Supplementary Material Available: Table I, a listing of NMR and mass spectroscopy data for the products prepared in this study (1 page). Ordering information is given on any current masthead page.

References and Notes

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(2) N. A. Cortese, C. B. Ziegler, Jr., B. J. Hrnjez, and R. F. Heck, *J. Org. Chem.*, **43**, 2952 (1978).
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(9) T. A. Stephenson, S. M. Morehousr, A. R. Powell, J. P. Heffler, and G. Wilkinson, *J. Chem. Soc.*, 3632 (1965).
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(15) R. Camps, *Arch. Pharm. (Weinheim, Ger.)*, **237**, 683 (1899).
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Lewis Acid Catalyzed Reactions of Methyl Propiolate with Unactivated Alkenes

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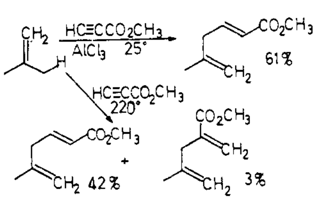
Received February 17, 1979

Abstract: Methyl propiolate undergoes Lewis acid catalyzed reactions with alkenes in high yield. Mono- and 1,2-disubstituted alkenes give mainly cyclobutenes. 1,1-Disubstituted, trisubstituted, and tetrasubstituted alkenes give only ene adducts. Use of ethylaluminum dichloride as catalyst allows the isolation of pure products from acid-sensitive alkenes. Functionalized alkenes containing nonbasic functional groups are suitable substrates. Alkenes containing more basic functional groups are suitable if 2 equiv of catalyst is used.

The use of carbon-carbon double bonds as activating groups for the formation of new carbon-carbon bonds under mild conditions is of considerable interest in organic synthesis. The ene reaction provides a potential solution to this problem. We have recently found that methyl propiolate[1] and 3-butyn-2-one[2] undergo Lewis acid catalyzed reactions at room temperature with a wide variety of alkenes giving either stereospecific [2 + 2] cycloadducts or ene adducts[3] depending on the substitution pattern of the alkene (Scheme I). These results contrast with the thermal reactions of methyl propiolate which proceed in low yield at 200-300 °C and give only ene adducts as mixtures of regioisomers.[4] The [2 + 2] cycloaddition has precedent in the cycloaddition of propiolate esters with enamines.[5] It has not been previously observed in nonphotochemical reactions of propiolates with unactivated alkenes.

In this paper we report significantly improved reaction conditions for the Lewis acid catalyzed reaction of propiolate esters with alkenes and describe our studies on the scope and limitations of this reaction, application to functionalized alkenes and studies directed toward elucidation of the mechanism of this reaction. The results of these studies are shown in Table I. The majority of these addition reactions were carried out with our initial conditions. Methyl propiolate is added to aluminum chloride in benzene. After the aluminum chloride has dissolved, the alkene is then added.[6] Although this procedure works well, isomerization of the alkene and addition of hydrogen chloride to the alkene or ene adduct often lead to byproducts. *We have recently found that ethylaluminum dichloride in either benzene or methylene chloride gives excellent yields of products uncontaminated with chlorine containing products or products resulting from isomerized alkene.* We believe that this dramatic improvement is due to the ability of ethylaluminum dichloride to act as a proton scavenger as well as a Lewis acid. Recent kinetic studies seem to indicate that the Lewis acid complexes preferentially with the product. *Therefore optimal yields are usually obtained with close to 1 equiv of ethylaluminum dichloride and reaction times of ca. 1 day.* In most of the cases in Table I, no attempt was made to optimize the amount of catalyst used. Yields greater than 80% can usually be obtained.

Scheme I



The formation of ene adducts is the exclusive reaction with alkenes containing at least one disubstituted carbon. 1,1-Disubstituted alkenes (cases 1-5), trisubstituted alkenes (cases 6-10), and tetrasubstituted alkenes (case 11) give ene adducts cleanly in good yield. Monosubstituted alkenes (cases 12 and 13) give mixtures of ene adduct and both of the possible cyclobutenes. Because of the ability of the trimethylsilyl group to stabilize positive charge at the β position, allyltrimethylsilane (**14**) gives only a single cyclobutene. This contrasts with the titanium tetrachloride catalyzed reactions of **14** with enones which give β-allylketones[7] but is similar to the cycloaddition of **14** with TCNE in nonpolar solvents which gives cyclobutanes.[8]

Cases 2 and 4 indicate that, with aluminum chloride as catalyst, isomerization of the alkene is sometimes a problem. This isomerization is probably catalyzed by hydrogen chloride. Use of ethylaluminum dichloride, which is both a milder catalyst and a hydrogen chloride scavenger, alleviates isomerization and allows the use of methylene chloride as solvent (cases 4, 31, 34, and 40). Under these conditions, optimal yields

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Table I. Aluminum Chloride Catalyzed Reactions with Methyl Propiolate

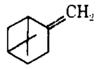
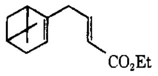
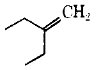
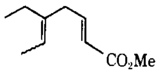
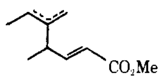
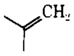
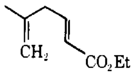
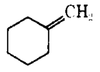
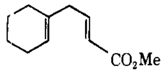
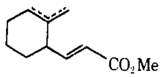
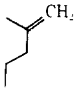
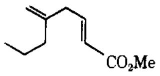
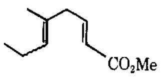
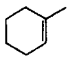
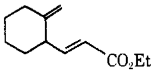
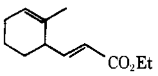
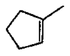
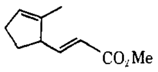
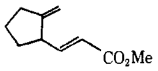
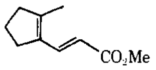
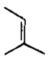
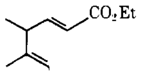
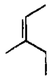
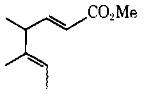
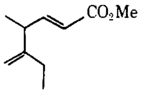
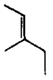
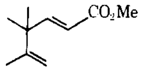
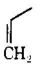
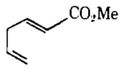
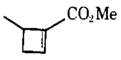
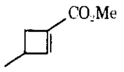
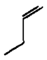
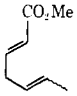
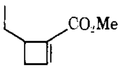
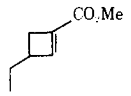
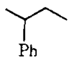
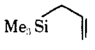
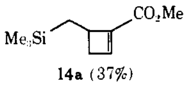
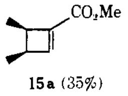
case		mol % catalyst (AlCl$_3$, reaction for 7 days in benzene unless specified)	products (% yield)		
1		19%	 **1a**[a] (82%)		
2		33%	 **2a**[b] (51%)	 **2b**[c] (4%)	
3		50%	 **3a**[a] (61%)		
4			 **4a**	 **4b**[c]	
		50%	(57%)	(13%)	
		50% (EtAlCl$_2$) 4 days	(58%)	—	
		50% (EtAlCl$_2$) 1 day, CH$_2$Cl$_2$	(32%)	—	
		90% (EtAlCl$_2$) 7 days, CH$_2$Cl$_2$	(92%)	—	
		150% (EtAlCl$_2$) 1 day, CH$_2$Cl$_2$	(89%)	—	
5		50%	 **5a** (39%)	 **5b** (26%)	
6		87%	 **6a**[a] (62%)	 **6b**[a] (25%)	
7		50%	 **7b** (26%)	 **7a** (36%)	 **7c**[d] (10%)
8		83%	 **8a**[a] (74%)		
9		62%	 **9a** (42%)	 **9b** (42%)	
10		62%	**9a** (40%) **9b** (40%)		
11		87%	 **11a** (90%)		
12		80%	 **12c** (16%)	 **12a** (29%)	 **12b** (22%)
13		80%	 **13c** (10%)	 **13a** (22%)	 **13b** (17%)
			 (11%)	**15a**[c] (6%)	**16a**[c] (3%)
14		50%	 **14a** (37%)		
15		47%	 **15a** (35%)		

Table I (*Continued*)

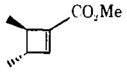
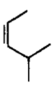
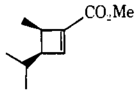
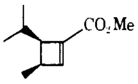
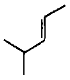
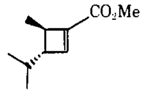
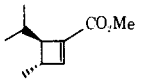
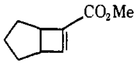
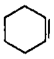
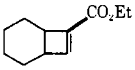
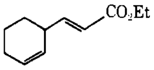
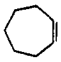
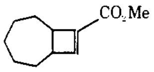
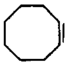
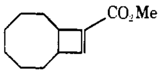
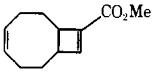
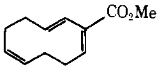
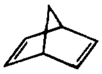
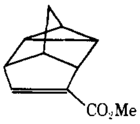
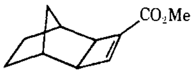
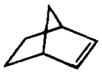
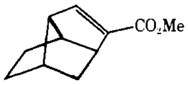
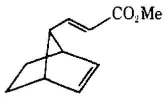
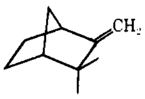
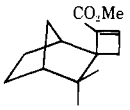
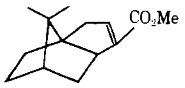
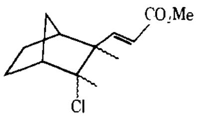
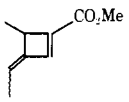
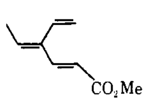
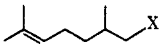
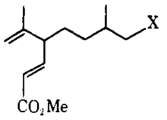
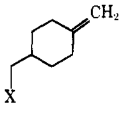
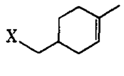
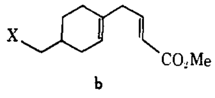
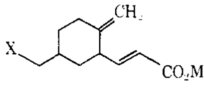
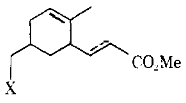
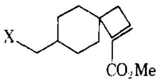
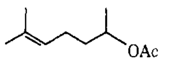
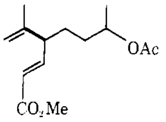
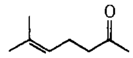
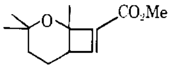
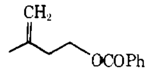
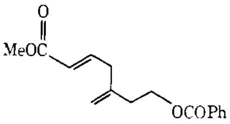
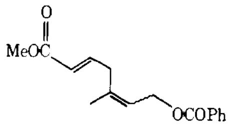
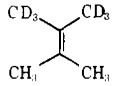
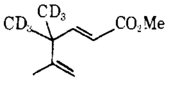
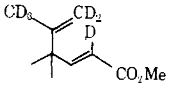
case	mol % catalyst ($AlCl_3$, reaction for 7 days in benzene unless specified)	products (% yield)
16 	47%	 **16a** (35%)
17 	50%	 **17a** (19%)  **17b** (8%)
18 	50%	 **18a** (7%)  **18b** (7%)
19 	50%	 **19a** (43%)
20 	86%	 **20a**[a] (72%)  **20b**[a] (15%)
21 	50%	 **21a** (36%)
22 	50%	 **22a** (60%)
23 	49%	 **23a** (38%)  **23b** (7%)
24 	50%	 **24b** (12%)  **24a** (28%)
25 	50%	 **25a** (22%)  **25b** (6%)  **25c** (4%)
26 	50%	 **26a** (16%)  **26b** (6%)  **26c** (3%)
27 	50%	 **27a**[e] (23%)  **27b** (4%)
		
28, X = CH_2OAc	50%	**28a**[f] (50%)
29, X = CH_2OMe	50%	**29a** (54%)
30, X = CO_2Me	50%	**30a** (53%)
31, X = CH_2NH_2	200% $EtAlCl_2$, CH_2Cl_2	complex mixture
32, X = $CH_2NHCOCF_3$	200% $EtAlCl_2$, CH_2Cl_2	**32a** (87%)
		 a  b

