Thermal Pericyclic Tandem Reactions[‡]

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Gas phase thermal isomerizations of twelve acetylenic systems, all of which can in principle undergo two successive pericyclic steps, are described. The substrates, the syntheses and spectroscopic properties of which are presented, are formal derivatives of but-2-yne, with different functional groups in the 1- and the 4-positions. The Cope, Claisen, Claisen ester, retro-ene, 1,5-hydrogen shift, and 1,5-homo hydrogen-shift processes were employed as the pericyclic steps from which the tandem processes were composed. The compositions of the pyrolysates obtained were determined over broad temperature ranges, and the mechanisms of the individual steps producing the pyrolysis products are discussed.

Introduction

In the current discussion on improvement of the efficiency of chemical transformations, concepts such as atom economy,[2] tandem and domino reactions,[3] solvent-free processes,[4] and catalytic transformations with high stereoselectivities[5] play important roles. While it would probably be very difficult to design chemical reactions involving *all* of these features, it is attractive to develop processes incorporating at least *several* of them. As far as atom economy is concerned, two types of chemical reactions clearly stand out: isomerizations and additions. Whereas the molecular masses of starting material and product are identical in the former transformations, the mass of the product in the latter is the sum of the masses of the reaction partners, as no atoms are lost in the process. The second and the third points on the above list are often encountered in thermal processes, and when these proceed according to a pericyclic mechanism they often also take place in highly stereoselective fashion. During the course of our work on the pyrolytic behavior of alkynes, allenes, and cumulenes, we have observed several thermal isomerizations (see below), which may best be described as tandem reactions composed of several pericyclic steps. That acetylenes and/or their isomeric allenes are particularly prone to participation in these processes is not surprising; they are energy-rich substrates, which may experience considerable stabilization as a result of redistribution of their π-electrons over the σ-framework: i.e., isomerization. A simple example illustrating this "delocalization" of π-electrons over a more extended σ-skeleton is provided by the heats of formation of the three C_4H_6 isomers but-1-yne ($\Delta H°_{f(g)}$ = 33.9 kcal·mol^{-1}), buta-1,2-diene (33.2 kcal·mol^{-1}), and buta-1,3-diene (20.7 kcal·mol^{-1}).[6] In the other characteristic type of reaction − addition − in which acetylenes normally participate, the thermodynamically less favorable π-bonds are replaced totally or partially by σ-bonds, and a countless number of inter- and intramolecular addition reactions involving acetylenes are known.[7] Finally, acetylenes are attractive as starting materials or intermediates in organic chemistry because they are often very easily available. By exploitation of the acidity of terminal alkynes, all types of functional groups may be introduced and chain extensions of different complexity can readily be carried out.

In this paper we present a comprehensive study of the thermal isomerization of various acetylenic systems, all of which can in principle undergo two pericyclic steps in tandem fashion. In these substrates the triple bond serves two functions: on the one hand it is the "energy reservoir" and "molecular fuse" for the isomerization under consideration, and on the other it "holds together" the two pericyclic steps.

Results and Discussion

Selection of Substrates to be Studied

The different acetylenes we wished to subject to gas phase (i.e., solvent-free) pyrolysis are summarized in Scheme 1. This reaction matrix begins with deca-1,9-dien-5-yne (**1**), a hydrocarbon that can undergo two successive Cope isomerizations, and the thermal conversion of which into 3,4-bismethylenehexa-1,5-diene ("2,3-bisallyl-1,3-butadiene") we already described many years ago (see below).[8] Proceeding along the first row of the scheme, we next arrive at the enolether **2**, in which a succession of Claisen and Cope steps (or vice versa, see below) appears feasible. Entry number 3 allows for the combination of the Cope process with a Claisen ester isomerization, entry number 4 that of a Cope with a retro-ene step (i.e., in this latter case we are losing some of the atoms of the substrate). To combine a

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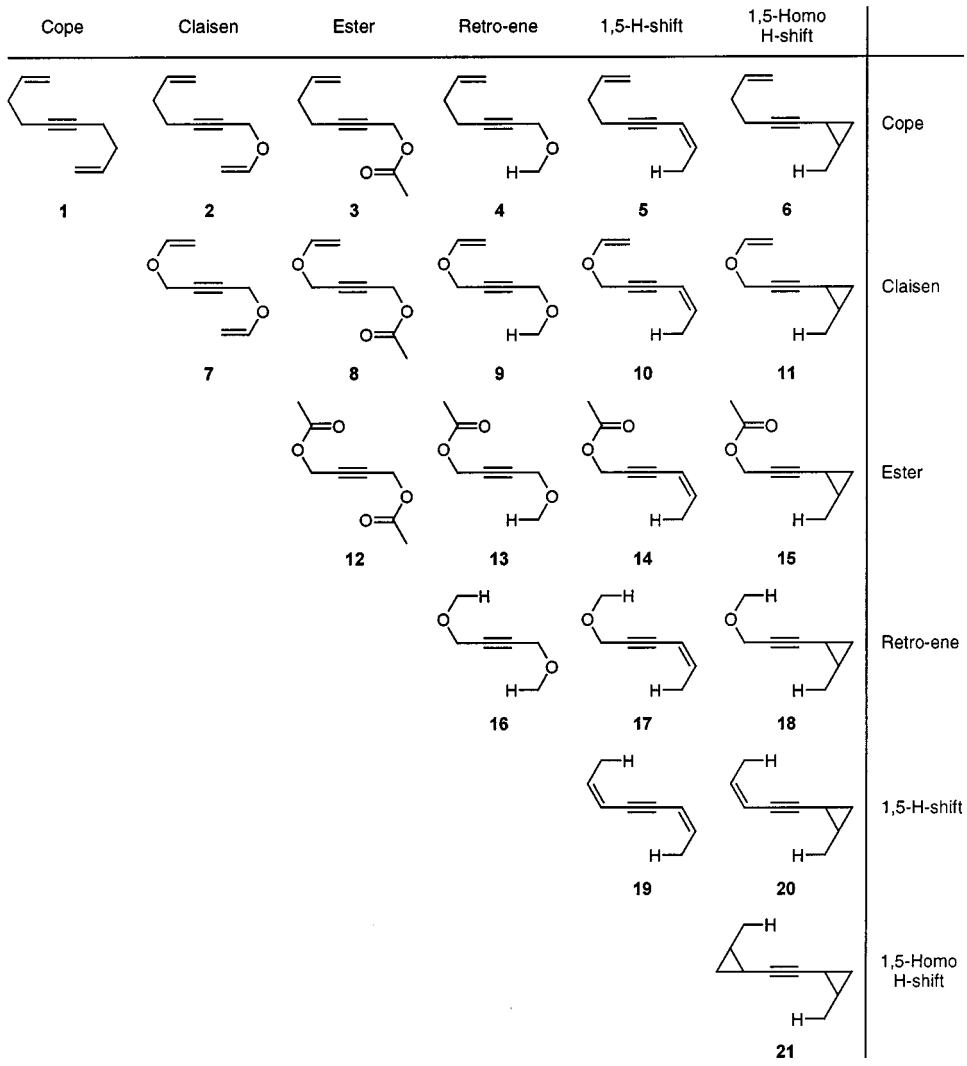


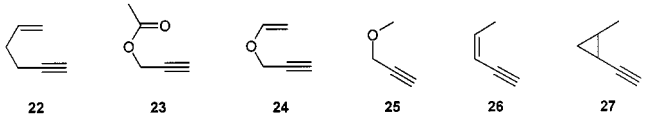
Scheme 1. A selection of substrates for tandem reactions involving disubstituted alkynes

1,5-hydrogen shift process with a Cope rearrangement, we proposed to study the hydrocarbon **5** as a model system, while with the cyclopropane derivative **6**, allowing the inclusion of a 1,5-sigmatropic homo hydrogen shift reaction, our combinatorial scheme grows still further. The remaining entries in the scheme are self-explanatory.

It is also of interest to include cyclopropane rings in some of the substrate molecules, because the ring strain of the three-membered ring results in the energy content of the starting material being increased still further. We had already previously demonstrated that the subsystem *cis*-1-ethynyl-2-methylcyclopropane readily undergoes the anticipated hydrogen shift process.[9] Although the concept of using highly unsaturated starting materials that also contain a strained ring is attractive for the design of systems capable of undergoing multiple pericyclic tandem reactions, the synthesis of these doubly activated starting materials could become a problem in certain cases. Cyclopropane and cyclobutane chemistry has experienced phenomenal growth in the last two decades,[10] but it still cannot compete with acetylene chemistry as far as (commercial) availability of substrates and simplicity of performing chemical transformations with them are concerned. In the following sections we describe the preparation and gas phase pyrolysis of 12 of the 21 derivatives presented in Scheme 1, systems particularly well suited in our opinion to demonstrate the scope and limitations of the sequential processes.

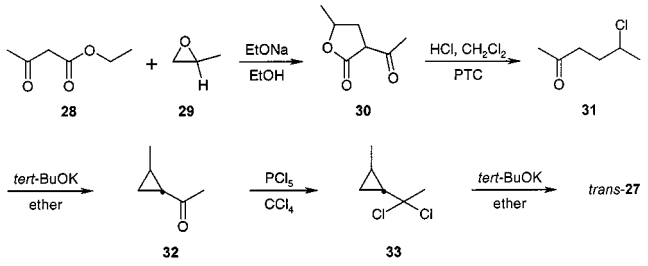
Preparation of Starting Materials

From the retrosynthetic viewpoint, it is advantageous to cleave the molecules collected in Scheme 1 between the triple bonds and a neighboring carbon atom, since the resulting six building blocks **22**–**27** (Scheme 2) have all been described in the chemical literature.



Scheme 2. Starting materials for the synthesis of the acetylenes shown in Scheme 1

Of these, the cyclopropylacetylene **27** was the most difficult to prepare at the outset of our studies, the others being available by published procedures (see Exp. Sect.). The cyclopropane **27** had originally been obtained as a mixture of isomers by cyclopropanation of pent-2-en-4-yne with diazomethane/cuprous chloride.[9] However, the yields of this reaction were so low that it was impossible to synthesize the hydrocarbon in amounts large enough for subsequent steps. The route presented in Scheme 3, arrived at after much optimization work, finally furnished *trans*-**27** in multigram amounts.



Scheme 3. Preparation of *trans*-1-ethynyl-2-methylcyclopropane (*trans*-**27**)

The synthesis began with the alkylation of ethyl acetoacetate (**28**) with propylene oxide (**29**), a process described in the literature,[11] and which provided 3-acetyl-5-methyldihydro-2-furanone (**30**) in one step in acceptable yield (50%). When the ring-opening of this lactone was carried out with a mixture of dichloromethane/conc. hydrochloric acid under phase-transfer conditions (PTC), 5-chlorohexan-2-one (**31**) was obtained in 42% yield. Subsequent ring-closure of **31** under the conditions reported in the literature with sodium amide provided *trans*-1-acetyl-2-methylcyclopropane (**32**), but the yields were disappointing. When potassium *tert*-butoxide was employed as base, however, compound **32** was isolated in yields between 70 and 80%. Chlorination of **32** to give the dichloride **33** was problematic,[12] and in our hands yields in the 40% range could not be exceeded. Under the drastic reactions conditions used (see Exp. Sect.), ring-opening to 2,5-dichlorohex-2-ene (inter alia) was observed. The final dehydrochlorination step with potassium *tert*-butoxide in ether to give *trans*-**27** could again be carried out in acceptable yield (61%).

Trapping of the acetylides prepared from **22**−**27** with different electrophiles permits most of the alkynes summarized in Scheme 1 to be prepared. These derivatives fall into two categories: unsymmetrically and symmetrically substituted acetylenes.

a) Unsymmetrically Substituted Acetylenes

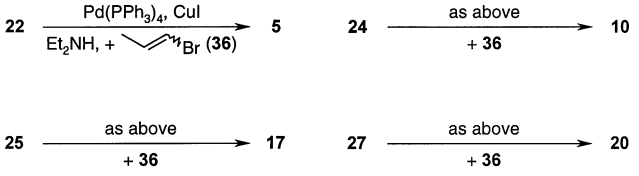
Methyl Propargyl Ethers 4, 9, and 18: These three methyl propargyl ethers were prepared by coupling the lithium salts of **22**, **24**, and **27**, respectively, with bromomethyl methyl ether (**34**), as shown in Scheme 4.

Scheme 4. Preparation of the methyl propargyl ethers **4**, **9**, **18**, and the but-3-enylalkyne **6**

The acetylenes, obtained in 30−40% yields, were stable, colorless liquids that could be purified by vacuum distillation; they were characterized by the usual spectroscopic and analytical methods (see Exp. Sect.). In principle, **22**, **24**, and **27** could also be used as starting materials for other derivatives shown in Scheme 1 for **2**, **7**, and **11** by use of bromomethyl vinyl ether as the trapping reagent, for example. Since this compound is not readily available, however, the corresponding coupling reactions were not attempted.

***trans*-1-Hex-5-en-1-ynyl-2-methylcyclopropane (6):** When acetylides are treated with a non-activated electrophile, such as 4-bromobut-1-ene (**35**), much harsher reaction conditions are necessary. In fact, this process was only used for the synthesis of **6**, since this hydrocarbon could not be obtained by any other route (Scheme 4). When the reaction was carried out in THF solution, no coupling of **27** with **35** could be accomplished; only when HMPT was added as more polar co-solvent was the cyclopropylacetylene derivative produced, although only in poor yield (10%). The reason for this disappointing result can be seen in the low reactivity of **35** and its high tendency to undergo dehydrobromination in the presence of base, to give buta-1,3-diene.

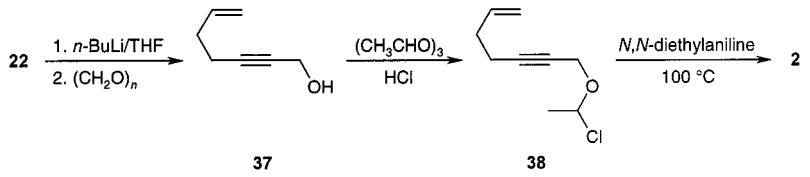
Enynes 5, 10, 17, and 20: These conjugated enynes were prepared by Hagihara coupling of **22**, **24**, **25**, and **27** with 1-bromoprop-1-ene (**36**, mixture of isomers, Scheme 5).



Scheme 5. Preparation of the conjugated enynes **5**, **10**, **17**, and **20**

The yields of these reactions were acceptable (40−50%), and since **36** was employed as a (*E*)/(*Z*) mixture the enynes were also produced as mixtures of diastereomers. In most cases the coupling provided decidedly more of the (*Z*) isomer. Separation was achieved by preparative gas chromatography, allowing full spectroscopic identification of the different enynes.

7-Vinyloxyhept-1-en-5-yne (2): As mentioned above, since bromomethyl vinyl ether is not a readily obtainable reagent, its direct coupling with terminal acetylenes was not a viable option for preparation of propargyl vinyl ethers. Since, moreover, the addition of alcohols to acetylenes can be quite demanding from the practical viewpoint,[13] we decided



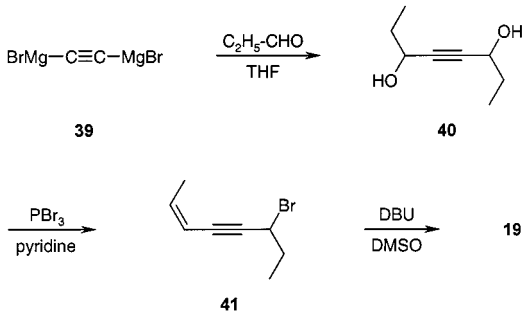
Scheme 6. Preparation of the unsymmetrical propargyl vinyl ether **2**

to use a procedure originally proposed by Brandsma for the synthesis of **24**[14] to prepare the propargyl vinyl ether **2**. As shown in Scheme 6, compound **22** was first chain-elongated to afford the propargyl alcohol **37**, which was subsequently converted into 7-(1-chloroethoxy)hept-1-en-5-yne (**38**) by treatment with paraldehyde in the presence of hydrogen chloride.

In this conversion, the initially produced hemiacetal reacted further, to give **38** by a nucleophilic substitution. When **38** was added to hot *N*,*N*-diethylaniline, dehydrochlorination took place and **2** was formed in approximately 40% yield, the product having to be removed from the reaction flask immediately on formation.

b) Symmetrically Substituted Acetylenes 19 and 12, and also 7

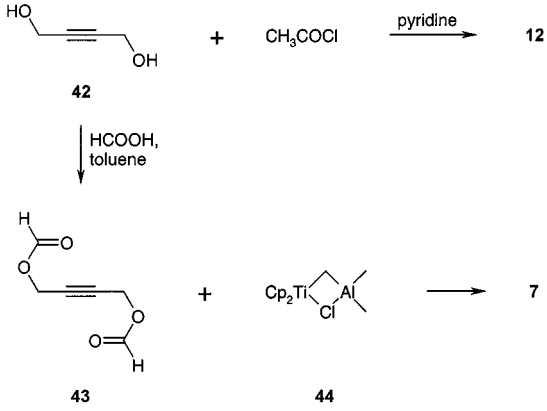
For acetylenes bearing two identical substituents, the best starting materials are acetylene and but-2-yne-1,4-diol (**42**, see Scheme 8). As shown in Scheme 7, the bis-Grignard reagent derived from acetylene, **39**, reacted with propanal to give the expected diol **40** (mixture of diastereomers), which yielded the vinylacetylene **41**, as a mixture of isomers, on treatment with phosphorous tribromide in pyridine (yield 50%, *Z*/*E* ratio 2:1).



Scheme 7. Preparation of octa-2,6-dien-4-yne (**19**)

With diazabicycloundecane (DBU) in DMSO, compound **41** underwent the second dehydrobromination step and furnished the dienyne **19** as a mixture of isomers [(*Z*,*Z*)/(*Z*,*E*)/(*E*,*E*) = 3:5:17, GC analysis] in 39% yield; the hydrocarbons could be separated by preparative gas chromatography and were fully characterized spectroscopically (see Exp. Sect.).

1,4-Diacetoxybut-2-yne (**12**) is easily made by esterification of **42** with acetyl chloride in dichloromethane (70−80% yield). When compound **42** is first esterified with formic acid in toluene, the resulting diester **43** was converted in 26% yield into 1,2-bis(vinyloxy)but-2-yne (**7**) on treatment with Tebbe's reagent (**44**) (Scheme 8).



