$EtAlCl_2$-Catalyzed Reactions of Alkenes with Electrophilic Cyclopropanes. A New Cyclopentane Annelation Reaction

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Treatment of 1,1-di-, tri-, and tetrasubstituted alkenes with diethyl cyclopropane-1,1-dicarboxylate (1) and 2 equiv of $EtAlCl_2$ gives zwitterions which collapse to cyclopentanedicarboxylates in good to excellent yield. This reaction provides a general procedure for the annelation of cyclopentanes to alkenes. The intermediate zwitterions undergo the 1,2-hydride and -methyl shifts characteristic of carbocations, although these side reactions are generally minor. Diethyl 2-methylcyclopropane-1,1-dicarboxylate (**38**) reacts similarly with alkenes at the more substituted carbon of **38** to give 3-methylcyclopentane-1,1-dicarboxylates. Diethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate (**46**) rearranges in the presence of $EtAlCl_2$ to diethyl isobutylidenemalonate, which reacts with alkenes and is reduced by $EtAlCl_2$. The intramolecular Lewis acid induced addition of alkenes to cyclopropanedicarboxylate esters occurs analogously.

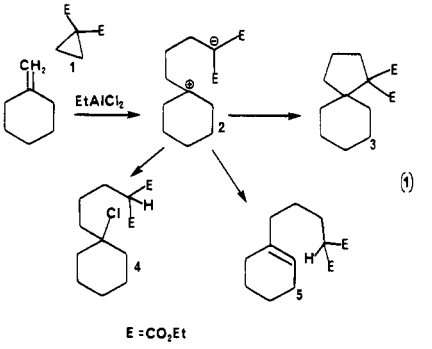
Introduction

As part of our ongoing interest in the development of new procedures for the carbofunctionalization of alkenes, we have extensively explored Lewis acid induced reactions of alkenes with carbonyl compounds and α,β-unsaturated esters, ketones, and aldehydes.[2] In general, ene adducts are produced in good to excellent yield from these reactions. We have now turned our attention to Lewis acid induced reactions of electrophilic cyclopropanes with alkenes. The use of electrophilic cyclopropanes in organic synthesis has been extensively developed.[3] Typical nucleophilic components in these reactions are enamines,[4] amines,[5] or organometallic reagents such as cuprates.[6] Cyclopropyl esters and ketones have also been reported to undergo intermolecular[7] and intramolecular[8] Friedel–Crafts reactions.

To the best of our knowledge, the intermolecular reactions of electrophilic cyclopropanes with alkenes have not been reported. On the other hand, intramolecular reactions of electrophilic cyclopropanes with alkenes have been explored. Stork,[9] Grieco,[10] and Corey[11] have used Lewis acid complexes of cyclopropyl ketones for the initiation of cation–olefin cyclizations. In some cases the initially formed zwitterion collapses to a cyclopentyl ketone. Since the intramolecular reactions of electrophilic cyclopropanes with alkenes have been shown to give useful products, we set out to explore Lewis acid induced intermolecular reactions of electrophilic cyclopropanes with alkenes. Cyclopropyl methyl ketone does not undergo Lewis acid induced reaction with alkenes. Therefore, we chose to explore the reactions of a doubly activated cyclopropane such as diethyl cyclopropane-1,1-dicarboxylate (1) with alkenes.

Results and Discussion

Reactions of 1. The Lewis acid induced reaction of **1** with methylenecyclohexane was examined initially since 1,1-disubstituted alkenes are the most reactive class of alkenes toward electrophiles.[2] A priori, it was expected that electrophilic addition of the $1\cdot EtAlCl_2$ complex to methylenecyclohexane will give the zwitterion **2** which could collapse to give **3**, transfer a chloride ion to give **4**, or transfer a proton to give **5** (see eq 1). In practice, only the first of these processes, collapse of zwitterion **2** to give cyclopentanedicarboxylate **3**, was observed. Optimal results were obtained by treatment of methylenecyclohexane with **1** and 2 equiv of $EtAlCl_2$ in 1,2-dichloroethane for 48 h which gives a virtually quantitative yield of diethyl spiro[4.5]decane-1,1-dicarboxylate (**3**). This reaction therefore promises to be an important new cyclopentane annelation reaction.[12] The formation of a bond between two quaternary carbons makes this a valuable route to highly substituted cyclopentanes.[13]



(1)