Table I (*Continued*)

case	mol % catalyst ($AlCl_3$, reaction for 7 days in benzene unless specified)	products (% yield)
		 c  d[c]  e
33, X = OMe	50%	**33a** (28%), **33b** (20%), **33c** (9%), **33d** (7%)
34, X = CN	50%	**34a** (28%), **34b** (16%), **34e** (4%)
35, X = NO_2	50%	**35b** (67%)
36, X = OAc	50%	**36b** (3%)
	150%	**36b** (26%), **36c** and **36d**[f] (12%)
	190% $EtAlCl_2$, CH_2Cl_2	**36b** (71%)
37, X = $OCOPhNO_2$	50%	**37b** (25%), **37c** and **37d**[f] (2.5%)
38, X = $OCOPh(NO_2)_2$	50%	**38b** (27%), **38c** and **38d**[f] (1%)
39, X = $OCOCF_3$	50% $EtAlCl_2$, CH_2Cl_2	**39b** (44%)
40 		 **40a**
	50%	12%
	150%	50%[f]
	150% $EtAlCl_2$	48%
41 	50% $EtAlCl_2$	 **41a** (53%)
42 	50%	 **42a** (9%)  **42b** (0%)
43 	50%	 **43a** (34.8%)  **43b** (13.2%)

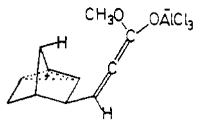
[a] Ethyl propiolate was used instead of methyl propiolate. [b] A 60:40 isomer mixture was obtained as determined by NMR. [c] Obtained from isomerized starting material. [d] Derived from isomerization of the ene adduct. This is the only case in which such a product was obtained from propiolate. [e] Obtained as a 55:45 isomer mixture. [f] The unreacted starting material is contaminated with hydrogen chloride adduct and the product of Friedel-Crafts addition to benzene.

are obtained with 1 equiv of catalyst per functional group. More than 1 equiv can be used with no ill effects with simple alkenes, but with functionalized alkenes more than 1 equiv of catalyst per functional group often leads to decomposition.

1,2-Disubstituted alkenes give stereospecific [2 + 2] cycloaddition (cases 15-23). The stereochemistry of **15a** and **16a** is determined by comparison with authentic samples[9] and the vicinal coupling of the cyclobutyl protons $J_{H_aH_b}$ = 4.5 Hz for **15a** and 1.4 Hz for **16a**.[10] Cyclohexene is unusual in that it gives ene adduct in addition to cyclobutene. Diene **23** does not give any 1:2 adduct even when 2 equiv of methyl propiolate is used. Complexation of the monoadduct with aluminum chloride inductively deactivates the second double bond.

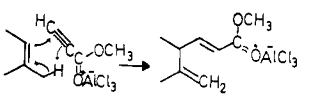
The reaction with norbornadiene (case 24) gives a mixture of the homo Diels-Alder adduct **24a** and the exo [2 + 2] adduct **24b**. The thermal reaction of **24** and methyl propiolate gives only the homo Diels-Alder adduct **24a**.[11] Cyclobutene **24b** has been previously obtained by thermal reaction of methyl propiolate and quadricyclene.[12] The reactions with norbornene and camphene (cases 25 and 26) were investigated to determine the mechanism of the [2 + 2] cycloaddition. Norbornene gives the three products expected from a zwitterionic intermediate[13] (Scheme II). Camphene similarly gives a complex mixture of products derived from rearrangement of the intermediate cation.[14] Thus, in these two cases the cycloaddition is a polar two-step reaction.

Scheme II



If these ene and cycloaddition reactions are to be of general synthetic value, then they must be compatible with functionalized alkenes. If the required propiolate-Lewis acid complex is to be present, the functionality must have a basicity less than that of propiolate or an additional equivalent of Lewis acid must be used. An examination of the available data[15,16] indicates that nitriles, nitro compounds, and of course esters may be less basic than propiolate. Although ethers are more basic toward protons than esters, it is possible to form the methyl acrylate-aluminum chloride complex from the aluminum

Scheme III



chloride-diethyl ether complex[17] so that ethers may be less basic toward Lewis acids. Our initial studies indicate that, in some cases at least, esters, nitriles, ethers, and nitro compounds do not interfere with the reaction and do not require an extra equivalent of catalyst. The citronellyl system was initially investigated because **28a** was needed as an intermediate in the synthesis of the A-1 component of the female sex pheromone of the California Red Scale.[18] Cases 28-30 indicate that the ester, acetate, or methyl ether does not interfere with the ene reaction. Citronellylamine (case 31) undergoes the ene reaction when 2 equiv of catalyst is used but the amine also reacts with the propiolate. Citronellyl trifluoroacetamide (case 32) with 1 equiv of catalyst gives a complex mixture in which ~50% ene adduct is formed and ~50% of the amide has added to the propiolate. With 2 equiv of catalyst, an 87% yield of the desired ene adduct is isolated. Dimethyl citronellamide is recovered unchanged, even with 2 equiv of catalyst, while citronellal and its ethylene acetal are decomposed under the reaction conditions.

An investigation of a series of methylenecyclohexane derivatives gives similar results. Since the exocyclic double bond is very susceptible to isomerization, ca. 20% of the ene adduct is derived from 1-methylcyclohexene with the parent system when aluminum chloride is used as catalyst (case 4). The methoxymethyl, cyanomethyl, and nitromethyl derivatives (cases 33-35) give similar results with varying amounts of isomerization. In case 33 this isomerization is prevented by the use of ethylaluminum dichloride.

The acetate **36** behaves differently giving only a 4% yield of ene adduct with 0.5 equiv of catalyst, presumably due to preferential aluminum chloride complexation with the acetate. However, by using an extra equivalent of aluminum chloride to complex the acetate, a 50% yield of a mixture of isomeric ene adducts is obtained, along with the chloride and Friedel-Crafts product derived from starting material. Use of 1.5 equiv of ethylaluminum dichloride gives a 50% yield of a single ene adduct and 50% of unreacted starting material. With 1.9 equiv of ethylaluminum dichloride, the yield is 78%. If more than 2 equiv of catalyst is used, extensive decomposition occurs. Alternatively, use of a less basic ester such as 4-nitrobenzoate (case 37), 3,5-dinitrobenzoate (case 38), or trifluoroacetate (case 39) gives respectable yields with 0.5 equiv of catalyst.

The acetate **40** behaves similarly to **34** giving a low yield of **40a** with 0.5 equiv of aluminum chloride and a 50% yield with 50% recovered **40** with 1.5 equiv of ethylaluminum dichloride. The ene adduct **40a** should be a useful intermediate for the synthesis of tobacco isoprenoids.[19] Methylheptenone (**41**) reacts to give the cyclobutene resulting from the rearranged dihydropyran.[20] Isopentenyl benzoate (**42**) reacts to give a low yield of a single ene adduct **42a**. The acetate and ethyl carbonate behave similarly. The absence of the other adduct **42b** may be due to the electron-withdrawing acetate preventing its formation or to selective destruction of **42b** which is an allylic acetate. The latter is plausible since geranyl acetate is decomposed under the reaction conditions.

Mechanism. These reactions probably occur between the alkene and the methyl propiolate-Lewis Acid complex (Scheme III) as do aluminum chloride catalyzed Diels-Alder reactions.[21] The greater electron-withdrawing character of the ester complexed to aluminum chloride is responsible for the tremendous rate acceleration observed. Although all types of alkenes react, more electron rich alkenes react faster. This reaction is probably quite different from the aluminum chloride catalyzed dimerization of 2-butyne in which the aluminum is bonded to carbon.[22] The reaction of 2-methyl-2-butene with methyl propiolate and 0.16 equiv of aluminum chloride in benzene-d_6 was monitored by NMR (Figure 1). The reaction was clearly not second order. The rate was initially very rapid and then dropped off rapidly after ~15-20% reaction in a manner that is qualitatively consistent with the expected second order reaction if the product α,β-unsaturated ester is more basic toward aluminum chloride than the starting propiolate. This is expected, since an ethynyl group is strongly electron withdrawing relative to an alkenyl group.[23,24] Since α,β-unsaturated esters and saturated esters have similar basicities,[25] second-order kinetics are observed in the aluminum chloride catalyzed Diels-Alder reactions of methyl acrylate.[21] Since the product complexes more strongly to the catalyst than the methyl propiolate, better yields are obtained when close to 1 equiv of aluminum chloride is used. If more than 1 equiv of aluminum chloride is used, isomerization and Friedel-Crafts reaction occur. With ethylaluminum dichloride, more than 1 equiv of catalyst can be used. One to two equivalents of catalyst is usually optimal for functionalized alkenes. More than 1 equiv of catalyst per functional group often leads to decomposition.

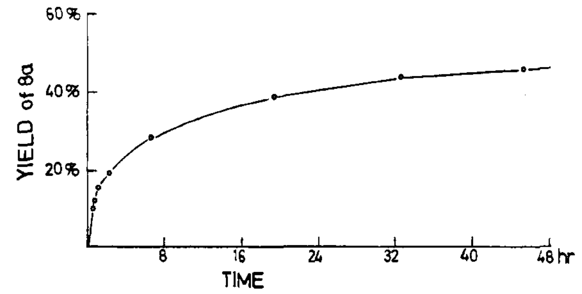


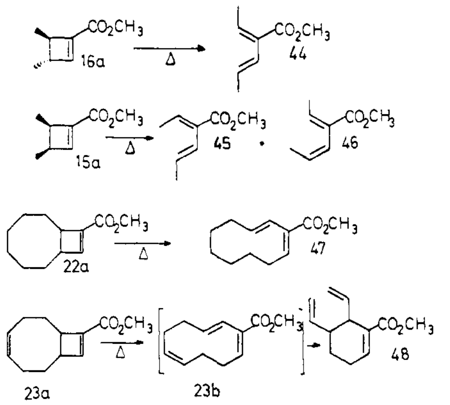
Figure 1. Reaction of 2-methyl-2-butene with methyl propiolate and 0.16 equiv of aluminum chloride in benzene-d_6. After 500 h, 71% of **8a** and 25% of 2-chloro-2-methylbutane were present.

The choice of solvent is essential to the success of the aluminum chloride catalyzed reaction. Benzene or other aromatic solvents such as toluene, xylene, or chlorobenzene apparently deactivate the aluminum chloride sufficiently by formation of a weak complex so that isomerization of the alkene is usually not a problem. This has been previously observed in Diels-Alder reactions of methyl acrylate.[6] Use of methylene chloride or carbon disulfide as solvent in the reaction with 2-ethyl-1-butene gives a mixture containing 30-50% of ene adducts derived from isomeric 3-methyl-2-pentene. Ether, which binds competitively to aluminum chloride, gives low yields of ene adduct, also derived in large part from isomerized alkene. With ethylaluminum dichloride, methylene chloride is a suitable solvent giving slightly faster reactions than in aromatic solvents.

The two most probable mechanisms for these reactions are a dipolar two-step mechanism in which a common intermediate goes on to give either ene adduct and/or cyclobutene or two competing concerted reactions. Due to the nature of the reaction, the concerted pathways would also have a large degree polar character. At this time, the evidence is somewhat contradictory in nature, but we believe it is consistent with a concerted ene and $[{}_\pi 2_s + {}_\pi 2_a]$ cycloaddition[26,27] except in cases such as norbornene where a carbonium ion of exceptional stability can be produced. β-Pinene gives very high yields of ene adducts uncontaminated with products resulting from skeletal rearrangement. If an intermediate were present, it would have to transfer hydrogen faster than it isomerized. The cycloaddition reactions of isomeric 2-butenes and 4-methyl-2-pentenes are stereospecific. This requires that the intermediates, if formed, collapse faster than rotation occurs. Monosubstituted alkenes give mixtures of cyclobutenes which, if formed by a two-step mechanism, imply that a primary carbonium ion would be formed almost as easily as a secondary carbonium ion.