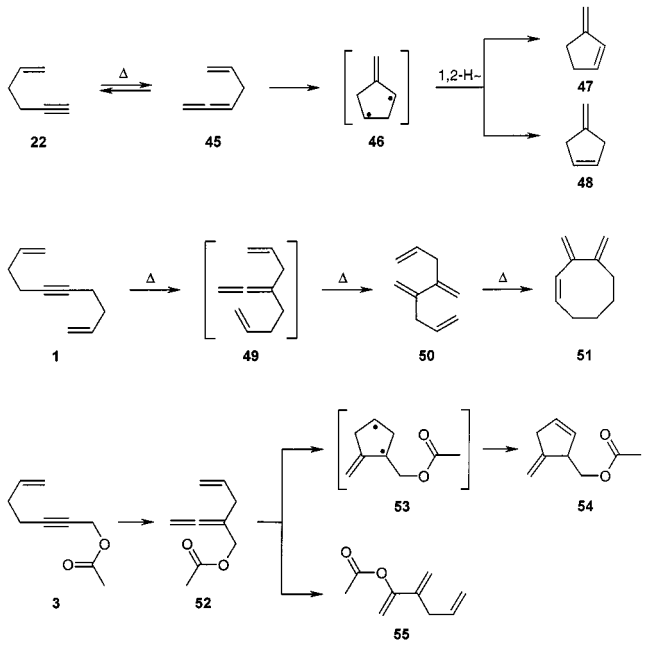
Scheme 8. Preparation of the diester **12** and the divinyl ether **7**

Pyrolyses

Pyrolysis experiments were carried out in a conventional tubular furnace equipped with an empty quartz tube connected on one side to an evaporation system (kugelrohr oven with evaporation flask) and on the other to a cold trap cooled with liquid nitrogen. This set-up allowed experiments to be performed both in the mg range (product analysis by GC or GC/MS analysis) and also on a preparative, gram scale (product analysis after gas chromatographic separation by conventional spectroscopic methods). Contact times were estimated as several seconds, and in all experiments a complete temperature profile was determined: the reaction temperature at which isomerization was just beginning to occur was determined, as was the highest temperature at which the starting material was fully consumed. The temperature increase was carried out in 25−30-degree steps.

The first sigmatropic tandem isomerization of simple acetylene derivatives were studied by us as early as 1985 and involved the hydrocarbon **1** and the ester **3**.[8] The prototype for the thermal isomerization of **1** was the propargyl Cope rearrangement[15] of hex-1-en-5-yne (**22**) to hexa-1,2,5-triene (**45**), studied extensively by Huntsman and coworkers[16] (Scheme 9).

As pyrolysis temperatures increased, this reversible process more and more became accompanied by an irreversible cyclization reaction producing 3- and 4-methylenecyclopentene (**47** and **48**). The cyclization was initiated by a 1,5-*C*,*C*-bridging step, which generated the diradical **46**; this species that underwent 1,2-hydrogen shifts in two different directions to furnish the dienes **47** and **48**. Incorporation of a second butenyl substituent into **22** created the prerequisites for a tandem Cope rearrangement process, and when **1**



Scheme 9. Tandem pericyclic reactions of **1** and **3**

was heated to 410 °C compound **1** indeed isomerized to give 4,5-dimethyleneocta-1,7-diene (**50**). The primary isomerization product, the allene intermediate **49**, could not be isolated under the reaction conditions. An increase in the pyrolysis temperature to 470 °C caused the formation of 3,4-dimethylenecyclooctene (**51**), presumably through an intramolecular ene reaction. Thus, compound **1** experienced three consecutive pericyclic steps in total, and since the resulting cross-conjugated triene, a cyclic [3]dendralene derivative,[17] is set up for a Diels–Alder addition, even a fourth pericyclic step appears feasible in principle. Because the activation energies of allyl ester rearrangements are higher than those of pure Cope isomerizations (see below), it has been argued[8] that an allene intermediate should be isolable if one of the allyl subsystems of **1** were replaced by an ester function. This was indeed the case. At 460 °C the allene **52** was obtained from **3** as the primary product, and when the temperature was raised to 540 °C the expected tandem product **55** was formed, accompanied by the five-membered ring compound **54**. This latter ester was produced since the harsher reaction conditions necessary for the **52** → **55** isomerization to take place also induced five-membered ring formation by way of **53**. That the conjugated isomer of **54**, corresponding to **47**, could not be isolated under these conditions might well be the result of still another [3.3]sigmatropic shift. This would produce 1-acetoxy-2,3-dimethylenecyclopentane, which, with its now exocyclic conjugated diene system, could participate in cycloaddition reactions to afford higher molecular weight material.

1. Pyrolyses of the Hex-1-en-5-yne Derivatives 2, 4, 5, and 6

a) Pyrolysis of 7-Vinyloxyhept-1-en-5-yne (2): In view of the above complex thermal behavior, the pyrolysis of the vinyl ether **2**, more highly oxidized than **1** but less so than **3**, was of particular interest. Its thermal isomerization between 190 and 500 °C is represented by the yield vs. temperature diagram in Figure 1.

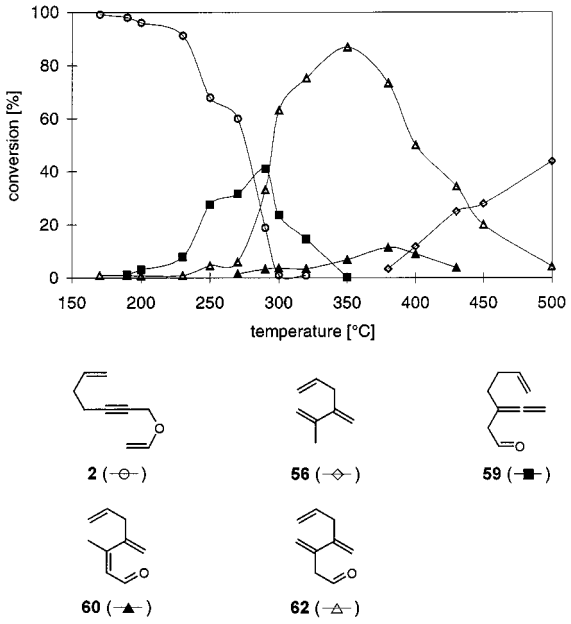
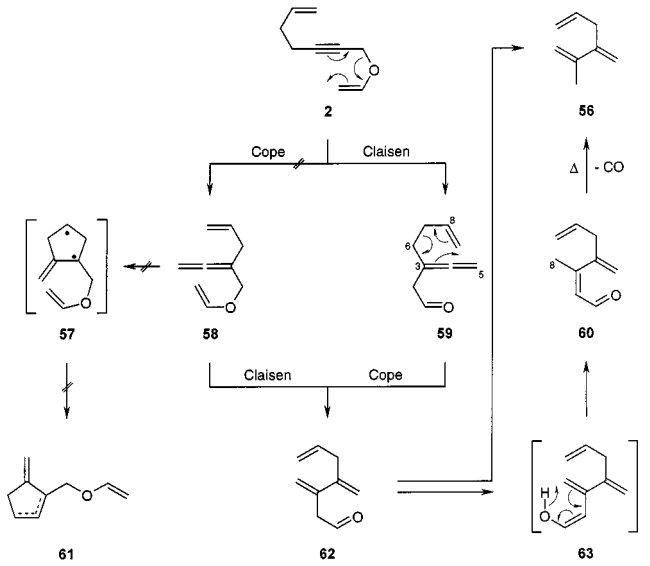


Figure 1. Temperature profile for the pyrolysis of 7-vinyloxyhept-1-en-5-yne (**2**)

The rearrangement set in at a comparatively low temperature (see the other isomerizations described below), and at 300 °C the substrate had been fully converted. The primary product was the allene **59**, which reached its peak concentration of 41% at 290 °C. Beginning at ca. 250 °C, 3,4-dimethylenehept-6-enal (**62**) was produced, and reached its maximum concentration (87%) in the product mixture at 350 °C. As well as these two main isomerization products of **2**, up to 12% of 3-methyl-4-methylenehept-6-enal (**60**) was produced. At higher temperatures (400–500 °C), increasing amounts of 2-methyl-3-methylenehexa-1,5-diene (**56**) could be detected; this hydrocarbon was the main pyrolysis product above 450 °C. Up to 400 °C these products were the only ones produced, but at higher temperatures the reaction becomes increasingly complex, yielding numerous other isomerization and fragmentation products as shown by GC/MS analysis. Altogether the process constitutes a preparatively useful route to the trienal **62**. The sequence of events during the pyrolysis of **2** is charted in Scheme 10.

The initial [3.3]sigmatropic rearrangement of the substrate can follow either a Cope or a Claisen path. Since neither the product of the former process (**58**) or its cyclization product (**61**), which might be produced through the intermediate **57** in analogy to the **52** → **54** cyclization, could be detected in the pyrolysate, the Claisen process evidently won the competition in this first step. Actually this is not surprising, since a C–O double bond is generated in this isomerization (see below). Intermediate **59** then underwent the expected Cope process to furnish the main product, **62**. To account for the other identified pyrolysis products we propose that **62** then enolized, resulting in the generation



Scheme 10. Tandem pericyclic processes in the pyrolysis of **2**

of the cross-conjugated enol **63**, which was converted into **60** by way of a 1,5-hydrogen shift. Finally, the triene **56** could be produced by decarbonylation of **60** and/or **62**, carbon monoxide loss being a well established process at higher temperatures.[18]

b) Pyrolysis of 7-Methoxyhept-1-en-5-yne (4): Proceeding from **2** to **4**, we now encountered a rearrangeable system that for the first time contained a subunit that could be split off during the cascade process. This was disadvantageous from the point of view of atom economy, but it could in principle result in a simpler product mixture composition. Actually, this was not the case for **4**, at least not at higher reaction temperatures. The temperature profile for the pyrolysis of this ether between 200 and 600 °C is shown in Figure 2.

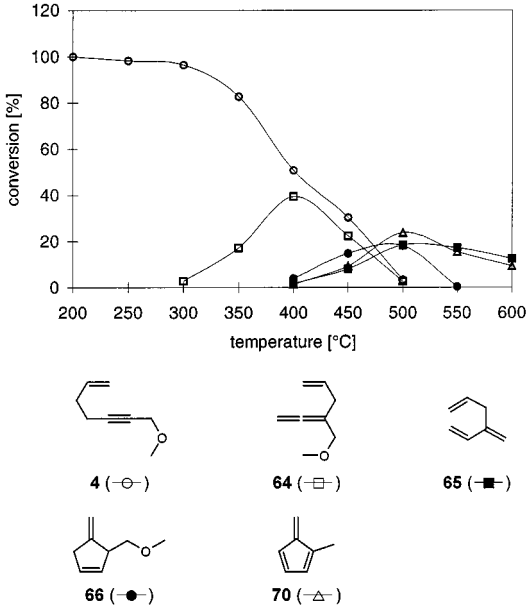
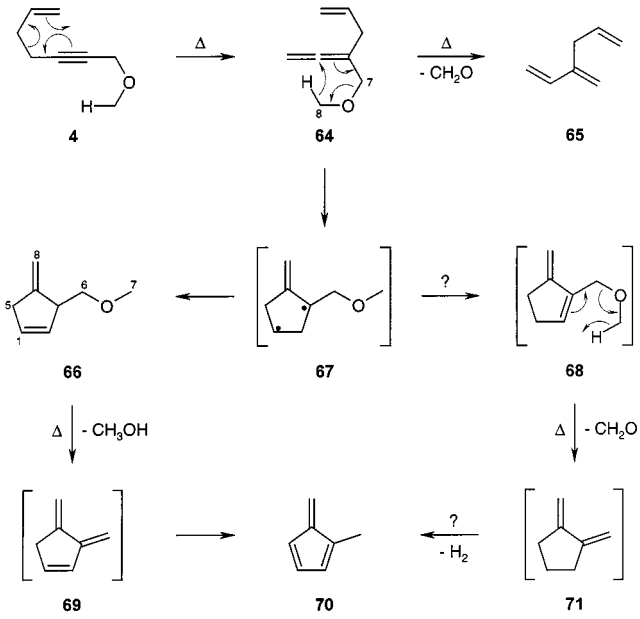


Figure 2. Temperature profile for the pyrolysis of 7-methoxyhept-1-en-5-yne (**4**)

As can be seen from the diagram, this substrate was thermally more stable than **2**. Whereas **4** was still the predominant component of the pyrolysate at about 400 °C, no **2** survived under these conditions. The only product generated from **4** up to this temperature was the allene **64**, produced in ca. 40% yield. From there on, essentially three products were formed: 3-methylenehexa-1,5-diene (**65**), 3-methoxymethyl-4-methylenecyclopentene (**66**), and 2-methylfulvene (**70**); at ca. 500 °C these were present in roughly equal amounts. Above this temperature, aromatization set in, and benzene and toluene were chiefly formed from the above precursors. The formation of **64** and **65** is self-explanatory (Scheme 11): the former is the result of a Cope rearrangement that clearly requires less energy (see below) than the ene reaction producing the latter product.



Scheme 11. Tandem pericyclic processes in the pyrolysis of **4**

Higher temperatures favored five-membered ring formation, and **64** was converted into **66** by way of **67** through a mechanism similar to the one discussed above. The simplest route to the fulvene **70** could involve loss of methanol from **68** to give the [3]dendralene[17] **69**, which would stabilize itself in turn by a hydrogen shift. The thermal cleavage of unsaturated methyl ethers to dienes and methanol is a known process that takes place in high yield.[19]

It was again surprising that the conjugated isomer of **66**, the ether **68**, was missing from the pyrolysate, although it could in principle easily have been generated through a 1,2-hydrogen shift. Derivative **68**, however, meets the prerequisites for undergoing retro-ene cleavage to give **71** (loss of formaldehyde). To reach **70** from this diene intermediate, though, would require hydrogen loss. 1,2-Bismethylenecyclopentane (**71**) could not be detected among the pyrolysis products.

c) Pyrolysis of Nona-1,7-diene-5-yne (5): In this hydrocarbon the initial isomerization step could be either a Cope rearrangement or a 1,5-hydrogen shift. Since both processes

occur with comparable activation energies (see below) it was difficult to predict the outcome of this primary competition. When a mixture of *cis*/*trans*-**5** was pyrolyzed between 300 and 500 °C, essentially three products were formed (Figure 3), two of them − 1-allyl-3-methyl-2-methylenecyclobutene (**73**) and 2-allylcyclohexa-1,3-diene (**75**) − clearly being intermediates, and the other, benzene (**76**), being produced as a final product. It was shown by GC analysis that thermal equilibration between the diastereomers of the starting material took place.

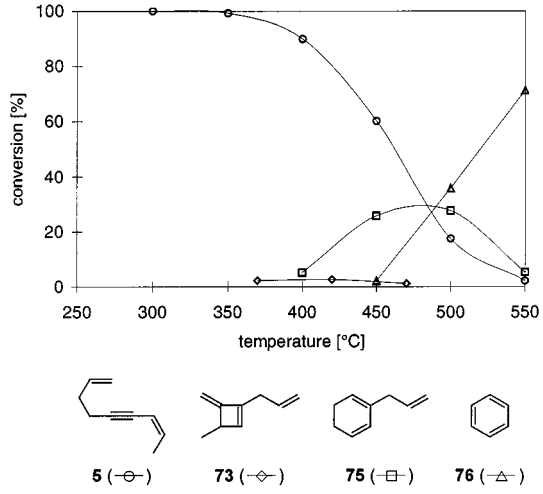
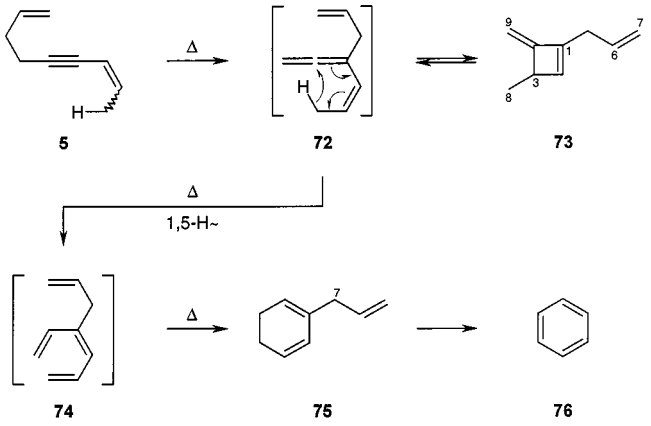


Figure 3. Temperature profile for the pyrolysis of nona-1,7-dien-5-yne (**5**)

At the relatively high temperature of 450 °C, about 60% of the substrate still survived, whereas **75** made up 26% of the pyrolysate. While **73** was vanishing from the product mixture (ca. 2%), **76** was beginning to become detectable (ca. 2%). In interpretation of the formation of these hydrocarbons we propose that the initial step of this tandem sequence was the formation of the Cope product **72**. With its hexa-1,2,4-triene substructure it was able to participate in the expected 1,5-hydrogen shift, which would produce 3-vinylhexa-1,3,5-triene (**74**) as a reactive intermediate. 1,5-Hydrogen shifts of this type have been investigated thoroughly by Okamura and co-workers, who used them in their extensive studies on novel routes to Vitamin A and D derivatives.[20] Conjugated trienes are known to electrocyclize between 350 and 400 °C,[21] and the ring-closure of **74** to the cyclohexadiene **75** hence comes as no surprise (Scheme 12).

