Preparation of δ-Chloro-α-allenyl Ketones by Acylation of 3-Buten-1-ynes†

Christiane Santelli-Rouvier, Sophie Lefrère, and Maurice Santelli*

Laboratoire de Synthèse Organique, URA au CNRS no. 1411, Centre. de St-Jérôme, Av. Esc. Normandie-Niemen, 13397 Marseille Cedex 20, France

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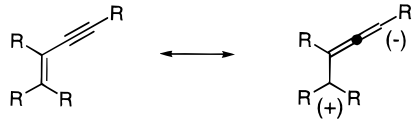
$AlCl_3$-mediated acylation of 3-buten-1-yne derivatives with acyl chlorides yields a mixture of 5-chloro-2,3-pentadienones and 3-chloro-2,4-pentadienones. The proportion of allenyl ketones vs conjugated dienic ketones depends on the substitution pattern of the starting enyne. Acylation of 5-acetoxy-3-buten-1-ynes leads to the corresponding allenyl ketones (6-acetoxy-5-chloro-2,3-pentadienones).

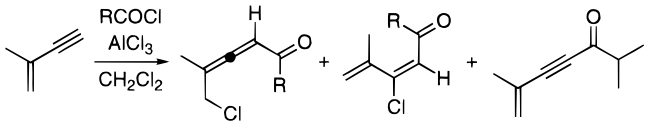
The acylation of olefins is a well-known reaction in the preparation of α,β-enones. However, the scope of this reaction is generally limited by the presence of numerous byproducts (β-halo ketones, β,γ-enones, or β-acyloxy ketones).[1] In a similar manner, the acylation of alkynes gives rise to β-chloro-α,β-enones as major products.[2] Sometimes more interesting products have been obtained. For example, when the acylation reaction was carried out in the presence of aromatic compounds, various β-aryl-α,β-enones were obtained.[3] In addition, intramolecular hydride migration has been observed[4] and cyclopentenones may also result from this process.[5] In the acylation of butenynes, one experiment resulted in the formation of β-chloro-α,β−γ,δ-dienones.[6,7] In contrast, very interesting results are obtained from the acylation of dicobalthexacarbonyl complexes of 1,3-enynes. Efficient stepwise reactions led to multifunctional compounds including a cyclopentenone moiety resulting from a subsequent Pauson−Khand reaction.[8,9]

Electrophilic addition reactions to conjugated enynes are known to take place in an unselective fashion and give a mixture of products resulting from the addition to both the double and the triple bonds. However, some allenic compounds are also formed from a 1,4-addition reaction corresponding to the polarization of the 3-buten-1-yne moiety as shown.[10]



Herein we describe some of our recent work on the acylation of the 3-buten-1-yne moiety, an approach that seemed ideally suitable for the synthesis of allenic ketones.[11]

The acylation of 3-methyl-3-buten-1-yne **1** yields a mixture of allenyl ketone **2** and conjugated dienic ketone **3**.



1 **2a**: R = Me, 60% **3a**: R = Me, 19% **4b**
2b: R = *i*-Pr, 68% **3b**: R = *i*-Pr, 22%

On purification by chromatography over silica gel, ketone **2a,b** partially isomerizes into ketone **3a,b** [**2a**, 64%; **3a**, 16% yield (^{1}H NMR integration); isolated products, **2a**, 60%; **3a**, 19% yield. **2b**, 80%; **3b**, 10% (by NMR); isolated products, **2b**, 68%; **3b**, 22% yield]. According to semiempirical PM3 calculations,[12] the dienic ketone **3a** is significantly more stable ($\Delta H_f = -26.6$ kcal/mol) than the corresponding allenic ketone **2a** ($\Delta H_f = -16.1$ kcal/mol). With the aim of suppressing this isomerization, triethylamine (3% v/v) was added to the eluent of the flash chromatography of **2b**, but this led to the formation of enynone **4b**.

Interestingly, allenyl ketones were obtained even in

† Gratefully dedicated to Professor A. Guillemonat who introduced allene chemistry at the University of Marseille.

* Author to whom correspondence should be addressed. Fax: (33) 91 98 38 65. E-mail: m.santelli@lso.u-3mrs.fr.

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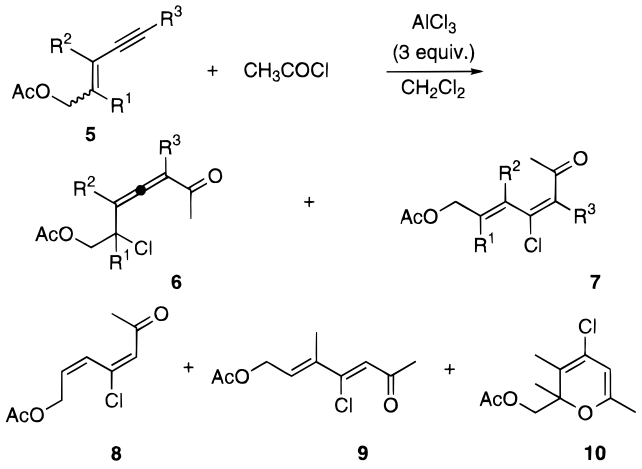
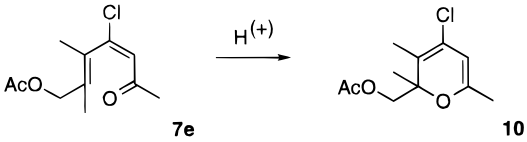
the case of the acylation of 5-acetoxy-3-buten-1-ynes **5**.[13] The stability of the allenyl ketones **6** increased with the substitution pattern of the enyne moiety. Allenyl ketones **6** were obtained as an inseparable mixture of diastereomers.