The two mechanistic alternatives for the ene reaction should have very different isotope effects.[28] The two-step reaction should show only secondary effects while a concerted reaction should show a primary effect along with secondary effects due to rehybridization. The intramolecular deuterium isotope effect obtained with **43**,[29] $K_H/K_D = 2.64$, is similar to values obtained in the thermal reaction of **43** and dimethyl acetylenedicarboxylate ($K_H/K_D = 2.33$ at 125 °C)[28] and in the reaction of **43** with diethyl azodicarboxylate.[28] The observed ratio is consistent with a concerted mechanism, but does not rule out a stepwise mechanism. The reactions of norbornene and camphene clearly proceed via a two-step mechanism. However, there may be special cases since an ene reaction is impossible, the intermediate cation is very stable, and the transition state required for a $[_{\pi}2_s + _{\pi}2_a]$ cycloaddition is hindered.[30] Similar atypical behavior of norbornene has also been observed in the reaction of alkenes with acyl cations.[31]

The cyclobutene carboxylates undergo the expected thermal conrotatory ring opening reactions.[32] *trans*-3,4-Dimethylcyclobutene **16a** opens completely in 3 h at 100 °C giving only the *trans,trans*-diene **44**. The *cis*-3,4-dimethylcyclobutene **15a** requires higher temperature, opening completely in 72 h at 120 °C to give a 5:1 mixture of **45** and **46**. The bicyclodiene **22a** undergoes clean opening to **47** in 50 h at 120 °C.[30] Only one isomer is formed. The bicyclodiene **23a** is converted quantitatively to the *cis*-divinylcyclohexene **48** after 12 h at 120 °C.[33] The intermediate cyclodecatriene **23b** could not be observed at any point. However, 7% of the cyclodecatriene **23b** was isolated from the cycloaddition reaction. We hypothesized that the formation of **23b** from **23a** during the cycloaddition reaction was catalyzed by aluminum chloride, which would not catalyze the Cope reaction. To test this, **23a** was treated with 0.5 equiv of aluminum chloride. Complete reaction required 4 days at 75 °C giving an 8:2 mixture of **48** and an unidentified product probably derived from isomerization of **48**. In the absence of aluminum chloride a 6:4 mixture of **23a** and **48** is obtained.



The results described above indicate the broad scope of this ene and cycloaddition reaction and the high yields obtainable which we feel will make this a valuable synthetic method.

Experimental Section

Materials and Methods. Infrared spectra were obtained as thin films on sodium chloride plates on a Perkin-Elmer 237 or 283. NMR spectra were determined on a Varian A-60, XL-100 or Perkin-Elmer R32 spectrometer in $CDCl_3$ using Me_4Si as an internal standard. Mass spectra were obtained on an AEI MS9 mass spectrometer. Gas-chromatographic separations were accomplished on a 6-ft 5% DEGS on Chromosorb W column. Benzene and toluene were dried by distillation from sodium benzophenone ketyl. Methylene chloride was dried by distillation from calcium hydride. Methyl propiolate was used as purchased from Farchan Co. Alkenes were purchased from Aldrich or Chemical Samples Co. and used without further purification. Aluminum chloride was sublimed before use and stored in vacuo. Ethylaluminum dichloride was purchased as a 25% solution in heptane from Texas Alkyls.

General Procedure. To anhydrous powdered aluminum chloride under nitrogen in a 50-mL flask is added benzene and methyl propiolate. The mixture is stirred until most of the aluminum chloride has dissolved (15–45 min) and a homogeneous yellow solution has formed. The alkene is then added and the solution stirred 2–7 days giving an orange to brown solution containing some precipitate. In some cases the initial reaction is exothermic and the vessel should be cooled in an ice bath before the alkene is added.

Workup is accomplished by pouring the solution into a saturated sodium dihydrogen phosphate solution. After stirring for 10 min, 10% hydrochloric acid is added until the precipitated alumina dissolves. The aqueous layer is washed with three portions of ether and the combined organic layers are washed with brine and dried over magnesium sulfate, and the solvent is removed in vacuo.

For acid-sensitive products, the reaction is quenched in saturated sodium bicarbonate solution, followed by suction filtration through Celite to remove the precipitated alumina. Extraction with ether is then carried out as described above.

For the ethylaluminum dichloride catalyzed reactions, 25% ethylaluminum dichloride in heptane is added to the solvent under nitrogen. Methyl propiolate and then the alkene are added and the reaction stirred at room temperature and worked up as described above.

Reaction of β-Pinene (1) with Ethyl Propiolate. Ethyl propiolate (1.00 g, 10.2 mmol), aluminum chloride (260 mg, 1.93 mmol, 0.19 equiv) and β-pinene (1.55 g, 11.4 mmol) were stirred 2 days in 20 mL of benzene. Normal workup followed by evaporative distillation at 110 °C at 0.1 Torr gave 1.912 g (82%) of pure ene adduct: NMR ($CDCl_3$) δ 6.90 (1 H, d of t, J = 16, 7 Hz), 5.80 (1 H, d of t, J = 16, 1.5 Hz), 5.28 (1 H, br s), 4.18 (2 H, q, J = 7 Hz), 2.8 (2 H, d of d of d, J = 7, 1.5, 1.5 Hz), 2.5–1.0 (9 H, m), 1.27 (3 H, s), and 0.85 ppm (3 H, s); IR (neat) 1730, 1650, and 970 cm^{-1}.

Reaction of 2-Ethyl-1-butene (2) with Methyl Propiolate. Methyl propiolate (1.00 g, 12 mmol), aluminum chloride (0.54 g, 4 mmol), and excess 2-ethyl-1-butene were stirred 6 days in 20 mL of benzene. After normal workup, 1.143 g of crude product was obtained which was purified by evaporative distillation at 110 °C at 25 Torr giving 1.11 g (55%) of ene adducts. GC (6-ft 5% DEGS at 135 °C) showed this to consist of 6–8% of **2b** and 92–94% of **2a** as a 60:40 inseparable isomer mixture. Preparative gas chromatography gave a pure sample of the isomers of **2a**: NMR ($CDCl_3$) δ 6.98, 6.96 (1 H, 2 d of t, J = 16, 7 Hz), 5.90 (1 H, d of t, J = 16, 1 Hz), 5.28 and 5.40 (1 H, 2 br q, J = 7 Hz), 3.71 (3 H, s), 2.97 and 2.85 (2 H, 2 br d, J = 7 Hz), 2.05 (2 H, br q, J = 7 Hz), 1.61 (3 H, d, J = 7 Hz), and 1.00 ppm (3 H, t, J = 7 Hz); IR (neat) 1725, 1660, and 990 cm^{-1}.

Reaction of Methyl Propiolate with 2-Ethyl-1-butene in Nonaromatic Solvents. In all cases methyl propiolate (0.5 g, 6 mmol), aluminum chloride (0.2 g, 1.5 mmol, 0.25 equiv), and 2-ethyl-1-butene (1 g, 12 mmol) were stirred 1 week in 10 mL of solvent. The reactions were monitored by GC and NMR.

In toluene, 607 mg (60%) of product was obtained which contained ~5% of ene adducts derived from 3-methyl-2-pentene. In chlorobenzene, 290 mg (21.5%) of a similar mixture was obtained. In methylene chloride, 860 mg (85%) was obtained of a complex mixture which appeared to be roughly 50% derived from isomerized alkene. In ether, only 176 mg (17%) of a similar mixture was obtained. In carbon disulfide, 687 mg (68%) was obtained of a mixture of ene adducts of which ca. 30% was derived from rearranged alkene.

Reaction of Ethyl Propiolate with Isobutylene (3). Ethyl propiolate (1.018 g, 10.4 mmol) and aluminum chloride (670 mg, 5 mmol) were dissolved in 15 mL of benzene in a resealable tube. An excess of isobutylene was then condensed into the solution and the tube was sealed and stirred at 25 °C for 5 days. The reaction mixture was poured into saturated sodium bicarbonate solution and filtered to remove precipitated aluminum salts. Extraction with three portions of ether which were dried and evaporated gave 1.428 g of crude product. Evaporative distillation at 100 °C at 30 Torr gave 0.97 g (61%) of ene adduct: NMR ($CDCl_3$) δ 6.95 (1 H, d of t, J = 15.5, 7 Hz), 5.83 (1 H, d of t, J = 15.5, 1.5 Hz), 4.7–4.9 (2 H, br s), 4.2 (2 H, q, J = 7 Hz), 2.89 (2 H, d, J = 7 Hz), 1.77 (3 H, br s), and 1.27 ppm (3 H, t, J = 7 Hz); IR (neat) 3070, 1730, 1650, 980, and 895 cm^{-1}; MS *m/e* 154, 139, 126, 125, 111, 109, 81, and 80. The IR spectrum is superimposable with a published spectrum.[31] Anal. Calcd for $C_9H_{14}O_2$: *m/e* 154.0993. Found: *m/e* 154.0997.

Reaction of Methyl Propiolate with Methylenecyclohexane (4). Methylpropiolate (1.02 g, 12.16 mmol), aluminum chloride (0.8105 g, 6.08 mmol, 0.5 equiv), and methylenecyclohexane (1.28 g, 13.38 mmol, 1.10 equiv) were stirred 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 10/1 pentane/ether as eluent gave 1.4863 g (68%) of an ~8:2 mixture of desired ene adduct **4a** and ene adducts **4b** derived from 1-methylcyclohexene.

Methyl propiolate (0.64 g, 1 equiv), ethylaluminum dichloride (2.44 mL, 1.57 M in heptane, 0.5 equiv) and methylenecyclohexane (0.807 g, 1.1 equiv) were stirred 4 days in 15 mL of benzene. Normal workup gave 0.795 g (58%) of pure **4a**: NMR ($CDCl_3$) δ 6.93 (1 H, d of t, J = 15, 7 Hz), 5.77 (1 H, d of t, J = 15, 2 Hz), 5.48 (1 H, br s), 3.70 (3 H, s), 2.78 (2 H, br d, J = 6 Hz), and 1.27–2.27 ppm (8 H, m); IR (neat) 1730 and 1630 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.22; H, 8.67.

A solution of methylenecyclohexane (874 mg, 8.4 mmol), methyl propiolate (643 mg, 7.65 mmol), and ethylaluminum dichloride (2.44 ml of 1.57 M, 3.83 mmol, 0.5 equiv) in 24 mL of methylene chloride was stirred for 1 day. Normal workup gave 447 mg (32%) of ene adduct **4a**.

A solution of methylenecyclohexane (404 mg, 4.21 mmol), methyl propiolate (354 mg, 4.21 mmol), and ethylaluminum dichloride (2.41 mL of 1.57 M, 3.79 mmol, 0.9 equiv) in 15 mL of methylene chloride was stirred 7 days. Normal workup gave 694 mg (92%) of ene adduct **4a**.

A solution of methylenecyclohexane (404 mg, 4.21 mmol), methyl propiolate (353 mg, 4.21 mmol), and ethylaluminum dichloride (4.03 mL of 1.57 M, 6.32 mmol, 1.5 equiv) in 12 mL of methylene chloride was stirred 1 day. Normal workup gave 677 mg (89%) of pure ene adduct **4a**.

