Lewis Acid Catalyzed Inter- and Intramolecular [2 + 2] Cycloadditions of Conjugated Allenic Esters to Alkenes

Barry B. Snider* and Eyal Ron

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

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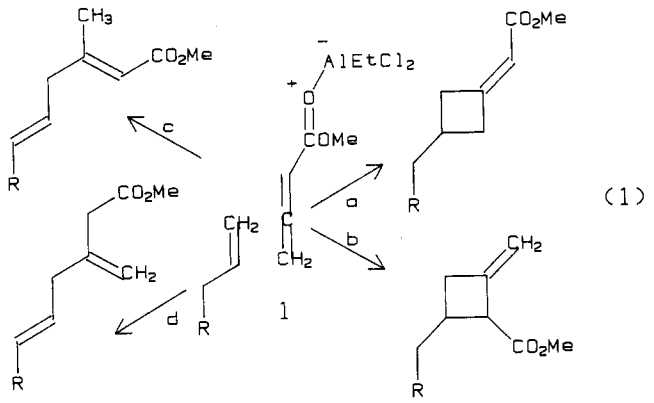
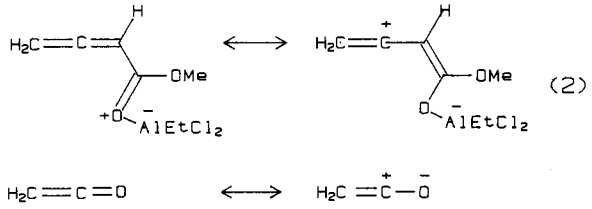
The [2 + 2] cycloadditions of the substituted allenic esters methyl 2,3-pentadienoate (**2**), methyl 4-methyl-2,3-pentadienoate (**3**), and methyl 2-methyl-2,3-butadienoate (**4**) with alkenes occur at carbons 3 and 4 as with methyl 2,3-butadienoate to give similar mixtures of products. The stereo- and regioselectivities of these Lewis acid catalyzed reactions are remarkably similar to the thermal cycloaddition reactions of the corresponding ketenes, which indicates that the mechanistic models used to rationalize ketene cycloaddition reactions are probably also applicable to the allenic ester cycloadditions. In particular, the cycloaddition of **2** with *cis*-3-hexene is selective for the cycloadduct **12** expected from a concerted reaction proceeding through a $[_\pi2_s + _\pi2_a]$ transition state. Cycloadditions of the intramolecular allenic esters **41**, **44**, and **48** proceed in excellent yield to give primarily the [2 + 2] cycloadducts. These reactions complement intramolecular ketene cycloadditions which often proceed in reasonable yield only when activated ketenes are used.

Lewis acid catalyzed reactions of allenic esters with alkenes are of considerable mechanistic interest since there are, in principle, four types of products which can be obtained (see eq 1). Pathways a and b have been observed



(1)

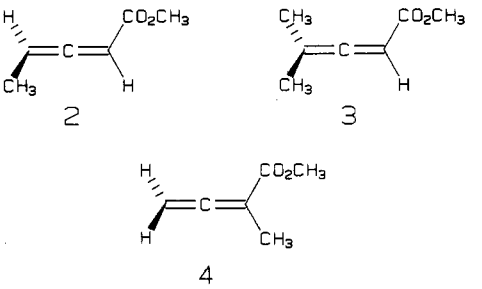
in the reactions of enamines with electron-deficient allenes.[1] We have investigated the $EtAlCl_2$-catalyzed reactions of methyl 2,3-butadienoate (**1**) with alkenes.[1,2] In all cases cyclobutylideneacetates (path a) were formed as the major product. The ene adduct (path d) was formed as a minor product from 2-ethyl-1-butene. In all cases leading bond formation occurred between the less substituted olefinic carbon and carbon 3 of **1**. Neither adducts from paths b or c nor those with opposite regiochemistry were observed. These results can be rationalized by considering that the Lewis acid complex of methyl 2,3-butadienoate is very similar to a ketene and should therefore undergo similar reactions (see eq 2).



(2)

[2 + 2] cycloadditions of ketenes or allenes with alkenes are mechanistically complex and diverse.[3] Stepwise cycloaddition reactions can proceed through diradical or zwitterionic intermediates. Both $[_\pi2_s + _\pi2_a]$ and $[_\pi2_s + (_\pi2_s + _\pi2_s)]$ concerted mechanisms have also been proposed. The $[_\pi2_s + _\pi2_a]$ model for the cycloaddition of ketenes with alkenes is attractive since it explains both the stereospecificity of the reaction and provides a rationale for the formation of the more hindered endo products from the addition of aldo ketenes to cyclopentadiene.[3a] If the Lewis acid catalyzed addition of **1** to alkenes does resemble the cycloaddition of ketenes to alkenes as we have proposed,[1] then the $[_\pi2s + _\pi2_a]$ model should also be useful for explaining the stereoselectivity of the cycloaddition reactions of **1**. Reaction of a cis-1,2-disubstituted alkene with **1** gave primarily the *E* isomer as expected from this model. However, this is not a very demanding test of this mechanism. If a $[_\pi2_s + _\pi2_a]$ mechanism is operative the more hindered *all-cis* isomer should be formed selectively from the reaction of methyl 2,3-pentadienoate (**2**) with cis-1,2-disubstituted alkene.

Therefore, we decided to examine the Lewis acid catalyzed reactions of the allenic esters methyl 2,3-pentadienoate (**2**), methyl 4-methyl-2,3-pentadienoate (**3**), and methyl 2-methyl-2,3-butadienoate (**4**) with alkenes. The



stereochemistry of the adducts formed from Lewis acid catalyzed cycloadditions of **2** with alkenes will provide information on the mechanism of the cycloaddition. The

(1) Snider, B. B.; Spindell, D. K. *J. Org. Chem.* **1980**, *45*, 5017 and references cited therein.

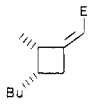
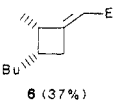
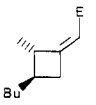
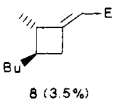
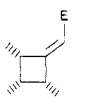
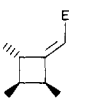
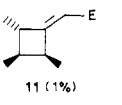
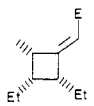
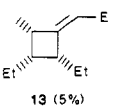
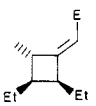
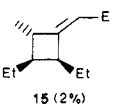
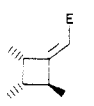
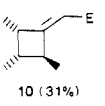
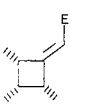
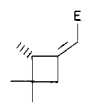
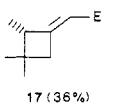
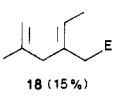
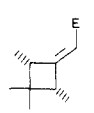
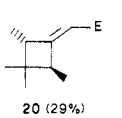
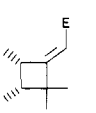
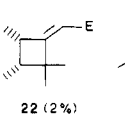
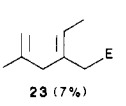
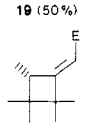
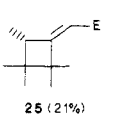
(2) For a related study, see: Hoffmann, H. M. R.; Ismail, Z. M.; Weber, A. *Tetrahedron Lett.* **1981**, *22*, 1953.

(3) For reviews see: (a) Ghosez, L.; O'Donnell, M. J. In *Pericyclic Ractions, Volume II*; Marchand, A. P., Lehr, R. E., Eds., Academic Press: New York, 1977; pp 79–140. (b) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805. (c) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984. (d) Hopf, H. In *The Chemistry of Allenes, Volume 2*; Landor, S. R., Ed.; Academic Press: London, 1982; pp 525–562. (e) Lukas, J. H.; Kouwenhoven, A. P.; Baardman, F. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 709.

(4) Lang, R. W.; Hansen, H. J. *Org. Synth.* **1984**, *62*, 202. Lang, R. W.; Hansen, H. J. *Helv. Chim. Acta* **1980**, *63*, 438. Lang, R. W.; Hansen, H. J. *Helv. Chim Acta* **1979**, *62*, 1025.

0022-3263/86/1951-3643$01.50/0

Table I. $EtAlCl_2$-Catalyzed Cycloadditions of Alkenes to Methyl 2,3-Pentadienoate (2)

entry	alkene	products (yield) E = CO_2Me				
1		 5 (47%)	 6 (37%)	 7 (5%)	 8 (3.5%)	
2		 9 (70%)	 10 (3%)	 11 (1%)		
3		 12 (63%)	 13 (5%)	 14 (6%)	 15 (2%)	
4		 11 (44%)	 10 (31%)	 9 (9%)		
5		 16 (33%)	 17 (36%)	 18 (15%)		
6		 19 (50%)	 20 (29%)	 21 (9%)	 22 (2%)	 23 (7%)
7		 24 (64%)	 25 (21%)			

presence of additional alkyl groups on the allenic ester may perturb the choice between the four reaction pathways of eq 1 due to steric interactions.

We have recently begun a systematic exploration of the intramolecular [2 + 2] cycloaddition reactions of ketenes.[5] Since we have proposed that the Lewis acid catalyzed cycloadditions of allenic esters with alkenes mechanistically resemble the corresponding ketene cycloadditions, it was important to compare the intramolecular Lewis acid catalyzed cyclization reactions of allenic esters with those of the corresponding ketenes.

Results and Discussion

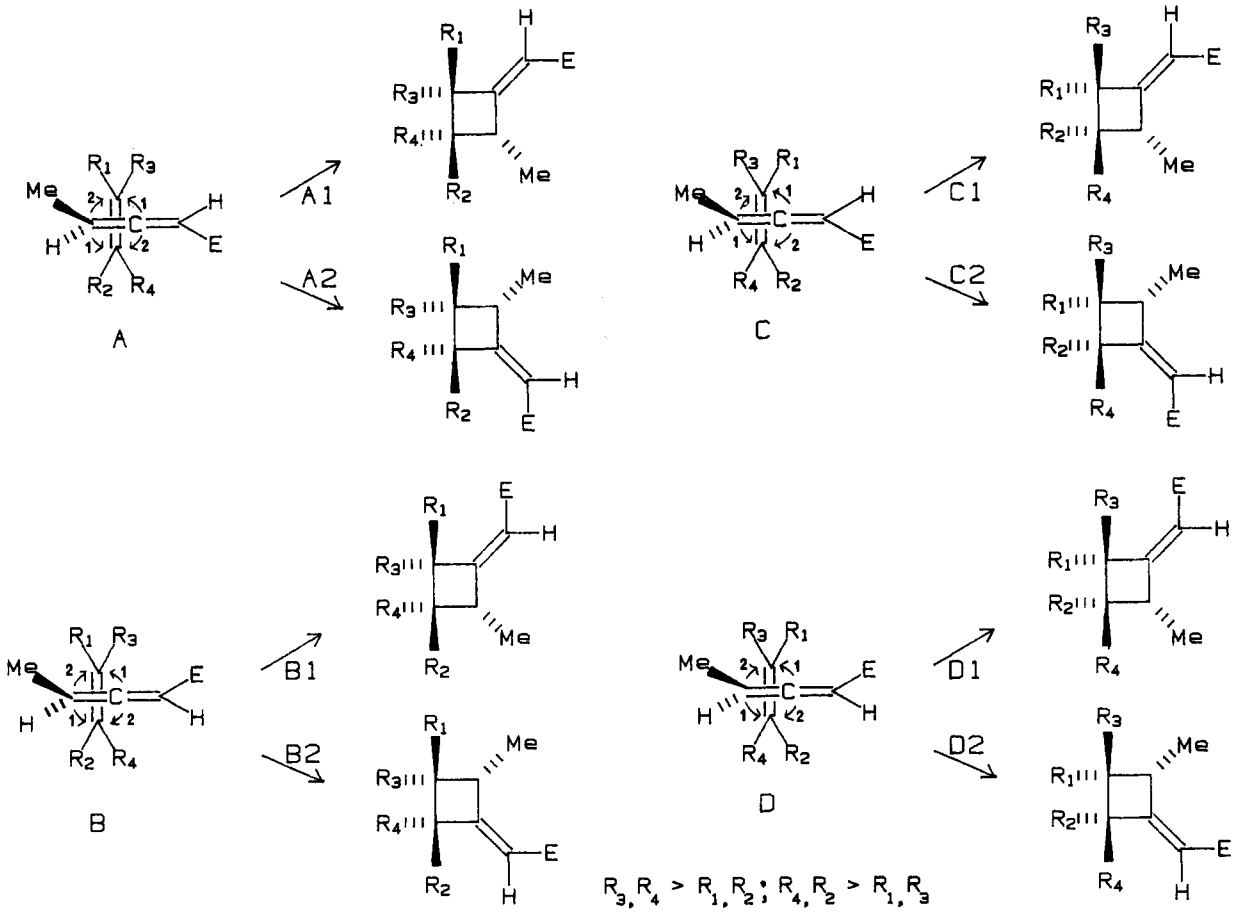
Allenic esters **2**, **3**, and **4** were prepared from the acid chloride and appropriate phosphorane by the procedure of Lang and Hansen,[4] a new method for the preparation of allenic esters which greatly facilitated this study. Treatment of the allenic ester **2**, alkene, and 0.5–0.7 equiv of $EtAlCl_2$ in CH_2Cl_2 at 25 °C for 1–25 days gave a mixture of adducts, generally in excellent yield (see Table I). Yields were determined from GC and NMR analysis of crude reaction mixtures which indicated that only those products indicated in Tables I and II were formed with the exception of isobutylene which also formed oligomers. Pure samples were obtained by preparative GC. Other Lewis acids were not investigated since our previous studies have indicated that $EtAlCl_2$ is optimal for Lewis acid catalyzed reactions of unsaturated esters. The reaction times were determined arbitrarily due to technical problems monitoring the disappearance of starting materials. Many of these reactions are probably complete at much shorter reaction times. The intramolecular cycloaddition of **48** (vide infra) was complete in an hour. Mixtures of isomeric cyclobutylideneacetates were formed in all cases. As we have previously noted in the reactions of **1** with alkenes,[1] ene adducts were formed as minor byproducts from 1,1-di- and trisubstituted alkenes.