The aromatization of cyclohexa-1,3-diene at temperatures above 500 °C by radical processes is well known,[22] and since **75** had to eject a (resonance-stabilized) allyl radical during this process, benzene (**76**) formation was already active at lower temperatures. Unexpected in view of the reaction matrix (Scheme 1) was hydrocarbon **73**. It should be kept in mind, though, that the number and type of pericyclic processes were deliberately restricted when this scheme was composed. Had other pericyclic reactions, such as the important electrocyclizations, been included, the scheme would, of course, have been more complex. Cyclobutene **73** is indeed an electrocyclization product. Normally the equilibrium between a 1,3-butadiene and its cyclobutene



Scheme 12. Tandem pericyclic processes in the pyrolysis of **5**

valence isomer lies completely on the side of the open-chain product. If, however, one of the double bonds of the diene is replaced by an allene group, the situation begins to reverse, because the high endothermicity of the allene grouping can overcome the ring strain of the cyclobutene ring. Thus, an equilibrium between penta-1,2,4-triene (vinylallene) and 3-methylenecyclobutene is established when these hydrocarbons are heated to approximately 170 °C in a static reactor.[23] The vinylallene derivative **72** cyclized analogously to **73**, with the additional double bond presumably contributing to the ring-forming process. Note that no methylenecyclopentene derivative was produced from **72**, although the structural prerequisites were fulfilled (see above); probably the cyclization temperature was too low for this process to compete.

d) Pyrolysis of *trans*-1-Hex-5-en-1-ynyl-2-methylcyclopropane (6): The pyrolysis of the cyclopropylacetylene **6** completed the prototype tandem processes summarized in the first row of Scheme 1. As shown in the conversion diagram (Figure 4), *trans*-**6** was stable up to 300 °C under flow conditions.

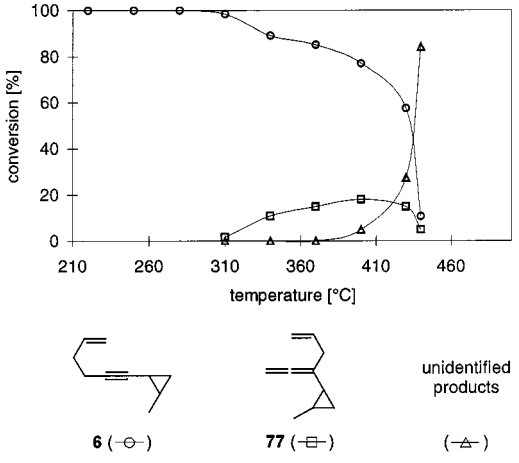
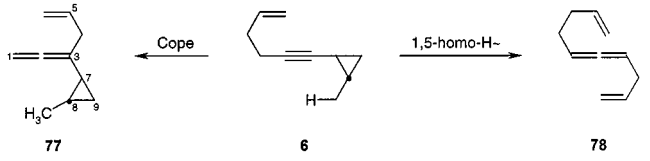


Figure 4. Temperature profile for the pyrolysis of 1-(hex-5-en-1-ynyl)-2-methylcyclopropane (**6**)

At ca. 310 °C, small amounts of 3-(2-methylcyclopropyl)hexa-1,2,4-triene (**77**) were formed. Increases in the

temperature in small steps caused an increase in the yield, near 20% conversion being attainable at 430 °C. At that point a veritable explosion of complexity set in, resulting in at least 20 different products, all of them isomers of the starting material **6** as shown by GC/MS analysis. Needless to say, separation of this mixture was impossible. In the hope of reducing the number of isomerization products, the pyrolysis was repeated at 200 °C in a static system. In addition to **6** (78%) and **77** (8%, GC analysis), the same complex pyrolysate was generated again. Whether **6** really preferred the Cope process over the 1,5-homo hydrogen shift, which would produce the $C_{10}H_{14}$ hydrocarbon **78**, could not be determined. The activation energy of the conversion of 1-ethynyl-2-methylcyclopropane to hexa-1,2,4-triene is unknown[9] (Scheme 13).



Scheme 13. Tandem pericyclic processes in the pyrolysis of **6**

From what we have learned so far, it is obvious that both **77** and **78** could serve as entries for other thermal interconversions. For example, they could both participate in a subsequent pericyclic step that would produce 4-vinylocta-1,4,7-triene or − as allylallenes − they could form methylene cyclopentane-1,3-diyl intermediates (see above). Other reaction channels could be opened up from either of these species, yielding still further $C_{10}H_{14}$ isomers. Clearly, this thermal process of a hydrocarbon without a built-in point of fracture is preparatively useless (see below).

2. Thermal Isomerization of the Enol Ethers 7, 9, and 10

The second row of Scheme 1 displays a collection of enol ethers. Comparing these substrates with those of row 1, we note that the allyl group in **2**−**6** has been replaced by a vinyloxy substituent. In the section below, the pyrolyses of the model systems **7**, **9**, and **10** are discussed. Since CC double bonds are converted into carbonyl groups in all these processes the driving force for the respective isomerizations should be high.

a) Pyrolysis of 1,4-Bis(vinyloxy)but-2-yne (7): As seen in Figure 5, and in line with expectations, the isomerization set in at very low temperatures (< 180 °C), and at 280 °C none of the starting material remained. Unfortunately, the primary product, produced in approximately 60% yield at 240 °C, could not be isolated by preparative gas chromatography because of its low stability. By GC/FT-IR analysis, however, it could be identified as 3-vinyloxymethylpenta-3,4-dienal (**79**), its intense allene band at 1969 cm^{-1} being of particular diagnostic value.

Between 280 and 320 °C the main product of the isomerization was 3,4-dimethylenehexane-1,6-dial (**80**), separable by preparative gas chromatography and identified by the usual spectroscopic methods (see Exp. Sect.). Beginning at 280 °C, small amounts of 4-methyl-3-methylenepenten-4-

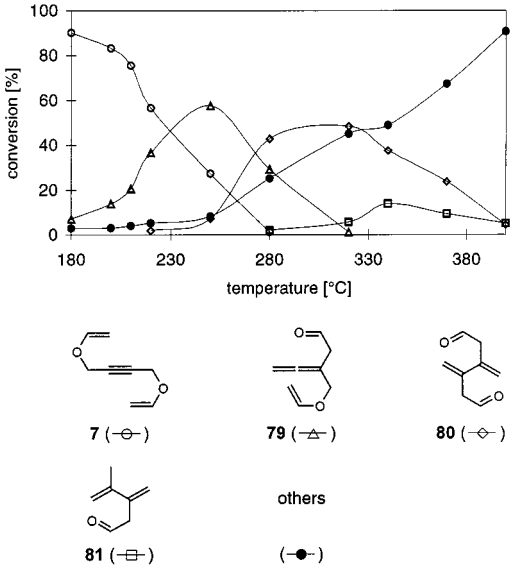
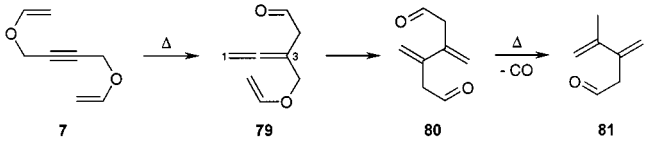


Figure 5. Temperature profile for the pyrolysis of 1,4-bis(vinyloxy)but-2-yne (**7**)

al (**81**) were produced. Clearly, the reaction had taken place as expected, as a tandem Claisen rearrangement to yield the desired **80** (Scheme 14).



Scheme 14. Tandem pericyclic processes in the pyrolysis of **7**

This dialdehyde, however, was unstable under the reaction conditions, and it was decarbonylated to the aldehyde **81**. Looking back to Figure 5, it is apparent that the reaction is not a "clean" one; side products were already being formed at ca. 250 °C and dominated the reaction above 310 °C. According to GC/MS analysis, these (unidentified) products were either isomers of **7**, **79**, and/or **80** or cleavage products. Before judgment is passed on the preparative value of the **7** → **80** isomerization, it should be kept in mind that 2,3-difunctionalized buta-1,3-dienes are difficult to prepare by other routes, fulgenic acid (buta-1,3-diene-2,3-dicarboxylic acid) and its anhydride being particularly well known examples.[24]

b) Pyrolysis of 1-Methoxy-4-vinyloxybut-2-yne (9): The pyrolysis of **9** was a remarkable process: it was clean (no side products), and it yielded only two products (Figure 6).

Surprisingly, however, these were not the expected products (see below), but 2-methoxymethylbuta-1,3-diene (**83**) and isoprene (**86**, Scheme 15).

If it is postulated that **9** should prefer the Claisen process over the retro-ene cleavage (see above), the initial pyrolysis product should be **82**, not the allene vinyl ether **84**. If **82** were subsequently to fragment by a retro-ene process, the dienal **85** should result. Neither **82** nor **85** were isolated, however, although we should at least expect **85** not to be particularly sensitive. After all, the dialdehyde **80** is an isol-

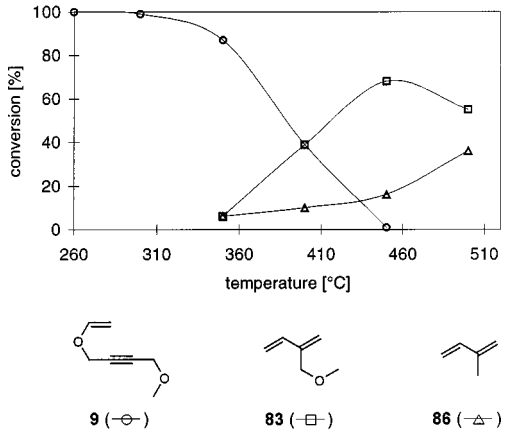
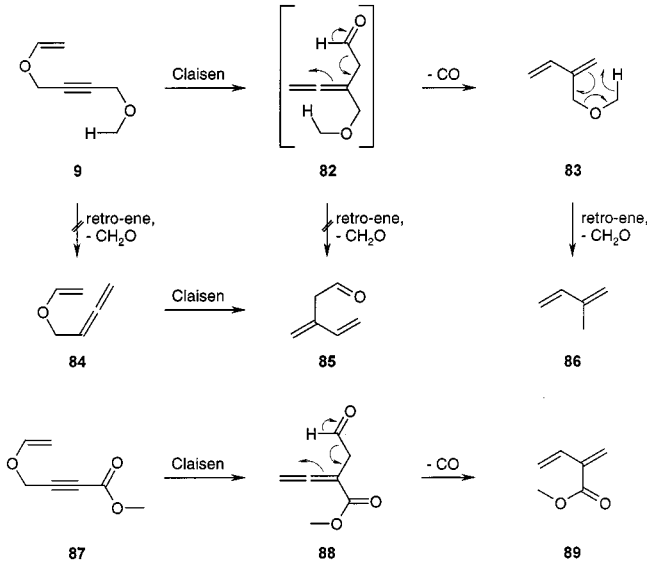


Figure 6. Temperature profile for the pyrolysis of 1-methoxy-4-vinyloxybut-2-yne (**9**)



Scheme 15. Tandem pericyclic processes in the pyrolysis of **9**

able product in the pyrolysis of **7**. Intermediate **82** bypassed retro-ene cleavage by splitting off carbon monoxide to produce **83**, the main pyrolysis product. For this latter ether, only one reaction path was open. This was the retro-ene cleavage to **86**, evidently the most energy-demanding step in the whole cascade. Interestingly, Jung and Zimmerman observed a similar process during flash vacuum pyrolysis of methyl 4-vinyloxybut-2-ynoate (**87**), which initially resulted in the allene ester **88**.[25] At higher temperatures, **88** was converted into methyl 2-methylene-but-3-enoate (**89**) by decarbonylation, in a fragmentation process involving hydrogen transfer from the formyl substituent to the central carbon atom of the allene group by way of a five-membered transition state.

c) Pyrolysis of 6-Vinyloxyhex-2-en-4-yne (10): The pyrolysis of this substrate, carried out between 100 and 600 °C, produced one of the most complex product mixtures encountered in this study. As shown in Figure 7, isomerization of the vinyl ether set in at low temperatures, and conversion of **10** was already complete at 300 °C.

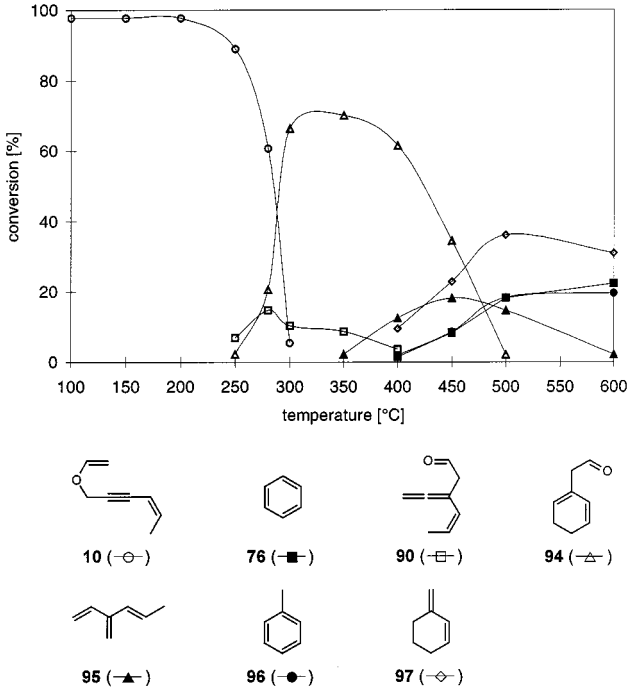
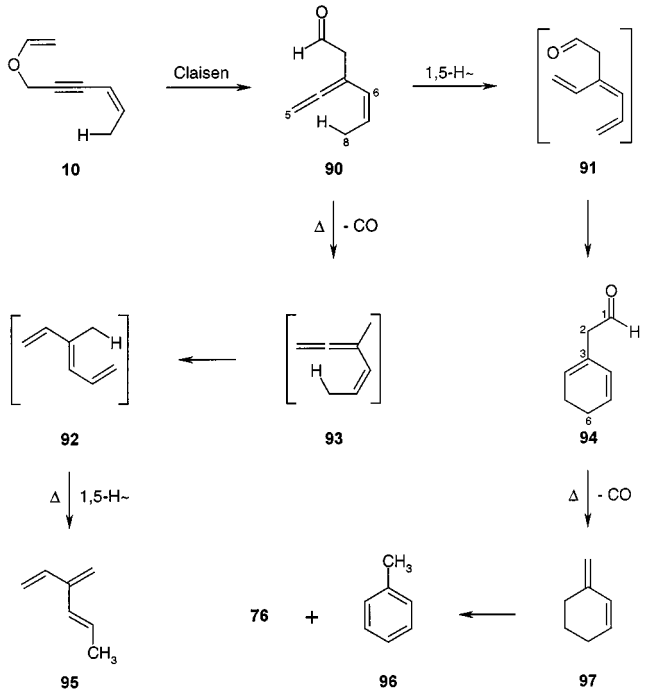


Figure 7. Temperature profile for the pyrolysis of 6-vinyloxyhex-2-en-4-yne (**10**)

The main product obtained up to this temperature was the cyclohexadienyl acetaldehyde **94**. It was produced in 60−70% yield between 300 and 400 °C, making this process an attractive preparative route to this diene system. As a side product, 3-(prop-1-enyl)penta-3,4-dienal (**90**) was generated. Above this temperature the thermolysis became more and more intricate and the product mixture was increasingly composed of degradation products. Among these, the cross-conjugated hydrocarbon 3-methylenehexa-1,4-diene (**95**), benzene (**76**), toluene (**96**), and 3-methylenecyclohexene (**97**) could be found, the aromatic products becoming − as expected − more and more important as the temperature increased. The formation of all of these products can be interpreted by the transformations summarized in Scheme 16.

The tandem sequence began with the Claisen isomerization of **10** to the aldehyde **90**, which subsequently evidently underwent the expected 1,5-hydrogen shift. The anticipated isomerization product, **91**, however, did contain a hexa-1,3,5-triene subsystem and so could readily undergo electrocyclization to give the cyclohexadiene derivative **94**. Since **90** and **94** are both aldehydes, we should not be surprised to see them suffer decarbonylation as the temperature is increased. Whereas the cleavage product from **94** (hydrocarbon **97**) was indeed isolated, the intermediate produced from **90** (the vinyl allene **93**) still had several steps ahead of itself before it could reach a stable situation. Through a 1,5-hydrogen shift, a process known to take place in methyl-substituted vinyl allenes,[20] it rearranged to its linearly conjugated isomer **92**, which again fulfilled the prerequisites for a 1,5-hydrogen shift and isomerized in turn to the [3]den-



Scheme 16. Tandem pericyclic processes in the pyrolysis of **10**

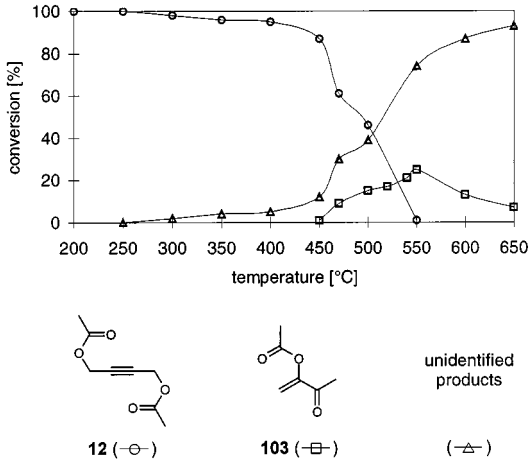
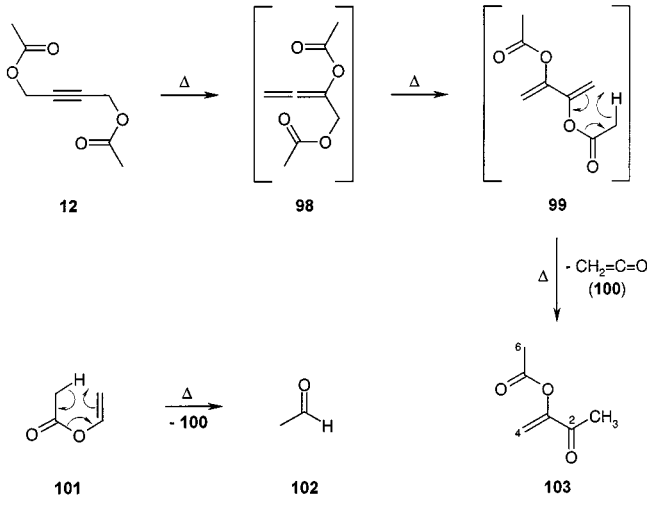


Figure 8. Temperature profile for the pyrolysis of 1,4-bis(acetoxy)-but-2-yne (**12**)



Scheme 17. Tandem pericyclic processes in the pyrolysis of **12**

dralene **95**. Remarkable in these latter processes are the observations that the vinyl allene **93** did not cyclize to a methylenecyclobutene derivative (see above) and that the *trans* isomer of **95** was formed, the *cis* diastereomer being the expected isomerization product. In view of the relatively high temperatures it seems reasonable to assume that both **93** and **95** preferred their thermodynamically more stable isomers under the conditions of their generation. Finally, aromatization and cleavage of **97** to give toluene (**96**) and benzene (**76**) is a known high temperature process.[26]

3. Thermal Isomerization of 1,4-Diacetoxybut-2-yne (12)

In this third category (row three in Scheme 1) we had so far studied only the pyrolysis of the diester **12**; this, however, is a relative of the monoester **3**, the thermal behavior of which was already discussed in the introductory chapter. Although **12**, with its two ester groups as the only rearrangeable substituents, was expected very probably to require high isomerization temperatures and so presumably yield complex product mixtures, it was not expected that its pyrolysis would give such disappointing results as were actually observed (Figure 8).