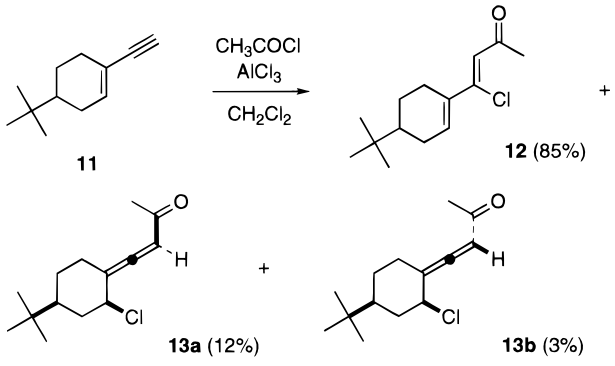
a, $R^1 = R^2 = R^3 = H$; **7a** : 48%; **8** : 32%
b, $R^1 = R^3 = H$; $R^2 = Me$; **6b** : 35% (mixt. of diaster., 3.3 : 1); **9** : 48%
c, $R^1 = R^2 = H$; $R^3 = Me$; **6c** : 57% (mixt. of diaster., 8 :1); **7c** : 38%
d, $R^1 = H$; $R^2 = R^3 = Me$; **6d** : 85% (mixt. of diaster., 1.8 : 1); **7d** : 5%
e, $R^1 = R^2 = Me$; $R^3 = H$; **6e** : 40% (mixt. of diaster., 9 : 1); **10** : 52%

The proportion of allenyl ketones **6** increased with the substitution of the starting enyne moiety and particularly at the acetylenic end.

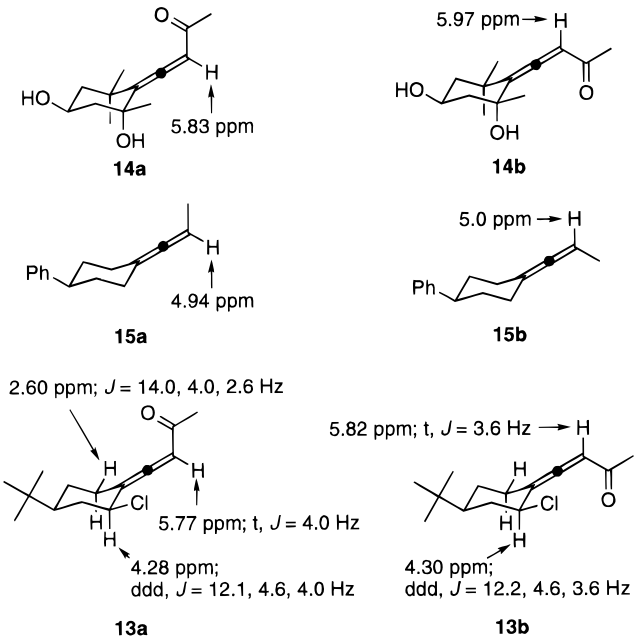
The pyran derivative **10** probably results from a proton-induced cyclization of the dienic ketone **7e** (not isolated).



The acylation of 1-ethynyl-4-*tert*-butylcyclohexene **11** led, after chromatography over silica gel, mainly to the dienic ketone **12** with only small amounts of the allenic ketones **13a** and **13b**.



The stereochemistry of **13a** and **13b** was determined by examining the ^1H NMR spectrum. The magnitude of the coupling constants ($^3J_{ax.-ax.} = 12.1$ Hz) of the signals due to the geminate proton to the chlorine showed that the latter was equatorial.[14] We noted that the allenic protons were coupled only with the ring axial protons (^5J coupling constant), in agreement with the previous quantitative relation between molecular conformation and dihedral angle.[15] For the major allenic ketone, we tentatively assign the configuration **13a** by analogy with the known vinylidenecyclohexanes such as the grasshopper ketone **14a**,[16] its epimeric racemate **14b**,[17] the propenylidenecyclohexanes **15a** and **15b**,[18] and an allenic epoxycyclohexane.[19] For these compounds, structures were determined by X-ray crystallographic analysis. From these few examples, it appears that the pseudo-axial allenic proton has a chemical shift which is deshielded relative to its equatorial counterpart.



An increased yield of allenic ketone was observed during the acylation of ethynylcyclohexene. The diastereomeric allenyl ketones **16** and **17** were isolated by flash chromatography on silica gel with partial isomerization into dienic ketone **18**. The structure of the allenic ketones was confirmed by ^1H NMR data with decoupling experiments. The C−Cl bond appears to be axial (Cl−C−*H*, **16a**, $\delta = 4.71$ ppm; t, $J = 4.2$ Hz; **17a**, $\delta = 4.66$ ppm; t, $J = 4.4$ Hz; **16b** or **17b**, $\delta = 4.69$ ppm; t, $J = 4.0$ Hz). To confirm the stability of the axial C−Cl bond, we have carried out a semiempirical PM3 study.[12] Calculations reveal that from the four possible stereomers, the more stable compounds were **16a** (or **16b)** and then **17a** (or **17b**) (Chart 1). We propose that the preferential

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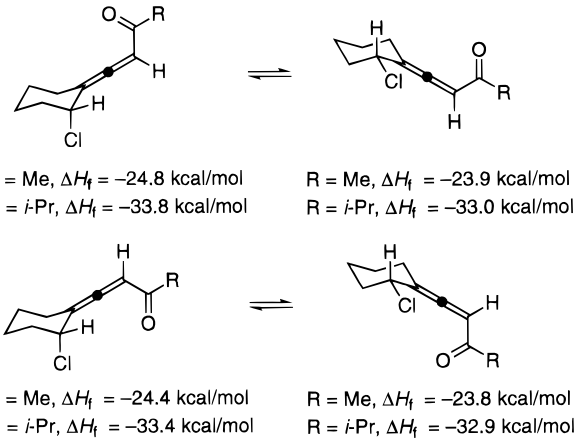
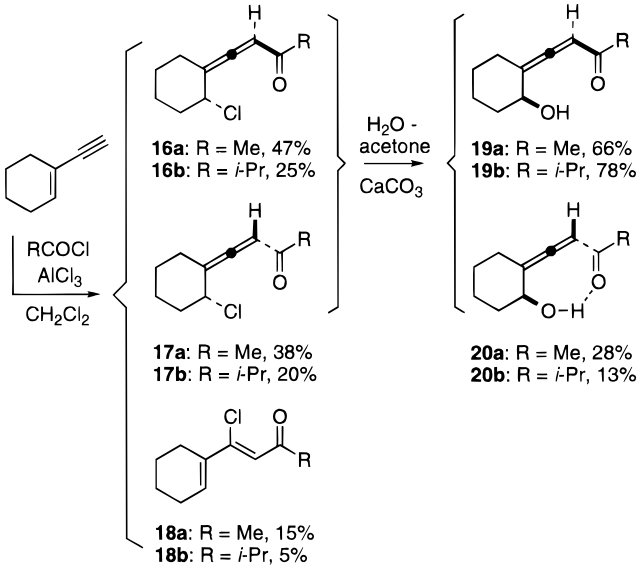
Chart 1. PM3 Calculated Heat of Formation of Chloroallenic Ketones 16 and 17



formation of the more stable stereomers results from chlorine exchange occurring during the reaction.