The structures of the cyclobutylideneacetates were established by examination of the high-field ^1H and ^{13}C NMR spectra. The olefinic proton was coupled to the allylic protons on carbons 2 and 4 with a coupling constant of 1–3 Hz. The coupling pattern of the olefinic proton at $\delta \sim 5.55$ thus provided sufficient information to unambiguously assign the regiochemistry of the cycloadduct with unsymmetrical alkenes. The ester group deshielded the proton or protons on the cis allylic carbon by δ 0.2–0.5 and the methyl group or groups by $\delta \lesssim 0.2$.[1] In general this was sufficient to assign the stereochemistry of the double bond. In all cases, protons and methyl groups on carbons 2 and 4 absorb downfield of those on carbon 3. This observation facilitates the assignment of the spectrum. Finally, alkyl substituents on the cyclobutane shield cis protons and methyl groups on adjacent carbons.[6] For instance, the two methyl groups on carbon 3 in **20**, which are both shielded by one methyl group, absorb at δ 0.95 and 1.04. The methyl group on carbon 3 in **19** which is shielded by two

(5) Snider, B. B.; Hui, R. A. H. F. *J. Org. Chem.* **1985**, *50*, 5167 and reference 3 therein. Kulkarni, Y. S.; Burbaum, B. W.; Snider, B. B. *Tetrahedron Lett.* **1985**, *26*, 5619 and references cited therein.

(6) Auchter, G.; Kunzmann, E.; Hanack, M. *Tetrahedron Lett.* **1983**, *24*, 577.

Scheme I



cis methyl groups absorbs at δ 0.82 while the other methyl group, which is not shielded, absorbs at δ 1.13. Vicinal coupling constants, as have been previously noted,[7] are not very useful for assigning stereochemistry to cyclobutanes since both cis and trans coupling constants vary widely. The ^{13}C NMR spectra are consistent with the expected values on the basis of literature models.[8]

The stereochemistry of the products formed from **2** is an invaluable source of mechanistic information. The formation of **21** and **22** from the reaction of 2-methyl-2-butene and **2** and **28** from the reaction of 1-hexene and **3** precludes a two-step reaction proceeding through a simple zwitterionic intermediate, since an intermediate containing a primary carbocation would be necessary to form **28**. A two-step mechanism proceeding through a diradical intermediate has been widely used to explain cycloadditions of allenes.[3] It is unlikely, however, that a Lewis acid catalyzed reaction would proceed through a diradical intermediate. We have recently shown that some Lewis acid catalyzed ene reactions proceed by two-step mechanism with rate-determining formation of a π complex.[9] Such a mechanism is quite likely to be operable in these cycloadditions. Unfortunately, the lack of a more specific description of the intermediate makes this model of little value for the rationalization of the stereoselectivity of the reaction.

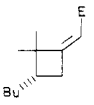
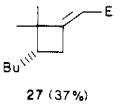
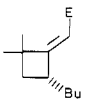
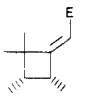
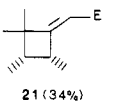
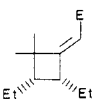
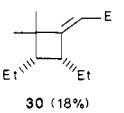
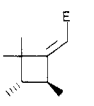
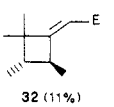
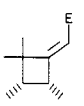
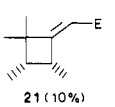
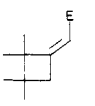
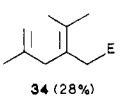
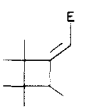
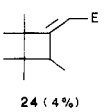
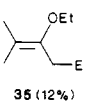
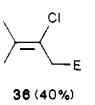
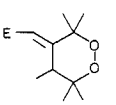
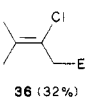
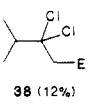
A concerted mechanism for this cycloaddition is also possible. Both $[_\pi2_s + _\pi2_a]$ and $[_\pi2_s + (_\pi2_s + _\pi2_s)]$ concerted mechanisms have been proposed for the cycloadditions of ketenes and allenes and the $[_\pi2_s + _\pi2_a]$ mechanism has been extensively used to rationalize the stereochemistry of ketene cycloadditions.[3a] This interpretation may also be valid for a two-step mechanism proceeding through a π-complex if the geometry of that complex resembles the transition state for a $[_\pi2_s + _\pi2_a]$ mechanism. *The results presented in Table I will therefore be considered in the context of a $[_\pi2_s + _\pi2_a]$ mechanism since this model leads to stereochemical predictions which can be tested and is useful for comparing these reactions to those of ketenes. As indicated above, these reactions may be occurring by another mechanism.*

To completely examine the possible $[_\pi2_s + _\pi2_a]$ reaction possibilities, two pathways must be considered from each of four possible transition states A–D (see Scheme I). The substituents on the alkene are defined such that R_3, $R_4 > R_1$, R_2 and R_4, $R_2 > R_3$, R_1. Transition states A and B should be strongly preferred since the hydrogen on carbon 4 of the allenic ester is interacting with the smaller substituents on the alkene. Four additional transition states with the methyl group and hydrogen switched have not been considered since they are too hindered. Transition states corresponding to A and B are identical in ketene cycloadditions. The presence of the allenic ester complicates the analysis.

The addition of **2** to symmetrical alkenes will be considered initially since in these cases only two (A and C) of the four transition states need be considered. Examination of entry 2 in Table I indicates that the major product from *cis*-2-butene, **9**, was formed from transition state A. Transition state C is much higher in energy. However, pathways 1 and 2 from transition state A cannot be distinguished because of the accidental symmetry of the product. Reaction of *cis*-3-hexene with **2** (entry 3) was

(7) Fleming, I.; Williams, D. H. *Tetrahedron* **1967**, *23*, 2747.
(8) Eliel, E. L.; Pietrusiewicz, K. M. *Org. Magn. Reson.* **1980**, *13*, 193. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.
(9) Snider, B. B.; Ron, E. *J. Am. Chem. Soc.* **1985**, *107*, 8160.

Table II. $EtAlCl_2$-Catalyzed Cycloadditions of Alkenes to Methyl 4-Methyl-2,3-pentadienoate (3)

entry	alkene	products (yield) E = CO_2Me				
1		 26 (10%)	 27 (37%)	 28 (43%)		
2		 22 (51%)	 21 (34%)			
3		 29 (67%)	 30 (18%)			
4		 31 (26%)	 32 (11%)	 22 (12%)	 21 (10%)	
5		 33 (12%)			 34 (28%)	
6		 25 (6%)	 24 (4%)	 35 (12%)	 36 (40%)	 37 (19%)
7		 36 (32%)	 38 (12%)			

equally selective for transition state A and exhibited very high selectivity for **12**, the product of pathway 1, presumably because this pathway minimizes steric interactions between the ester group and R_3 and R_4. The selective formation of **9** and **12** indicates that the $[{}_\pi 2_s + {}_\pi 2_a]$ mechanism is a useful model for this cycloaddition since the more stable trans products **10**, **11**, **14**, and **15** were formed in only trace amounts since transition state C is very hindered.

Only transition states A and B, which are similar in energy, need to be considered for the reaction of *trans*-2-butene with **2**. Only the less stable trans,cis isomers were formed by pathways A1 and B1 (R_1, R_4 = Me) since these pathways minimized steric interactions during the cycloaddition. The formation of a small amount of **9** is, at first glance, disconcerting since a concerted reaction should be stereospecific. However, related phenomena have been observed in the cycloaddition of ketenes with alkenes. Loss of stereospecificity in the cycloaddition of dimethylketene to *trans*-2-butene, but not *cis*-2-butene, has been reported[10] and *cis*-alkenes are much more reactive than their trans isomers in related cycloadditions of ketenes.[3a] A competition experiment with a large excess of a 1:1 mixture of *cis*- and *trans*-2-butene gave a 3.3:1 mixture of **9**:**10** and **11**, indicating that the cis isomer reacted 3.7 times as fast as the trans isomer. The loss of stereochemistry in the cycloaddition to *trans*-2-butene may be due to a change in mechanism with the less reactive isomer or to partial isomerization to the more reactive cis isomer.

Although four possible transition states exist for the reaction of 1-hexene with **2**, transition states A and B should be strongly favored. The two major products, **5** and **6**, were formed by pathways A1 and B1 which minimize steric interactions between the ester and butyl groups.

The formation of **21** and **22** in the reaction of 2-methyl-2-butene with **2** indicates a surprising loss of regiochemical control. These results are consistent with a concerted mechanism but not with a stepwise mechanism proceeding through zwitterionic or diradical intermediates. Similar results have occasionally been obtained in related ketene cycloadditions.[11] Ene adducts **18** and **23** were obtained as minor byproducts in the reactions of **2** with 2-methyl-2-butene and isobutylene. The presence of a disubstituted olefinic carbon in the alkene increases the steric hindrance in the transition state for the cycloaddition and stabilizes the transition state for the ene reaction.[12] The failure of **2** and **3** to react with 2-ethyl-1-butene further delineates the steric requirements of this reaction. Ester **2** also failed to react with the unhindered but nonnucleophilic substrate ethylene.

The reactions of **3** with alkenes shown in Table II gave less complex mixtures because of the higher symmetry of the products. The formation of **28** as the major product from 1-hexene and **3** indicates that steric interactions dominate electronic effects in this reaction. As in the reactions with **2**, the reactions of *cis*-alkenes were stereospecific while those of *trans*-2-butene were not. Reaction of **3** with isobutylene gave mainly the ene adduct **34**. 2-

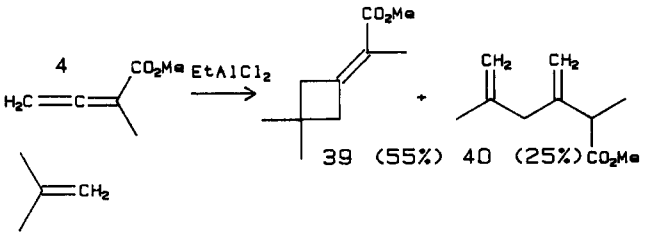
(10) Frey, H. M.; Isaacs, N. S. *J. Chem. Soc. B* **1970**, 830.

(11) Bak, D. A.; Brady, W. T. *J. Org. Chem.* **1979**, *44*, 107.

(12) For related competitions between ene and [2 + 2] cycloadditions in the Lewis acid catalyzed additions of propiolate esters and alkenes, see: Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283. Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D.; Spindell, D.; *J. Org. Chem.* **1980**, *45*, 2773.

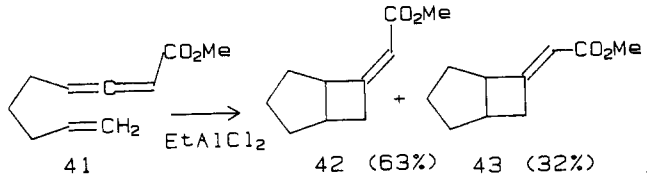
Methyl-2-butene reacted very slowly with **3** and 2,3-dimethyl-2-butene was too hindered to react with **3**. Addition of chloride to give **36** and **38** or ethoxide (formed from $EtAlCl_2$ and adventitious oxygen) to give **35** were the major processes. The peroxide **37** was formed via opening of the cyclobutane and reaction with adventitious oxygen or reaction of an intermediate with adventitious oxygen. Related peroxides are known to be stable.[13]

The $EtAlCl_2$-catalyzed reaction of **4** with excess isobutylene gave the cyclobutane **39** (≃55%), and the ene adduct **40** (≃25%). Oligomers of isobutylene were also isolated.