Reaction conditions were carefully investigated to optimize the yield of **3**. Slightly lower yields were obtained in the slightly less polar solvent dichloromethane. Poorer yields were obtained in aromatic solvents or in 1:1 dichloromethane–nitromethane. Two equivalents of $EtAlCl_2$ appeared to be optimal. More complex mixtures containing chloride **53** were obtained with less than 2 equiv of Lewis acid and with 2 equiv of $EtAlCl_2$ in other solvents. Methylaluminum sesquichloride and Me_2AlCl were less

(1) Camille and Henry Dreyfus Teacher-Scholar 1982–1987.
(2) (a) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426. (b) Snider, B. B.; Rodini, D. J.; Conn, R. S. E.; Sealfon, S. *J. Am. Chem. Soc.* **1979**, *101*, 5283. (c) Snider, B. B.; Roush, D. M.; Rodini, D. J.; Gonzalez, D. M.; Spindell, D. *J. Org. Chem.* **1980**, *45*, 2773. (d) Duncia, J. V.; Lansbury, P. T., Jr.; Miller, T.; Snider, B. B. *J. Am. Chem. Soc.* **1982**, *104*, 1930. (e) Snider, B. B.; Deutsch, E. A. *J. Org. Chem.* **1983**, *48*, 1822. (f) Snider, B. B.; Rodini, D. J.; Kirk, T. C.; Cordova, R. *J. Am. Chem. Soc.* **1982**, *104*, 555. (g) Snider, B. B.; Phillips, G. B. *J. Org. Chem.* **1983**, *48*, 464.
(3) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66.
(4) Dolfini, J. E.; Menich, K.; Corliss, P.; Cavanaugh, R.; Danishefsky, S.; Chakrabartty, S. *Tetrahedron Lett.* **1966**, 4421.
(5) Blanchard, L. A.; Schneider, J. A. *J. Org. Chem.* **1986**, *51*, 1372.
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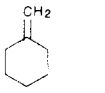
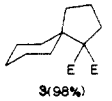
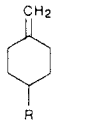
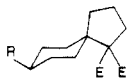
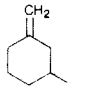
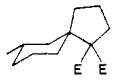
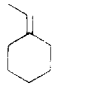
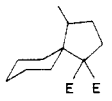
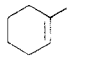
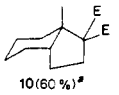
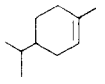
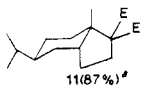
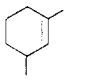
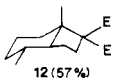
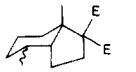
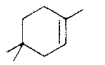
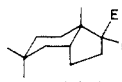
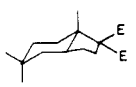
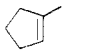
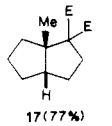
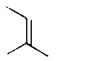
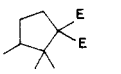
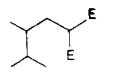
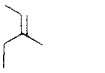
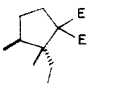
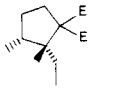
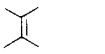
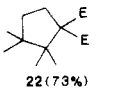
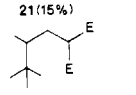
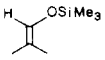
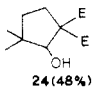
(7) Pinnick, H. W.; Brown, S. P.; McLean, E. A.; Zoller, L. W., III *J. Org. Chem.* **1981**, *46*, 3758.
(8) (a) Magnus, P.; Schultz, J.; Gallagher, T. *J. Am. Chem. Soc.* **1985**, *107*, 4984. (b) Murphy, W. S.; Wattanasin, S. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2920; **1982**, 271, 1029. (c) Stork, G.; Gregson, M. *J. Am. Chem. Soc.* **1969**, *91*, 2373.
(9) (a) Stork, G.; Marx, M. *J. Am. Chem. Soc.* **1969**, *91*, 2371. (b) Stork, G.; Grieco, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 2407. (c) Stork, G.; Grieco, P. A. *Tetrahedron Lett.* **1971**, 1807.
(10) Grieco, P. A.; Finkelhor, R. S. *Tetrahedron Lett.* **1974**, 527.
(11) Corey, E. J.; Balanson, R. D. *Tetrahedron Lett.* **1973**, 3153.
(12) For recent reviews of cyclopentane annelation reactions see: (a) Ramaiah, M. *Synthesis* **1984**, 529. (b) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1.
(13) Godleski, S. A.; Valpey, R. S. *J. Org. Chem.* **1982**, *47*, 381.