Interestingly, the diastereomeric mixture of allenyl ketones **16a** and **17a** or **16b** and **17b** can be hydrolyzed in good yield into the allenic ketols **19a** and **20a** or **19b** and **20b**, respectively. Each of these pairs was separable by flash chromatography on silica gel. In contrast to the precursors, the hydroxy group in these alcohols is located in an equatorial position. In each case, the relative proportion of stereomers was modified in favor of the *R*,S**-diastereomer.

Acylation of trimethylethynylcyclohexene **21**[20] led to the very interesting allenic ketone **22**, a convenient precursor of ionone. Although this reaction provides a straightforward access to a class of natural products, the yield for the addition was only modest.

Discussion

Two mechanisms have been invoked to account for the acylation of olefins: electrophilic attack[21] to give a β-ketocation possibly followed by a cyclic transfer of the γ-hydrogen to oxygen,[1b] or a heteroene reaction.[22] In the case of the acylation of butenynes, electrophilic attack would be expected to occur only at the end of the conjugated system. The answer to the problem of the orientation of the electrophilic addition to an unsymmetrical substrate is given by Markovnikov's rule: *the positive portion of the reagent goes to the end of the double or triple bond that has more hydrogens.* A number of explanations have been suggested for this regioselectivity, but the most probable is that the electrophilic reagent adds to the end that will give the more stable carbocation.[23] The rule would predict that the attack should be at C(4) of 3-methylbut-3-en-1-yne, leading to the mesomeric 5-oxo-1-butyn-3-yl cation **25**. However, in our study all the addition products obtained came from attack at C(1), which involves the mesomeric 5-oxo-2,3-butadien-1-yl cation **24**. With the aim of understanding the origin of this regioselectivity, we have carried out molecular orbital calculations, with the object of finding a theoretical interpretation (Figure 1).

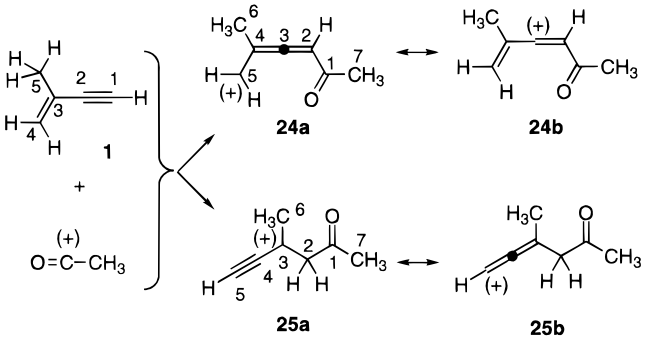
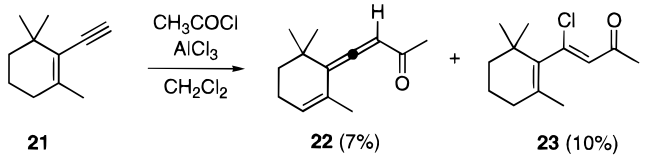


Figure 1. Addition of acetyl cation to 3-methyl-3-buten-1-yne.



Firstly, we calculated charges and HOMO coefficients for 3-methylbut-3-en-1-yne using the *ab initio* UHF/6-31G** level[24] and also by the PM3 method (Table 1). Calculations indicated that the magnitude of the HOMO coefficient at C(4) is greater than at C(1) [6-31G** (PM3); C(1), 0.513 (0.427); C(2), 0.380 (0.275); C(3), −0.504 (−0.518); C(4), −0.602 (−0.643)]. In contrast, the net atomic charge is mainly present at C(1) [6-31G** (PM3); C(1), −0.450 (−0.172); C(2), 0.102 (−0.140); C(3), 0.024 (0.022); C(4), −0.274 (−0.154)]. This would indicate that the regioselectivity of the acylation addition to the conjugated enyne is a charge-controlled reaction.[25,26]

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(29) Cf. ref 24, p 251.

Table 1. Optimized Bond Lengths and Angles of 3-Methylbut-3-en-1-yne Calculated Using the *Ab Initio* UHF/6-31G Level and by the PM3 Method[b]**

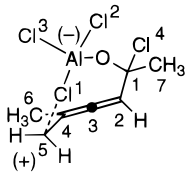
	6-31G**	PM3		6-31G**	PM3
HOMO, eV[c]	−9.05 eV	−9.65 eV	C(1)−C(2)−C(3)	178.5	179.9
C(1)−C(2)	1.189	1.192	C(2)−C(3)−C(4)	120.2	121.1
C(2)−C(3)	1.445	1.419	C(2)−C(3)−C(5)	117.0	116.6
C(3)−C(4)	1.323	1.336	H−C(1)−C(2)	179.5	179.9
C(3)−C(5)	1.519	1.490	C(3)−C(4)−H	121.6	123.1
			H−C(4)−H	117.3	114.8

[a] Bond lengths and angles are expressed in Å and deg, respectively. [b] Atom numbering is as in Figure 1. [c] HOMO energies (6-31G*) of 1,3-pentadiene, −8.53 eV (ref 27); isoprene, −8.70 eV (ref 28).

Secondly, we determined the structures and energies at the RHF/6-31G** and RHF/3-21G level and with the PM3 method for the isomeric cations **24** and **25** which arise from attack at C(1) or C(4), respectively (Table 2). The difference of total energies *E*(**24**)−E(**25**) is calculated to be −2.50 kcal/mol at the 6-31G** level, 1.48 kcal/mol at the 3-21G level, and 6.40 kcal/mol with the PM3 method, in favor of the mesomeric cation **25**. Although these calculations are not a reliable measure of the relative energy of **24** and **25** in solution, they are in line with the intuitive idea that electrophilic attack at C(1) would give the less stable of the two cations resulting from a formal addition of an acetyl cation to 3-methylbut-3-en-1-yne.