Reaction of Methyl Propiolate with 2-Methyl-1-pentene (5). Methyl propiolate (0.557 g, 6.63 mmol), aluminum chloride (0.447 g, 3.3 mmol, 0.5 equiv) and 2-methyl-1-pentene (0.84 g, 10 mmol) were stirred 7 days in 15 mL of benzene. Normal workup gave 0.723 g (65%) of crude ene adduct which was shown by NMR to be a pure 6:4 mixture of **5a** and **5b**: NMR ($CDCl_3$) δ 6.95, 6.93, 6.88 (0.6, 0.25, 0.15 H, 3 t of d, J = 7, 16 Hz), 5.82 (1 H, br d, J = 15 Hz), 5.30 and 5.20 (0.4 H, 2 br t, J = 7 Hz), 4.80 (0.6 × 2 H, br s), 3.70 (3 H, s), 2.87 (2 H, br d, J = 7 Hz), and 0.7–2.2 ppm (7.4 H, m); IR 1730 and 1630 cm^{-1}.

Reaction of Ethyl Propiolate and 1-Methylcyclohexene (6). Ethyl propiolate (550 mg, 5.6 mmol), aluminum chloride (650 mg, 4.86 mmol, 0.87 equiv), and 1-methylcyclohexene (800 mg, 8.33 mmol) were stirred for 6 days in 12 mL of benzene. Normal workup followed by evaporative distillation at 125 °C and 25 Torr gave 962 mg (89%) of a 7:3 mixture of ene adducts **6a** and **6b** which were not separated: NMR ($CDCl_3$) δ 7.10 (0.7 × 1 H, d of d, J = 16.5, 7.5 Hz), 6.90 (0.3 × 1 H, d of d, J = 16.5, 9 Hz), 5.79 (1 H, br d, J = 16.5 Hz), 5.53 (0.3 × 1 H, br s), 4.75 (0.7 × 1 H, br s), 4.85 (0.7 × 1 H, br s), 4.18 (2 H, q, J = 7 Hz), 2.91 (1 H, m), 1.3–2.5 (8.3 H, m), and 1.23 ppm (3 H, t, J = 7 Hz); IR (neat) 3040, 1725, 1650, 980 and 890 cm^{-1}; MS *m/e* 194, 192, 179, 165, 151, 149, 121, and 120. Anal. Calcd for $C_{12}H_{18}O_2$: *m/e* 194.1307. Found: *m/e* 194.1302.

Reaction of 1-Methylcyclopentene with Methyl Propiolate (7). Methyl propiolate (0.739 g, 8.79 mmol), aluminum chloride (0.584 g, 4.39 mmol, 0.5 equiv), and 1-methylcyclopentene (840 mg, 10 mmol) were stirred 5 days in 15 mL of benzene. Normal workup gave 1.06 g (72.6%) of a 49:38:13 mixture of **7a**, **7b**, and **7c** as determined by examination of the NMR spectrum and GC (6-ft 5% DEGS, 150 °C). The data for **7a** are: Tr = 8.4 min; NMR ($CDCl_3$) δ 6.85 (1 H, d of d, J = 15, 8 Hz), 5.82 (1 H, d, J = 15 Hz), 4.99 (1 H, m), 4.78 (1 H, m), 3.7 (3 H, s), and 1.3–3.5 (7 H, m). The data for **7b** are: Tr = 6.8 min; NMR ($CDCl_3$) δ 6.83 (1 H, d of d, J = 15, 8 Hz), 5.82 (1 H, d, J = 15 Hz), 5.46 (1 H, m), 3.7 (3 H, s), and 1–3.3 ppm (8 H, m). The data for **7c** are: Tr = 15.7 min; NMR ($CDCl_3$) δ 7.65 (1 H, d, J = 16 Hz), 5.75 (1 H, d, J = 16 Hz), 3.71 (3 H, s), and 0.9–2.5 ppm (9 H, m).

Reaction of Ethyl Propiolate with 2-Methyl-2-butene (8). Ethyl propiolate (570 mg, 5.82 mmol), aluminum chloride (0.65 g, 4.86 mmol, 0.83 equiv) and excess 2-methyl-2-butene in 10 mL of benzene for 7 days gave after normal workup 0.93 g of crude product which was purified by evaporative distillation at 100 °C at 20 Torr to give 0.724 g (74%) of pure ene adduct: NMR ($CDCl_3$) δ 7.05 (1 H, d of d, J = 16, 7 Hz), 5.90 (1 H, d of d, J = 16, 1.5 Hz), 4.88 (2 H, br s), 4.28 (2 H, q, J = 7 Hz), 3.04 (1 H, d of q, J = 7, 7 Hz), 1.74 (3 H, br s), 1.30 (3 H, t, J = 7 Hz), and 1.23 ppm (3 H, d, J = 7 Hz); IR (neat) 3060, 1730, 1650, 980, and 895 cm^{-1}; MS *m/e* 168, 153, 139, 125, 123, 95, and 94. Anal. Calcd for $C_{10}H_{16}O_2$: *m/e* 168.1150. Found: *m/e* 168.1146.

Reaction of Methyl Propiolate with *cis*-3-Methyl-2-Pentene (9). Methyl propiolate (0.458 g, 5.45 mmol), aluminum chloride (0.455 g, 2.73 mmol, 0.62 equiv) and *cis*-3-methyl-2-pentene (0.5 g, 6.0 mmol, 1.1 equiv) were stirred 7 days in 10 mL of benzene. Normal workup gave virtually pure ene adducts in 84% yield. Examination of the NMR showed a ca. 1/1 mixture of **9a** and **9b**: NMR ($CDCl_3$) δ 7.02 (1 H, d of d, J = 7, 15 Hz), 5.83 (1 H, d of d, J = 2, 15 Hz), 5.13–5.63 (1 H, m, **9a**), 4.87 (2 H, br s, **9b**), 3.73 (3 H, s), 2.95 (1 H, br, q), 2.07 (2 H, br q, J = 7 Hz, **9b**), 1.67 (3 H, d, J = 6 Hz, **9a**), 1.63 (3 H, s, **9a**), 1.17 (3 H, d, J = 7 Hz), and 1.17 ppm (3 H, t, J = 7 Hz, **9b**): IR (neat) 1730, 1640 cm^{-1}.

Reaction of Methyl Propiolate with *trans*-3-Methyl-2-pentene (10). Reaction of *trans*-3-methyl-2-pentene as described for the cis isomer gave a virtually identical mixture of isomers in 80% yield.

Reaction of 2,3-Dimethyl-2-butene with Ethyl Propiolate (11). Ethyl propiolate (550 mg, 5.6 mmol), aluminum chloride (650 mg, 4.86 mmol, 0.87 equiv), and 2,3 dimethyl-2-butene (1 g, 11.9 mmol) were stirred for 6 days in 12 mL of benzene. Normal workup gave 0.995 g of brown oil which was purified by evaporative distillation at 110 °C at 25 Torr giving 0.922 g (90%) of **11a** as a colorless oil: NMR ($CDCl_3$) δ 7.07 (1 H, d, J = 16 Hz), 5.87 (1 H, d, J = 16 Hz), 4.90 (2 H, br s), 4.27 (2 H, q, J = 7 Hz), 1.73 (3 H, br s), 1.33 (3 H, t, J = 7 Hz), and 1.22 ppm (6 H, s); IR (neat) 3060, 1730, 1650, 1000, and 900 cm^{-1}; MS *m/e* 182, 167, 153, 139, 137, and 109. Anal. Calcd for $C_{11}H_{18}O_2$: *m/e* 182.1307. Found: *m/e* 182.1305.

Reaction of Methyl Propiolate with Propylene (12). Methyl propiolate (1.05 g, 12.5 mmol), aluminum chloride (1.33 g, 10 mmol, 0.8 equiv) and excess propylene were stirred for 4 days in 25 mL of benzene at 25 °C in a resealable tube. Normal workup gave 1.07 g (68%) of a mixture which was shown by GC (6-ft, 5% DEGS, 80 °C) to consist of 43% **12a**, 33% **12b**, and 24% of ene adduct **12c**. Preparative gas chromatography gave pure samples. The spectral data for **12a** are: GC, Tr = 10.3 min; NMR ($CDCl_3$) δ 6.80 (1 H, t, J = 1 Hz), 3.73 (3 H, s), 2.8–3.3 (1 H, m), 2.68 (1 H, d of d of d, J = 15, 4, 1 Hz), 2.00 (1 H, d of d of d, J = 15, 1, 1 Hz), and 1.28 ppm (3 H, d, J = 7 Hz); IR (CCl_4) 1725, 1610 cm^{-1}. The spectral data for **12b** are: GC, Tr = 13.1 min; NMR ($CDCl_3$) δ 6.85 (1 H, d, J < 1 Hz), 3.72 (3 H, s), 2.7–3.0 (1 H, m), 2.82 (1 H, d of d, J = 12, 4 Hz), 2.15 (1 H, d of d, J = 12, 1 Hz), and 1.18 ppm (3 H, d, J = 7 Hz); IR (CCl_4) 1725, 1610 cm^{-1}. The spectral data for ene adduct **12c** are: GC, Tr = 19.3 min; NMR ($CDCl_3$) δ 7.0 (1 H, d of t, J = 16, 7 Hz), 5.87 (1 H, d of t, J = 16, 1 Hz), 5.5–6.0 (1 H, m), 4.9–5.3 (2 H, m), 3.75 (3 H, s), and 2.95 ppm (2 H, br t, J = 7 Hz); IR (CCl_4), 1730, 1650, and 1640 cm^{-1}.

Reaction of Methyl Propiolate with 1-Butene (13). Methyl propiolate (1.05 g, 12.5 mmol), aluminum chloride (1.33 g, 10 mmol, 0.80 equiv), and excess 1-butene were stirred 5 days in 25 mL of benzene. Normal workup gave 1.25 g (71%) of crude product which GC (6-ft, 5% DEGS, 80 °C) showed to be 14% ene adduct **13c**, 31 and 25% of cyclobutenes, **13a** and **13b**, 15% *sec*-butylbenzene, 5% **16a** and 10% **15a**. Preparative gas chromatography gave pure **13a**: GC, Tr = 18 min; NMR ($CDCl_3$) δ 6.82 (1 H, t, J = 1.3 Hz), 3.73 (3 H, s), 2.8–3.3 (1 H, m), 2.60 (1 H, d of d of d, J = 15, 4, 1.3 Hz), 2.04 (1 H, d of d of d, J = 15, 1.5, 1.3 Hz), 1.4–1.8 (2 H, m), and 0.97 ppm (3 H, br t, J = 7 Hz); IR (CCl_4) 1730 and 1610 cm^{-1}. Cyclobutene **13b** eluted after 24 min; NMR ($CDCl_3$) δ 6.88 (1 H, d, J = 1 Hz), 3.73 (3 H, s), 2.85 (1 H, d of d, J = 12, 4 Hz), 2.4–2.8 (1 H, m), 2.27 (1 H, d of d, J = 12, 1.5 Hz), 1.55 (2 H, d of q, J = 7, 7 Hz), and 0.95 ppm (3 H, t, J = 7 Hz); IR (CCl_4) 1725 and 1610 cm^{-1}. The ene adduct **13c** eluted after 38 min; NMR ($CDCl_3$) δ 6.98 (1 H, d of t, J = 16, 7 Hz), 5.87 (1 H, d of t, J = 16, 1.5 Hz), 5.4–5.7 (2 H, m), 3.73 (3 H, s), 2.7–3 (2 H, m), 1.6–1.8 (3 H, 2 d, J = 7 Hz); IR (CCl_4) 1730, 1660 cm^{-1}.