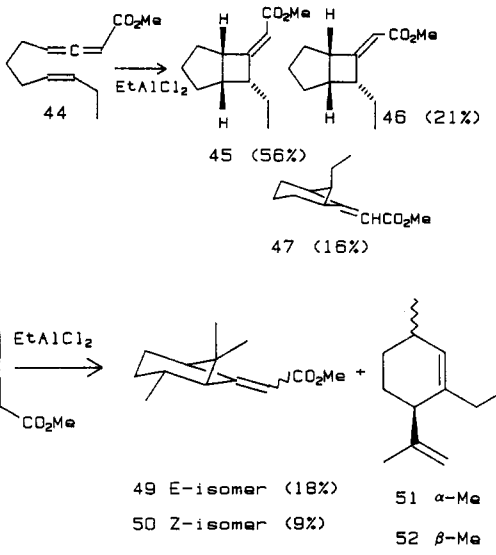
Intramolecular Cycloadditions. We and others have recently shown that the intramolecular [2 + 2] cycloadditions of ketenes to alkenes is a versatile synthetic method.[5] The ready availability of allenic esters by the reaction of acid chlorides with ((methoxycarbonyl)methylene)triphenylphosphorane[4] and the desire to compare these cycloadditions with related intramolecular ketene cycloadditions prompted us to explore the intramolecular Lewis acid catalyzed cycloadditions of allenic esters. Two examples of related intramolecular ene reactions in which the allene functions as the enophile are known.[14] Both of these cases involve thermal ene reactions of allenes.

Treatment of **41** with $EtAlCl_2$ for 14 days in CH_2Cl_2 at 25 °C gave a 95% yield of a 2:1 mixture of **42** and **43**. These adducts are also available from the intermolecular cycloaddition of cyclopentene and methyl 2,3-butadienoate,[2] a process which was used to prepare authentic samples of **42** and **43**. However, the intermolecular cycloaddition gave a 5:95 mixture of **42** and **43**. The formation of the fused ring system in the cyclization of **41** is expected on electronic grounds.



The intramolecular [2 + 2] cycloaddition of **44** was examined to determine the regiochemistry of the cycloaddition in the absence of electronic effects from the alkene substituents. Bridged adduct **47** (16%) was now formed, although the fused adducts **45** (21%) and **46** (56%) were still the major products. Similar ratios of bridged and fused products have been observed in related intramolecular ketene cycloadditions.[5]

Lewis acid catalyzed cyclization of **48** proceeded to give a complex mixture of the expected cycloadducts **49** (18%) and **50** (9%) and the ene adducts **51** (36%) and **52** (13%).



Similar bicyclo[3.1.1]heptanes have been obtained from related ketene cycloadditions.[5] The formation of the ene adduct as well as the cyclobutane was observed in intermolecular cycloadditions of **1**–**4** with alkenes containing a disubstituted olefinic carbon.[1]

Conclusion. These results indicate that the intermolecular and intramolecular [2 + 2] cycloadditions of substituted allenic esters with alkenes occur at carbons 3 and 4 as with methyl 2,3-butadienoate to give similar mixtures of products. The stereo- and regioselectivity of these Lewis acid catalyzed reactions are remarkably similar to the thermal cycloaddition reactions of the corresponding ketenes, which indicates that the mechanistic models used to rationalize ketene cycloaddition reactions are probably also applicable to the allenic ester cycloadditions. The intramolecular allenic ester cycloadditions complement intramolecular ketene cycloadditions which often proceed in reasonable yield only when activated ketenes are used.[5]

Experimental Section

Materials and Methods. NMR spectra were recorded in $CDCl_3$ solution on Perkin-Elmer R-32 or Varian EM-390 spectrometers at 90 MHz and on a Varian XL-300 spectrometer at 300 MHz. ^{13}C NMR were recorded on a Varian XL-300 spectrometer. Chemical shifts are reported in ppm down field from Me_4Si (δ). IR spectra were obtained in $CDCl_3$ on a Perkin-Elmer 683 spectrometer and are reported in wavenumbers (cm^{-1}). Gas chromatography was carried out on a 7 ft × $^1/_4$ in. 10% XF-1150 on Chromosorb PAW column at 105 °C with a flow rate of 35 mL/min. Products are listed in order of elution. Preparative GC was carried out on a 6 ft × $^3/_8$ in. 10% XF-1150 on Chromosorb PNAW column. $EtAlCl_2$ was obtained from Texas Alkyls (1.44 M in hexane). Dichloromethane was distilled from CaH_2 under N_2.

Preparation of Starting Materials. Methyl 2,3-pentadienoate (**2**), methyl 4-methyl-2,3-pentadienoate (**3**), and methyl 2-methyl-2,3-butadienoate (**4**) were prepared from the acid chloride and the appropriate triphenylphosphorane by the procedure of Lang and Hansen.[4] Commercial samples of alkenes were used without further purification. (*Z*)-6-Octenal and citronellal were oxidized to the carboxylic acids with Ag_2O. The resulting acids and 6-heptenoic acid were converted to the acid chlorides with oxalyl chloride in benzene (1 h, 25 °C; 1 h, reflux).

Reaction of 1-Hexene with 2. Ester **2** (112 mg, 1.0 mmol) followed by 1-hexene (92.6 mg, 1.1 mmol) and $EtAlCl_2$ (0.55 mL of 1.44 M, 0.8 mmol) were added to 1.5 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction mixture was stirred for 5 days at 25 °C, diluted with ether, and quenched by slow addition of saturated NaH_2PO_4 solution. Hydrochloric acid (10%) was added to dissolve the precipitated alumina. The two layers were separated and the aqueous layer was washed with three portions of ether. The combined organic layers were dried over

(13) Bloodworth, A. J.; Khan, J. A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2450.
(14) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1976**, *17*, 478. See reference 36b,c.

$MgSO_4$ and filtered through silica gel. Evaporation in vacuo gave 184.2 mg (94%) of crude product which consisted of a 1.7:14.0:1.0:11.0 mixture, of **7**, **5**, **8**, and **6** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (2α-methyl-3β-butyl-(*Z*)-cyclobutylidene)acetate (**7**) follow: ^{1}H NMR 5.61 (ddd, 1, J = 2.2, 2.2, 2.2 Hz), 3.68 (s, 3), 2.95 (m, 2, $H_{2\beta}$ and $H_{4\alpha}$), 2.25 (dddd, 1, J = 16.6, 7.0, 3.5, 2.2 Hz, $H_{4\beta}$), 1.90 (m, 1, $H_{3\alpha}$), 1.30 (d, 3, J = 7.1 Hz, $Me_{2\alpha}$), 1.80–1.40 (m, 6), and 0.90 (t, 3, J = 7.1 Hz); IR 2987, 2929, 1713, 1674, 1468, 1438, 1383, 1347, 1279, 1200, 1035 cm^{-1}; GC t_R 18.5 min.

The spectral data for methyl (2α-methyl-3α-butyl-(*Z*)-cyclobutylidene)acetate (**5**) follow: ^{1}H NMR 5.57 (ddd, 1, J = 2.8, 2.8, 1.4 Hz), 3.69 (s, 3), 3.47 (dddq, 1, J = 6.4, 3.8, 2.8, 2.2, 7.6 Hz, $H_{2\beta}$), 2.78 (dddd, 1, J = 16.4, 7.9, 3.8, 1.4 Hz, $H_{4\beta}$), 2.50 (dddd, 1, J = 16.4, 8.8, 2.8, 2.8 Hz, $H_{4\alpha}$), 2.37 (dddt, 1, J = 8.8, 7.9, 6.4, 8.5 Hz, $H_{3\beta}$), 1.60–1.20 (m, 6, 3α Bu), 1.22 (d, 3, J = 7.6 Hz, $Me_{2\alpha}$), 0.90 (t, 3, J = 7.3 Hz, 4′ Me); ^{13}C NMR 170.2, 166.6, 111.3, 50.8, 42.8 (C_2), 36.8 (C_4), 34.1 (C_3), 30.2, 29.9, 22.7, 14.1, 12.3 ($Me_{2\alpha}$); IR 2962, 2933, 2875, 2860, 1711, 1676, 1462, 1439, 1372, 1347, 1280, 1205, 1131, 1107, 1030 cm^{-1}; GC t_R 26.5 min.

The spectral data for methyl (2α-methyl-3β-butyl-(*E*)-cyclobutylidene)acetate (**8**) follow: ^{1}H NMR 5.60 (ddd, 1, J = 2.4, 2.4, 2.4 Hz), 3.69 (s, 3), 3.25 (m, 1, $H_{4\alpha}$), 2.94 (m, 1, $H_{4\beta}$), 2.64 (m, 1, $H_{2\beta}$), 1.87 (m, 1, $H_{3\alpha}$), 1.60–1.20 (m, 6), 1.15 (d, 3, J = 7.5 Hz, $Me_{2\alpha}$), 0.90 (t, 3, J = 7.3 Hz); GC t_R 26.5 min.

The spectral data for methyl (2α-methyl-3α-butyl-(*E*)-cyclobutylidene)acetate (**6**) follow: ^{1}H NMR 5.63 (ddd, 1, J = 2.4, 2.4, 2.4 Hz), 3.69 (s, 3), 3.19 (ddddq, 1, J = 4.3, 3.5, 2.4, 0.7, 7.1 Hz, $H_{2\beta}$), 3.13 (dddd, 1, J = 17.5, 9.0, 2.4, 0.7 Hz, $H_{4\beta}$), 2.70 (dddd, 1, J = 17.5, 4.8, 3.5, 2.4 Hz, $H_{4\alpha}$), 2.38 (dddt, 1, J = 9.0, 4.8, 4.4, 7.4 Hz, $H_{3\beta}$), 1.60–1.20 (m, 6), 1.06 (d, 3, J = 7.1 Hz, $Me_{2\alpha}$), 0.90 (t, 3, J = 7.0 Hz); ^{13}C NMR 172.4, 167.3, 110.7, 50.9, 41.6 (C_2), 37.5 (C_4, CH_2), 34.5 (C_3, CH), 29.9, 29.7, 22.8, 14.1, 12.4 ($Me_{2\alpha}$); IR 2962, 2933, 2875, 2860, 1708, 1674, 1458, 1439, 1348, 1281, 1227, 1203, 1187, 1143, 1115, 1053, 1036, 1007 cm^{-1}; GC t_R 33.5 min.

Reaction of *cis*-Butene with 2. Excess *cis*-2-butene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) and ester **2** (108.4 mg, 0.97 mmol) in 2.5 mL of CH_2Cl_2. After 15 days at 25 °C the reaction mixture was worked up in the normal manner to give 121.6 mg (75%) of crude product which consisted of a 1:2.5:52.0 mixture of **11**, **10**, and **9** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (2β,3β,4α-trimethyl-(*Z*)-cyclobutylidene)acetate (**11**) follow: ^{1}H NMR 5.52 (dd, 1, J = 2.2, 1.7 Hz), 3.67 (s, 3), 3.41 (ddq, 1, J = 8.5, 1.7, 7.6 Hz, $H_{2\alpha}$), 2.72 (ddq, 1, J = 8.8, 2.2, 6.8 Hz, $H_{4\beta}$), 2.04 (ddq, 1, J = 8.8, 8.5, 6.8 Hz, $H_{3\alpha}$), 1.20 (d, 3, J = 7.6 Hz, $Me_{2\beta}$), 1.11 (d, 3, J = 6.8 Hz, $Me_{4\alpha}$), 1.04 (d, 3, J = 6.8 Hz, $Me_{3\beta}$); ^{13}C NMR 175.7, 166.9, 109.1, 50.8, 45.4 (C_4), 41.1 (C_2), 37.1 (C_3), 15.9, 14.0, 12.7; IR 2964, 2928, 2870, 1705, 1671, 1451, 1436, 1371, 1347, 1280, 1239, 1201, 1148, 1107, 1046, 1009, 959 cm^{-1}; GC t_R 8 min.