0022-3263/86/1951-4391$01.50/0

Table I. Lewis Acid Induced Reactions of Diethyl Cyclopropane-1,1-dicarboxylate (1) with Alkenes

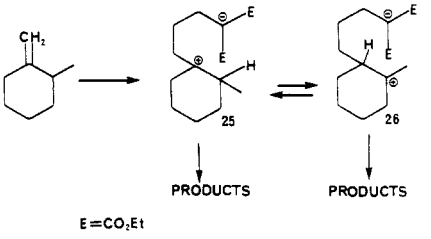
alkene	adducts (% yield)[b]
	 3(98%)
	 6, R = Me(74%) 7, R = *t*-Bu(79%)
	 8(50%)
	 9(87%)
	 10(60%)[a]
	 11(87%)[a]
	 12(57%)  13, β-Me(19%) 14, α-Me(19%)
	 15(50%)  16(25%)
	 17(77%)
	 18(83%)  19(3%)
	 20(58%)  21(15%)
	 22(73%)  23(6%)
	 24(48%)

[a] The product was contaminated with small amounts of the trans-fused isomer [b] E = CO_2Et.

effective catalysts for this reaction. Our previous studies have shown that alkylaluminum halides are optimal Lewis acids when an excess of Lewis acid is required and sensitive alkenes are used since they are proton scavengers in addition to Lewis acids.[14] $EtAlCl_2$ was also the optimal catalyst for Lewis acid catalyzed ene reactions of α,β-unsaturated esters.[2,14]

The reactions of a variety of alkenes with 1 and 2 equiv of $EtAlCl_2$ are shown in Table I. Substituted methylenecyclohexanes were examined to determine the stereochemistry of the closure of zwitterion **2** to give **3**. 4-Methylmethylenecyclohexane gives adduct **6** which results from equatorial attack on the cyclohexyl cation. The stereochemistry of **6** was established by comparison of its ^{13}C NMR spectrum to that of **3**[15] which shows the expected shielding for an equatorial methyl group at C_8 of +6.3 ppm on C_8, +9.3 ppm on $C_{7,9}$, and +0.2 ppm on $C_{6,10}$. Identical results were obtained with 4-*tert*-butylmethylenecyclohexane which gives **7** whose ^{13}C NMR spectrum shows the expected shielding for an equatorial *tert*-butyl group at C_8 of +15.4 ppm on C_8, +0.7 ppm on $C_{7,9}$, and +0.5 ppm on $C_{6,10}$. Comparable results were obtained with 3-methylmethylenecyclohexane which gives mainly **8** with an equatorial methyl group at C_7 whose ^{13}C NMR spectrum shows the expected shielding for an equatorial methyl group at C_7 of +6.1 ppm on C_7, +8.9 ppm on C_6, +8.9 ppm on C_8, +1.0 ppm on C_5, and −0.2 ppm on C_9.

Reaction of **1** with 2-methylmethylenecyclohexane gives a complex mixture of products, indicative of a major limitation of this reaction. Zwitterion **25** undergoes a facile 1,2-hydride shift to give **26** which closes to give isomeric decalin derivatives. Similarly, reaction of 1,6-dimethylcyclohexene with **1** gives a complex mixture of products.



Reaction of **1** with ethylidenecyclohexane gives an 87% yield of **9**, indicating that trisubstituted alkenes are suitable substrates for this reaction. Reaction of **1** with 1-methylcyclohexene gives a 65% yield of **10**. The expected cis ring fusion of **10** is established by the methyl singlet at δ 1.20. A trace of the trans isomer is present as indicated by a singlet at δ 0.77.[16] Reaction of menthene with **1** gives **11** in 87% yield. The stereochemistry of **11** is assigned based on the expected attack trans to the isopropyl group.[2d] Traces of a trans-fused isomer are again formed. 1-Methylcyclopentene reacts to give exclusively the cis-fused adduct **17** in 77% yield.