Reaction of Methyl Propiolate with Allyltrimethylsilane (14). Methyl propiolate (0.84 g, 10 mmol), aluminum chloride (0.67 g, 5 mmol, 0.5 equiv), and allyltrimethylsilane (1.25 g, 11 mmol, 1.1 equiv) were stirred for 7 days in 15 mL of benzene. Normal workup followed by evaporative distillation (0.5 Torr, 25 °C) gave 0.727 g (36.7%) of pure **14a**: NMR ($CDCl_3$) δ 6.68 (1 H, t, J = 1.5 Hz), 3.68 (3 H, s), 3.03

(1 H, d of d of d of d, J = 12, 4, 3, 1.5 Hz), 2.65 (1 H, d of d of d, J = 15, 4, 1.5 Hz), 1.97 (1 H, d of d of d, J = 15, 1.5, 1.5 Hz), 1.28 (1 H, d of d, J = 15, 3 Hz), 0.53 (1 H, d of d, J = 12, 15 Hz), and 0.05 ppm (9 H, s); IR 1730 and 1608 cm^{-1}; MS *m/e* 198 (M^+), 183 and 160. Anal. Calcd for $C_{10}H_{18}O_2Si$: *m/e* 198.1076. Found: *m/e* 198.1071.

Reaction of Methyl Propiolate with *cis*-2-Butene (15). Methyl propiolate (1.05, g, 12.5 mmol) and aluminum chloride (0.78 g, 5.84 mmol, 0.47 equiv) were stirred for 2 days in 20 mL of benzene containing an excess of *cis*-2-butene in a resealable tube. Normal workup gave 618 mg of crude product which was purified by evaporative distillation at 25 °C at 2 Torr giving 584 mg (33%) of cyclobutene **15a** which was greater than 95% pure as determined by GC and contained less than 1% of **16a**. An analytical sample was prepared by GC (6-ft, 5% DEGS at 80 °C), Tr = 17.2 min; NMR ($CDCl_3$) δ 6.82 (1 H, d, J = 1 Hz), 3.73 (3 H, s), 2.75–3.4 (2 H, m), 1.12 (3 H, d, J = 7 Hz), and 1.05 ppm (3 H, d, J = 7 Hz); NMR (benzene-d_6) δ 6.63 (1 H, d, J = 1 Hz), 3.41 (3 H, s), 3.03 (1 H, q of d, J = 7.4, 4.7 Hz), 2.58 (1 H, q of d of d, J = 7.4, 4.7, 1 Hz), 1.08 (3 H, d, J = 7.4 Hz), and 0.80 ppm (3 H, d, J = 7.4 Hz); IR (neat) 3040, 1725, and 1605 cm^{-1}. Cyclobutene **15a** was identical by spectroscopic comparison with an authentic sample.[9]

Reaction of Methyl Propiolate with *trans*-2-Butene (16). Methyl propiolate (1.05 g, 12.5 mmol) and aluminum chloride (0.78 g, 5.84 mmol, 0.47 equiv) were stirred 3 days in 20 mL of benzene containing an excess of *trans*-2-butene in a resealable tube giving 631 mg of crude product. Evaporative distillation gave 525 mg (30%) of cyclobutene **16a**, contaminated by a small amount of diene resulting from ring opening. An analytical sample was prepared by preparative gas chromatography on a 6-ft, 5% DEGS column at 80°C, Tr = 12 min; NMR ($CDCl_3$) δ 6.83 (1 H, d, J = 1 Hz), 3.75 (3 H, s), 2.2–2.8 (2 H, m), 1.25 (3 H, d, J = 7 Hz), and 1.19 ppm (3 H, d, J = 7 Hz); NMR (benzene-d_6) δ 6.67 (1 H, d, J = 1 Hz), 3.40 (3 H, s), 2.48 (1 H, q of d, J = 7, 1.5 Hz), 2.07 (1 H, q of d of d, J = 7, 1.5, 1 Hz), 1.25 (3 H, d, J = 7 Hz), and 0.91 ppm (3 H, d, J = 7 Hz); IR (neat) 3045, 1730, 1615, and 1610 cm^{-1}. Gas chromatography indicated that less than 1% of **15a** is present. Cyclobutene **16a** was identical by spectroscopic comparison with an authentic sample.[9]

Reaction of Methyl Propiolate with *cis*-4-Methyl-2-pentene (17). Methyl propiolate (0.908 g, 10.8 mmol), aluminum chloride (0.72 g, 5.41 mmol, 0.5 equiv), and *cis*-4-methyl-2-pentene were stirred 5 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 4/1 pentane/ether as eluent gave 0.4932 g (27.2%) of a 7:3 mixture of cyclobutenes **17a** and **17b** as indicated by NMR. The data for **17a** are: NMR ($CDCl_3$) δ 6.83 (1 H, d, J = 2 Hz), 3.70 (3 H, s), 2.00 (1 H, d of q, J = 4, 7 Hz), 2.38 (1 H, d of d of d, J = 10, 4, 2 Hz), 1.5–1.9 (1 H, m), 1.2 (3 H, d, J = 6 Hz), 0.97 (3 H, d, J = 6 Hz), and 0.90 ppm (3 H, d, J = 6 Hz); IR (neat) 1725 and 1610 cm^{-1}. The data for **17b** are: NMR ($CDCl_3$) δ 6.78 (1 H, d, J = 2 Hz), 3.70 (3 H, s), and 2.5–3.00 ppm (2 H, m).

Reaction of Methyl Propiolate of *trans*-4-Methyl-2-pentene (18). Methyl propiolate (0.908 g, 10.8 mmol), aluminum chloride (0.72 g, 5.41 mmol, 0.5 equiv), and *trans*-4-methyl-2-pentene (1.0 g, 11.9 mmol, 1.1 equiv) were stirred 5 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 4/1 pentene/ether gave 0.2919 g (14.6%) of a ca. 1:1 mixture of **18a** and **18b** as determined by NMR. The data for **18a** are: NMR ($CDCl_3$) δ 6.87 (1 H, d, J = 1 Hz), 3.72 (3 H, s), 2.67 (1 H, d of d of q, J = 1, 1.5, 7 Hz), 1.85 (1 H, d of d, J = 1.5, 13 Hz), and 0.8–1.7 ppm (10 H, m); IR 1725 and 1608 cm^{-1}. The data for **18b** are: NMR ($CDCl_3$) 6.83 (1 H, d, J = 1 Hz), 3.72 (3 H, s), 2.40 (1 H, d of d of d, J = 1, 1.5, 6 Hz), 1.9 (1 H, d of q, J = 1.5, 7 Hz), and 1.7–0.8 ppm (10 H, m).

Reaction of Cyclopentene (19) with Methyl Propiolate. Methyl propiolate (0.81 g, 9.6 mmol), aluminum chloride (0.643 g, 4.84 mmol, 0.5 equiv), and cyclopentene (800 mg, 11.8 mmol) were stirred in 15 mL of benzene for 7 days. Normal workup gave 0.6312 g (43%) of cycloadduct which was greater than 95% pure by GC and NMR: NMR ($CDCl_3$) δ 6.65 (1 H, d of d, J = 0.5, 0.5 Hz), 3.73 (3 H, s), 3.35 (1 H, br d of d, J = 6.5, 3.4 Hz), 3.08 (1 H, br d of d, J = 6.5, 3.4 Hz), and 1.4–2.0 (6 H, m): IR (CCl_4) 1725, 1612, and 1601 cm^{-1}; MS *m/e* (%) 152, (M^+, 35), 137 (11), 124 (9), 121 (15), 93 (100), 92 (31), 91 (53), and 77 (52). Anal. Calcd for $C_9H_{12}O_2$: *m/e* 152.0837. Found: *m/e* 152.0841. Cyclobutene **19a** was identical with an authentic sample by spectroscopic comparison.[35]

Reaction of Ethyl Propiolate with Cyclohexene (20). Ethyl propiolate (550 mg, 5.6 mmol) and aluminum chloride (650 mg, 4.87 mmol, 0.86 equiv) in 12 mL of benzene were stirred with excess cyclohexene for 7 days. Normal workup gave 936 mg (92% of crude product) which consisted of 5% cyclohexylbenzene, 79% of cyclobutene **20a**, and 16% of ene adduct **20b**. Pure samples were prepared by GC (6-ft, 5% DEGS, 150 °C). The data for **20a** are: Tr = 7.7 min; NMR ($CDCl_3$) δ 6.91 (1 H, d, J = 1 Hz), 4.21 (2 H, q, J = 1 Hz), 2.6–3.3 (2 H, m), 1.2–2.0 (8 H, m), and 1.25 ppm (3 H, t, J = 7 Hz); IR 1730 and 1610 cm^{-1}; MS *m/e* (%) 180 (M^+, 9), 152 (23), 151 (18), 135 (28), 134 (31), 123 (23), 107 (91), and 79 (100). The data for ene adduct **20b** are: Tr = 12.0 min; NMR ($CDCl_3$) δ 7.00 (1 H, d of d, J = 16, 7 Hz), 5.82 (1 H, d of d, J = 16, 1 Hz), 5.4–6.0 (2 H, m), 4.25 (2 H, q, J = 7 Hz), 2.7–3.3 (1 H, m), 2.3–1.3 (6 H, m), and 1.22 ppm (3 H, t, J = 7 Hz); IR (CCl_4) 1725, 1650, and 970 cm^{-1}; MS *m/e* (%) 180 (M^+, 100), 152 (30), 151 (74), 135 (34), 134 (21), 107 (91), 105 (29), and 79 (92).

Reaction of Cycloheptene (21) with Methyl Propiolate. Methyl propiolate (701 mg, 8.35 mmol), aluminum chloride (0.557 g, 4.18 mmol, 0.5 equiv), and cycloheptene (0.96 g, 10 mmol) were stirred 5 days in anhydrous benzene. Normal workup gave 0.540 g (36%) of cycloadduct **2a** contaminated with less than 5% of chlorocycloheptane and cycloheptylbenzene. An analytical sample was prepared by Prep GC, 6-ft, 5% DEGS at 150 °C; Tr = 12 min; NMR ($CDCl_3$) δ 6.88 (1 H, d, J = 1 Hz), 3.74 (3 H, s), 2.6–3.3 (2 H, m) and 1.1–2.0 ppm (10 H, m); IR (neat) 1722, 1613, and 1605 cm^{-1}; MS *m/e* (%) 180 (M^+, 15), 165 (9), 149 (15), 148 (10), 138 (20), 137 (25), 121 (95), 120 (35), 91 (8), and 79 (100). Anal. Calcd for $C_{11}H_{16}O_2$: *m/e* 180.1150. Found: *m/e* 180.1153.

Reaction of Cyclooctene (22) with Methyl Propiolate. Methyl propiolate (0.81 g, 9.64 mmol), aluminum chloride (0.643 g, 4.84 mmol, 0.5 equiv), and cyclooctene (1.12 g, 10.2 mmol) were stirred in 15 mL of benzene for 10 days. Normal workup gave 1.457 g of crude product. A portion (0.7 g) was purified by chromatography on silica gel. Elution with 96:4 petroleum ether:ether gave 0.535 g (60%) of pure cycloadduct **22a**: NMR ($CDCl_3$) δ 6.69 (1 H, d, J = 1 Hz), 3.71 (3 H, s), 2.5–3.2 (2 H, m), and 1.2–2.0 ppm (12 H, m); IR (neat) 1723 and 1609 cm^{-1}; MS *m/e* (%) 194 (M^+, 38), 179 (8), 162 (16), 161 (16), 152 (45), 135 (91), 91 (100), and 79 (85). Anal. Calcd for $C_{12}H_{28}O_2$: *m/e* 194.1307. Found: *m/e* 194.1311.