The spectral data for methyl (2β,3α,4α-trimethyl-(*Z*)-cyclobutylidene)acetate (**10**) follow: ^{1}H NMR 5.60 (dd, 1, J = 2.4, 2.2 Hz), 3.69 (s, 3), 3.29 (dddq, 1, J = 9.8, 3.5, 2.4, 7.3 Hz, $H_{4\beta}$), 2.87 (dddq, 1, J = 3.4, 3.4, 2.2, 7.1 Hz, $H_{2\alpha}$), 2.11 (ddq, 1, J = 9.8, 3.4, 7.1 Hz, $H_{3\beta}$), 1.33 (d, 3, J = 7.1 Hz, $Me_{2\beta}$), 1.00 (d, 3, J = 7.3 Hz, $Me_{4\alpha}$), 0.99 (d, 3, J = 7.1 Hz, $Me_{3\alpha}$); ^{13}C NMR 176.9, 166.8, 111.1, 50.8, 46.7, 38.8, 36.6, 18.4, 14.6, 11.8; IR 2960, 2929, 2870, 1705, 1669, 1459, 1436, 1371, 1348, 1281, 1242, 1201, 1148, 1108, 1039, 1007, 977 cm^{-1}; GC t_R 8 min.

The spectral data for methyl (2α,3α,4α-trimethylcyclobutylidene)acetate (**9**) follow: ^{1}H NMR 5.60 (dd, 1, J = 2.4, 1.7 Hz), 3.68 (s, 3), 3.40 (dddq, 1, J = 9.3, 1.3, 2.4, 7.3 Hz, $H_{2\alpha}$), 3.06 (dddq, 1, J = 9.3, 1.7, 1.3, 7.3 Hz, $H_{4\alpha}$), 2.60 (ddq, 1, J = 9.3, 9.3, 7.3 Hz, $H_{3\alpha}$), 1.20 (d, 3, J = 7.3 Hz, $Me_{2\beta}$), 1.05 (d, 3, J = 7.3 Hz, $Me_{4\beta}$), 0.91 (d, 3, J = 7.3 Hz, $Me_{3\beta}$); ^{13}C NMR 176.4, 166.6, 111.0, 50.9, 41.6, 40.1, 31.5 (C_3), 12.8, 12.6, 9.7 ($Me_{3\beta}$); IR 2966, 2935, 2875, 2847, 1711, 1673, 1438, 1372, 1350, 1284, 1197, 1137, 1085, 1057, 1013 cm^{-1}; GC t_R 12 min.

Reaction of 3-*cis*-Hexene with 2. Ester **2** (107 mg, 0.95 mmol) followed by 3-cis-hexene (84 mg, 1.0 mmol) and $EtAlCl_2$ (0.4 mL of 1.44 M, 0.6 mmol) were added to 3 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction mixture was stirred for 9 days at 25 °C and worked up in the normal manner to give 143 mg (77%) of crude product which consisted of a 2.6:1.0:2.3:27 mixture of **14**, **15**, **13**, and **12** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (2α,3α-diethyl-4β-methyl-(*E*)-cyclobutylidene)acetate (**14**) follow: ^{1}H NMR 5.65 (dd, 1, J = 2.1, 2.1 Hz), 3.69 (s, 3), 3.06 (m, 1, $H_{2\beta}$), 2.95 (m, 1, $H_{4\alpha}$), 1.90 (m, 1, $H_{3\beta}$), 1.6–1.4 (m, 4, ethyl CH_2), 1.33 (d, 3, J = 7.0 Hz, $Me_{4\beta}$), 0.92 (t, 3, J = 7.3 Hz, 2α ethyl Me), 0.88 (t, 3, J = 7.3 Hz, 3α ethyl Me); GC t_R 16.5 min.

The spectral data for methyl (2α,3α-diethyl-4β-methyl-(*Z*)-cyclobutylidene)acetate (**15**) follow: ^{1}H NMR 5.57 (dd, 1, J = 2.1, 2.1 Hz), 3.69 (s, 3), 3.37 (m, 1, $H_{2\beta}$), 2.76 (m, 1, $H_{4\alpha}$), 1.90 (m, 1, $H_{3\beta}$), 1.6–1.4 (m, 4, ethyl CH_2), 1.13 (d, 3, J = 7.0 Hz, $Me_{4\beta}$), 0.96 (t, 3, J = 7.3 Hz, 2α ethyl Me), 0.90 (t, 3, J = 7.3 Hz, 3α ethyl Me); GC t_R 17.5 min.

The spectral data for methyl (2β,3β-diethyl-4β-methyl-(*Z*)-cyclobutylidene)acetate (**13**) follow: ^{1}H NMR 5.61 (dd, 1, J = 2.1, 2.1 Hz), 3.69 (s, 3), 3.23 (m, 1, $H_{2\alpha}$), 3.02 (m, 1, $H_{4\beta}$), 2.43 (m, 1, $H_{3\alpha}$), 1.6–1.4 (m, 4, ethyl CH_2), 1.12 (d, 3, J = 7.6 Hz, $Me_{4\beta}$), 0.93 (t, 3, J = 7.3 Hz, 2β ethyl Me), 0.89 (t, 3, J = 7.3 Hz, 3β ethyl Me); GC t_R 30.5 min.

The spectral data for methyl (2β,3β-diethyl-4β-methyl-(*E*)-cyclobutylidene)acetate (**12**) follow: ^{1}H NMR 5.64 (dd, 1, J = 2.0, 2.0 Hz), 3.69 (s, 3), 3.45 (dddq, 1, J = 8.9, 3.1, 2.0, 7.6 Hz, $H_{4\alpha}$), 2.79 (dddt, 1, J = 9.1, 3.1, 2.0, 9.3 Hz, $H_{2\alpha}$), 2.43 (ddt, 1, J = 9.1, 8.9, 7.5 Hz, $H_{3\alpha}$), 1.7–1.4 (m, 4, ethyl CH_2), 1.26 (d, 3, J = 7.6 Hz, $Me_{4\beta}$), 0.94 (t, 3, J = 7.3 Hz, 2β ethyl Me), 0.88 (t, 3, J = 7.3 Hz, 3β ethyl Me); ^{13}C NMR 174.4, 166.6 (C_1), 112.1, 50.8, 48.1 (C_2), 41.5, 38.8, 22.9 (2β ethyl CH_2), 18.2 (3β ethyl CH_2), 13.5, 13.2, 12.6; IR 3693, 3023, 2970, 2938, 2878, 1709, 1670, 1461, 1439, 1350, 1284, 1217, 1207, 1179, 1138; GC t_R 30.5 min.

Reaction of *trans*-2-Butene with 2. Excess *trans*-2-butene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.40 mL of 1.44 M, 0.58 mmol) and ester **2** (107 mg, 0.95 mmol) in 2.0 mL of CH_2Cl_2. After 19 days at 25 °C the reaction mixture was worked up in the normal manner to give 135.6 mg (85%) of crude product which consisted of a 3.4:4.8:1 mixture of **10**, **11**, and **9** as determined by GC analysis. Pure samples were obtained by preparative GC.

Reaction of Isobutylene with 2. Excess isobutylene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.23 mL of 1.44 M, 0.33 mmol) and ester **2** (53 mg, 0.47 mmol) in 1 mL of CH_2Cl_2. After 30 days at 25 °C the reaction mixture was worked up in the normal manner to give 244 mg of gummy crude product which consisted of a 1.0:2.2:2.4 mixture of **18**, **16**, and **17** and long chain polymers as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 3-(*Z*)-ethylidene-5-methyl-5-hexenoate (**18**) follow: NMR 5.51 (q, 1, J = 6.4 Hz), 4.80 (br, 1, H_6), 4.72 (br, 1, H_6), 3.67 (s, 3), 3.04 (s, 2, H_2), 2.78 (s, 2, H_4), 1.66 (d, 3, J = 6.4 Hz, ethylidene CH_3), 1.55 (s, 3, Me_5); IR 2980, 2935, 2905, 1731, 1702, 1459, 1376, 1270, 1216, 1167 cm^{-1}; GC t_R 6.2 min.

The spectral data for methyl (2β,3,3-trimethyl-(*Z*)-cyclobutylidene)acetate (**16**)[1] follow: ^{1}H NMR 5.63 (ddd, 1, J = 2.7, 2.2, 1.7 Hz), 3.69 (s, 3), 2.97 (dddq, 1, J = 2.9, 2.7, 2.2, 7.3 Hz, $H_{2\alpha}$), 2.57 (ddd, 1, J = 16.5, 2.7, 2.7 Hz, $H_{4\alpha}$), 2.39 (ddd, 1, J = 16.5, 2.9, 1.7 Hz, $H_{4\beta}$), 1.20 (d, 3, J = 7.3 Hz, $Me_{2\beta}$), 1.15 (s, 3, $Me_{3\alpha}$), 1.05 (s, 3, $Me_3\beta$); ^{13}C NMR 176.9, 148.8, 113.2, 50.8, 49.4 (C_2), 43.7 (C_4), 29.3 ($Me_{3\alpha}$), 23.0 ($Me_{3\beta}$), 13.1 ($Me_{2\beta}$), one carbon was not observed; IR 2957, 2909, 2870, 1711, 1675, 1466, 1437, 1371, 1348, 1280, 1216, 1194, 1183, 1161 cm^{-1}; GC t_R 6.8 min.

The spectral data for methyl (2β,3,3-trimethyl-(*E*)-cyclobutylidene)acetate (**17**)[1] follow: ^{1}H NMR 5.63 (ddd, 1, J = 2.4, 2.4, 2.3 Hz), 3.68 (s, 3), 2.82 (ddd, 1, J = 16.8, 2.3, 2.3 Hz, $H_{4\alpha}$), 2.74 (dddq, 1, J = 2.4, 2.3, 2.3, 7.1 Hz, $H_{2\alpha}$), 2.71 (ddd, 1, J = 16.8, 2.4, 2.3 Hz, $H_{4\beta}$), 1.19 (s, 3, $Me_{3\alpha}$), 1.00 (d, 3, J = 7.1 Hz, $Me_{2\beta}$), 0.97 (s, 3, $Me_{3\beta}$); ^{13}C NMR 179.0, 163.1, 110.6, 50.9, 48.9 (C_4), 45.5 (C_2), 35.3 (C_3), 29.2 ($Me_{3\alpha}$), 22.2 ($Me_{3\beta}$), 11.6 ($Me_{2\beta}$); IR 2957, 2869, 1705, 1675, 1466, 1437, 1346, 1281, 1216, 1174, 1114 cm^{-1}; GC t_R 9 min.

Reaction of 2-Ethyl-1-butene with 2 and 3. $EtAlCl_2$ (0.55 mL of 1.44 M, 0.8 mmol) was added to a solution of **2** or **3** (1 mmol) and 2-ethyl-1-butene (92.4 mg, 1.1 mmol) in 2 mL of CH_2Cl_2. After 11 days at 25 °C the reaction mixture was worked up in the normal manner. No product was recovered.

Reaction of 2-Methyl-2-butene with 2. $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) was added to a solution of **2** (120 mg, 1.07 mmol) and 2-methyl-2-butene (77 mg, 1.1 mmol) in 1.5 mL of CH_2Cl_2. After 3 days at 25 °C the reaction mixture was worked up in the normal manner to give 193.6 mg (98%) of crude product which consisted of a 3.9:16.0:1.0:5.0:27.4 mixture of **23**, **20**, **22**, **21**, and **19** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 3(*Z*)-ethylidene-4,5-dimethyl-5-hexenoate (**23**) follow: ^1H NMR 5.53 (q, 1, J = 6.4 Hz), 4.80 (br, 1), 4.77 (br, 1), 3.65 (s, 3, OMe), 3.03 (d, 1, J = 15.8 Hz), 2.99 (d, 1, J = 15.8 Hz), 2.84 (q, 1, J = 7.1 Hz, H_4), 1.65 (d, 3, J = 6.4 Hz), 1.56 (s, 3), 1.12 (d, 3, J = 7.1 Hz); ^{13}C NMR 163.1, 147.9, 123.0, 122.9, 110.8, 51.7, 48.8, 47.9, 34.0, 17.4, 17.3; IR 2976, 2933, 2922, 2881, 1733, 1645, 1458, 1438, 1377, 1329, 1269, 1200, 1159, 1024 cm^{-1}; GC t_R 7.5 min.