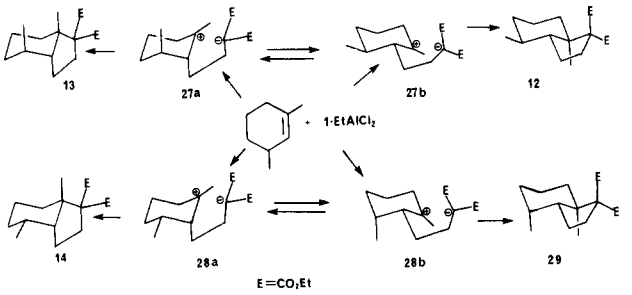
Reaction of 1,3-dimethylcyclohexene gives a mixture of three products: **12**, **13**, and **14**. This result was unexpected since there are only two possible cis-fused isomers. A more complete analysis suggests that one of the two possible trans-fused isomers should also be formed in this case. Zwitterions **27** and **28** can each exist in two conformations. If we assume that equatorial attack of the hindered malonate nucleophile is strongly preferred, as is indicated by the selective formation of **6**, **7**, and **8**, then each conformer will give only a single adduct. Zwitterions **27a** and **28a** with an axial side chain must give the cis-fused adducts **13** and **14**, while the zwitterions **27b** and **28b** will give the trans-fused adducts **12** and **29** from equatorial attack rather than

(14) Snider, B. B.; Rodini, D. J.; Karras, M.; Kirk, T. C.; Deutsch, E. A.; Cordova, R.; Price, R. T. *Tetrahedron* **1981**, *37*, 3927.

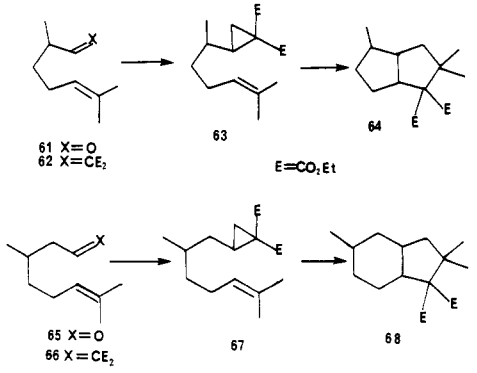
(15) ^{13}C NMR spectra were assigned by comparison with appropriate model compounds. (a) Spiro[4.5]decane: Kutschan, R.; Ernst, L.; Wolf, H. *Tetrahedron* **1977**, *33*, 1833. (b) *cis*-1-Methylbicyclo[3.3.0]octane: Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878. (c) *cis*-1-Methylbicyclo[4.3.0]nonane: Gooding, K. R.; Jackson, W. R.; Pincombe, C. F; Rash, D. *Tetrahedron Lett.* **1979**, 263. (d) *cis*- and *trans*-bicyclo[3.3.0]octane and bicyclo[4.3.0]nonane: Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 68. (e) Diethyl cyclopentane-1,1-dicarboxylate: Stadtler ^{13}C NMR spectra 12815M.

(16) These values are in good agreement with those calculated for the 18-CH_3 groups of 14α and 14β steroids with two ester groups at C_{17}. See: Bhacca, N. S.; Williams, D. H. *Applications of NMR Spectroscopy in Organic Chemistry*; Holden-Day: San Francisco, 1964. Arnold, W.; Meister, W.; Englert, G. *Helv. Chim. Acta* **1974**, *57*, 1559.

the cis-fused adducts which would result from axial attack. The selective formation of **10** from 1-methylcyclohexene indicates that formation of the cis-fused isomer from the axial conformer is preferred in the absence of substituents.[17] Conformers **28a** and **28b** are similar in energy so that formation of **14** should be strongly favored over **29**. However, the presence of the *trans*-methyl group in **27** strongly favors conformer **27b** so that formation of the trans adduct **12** becomes a major process. The singlet at δ 0.80 in the NMR spectrum of the major isomer indicates that it is the trans-fused adduct **12**.[16]



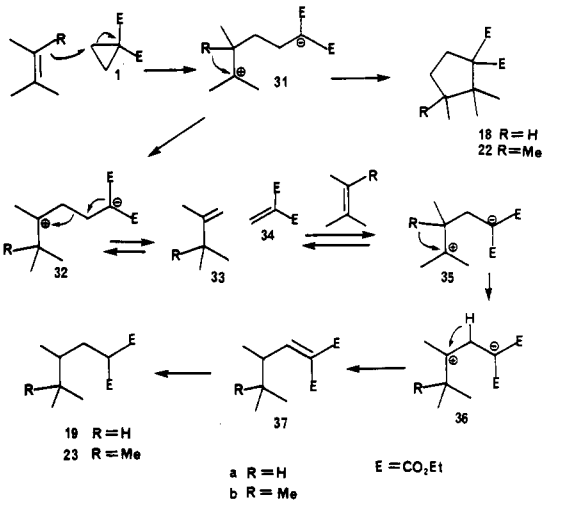
In order to test this analysis, the reaction of **1** with 1,4,4-trimethylcyclohexene was examined. Conformation **30a** of the zwitterionic intermediate is destabilized by a 1,3-diaxial interaction so that the trans-fused isomer **16** should be formed from **30b** in addition to the cis-fused isomer **15** from **30a**. The formation of a 2:1 mixture of **15** and **16** indicates that formation of the trans-fused isomer is a significant process from the equatorial conformer **30b**.