Reaction of 1,5-Cyclooctadiene (23) with Methyl Propiolate. Methyl propiolate (1.19 g, 14.15 mmol), aluminum chloride (0.925 g, 6.96 mmol, 0.49 equiv), and 1,5-cyclooctadiene (3.024 g, 28 mmol) were stirred 6 days in 15 mL of benzene. Normal workup gave 2.204 g of crude product which contained some 1,5-cyclooctadiene. Chromatography on silica using 25:1 petroleum ether:ether as eluent gave 1.04 g (38%) of cyclobutene **23a** and 0.21 g (7%) of the ring opened adduct **23b**. The spectral data for **23a** are: NMR ($CDCl_3$) δ 6.70 (1 H, d, J = 1 Hz), 5.69 (2 H, br t, J = 5 Hz), 3.68 (3 H, s), 2.8–3.4 (2 H, m), and 1.3–2.5 ppm (8 H, m); IR (neat) 1723 and 1612 cm^{-1}. The spectral data for **23b** are: NMR ($CDCl_3$) δ 6.95 (1 H, t, J = 6 Hz), 5.2–6.8 (4 H, m), 3.71 (3 H, s), and 2.0–2.8 ppm (8 H, m); IR (neat) 1725, 1610–1635 cm^{-1}.

Reaction of Norbornadiene (24) with Methyl Propiolate. Methyl propiolate (0.726 g, 8.63 mmol), aluminum chloride (0.576 g, 4.33 mmol, 0.5 equiv), and freshly distilled norbornadiene (920 mg, 10.0 mmol) were stirred 5 days in 15 mL of benzene. Normal workup gave 0.620 g (40.8%) of a 68:32 mixture of **24a** and **24b** which were purified by GC on a 6-ft, 5% DEGS column at 150 °C. The data for **24a** are: Tr = 10.9 min; NMR ($CDCl_3$) δ 6.99 (1 H, br s), 6.18 (2 H, d of d, J = 1, 1 Hz), 3.73 (3 H, s), 2.3–2.8 (4 H, m), and 1.3–1.5 ppm (2 H, m); IR (neat) 3130, 1725, 1600, and 1585 cm^{-1}. MS *m/e* (%) 176 (M^+, 9), 145 (8), 118 (12), 117 (100), 116 (39), 115 (59), and 91 (32). The spectral data for **24b** are: Tr = 17.2 min; NMR ($CDCl_3$) δ 6.83 (1 H, d of d, J = 4, 1 Hz), 3.65 (3 H, s), 2.95 (1 H, br s), 2.68 (1 H, br s), 2.05 (1 H, br s), and 1.2–1.8 ppm (5 H, m); IR (neat 1720 and 1540 cm^{-1}; MS *m/e* (%) 176 (M^+, 8), 145 (8), 118 (11), 117 (100), 116 (55), 115 (71), and 91 (31).

Adducts **24a**[12] and **24b**[11] are identical with authentic samples by spectroscopic comparisons.

Reaction of Norbornene (25) with Methyl Propiolate. Methyl propiolate (0.908 g, 10.8 mmol), aluminum chloride (0.705 g, 5.3 mmol, 0.49 equiv), and norbornene (1.2 g, 12.8 mmol) were stirred at 25 °C in 15 mL of benzene for 7 days. Normal workup gave 0.635 g (33%) of crude product which was a 68:19:13 mixture of **25a**, **25b**, and **25c**. Analytical samples were prepared by preparative GC on 8-ft, 5% DEGS at 140 °C. The data for **25a** are: Tr = 14.7 min; NMR ($CDCl_3$) δ 6.64 (1 H, d, J < 1 Hz), 3.72 (3 H, s), 2.72 (1 H, br d, J = 3.5 Hz), 2.44 (1 H, br d, J = 3.5 Hz), 2.15 (1 H, m), 2.02 (1 H, m), and 0.85–1.70 (6 H, m); **IR** (neat) 1720 and 1600 cm^{-1}; MS *m/e* (%) 178 (M$^+$, 1.0), 150 (3.3), 137 (38.0), 136 (15.4), 119 (26.5), 105 (44.7), 93 (70.5), 91 (100.0), and 77 (60.2). Adduct **25a** is identical with an authentic sample of spectroscopic comparison.[12] The data for **25b** are: Tr = 17.6 min; NMR ($CDCl_3$) δ 6.81 (1 H, d of d, J = 3, 1 Hz), 3.71 (3 H, s), 2.86 (1 H, m), 2.70 (1 H, m), 2.31 (1 H, m), and 1.0–2.0 ppm (7 H, m); **IR** (neat) 1718 and 1600 cm^{-1}; MS *m/e* (%) 178 (18.6), 150 (12.1), 147 (12.4), 137 (48.9), 124 (17.3), 119 (100.0), 118 (37.6), 117 (15.0), 109 (14.3), 105 (30.7), and 91 (85.8).

The data for **25c** are: Tr = 21.1 min; NMR ($CDCl_3$) δ 6.98 (1 H, d of d, J = 16.8 Hz), 5.96 (2 H, d, J = 2 Hz), 5.76 (1 H, d, J = 16 Hz), 3.69 (3 H, s) 2.72 (2 H, br s), 2.32 (1 H, br d, J = 8 Hz), and 0.9–1.9 (4 H, m); **IR** (neat) 1725, 1650, and 970 cm^{-1}; MS *m/e* (%) 178 (M$^+$, 3.7), 150 (2.1), 147 (6.6), 119 (33.1), 118 (54.5), 117 (20.3), 98 (12.3), 91 (37.9), 79 (30.5), and 28 (100.0).

Reaction of Methyl Propiolate with Camphene (26). Methyl propiolate (1.02 g, 12.2 mmol), aluminum chloride (0.814 g, 6.1 mmol, 0.5 equiv) and camphene (1.8 g, 13.2 mmol, 1.1 equiv) were stirred 4 days in 15 mL of benzene. Normal workup followed by evaporative distillation (150 °C, 0.1 mm) gave 0.735 g (27.3%) of a mixture of 60% **26a,** 8% of several unknown components, 21% of **26b** and 11% of **26c** as determined by GC on 8-ft, 5% DEGS at 140 °C. The data for **26a** are: GC Tr = 34 min; NMR ($CDCl_3$) δ 6.89 (1 H, t, J = 1.5 Hz), 3.67 (3 H, s), 2.42 (1 H, d of d, J = 8.5, 1.5 Hz), 2.20 (1 H, d of d, J = 8.5, 1.5 Hz), 1.2–2.73 (8 H, m), 1.12 (3 H, s), and 0.93 (3 H, s); **IR** (CCl_4) 1725 and 1600 cm^{-1}; MS *m/e* 220 (M$^+$), 205, 188, and 177. The data for **26b** are: GC Tr = 45.5 min; NMR ($CDCl_3$) δ 6.40–6.65 (1 H, m), 3.86 (3 H, s), 1.05–3.0 (10 H, m), 0.86 (3 H, s), and 0.70 ppm (3 H, s); **IR** (CCl_4) 1720 and 1610 cm^{-1}; MS *m/e* 220 (M$^+$). The data for **26c** are: GC Tr = 49 min; NMR ($CDCl_3$) δ 6.9 (1 H, m), 5.8 (1 H, br d, J = 16 Hz), 3.70 (3 H, s), 0.9–2.8 (10 H, m), 1.53 (3 H, s), and 0.85 ppm (3 H, s); **IR** (CCl_4) 1723 and 1650 cm^{-1}; MS *m/e* 220 (M$^+$ − HCl).

Reaction of Methyl Propiolate with 2,3-Pentadiene (27). Methyl propiolate (0.84 g, 10 mmol), aluminum chloride (0.673 g, 5 mmol, 0.5 equiv), and 2,3-pentadiene (0.748 g, 11 mmol, 1.1 equiv) were stirred 7 days in 15 mL of benzene. Normal workup followed by evaporative distillation gave 0.42 g (27%) which consisted of 85% of a 55:45 mixture of the isomers of **27a** and 15% of **27b** which were separated by preparative GC (6-ft, XF-1150, 100 °C). The data for **27a** are: GC (6-ft, 10% XF-1150, 150 °C) Tr = 3.7 and 4.0 min; NMR ($CDCl_3$) δ 7.03 and 6.79 (1 H, 2 s), 5.45 and 5.29 (1 H, 2 br q, J = 7 Hz), 3.72 (3 H, s), 3.50 and 3.38 (1 H, 2 br q, J = 7 Hz), 1.74 and 1.71 (3 H, 2 d, J = 7 Hz), and 1.31 and 11.8 ppm (3 H, 2 d, J = 7 Hz); **IR** (neat) 1720, 1685 and 1565 cm^{-1}; UV (cyclohexane) λ_{max}, 276 nm (ϵ 8300), 218 nm (ϵ 890). The data for **27b** are; GC (6 ft, 10% XF-1150, 150 °C) Tr = 7.2 min; NMR ($CDCl_3$) δ 7.35 (1 H, d, J = 16 Hz), 6.37 (1 H, d of d, J = 17, 11 Hz), 6.03 (1 H, q, J = 7 Hz), 5.93 (1 H, d, J = 16 Hz), 5.40 (1 H, d of d, J = 11, 2 Hz), 5.30 (1 H, d of d, J = 17, 2 Hz), 3.75 (3 H, s), and 1.85 ppm (3 H, d, J = 7 Hz); **IR**, 1720, 1630, and 1620 cm^{-1}.

Repetition of this experiment with 0.68 g (8.1 mmol) of methyl propiolate, 0.5 g (7.35 mmol) of 2,3-pentadiene, and 5.16 mL of 1.57 M (8.1 mmol, 1.0 equiv) ethylaluminum dichloride for 7 days in methylene chloride gave 1.005 g of crude product. Purification on silica gave 0.584 g (47%) of a mixture of **27a** and **27b** followed by 0.149 g of an unidentified mixture.

Reaction of Methyl Propiolate with Citronellyl Acetate (28). Methyl propiolate (1.8 g, 21.4 mmol), aluminum chloride (1.44 g, 10.7 mmol, 0.5 equiv), and citronellyl acetate (4.66 g, 23.52 mmol, 1.1 equiv) were stirred for 7 days in 30 mL of benzene. Normal workup followed by chromatography on silica using 10/1 pentane/ether as eluent gave 3.02 g (50%) of ene adduct **28a.** The spectral data for **28a** are: NMR ($CDCl_3$) δ 6.90 (1 H, d of d, J = 16, 8 Hz), 5.83 (1 H, d of d, J = 16, 1 Hz), 4.85 (2 H, m), 4.15 (2 H, 5, J = 6 Hz), 3.75 (3 H, s), 2.77 (1 H, t of d, J = 6, 8 Hz), 2.03 (3 H, s), 1.70 (3 H, d, J = 1 Hz), 1.05–1.82 (7 H, m), and 0.93 ppm (3 H, d, J = 6 Hz); IR (neat) 1730 and 1645 cm^{-1}; mass spectrum (m/e) 137, 123, 109, and 96. ^{13}C NMR indicates that a ca. 1:1 mixture of diastereomers is present. Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 68.25; H, 9.36.

Reaction of Methyl Propiolate with Citronellyl Methyl Ether[36] (29). Methyl propiolate (0.459 g, 5.46 mmol), aluminum chloride (0.3571 g, 2.73 mmol, 0.5 equiv), and citronellyl methyl ether[36] (1.02 g, 6.00 mmol, 1.1 equiv) were stirred 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 10/1 pentane/ether gave 0.358 g (35%) of recovered starting material followed by 0.749 g (53.8%) of ene adduct **29a:** NMR ($CDCl_3$) δ 6.83 (1 H, d of d, J = 15, 7 Hz), 5.72 (1 H, d of d, J = 15, 1 Hz), 4.85 (2 H, m), 3.68 (3 H, s), 3.37 (2 H, t, J = 6 Hz), 3.28 (3 H, s), 2.70 (1 H, t of d, J = 6, 7 Hz), 1.67 (3 H, d, J = 1 Hz), 1–2 (7 H, m), and 0.9 ppm (3 H, d, J = 6 Hz); **IR** (neat) 1725 and 1640 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.82; H, 10.30. Found: C, 70.70; H, 10.39.