As shown in this diagram, **12** was indeed thermally very stable. Significant conversion of starting material only set in at approximately 450 °C, a temperature at which numerous products were also beginning to be formed in small concentrations. As the only isolable and identifiable product, 3-acetoxybut-3-en-2-one (**103**) was obtained in 25% yield at 550 °C. To explain these results we postulate that the intended tandem process from **12** to **99** by way of **98** did occur as anticipated, but that both intermediates fragmented under the harsh reaction conditions (Scheme 17).

The butadiene **99** was also able to lose ketene (**100**) to furnish **103**, in a process similar to the one described by Allan and co-workers[27] for the vinyl ester of acetic acid (**101**), which on heating between 500 and 550 °C in the gas phase fragmented into acetaldehyde (**102**) and ketene (**100**).

4. Thermal Isomerization of the Methyl Propargyl Ethers 17 and 18

a) Pyrolysis of 6-Methoxyhex-2-en-4-yne (17): The ether **17** (mixture of isomers) represented an attempt to couple a retro-ene process to a 1,5-hydrogen shift. Although results of preparative significance were not expected (see below), the compound was pyrolyzed between 300 and 650 °C to add another piece to our increasingly complete mosaic of thermal pericyclic tandem processes. As shown in Figure 9, the ether was thermally very stable. Significant isomerization was observed only above 450 °C and gave only one product: 1,3-cyclohexadiene (**107**). This constituted ca. 60% of the pyrolysate at 600 °C. The only other product formed was benzene (**76**), which became the major component

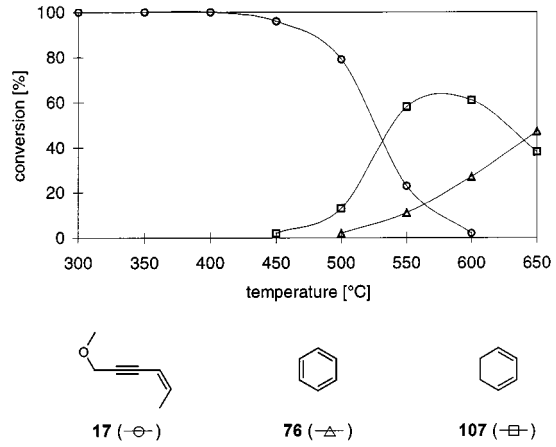
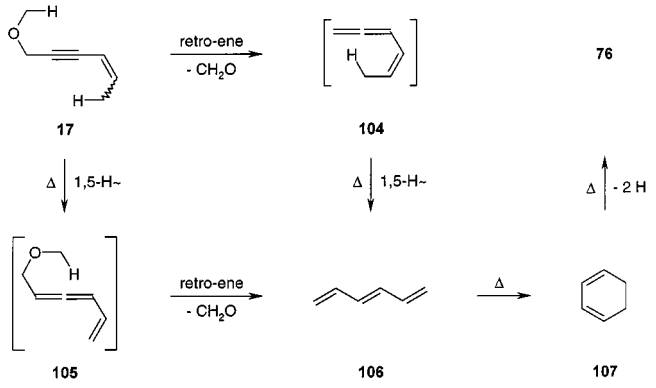


Figure 9. Temperature profile for the pyrolysis of 6-methoxyhex-2-en-4-yne (**17**)



Scheme 18. Tandem pericyclic processes in the pyrolysis of **17**

above 650 °C. Scheme 18 effortlessly explains these observations.

In a manner comparable to a knight′s move in chess, the triene **106** was produced either by a retro-ene process followed by a 1,5-hydrogen shift, by way of **104**, or by the reversed sequence of these steps, via **105**. Since neither **104** nor **105** accumulated during the process, the activation energies of both pericyclic steps appear to be quite similar (see below). Although both **104** and **105** are vinylallene derivatives, neither cyclized to a methylenecyclobutene at these high temperatures, as discussed previously. The cyclization of **106** to **107** was expected, as was its aromatization to **76** (see above).

b) Pyrolysis of *trans*-1-(3-Methoxy-prop-1-ynyl)-2-methylcyclopropane (18): With its multifarious structural features, we would expect a varied thermal behavior for the cyclopropylacetylene **18**. This was indeed the case, although, unfortunately, at no temperature was one single pyrolysis product favored over its isomers or cleavage products. The tandem process was triggered relatively late (at ca. 400 °C) and first produced small amounts of 7-methoxyhepta-1,4,5-triene (**108**). From 450 °C onwards three additional products were generated; these were cyclopentenes **111** and **112** (formed as a mixture of (*E*)/(*Z*) isomers that could not be separated by gas chromatography) and toluene (**96**). A further increase in the pyrolysis temperature caused increased toluene production, accompanied above ca. 570 °C by rising quantities of benzene (**76**) (Figure 10).

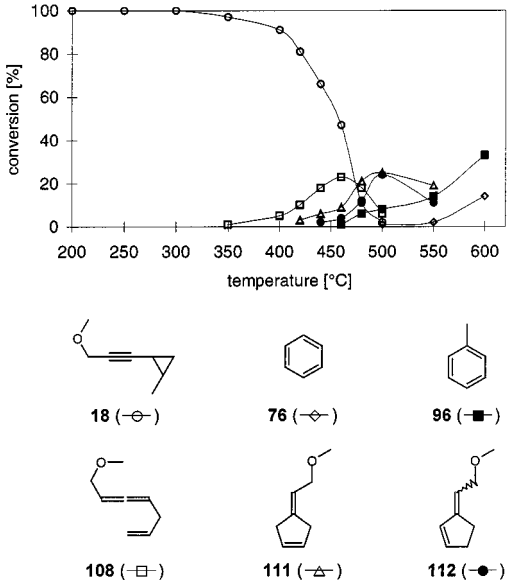
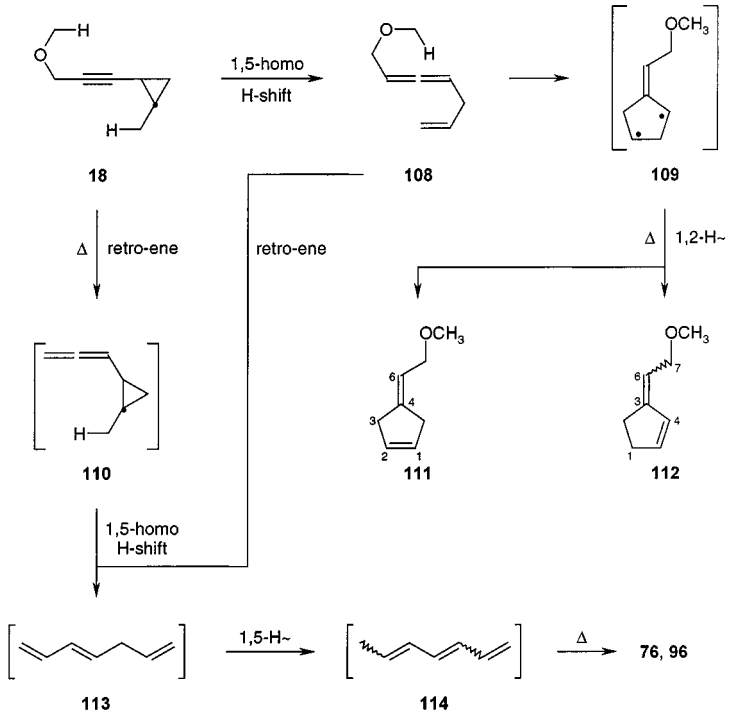


Figure 10. Temperature profile for the pyrolysis of 1-(3-methoxy-prop-1-ynyl)-2-methylcyclopropane (**18**)

Altogether, the pyrolysis was not very "clean" and many other products were produced in small yields (Scheme 19). At ca. 450 °C the sum of these "impurities" amounted to 25−35% of the pyrolysate. The most interesting products in these experiments were the five-membered ring compounds **111** and **112**. All the other components of the thermolysis mixture could be accounted for by mechanisms similar to those already presented several times in this study. In other words, **18** entered into the isomerization sequence by conversion into **108** (1,5-homo hydrogen shift). By a retro-ene process this lost formaldehyde to provide hepta-1,3,6-triene (**113**), which rearranged by a 1,5-hydrogen shift into its conjugated isomer **114**. The most likely thermal reaction path available for this hydrocarbon was its cyclization to toluene (**96**) and benzene (**76**). Obviously, **113** could also be reached from **18** by way of **110**. The primary product was a derivative of allylallene (**45**, see above) and, as such, prone to intramolecular cycloaddition (by 1,5-carbon bridging) to yield the diradical **109**. Like the parent system **46**, **109** was able to undergo 1,2-hydrogen shift reactions in two different directions, furnishing the nonconjugated diene ether **111** or its conjugated isomer **112** as a mixture of diastereomers. As methyl allyl ethers, both of these pyrolysis products in principle could in principle participate in further pericyclic reactions, and this may be part of the reason why the composition of the product mixture is so complex in this case.

5. Thermal Isomerization of the Enyne Hydrocarbons 19 and 20

This study began with the presentation of the pyrolytic behavior of a hydrocarbon, deca-1,9-dien-5-yne (**1**), and we also wish to end it with the description of the behavior of two hydrocarbons under flash vacuum conditions: octa-2,6-



Scheme 19. Tandem pericyclic processes in the pyrolysis of **18**

dien-4-yne (**19**) and 1-methyl-2-(pent-3-en-1-ynyl)cyclopropane (**20**).

a) Pyrolysis of Octa-2,6-dien-4-yne (19): Although this divinylacetylene in principle had many interesting options to undergo sequential reactions after an initial 1,5-hydrogen shift had converted it into octa-1,3,4,6-tetraene, these possibilities evidently could not be seized under the prevailing reaction conditions. As shown in Figure 11, the substrate was essentially stable up to 500 °C.

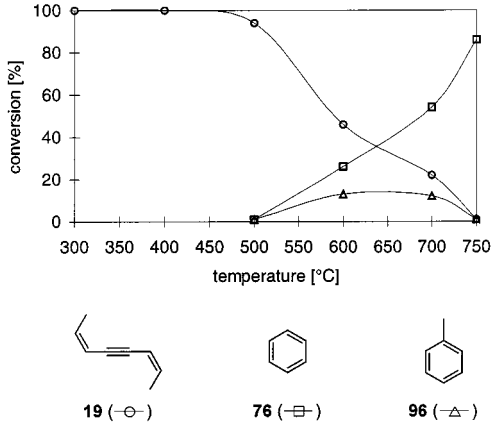


Figure 11. Temperature profile for the pyrolysis of octa-2,6-dien-4-yne (**19**)

Above this temperature, only two (unremarkable) products were produced: toluene (**96**) and benzene (**76**). Since not a trace of any intermediate could be isolated in this case it appears futile to speculate on the pathways producing these simple aromatics. The primary divinylallene mentioned could in principle give rise to acyclic four-, five-, and six-membered isomerization products, all of which could be degraded to **76** and **96**. Clearly, the initiation step in this transformation produced such an energy-rich intermediate that no discrimination between the ensuing isomerizations and/or fragmentations could take place any longer.

b) Pyrolysis of *trans*-1-Methyl-2-(pent-3-en-1-ynyl)cyclopropane (20): Replacement of one of the double bonds in **19** by a cyclopropane ring gives hydrocarbon **20**. Since this is clearly more strained than the divinylacetylene **19**, one would expect it to isomerize under milder conditions and hence engage in a more specific pericyclic tandem sequence. On the other hand, because of the numerous isomerization possibilities "built" into **20**, we might expect a rather complex composition of the pyrolysis mixture. By and large these assumptions were born out by experiment. The rearrangement began at ca. 320 °C, 100 degrees lower than that of **19**, and at 460 °C all of the starting material had been transformed. Depending on the temperature, three hydrocarbons were obtained: 2-vinylcyclohexa-1,3-diene (**75**), 3-but-2-enylidenecyclopentene (**119**), and benzene (**76**), which constituted ca. 50% of the pyrolysate at 500 °C (Figure 12).

Preparatively, the tandem process is of very limited use, since these three hydrocarbon products are − as shown by GC/MS analysis − accompanied by numerous other products formed in yields too low to enable separation and characterization. Note also that four diastereomers of **119** are possible. Since the GC fraction containing this hydrocarbon could not be further separated, the structure assignment shown must remain speculative. A mechanistic scheme accounting for the formation of **119**, **75**, and **76** is shown in Scheme 20.

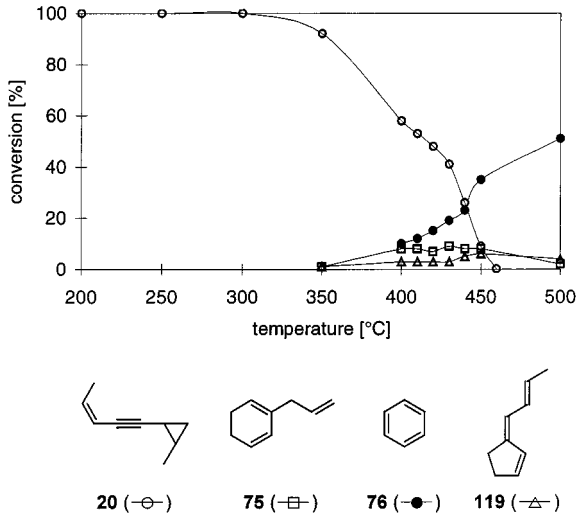
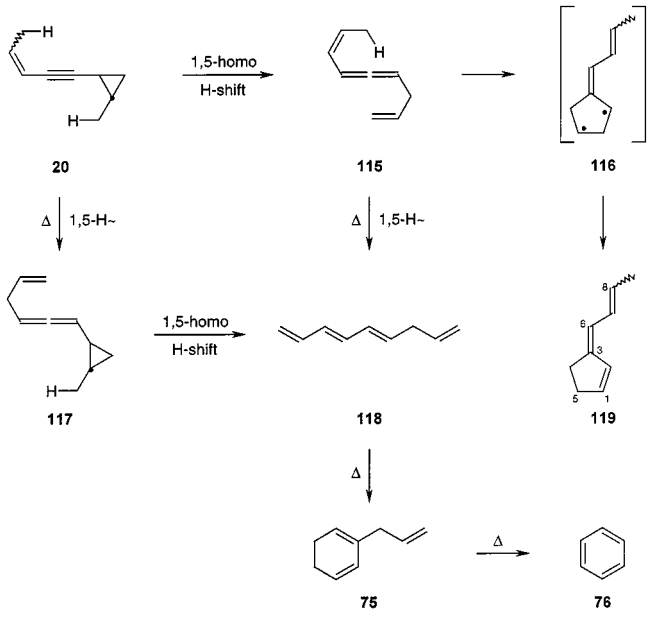


Figure 12. Temperature profile for the pyrolysis of 5-(2-methylcyclopropyl)pent-2-en-4-yne (**20**)



Scheme 20. Tandem pericyclic processes in the pyrolysis of **20**

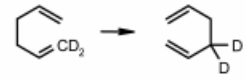
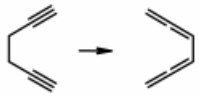
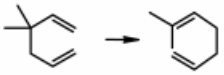
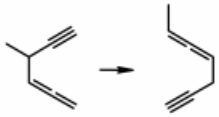
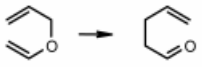
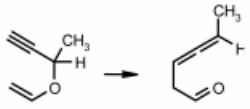
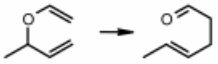
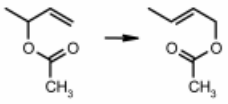
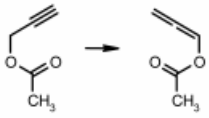
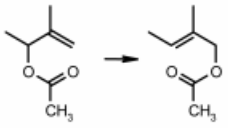
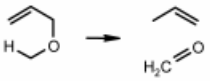
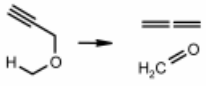
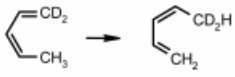
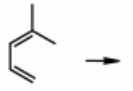
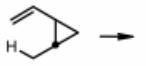
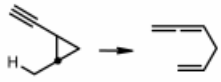
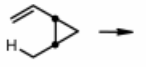
Compound **20** was converted into **118** either through a 1,5-homo hydrogen-shift/1,5-hydrogen shift tandem sequence, or by the reverse sequence of these steps, passing through intermediates **115** and **117** en route. As an allyl allene, **115** was able to participate in the cyclization step so characteristic of this arrangement of double bonds, to provide **119** by way of the diyl **116**. Since **118** is the linear isomer of the branched tetraene **74** (2-allylhexa-1,3,5-triene) discussed above in the pyrolysis of **5** (**20** and **5** are both C_9H_{12} hydrocarbons), we would expect comparable behavior in this intermediate. This was the case, both compounds first cyclizing to 2-allylcyclohexa-1,3-diene (**75**), which subsequently fragmented to become **76** by loss of an allyl radical − presumably after having equilibrated to other cyclohexadiene isomers through a succession of 1,5-hydrogen shifts.

Discussion

In this study we have investigated the flash vacuum pyrolyses of 12 substrates with the common feature that they all possess a core unit derived from but-2-yne. These acetylenes can in principle all undergo tandem isomerizations composed of various sigmatropic steps. These pericyclic processes belong to six different categories: the Cope, Claisen, Claisen ester, retro-ene, 1,5-hydrogen shift, and 1,5-homohydrogen shift rearrangements. Before the above tandem reactions are discussed and compared, it is appropriate to recall the activation parameters for the partial steps out of which the sequential processes are composed. Although not known for all these model reactions, detailed kinetic investigations have been performed for some of them. Furthermore, comparison with the corresponding model compounds in which the triple bond has been replaced by a double bond should turn out to be helpful.