The spectral data for methyl (2α,3,3,4β-tetramethyl-(*Z*)-cyclobutylidene)acetate (**20**) follow: ^1H NMR 5.59 (dd, J = 2.4 1.7 Hz), 3.69 (s, 3), 2.91 (ddq, 1, J = 2.9, 1.7, 7.6 Hz, $H_{2\beta}$), 2.83 (ddq, 1, J = 2.9, 2.4, 7.1 Hz, $H_{4\alpha}$), 1.22 (d, 3, J = 7.6 Hz, $Me_{2\alpha}$), 1.04 (s, 3, 3-Me), 0.96 (d, 3, J = 7.1 Hz, $Me_{4\beta}$), 0.95 (s, 3, 3-Me); ^{13}C NMR 175.5, 166.8, 110.2, 50.8, 48.8, 46.6, 37.0 (C_3), 23.7, 22.8, 13.7, 10.8; IR 2968, 2939, 2871, 1708, 1672, 1460, 1438, 1369, 1327, 1281, 1215, 1170, 1112, 1045, 1021 cm^{-1}; GC t_R 9 min.

The spectral data for methyl (2,2,3β,4β-tetramethyl-(*Z*)-cyclobutylidene)acetate (**22**) follow: ^1H NMR 5.55 (d, 1, J = 2.2 Hz), 3.68 (s, 3), 3.15 (ddq, 1, J = 10.0, 2.2, 7.3 Hz, $H_{4\alpha}$), 2.19 (dq, 1, J = 10.0, 7.3 Hz, $H_{3\alpha}$), 1.37 (s, 3, $Me_{2\alpha}$), 1.19 (s, 3, $Me_{2\beta}$), 1.02 (d, 3, J = 7.3 Hz, $Me_{4\beta}$), 0.91 (d, 3, J = 7.3 Hz, $Me_{3\beta}$); ^{13}C NMR 172.3, 159.1, 110.9, 50.8, 46.8 (C_2), 39.0, 37.2, 27.6 ($Me_{2\alpha}$), 20.1 ($Me_{2\beta}$), 12.5 ($Me_{4\beta}$), 10.3 ($Me_{3\beta}$); IR 2973, 2963, 2923, 1707, 1671, 1461, 1438, 1371, 1348, 1269, 1200, 1180, 1131, 1072, 1022 cm^{-1}; GC t_R 9 min.

The spectral data for methyl (2,2,3β,4β-tetramethyl-(*E*)-cyclobutylidene)acetate (**21**) follow: ^1H NMR 5.59 (d, 1, J = 2.3 Hz), 3.69 (s, 3), 3.46 (ddq, 1, J = 9.6, 2.3, 7.6 Hz, $H_{4\alpha}$), 2.29 (dq, 1, J = 9.6, 7.3 Hz, $H_{3\alpha}$), 1.23 (d, 3, J = 7.6 Hz, $Me_{4\beta}$), 1.14 (s, 3, $Me_{2\alpha}$), 1.08 (s, 3, $Me_{2\beta}$), 0.94 (d, 3, J = 7.3 Hz, $Me_{3\beta}$); ^{13}C NMR 181.1, 166.9, 110.0, 50.9, 45.0 (C_2), 39.2, 39.1, 28.4 ($Me_{2\alpha}$), 22.4 ($Me_{2\beta}$), 13.0 ($Me_{4\beta}$), 9.6 ($Me_{3\beta}$); IR 2974, 2925, 2872, 1710, 1669, 1446, 1438, 1349, 1262, 1227, 1198, 1178, 1145, 1086, 1046, 1013 cm^{-1}; GC t_R 10.5 min.

The spectral data for methyl (2α,3,3,4α-tetramethylcyclobutylidene)acetate (**19**) follow: ^1H NMR 5.59 (dd, 1, J = 2.7, 2.0 Hz), 3.68 (s, 3), 2.91 (dq, 1, J = 2.7, 7.3 Hz, $H_{2\beta}$), 2.59 (dq, 1, J = 2.0, 7.1, $H_{4\beta}$), 1.14 (d, 3, J = 7.1 Hz, $Me_{2\alpha}$), 1.13 (s, 3, $Me_{3\beta}$), 0.98 (d, 3, J = 7.1 Hz, $Me_{4\alpha}$), 0.82 (s, 3, $Me_{3\alpha}$); ^{13}C NMR 173.8, 166.6, 110.3, 50.9, 49.0, 47.6, 37.0 (C_3), 29.1 ($Me_{3\beta}$), 17.2 ($Me_{3\alpha}$), 11.9, 11.5; IR 2956, 2871, 1712, 1675, 1467, 1456, 1438, 1373, 1357, 1286, 1211, 1175, 1112, 1041, 1025 cm^{-1}; GC t_R 12 min.

Reaction of 2,3-Dimethyl-2-butene with 2. $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) was added to a solution of **2** (112.1 mg, 1 mmol) and 2,3-dimethyl-2-butene (92.6 mg, 1.1 mmol) in 2.0 mL of CH_2Cl_2. After 44 h at 25 °C the reaction mixture was worked up in the normal manner to give 167 mg (85%) of crude product which consisted of a 1:3.1 mixture of **25** and **24** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for the methyl (2,2,3,3,4-pentamethyl-(*Z*)-cyclobutylidene)acetate (**25**) follow: ^1H NMR 5.53 (d, 1, J = 2.2 Hz), 3.69 (s, 3), 2.79 (dq, 1, J = 2.2, 7.0 Hz, $H_{4\beta}$), 1.29 (s, 3, $Me_{2\beta}$), 1.14 (s, 3, $Me_{2\alpha}$), 1.00 (s, 3, $Me_{3\beta}$), 0.96 (d, 3, J = 7.0 Hz, $Me_{4\alpha}$), 0.87 (s, 3, $Me_{3\alpha}$); ^{13}C NMR 178.7, 166.3 (C_1), 109.5, 50.9, 49.4 (C_2), 45.8 (C_4), 38.9 (C_3), 23.1, 22.8, 20.4, 20.0, 10.4 ($Me_{4\alpha}$); IR 2976, 2930, 2871, 1707, 1672, 1456, 1438, 1376, 1349, 1282, 1246, 1198, 1181, 1144, 1108, 1024 cm^{-1}; GC t_R 12 min.

The spectral data for the methyl (2,2,3,3,4-pentamethyl-(*E*)-cyclobutylidene)acetate (**24**) follow: ^1H NMR 5.59 (d, 1, J = 2.5 Hz), 3.66 (s, 3), 3.00 (dq, 1, J = 2.5, 7.3 Hz, $H_{4\beta}$), 1.19 (d, 3, J = 7.3 Hz, $Me_{4\alpha}$), 1.05 (s, 6), 1.01 (s, 3), 0.90 (s, 3); ^{13}C NMR 179.8, 166.8, 110.0, 50.9, 47.8 (C_4), 47.0 (C_2), 39.3 (C_3), 25.0, 23.8, 23.2, 19.2, 12.8 ($Me_{4\alpha}$); IR 2958, 2931, 1707, 1673, 1460, 1438, 1374, 1347, 1282, 1266, 1239, 1200, 1177, 1077, 1023 cm^{-1}; GC t_R 14 min.

Reaction of Ethylene with 2. A balloon filled with ethylene was connected to a Schlenk flask which contained a mixture of $EtAlCl_2$ (0.40 mL of 1.44 M, 0.58 mmol) and ester **2** (107 mg, 0.95 mmol) in 2.5 mL of CH_2Cl_2. After 10 days at 25 °C, the reaction mixture was worked up in the normal manner to give 155 mg of crude product which consisted of a 1.0:1.4 mixture of (*Z*)- and (*E*)-methyl 3-chloro-3-pentenoate as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (*Z*)-3-chloro-3-pentenoate follow: ^1H NMR 5.73 (tq, 1, J = 1.0, 6.6 Hz, H_4), 3.74 (s, 3), 3.34 (dq, 2, J = 1.1, 1.1 Hz, H_2), 1.78 (dt, 3, J = 6.6, 1.1 Hz, H_5); ^{13}C NMR 170.0 (C_1), 126.9 (C_3), 125.1 (C_4), 52.2 (OMe), 44.7 (C_2), 14.3 (C_5); IR 3030, 3001, 2955, 2923, 2861, 1741, 1669, 1438, 1405, 1344, 1302, 1269, 1209, 1176, 1136, 1016, 974, 934 cm^{-1}; GC t_R 6.5 min.

The spectral data for methyl (*E*)-3-chloro-3-pentenoate follow: ^1H NMR 5.89 (q, 1, J = 7.2 Hz, H_4), 3.74 (s, 3, OMe), 3.40 (q, 2, J = 0.7 Hz, H_2), 1.70 (dt, 3, J = 7.2, 0.7 Hz, H_5); ^{13}C NMR 169.8 (C_1), 127.0 (C_3), 126.5 (C_4), 52.3 (OMe), 39.2 (C_2), 14.3 (C_5); IR 2956, 2927, 2901, 2861, 1742, 1661, 1438, 1411, 1349, 1317, 1273, 1197, 1176, 1124, 1025, 1001 cm^{-1}; GC t_R 7.8 min.

Reaction of 1-Hexene with 3. $EtAlCl_2$ (0.55 mL of 1.44 M, 0.8 mmol) was added to a solution of **3** (126 mg, 1.0 mmol) and 1-hexene (92.6 mg, 1.1 mmol) in 1.5 mL of CH_2Cl_2. After 11 days at 25 °C the reaction mixture was worked up in the normal manner to give 186.6 mg (89%) of crude product which consisted of a 4.2:1:3.6 mixture of **28**, **26**, and **27** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (2-butyl-4,4-dimethyl-(*E*)-cyclobutylidene)acetate (**28**) follow: ^1H NMR 5.56 (d, 1, J = 2.1 Hz), 3.65 (s, 3), 2.86 (dddt, 1, J = 9.7, 7.5, 2.1, 6.8 Hz, $H_{2\alpha}$), 1.98 (dd, 1, J = 10.9, 9.7 Hz, $H_{3\alpha}$), 1.51 (dd, 1, J = 10.9, 7.5 Hz, $H_{3\beta}$), 1.33 (s, 3), 1.30 (s, 3), 1.2–1.6 (m, 6), 0.87 (t, 3, J = 6.8 Hz); ^{13}C NMR 179.6, 166.1, 110.9, 50.8, 43.5 (C_4), 38.9 (C_3, CH_2), 38.4 (C_4, CH), 33.9, 29.1, 26.4 (4-Me), 26.3 (4-Me), 22.6, 14.0; IR 2961, 2933, 2864, 1716, 1709, 1467, 1459, 1438, 1362, 1347, 1283, 1263, 1197, 1184, 1166, 1041, 1026 cm^{-1}; GC t_R 15 min.

The spectral data for methyl (3-butyl-2,2-dimethyl-(*Z*)-cyclobutylideneacetate) (**26**) follow: ^1H NMR 5.55 (dd, 1, J = 2.2, 1.5 Hz), 3.70 (s, 3), 2.79 (ddd, 1, J = 17.0, 7.1, 1.5 Hz, $H_{4\alpha}$), 2.33 (ddd, 1, J = 17.0, 8.3, 2.2 Hz, $H_{4\beta}$), 2.00 (ddt, 1, J = 8.3, 7.1, 6.8 Hz, $H_{3\alpha}$), 1.35 (s, 3, $Me_{2\alpha}$), 1.26 (s, 3, $Me_{2\beta}$), 1.2–1.6 (m, 6), 0.92 (t, 3, J = 6.8 Hz); ^{13}C NMR 173.6, 169.8, 111.8, 50.8, 41.5, 34.1, 30.4, 29.9, 26.5, 22.8, 19.4, three carbons were not observed; IR 2960, 2932, 2863, 1716, 1672, 1467, 1438, 1347, 1283, 1217, 1195, 1183, 1163, 1079 cm^{-1}; GC t_R 19.2 min.

The spectral data for methyl (3-butyl-2,2-dimethyl-(*E*)-cyclobutylidene)acetate (**27**) follow: ^1H NMR 5.57 (dd, 1, J = 2.5, 2.2 Hz), 3.67 (s, 3), 3.20 (ddd, 1, J = 17.8, 8.5, 2.2 Hz, $H_{4\alpha}$), 2.60 (ddd, 1, J = 17.8, 7.6, 2.5 Hz, $H_{4\beta}$), 1.99 (ddt, 1, J = 8.5, 7.6, 6.6 Hz, $H_{3\alpha}$), 1.16 (s, 3, $Me_{2\alpha}$), 1.07 (s, 3, $Me_{2\beta}$), 1.2–1.6 (m, 6), 0.88 (t, 3, J = 7.1 Hz); ^{13}C NMR 175.4, 167.5, 109.1, 50.9, 46.7 (C_2), 42.2 (C_3, CH), 35.7 (C_4, CH_2), 30.5, 30.1, 27.4 ($Me_{2\alpha}$), 22.8, 21.2 ($Me_{2\beta}$), 14.1; IR 2961, 2930, 2862, 1705, 1674, 1463, 1439, 1366, 1346, 1281, 1201, 1184, 1062, 1021 cm^{-1}; GC t_R 28.8 min.