The PM3-optimized geometry of **24** resembles that calculated *ab initio*. The chief discrepancy is that the dihedral angle O−C(1)−C(2)−C(3) is larger. Consequently, the O−C(3) length is increased at the PM3 level. The main feature of these calculations was the nonplanar structure of the *s-cis*-α,*β*-ethylenic ketone moiety and the relatively short length of the O−C(3) distance. This nonplanar conformation can be attributed to the stabilizing interaction of the lone pair orbital at O with the allylic cation moiety. As for **24**, PM3 and *ab initio* calculations for propargyl cation **25** indicate a hairpin structure with the possibility of interaction of the oxygen lone pair with the tertiary carbon. The propargyl structure of the cation moiety was confirmed by the charge density [6-31G**, 3-21G, PM3, respectively; C(3), 0.233, 0.241, 0.545; C(5), −0.169, −0.101, 0.242].

Thirdly, since the regioselectivity of the acylation cannot be explained by the formation of the keto cation **24**, we calculated energies by the PM3 method for the 1:1:1 $AlCl_3$−acetyl chloride−methylbutenyne complexes **26** and **27**. Such tetrahedral intermediates have previously been invoked during the course of the Friedel−Crafts acylation.[30,31]



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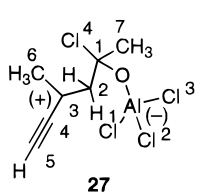
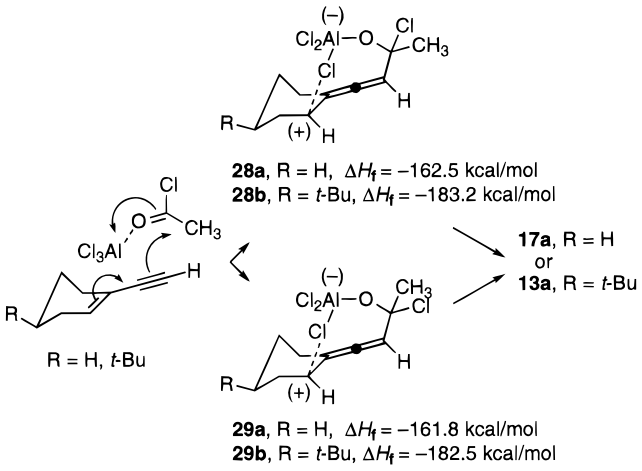


27

In this case, the PM3 method calculations show a significant difference between the two possible zwitterionic intermediates **26** and **27**. Thus **26** has $H_f = -153.8$ kcal/mol, whereas **27** has $H_f = -121.5$ kcal/mol ($\Delta H_f = 32.3$ kcal/mol). In **26**, the origin of this stabilization seems to be the proximity of one chlorine to C(5) with a lengthening of the bond distance of the same chlorine and aluminum ($d_{(C(5)-Cl)} = 1.80$ Å, $d_{(Cl-Al)} = 2.47$ Å).[32] The charge distributions reflect this interaction; the carbons of the allyl cation moiety bear a negative charge (C(3), −0.22; C(4), −0.02; C(5), −0.07). The opposite charges are present on the singular chlorine atom and the aluminum atom (Cl, 0.13; Al, 0.83). In contrast, in the zwitterionic intermediate **27**, the carbon atoms C(3) and C(5) of the propargyl cation bear a positive charge and all the chlorine atoms are remote from C(3) or C(5).

PM3 calculations of the zwitterionic intermediates arising from the acylation of ethynylcyclohexene displayed a low diastereoselectivity. In diastereomer **28a**, one chlorine is near C(1) ($d_{(C(1)-Cl)} = 1.82$ Å, $d_{(Cl-Al)} = 2.47$ Å; charge density, C(1), −0.024). According to these calculations, the isolated major compound should be **17a**, but $AlCl_3$-promoted chlorine exchange should lead to an equilibrium between **16a** and **17a**. Similar results account for the formation of **13a** through the zwitterionic intermediates **28b** or **29b**.



The formation of the hydroxy allenic ketone derivatives **19** or **20** could result from nucleophilic reagent addition to a mesomeric 5-oxo-2,3-butadien-1-yl cation similar to **24**.[33] Of previous results on the trapping of the 2,3-butadien-1-yl cation, only a few report the formation of allenic derivatives by nucleophilic attack of water or ethanol.[34] In the mesomeric cation **24**, PM3 calculations indicated that the magnitude of the LUMO coefficient at C(3) (0.615) is slightly greater than at C(5) (−0.570), but 3-21G calculations reveal the reverse trend (C(3), 0.424; C(5), −0.445). The calculated value of the charge density is 0.261 for C(5) and 0.228 for C(3). In conclusion, FMO theory cannot explain completely the regioselectivity of the nucleophilic attack favoring C(5). Neverthe-

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(32) Measured bond distances: C(sp^2)−Cl, 1.73 Å (see, Rajput, A. S.; Chandra, S., *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1854−1857); Al-Cl in $Al_2Cl_7^-$, 2.10 Å (see, Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience Publishers: New York, 1972; p 269).

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Table 2. Optimized Energies, Bond Lengths and Angles[a] of 2-Methyl-5-oxo-2,3-pentadien-1-yl Cation 24 and 3-Methyl-5-oxo-1-pentyn-3-yl Cation 25 Calculated Using the *Ab Initio* RHF/6-31G or 3-21G Level and by the PM3 Method[b]**

	24			25		
	6-31G**	3-21G	PM3	6-31G**	3-21G	PM3
energy (a.u.)	−344.85976	−342.91218	−45.99243	−344.85517	−342.91453	−46.00263
ZPE (kcal/mol)[c]	83.19			82.82		
O−C(1)	1.180	1.198	1.202	1.186	1.202	1.208
C(1)−C(2)	1.549	1.557	1.533	1.556	1.581	1.550
C(2)−C(3)	1.277	1.272	1.279	1.492	1.483	1.470
C(3)−C(4)	1.372	1.367	1.369	1.381	1.370	1.386
C(4)−C(5)	1.363	1.361	1.373	1.199	1.199	1.207
C(1)−C(7)	1.500	1.500	1.495	1.502	1.502	1.496
C(4)−C(6)	1.517	1.525	1.494			
C(3)−C(6)				1.477	1.478	1.452
O−C(3)	2.748	2.774	2.948	2.654	2.734	2.800
O−C(1)−C(2)	118.3	119.0	119.2	119.6	120.6	120.7
C(1)−C(2)−C(3)	119.2	119.8	123.7	108.8	108.9	114.3
C(2)−C(3)−C(4)	177.7	177.5	178.3	119.1	119.3	119.1
C(3)−C(4)−C(5)	113.2	115.3	119.4	179.8	179.1	179.6
O−C(1)−C(7)	126.4	127.2	127.6	124.9	126.0	125.6
C(3)−C(4)−C(6)	121.6	120.2	118.7			
C(2)−C(3)−C(6)				121.0	120.2	121.2
O−C(1)−C(2)−C(3)	−15.4	−7.4	−46.3	−7.6	−20.5	−12.5
C(1)−C(2)−C(3)−C(4)				−97.3	−101.9	−107.9
C(1)−C(2)−C(4)−C(5)	84.3	86.0	87.3	−87.2	−92.2	−92.5

[a] Bond lengths and angles are expressed in Å and deg, respectively. [b] Atom numbering is as in Figure 1. [c] ZPEs (zero point energies) are scaled by 0.90.[29]

less, our experimental results (hydrolysis of **16** or **17**) strongly indicate that the kinetic products are the corresponding allenic ketone derivatives.