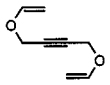
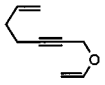
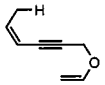
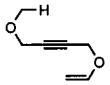
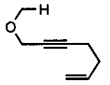
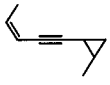
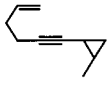
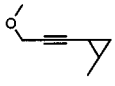
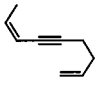
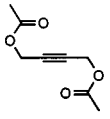
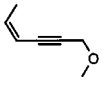
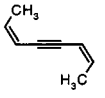
As a first glance at Scheme 21 (which lists the activation parameters for thermal pericyclic reactions of pertinent olefinic and acetylenic substrates) shows, many more kinetic data have been reported for the olefinic model reactions.

Comparing the entries of the left half of this collection, we note that the Cope and the Claisen rearrangements possess the lowest Arrhenius activation energies and A factors. Hydrogen shifts, whether of the 1,5- or 1,5-homo-type, come next. In the latter case there is a pronounced difference between the *cis* and the *trans* isomers of 1-methyl-2-vinylcyclopropane (last entry, left half of Scheme 21). Whereas the activation parameters for the *cis* compound indicate a concerted process (symmetry-allowed homodienyl-1,5-hydrogen shift or retro-ene rearrangement), the isomerization of the *trans* isomer to the diene, which requires more drastic conditions, is thought to be triggered by a *trans*→*cis* isomerization through a diradical intermediate.[37] Finally, the highest activation energies were found for the Claisen ester rearrangement and the retro-ene cleavage. Because of the linearity of the triple bond, one would intuitively expect that replacement of a CC double bond by a CC triple bond in any of the model systems (see right half of the scheme) should result in an increase in the activation energies. After all, this functional group interchange should increase the distance between the terminal atoms of the reacting system. As has been known for a long time, however, this rate retardation is not observed.[16] Acetylenes are known to participate in many pericyclic reactions, with rates usually of the same order as those of their olefinic counterparts, and sometimes isomerize even faster. The reason can be found in the considerable deformability of the triple bond, a fact also illustrated by the generation of cycloalkynes such as cyclopentyne and cyclohexyne.[42] Obviously, the geometric and stereochemical properties and requirements of the transition states of the olefinic and acetylene processes will differ considerably, but both systems can

	olefinic	E_a, kcal · mol^{-1}	log A	ref	acetylenic	E_a, kcal · mol^{-1}	log A	ref.
Cope		34.3	10.36	[28]		32.7	10.49	[16d]
		34.2	10.55	[29]		34.4	11.4	[38]
		34.6	11.13	[30]		30.8	10.84	[15]
Claisen		30.6	11.7	[31]		act. parameters unknown; isom. temp.: 250 °C		[16a]
		27.9	11.3	[32]				
Ester		40	11.3	[33]		act. parameters unknown; isom. temp.: 630 °C		[39]
		45.4	13.5	[34]				
Retro--ene		39.2-43.5	$\Delta S^{\neq}$ = -8.4 to -12.7 e.u. at 300 °C	[16c]		39.5-43.3	$\Delta S^{\neq}$ = -6.3 to -12.8 e.u. at 300 °C	[16c]
1,5-H~		36.3	11.93	[35]		47.6	12.3	[40]
		36.2	11.72	[36]		47.4		[41]
1,5-homo--H~		48.6	14.7	[37]		act. parameters unknown; isom. temp. for *trans*-isomer: > 300 °C		[9]
		31.2	11.03	[37]				

Scheme 21. Activation parameters for olefinic and acetylenic pericyclic processes

achieve bonding between the termini of the reacting systems with comparable ease. The entries of the ''acetylenic half'' of Scheme 21 illustrate these generalizations clearly. Replacement of a double bond in hexa-1,5-diene by a triple bond (generation of **22**) influences the activation parameters only slightly. Even with a second ethynyl group the corresponding hydrocarbon, hexa-1,5-diyne, shows the typical Cope parameters. Although no quantitative data for acetylenic Claisen and Claisen ester isomerizations have so far been reported, the observed rearrangement temperatures, 250 and 630 °C, respectively, are in accordance with a prediction based on the thermal behavior of the respective olefinic substrates. Agreement between the activation parameters for retro-ene processes of the two classes of compounds is again excellent. And although the known and calculated activation energies for 1,5-hydrogen shifts in

50 % - T, °C		
220		**7**
280		**2**
290		**10**
385		**9**
415		**4**
420		**20**
440		**6**
460		**18**
470		**5**
490		**12**
540		**17**
600		**19**

Scheme 22. Temperatures at which half of the substrate had been consumed

acetylenic and allenic substrates are considerably higher than those of their olefinic counterparts, the pericyclic processes in these cases also require higher activation than, for example, a Cope or Claisen process. Finally, the scarce data available for *trans*-2-ethynynl-1-methylcyclopropane (*trans*-**27**) also seem to indicate that this diastereomer prefers a radical route over a concerted one, for which a far lower isomerization temperature would be expected. It appears, then, that in those acetylenic cases for which no detailed kinetic studies have been carried out, we can employ the corresponding data for their olefin pendants to estimate the relative reactivity of the former with a high degree of confidence. We can hence postulate the following reactivity order: Claisen ≥ Cope > 1,5-hydrogen shift > retro-ene > Claisen ester. For the 1,5-homo-H shift, the position within this series is determined by the stereochemistry of the substituents at the three-membered ring: closer to the high-reactivity end for the *cis* isomer and closer to the retro-ene and ester end for the *trans* isomer.

Can the above considerations also be used to account for the thermal behavior of the tandem processes described in this study? By and large, the answer is yes. Since no kinetic experiments have so far been carried out for any of the coupled isomerizations summarized in Scheme 1, our explanations must obviously remain qualitative. In Scheme 22 we list the 12 acetylenes studied here according to the temperature at which half of the substrate has been isomerized ("50%-T").

The clear "winners" in this table are the Claisen and the Cope processes: the first four entries all incorporate the vinyloxy function. The "losers", on the other end of this list, possess ester functions and have to undergo 1,5-hydrogen shifts involving acetylenes. The center positions are occupied by the three cyclopropane derivatives **20**, **6**, and **18**. These react relatively slowly because of the *trans* arrangement of the substituents at the three-membered ring. It would have been interesting to study a *cis*-substituted cyclopropane able to participate in a Claisen or Cope process, but we have unfortunately been unable to prepare the required substrates.

From the preparative viewpoint, some of the above tandem processes are useful (**1** → **50**, **2** → **62**, **4** → **64**, **10** → **94**). Whether higher selectivity – i.e., less complex pyrolysis mixtures – might on occasion be achievable by introduction of functional groups into the above model compounds is an open question.

Experimental Section

General Remarks: All moisture-sensitive reactions were carried out in flame-dried glassware under nitrogen or argon. Commercially available reagents and solvents were purified and dried when necessary by standard methods immediately prior to use. – IR: Nicolet 320 FT-IR spectrometer. – UV/Vis: HP 8452A Diode Array spectrophotometer. – ^{1}H and ^{13}C NMR: Bruker AC 200 or Bruker DRX 400 at 200.1 and 50.3 or 400.1 and 10.6 MHz, respectively; chemical shifts refer to TMS as internal standard. – MS: Finnigan MAT 8430. – GC/MS: Carlo Erba HRGC 5160 combined with a Finnigan 4515 mass spectrometer. – HRMS: Finnigan MAT 8430 using the peak matching method. – Elemental analyses: Institute of Inorganic and Analytical Chemistry of the Technical University of Braunschweig. – 1-Hexen-5-yne (**22**),[43] 3-vinyloxypropyne (**24**),[14] and 3-methoxypropyne (**25**)[44] were prepared according to published procedures.

Preparation of the Building Block *trans*-1-Ethynyl-2-methylcyclopropane (27): Although both **27** and its precursors have been described previously,[11] we describe the synthesis of this intermediate in full, since the reported spectroscopic data are incomplete. **a) 3-Acetyl-5-methyldihydro-2-furanone (30):** Anhydrous ethanol (2.5 L) was

placed in a 4-L three-necked flask, and sodium (108.0 g, 4.7 mol) was slowly added. The resulting solution of sodium ethoxide in ethanol was cooled to 0 °C and ethyl acetoacetate (**28**) (650 g, 5.0 mol) was added rapidly. Propylene oxide (**29**) (290 g, 5.0 mol) was added over 30 min, and the solution was stirred for 18 h. The ethanol was distilled off in a rotary evaporator, keeping the temperature below 50 °C. Glacial acetic acid (315 g, 5.25 mol) was added to the syrupy residue, followed by ice-water (500 mL). The oily layer was separated and the water phase was extracted with ether. The combined organic phases were neutralized with sodium bicarbonate solution and dried with $MgSO_4$, and after the solvent had been removed by rotary evaporation the remaining oil was fractionated. At 95−97 °C (0.3 mbar), 355 g (50%) of **30** distilled as a colorless liquid. Since the lactone was produced as a mixture of diastereomers, the NMR spectra showed two sets of signals. − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.42/1.45 (d, ^3J = 6.1 Hz, 3 H, CH_3), 2.38/2.40 (m, 2 H, 4-H), 2.43/2.47 (s, 3 H, Ac), 3.78/3.80 (m, 1 H, 5-H), 4.62/4.69 (m, 1 H, 3-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.04/20.97 (q, CH_3), 29.11/29.61 (q, Ac), 31.22/31.80 (t, C-4), 54.36/54.77 (d, C-5), 75.64/76.82 (d, C-3), 172.12 (s, C-2), 199.90/200.10 (s, C-6). − IR (film): $\tilde{\nu}$ = 2983 cm^{-1} (m), 1767 (vs), 1655 (m), 1455 (s), 1423 (m), 1361 (s), 1273 (m), 1181 (m), 1122 (s), 1055 (m), 951 (s). − UV (acetonitrile): λ_{max} (log ε) = 254 nm (2.67).

b) 5-Chlorohexan-2-one (31): Concd. hydrochloric acid (500 mL) was added to a solution of **30** (113.7 g, 0.8 mol) and benzyltriethylammonium chloride (18.2 g, 0.08 mol) in dichloromethane (500 mL), and the reaction mixture was stirred at room temp for 18 h. The aqueous phase was separated and extracted with dichloromethane. The combined organic layers were neutralized with sodium bicarbonate solution and dried with $MgSO_4$. The solvent was removed in vacuo and the residue was purified by fractional distillation: 44.1 g (42%) of **31**, colorless liquid.[11] − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.53 (d, ^3J = 6.1 Hz, 3 H, 6-H), 1.85−2.09 (m, 2 H, 4-H), 2.18 (s, 3 H, 1-H), 2.67 (m, 2 H, 3-H), 3.96 (m, 1 H, 5-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.45 (q, C-6), 30.03 (q, C-1), 33.68 (t, C-4), 40.37 (t, C-3), 58.08 (d, C-5), 207.71 (s, C-2). − IR (film): $\tilde{\nu}$ = 2929 cm^{-1} (m), 2873 (m), 1739 (vs), 1414 (m), 1380 (m), 1359 (m), 1271 (m), 1189 (m), 966 (w). − UV (acetonitrile): λ_{max} (log ε) = 248 nm (2.00). − GC/MS (40 eV): *m*/*z* (%) = 136 [M^+ ^{37}Cl] (2), 134 [M^+ ^{35}Cl] (6), 119 (5), 98 (4), 58 (74), 56 (17), 55 (23), 43 (100), 41 (18).

c) *trans*-1-Acetyl-2-methylcyclopropane (32): Potassium *tert*-butoxide (37.0 g, 0.33 mol) was suspended in anhydrous ether (600 mL) in a 1-L three-necked flask, equipped with mechanical stirrer and reflux condenser. The mixture was stirred and **31** (44.1 g, 0.33 mol) was added at such at rate that the ether refluxed gently. The reaction mixture became increasingly viscous during the addition, requiring vigorous stirring. After addition of the chloride was complete, stirring was continued for 15 min, followed by addition of ice-water until the solid residue had dissolved completely. The aqueous phase was separated and washed thoroughly with water. The combined ether extracts were dried ($MgSO_4$), the solvent was removed by rotary evaporation, and the remaining residue was purified by fractional distillation by using a spinning-band column. At 58−59 °C (85 mbar), 23.5 (73%) of **32** was obtained as a colorless liquid.[45] − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.12 (d, ^3J = 6.0 Hz, 3 H, CH_3), 0.73, 1.24, 1.40, 1.68 (4 × m, 4 H, 1-H − 3-H), 2.22 (s, 3 H, Ac). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.02 (q, CH_3), 19.27 (t, C-3), 19.96 (d, C-2), 30.22 and 30.27 (d and q, C-1, C-5), 208.30 (s, C-4, Ac). − IR (film): $\tilde{\nu}$ = 2303 cm^{-1} (w), 2960 (w), 1697 (vs), 1438 (w), 1403 (s), 1345 (m), 1177 (s), 855 (m). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (3.75). − GC/MS (40 eV): *m*/*z* (%) = 98 [M^+] (10), 83 (28), 55 (27), 53 (5), 43 (100).

d) *trans*-1-(1,1-Dichloroethyl)-2-methylcyclopropane (33): Compound **32** (12.8, 0.13 mol) was added at 0−5 °C to a suspension of phosphorous pentachloride (52 g, 0.25 mol) in 150 mL of carbon tetrachloride. After the reaction mixture had been stirred for 5 h at this temperature, the solution was poured into ice-cold aqueous sodium bicarbonate solution. The mixture was neutralized by addition of further sodium bicarbonate, the aqueous phase was separated and carefully washed with ether, and the organic phases were combined and dried with $MgSO_4$. The organic solvents were removed in vacuo and the remaining oil was fractionated by using a spinning-band column. At 38−39 °C (25 mbar), compound **33** (7.7 g, 38%) was obtained as a colorless liquid.[12,46] − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.10 (d, ^3J = 5.4 Hz, 3 H, CH_3), 0.50, 0.93, 1.13, 1.38 (m, 4 H, 1-H − 3-H), 2.13 (s, 3 H, CH_3CCl_2). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 13.30 (d, C-2), 13.33 (t, C-3), 17.83 (q, CH_3), 36.03 and 37.05 (d and q, C-1 and CH_3CCl_2), 91.79 (s, C-4). − IR (film): $\tilde{\nu}$ = 3023 cm^{-1} (w), 3003 (m), 2959 (s), 2932 (m), 2871 (m), 1455 (m), 1378 (s), 1183 (s), 1116 (s), 1070 (s), 1036 (m), 691 (vs). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (3.11).

e) *trans*-1-Ethynyl-2-methylcyclopropane (*trans*-27): 18-Crown-6 (1.32 g, 0.005 mol) and compound **33** (23.20 g, 0.15 mol) were added to a suspension of potassium *tert*-butoxide (50.5 g, 0.45 mol) in pentane (600 mL). The mixture was stirred at room temp. for 18 h and then hydrolyzed with ice water until the solid residue dissolved. The pentane phase was separated and carefully washed with water to remove the *tert*-butyl alcohol formed. After drying ($MgSO_4$) and removal of the solvent, the remaining oil was purified by distillation with a spinning-band column. At 69−71 °C *trans*-**27** (7.3 g, 61%) of *trans*-**27** distilled as a colorless liquid.[9,12,45] − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.07 (d, ^3J = 4.0 Hz, 3 H, CH_3), 0.53, 0.85, 0.91, 1.09 (4 × m, 4 H, 1-H − 3-H), 1.78 (d, ^4J = 2.0 Hz, 1 H, HC≡C). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.11 (d, C-1), 16.24 (t, C-3), 16.62 (d, C-2), 18.13 (q, CH_3), 63.58 (d, H*C*≡C), 87.36 (d, HC≡*C*). − IR (film): $\tilde{\nu}$ = 3301 cm^{-1} (s), 3314 (vs), 3083 (w), 3022 (w), 3007 (m), 2959 (s), 2933 (m), 2901 (m), 2115 (s), 1463 (m), 1445 (m), 1037 (m). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (3.37).