Reaction of Methyl Propiolate with Methyl Citronellate[37] (30). Methyl propiolate (0.402 g, 4.78 mmol), aluminum chloride (0.318 g, 2.39 mmol, 0.5 equiv), and methyl citronellate[37] (0.968 g, 5.26 mmol, 1.1 equiv) were stirred 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 4/1 pentane/ether gave 0.216 g (22.3%) of recovered starting material followed by 0.676 g (53.2%) of **30a;** NMR ($CDCl_3$) δ 6.85 (1 H, d of d, J = 15, 7 Hz), 5.78 (1 H, d of d, J = 15, 1 Hz), 4.85 (2 H, m), 3.68 (3 H, s), 3.63 (3 H, s), 2.75 (1 H, t of d, J = 7, 7 Hz), 0.8–2.5 (7 H, m), 1.62 (3 H, bd s), and 0.92 ppm (3 H, d, J = 6 Hz); **IR** (neat) 1725 and 1650 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 66.95; H, 9.13.

Reaction of Methyl Propiolate with Citronellyl Trifluoroacetamide (32). A solution of **32** (0.5 g, 2.0 mmol), methyl propiolate (0.168 g, 2 mmol), and ethylaluminum dichloride (2.48 mL of 1.57 M, 3.9 mmol, 1.95 equiv) in 6 mL of methylene chloride was stirred 7 days at 25 °C. Normal workup gave 0.658 g. Evaporative distillation gave 0.584 g (87%) of ene adduct **32a:** NMR ($CDCl_3$) δ 7.15 (1 H, br s), 6.87 (1 H, d of d, J = 14, 8 Hz), 5.81 (1 H, d of d, J = 14, 1 Hz), 4.84 (2 H, br s), 3.74 (3 H, s), 3.4 (2 H, d of t, J = 5, 7 Hz), 2.8 (1 H, d of t, J = 8, 7 Hz), 1.69 (3 H, s), 0.92 (3 H, d, J = 6 Hz), and 0.8–1.99 ppm (7 H, m); IR (neat) 3210, 1725, 1705, 1658, and 1648 cm^{-1}. Anal. Calcd for $C_{16}H_{24}F_3NO_3$: C, 57.30; H, 7.21; F, 17.00; N, 4.18. Found: C, 57.42; H, 7.32; F, 17.18; N, 3.96.

Reaction of Methyl Propiolate with 4-Methylenecyclohexylmethyl Methyl Ether[36] (33). Methyl propiolate (0.551 g, 6.5 mmol), aluminum chloride (0.430 g, 3.25 mmol, 0.5 equiv), and **33**[36] (1.00 g, 7.14 mmol, 1.1 equiv) were stirred for 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 10/1 pentane/ether as eluent gave 0.3536 g (28.1%) of isomerized starting material **33a** followed by 0.5839 g (36.5%) of a mixture consisting of 55% **33b** and 25% **33c** and 20% of **33d.** The spectral data for **33a** are: NMR ($CDCl_3$) δ 5.38 (1 H, br s), 3.32 (3 H, s), 3.28 (2 H, d, J = 6 Hz), and 1.1–3.1 ppm (10 H, m). The data for **33b** are: NMR ($CDCl_3$) δ 7.03 (1 H, d of t, J = 16, 7.5 Hz), 5.82 (1 H, d of t, J = 16, 1 Hz), 5.55 (1 H, m), 3.70 (3 H, s), 3.30 (3 H, s), 3.22 (2 H, d, J = 6 Hz), 2.80 (2 H, d, J = 7 Hz), and 0.8–2.3 ppm (7 H, m); IR (neat) 1720 and 1640 cm^{-1}; MS *m/e* 224 (M$^+$). Anal Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.79; H, 8.78. The data for **33c** are: NMR ($CDCl_3$) δ 7.08 (1 H, d of d, J = 16, 5 Hz), 5.82 (1 H, d of d, J = 16, 1 Hz), 4.75 (2 H, br s), 3.7 (3 H, s), 3.3 (3 H, s), 3.28 (1 H, m), 3.22 (2 H, d, J = 6 Hz), 0.8–2.4 ppm (7 H, m). The data for **33d** are: NMR ($CDCl_3$) δ 6.98 (1 H, d of d, J = 16, 6 Hz), 5.82 (1 H, d of d, J = 16, 1 Hz), 5.55 (1 H, m), 3.70 (3 H, s), 3.3 (3 H, s), 3.28 (1 H, m), 3.22 (2 H, d, J = 6 Hz), and 0.8–2.3 ppm (8 H, m).

Reaction of Methyl Propiolate with 4-Methylenecyclohexylacetonitrile (34).[39] Methyl propiolate (0.595 g, 7.10 mmol), aluminum chloride (0.49 g 3.67 mmol, 0.5 equiv), and **34**[39] (0.951 g, 7.04 mmol, 1 equiv) were stirred for 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica using 10/1 pentane/ether as eluent gave 0.450 g (47%) of a 2:3 mixture of **34** and its isomer **34a,** 0.068 g (4%) of [2 + 2] adduct **34e,** and 0.310 g (18%) of a 9:1 mixture of **34b** and **34c,d.** The spectral data for **34e** are: NMR ($CDCl_3$) δ 7.08 (1 H, t, J = 1 Hz), 3.75 (3 H, s), 1.0–3.1 ppm (13 H, m); IR (CCl_4) 1725 and 1605 cm^{-1}. The spectral data for **34b** are: NMR ($CDCl_3$) δ 6.98 (1 H, d of t, J = 15, 7 Hz), 5.83 (1 H, d of t, J = 15, 1 Hz), 5.48 (1 H, m), 3.72 (3 H, s), 2.85 (2 H, d, J = 7 Hz), 1.1–2.5 ppm (9 H, m); IR (neat) 1725 and 1605 cm^{-1}; MS *m/e* 219 (M$^+$) 188 and 160.

Reaction of Methyl Propiolate with 4-Nitromethylmethylenecyclohexane (35).[40] Methyl propiolate (0.1 g, 1.2 mmol), aluminum chloride (0.81 g, 0.61 mmol, 0.5 equiv), and **35**[40] (0.210 g, 1.32 mmol, 1.1 equiv) were stirred for 7 days in 5 mL of benzene. Normal workup followed by preparative layer chromatography using 1:1 pentane:ether gave 0.1955 g (67.0%) of ene adduct **35b:** NMR ($CDCl_3$) δ 6.90 (1 H, d of t, J = 15, 6 Hz), 5.78 (1 H, d of t, J = 15, 1 Hz), 5.45 (1 H, m), 4.3 (2 H, d, J = 6 Hz), 3.70 (3 H, s), 2.83 (2 H, bd d, J = 6 Hz), and 0.82–2.68 ppm (7 H, m); IR 1725, 1650, and 1550 cm^{-1}.

Reaction of Methyl Propiolate with 4-Methylenecyclohexylmethyl Acetate (36). Methyl propiolate (0.487 g, 5.80 mmol), aluminum chloride (0.37 g, 2.90 mmol, 0.5 equiv), and **36** (1.072 g, 6.38 mmol, 1.1 equiv) were stirred for 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica in 10/1 pentane/ether gave 0.694 g (65%) of recovered **36** followed by 0.0445 g (3.0%) of ene adduct **36b**: NMR ($CDCl_3$) δ 6.97 (1 H, d of t, J = 15, 7 Hz), 5.82 (1 H, d of t, J = 15, 1 Hz), 3.98 (2 H, d, J = 5 Hz), 3.73 (3 H, s), 2.83 (2 H, d, J = 7 Hz), 2.05 (3 H, s), and 1.1–2.5 (7 H, m); IR (neat) 1730, 1650 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.78; H, 7.73.

Treatment of methyl propiolate (0.539 g, 6.42 mmol) and **36** (1.08 g, 6.43 mmol) with 1.5 equiv of aluminum chloride (1.28 g, 9.63 mmol) for 7 days in 15 mL of benzene gave after workup 1.408 g of crude product which was purified on silica with 10/1 pentane/ether. Fraction 1 consisted of a mixture of hydrogen chloride adduct and Friedel-Crafts product (0.541 g, 41%). Fraction 2 consisted of a 67:33 mixture of **36b** and **36c,d** (0.616 g, 38%).

A solution of **36** (840 mg, 5.0 mmol), methyl propiolate (407 mg, 4.55 mmol), and ethylaluminum dichloride (4.3 mL of 1.57 M, 6.83 mmol, 1.5 equiv) in 15 mL of methylene chloride was stirred 7 days. Normal workup gave 1.041 g of crude product. Chromatography of 0.858 g on silica gave 262 mg of recovered **36**, 47 mg of an unidentified compound, and 282 mg (30%) of ene adduct **36b**.

Use of 5.5 mL of 1.57 M ethylaluminum dichloride (1.9 equiv) gave 1.24 g of crude adduct. Purification of 844 mg on silica gave 116 mg of recovered **36** and 542 mg (71%) of pure ene adduct **36b**.

Reaction of Methyl Propiolate with 4-Methylenecyclohexylmethyl *p*-Nitrobenzoate (37). A solution of methyl propiolate (0.558 g, 6.61 mmol), **37** (2.00 g, 7.3 mmol, 1.1 equiv), and aluminum chloride (0.443 g, 3.32 mmol, 0.5 equiv) was stirred 7 days in 20 mL of benzene. Normal workup gave 2.255 g of crude product which was purified on silica with 5/1 hexane/ethyl acetate. Fraction 1 (0.535 g, 27%) consisted of partially isomerized starting material. Fraction 2 (0.311 g, 13%) consisted of the hydrogen chloride adduct of starting material. Fraction 3 (0.654 g, 27.5%) consisted of a 9/1 mixture of **37b** and **37c,d**. The spectral data of **37b** are: NMR ($CDCl_3$) δ 8.10 (4 H, s), 6.83 (1 H, d of t, J = 15, 7 Hz), 5.72 (1 H, d of t, J = 15, 1 Hz), 5.3 (1 H, m), 4.18 (2 H, d, J = 5 Hz), 3.70 (3 H, s), 2.78 (2 H, br d, J = 7 Hz), and 1.0–2.5 (7 H, m); IR 1730, 1650, and 1530 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.77; H, 6.09; N, 3.85.

Reaction of Methyl Propiolate with 4-Methylenecyclohexylmethyl 3,5-Dinitrobenzoate (38). A solution of methyl propiolate (0.773 g, 9.2 mmol), **38** (3.25 g, 10.1 mmol, 1.1 equiv), and aluminum chloride (0.614 g, 4.6 mmol, 0.5 equiv) was stirred 7 days in 30 mL of benzene. Normal workup gave 3.823 g of product which was purified on silica using 5/1 hexane/ethyl acetate. Fraction 1 (0.667 g, 21%) consisted of partially isomerized starting material. Fraction 2 (0.900 g, 24%) consisted of the hydrogen chloride adduct of **38** and fraction 3 (1.055 g, 28.3%) consisted of virtually pure **38b**, mp 99–107 °C. Recrystallization from cyclohexane/benzene gave an analytical sample, mp 105–107 °C; NMR ($CDCl_3$) δ 9.1 (3 H, m), 6.92 (1 H, d of t, J = 15, 7 Hz), 5.80 (1 H, d of t, J = 15, 1.5 Hz), 5.52 (1 H, m), 4.38 (2 H, d, J = 5.5 Hz), 3.70 (3 H, s), 2.87 (2 H, d, J = 7 Hz), and 1.2–2.5 (7 H, m); IR ($CHCl_3$) 1730, 1630, and 1547 cm^{-1}. Anal. Calcd for $C_{19}H_{20}N_2O_8$: C, 56.43; H, 4.99; N, 6.93. Found: C, 56.62; H, 5.05; N, 6.81.