Reaction of *cis*-Butene with 3. Excess *cis*-2-butene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) and ester **3** (126 mg, 1 mmol) in 2 mL of CH_2Cl_2. After 22 days at 25 °C the reaction mixture was worked up in the normal manner to give 212 mg (90%) of crude product which consisted of a 1.3:1 mixture of **22** and **21** as determined by GC analysis. Pure samples were obtained by preparative GC.

Reaction of 3-*cis*-Hexene with 3. Ester **3** (63 mg, 0.5 mmol) followed by 3-*cis*-hexene (46 mg, 0.55 mmol) and $EtAlCl_2$ (0.21 mL of 1.44 M, 0.3 mmol) were added to 1.5 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction mixture was stirred for 19 days at 25 °C and worked up in the normal manner to give 88.5 mg (85%) of crude product which consisted of a 1.0:3.8 mixture of **30** and **29** as determined by GC analysis. A pure mixture of **30** and **29** was obtained by preparative GC.

The spectral data for methyl (2β,3β-diethyl-4,4-dimethyl-(*E*)-cyclobutylidene)acetate (**30**) follow: ^1H NMR 5.61 (d, 1, J = 2.0 Hz), 3.68 (s, 3), 2.78 (ddt, 1, J = 9.8, 2.0, 7.6 Hz, $H_{2\alpha}$), 2.06 (dt, 1, J = 9.8, 7.6 Hz, $H_{3\alpha}$), 1.9–1.4 (m, 4, ethyl CH_2), 1.34 (s, 3, 4-Me), 1.29 (s, 3, 4-Me), 0.94 (t, 3, J = 7.2 Hz), 0.90 (t, 3, J = 7.2 Hz); ^{13}C NMR 178.3, 166.0, 111.9, 50.8, 46.9 (C_4), 46.7, 44.5, 27.7 ($Me_{4\alpha}$), 22.3 (2β ethyl CH_2), 20.3 ($Me_{4\beta}$), 18.6 (3β ethyl CH_2), 13.7, 13.6; IR 2967, 2906, 2879, 1712, 1667, 1606, 1463, 1439, 1380, 1348, 1285, 1198, 1176, 1165, 1140, 1025; GC t_R 18 min.

The spectral data for methyl (2β,3β-diethyl-4,4-dimethyl-(Z)-cyclobutylidene)acetate (**29**) follow: ^{1}H NMR 5.60 (d, 1, J = 2.1 Hz), 3.68 (s, 3), 3.30 (dddd, 1, J = 9.2, 9.2, 5.1, 2.1 Hz, $H_{2\alpha}$), 2.12 (ddd, 1, J = 9.2, 8.3, 7.3 Hz, $H_{3\alpha}$), 1.9–1.4 (m, 4, ethyl CH_2), 1.15 (s, 3, $Me_{4\alpha}$), 1.08 (s, 3, $Me_{4\beta}$), 0.96 (t, 3, J = 7$_4$ Hz), 0.92 (t, 3, J = 7.3 Hz); ^{13}C NMR 178.8, 167.0, 109.8, 50.8, 47.3, 45.7, 27.6 ($Me_{4\alpha}$), 22.9 (2β ethyl CH_2), 22.2 ($Me_{4\beta}$), 4 carbons were not observed; GC t_R 19 min.

Reaction of *trans*-2-Butene with 3. Excess *trans*-2-butene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) and ester **3** (126 mg, 1.0 mmol) in 2.0 mL of CH_2Cl_2. After 11 days at 25 °C the reaction mixture was worked up in the normal manner to give 130 mg (70%) of crude product which consisted of a 2.6:1.1:1.2:1 mixture of **31**, **32**, **22**, and **21** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl (2,2,3α,4β-tetramethyl-(Z)-cyclobutylidene)acetate (**31**) follow: ^{1}H NMR 5.52 (d, 1, J = 2.2 Hz), 3.68 (s, 3), 2.48 (ddq, 1, J = 8.5, 2.2, 6.8 Hz, $H_{4\alpha}$), 1.66 (dq, 1, 8.5, 6.8 Hz, $H_{3\beta}$), 1.27 (s, 3, $Me_{2\beta}$), 1.20 (s, 3, $Me_{2\alpha}$), 1.11 (d, 3, J = 6.8 Hz, $Me_{4\beta}$), 1.00 (d, 3, J = 6.8 Hz, $Me_{3\alpha}$); ^{13}C NMR 178.9, 166.2, 109.6, 50.8, 46.3 (C_2), 44.7, 42.4, 26.2 ($Me_{2\beta}$), 19.9 ($Me_{2\alpha}$), 16.6 ($Me_{4\beta}$), 13.6 ($Me_{3\alpha}$); IR 2961, 2925, 2902, 2868, 1708, 1668, 1453, 1436, 1373, 1346, 1261, 1234, 1196, 1161, 1114, 1085, 1041, 1015 cm^{-1}; GC t_R 6.8 min.

The spectral data for methyl (2,2,3α,4β-trimethyl-(E)-cyclobutylidene)acetate (**32**) follow: ^{1}H NMR 5.61 (d, 1, J = 2.5 Hz), 3.68 (s, 3), 2.83 (ddq, 1, J = 7.3, 2.5, 6.9 Hz, $H_{4\alpha}$), 1.75 (dq, 1, J = 7.3, 7.1 Hz, $H_{3\beta}$), 1.32 (d, 3, J = 6.9 Hz, $Me_{4\beta}$), 1.17 (s, 3, $Me_{2\beta}$), 1.02 (d, 3, J = 7.1 Hz, $Me_{3\beta}$), 1.02 (s, 3, $Me_{2\beta}$); ^{13}C NMR 180.0, 166.8, 110.0, 50.9, 44.8, 44.3, 43.3, (C_2), 28.0 ($Me_{2\beta}$), 22.2 ($Me_{2\alpha}$), 17.9 ($Me_{4\beta}$), 14.3 ($Me_{3\alpha}$); IR 2959, 2929, 2905, 2868, 1705, 1670, 1460, 1454, 1436, 1373, 1349, 1269, 1196, 1180, 1167, 1089, 1037, 1011, 964 cm^{-1}; GC t_R 7.8 min.

Reaction of Isobutylene with 3. Excess isobutylene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.23 mL of 1.44 M, 0.33 mmol) and ester **3** (63 mg, 0.5 mmol) in 1.5 mL of CH_2Cl_2. After 28 days at 25 °C the reaction mixture was worked up in the normal manner to give 127 mg of crude product which consisted of a 3.3:2.3:1.0 mixture of an unidentified mixture, **34** and **33** and long chain polymers as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 3-(methylethylidene)-5-methyl-5-hexenoate (**34**) follow: ^{1}H NMR 4.74 (br, 1, H_6), 4.64 (br, 1, H_6), 3.65 (s, 3, OMe), 3.04 (br, 2, H_2), 2.83 (s, 2, H_4), 1.74 (s, 3), 1.72 (s, 3), 1.67 (s, 3); ^{13}C NMR 172.8 (C_1), 143.4, 131.2, 122.9, 110.9 (C_6), 51.6 (OMe), 41.1, 37.0, 22.3, 20.9, 20.7; IR 3697, 3611, 3160, 2926, 2868, 1732, 1647, 1606, 1443, 1381, 1338, 1274, 1171, 1106, 1014 cm^{-1}; GC t_R 9 min.

The spectral data for methyl (2,2,3,3-tetramethyl-(E)-cyclobutylidene)acetate (**33**) follow: ^{1}H NMR 5.63 (t, 1, J = 2.5 Hz), 3.68 (s, 3), 2.82 (d, 2, J = 2.5 Hz, H_4), 1.08 (s, 6), 1.05 (s, 6); ^{13}C NMR 109.8, 50.9, 48.4, 44.2 (C_4), 37.2 (C_2), 24.3, 22.7, two carbons were not observed; IR 3695, 3025, 2963, 2873, 1710, 1676, 1604, 1444, 1346, 1279, 1212, 1176, 1021 cm^{-1}; GC t_R 11 min.

Reaction of 2-Methyl-2-butene with 3. $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) was added to a solution of **3** (126 mg, 1.0 mmol) and 2-methyl-2-butene (77 mg, 1.1 mmol) in 1.5 mL of CH_2Cl_2. After 18 days at 25 °C the reaction mixture was worked up in the normal manner to give 229 mg (98%) of crude product which consisted of a 2.8:9.5:1.4:1.0:4.5 mixture of **35**, **36**, **25**, **24**, and **37** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 3-ethoxy-4-methyl-2-pentenoate (**35**) follow: ^{1}H NMR 4.87 (s, 1, H_2), 3.99 (qq, 1, J = 6.8, 6.8 Hz, H_4), 3.79 (q, 2, J = 6.9 Hz), 3.66 (s, 3, OMe), 1.33 (t, 3, J = 6.9 Hz), 1.08 (d, 6, J = 6.8 Hz); IR 2984, 2941, 2877, 1710, 1612, 1471, 1438, 1317, 1279, 1153, 1051 cm^{-1}; GC t_R 6.8 min.

The spectral data for methyl 3-chloro-4-methyl-3-pentenoate (**36**) follow: ^{1}H NMR 3.73 (s, 3, OMe), 3.44 (s, 2, H_2), 1.89 (s, 3), 1.84 (s, 3); ^{13}C NMR 170.2, 132.1, 119.3, 52.2, 41.0, 21.9, 20.6; IR 3001, 2956, 2925, 2862, 1741, 1439, 1342, 1279, 1197, 1175, 1134, 1046, 1014 cm^{-1}; GC t_R 10.5 min.

The spectral data for **37** follow: ^{1}H NMR 5.68 (d, 1, J = 1.4 Hz), 3.74 (s, 3), 3.43 (dq, 1, J = 1.4, 7.2 Hz), 1.41 (s, 3), 1.36 (s, 3), 1.27 (s, 3), 1.18 (d, 3, J = 7.2 Hz), 1.17 (s, 3); ^{13}C NMR 169.8, 111.1, 81.9, 81.8, 51.2, 47.0, 32.4, 30.6, 16.4, two carbons were not observed; IR 2981, 1714, 1666, 1462, 1438, 1371, 1354, 1281, 1271, 1232, 1150, 1106, 1040, 979 cm^{-1}; GC t_R 14 min.

Reaction of 2,3-Dimethyl-2-butene with 3. $EtAlCl_2$ (0.42 mL of 1.44 M, 0.6 mmol) was added to a solution of **3** (126 mg, 1.0 mmol) and 2,3-dimethyl-2-butene (92.6 mg, 1.1 mmol) in 2.0 mL of CH_2Cl_2. After 17 days at 25 °C the reaction mixture was worked up in the normal manner to give 127.6 mg (60%) of crude product which consisted of a 2.6:1 mixture of **36** and **38** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 3,3-dichloro-4-methylpentanoate (**38**) follow: ^{1}H NMR 3.72 (s, 3), 3.50 (s, 2, H_2), 2.70 (qq, 1, J = 6.8, 6.8 Hz), 1.12 (d, 6, J = 6.8 Hz); ^{13}C NMR 170.2, 52.3, 46.8, 41.3, 17.9 (2 carbons), one carbon was not observed; IR 2981, 2939, 2879, 1748, 1717, 1657, 1625, 1468, 1440, 1406, 1318, 1272, 1233, 1193, 1051, 1006 cm^{-1}; GC t_R 13.5 min.

Reaction of Isobutylene with 4. Excess isobutylene was condensed, using a dry ice–acetone bath, into a pressure bottle which contained a mixture of $EtAlCl_2$ (0.45 mL of 1.44 M, 0.65 mmol) and ester **4** (105 mg, 0.94 mmol) in 2 mL of CH_2Cl_2. After 16 days at 25 °C the reaction mixtures was worked up in the normal manner to give 340 mg of crude product which consisted of a 1.0:2.2:1.7 mixture of **40**, **39**, and 2,4,4,6,6,8,8-heptamethyl-1-nonene as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl 2,5-dimethyl-3-methylene-5-hexenoate (**40**) follow: ^{1}H NMR 5.01 (br, 1), 4.96 (br, 1), 4.85 (br, 1), 4.76 (br, 1), 3.67 (s, 3), 3.16 (q, 1, J = 7.2 Hz, H_2), 2.80 (s, 2, H_4), 1.68 (s, 3, C_5-Me), 1.28 (d, 3, J = 7.2 Hz); ^{13}C NMR 169.8 (C_1), 142.9, 140.6, 113.1, 113.0, 51.8 (OMe), 44.3, 44.2, 22.7; IR 3697, 3613, 3158, 2986, 1799, 1735, 1605, 1468, 1381, 1219, 1098 cm^{-1}; GC t_R 16 min.