General Procedure for the Preparation of the Methyl Propargyl Ethers 4, 9, and 18: *n*-Butyllithium in hexane (15.7 mL, 0.025 mol of a 1.6 M solution) was added over 15 min to a cooled (−40 °C) solution of the 1-alkyne (0.025 mol) in 25 mL of anhydrous ether. A solution of bromomethyl methyl ether (**34**) (3.12 g, 0.025 mol) in 10 mL of anhydrous ether was added, the temperature of the reaction mixture was slowly allowed to rise to room temp., and after a further 1 h stirring, 50 mL of ice-water was added. The aqueous phase was extracted with ether, the organic phases were combined, and, after removal of the solvent by rotary evaporation, the residue was purified by vacuum distillation.

a) 7-Methoxyhept-1-en-5-yne (4): Preparation from **22**, colorless liquid, 0.95 g (31%), b.p. 33−34 °C (4 mbar). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.23−2.45 (m, 4 H, 3-H, 4-H), 3.37 (s, 3 H, CH_3), 4.18 (t, ^5J = 1.9 Hz, 2 H, 7-H), 5.03 (dd, ^2J = 1.5, ^3J = 10.5 Hz, 1 H, 1-H), 5.18 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 1-H), 5.86 (ddt, ^3J = 10.5, ^3J = 17.1, ^3J = 6.4 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.50 (t, C-4), 32.71 (t, C-3), 57.28 (q, CH_3), 60.07 (t, C-7), 76.13 (s, C-5), 86.22 (s, C-6), 115.56 (t, C-1), 136.77 (d, C-2). − IR (film): $\tilde{\nu}$ = 3295 cm^{-1} (w), 3080 (w), 2240 (w), 1639 (s), 1618 (s), 1449 (m), 1360 (m), 1270 (s), 1136 (m), 1094 (m), 944 (w), 871 (m). − UV (acetonitrile): λ_{max} (log ε) = 192 nm

(3.96), 262 (2.46). − GC/MS (40 eV): *m*/*z* (%) = 124 [M$^+$] (2), 123 (24), 109 (24), 93 (22), 92 (14), 91 (60), 81 (22), 79 (87), 77 (48), 65 (17), 53 (49), 52 (29), 51 (21), 45 (100), 41 (45). − $C_8H_{12}O$ (124.18): calcd. C 77.38, H 9.74; found C 77.36, H 9.70.

b) 1-Methoxy-4-vinyloxybut-2-yne (9): Preparation from **24**, colorless liquid, 0.8 g (28%), b.p. 69−70 °C (8 mbar). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.38 (s, 3 H, CH_3), 4.13 (dd, ^2J = 2.4, ^3J = 6.7 Hz, 1 H, =CH_2), 4.14 (t, ^5J = 1.7 Hz, 2 H, 1-H), 4.31 (dd, ^2J = 2.4, ^3J = 14.3 Hz, 1 H, =CH_2), 4.44 (t, ^5J = 1.7 Hz, 2 H, 4-H), 6.45 (dd, ^3J = 6.7, ^3J = 14.3 Hz, 1 H, -CH=). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.94 (t, C-4), 57.51 (q, CH_3), 59.69 (t, C-1), 81.02 (s, C-3), 83.02 (s, C-2), 88.24 (t, =*C*H_2), 150.29 (d, -*C*H=). − IR (film): $\tilde{\nu}$ = 2934 cm^{-1} (m), 2908 (m), 2879 (m), 2824 (m), 1639 (s), 1620 (s), 1450 (m), 1356 (s), 1320 (s), 1271 (m), 1189 (vs), 1153 (s), 1123 (s), 1098 (vs), 1059 (s), 988 (m), 960 (m), 949 (m). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (3.81). − GC/MS (40 eV): *m*/*z* (%) = 126 [M$^+$] (7), 97 (8), 96 (8), 95 (8), 94 (10), 83 (19), 82 (18), 81 (45), 68 (30), 55 (43), 53 (100), 52 (40), 51 (38), 50 (18), 45 (45). − $C_7H_{10}O_2$ (126.15): calcd. C 66.65, H 7.99; found C 66.51, H 8.02.

c) 1-(3-Methoxyprop-1-ynyl)-2-methylcyclopropane (18): Preparation from *trans*-**27**, colorless liquid, 1.2 g (37%), b.p. 50−51 °C (8 mbar). − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.54, 0.84, 0.94, 1.08 (4 × m, 4 H, 1-H − 3-H), 1.07 (d, ^3J = 1.0 Hz, 3 H, CH_3), 3.35 (s, 3 H, OCH_3), 4.04 (d, ^5J = 2.0 Hz, 2 H, CH_2). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.43 (d, C-1), 16.41 (t, C-3), 16.73 (d, C-2), 18.18 (q, CH_3), 57.26 (q, OCH_3), 60.16 (t, *C*H_2), 71.28 (s, C-5), 89.93 (s, C-6). − IR (film): $\tilde{\nu}$ = 3004 cm^{-1} (m), 2989 (m), 2957 (s), 2932 (s), 2900 (m), 2872 (m), 2844 (m), 2821 (m), 2242 (m), 2225 (m), 1463 (m), 1448 (m), 1379 (m), 1357 (m), 1187 (s), 1098 (vs), 1067 (s), 1001 (m), 898 (m), 849 (m). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (3.49). − GC/MS (40 eV): *m*/*z* (%) = 124 [M$^+$] (46), 123 (29), 109 (67), 95 (29), 93 (36), 91 (74), 82 (25), 81 (48), 79 (81), 78 (28), 77 (100), 66 (24), 65 (31), 53 (55). − $C_8H_{12}O$ (124.18): calcd. C 77.38, H 9.74; found C 77.30, H 9.84.

General Procedure for the Preparation of the Enynes 5, 10, 17, and 20: Copper(I) iodide (760 mg, 4.0 mmol) was added to a solution of 1-bromo-1-propene (**36**, 1:1 mixture of the (*E*) and (*Z*) isomers according to ^{1}H NMR analysis, 8.46 g, 0.07 mol), the 1-alkyne (0.05 mol), and tetrakis(triphenylphosphane)-palladium(0) (230 mg, 0.2 mmol) in diethylamine (60 mL). The mixture was stirred for 3 h at room temp., hydrolyzed with 100 mL of ice-water, and thoroughly extracted with pentane. The combined organic phases were filtered through a short alumina column, the solvent was removed in vacuo, and the remaining oil was fractionated by vacuum distillation.

a) Nona-1,7-dien-5-yne (5): Preparation from **22**, colorless liquid, 2.46 g (40%), b.p. 52−53 °C (8 mbar). According to GC analysis, a (*Z*)/(*E*) mixture in 2:1 ratio was obtained; the pure diastereomers were obtained by preparative gas chromatography (Carbowax, 3 m, 120 °C). − **(*Z*)-nona-1,7-dien-5-yne [(*Z*)-5]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.85 (dd, 3 H, ^3J = 6.9, ^4J = 1.9 Hz, 9-H), 2.30 (dt, 2 H, ^3J = 6.6, ^3J = 6.8 Hz, 3-H), 2.44 (t, ^3J = 6.8 Hz, 2 H, 4-H), 5.04 (dd, ^2J = 1.6, ^3J = 10.3 Hz, 1 H, 1-H), 5.10 (dd, ^2J = 1.6, ^3J = 17.1 Hz, 1 H, 1-H), 5.47 (dq, ^3J = 15.8, ^4J = 1.9 Hz, 1 H, 7-H), 5.89 (m, 2 H, 2-H, 8-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.64 (q, C-9), 19.35 (t, C-4), 33.07 (t, C-3), 77.52 (s, C-6), 93.96 (s, C-5), 110.22 (d, C-7), 115.54 (t, C-1), 136.97 (d, C-2), 137.07 (d, C-8). − **(*E*)-Nona-1,7-dien-5-yne [(*E*)-5]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.76 (dd, ^3J = 6.9, ^4J = 1.9 Hz, 3 H, 9-H), 2.27 (dt, 2 H, ^3J = 6.6, ^3J = 6.8 Hz, 3-H), 2.37 (t, ^3J = 6.8 Hz, 2 H, 4-H), 5.02 (dd, ^2J = 1.6, ^3J = 10.3 Hz, 1 H, 1-H), 5.09 (dd, ^2J = 1.6, ^3J = 17.1 Hz, 1 H, 1-H), 5.47 (dq, ^3J = 15.8, ^4J = 1.9 Hz, 1 H, 7-H), 5.86 (ddt, ^3J = 10.3, ^3J = 17.1, ^3J = 6.6 Hz, 1 H, 2-H), 6.06 (dq, ^3J = 15.8, ^3J = 6.9 Hz, 1 H, 8-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.37 (q, C-9), 19.12 (t, C-4), 32.96 (t, C-3), 79.50 (s, C-6), 87.50 (s, C-5), 110.91 (d, C-7), 115.46 (t, C-1), 136.99 (d, C-2), 138.15 (d, C-8). − IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (m), 3028 (m), 2981 (m), 2936 (s), 2914 (s), 2851 (m), 1642 (m), 1441 (m), 1362 (m), 1331 (m), 981 (m), 953(s), 915 (m), 722 (s). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (3.68), 226 (4.08), 234 (sh, 4.00). − GC/MS (40 eV): *m*/*z* (%) = 120 [M$^+$] (65), 105 (47), 93 (39), 91 (76), 79 (100), 78 (47), 77 (74), 66 (17), 85 (18), 53 (14). − C_9H_{12} (120.19): calcd. C 89.94, H 10.16; found C 89.88, H 9.97.

b) 6-Vinyloxyhex-2-en-4-yne (10): Preparation from **24**, colorless liquid, 3.2 g (52%), b.p. 57−58 °C (8 mbar). According to GC analysis a (*Z*)/(*E*) mixture in 2:1 ratio was obtained; the pure diastereomers were obtained by preparative gas chromatography (Carbowax, 3 m, 120 °C). − **(*E*)-6-Vinyloxyhex-2-en-4-yne [(*E*)-10]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.79 (dd, ^3J = 6.8, ^4J = 1.7 Hz, 3 H, 1-H), 4.12 (dd, ^2J = 2.3, ^3J = 6.8 Hz, 1 H, =CH_2), 4.31 (dd, ^2J = 2.3, ^3J = 14.3 Hz, 1 H, =CH_2), 4.49 (d, ^5J = 1.7 Hz, 2 H, 6-H), 5.52 (dtq, ^3J = 15.9, ^4J = 1.9, ^5J = 1.7 Hz, 1 H, 3-H), 6.20 (dq, ^3J = 6.8, ^3J = 15.9 Hz, 1 H, 2-H), 6.46 (dd, ^3J = 6.8, ^3J = 14.3 Hz, 1 H, 7-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.56 (q, C-1), 56.64 (t, C-6), 81.71 (s, C-4), 85.74 (s, C-5), 88.17 (t, = CH_2), 109.87 (d, C-3), 140.88 (d, C-2), 150.44 (d, -CH=). − **(*Z*)-6-Vinyloxyhex-2-en-4-yne [(*Z*)-10]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.88 (dd, ^3J = 6.8, ^4J = 1.6 Hz, 3 H, 1-H), 4.14 (dd, ^2J = 2.3, ^3J = 6.8 Hz, 1 H, =CH_2), 4.33 (dd, ^2J = 2.3, ^3J = 14.3 Hz, 1 H, = CH_2), 4.55 (d, ^5J = 1.9 Hz, 2 H, 6-H), 5.51 (dtq, ^3J = 10.7, ^4J = 1.6, ^{5}J = 1.9 Hz, 1 H, 3-H), 6.02 (dq, 1 H, ^3J = 6.8, ^3J = 10.7 Hz, 2-H), 6.48 (dd, ^3J = 6.8, ^3J = 14.3 Hz, 1 H, 7-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.94 (q, C-1), 56.63 (t, C-6), 83.69 (s, C-4), 87.99 (s, C-5), 88.23 (t, =CH_2), 109.20 (d, C-3), 139.67 (d, C-2), 150.40 (d, -CH=). − IR (film): $\tilde{\nu}$ = 3031 cm^{-1} (w), 2970 (w), 2218 (w), 1639 (vs), 1618 (vs), 1448 (m), 1372 (s), 1359 (s), 1319 (s), 1268 (m), 1189 (vs), 1152 (vs), 1077 (m), 1056 (s), 1029 (m), 985 (s), 957 (s). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.01), 226 (4.08). − GC/MS (40 eV): *m*/*z* (%) = 122 [M$^+$] (1), 107 (20), 91 (2), 79 (50), 78 (14), 77 (100), 69 (11), 53 (14), 51 (20). − $C_8H_{10}O$ (122.17): calcd. C 78.65, H 8.25; found C 78.89, H 8.34.

c) 6-Methoxyhex-2-en-4-yne (17): Preparation from **25**, colorless liquid, 3.1 g (47%), b.p. 38 °C (10 mbar). According to GC analysis a (*Z*)/(*E*) mixture in 4:1 ratio was obtained; the pure diastereomers were obtained by preparative gas chromatography (Carbowax, 3 m, 100 °C). − **(*Z*)-6-Methoxyhex-2-en-4-yne [(*Z*)-17]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.89 (dd, ^3J = 6.9, ^4J = 1.6 Hz, 3 H, 1-H), 3.41 (s, 3 H, OCH_3), 4.27 (d, ^5J = 1.9 Hz, 2 H, 6-H), 5.52 (dtq, ^3J = 10.8, ^4J = 1.6, ^5J = 1.9 Hz, 1 H, 3-H), 6.00 (dq, ^3J = 10.8, ^3J = 6.9 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.87 (q, C-1), 57.40 (q, OCH_3), 60.37 (t, C-6), 85.02 (s, C-4), 91.12 (s, C-5), 109.41 (d, C-3), 138.96 (d, C-2). − **(*E*)-6-Methoxyhex-2-en-4-yne [(*E*)-17]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.79 (dd, 3 H, ^3J = 6.8, ^4J = 1.9 Hz, 1-H), 3.38 (s, 3 H, OCH_3), 4.19 (d, ^5J = 1.8 Hz, 2 H, 6-H), 5.51 (dtq, ^3J = 15.8, ^4J = 1.9, ^5J = 1.8 Hz, 1 H, 3-H), 6.18 (dq, ^3J = 15.8, ^3J = 6.8 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.50 (q, C-1), 57.40 (q, OCH_3), 60.30 (t, C-6), 85.02 (s, C-4), 91.12 (s, C-5), 110.08 (d, C-3), 140.23 (d, C-2). − IR (film): $\tilde{\nu}$ = 3030 m^{-1} (m), 2990 (m), 2937 (s), 2916 (s), 2894 (s), 2821 (s), 2190 (w), 1465 (m), 1448 (s), 1399 (m), 1376 (s), 1357 (vs), 1279 (m), 1187 (vs), 1151 (vs), 1135 (vs), 1099 (vs), 1000 (m), 952 (s), 905 (s). − UV (acetonitrile): λ_{max} (log ε) = 226 nm

(4.02) − GC/MS (40 eV): *m*/*z* (%) = 110 [M^+] (56), 95 (79), 79 (67), 77 (100), 67 (60), 53 (23), 51 (41). The ether has been described in the literature;[47] however, the reported spectroscopic data are incomplete.

d) 5-(2-Methylcyclopropyl)pent-2-en-4-yne (20): Preparation from *trans*-**27**, colorless liquid, 1.5 g (48%), b.p. 39 °C (5 mbar). According to GC analysis a (*Z*)/(*E*) mixture in 4:1 ratio was obtained; the pure diastereomers were procured by preparative gas chromatography (Carbowax, 3 m, 120 °C). − **(*Z*)-5-(2-Methylcyclopropyl)pent-2-en-4-yne [(*Z*)-20]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.58, 0.97, 1.08 (3 × m, 4 H, 6-H − 8-H), 1.09 (d, ^3J = 4.1 Hz, 3 H, 9-H), 1.83 (dd, ^3J = 6.8, ^4J = 1.6 Hz, 3 H, 1-H), 5.42 (dq, ^3J = 10.6, ^4J = 1.6 Hz, 1 H, 3-H), 5.85 (dq, ^3J = 10.6, ^3J = 6.8 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 8.34 (d, C-6), 15.66 (q, C-1), 16.96 (t, C-7), 17.24 (d, C-8), 18.31 (q, C-9), 72.71 (s, C-5), 97.78 (s, C-4), 110.23 (d, C-3), 136.79 (d, C-2). − **(*E*)-5-(2-Methylcyclopropyl)pent-2-en-4-yne [(*E*)-20]:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.58, 0.97, 1.08 (3 × m, 4 H, 6-H − 8-H), 1.09 (d, ^3J = 4.1 Hz, 3 H, 9-H), 1.74 (dd, ^3J = 6.8, ^4J = 1.6 Hz, 3 H, 1-H), 5.44 (dq, ^3J = 10.6, ^4J = 1.6 Hz, 1 H, 3-H), 6.03 (dq, ^3J = 15.7, ^3J = 6.8 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 8.12 (d, C-6), 15.66 (q, C-1), 16.68 (t, C-7), 17.24 (d, C-8), 18.40 (q, C-9), 74.62 (s, C-5), 91.34 (s, C-4), 110.92 (d, C-3), 137.98 (d, C-2). − IR (film): $\tilde{\nu}$ = 3081 cm^{-1} (w), 3026 (s), 3005 (m), 2958 (vs), 2930 (m), 2913 (m), 2869 (m), 2213 (m), 1619 (w), 1460 (m), 1444 (m), 1362 (m), 1067 (m), 1034 (m), 952 (m), 932 (m), 848 (s), 720 (s). − UV (acetonitrile) λ_{max} (log ε) = 192 nm (3.70), 230 (3.95), 238 (3.95). − GC/MS (40 eV): *m*/*z* (%) = 120 [M^+] (100), 105 (85), 103 (33), 91 (80), 79 (75), 78 (28), 77 (84), 65 (25), 63 (24), 52 (25). − C_9H_{12} (120.19): calcd. C 89.94, H 10.06; found C 90.70, H 10.38.

6-(*trans*-2-Methylcyclopropyl)hex-1-en-5-yne (6): *n*-Butyllithium solution (1.6 M in hexane, 32 mL) was added at 15−20 °C to a solution of *trans*-**27** (4.0 g, 50 mmol) in anhydrous THF (40 mL). The mixture was stirred for 10 min and a solution of 1-bromo-3-butene (**35**) (6.7 g, 50 mmol) in HMPTA (30 mL) was added. After 3 h of additional stirring at 15−20 °C, ice-water was added for hydrolysis. The aqueous phase was separated and washed carefully with ether, and the organic phases were combined and dried with $MgSO_4$. The solvents were removed in vacuo and the remaining oil was fractionated at 42−45 °C and 0.3 mbar: 0.7 g (10%) of **6**, colorless liquid. − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.46, 0.75, 0.88, 0.90 (4 × m, 4 H, 7-H − 9-H), 1.05 (d, ^3J = 5.5 Hz, 3 H, CH_3), 2.21 (m, 4 H, 3-H, 4-H), 5.00 (dd, ^2J = 1.5, ^3J = 16.9 Hz, 1 H, 1-H), 5.05 (dd, ^2J = 1.5, ^3J = 10.1 Hz, 1 H, 1-H), 5.84 (ddt, ^3J = 10.1, ^3J = 16.9, ^3J = 6.4 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 7.65 (d, C-7), 16.25 (d, C-9), 16.41 (t, C-8), 18.28 (q, CH_3), 18.62 (t, C-4), 33.29 (t, C-3), 75.05 (s, C-6), 83.44 (s, C-5), 115.23 (t, C-1), 137.19 (d, C-2). − IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (m), 3003 (m), 2979 (m), 2956 (s), 2928 (s), 2869 (m), 2245 (w), 2231 (w), 1642 (m), 1469 (m), 1444 (m), 1068 (m), 1034 (m), 913 (s). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (3.78), 240 (3.20). − GC/MS (40 eV): *m*/*z* (%) = 143 [M^+] (3), 119 (23), 106 (18), 105 (24), 93 (10), 92 (16), 91 (100), 79 (13), 78 (20), 77 (79), 65 (24). − $C_{10}H_{14}$ (134.22): calcd. C 89.49, H 10.51; found C 89.61, H 10.53.