Reaction of Methyl Propiolate with 4-Methylenecyclohexylmethyl Trifluoroacetate (39). A solution of **39** (1.055 g, 5.00 mmol), methyl propiolate (382 mg, 4.55 mmol), and ethylaluminum dichloride (1.45 mL of 1.57 M, 2.28 mmol, 0.5 equiv) in methylene chloride was stirred for 7 days. Normal workup gave 1.170 g of crude product. Chromatography on silica eluting with 5/1 hexane/ethyl acetate gave 326 mg (31%) of recovered **39** and 615 mg (44%) of ene adduct **39b**. The spectral data for **39b** are: NMR ($CDCl_3$) δ 6.95 (1 H, d of t, J = 15, 7 Hz), 5.80 (1 H, d of t, J = 15, 1.5 Hz), 5.29 (1 H, br s), 4.23 (2 H, d, J = 5.5 Hz), 3.68 (3 H, s), 2.83 (2 H, br d, J = 7 Hz), and 1.5–2.5 ppm (7 H, m); IR (neat) 1722, 1653, and 985 cm^{-1}. Anal. Calcd for $C_{14}H_{17}F_3O_4$: C, 54.90; H, 5.60; F, 18.60. Found: C, 54.69; H, 5.84; F, 18.36.

Reaction of 6-Methyl-5-hepten-2-yl Acetate (40) with Methyl Propiolate. A solution of **40** (767 mg, 4.51 mmol), methyl propiolate (379 mg, 4.51 equiv), and aluminum chloride (903 mg, 6.76 mmol, 1.5 equiv) in 15 mL of benzene was stirred for 7 days. Normal workup gave 1.043 g of crude product. Chromatography on silica gel eluting with 10/1 petroleum ether/ether gave 213 mg of a mixture of the hydrogen chloride adduct of **40** and the product of Friedel-Crafts alkylation of benzene. Pure ene adduct **40a** was obtained as the second fraction (574 mg, 50%); NMR ($CDCl_3$) δ 6.55 (1 H, d of d, J = 15, 8 Hz), 5.83 (1 H, d of d, J = 15, 1.5 Hz), 4.86 (2 H, br s), 4.85 (1 H, m), 3.72 (3 H, s), 2.83 (1 H, m), 2.02 (3 H, s), 1.4–2.0 (4 H, m), 1.68 (3 H, bd s), and 1.20 ppm (3 H, d, J = 6.5 Hz); IR 1740, 1730, 1658, and 1645 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.70. Found: C, 65.94; H, 8.52.

A solution of **40** (1.00 g, 5.88 mmol), methyl propiolate (0.45 g, 5.35 mmol), and ethylaluminum dichloride (5.11 mL of 1.57 M, 8.03 mmol, 1.5 equiv) in 15 mL of methylene chloride was stirred for 7 days. Normal workup gave 1.193 g of crude product which was purified on silica giving 0.452 g (45%) of recovered **40**, and 0.601 g (48%) of ene adduct of **40a**.

Reaction of Methyl Propiolate with 6-Methyl-5-hepten-2-one (41). A solution of **41** (630 mg, 5.00 mmol), methyl propiolate (0.407 g, 4.55 mmol), and ethylaluminum dichloride (1.45 mL of 1.57 M, 2.28 mmol, 0.5 equiv) in 15 mL of methylene chloride was stirred 7 days. Normal workup gave 0.940 g. Chromatography of 0.624 g on silica eluting with 5:1 hexane:ethyl acetate gave 0.334 g (53%) of **41a**: NMR ($CDCl_3$) δ 6.78 (1 H, d, J = 1.5 Hz), 3.70 (3 H, s), 2.77 (1 H, d of d of d, J = 4, 4, 1.5 Hz), 1.46 (3 H, s), 1.14 (6 H, s), and 1.1–2.3 ppm (4 H, m); ^{13}C NMR ($CDCl_3$) δ 161.4 (s), 147.5 (d), 146.6 (s), 76.1 (s), 72.7 (s), 50.8 (q), 47.3 (d), 30.6 (q), 30.5 (t), 29.97 (q), 25.0 (q), and 21.2 ppm (t); IR (neat) 3060, 2980, 2940, 2880, 1725, and 1609 cm^{-1}; MS *m/e* (%), 211 (5), 210 (M^+, 27.4), 195 (6), 192 (5), 178 (26), 167 (12), 163 (41), 154 (18), 153 (32), 152 (14), 151 (10), 150 (15), 142 (15), 135 (34), 126 (28), 124 (15), 123 (30), 121 (25), 111 (32), 107 (21), 95 (77), 93 (34), 82 (54), 81 (41), 69 (55), 56 (56), 43 (100). Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.33; H, 8.76.

Reaction of Methyl Propiolate with Isopentenyl Benzoate (42). Methyl propiolate (0.831 g, 9.89 mmol), aluminum chloride (0.591 g, 4.4 mmol, 0.45 equiv), and **42** (2.11 g, 11.1 mmol, 1.12 equiv) were stirred for 7 days in 15 mL of benzene. Normal workup followed by chromatography on silica eluting with 10/1 pentane/ether gave 0.264 g (9%) of ene adduct **42a**: NMR ($CDCl_3$) δ 7.3–8.15 (5 H, m), 7.01 (1 H, d of t, J = 16, 6 Hz), 5.90 (1 H, d of t, J = 16, 2 Hz), 4.97 (2 H, br s) 4.43 (2 H, t, J = 6 Hz), 3.70 (3 H, s), 2.98 (2 H, t, J = 6 Hz), and 2.50 ppm (2 H, d, J = 6 Hz).

Reaction of Methyl Propiolate with 1,1,1-Trideuterio-2-trideuteriomethyl-3-methyl-2-butene (43). Methyl propiolate (125 mg, 1.5 mmol), aluminum chloride (100 mg, 0.75 mmol, 0.5 equiv) and **43** (150 mg, 1.66 mmol, 1.1 equiv) were stirred for 7 days in 1 mL of benzene. Normal workup followed by chromatography on silica eluting with 40/1 pentane/ether gave 116 mg (48%) of a 2.63/1 (run 1) and 2.67/1 (run 2) mixture of **43a** and **43b** as determined by NMR. The spectral data for **43a** are: NMR ($CDCl_3$) δ 7.01 (1 H, d, J = 15 Hz), 5.80 (1 H, d, J = 15 Hz), 4.87 (2 H, br s), 3.75 (3 H, s), and 1.73 ppm (3 H, br s). The data for **43b** are: NMR ($CDCl_3$) δ 7.01 (1 H, J_{HD} = 2.5 Hz), 3.75 (3 H, s), and 1.22 ppm (6 H, s).

Kinetic Study of the Ene Reaction of Methyl Propiolate with 3-Methyl-2-butene. Methyl propiolate (70 mg, 0.83 mmol), aluminum chloride (17.7 mg, 0.133 mmol, 0.16 equiv), and 3-methyl-2-butene (64 mg, 0.913 mmol. 1.1 equiv) were dissolved in 0.25 mL of benzene-d_6 and sealed in an NMR tube. The reaction was monitored by NMR (time (h), % conversion): 0.6, 10; 0.9, 12.4; 1.2, 15; 2.5, 19, 3.25, 23; 6.25, 28; 19.3, 38; 32.5, 43; 45.5, 46.2; 120, 56.6; 332, 65; 501, 71; and 672, 73.5. At this point, most of the unreacted alkene had been converted to 2-chloro-2-methylbutane. The results are shown in Figure 1.

Ring Opening of 16a. Heating **16a** for 3 h at 100 °C in $CDCl_3$ gave complete conversion to the diene **44**. The reaction was 55% complete after 30 min. The spectral data for **44** are: NMR ($CDCl_3$) δ 6.3–5.7 (3 H, m), 3.80 (3 H, s), 1.87 (3 H, d, J = 8 Hz), and 1.76 ppm (3 H, d, J = 5 Hz).

Ring Opening of 15a. Heating **15a** for 72 h at 120 °C gives quantitative conversion to a ~5:1 mixture of two isomers. The major isomer is **45**. The structure of the minor compound is tentatively assigned as **46**. The spectral data for **45** are: NMR ($CDCl_3$) δ 6.80 (1 H, q, J = 7.7 Hz), 6.25 (1 H, d, J = 16 Hz), 6.15 (1 H, d of d, J = 16, 5 Hz), 3.80 (3 H, s), 1.93 (3 H, d, J = 8 Hz), and 1.86 (3 H, d, J = 5 Hz). The partial spectral data for the minor isomer are: NMR ($CDCl_3$) δ 3.82 (3 H, s), 2.05 (3 H, d, J = 8 Hz), and 1.73 ppm (3 H, d of d, J = 6, 1.5 Hz). The reaction is 50% complete after 12 h at 120 °C.

Ring Opening of Methyl Bicyclo[6.2.0]dec-8-ene-8-carboxylate (22a). A sample of **22a** in $CDCl_3$ was heated 50 h at 120 °C in a sealed

NMR tube giving a virtually quantitative yield of **47**: NMR ($CDCl_3$) δ 6.84, (1 H, t of d, J = 7.8, 1.3 Hz), 5.98 (1 H, br d, J = 16 Hz), 5.49 (1 H, d of t, J = 16, 7 Hz), 3.7 (3 H, s), 2.0–2.4 (4 H, m), and 1.2–1.5 ppm (8 H, m); IR (neat) 1720, 1650, 1610, and 970 cm^{-1}; MS *m/e* (%) 194 (M^+, 12), 115 (42), 105 (47), 83 (12), 78 (12), and 77 (100). Anal. Calcd for $C_{12}H_{18}O_3$: *m/e* 194.1307. Found: *m/e* 194.1305.

Ring Opening of Bicyclo[6.2.0]deca-4,8-diene-8-carboxylate (23a). A solution of **23a** in $CDCl_3$ was heated 12 h at 120 °C giving quantitative conversion to the *cis*-divinylcyclohexene **48**. The reaction proceeded slowly at 75–90 °C but in no case could any of **23b** be detected. The spectral data for **48** are: NMR ($CDCl_3$) δ 7.07 (1 H, d of d, J = 3.5 Hz), 5.5–6.0 (2 H, m), 4.7–5.2 (4 H, m), 3.7 (3 H, s), 3.43 (1 H, br d of d, J = 5.0, 6.0 Hz), 2.1–2.4 (3 H, m), and 1.5–1.7 ppm (2 H, m); IR (neat) 1720, 1650, 990, and 905 cm^{-1}.

Aluminum Chloride Catalyzed Reaction of 23a. Aluminum chloride (22.7 mg, 0.17 mmol) and **23a** (6.5 mg, 0.34 mmol) in 0.25 mL of benzene-d_6 were sealed in an NMR tube. A similar sample lacking aluminum chloride was prepared as a control. After 11 days at 75 °C, the control consisted of 60% **23a** and 40% divinylcyclohexene **48**. The aluminum chloride catalyzed reaction contained less than 10% of **23a** and an 8:2 mixture of **48** and an unidentified product probably derived from isomerization of **48**.

Acknowledgment. We wish to thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Institutes of Health for financial support.

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