The absence of significant amounts of the trans-fused adduct in the reaction of **1** and 1-methylcyclohexene confirms that the cis-fused isomer **10** is formed mainly from the conformer of the zwitterion with an axial side chain by equatorial attack.

The reaction of 2-methyl-2-butene with **1** gives a 30:1 mixture of **18** and **19** in 86% yield. Since **19** appears to have lost a carbon, the structure was confirmed by synthesis. Alkylation[18] of diethyl malonate with 1-bromo-2,3-dimethylbutane[19] gives **19** which was spectroscopically

Scheme I



and chromatographically identical with the isolated material.

A possible mechanism for the formation of **19** is indicated in Scheme I. Zwitterion **31a** can collapse to give **18** or undergo a 1,2-hydride shift to give **32a**. Zwitterion **32a** can collapse reversibly to give a cyclobutane[20] or fragment to give **33a** and diethyl methylenemalonate (**34**). Addition of the reactive electrophile **34** to 2-methyl-2-butene, which is present in greater amounts than **33a**, will give **35a**. Two 1,2-hybride shifts will give **37a** which will be reduced by $EtAlCl_2$, which can donate a β-hydride, to give **19**. Similar products are also undoubtedly formed from other trisubstituted alkenes but could not be characterized due to their greater structural complexity.

Reaction of either (*E*)- or (*Z*)-3-methyl-2-pentene with **1** gives an identical 4:1 mixture of **20** and **21**. This indicates that the stereochemistry of the alkene is not preserved. The zwitterion undergoes free rotation which scrambles the stereochemistry. The major product is the more stable isomer which suggests that the stereochemical interactions present in the product are also present in the transition state leading to ring closure. The stereochemistry is established by analysis of the NMR spectra. The C_2 methyl protons of **21** absorb at δ 1.10 while the C_2 methyl protons of **20**, which are shielded by the *cis*-C_3-methyl group, absorb at δ 0.87. Similar shielding is observed in the ^{13}C NMR spectra. The C_2 methyl carbon absorbs at δ 25.1 in **21** and δ 15.7 in **20**.

Reaction of 2,3-dimethyl-2-butene with **1** gives a 12:1 mixture of **22** and **23** in 79% yield. The substituted malonate **23** is formed as indicated in Scheme I. In this case 1,2-methyl shifts occur in the formation of **32b** and **37b**. 2-Methyl-1-propenyl trimethylsilyl ether reacts with **1** to give a 48% yield of cyclopentanol **24**, indicating that silyl enol ethers are suitable substrates. Further studies on the utility of enol ethers in this reaction are in progress.

These results clearly indicate the scope and limitations of this cyclopentane annelation reaction. Alkenes containing a disubstituted vinylic carbon, which give rise to a zwitterion containing a tertiary carbocation, are generally suitable substrates. Tri- and tetrasubstituted alkenes give zwitterions such as **31** which can undergo a 1,2-hydride or methyl shift which initiates a process leading to side products such as **19** or **23**. Fortunately, this appears to be a relatively minor side reaction in most cases. Alkenes such as 1,6-dimethylcyclohexene and 2-methylmethylenecyclo-