7-Vinyloxyhept-1-en-5-yne (2): Gaseous hydrochloric acid was passed for 1 h at −5 °C through a mixture of hept-6-en-2-yn-1-ol (**37**, from **22** by treatment of its lithium salt with paraldehyde, 3.36 g, 30.5 mmol) and paraldehyde (1.52 g, 0.12 mol). The reaction flask was placed in a cooling bath (−70 °C), and after a short time a solid layer (conc. HCl) had formed. The supernatant phase was carefully decanted and dried with magnesium sulfate. According to NMR analysis, the liquid consisted of **38** and the target molecule **2**. This mixture was added slowly to *N*,*N*-diethylamine (10 mL) heated to 95−105 °C. When the addition was complete, the reaction mixture was stirred for 30 min at this temperature. The flask was connected to a distillation apparatus and the vinyl ether formed was distilled off directly at 33 °C and 0.7 mbar: 1.56 g (38%) of **2**, colorless liquid. − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.24−2.35 (m, 4 H, 3-H, 4-H), 4.11 (dd, ^2J = 2.3, ^3J = 6.8 Hz, 1 H, H_2C=CHO), 4.29 (dd, ^2J = 2.3, ^3J = 14.3 Hz, 1 H, H_2C=CHO), 4.37 (t, ^4J = 2.1 Hz, 2 H, 7-H), 5.03 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 1-H), 5.08 (dd, ^2J = 1.5, ^3J = 10.4 Hz, 1 H, 1-H), 5.85 (ddt, ^3J = 10.4, ^3J = 17.1, ^3J = 6.4 Hz, 1 H, 2-H), 6.45 (dd, ^3J = 6.8, ^3J = 14.3 Hz, 1 H, H_2C=C*H*O). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.53 (t, C-4), 32.55 (t, C-3), 56.46 (t, C-7), 75.01 (s, C-5), 87.15 (s, C-6), 88.03 (t, H_2C=CHO), 115.68 (t, C-1), 136.65 (d, C-2), 150.46 (d, H_2C=*C*HO). − IR (film): $\tilde{\nu}$ = 3118 cm^{-1} (m), 2982 (m), 2289 (w), 2225 (w), 1638 (m), 1374 (s), 1270 (s), 1154 (s), 1128 (s), 989 (m), 944 (s), 871 (s), 630 (s). − UV (acetonitrile): λ_{max} (log ε) = 192 nm (4.04), 262 (2.52). − GC/MS (40 eV): *m*/*z* (%) = 136 [M^+] (1), 121 (5), 107 (10), 93 (28), 91 (78), 81 (10), 79 (28), 78 (27), 77 (100), 65 (39), 55 (17), 53 (29). − $C_9H_{12}O$ (136.19): calcd. C 79.37, H 8.88; found C 79.38, H 8.95.

Octa-2,6-dien-4-yne (19). − a) 6-Bromo-oct-2-en-4-yne (41): Phosphorous(III) bromide (35.2 g, 0.13 mol) was added at −20 °C over 30 min to a solution of oct-4-yne-3,6-diol (**40**, prepared by addition of propanal to acetylene bis-Grignard **39** according to ref.,[48] 22.0 g, 0.15 mol) and pyridine (4.0 g, 50 mmol) in anhydrous ether (400 mL). The reaction mixture was stirred for 2 h at room temp. and hydrolyzed by addition of ice-water (200 mL). The aqueous phase was separated and washed carefully with ether, and the combined organic phases were neutralized with bicarbonate solution and finally dried with $MgSO_4$. The solvent was removed in vacuo and the remaining oil was fractionated by distillation through a 40 cm Vigreux column; at 60−62 °C and 0.6 mbar 20.3 g (50%) of **41** was obtained as a colorless liquid. According to GC analysis the mixture consisted of (*Z*)- and (*E*)-**41** in 2:1 ratio. For analytical purposes the pure diastereomers were separated by preparative gas chromatography (Carbowax, 3 m, 150 °C): **(*Z*)-6-bromo-oct-2-en-4-yne**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.12 (t, ^3J = 7.3 Hz, 3 H, 8-H), 1.88 (dd, ^3J = 6.8, ^4J = 1.8 Hz, 3 H, 1-H), 2.06 (dq, ^3J = 6.0, ^3J = 7.3 Hz, 2 H, 7-H), 4.72 (dt, ^3J = 6.0, ^5J = 1.8 Hz, 1 H, 6-H), 5.53 (ddt, ^3J = 10.7, ^4J = 1.8, ^5J = 1.8 Hz, 1 H, 3-H), 6.03 (dq, ^3J = 6.8, ^3J = 10.7 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.72 (q, C-8), 15.98 (q, C-1), 33.18 (t, C-7), 39.92 (d, C-6), 83.87 (s, C-5), 92.23 (s, C-4), 109.25 (d, C-3), 139.84 (d, C-2). − **(*E*)-6-bromo-oct-2-en-4-yne:** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.12 (t, ^3J = 7.3 Hz, 3 H, 8-H), 1.80 (dd, ^3J = 6.8, ^4J = 1.8 Hz, 3 H, 1-H), 2.06 (dq, ^3J = 6.3, ^3J = 7.3 Hz, 2 H, 7-H), 4.65 (dt, ^3J = 6.3, ^5J = 1.8 Hz, 1 H, 6-H), 5.53 (ddt, ^3J = 15.8, ^4J = 1.8, ^5J = 1.8 Hz, 1 H, 3-H), 6.19 (dq, ^3J = 6.8, ^3J = 15.8 Hz, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 11.72 (q, C-8), 18.60 (q, C-1), 33.18 (t, C-7), 40.09 (d, C-6), 85.56 (s, C-5), 92.98 (s, C-4), 109.94 (d, C-3), 141.03 (d, C-2). − IR (film): $\tilde{\nu}$ = 3031 cm^{-1} (m), 2974 (vs), 2938 (s), 2914 (s), 2877 (m), 2204 (w), 2180 (w), 1737 (m), 1671 (m), 1462 (m), 1363 (s), 1171 (vs), 1087 (s), 722 (vs), 665 (s), 598 (s), 577 (s). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (3.93), 236 (3.13). − GC/MS (40 eV): *m*/*z* (%) = 188 [$M^{+\,81}$Br] (4), 186 [$M^{+\,79}$Br] (4), 107 (100), 91 (72), 79 (39), 78 (29), 65 (16). − $C_8H_{11}Br$ (187.08): calcd. C 51.36, H 5.93; found C 51.22, H 5.81. − b) **Octa-2,6-dien-4-yne (19)**: DBU (14.3 g, 0.09 mol) was added to a solution of (*E*/*Z*)-**41** (17.5 g, 0.07 mol) in anhydrous DMSO (120 mL). The reaction temperature increased to 45−50 °C, and the solution was stirred until it had reached room temp. again.

After hydrolysis with aqueous HCl (400 mL, 0.05 N), the aqueous phase was separated and extracted with pentane. The organic phases were combined, washed carefully with saturated ammonium chloride solution, and dried with $MgSO_4$. The pentane was removed in a rotary evaporator and the residue was fractionated by vacuum distillation, using a 40 cm Vigreux column. At 45−47 °C and 8 mbar, 2.7 g (39%) of a colorless liquid distilled. This was shown by GC analysis to consist of (*Z*,*Z*)-, (*Z*,*E*)-, and (*E*,*E*)-**19** in 3:5:1 ratio. For analytical purposes the pure diastereomers were separated by preparative gas chromatography (Carbowax, 3 m, 120 °C). Although these hydrocarbons are known, the spectroscopic data are incomplete and not readily available.[49] − (*Z*,*Z*)-**19**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.91 (dd, ^3J = 6.9, ^4J = 1.6 Hz, 3 H, 1-H, 8-H), 5.65 (dq, ^3J = 10.8, ^4J = 1.6 Hz, 1 H, 3-H, 6-H), 6.00 (dq, ^3J = 10.8, ^3J = 6.9 Hz, 1 H, 2-H, 7-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 15.93 (q, C-1, C-8), 91.56 (s, C-4, C-5), 110.30 (d, C-3, C-6), 137.69 (d, C-2, C-7). − (*E*,*E*)-**19**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.80 (dd, ^3J = 6.9, ^4J = 1.6 Hz, 3 H, 1-H, 8-H), 5.60 (dq, ^3J = 15.8, ^4J = 1.6 Hz, 1 H, 3-H, 6-H), 6.10 (dq, ^3J = 15.8, ^3J = 6.9 Hz, 1 H, 2-H, 7-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.66 (q, C-1, C-8), 68.34 (s, C-4, C-5), 110.90 (d, C-3, C-6), 138.93 (d, C-2, C-7). − (*E*,*Z*)-**19**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.82 (dd, ^3J = 6.9, ^4J = 1.6 Hz, 3 H, 8-H), 1.89 (dd, ^3J = 6.9, ^4J = 1.6 Hz, 3 H, 1-H) 5.59 (dq, ^3J = 15.8, ^4J = 1.6 Hz, 1 H, 6-H), 5.67 (dq, ^3J = 10.8, ^4J = 1.6 Hz, 1 H, 3-H), 5.95 (dq, ^3J = 10.8, ^3J = 6.9 Hz, 1 H, 2-H), 6.15 (dq, ^3J = 15.8, ^3J = 6.9 Hz, 1 H, 7-H). − IR (film): $\tilde{\nu}$ = 3080 cm^{-1} (m), 3028 (m), 2981 (m), 2936 (s), 2914 (vs), 2851 (m), 2227 (w), 2205 (w), 1642 (s), 1441 (s), 1362 (m), 1331 (m), 991 (m), 953 (m), 915 (vs), 722 (s). − UV (acetonitrile): λ_{max} (log ε) = 234 nm (3.95). − GC/MS (40 eV): *m*/*z* (%) = 106 [M$^+$] (100), 105 (18), 91 (65), 79 (28), 78 (24), 77 (33), 65 (20), 63 (12), 52 (13), 51 (24).

1,4-Bis(acetoxy)but-2-yne (12): The diester was prepared according to,[50] by esterification of but-2-yne-1,4-diol (**42**) with acetyl chloride; its spectroscopic data have all been reported in the chemical literature.

1,4-Bis(vinyloxy)but-2-yne (7): Titanocene dichloride (9.00 g, 0.036 mol) was placed under nitrogen in a flame-dried 250 mL three-necked flask, and a toluene solution of trimethyl aluminum (2.0 M solution, 52 mL, 0.104 mol) was added by syringe. The dark red solution was stirred for 3 days at room temp. The resulting solution of Tebbe's reagent **44** was then added by syringe over 30 min to a solution of 1,4-bis(formyloxy)but-2-yne (**43**, prepared from **42** according to,[51] 2.51 g, 18 mmol) in anhydrous THF (80 mL) at −40 °C. The reaction mixture was stirred for 30 min at this temperature and then slowly warmed to room temp. After additional stirring for 2 h, THF (50 mL) was added, the temperature was lowered to −10 °C, and aqueous sodium hydroxide solution (15%, 40 mL) was added carefully (vigorous gas evolution). While the temperature was kept at −10 °C, a solid precipitate formed, the color of which changed from orange to blue, and finally disappeared. The residue was removed by filtration and carefully washed with pentane. The combined organic phases were concentrated in vacuo until an orange red toluene solutions was obtained. When pentane (300 mL) was added to this solution, an orange solid precipitated and was removed by filtration through a short alumina column. The resulting solution was fractionated at 34 °C/0.2 mbar, furnishing 0.65 g (26%) of **7** as a colorless liquid. − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 4.14 (dd, ^2J = 2.6, ^3J = 6.8 Hz, 2 H, =CH_2), 4.33 (dd, ^2J = 2.6, ^3J = 14.3 Hz, 2 H, =CH_2), 4.44 (s, 4 H, 1-H), 6.45 (dd, ^3J = 6.8, ^3J = 14.3 Hz, 2 H, -CH=). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.90 (t, C-1), 81.80 (s, C-2), 88.41 (t, =CH_2), 150.26 (d, -CH=). − IR (film): $\tilde{\nu}$ = 3118 cm^{-1} (w), 3060 (w), 1960 (w), 1639 (s), 1620 (w), 1357 (m), 1320 (s), 1188 (s), 1152 (s), 1061 (m), 986 (m), 826 (m). − UV (acetonitrile): λ_{max} (log ε) = 194 nm (4.23). − GC/MS (40 eV): *m*/*z* (%) = 138 [M$^+$] (1), 109 (3), 95 (25), 81 (9), 67 (32), 65 (25), 52 (37), 53 (26), 41 (100). − $C_8H_{10}O_2$ (138.16): calcd. C 69.55, H 7.29; found C 69.60, H 7.32

Pyrolysis Experiments: Pyrolyses were carried out as described in the main section. At the beginning of each experiment, the compound to be pyrolyzed was frozen out in the evaporation flask and the whole apparatus was evacuated to about 0.1 mbar by connecting the (receiving) cold trap to a high vacuum line. Air was removed from the substrate and the apparatus by carrying out several freeze-pump-thaw cycles. For the analytical runs, about 20−30 mg of the starting material was pyrolyzed and the progress of the reaction was monitored by GC and GC/MS analysis. In this manner the various temperature profiles shown in the main section were established. For preparative runs, ca. 0.5−1.0 g of the starting material was pyrolyzed, the product mixture was taken up in pentane, and the pyrolysis products were separated for spectroscopic identification by preparative gas chromatography on a Carbowax column. The spectroscopic properties of the main and/or novel pyrolysis products are described below; spectroscopic data for simple pyrolysis products such as benzene (**76**), toluene (**96**), 1,3-cyclohexadiene (**107**), etc. are not given; those products were identified by comparison with the authentic compounds. Pyrolysis experiments exclusively yielding such simple compounds are not described.

a) Pyrolysis of 7-Vinyloxyhept-1-en-5-yne (2). − 2-Methyl-3-methylenehexa-1,5-diene (56): Spectral data are identical with data reported in ref.[52] − **3-(But-3-enyl)penta-3,4-dienal (59):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.08 (dt, ^3J = 6.5, ^3J = 6.5 Hz, 2 H, 7-H), 2.20 (tt, ^3J = 6.5, ^5J = 3.0 Hz, 2 H, 6-H), 2.99 (dt, ^3J = 2.5, ^5J = 3.0 Hz, 2 H, 2-H), 4.82 (tt, ^5J = 3.0, ^5J = 3.0 Hz, 2 H, 5-H), 5.01 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 9-H), 5.08 (dd, ^2J = 1.5, ^3J = 10.4 Hz, 1 H, 9-H), 5.83 (ddt, ^3J = 10.5, ^3J = 17.1, ^3J = 6.5 Hz, 1 H, 8-H), 9.68 (t, ^3J = 2.5 Hz, 1 H, 1-H). − IR (film): $\tilde{\nu}$ = 3081 cm^{-1} (w), 3004 (m), 2999 (m), 2981 (m), 2917 (m), 2839 (m), 2256 (m), 1724 (vs), 1667 (m), 1641 (m), 1598 (m), 1440 (m), 1386 (m), 1191 (m), 1134 (m), 1096 (m), 1038 (m), 998 (m). − GC/MS (40 eV): *m*/*z* (%) = 136 [M$^+$] (1), 135 (6), 121 (16), 107 (22), 94 (35), 93 (35), 92 (21), 91 (50), 81 (39), 79 (39), 77 (42), 41 (100). − **3-Methyl-4-methylenehepta-2,6-dienal (60):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, 8-H), 3.07 (ddd, ^3J = 6.5, ^4J = 1.3, ^4J = 1.3 Hz, 2 H, 5-H), 5.06 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 7-H), 5.09 (dd, ^2J = 1.5, ^3J = 10.4 Hz, 1 H, 7-H), 5.37 and 5.63 (2 × s, 2 H, 9-H), 5.82 (ddt, ^3J = 10.5, ^3J = 17.1, ^3J = 6.5 Hz, 1 H, 6-H), 10.18 (d, ^3J = 7.4 Hz, 1 H, 1-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.59 (q, C-8), 37.64 (t, C-5), 116.89 and 119.48 (2 × t, C-7, C-9), 126.68 (d, C-2), 135.37 (d, C-6), 146.53 (s, C-4), 155.87 (s, C-3), 192.08 (d, C-1). − GC/IR: $\tilde{\nu}$ = 3091 cm^{-1} (w), 3014 (w), 2981 (m), 2950 (m), 2934 (m), 1795 (s), 1696 (vs), 1635 (w), 1593 (m), 912 (s). − GC/MS (40 eV): *m*/*z* (%) = 136 [M$^+$] (3), 135 (15), 121 (19), 108 (41), 107 (53), 106 (27), 105 (28), 95 (77), 93 (48), 91 (88), 79 (51), 77 (63), 65 (41), 41 (100). − **3,4-Dimethylenehept-6-enal (62):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.06 (ddd, ^3J = 6.5, ^4J = 1.3, ^4J = 1.3 Hz, 2 H, 5-H), 3.31 (dd, ^3J = 2.5, ^4J = 0.9 Hz, 2 H, 2-H), 5.10 (m, 6 H, 7-H − 9-H), 5.86 (ddt, ^3J = 10.5, ^3J = 17.1, ^3J = 6.5 Hz, 1 H, 6-H), 9.59 (t, ^3J = 2.5 Hz, 1 H, 1-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 37.93 (t, C-5), 49.45 (t, C-2), 114.98, 116.44, 117.55 (3 × t, C7 − C-9), 136.04 (d, C-6); the quaternary carbon atoms could not be detected, due to their low intensity. − GC/IR: $\tilde{\nu}$ = 3097 cm^{-1} (m),

3013 (w), 2925 (m), 2809 (m), 2715 (m), 1745 (vs), 1643 (m), 1596 (m), 1390 (m), 1037 (m), 909 (s). − GC/MS (40 eV): *m/z* (%) = 136 [M^+] (1), 121 (8), 117 (12), 107 (45), 93 (68), 92 (43), 91 (100), 79 (71), 77 (67), 41 (73).

