NaCl solution and dried with MgSO₄. After evaporation of the solvents, the residue was condensed (0.05 Torr, 30 $^{\circ}\text{C}$) into a cold (-78°C) flask to yield

541 mg (98%) of crude 2,2,3,3-tetramethyl-1-[(trimethylsilyl)ethynyl]cyclopropane (**8**).

To the solution of 541 mg of crude **8** in 5 ml of methanol was added a solution of 1.2 g of potassium hydroxide in 10 ml of methanol. The mixture was stirred at ambient temp. for 14 h, then diluted with 100 ml of water and extracted with 5 portions of 50 ml *n*-pentane. The combined organic layers were dried with MgSO₄, the solvent was slowly distilled and the residue condensed (0.05 Torr, 30 $^{\circ}\text{C}$) into a cold (-78°C) flask, yield: 269 mg of crude **9**, 91% pure according to ¹H-NMR spectrum and GC. The product was purified by preparative scale GC (1.5-m 3/8 "Teflon" tube with 10% SE 54 on Chromosorb W-AW-DMCS 60/80, 60 $^{\circ}\text{C}$) to yield 193 mg (57%) of analytically pure **9**. — ¹H-NMR (90 MHz, CDCl₃): δ = 0.85 (d, ⁴*J* = 2.2 Hz, 1H, Cycloprop.-H), 1.15 (s, 12H, 4 CH₃), 1.95 (d, ⁴*J* = 2.2 Hz, 1H, C \equiv CH). — IR (film): $\tilde{\nu}$ = 3300 cm⁻¹ (ν H-C \equiv C-), 2990, 2100 (ν C \equiv C), 1450, 1380, 1105. — MS (70 eV): *m/z* (%) = 122 (54) [M⁺], 107 (100), 91 (89), 79 (90).

C₉H₁₄ (122.2) Calcd. C 88.45 H 11.55
Found C 88.31 H 11.72

Pyrolysis of 9: A sample of 0.30 g (2.5 mmol) of **9** was submitted to a 400-ml ampoule and the latter sealed under high vacuum after several freeze-pump-thaw cycles. After 60 min at 250 $^{\circ}\text{C}$ the pyrolysate was dissolved in cyclohexane and the product mixture separated by preparative GC (6-m 20%-Carbowax column on Chromosorb W/AW; 50–90 $^{\circ}\text{C}$).

Fraction I (relative proportion 60%): 4,4,5-trimethyl-1,2,4-hexatriene (**10**), colorless liquid. — IR (CCl₄): $\tilde{\nu}$ = 3090 cm⁻¹ (w), 2975 (vs), 2930 (m), 1960 (s), 1638 (m), 1458 (m), 1380 (m), 1157 (m), 892 (s), 870 (m), 846 (s). — ¹H-NMR (300 MHz, CDCl₃): δ = 1.17 (s, 6H, 2 CH₃), 1.76 (ps-s, 3H, CH₃), 4.74 (m, 1H, =CH-), 4.76 (d, *J* = 6.8 Hz, 2H, =C=CH₂), 4.81 (m, 1H, =CH-), 5.12 (t, *J* = 6.8 Hz, 1H, -CH=C=). — ¹³C-NMR (100.6 MHz, C₆D₆/CCl₄): δ = 19.9 (q, CH₃), 27.3 (q, 2 CH₃), 39.7 (s, C-4), 76.9 (t, C-1), 93.9 (d, C-3), 109.7 (t, C-6), 151.8 (s, C-5), 207.3 (s, C-2). — MS (70 eV): *m/z* (%) = 122 (2) [M⁺], 107 (100), 105 (11), 91 (53), 83 (17), 79 (31), 77 (14), 55 (51), 53 (15), 41 (43).

C₉H₁₄ (122.2) Calcd. C 88.45 H 11.55
Found C 88.12 H 11.69

Fraction II (40%): 5,6-Dimethyl-5-hepten-1-yne (**11**), colorless liquid. — IR (CCl₄): $\tilde{\nu}$ = 3315 cm⁻¹ (vs), 2995 (m), 2920 (w), 2865 (s), 1430 (m), 1373 (m), 925 (w), 630 (s). — ¹H-NMR (300 MHz, CDCl₃): δ = 1.65 (s, 6H, 2 CH₃), 1.68 (s, 3H, CH₃), 1.93 (t, *J* = 2.7 Hz, 1H, -C=CH), 2.26 (m, 4H, -CH₂CH₂-). — ¹³C-NMR (100.6 MHz, C₆D₆/CCl₄): δ = 17.8 (t, C-5), 18.5, 20.5, 20.9 (q, 3 CH₃), 33.9 (t, C-4), 68.7 (d, C-7), 84.4 (s, C-6), 125.8, 126.5 (2 x s, C-2, -3). — MS (70 eV): *m/z* (%) = 122 (3) [M⁺], 107 (69), 83 (72), 55 (100), 53 (10), 43 (16), 41 (55).

C₉H₁₄ (122.2) Calcd. C 88.45 H 11.55
Found C 88.73 H 11.23

CAS Registry Numbers

6: 72866-04-7 / **7:** 80631-32-9 / **8:** 103304-21-8 / **9:** 103304-20-7 / **10:** 116351-18-9 / **11:** 116351-19-0

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