Conclusion

The acylation reaction of conjugated enynes has attracted interest due to the importance of natural allenyl ketones and the difficulty of their synthesis.[35] Further application of this direct method is expected in the synthesis of allenic compounds.

Experimental Section

General. All reactions were run under argon in oven-dried glassware. TLC was performed on silica gel 60 F_{254}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions at 400 and 200, and 100 and 50 MHz, respectively. Carbon−proton couplings were determined by DEPT sequence experiments.[36]

General Procedure for Acylation of Butenynes (or Acetoxybutenynes). Aluminum trichloride (3.33 g, 25 mmol) (or 10 g, 75 mmol), anhydrous CH_2Cl_2 (45 mL) (or 80 mL) and acyl chloride (27.5 mmol, 1.1 equiv) were stirred until dissolution. The resulting solution was stirred under vacuum (20 mmHg) for 3 min and cooled to −90 °C, and the enyne derivative (30 mmol, 1.2 equiv) in anhydrous CH_2Cl_2 (30 mL) was slowly added over 2 h. The solution was allowed to warm to −60 °C, the mixture was stirred until TLC showed the end of the reaction and then added to a vigorously stirred mixture of crushed ice and Et_2O. The organic layer was quickly stirred with a saturated solution of $NaHCO_3$ and dried using $MgSO_4$ with storage in a refrigerator. After filtration and concentration in vacuo at room temperature, the crude product was quickly flash chromatographed on silica gel eluting with a gradient of pentane−ether. δ-Chloro-α-allenyl ketones are unstable compounds and should be stored in a refrigerator.

Acylation of 2-Methyl-1,3-butenyne with Acetyl Chloride. 5-Methyl-6-chloro-3,4-hexadien-2-one (2a): IR 1954, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.63 (m, 1H), 4.03 (1/2 AB, d, J = 11.4, 1.4 Hz, 1H), 3.99 (1/2 AB, d, J = 11.4, 1.8 Hz, 1H), 2.10 (s, 3H), 1.85 (d, J = 2.93 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.6 (s), 198.1 (s), 101.6 (s), 97.6 (d), 45.4 (t), 26.6 (q), 15.6 (q). Anal. Calcd for C_7H_9OCl: C, 58.14; H, 6.27; Cl, 24.52. Found: C, 58.18; H, 6.20; Cl, 24.49.

5-Methyl-4-chloro-3,5-hexadien-2-one (3a): IR 1745 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.35 (s, 1H), 5.81 (s, 1H), 5.35 (s, 1H), 2.34 (s, 3H), 1.93 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 197.5 (s), 139.6 (s), 132.1 (s), 124.2 (d), 122.6 (t), 31.8 (q), 20.4 (q).

Acylation of 2-Methyl-1,3-butenyne with Isobutyryl Chloride. 2,6-Dimethyl-7-chloro-4,5-heptadien-3-one (2b): IR 1960, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.68 (m, 1H), 4.12 (1/2 AB, d, J = 11.4, 1.6 Hz, 1H), 4.05 (1/2 AB, d, J = 11.4, 1.9 Hz, 1H), 2.98 (sept, J = 6.9 Hz, 1H), 1.89 (d, J = 2.95 Hz, 3H), 1.03 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 210.7 (s), 204.2 (s), 101.4 (s), 95.7 (d), 45.5 (t), 37.1 (d), 18.9 (q), 18.8 (q), 15.6 (q). Anal. Calcd for $C_9H_{13}OCl$: C, 62.61; H, 7.59; Cl, 20.53. Found: C, 62.51; H, 7.55; Cl, 20.55.

2,6-Dimethyl-5-chloro-4,6-heptadien-3-one (3b): IR 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.45 (s, 1H), 5.80 (s, 1H), 5.34 (s, 1H), 2.74 (sept, J = 6.9 Hz, 1H), 1.95 (s, 3H), 1.06 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 197.6 (s), 139.5 (s), 126.4 (d), 124.7 (s), 122.0 (t), 47.9 (d), 20.2 (q), 15.5 (q) (2C).

2,6-Dimethyl-6-hepten-4-yn-3-one (4b): IR 2194, 1673 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.46 (s, 1H), 5.40 (s, 1H), 2.55 (sept, J = 6.9 Hz), 1.84 (s, 3H), 1.08 (d, J = 6.9 Hz, 6H).

Acylation of 1-Acetoxy-2-penten-4-yne (5a) with Acetyl Chloride. (3*E*,5*E*)-7-Acetoxy-4-chloro-3,5-heptadien-2-one (7a): IR 1743, 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.33 (d, J = 15.2 Hz, 1H), 6.23 (dt, J = 15.2, 5.25 Hz, 1H), 6.13 (s, 1H), 4.41 (d, J = 5.25 Hz, 2H), 1.88 (s, 3H), 1.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 194.6 (s), 169.3 (s), 144.8 (s), 136.4 (d), 125.0 (d), 124.7 (d), 62.5 (t), 31.2 (q), 19.8 (q). Anal. Calcd for $C_9H_{11}O_3Cl$: C, 53.35; H, 5.47; Cl, 17.50. Found: C, 53.46; H, 5.43; Cl, 17.47.

(3*E*,5*Z*)-7-Acetoxy-4-chloro-3,5-heptadien-2-one (8): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.35−6.07 (m, 2H), 6.13 (s, 1H), 4.45 (d, J = 5.0 Hz, 2H), 2.08 (s, 3H), 1.81 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 195.7 (s), 169.6 (s), 138.5 (s), 134.0 (d), 129.3 (d), 126.5 (d), 62.5 (t), 31.2 (q), 20.1 (q).