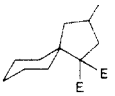
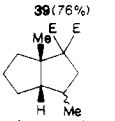
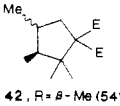
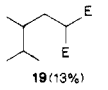
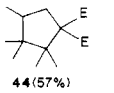
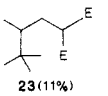
(17) For related discussions see: Crandall, J. K.; Magaha, H. S.; Widener, R. K.; Tharp, G. A. *Tetrahedron Lett.* **1980**, *21*, 4807. Macdonald, T. L.; Mahalingam, S.; O'Dell, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 6767. Crandall, J. K.; Magaha, H. S.; Henderson, M. A.; Widener, R. K.; Tharp, G. A. *J. Org. Chem.* **1982**, *47*, 5372. Crandall, J. K.; Magaha, H. S. *J. Org. Chem.* **1982**, *47*, 5368. Macdonald, T. L.; Mahalingam, S. *Tetrahedron Lett.* **1981**, *22*, 2077. Majetich, G.; Desmond, R. W., Jr.; Soria, J. J. *J. Org. Chem.* **1986**, *51*, 1753. Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778. These cases differ significantly in that the nucleophile is not sterically hindered so that there is no preference for equatorial attack.

(18) Marvel, C. S. *Org. Syn. Coll. Vol. 3*, **1955**, 495.

(19) Tsuda, K.; Kishida, Y.; Hayatsu, R. *J. Am. Chem. Soc.* **1960**, *82*, 3396. Giacomelli, G.; Menicagli, R.; Caporusso, A. M.; Lardicci, L. *J. Org. Chem.* **1978**, *43*, 1790.

(20) Snider, B. B.; Rodini, D. J.; van Straten, J. *J. Am. Chem. Soc.* **1980**, *102*, 5872.

Table II. Lewis Acid Induced Reactions of Diethyl 2-Methylcyclopropane-1,1-dicarboxylate (38) with Alkenes

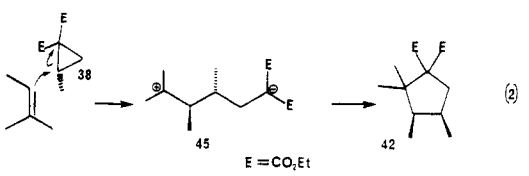
alkene	adducts (% yield)[a]
	 39(76%)
	 40, R = α-Me(54%) 41, R = β-Me(18%)
	 42, R = β-Me(54%) 43, R = α-Me(11%)  19(13%)
	 44(57%)  23(11%)

[a] E = CO_2Et.

hexane give zwitterions, e.g., **25**, which undergo facile 1,2-hydride shifts giving zwitterions, e.g., **26**, which can collapse to give cyclohexanes. In these cases complex mixtures of products are obtained. Mono- and 1,2-disubstituted alkenes give zwitterions containing unstable secondary carbocations which undergo rearrangements leading to complex mixtures of products.

Reactions of Substituted Cyclopropanedicarboxylates 38 and 46. The reactions of substituted cyclopropanedicarboxylates were examined to determine the scope of the reaction and the positional selectivity (see Table II). Reaction of methylenecyclohexane with diethyl 2-methylcyclopropane-1,1-dicarboxylate (**38**)[21] gives a 76% yield of **39**. Analysis of the ^1H and ^{13}C NMR spectra shows that the methyl group is at C_3 indicating that the alkene has added to the more substituted carbon of **38**.

Reaction of **38** with 1-methylcyclopentene gives a 3:1 mixture of **40** and **41**. The major isomer **40** has the methyl group endo as shown by the shielding of C_4, C_5, C_6, and C_4CH_3 in the ^{13}C NMR spectra relative to those of **41**. Treatment of **38** with 2-methyl-2-butene gives a 54:11 mixture of **42** and **43** in 65% yield and a 13% yield of **19**. The major isomer **42** has cis-methyl groups as indicated by the methyl doublets at δ 0.91 and 0.79 in the ^1H NMR spectrum. The methyl doublets of the trans isomer **43** absorb at δ 0.82 and 1.00. The formation of the less stable isomers **40** and **42** as the major products suggests that zwitterionic intermediates such as **45** are formed in an open transition state as indicated in eq 2. Treatment of **38** with 2,3-dimethyl-2-butene gives a 57% yield of **44** and an 11% yield of **23**. The formation of **19** and **23** from **38** provides support for the mechanism proposed in Scheme I.