b) Pyrolysis of 7-Methoxyhept-1-en-5-yne (4). − 3-(Methoxymethyl)hexa-1,2,5-triene (64): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.80 (m, 2 H, 4-H), 3.33 (s, 3 H, 8-H), 3.94 (t, ^5J = 3.2 Hz, 2 H, 7-H), 4.80 (tt, ^5J = 3.2, ^5J = 3.2 Hz, 2 H, 1-H), 5.04 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 6-H), 5.09 (dd, ^2J = 1.5, ^3J = 10.4 Hz, 1 H, 6-H), 5.85 (ddt, ^3J = 10.4, ^3J = 17.1, ^3J = 6.4 Hz, 1 H, 5-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 33.71 (t, C-4), 57.54 (q, C-8), 72.74 (t, C-7), 75.79 (t, C-1), 98.67 (s, C-3), 116.12 (t, C-6), 135.25 (d, C-5), 216.96 (s, C-2). − GC/IR: $\tilde{\nu}$ = 3070 cm^{-1} (w), 2993 (s), 2931 (s), 2900 (s), 2868 (m), 2830 (s), 1956 (m), 1181 (s), 1100 (vs), 998 (m), 917 (s), 849 (s). − GC/MS (40 eV): *m/z* (%) = 124 [M^+] (1), 123 (6), 109 (14), 91 (26), 79 (37), 77 (15), 51 (10), 45 (100), 41 (11). − **3-Methylenehexa-1,5-diene (65):** Spectral data are identical to those reported in ref.[53] − **3-Methoxymethylene-4-methylenecyclopent-1-ene (66):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.10 (m, 2 H, 5-H), 3.38 (s, 3 H, 7-H), 3.40 (m, 3 H, 3-H, 6-H), 5.07 (m, 2 H, 8-H), 5.82 (m, 2 H, 1-H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 39.01 (t, C-5), 50.00 (d, C-3), 58.92 (q, C-7), 76.81 (t, C-6), 107.64 (t, C-8), 130.35 and 132.07 (2 × d, C-1, C-2), 150.04 (s, C-4). − GC/IR: $\tilde{\nu}$ = 3074 cm^{-1} (m), 2989 (m), 2931 (s), 2904 (s), 2878 (s), 2835 (s), 1192 (m), 1125 (vs), 888 (s), 720 (m). − GC/MS (40 eV): *m/z* (%) = 124 [M^+] (3), 94 (8), 91 (38), 79 (72), 78 (20), 77 (52), 66 (25), 45 (100). − **1-Methylpentafulvene (70):** Spectra are identical to those reported in ref.[54]

c) Pyrolysis of Nona-1,7-dien-5-yne (5). − 1-Allyl-3-methyl-4-methylenecyclobutene (73): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.18 (d, ^3J = 6.9 Hz, 3 H, 8-H), 2.87 (m, 2 H, 5-H), 3.14 (m, 1 H, 3-H), 4.45 and 4.59 (2 × s, 2 H, 9-H), 5.05 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 7-H), 5.12 (dd, ^2J = 1.5, ^3J = 10.8 Hz, 1 H, 7-H), 5.88 (ddt, ^3J = 6.8, ^3J = 10.8, ^3J = 17.1 Hz, 1 H, 6-H), 6.40 (m, 1 H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 17.33 (q, C-8), 31.96 (t, C-5), 42.48 (d, C-3), 94.67 (t, C-9), 116.12 (t, C-7), 134.72 (d, C-6), 141.55 (d, C-2); the quaternary carbon atoms could not be detected, due to their low intensity. − GC/IR: $\tilde{\nu}$ = 3075 cm^{-1} (s), 2981 (m), 2916 (vs), 2870 (s), 1620 (m), 1141 (m), 891 (m), 853 (m). − GC/MS (40 eV): *m/z* (%) = 120 [M^+] (65), 105 (47), 92 (39), 19 (100), 78 (48), 77 (70), 66 (22), 65 (23). − **2-Allylcyclohexa-1,3-diene (75):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.18 (m, 4 H, 5-H, 6-H), 2.82 (t, ^3J = 6.3 Hz, 2 H, 7-H), 5.04 (dd, ^2J = 1.5, ^3J = 17.1 Hz, 1 H, 9-H), 5.09 (dd, ^2J = 1.5, ^3J = 10.3 Hz, 1 H, 9-H), 5.80 (m, 4 H, 1-H, 3-H, 4-H, 8-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 23.23 and 26.24 (2 × t, C-5, C-6), 41.71 (t, C-7), 116.15 (t, C-9), 119.46, 123.86, 124.56 (3 × d, C-1, C-3, C-4), 136.54 (d, C-8); C-2 could not be detected because of low signal intensity. − GC/IR: $\tilde{\nu}$ = 3086 cm^{-1} (m), 3040 (s), 298 (m), 2929 (vs), 2861 (m), 1843 (m), 1621 (m), 1443 (m), 1408 (m), 1366 (m), 1333 (m), 988 (m), 918 (s), 718 (m). − GC/MS (40 eV): *m/z* (%) = 120 [M^+] (56), 105 (38), 92 (31), 91 (67), 79 (100), 78 (37), 77 (67), 65 (16).

d) Pyrolysis of *trans*-6-(2-Methylcyclopropyl)hex-1-en-5-yne (6). − 1-(1-Allylpropa-1,2-dienyl)-2-methylcyclopropane (77): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.38, 0.60, 0.78, 0.91 (4 × m, 4 H, 7-H − 9-H), 1.07 (d, ^3J = 5.8 Hz, 3 H, 10-H), 2.79 (m, 2 H, 4-H), 4.79 (dt, ^5J = 2.8, ^5J = 2.3 Hz, 2 H, 1-H), 5.03 (ddt, ^2J = 1.7, ^3J = 10.1, ^4J = 1.6 Hz, 1 H, 6-H), 5.09 (ddt, ^2J = 1.7, ^3J = 17.0, ^4J = 1.6 Hz, 1 H, 6-H), 5.86 (ddt, ^3J = 10.1, ^3J = 17.0, ^3J = 6.8 Hz, 1 H, 5-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.50 (t, C-9), 15.21 (d, C-8), 18.75 (q, C-10), 20.19 (d, C-7), 37.32 (t, C-4), 76.63 (t, C-1), 104.89 (s, C-3), 115.57 (t, C-6), 136.02 (d, C-5), 204.95 (s, C-2). − GC/IR: $\tilde{\nu}$ = 3071 cm^{-1} (s), 3001 (vs), 2962 (vs), 2931 (s), 2912 (s), 2901 (s), 2884 (s), 1959 (m), 1948 (m), 1646 (m), 1454 (m), 1439 (m), 1141 (m), 914 (s), 888 (s), 851 (s). − GC/MS (40 eV): *m/z* (%) = 134 [M^+] (62), 119 (93), 117 (28), 115 (18), 105 (23), 91 (100), 79 (20), 78 (62), 77 (24).

e) Pyrolysis of 1,4-bis(vinyloxy)but-2-yne (7). − 3-Vinyloxymethylpenta-3,4-dienal (79): GC/IR: $\tilde{\nu}$ = 3074 cm^{-1} (w), 3058 (w), 3027 (m), 2885 (w), 1969 (m), 1811 (s), 1780 (m), 1427 (m), 1395 (m), 1145 (s), 1058 (s), 1027 (vs), 995 (s), 869 (s). − GC/MS (40 eV): *m/z* (%) = 110 [M^+ − CO] (2), 94 (13), 82 (14), 81 (100), 69 (11), 66 (52), 65 (30), 55 (14), 54 (13), 53 (43), 52 (12), 51 (23). − **3,4-Dimethylenehexanedial (80):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.39 (d, ^3J = 2.5 Hz, 4 H, 2-H, 5-H), 5.28 and 5.32 (2 × s, 4 H, 7-H, 8-H), 9.63 (t, ^3J = 2.5 Hz, 2 H, 1-H, 6-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 49.17 (t, C-2, C-5), 119.05 (t, C-7, C-8), 138.01 (s, C-3, C-4), 199.56 (d, C-1, C-6). − GC/IR: $\tilde{\nu}$ = 2966 cm^{-1} (w), 2942 (m), 2389 (m), 2831 (s), 1670 (vs), 1608 (m), 1393 (s), 1322 (s), 1227 (s), 1079 (m), 1038 (m), 885 (s). − GC/MS (40 eV): *m/z* (%) = 138 [M^+] (1), 120 (10), 109 (100), 95 (30), 91 (31), 82 (29), 79 (25), 77 (15), 67 (72), 65 (25), 53 (40), 41 (59). − **4-Methyl-3-methylenepent-4-enal (81):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.99 (s, 3 H, CH_3), 3.32 (d, ^3J = 2.3 Hz, 2 H, 2-H), 4.98, 5.08, 5.19, 5.40 (4 × s, 4 H, =CH_2), 9.60 (t, ^3J = 2.3 Hz, 1 H, 1-H). − GC/IR: $\tilde{\nu}$ = 2808 cm^{-1} (m), 2715 (m), 1745 (s), 1701 (w), 1601 (w), 1419 (m), 1034 (m), 912 (m). − GC/MS (40 eV): *m/z* (%) = 110 [M^+] (3), 95 (4), 82 (81), 79 (15), 67 (100), 65 (14), 54 (28), 53 (28), 51 (11), 41 (54).

f) Pyrolysis of 1-Methoxy-4-vinyloxybut-2-yne (9). − 2-(Methylmethoxy)buta-1,3-diene (83): The spectroscopic data of this pyrolysis product are incomplete in ref.[55] − ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 3.36 (s, 3 H, CH_3), 4.11 (s, 2 H, 5-H), 5.16 (dd, ^2J = 1.5, ^3J = 11.0 Hz, 1 H, 4-H), 5.25 (s, 2 H, 1-H), 5.30 (dd, ^2J = 1.5, ^3J = 17.7 Hz, 1 H, 4-H), 6.38 (dd, ^3J = 11.0, ^3J =17.7 Hz, 1 H, 3-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 58.00 (q, CH_3), 72.27 (t, C-5), 114.29 (t, C-1), 117.20 (t, C-4), 136.49 (d, C-3), 142.34 (s, C-2). − GC/IR: $\tilde{\nu}$ = 3097 cm^{-1} (w), 2993 (m), 2931 (s), 2910 (s), 2835 (m), 2823 (m), 1592 (m), 1194 (m), 1118 (vs), 993 (m), 906 (vs). − GC/MS (40 eV): *m/z* (%) = 98 [M^+] (2), 96 (33), 94 (20), 81 (37), 67 (11), 66 (11), 65 (19), 53 (11), 51 (18), 45 (100), 43 (12).

g) Pyrolysis of 6-Vinyloxyhex-2-en-4-yne (10): A (*Z*)/(*E*) mixture of **10** (ratio 2:1) was employed in the pyrolysis experiments. − **3-Propenylpenta-3,4-dienal (90)**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.81 (dd, ^2J = 1.7, ^3J = 6.9 Hz, 3 H, 8-H), 3.13 (d, ^3J = 2.9 Hz, 2 H, 2-H), 4.98 (m, 2 H, 5-H), 5.51 (dq, 1 H, ^3J = 15.4, ^3J = 6.9 Hz, 7-H), 6.00 (d, ^3J = 15.4 Hz, 1 H, 6-H), 9.64 (t, ^3J = 2.9 Hz, 1 H, 1-H). − GC/IR: $\tilde{\nu}$ = 3042 cm^{-1} (w), 2929 (m), 2805 (m), 2712 (m), 1942 (m), 1746 (vs), 1032 (m), 962 (s), 855 (s). − GC/MS (40 eV): *m/z* (%) = 122 [M^+] (6), 121 (12), 107 (45), 94 (24), 93 (13), 91 (31), 79 (84), 78 (20), 77 (100), 65 (24), 53 (25), 52 (16). − **2-Cyclohexa-1,3-dienyl-acetaldehyde (94)**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.20 (m, 4 H, 5-H, 6-H), 3.09 (d, ^3J = 2.6 Hz, 2 H, 2-H), 5.50−6.00 (m, 3 H, 4-H, 7-H, 8-H), 9.62 (t, ^3J = 2.6 Hz, 1 H, 1-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.96 and 22.38 (2 × t, C-5, C-6), 50.20 (t, C-2), 125.51, 126.20, 127.96 (3 × d, C-4, C-7, C-8), 139.14 (s, C-3), 200.33 (d, C-1). − GC/IR: $\tilde{\nu}$ = 3041 cm^{-1} (m), 2947 (s), 2889 (m), 2838 (m), 1742 (vs), 1042 (m), 1034 (m). − GC/MS (40 eV): *m/z* (%) = 122 [M^+] (55), 104 (27), 93 (47), 91 (72), 79 (47), 78 (63), 77 (100), 65 (24), 53 (11), 51 (12). − The spectroscopic properties of **3-methylenecyclohexene (97)**[56] and **3-methylenehexa-1,4-diene (95)**[57] were identical to those reported in the literature.

h) Pyrolysis of 1,4-Bis(acetoxy)but-2-yne (12). − 1-Acetylvinyl Acetate (103):[58] ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, 6-H), 2.38 (s, 3 H, 1-H), 5.14 and 5.94 (2 × d, ^2J = 2.3 Hz, 2 H, 4-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.40 (q, C-6), 21.47 (q, C-1), 101.33 (t, C-4), 156.11 (s, C-3), 170.06 (s, C-5), 196.51 (s, C-2). − GC/IR: $\tilde{\nu}$ = 1725 cm^{-1} (vs), 1620 (s), 1303 (s), 1260 (s), 969 (m), 891 (m).

i) Pyrolysis of *trans*-1-(3-Methoxyprop-1-ynyl)-2-methylcyclopropane (18). − 1-(Methoxymethyl)hexa-1,2,5-triene (108): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.70 (m, 2 H, 4-H), 3.36 (s, 3 H, 8-H), 3.96 (dd, ^3J = 5.7, ^5J = 4.0 Hz, 2 H, 7-H), 5.04 (dd, ^2J = 1.7, ^3J = 10.3 Hz, 1 H, 6-H), 5.10 (dd, ^2J = 1.7, ^3J = 17.4 Hz, 1 H, 6-H), 5.23 (m, 2 H, 1-H, 3-H), 5.87 (ddt, ^3J = 6.9, ^3J = 10.3, ^3J = 17.4 Hz, 5-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 33.65 (t, C-4), 57.41 (q, C-8), 71.87 (t, C-7), 88.23 and 90.03 (2 × d, C-1, C-3), 115.34 (t, C-6), 136.12 (d, C-5), 210.75 (s, C-2). − IR (film): $\tilde{\nu}$ = 2983 cm^{-1} (m), 2925 (m), 2894 (m), 2856 (m), 2819 (m), 1965 (m), 1640 (w), 1193 (m), 1187 (m), 1101 (s), 992 (m), 913 (s). − GC/MS (40 eV): *m*/*z* (%) = 124 [M$^+$] (1), 123 (10), 109 (11), 93 (14), 92 (18), 91 (33), 79 (23), 77 (19), 45 (100). − **4-(2-Methoxyethylidene)cyclopentene (111):** 3.05 and 3.12 (2 × m, 4 H, 3-H, 5-H), 3.35 (s, 3 H, 8-H), 3.92 (d, ^3J = 6.8 Hz, 2 H, 7-H), 5.54 (m, 1 H, 6-H), 5.77 (m, 2 H, 1-H, 2-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 35.48 and 38.96 (2 × t, C-3, C-5), 57.76 (q, C-8), 70.34 (t, C-7), 118.38 (d, C-6), 128.97 and 129.52 (2 × d, C-1, C-2), 144.09 (s, C-4). − GC/IR: $\tilde{\nu}$ = 3070 cm^{-1} (s), 2986 (m), 2973 (m), 2902 (vs), 2829 (s), 1624 (w), 1199 (m), 971 (m), 920 (m). − GC/MS (40 eV): *m*/*z* (%) = 124 [M$^+$] (1), 123 (1), 93 (11), 92 (100), 91 (63), 79 (27), 78 (10), 77 (30), 66 (28), 65 (11). − **3-(2-Methoxyethylidene)cyclopentene (112**, mixture of isomers**):** ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.52 (m, 4 H, 4-H, 5-H), 3.32 and 3.34 (2 × s, 3 H, 8-H), 3.98 and 4.01 (2 × d, 2 H, ^3J = 6.9 Hz, 7-H), 5.33 and 5.47 (2 × m, 1 H, 6-H), 6.13 and 6.16 (2 × dd, ^3J = 6.2, ^4J = 1.2 Hz, 1 H, 2-H), 6.23 and 6.46 (2 × m, 1 H, 1-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.83, 29.38, 31.19, 32.05 (t, C-4, C-5), 57.54, 57.71 (q, C-8), 69.76, 70.35 (t, C-7), 113.20, 114.71 (d, C-6), 129.43, 134.23, 138.74, 140.57 (d, C-1, C-2), 150.65, 150.98 (s, C-3). − GC/IR: $\tilde{\nu}$ = 2989 cm^{-1} (m), 2931 (vs), 2893 (s), 2866 (s), 2824 (s), 1381 (m), 1198 (m), 1117 (vs), 915 (m), 830 (m). − GC/MS (40 eV): *m*/*z* (%) = 124 [M$^+$] (70), 123 (23), 109 (19), 93 (59), 92 (43), 91 (100), 81 (20), 79 (29), 77 (56), 66 (13), 65 (19), 53 (12), 45 (25).

j) Pyrolysis of 5-(2-methylcyclopropyl)pent-2-en-4-yne (mixture of isomers, **20): 3-But-2-enylidenecyclopentene (119)**: ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.80 (d, ^3J = 6.3 Hz, 3 H, 9-H), 2.25 (m, 4 H, 4-H, 5-H), 5.60−6.20 (m, 5 H, 1-H, 2-H, 6-H − 8-H). − ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 18.36 (q, C-9), 22.20 and 22.86 (2 × t, C-4, C-5), 122.22, 123.72, 125.03, 125.96, 133.40 (5 × d, C-1, C-2, C-6 − C-8). − GC/IR: $\tilde{\nu}$ = 3078 cm^{-1} (m), 3044 (vs), 2981 (m), 2940 (vs), 2885 (s), 2836 (s), 1643 (w), 1442 (m), 1430 (m), 991 (m), 918 (m). − GC/MS (40 eV): *m*/*z* (%) = 120 [M$^+$] (30), 125 (25), 92 (21), 91 (47), 79 (100), 78 (29), 77 (49), 65 (10). − The spectroscopic data of **2-allylcyclohexa-1,3-diene (75)** are given under c).

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