Acylation of 1-Acetoxy-3-methyl-2-penten-4-yne (5b) with Acetyl Chloride. 7-Acetoxy-6-chloro-5-methyl-3,4-heptadien-2-one (6b). Unseparable 3.3:1 mixture of diastereomers: IR 1954, 1748, 1684, 1228 cm^{-1}. Major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.77 (br s, 1H), 4.59 (dd, J = 14.0, 7.5 Hz, 1H), 4.30 (m, 2H), 2.19 (s, 3H), 2.04 (s, 3H), 1.92 (d, J = 2.9 Hz); ^{13}C NMR ($CDCl_3$) δ 211.2 (s), 197.7 (s), 170.0

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(s), 102.4 (s), 98.5 (d), 64.7 (t), 57.5 (d), 26.8 (q), 20.5 (q), 14.4 (q). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 5.77 (br s, 1H), 4.59 (dd, J = 14.0, 7.5 Hz, 1H), 4.30 (m, 2H), 2.20 (s, 3H), 2.05 (s, 3H), 1.93 (d, J = 2.7 Hz); ^{13}C NMR ($CDCl_3$) δ 211.2 (s), 197.7 (s), 170.0 (s), 102.4 (s), 98.7 (d), 64.9 (t), 54.6 (d), 26.8 (q), 20.5 (q), 14.6 (q). Anal. Calcd for $C_{10}H_{13}O_3Cl$: C, 55.44; H, 6.05; Cl, 16.36. Found: C, 55.55; H, 6.09; Cl, 16.28.

(3*Z*,5*E*)-7-Acetoxy-4-chloro-5-methyl-3,5-heptadien-2-one (9): IR 1740, 1685, 1234 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.38 (s, 1H), 6.35 (t, J = 6.4 Hz, 1H), 4.70 (d, J = 6.4 Hz, 2H), 2.33 (s, 3H), 2.00 (s, 3H), 1.86 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 196.9 (s), 170.4 (s), 142.3 (s), 134.7 (s), 130.5 (d), 124.0 (d), 61.1 (t), 31.6 (q), 20.5 (q), 14.6 (q).

Acylation of 1-Acetoxy-2-hexen-4-yne (5c) with Acetyl Chloride. 7-Acetoxy-6-chloro-3-methyl-3,4-heptadien-2-one (6c). Unseparable 8:1 mixture of diastereomers: IR 1951, 1741, 1681, 1230 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.66 (m; 1H), 4.63 (m, 1H), 4.28 (dd, J = 5.47, 3.66 Hz, 2H), 2.24 (s, 3H), 2.02 (s, 3H), 1.73 (s, 3H). Major isomer: ^{13}C NMR ($CDCl_3$) δ 212.9 (s), 204.4 (s), 170.7 (s), 96.7 (s), 93.7 (d), 66.5 (t), 54.6 (d), 27.0 (q), 20.6 (q), 18.1 (q). Minor isomer (in part): ^{13}C NMR ($CDCl_3$) δ 212.7 (s), 93.8 (d), 26.8 (q). Anal. Calcd for $C_{10}H_{13}O_3Cl$: C, 55.44; H, 6.05; Cl, 16.36. Found: C, 55.59; H, 5.98; Cl, 16.46.

(3*E*,5*E*)-7-Acetoxy-4-chloro-3-methyl-3,5-heptadien-2-one (7c): ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.81 (d, J = 15.0 Hz, 1H), 6.26 (dt, J = 15.0, 4.9 Hz, 1H), 4.63 (d, J = 4.9 Hz, 2H), 2.22 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 201.7 (s), 170.2 (s), 136.1 (s), 134.5 (s), 130.8 (d), 127.3 (d), 63.7 (t), 29.8 (q), 20.8 (q), 13.2 (q).

Acylation of 1-Acetoxy-3-methyl-2-hexen-4-yne (5d) with Acetyl Chloride. 7-Acetoxy-6-chloro-3,5-dimethyl-3,4-heptadien-2-one (6d). Unseparable 9:1 mixture of diastereomers: IR 1953, 1746, 1683, 1233 cm^{-1}. Major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.58 (t, J = 6.8 Hz, 1H), 4.26 (m, 2H), 2.20 (s, 3H), 2.01 (s, 3H), 1.87 (s, 3H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 210.5 (s), 198.5 (s), 170.1 (s), 105.5 (s), 100.8 (s), 65.16 (t), 58.33 (d), 26.9 (q), 20.6 (q), 14.3 (q), 13.2 (q). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 4.50 (t, J = 7.0 Hz, 1H), 4.26 (m, 2H), 2.20 (s, 3H), 2.02 (s, 3H), 1.89 (s, 3H), 1.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 210.5 (s), 198.5 (s), 170.1 (s), 105.5 (s), 100.8 (s), 65.19 (t), 58.28 (d), 26.9 (q), 20.6 (q), 14.3 (q), 13.2 (q). Anal. Calcd for $C_{11}H_{15}O_3Cl$: C, 57.27; H, 6.55; Cl, 15.37. Found: C, 57.16; H, 6.58; Cl, 15.30.

Acylation of 1-Acetoxy-2,3-dimethyl-2-penten-4-yne (5e) with Acetyl Chloride. 7-Acetoxy-6-chloro-5,6-dimethyl-3,4-heptadien-2-one (6e): IR 1952, 1748, 1686, 1231 cm^{-1}. Major isomer: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.75 (q, J = 2.8 Hz, 1H), 4.24 (m, 2H), 2.16 (s, 3H), 2.01 (s, 3H), 1.92 (d, J = 2.8 Hz, 3H), 1.66 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 211.1 (s), 197.0 (s), 169.9 (s), 107.3 (s), 99.2 (d), 68.6 (t), 67.5 (s), 26.5 (q), 26.4 (q), 20.6 (q), 14.6 (q). Anal. Calcd for $C_{11}H_{15}O_3Cl$: C, 57.27; H, 6.55; Cl, 15.37. Found: C, 57.20; H, 6.54; Cl, 15.41.