The spectral data for methyl 2-(3,3-dimethylcyclobutylidene)propionate (**39**) follow: ^{1}H NMR 3.70 (s, 3), 2.78 (tq, 2, J = 2.7, 2.0 Hz, H_2), 2.49 (tq, 2, J = 2.7, 1.9 Hz, H_4), 1.70 (tt, 3, J = 2.0, 1.9 Hz), 1.18 (s, 6, C_3-Me); ^{13}C NMR 169.8, 109.8, 51.0, 46.8, 44.1, 31.2 (C_3), 29.0 (2 carbons), one carbon was not observed; IR 3697, 2956, 2930, 2870, 1705, 1675, 1605, 1439, 1324, 1295, 1219, 1153, 1066 cm^{-1}; GC t_R 17.8 min.

The spectral data for 2,4,4,6,6,8,8-heptamethyl-1-nonene follow: ^{1}H NMR 4.85 (q, 1, J = 1.4 Hz, H_1), 4.63 (q, 1, J = 1.0 Hz, H_1), 1.99 (s, 2, H_3), 1.78 (dd, 3, J = 1.4, 1.0 Hz, C_2-CH_3), 1.37 (s, 2, H_5), 1.33 (s, 2, H_7), 1.08 (s, 6, C_4-CH_3), 1.02 (s, 6, C_6-CH_3), 0.98 (s, 9, C_8-CH_3); ^{13}C NMR 114.3, 58.0, 56.2, 53.6, 36.1, 32.4, 32.3, 32.2, 30.6, 29.3, 25.7, carbon 2 was not observed; IR 3697, 3611, 2957, 1643, 1605 cm^{-1}; GC t_R 25 min.

Methyl 2,3,8-nonatrienoate (41) was prepared by the procedure of Lang and Hansen.[4] Into a 200-mL, round-bottomed flask equipped with a pressure equalizing dropping funnel containing a solution of 2.9 g (7 mmol) of (carbomethoxymethyl)-triphenylphosphonium bromide in 30 mL of CH_3CN was added 1.44 g (14 mmol) of triethylamine in 10 mL of CH_3CN dropwise over 5 min. After 10 min, 1.03 g (7 mmol) of 6-heptenoyl chloride in 10 mL of CH_3CN was added dropwise to the vigorously stirred solution over 15 min. The stirring was continued overnight at 25 °C. The brown mixture was filtered through Celite, washed with 40 mL of *n*-pentane, filtered again through the same Celite, and washed by an additional 40 mL of pentane. Water (50 mL) was added and the aqueous mixture was extracted with four portions of 40 mL of pentane. The organic layers were combined and dried over $MgSO_4$ and filtered through neutral alumina (grade III). Evaporation in vacuo gave 1.1830 g of crude product. Distillation under reduced pressure (0.15 torr 30–40 °C) yielded 939 mg (5.6 mmol, 73% from the acid) of pure **41**: ^{1}H NMR 5.86–5.72 (m, 2, allenic H), 5.64 (m, 1, H_8), 5.07–4.94 (m, 2, H_9), 3.74 (s, 3), 2.25–2.08 (m, 4), 1.56 (tt, 2, J = 7.3, 7.3 Hz, H_6); ^{13}C NMR 212.4 (C_3), 166.6 (C_1), 138.0 (C_8), 114.9 (C_9), 95.1 (C_2), 88.0 (C_4), 51.9 (OMe), 32.9, 27.8, 26.7; IR 3078, 2951, 2930, 2857, 1960, 1722, 1709, 1640, 1438, 1408, 1267, 1214, 1196, 1167, 1030; GC t_R 18 min.

Intramolecular Cycloaddition of Methyl 2,3,8-Nonatrienoate (41). Methyl 2,3,8-nonatrienoate (**41**) (190 mg, 1.1 mmol) and $EtAlCl_2$ (0.6 mL of 1.44 M, 0.86 mmol) were added to 2 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction

mixture was stirred for 14 days at 25 °C. Normal workup gave 180 mg (95%) of crude product which consisted of a 2:1 mixture of **42** and **43** as determined by GC analysis. Pure samples were obtained by preparative GC.

The spectral data for methyl ((*Z*)-bicyclo[3.2.0]hept-6-ylidene)acetate (**42**) follow: ^{1}H NMR 5.55 (ddd, 1, J = 2.2, 2.2, 2.2 Hz), 3.72 (m, 1, H_5), 3.70 (s, 3, CH_3), 2.93 (dddd, 1, J = 17.2, 9.0, 2.3, 2.2 Hz, H_7), 2.86 (ddd, 1, J = 3.8, 1.7, 1.6 Hz, H_2), 2.24 (dddd, 1, J = 17.2, 3.8, 3.6, 2.2 Hz, H_7), 1.8–1.6 (m, 6); ^{13}C NMR 112.7, 50.0, 35.4, 35.2, 33.2, 33.1, 32.1, 24.5, two carbons were not observed; IR 2955, 2863, 1712, 1673, 1439, 1351, 1235, 1201, 1092, 1036 cm^{-1}; GC t_R 19.5 min.

The spectral data for methyl ((*E*)-bicyclo[3.2.0]hept-6-ylidene)acetate (**43**)[2] follow: ^{1}H NMR 5.58 (ddd, 1, J = 2.5, 2.5, 1.7 Hz), 3.67 (s, 3), 3.38 (m, 1, H_5), 3.20 (dddd, 1, J = 19.3, 9.0, 2.5, 2.5 Hz, H_7), 2.85 (ddddd, 1, J = 9.0, 5.6, 5.0, 1.3, 1.3 Hz, H_1), 2.54 (dddd, 1, J = 19.3, 5.0, 4.0, 2.5 Hz, H_7), 1.8–1.5 (m, 6); ^{13}C NMR 171.9, 167.0, 112.2, 50.8, 48.6, 37.1, 35.7, 33.1, 32.5, 24.5; IR 2958, 2860, 1708, 1673, 1438, 1348, 1280, 1214, 1198, 1126, 1090, 1029 cm^{-1}; GC t_R 23 min.

Methyl (*Z*)-2,3,8-undecatrienoate (44) was prepared by the procedure of Lang and Hansen[4] from 4.6 g (11.1 mmol) of (carbomethoxymethyl)triphenylphosphonium bromide, 2.25 g (22.2 mmol) of triethylamine, and 1.92 g (11 mmol) of 6-*cis*-nonenoyl chloride as described above. Normal workup gave 1.6050 g of crude product. Distillation under reduced pressure (0.15 torr, 43–50 °C) yielded 1.170 g (6 mmol, 40% from the aldehyde) of pure **44**: ^{1}H NMR 5.64–5.60 (m, 2, allenic H), 5.43–5.25 (m, 2, olefinic H), 3.74 (s, 3), 2.20–2.00 (m, 6), 1.53 (tt, 2, J = 7.3, 7.3 Hz, H_6), 0.96 (t, 3, J = 7.4 Hz, H_{11}); ^{13}C NMR 212.3 (C_3), 166.6 (C_1), 132.3 (C_8), 128.2 (C_9), 95.2 (C_2), 88.0 (C_4), 51.9 (OMe), 28.6, 26.9, 26.3, 20.5 (C_{10}), 14.3 (C_{11}); IR 3005, 2932, 2859, 1960, 1712, 1455, 1438, 1267, 1214, 1165, 1029; GC t_R 43 min.

Intramolecular Cycloaddition of Methyl (*Z*)-2,3,8-Undecatrienoate (44). Methyl (*Z*)-2,3,8-undecatrienoate (**44**) (137 mg, 0.71 mmol) and $EtAlCl_2$ (0.34 mL of 1.44 M, 0.49 mmol) were added to 2 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction mixture was stirred for 7 days at 25 °C followed by a normal workup to give 137 mg (100%) of crude product which consisted of a 4.1:5.4:14.6 mixture of **47**, **46**, and **45** as determined by GC analysis. Pure samples were obtained by preparative GC. Three additional products were formed in very low yield. Since the starting material contained ≃10% of the *E* isomer, three isomers corresponding to **45**–**47** should be formed.

The spectral data for methyl (7-*syn*-ethylbicyclo[3.1.1]hept-6-ylidene)acetate (**47**) follow: ^{1}H NMR 5.67 (br, 1), 3.69 (s, 3), 3.24 (ddd, 1, J = 6.9, 4.1, 0.9 Hz, H_1), 2.63 (ddd, 1, J = 6.9, 3.3, 3.3 Hz, H_5), 2.24 (dddd, 1, J = 13.0, 8.0, 4.1, 4.1 Hz, H_2), 2.15–2.00 (m, 3), 1.75–1.65 (m, 3), 1.39 (dt, 2, J = 8.3, 7.3 Hz, CH_2-ethyl), 0.87 (t, 3, J = 7.3 Hz, Me-ethyl); ^{13}C NMR 175.5, 167.3, 108.9, 50.8, 49.5, 48.9, 46.4, 34.6, 34.5, 33.5, 25.0, 17.3; IR 3024, 2955, 2868, 1702, 1676, 1468, 1438, 1378, 1218 cm^{-1}; GC t_R 25 min.

The spectral data for methyl ((*E*)-7-*endo*-ethylbicyclo[3.2.0]-hept-6-ylidene)acetate (**46**) follow: ^{1}H NMR 5.57 (dd, 1, J = 2.8, 2.1 Hz), 3.67 (s, 3), 3.20 (m, 2, H_5 and H_7), 2.90 (ddd, 1, J = 7.8, 7.8, 7.8 Hz, H_1), 2.14 (ddq, 1, J = 12.9, 3.2, 7.3 Hz, CH_2-ethyl), 1.9–1.4 (m, 6), 1.31 (dq, 1, J = 12.9, 7.3 Hz, CH_2-ethyl), 0.85 (t, 3, J = 7.3 Hz); ^{13}C NMR 187.3, 112.1, 50.9, 46.8, 46.7, 38.1, 32.4, 26.8 (3 carbons), 17.9, one carbon was not observed; IR 2957, 2878, 1712, 1670, 1439, 1218, 1208, 1184 cm^{-1}; GC t_R 34 min.

The spectral data for methyl ((*Z*)-7-*endo*-ethylbicyclo[3.2.0]-hept-6-ylidene)acetate (**45**) follow: ^{1}H NMR 5.61 (dd, 1, J = 2.3, 2.3 Hz), 3.69 (m, 1, H_7), 3.68 (s, 3), 2.89 (m, 2, H_1 and H_5), 1.8–1.4 (m, 8), 0.91 (t, 3, J = 7.5 Hz); ^{13}C NMR 184.5, 166.5, 111.2, 50.8, 48.6, 45.5, 38.3, 31.5, 27.2, 27.1, 27.0, 19.8; IR 3023, 2956, 2874, 1705, 1669, 1438, 1350, 1219, 1201, 1156, 1027 cm^{-1}; GC t_R 41 min.

Methyl 5,9-dimethyl-2,3,8-decatrienoate (48) was prepared by the procedure of Lang and Hansen[4] from 2.325 g (5.6 mmol) of (carbomethoxymethyl)triphenylphosphonium bromide, 1.16 g (11.4 mmol) of triethylamine, and 0.8 g (4.2 mmol) of crude 3,7-dimethyl-6-octenoyl chloride in 5 mL of CH_3CN as described above. Normal workup yielded 1.635 g of red crude product. A 0.547-g sample of the crude product was purified by chromatography on neutral alumina (grade III, 9:1 hexane–EtOAc) to give 0.2743 g (95% from the acid chloride) of pure **48**: ^{1}H NMR 5.60 (m, 2, H_2 and H_4), 5.10 (m, 1, H_8), 3.73 (s, 3), 2.32 (m, 1, H_5), 2.05 (m, 2, H_7), 1.68 (d, 3, J = 1.2 Hz), 1.61 (s, 3), 1.42 (m, 2, H_6), 1.08 (d, 3, J = 6.8 Hz, 5-Me), [3.72 (s, 3, diastereomer OMe), 1.07 (d, 3, J = 6.8 Hz, diastereomer 5-Me)]; ^{13}C NMR 211.6 (C_3), 166.6 (C_1), 137.8 (C_9), 131.7 (C_8), 124.1 (C_2), 100.1 (C_4), 51.8, 36.9 (C_6), 32.6 (C_7), 25.5 (C_5), 20.2, 17.6, 14.0, [100.9 (diastereomer C_4), 20.0 (diastereomer C_5-Me)]; IR 2970, 2928, 2891, 2876, 1962, 1723, 1631, 1445, 1410, 1380, 1333, 1272, 1219, 1199, 1169, 1033 cm^{-1}; GC t_R 44 min.