2-(Acetoxymethyl)-4-chloro-2,3,6-trimethyl-2*H*-pyran (10): IR 1744, 1654, 1233 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 4.98 (br s, 1H), 4.33 (1/2 AB, J = 11.8 Hz, 1H), 3.90 (1/2 AB, J = 11.8 Hz, 1H), 2.05 (s, 3H), 1.74 (s, 3H), 1.73 (s, 3H), 1.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.9 (s), 151.9 (s), 124.6 (s), 118.6 (s), 100.8 (d), 81.7 (s), 64.9 (t), 30.0 (q), 20.8 (q), 17.0 (q), 14.3 (q).

Acylation of 4-*tert*-Butyl-1-ethynylcyclohexene (11) with Acetyl Chloride. (2*Z*)-4-Chloro-4-(4-*tert*-butyl-1-cyclohexenyl)-3-buten-2-one (12): IR 1658, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.67 (br s, 1H), 6.24 (s, 1H), 2.30 (s, 3H), 0.78 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 197.5 (s), 136.7 (d), 133.3 (s), 121.5 (d), 97.5 (s), 59.0 (s), 65.7 (t), 28.0 (t), 27.7 (t), 27.3 (q), 27.0 (q) (3C).

***cis*-4-*tert*-Butyl-2-chloro-1-(3-oxo-1-butenylidene)cyclohexane (13).** Unseparable 4:1 mixture of diastereomers: IR 1951, 1682, 1235 cm^{-1}. **13a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.77 (t, J = 4.0 Hz, 1H), 4.28 (ddd, J = 12.1, 4.6, 4.0 (suppressed by irradiation at 5.77 ppm) Hz, 1H), 2.60 (ddd, J = 14.0, 3.7, 3.0 Hz, 1H), 2.45−2.32 (m, 1H), 2.32−2.20 (m, 1H), 2.20 (s, 3H), 2.15−1.98 (m, 1H), 1.55−1.40 (m, 1H), 1.28−1.15 (m, 1H), 0.85 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 208.1 (s), 199.0 (s), 110.1 (s), 100.1 (d), 56.6 (d), 47.9 (t), 41.3 (d), 39.9 (t), 30.7 (s), 27.6 (q), 27.4 (q)(3C), 27.0 (t). **13b**: ^{1}H NMR δ (in part) 5.82 (t, J = 3.6 Hz, 1H), 4.30 (ddd, J = 12.2, 4.6, 3.6 Hz, 1H), 2.58 (ddd, J = 14.0, 3.7, 3.0 Hz, 1H), 2.14 (s, 3H), 0.84 (s, 9H). Anal. Calcd for $C_{14}H_{21}OCl$: C, 69.84; H, 8.79; Cl, 14.72. Found: C, 69.75; H, 8.82; Cl, 14.81.

Acylation of 1-Ethynylcyclohexene with Acetyl Chloride. 2-Chloro-1-(3-oxo-1-butenylidene)cyclohexane (16a and 17a) was separated by flash chromatography on silica gel: IR 1952, 1682, 1228 cm^{-1}. **16a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.67 (br d, J = 3.0 Hz, 1H), 4.71 (t, J = 4.2 Hz, 1H), 2.55 (dddd, J = 14.2, 10.4, 4.1, 3.0 Hz, 1H), 2.17 (s, 3H), 2.0−1.2 (m; 7H); ^{13}C NMR ($CDCl_3$) δ 208.2 (s), 199.3 (s), 107.2 (s), 97.6 (d), 58.0 (d), 35.3 (t), 26.1 (q), 25.9 (t), 25.3 (t), 20.6 (t); Anal. Calcd for $C_{10}H_{13}OCl$: C, 65.04; H, 7.10; Cl, 19.20. Found: C, 64.96; H, 7.08; Cl, 19.18. **17a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ (in part) 5.67 (d, J = 3.2 Hz, 1H), 4.66 (d, J = 4.4 Hz, 1H), 2.49 (dddd, J = 14.2, 10.4, 4.1, 3.2 (suppressed by irradiation at 5.67 ppm) Hz, 1H), 2.11 (s, 3H), 2.0−1.2 (m; 7H); ^{13}C NMR ($CDCl_3$) δ 207.5 (s), 197.4 (s), 107.5 (s), 97.5 (d), 57.7 (d), 35.7 (t), 26.5 (t), 26.1 (q), 25.6 (t), 20.8 (t).

4-Chloro-4-(1-cyclohexenyl)-3-buten-2-one (18a): IR 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.71 (t, J = 3.3 Hz, 1H), 6.29 (s, 1H), 2.35 (s, 3H), 2.10 (br s, 4H), 1.68−1.42 (br s, 4H); ^{13}C NMR ($CDCl_3$) δ 197.7 (s), 143.6 (s), 136.3 (d), 133.5 (s), 121.4 (d), 32.1 (q), 26.3 (t), 26.0 (t), 22.4 (t), 21.5 (t).

Acylation of 1-Ethynylcyclohexene with isobutyryl Chloride. 2-Chloro-1-(4-methyl-3-oxo-1-pentylidene)cyclohexane (16b and 17b) was separated by flash chromatography on silica gel: IR 1953, 1682 cm^{-1}. **16b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.62 (d, J = 3.0 Hz, 1H), 4.69 (t, J = 4.0 Hz, 1H), 3.00 (sept, J = 6.85 Hz, 1H), 2.60−2.46 (m, 1H), 2.26−2.15 (m, 1H), 2.02−1.94 (m, 2H), 1.90−1.67 (m, 2H), 1.59−1.44 (m, 2H), 1.01 (d, J = 6.85 Hz, 3H), 0.98 (d, J = 6.85 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 207.2 (s), 203.7 (s), 107.0 (s), 95.7 (d), 58.0 (d), 36.4 (d), 35.3 (t), 26.0 (t), 25.3 (t), 20.8 (t), 18.8 (q), 18.5 (q). **17b**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.69 (br d, J = 3.12 Hz, 1H), 4.69 (t, J = 4.0 Hz, 1H), 2.95 (sept, J = 6.85 Hz, 1H), 2.51 (m, 1H), 2.18 (dt, J = 14.1, 4.5 Hz, 1H), 1.99−1.92 (m, 2H), 1.899−1.64 (m, 2H), 1.57−1.18 (m, 2H), 1.06 (d, J = 6.85 Hz, 3H), 1.03 (d, J = 6.85 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 207.9 (s), 204.3 (s), 107.4 (s), 95.6 (d), 57.7 (d), 36.5 (d), 35.7 (t), 26.3 (t), 25.7 (t), 20.8 (t), 18.6 (q) (2C). Anal. Calcd for $C_{12}H_{17}OCl$: C, 67.76; H, 8.06; Cl, 16.67. Found: C, 67.80; H, 8.01; Cl, 16.72.