Intramolecular Cycloaddition of Methyl 5,9-Dimethyl-2,3,8-decatrienoate (48). Methyl 5,9-dimethyl-2,3,8-decantrienoate (**48**) (250 mg, 1.2 mmol) and $EtAlCl_2$ (0.45 mL of 1.44 M, 0.65 mmol) were added to 3 mL of CH_2Cl_2 in a flame-dried flask under nitrogen. The reaction mixture was stirred for 12 days at 25 °C, diluted with ether, and quenched by slow addition of saturated NaH_2PO_4 solution. Hydrochloric acid (10%) was added to dissolve the precipitated alumina. The two layers were separated and the aqueous layer was washed with three portions of ether. The combined organic layers were dried over $MgSO_4$ and filtered through neutral alumina (grade III). Evaporation in vacuo gave 190.6 mg (76%) of crude product which consisted of a 3.9:1.4:2.0:1.0 mixture of **51**, **52**, **49**, and **50** as determined by GC analysis. Pure samples were obtained by preparative GC. GC analysis of a similar run showed that the reaction was complete after 1 h and that the ene adducts (**51** and **52**) slowly decomposed at extended reaction times (10–25 days).

The spectral data for methyl *trans*-3-methyl-6-(methylethenyl)-1-cyclohexenacetate (**51**) follow: ^{1}H NMR 5.54 (dddd, 1, J = 2.5, 1.3, 1.2, 1.2 Hz, H_2), 4.83 (br, 1), 4.71 (br, 1), 3.65 (s, 3), 2.94 (dddd, 1, J = 15.5, 2.5, 1.2, 1.1 Hz), 2.87 (ddd, 1, J = 15.5, 1.2, 1.2 Hz), 2.87 (m, 1, H_6), 2.20 (br, 1, H_3), 1.8–1.7 (m, 3), 1.64 (br, 3, 6-Me), 1.2–1.1 (m, 1), 0.98 (d, 3, J = 7.5 Hz, C_3-Me); ^{13}C NMR 146.8, 134.1, 112.8, 51.6, 46.2, 40.6, 30.3, 28.6, 26.5, 19.8, 3 carbons were not observed; IR 2958, 2935, 2871, 1736, 1644, 1458, 1439, 1219, 1168 cm^{-1}; GC t_R 21.5 min.

The spectral data for methyl *cis*-3-methyl-6-(methylethenyl)-1-cyclohexeneacetate (**52**) follow: ^{1}H NMR 5.56 (ddd, 1, J = 2.0, 1.5, 1.2 Hz, H_2), 4.87 (br, 1), 4.59 (br, 1), 3.66 (s, 3), 2.95 (ddd, 1, J = 15.1, 1.7, 1.7 Hz), 2.90 (ddd, 1, J = 15.1, 1.3, 1.3 Hz), 2.7 (br, 1, H_6), 2.20 (br, 1, H_3), 1.73 (br, 3, 6-Me), 1.7–1.5 (m, 3), 1.25–1.1 (m, 1), 0.97 (d, 3, J = 7.1 Hz, C_3-Me); ^{13}C NMR 146.4, 134.1, 131.0, 112.4, 51.6, 44.4, 41.3, 30.7, 26.3, 26.0, 22.0, two carbons were not observed; IR 2958, 2939, 2872, 1734, 1660, 1460, 1440, 1380 cm^{-1}; GC t_R 23.5 min.

The spectral data for methyl ((*E*)-(1α,2β,5α)-2,7,7-trimethylbicyclo[3.1.1]hept-6-ylidene)acetate (**49**) follow: ^{1}H NMR 5.74 (dd, 1, J = 1.2, 1.0 Hz), 3.71 (s, 3), 3.03 (dddd, 1, J = 6.6, 4.8, 1.6, 1.2 Hz, H_5), 2.18 (dd, 1, J = 6.6, 1.0 Hz, H_1), 2.34 (m, 1), 2.05–1.80 (m, 3), 1.60 (m, 1), 1.11 (s, 3, endo-Me), 0.99 (s, 3, exo-Me), 0.88 (d, 3, J = 6.5 Hz, 2 Me); IR 2988, 2872, 1704, 1678, 1459, 1439, 1356, 1214, 1181, 1105 cm^{-1}; GC t_R 26 min.

The spectral data for methyl ((*Z*)-(1α,2β,5α)-2,7,7-trimethylbicyclo[3.1.1]hept-6-ylidene)acetate (**50**) follow: ^{1}H NMR 5.78 (dd, 1, J = 0.8, 0.8 Hz), 3.69 (s, 3), 2.93 (ddd, 1, J = 6.6, 1.5, 1.0 Hz, H_1), 2.42 (m, 1, H_5), 2.34 (m, 1), 2.05–1.80 (m, 3), 1.60 (m, 1), 1.10 (s, 3, endo-Me), 0.96 (s, 3, exo-Me), 0.88 (d, 3, J = 6.5 Hz, 2α Me); GC t_R 26 min.

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Registry No. **1**, 592-41-6; **2**, 22377-44-2; **3**, 17039-96-2; **4**, 18913-37-6; **5**, 103562-94-3; **6**, 103664-48-8; **7**, 103664-49-9; **8**, 103664-50-2; **9**, 103562-95-4; **10**, 103664-51-3; **11**, 103664-52-4; **12**, 103562-96-5; **13**, 103664-53-5; **14**, 103664-54-6; **15**, 103664-55-7; **16**, 75233-02-2; **17**, 75233-01-1; **18**, 103562-97-6; **19**, 103562-98-7; **20**, 103562-99-8; **21**, 103563-00-4; **22**, 103664-56-8; **23**, 103563-01-5; **24**, 103563-02-6; **25**, 103563-03-7; **26**, 103563-04-8; **27**, 103563-05-9; **28**, 103563-06-0; **29**, 103563-07-1; **30**, 103664-57-9; **31**, 103664-58-0; **32**, 103664-59-1; **33**, 75233-04-4; **34**, 103563-08-2; **35**, 103563-09-3; **36**, 103563-10-6; **37**, 103563-11-7; **38**, 103563-12-8; **39**, 103563-13-9; **40**, 103563-14-0; **41**, 103563-15-1; **42**, 103563-16-2; **43**, 103563-17-3; **44**, 103563-18-4; **45**, 103563-19-5; **46**, 103664-60-4; **47**, 103563-20-8; **48**, 103563-21-9; **49**, 103563-22-0; **50**, 103563-23-1; **51**, 103563-24-2;

52, 103563-25-3; (Z)-EtCH=CHEt, 7642-09-3; (E)-MeCH=CHMe, 624-64-6; $Me_2C=CH_2$, 115-11-7; $Me_2C=CHMe$, 513-35-9; $Me_2C=CMe_2$, 563-79-1; (Z)-MeCH=CHMe, 590-18-1; EtCOCl, 79-03-8; $Me_2CHCOCl$, 79-30-1; MeCOCl, 75-36-5; $Ph_3P^+CHMeCO_2MeBr^-$, 2689-62-5; (Z)-EtCH=CH$(CH_2)_4$CHO, 2277-19-2; $Me_2C=CH(CH_2)_2CH(Me)CH_2CHO$, 106-23-0; $Me_2C=CH(CH_2)_2CH(Me)CH_2CO_2H$, 502-47-6; (Z)-EtCH=CH$(CH_2)_4CO_2H$, 41653-99-0; $H_2C=CH(CH_2)_4CO_2H$, 1119-60-4; $H_2C=CEt_2$, 760-21-4; $H_2C=CH_2$, 74-85-1; (Z)-MeCH=C(Cl)CH_2CO_2Me, 103563-26-4; (E)-MeCH=C(Cl)CH_2CO_2Me, 103563-27-5; $H_2C=C(Me)(CH_2C(Me_2))_3CH_3$, 15796-04-0; $Ph_3P^+CH_2CO_2Me$ Br^-, 1779-58-4; $H_2C=CH(CH_2)_4COCl$, 21430-12-6; (Z)-EtCH=CH$(CH_2)_4COCl$, 103563-28-6; $Me_2C=CH(CH_2)_2CH(Me)CH_2COCl$, 36392-06-0; $EtACl_2$, 563-43-9.

Synthesis and Ring Expansion of Vinylazetidines. A Synthesis of Hydroazocines[1]

Alfred Hassner* and Norbert Wiegand

Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52100 Israel

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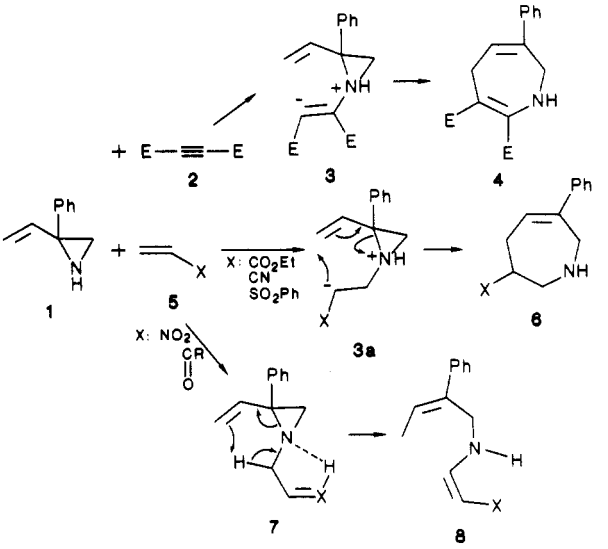
A synthesis of 2-vinylazetidines **11a–c** by means of $ClSO_2NCO$ addition to 1,3-dienes followed by AlH_3 reduction is described. One example (**11a**) underwent Michael additions with several olefinic and acetylenic substrates. The 1,2-divinylazetidines obtained with the latter reagents underwent Cope rearrangements when heated and gave rise to tautomeric mixtures of 3,4,7,8- and 1,4,7,8-tetrahydroazocines (**21** and **22**).

The chemistry of azocines and of their hydro derivatives is largely unexplored[2] because of the unavailability of good methods for their preparation. Recently we reported a ring expansion reaction of 2-vinylaziridines **1** to hydroazepines **4** or **6** during their reaction with olefinic or acetylenic substrates.[3] Thus vinylaziridine **1** reacts with dimethyl acetylenedicarboxylate (**2**) at 20 °C to produce dihydroazepine **4** in excellent yield. Since even olefins **5** (X: COOEt, CN, or SO_2Ph) react with **1** by way of ring expansion to the tetrahydroazepines **6**, both reactions were postulated to proceed via a Michael addition to produce the zwitterionic intermediates **3**; the latter then undergo ring closure with cleavage of the three-membered ring. However, not all olefinic Michael acceptors led to formation of seven-membered rings. When the intermediate carbanionic species **3a** is stabilized by a nitro or a carbonyl function, the reaction takes a different course and leads, via an ene reaction on **7**, to enamine species **8**. In order to test the scope of the above ring expansion reactions and whether they can be applied to the synthesis of hydroazocines, we decided to investigate the reaction of 2-vinylazetidines with unsaturated substrates. We report here the synthesis of vinylazetidines **11** and reaction of **11a** with olefinic and acetylenic Michael acceptors.

Results and Discussion

While 2-vinylaziridines **1** can be prepared from readily available azirines,[4] a general method for synthesis of 2-vinylazetidines is not available.[5] As an entry into vinylazetidines, we utilized the chlorosulfonyl isocyanate (CSI) addition to olefins.[6] Reaction of $ClSO_2NCO$ with isoprene



followed by sodium sulfite workup[7] furnished vinylazetidinone **10a**.[8] Reduction of **10a** to 2-vinylazetidine **11a** presented unexpected difficulties. Although lithium aluminium hydride reduction of azetidinones to azetidines is a well-known reaction,[9] its application to **10** led surprisingly to concomitant reduction of the vinyl side chain. The NMR spectrum of the product (**12**) revealed the absence of olefinic protons, and instead the typical pattern of a CH_3CH_2 group was visible. An additional highly coupled signal for the CH_2-4 group, centered at 3.4 ppm, indicated conversion to the azetidine system. An analogy for an intramolecular C=C reduction by LAH can be found during the reduction of a carbonyl adjacent to an allenic function.[10] On the other hand, DIBAL, $HAlCl_2$, or H_2AlCl, which were reported[11] to be reagents of choice for reduction of azetidinones, were ineffective for reduction of **10**. Finally, we succeeded in generating **11a** in 73% yield by AlH_3 reduction of **10a**. In a similar manner 2,3-di-

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