(4*Z*)-5-Chloro-5-(1-cyclohexenyl)-2-methyl-4-buten-3-one (18b). IR 1683 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.64 (t, J = 3.5 Hz, 1H), 6.33 (s, 1H), 2.70 (sept, J = 6.9 Hz, 1H), 2.15 (br s, 4H), 1.9−1.3 (m, 4H), 0.88 (d, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 203.0 (s), 143.3 (s), 135.7 (d), 133.5 (s), 118.8 (d), 41.7 (d), 26.25 (t), 26.18 (t), 22.4 (t), 21.4 (t), 18.1 (q) (2C). Differential nuclear Overhauser enhancement experiments confirm the *Z*-configuration. By irradiation at 6.33 ppm, enhancement was observed for signals at 2.70, 2.18, and 1.02 ppm.

Acylation of 1-Ethynyl-2,6,6-trimethylcyclohexene (21) with Acetyl Chloride. 2,4,4-Trimethyl-3-(3-oxo-1-butenylidene)-1-cyclohexene (22): IR 1936, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.85 (br, s, 1H), 5.56 (t, J = 2.7 Hz, 1H), 2.05 (s, 3H), 1.59 (br s, 3H), 1.40 (t, J = 6.2 Hz, 2H), 1.01 (s, 3H), 0.96 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 212.8 (s), 198.7 (s), 126.7 (d), 125.4 (s), 117.1 (s), 101.6 (d), 35.4 (t), 33.2 (s), 27.7 (q), 27.6 (q), 26.2 (q), 22.7 (t), 20.9 (q). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.98; H, 9.49.

4-Chloro-4-(2,6,6-trimethyl-1-cyclohexenyl)-3-buten-2-one (23): IR 1699 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 6.45 (s, 1H), 2.08 (s, 3H), 1.98 (t, J = 5.92 Hz, 2H), 1.73−1.50 (m, 2H), 1.57 (s, 3H), 1.42 (t, J = 4.88 Hz, 2H), 1.12 (s, 3H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 195.1 (s), 149.5 (s), 134.9 (s), 130.6 (s), 129.8 (d), 39.0 (t), 34.4 (s), 31.4 (t), 30.2 (q), 29.8 (q), 27.7 (q), 21.1 (q), 18.5 (t). Anal. Calcd for $C_{13}H_{19}OCl$: C, 68.86; H, 8.45; Cl, 15.64. Found: C, 68.79; H, 8.40; Cl, 15.70.

Hydrolysis of δ-Chloro-α-allenyl ketones 16 and 17. To a stirred suspension of $CaCO_3$ (4 g) in acetone (100 mL) and water (60 mL) was added chloro ketone (20 mmol). The suspension was submitted to reflux for 30 h. After that time,

TLC showed that the starting material had disappeared. The solvent was then evaporated and the residue obtained was extracted with ether. The resulting solution was dried using $MgSO_4$, concentrated, and purified by flash chromatography.

Hydrolysis of 2-Chloro-1-(3-oxo-1-butenylidene)cyclohexane (16a and 17a). 2-(3-Oxo-1-butenylidene)cyclohexanol (19a and 20a) was separated by flash chromatography on silica gel. **19a:** IR 3422, 1952, 1679 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.82 (dd, J = 3.85, 2.4 Hz, 1H), 4.25 (ddd, J = 8.7, 4.3, 2.4 (suppressed by irradiation at 5.82 ppm) Hz, 1H), 2.50 (dm, J = 13.7 Hz, 1H), 2.19 (s, 3H), 2.17 (m, 1H), 2.03 (dddd, J = 12.5, 6.6, 4.3 (suppressed by irradiation at 4.25 ppm), 3.1 Hz, 1H), 2.2−1.25 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 207.1 (s), 200.4 (s), 111.9 (s), 99.2 (d), 68.8 (d), 35.4 (t), 28.8 (t), 26.5 (q), 26.2 (t), 23.1 (t). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.35; H, 8.44. **20a**: ^{13}C NMR ($CDCl_3$, 400 MHz) δ 207.2 (s), 200.3 (s), 111.7 (s), 99.0 (d), 68.6 (d), 35.2 (t), 28.4 (t), 26.4 (q), 25.9 (t), 22.8 (t).

Hydrolysis of 2-Chloro-1-(4-methyl-3-oxo-1-pentylidene)cyclohexane (16b and 17b). 2-(4-Methyl-3-oxo-1-pentylidene)cyclohexanol (19b and 20b) was separated by flash chromatography on silica gel. **19b:** IR 3425, 1951, 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.77 (dd, J = 4.2, 2.5 Hz, 1H), 4.24 (ddd, J = 8.65, 4.2, 2.5 (suppressed by irradiation at 5.77 ppm) Hz, 1H), 3.0 (sept J = 6.9 Hz, 1H), 2.48 (d, J = 13.6 Hz, 1H), 2.14 (ddd, J = 13.6, 9.77, 4.2 Hz, 1H), 1.06 (d, J = 6.9 Hz, 3H), 1.05 (d, J = 6.9 Hz, 3H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.06; H, 9.29. **20b**: ^1H NMR ($CDCl_3$, 400 MHz) δ 5.79 (td, J = 3.3, 0.8 Hz, 1H), 4.19 (ddd, J = 9.3, 3.7, 3.3 Hz, 1H), 3.09 (sept, J = 6.9 Hz, 1H), 2.51 (dt, J = 12.9, 3.3 Hz, 1H), 2.09 (m, 1H), 1.10 (d, J = 6.9 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H).

Computational Methods. Computer modeling was carried out with the Hyperchem program (version 4.5) from Hypercube, Inc. on an ESCOM 100 MHz PC. Structures were minimized with the following parameters: PM3 or *ab initio* 3-21G basic set; restricted Hartree-Fock (RHF) level; minimization algorithm, until the root mean square energy gradient was less than 0.001 (PM3), 0.005 (3-21G), 0.01 kcal/mol Å (6-31G**); accelerated convergence. Calculation concerning **24** and **25** were carried out with Gaussian 94 on an IDRIS workstation.

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