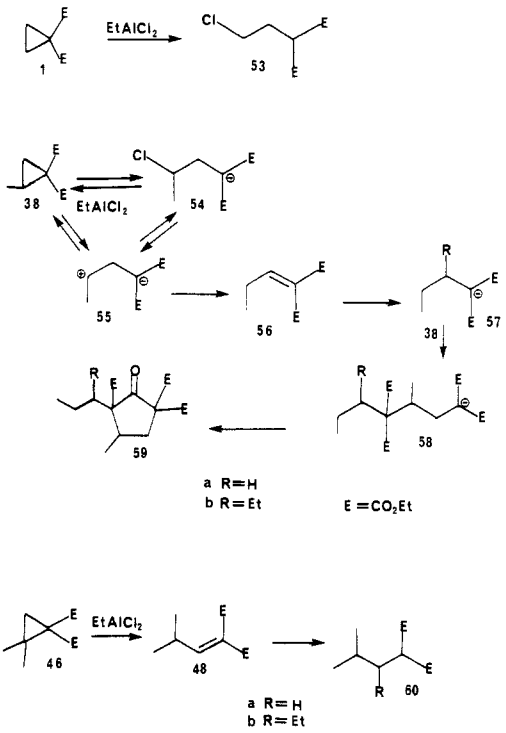


(2)

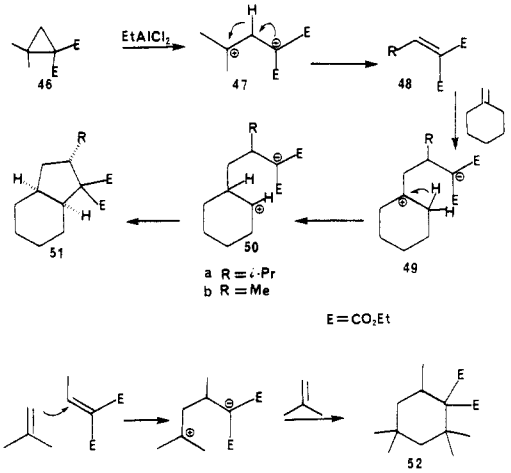
Treatment of methylenecyclohexane with diethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate (**46**)[21] and $EtAlCl_2$ gives a complex mixture of products from which **51a** was isolated in 28% yield. In the presence of Lewis acid **46** opens rapidly to **47** which undergoes a 1,2-hydride shift

(21) Landor, S. R.; Punja, N. *J. Chem. Soc. C* **1967**, 2495.

Scheme II



to give **48a**. Ester **48a** reacts with methylenecyclohexane to give **49a**. Zwitterion **49a** can fragment to regenerate **48a**, undergo reversible closure to give a cyclobutane,[20] or undergo a 1,2-hydride shift to give the unstable secondary carbocation **50a** which can collapse irreversibly to give **51a**. The gross structure of **51a** is established by the presence of three methine carbons in the ^{13}C NMR spectrum and confirmed by the reaction of methylenecyclohexane with diethyl ethylidenemalonate (**48b**) and $EtAlCl_2$ to give a 27% yield of **51b**. **51** is assumed to be the most stable isomer as shown since the stereochemistry is generated in the reversible hydride shift which gives **50**. Reaction of isobutylene with **48b** cannot proceed analogously since the zwitterion corresponding to **50b** would contain a primary carbocation. Instead the 2:1 adduct **52** is formed in 55% yield.



The reactions of cyclopropanes **1**, **38**, and **46** with 2 equiv of $EtAlCl_2$ in the absence of alkene were examined. The unsubstituted diester **1** reacts slowly undergoing 15% conversion to chloride **53** after 3 days. The monosubstituted diester **38** undergoes a complicated series of reactions as indicated in Scheme II and Table III. Chloride **54** is formed rapidly and reversibly. Zwitterion **55** rearranges

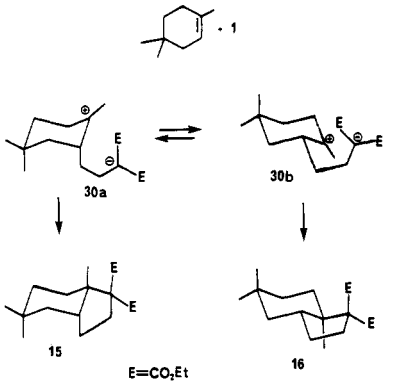
Table III. Reaction of Diethyl 2-Methylcyclopropane-1,1-dicarboxylate (38) with 2 Equiv of $EtAlCl_2$

time, h	54, %	57b, %	38, %	57a, %	59a, %	59b, %
0.25	11.3	3.6	85.1	*a*		
0.50	9.6	5.7	84.7	*a*		
1.0	9.3	9.9	80.7	*a*		
2.0	7.8	13.7	78.5	*a*		
4.0	10.2	29.3	60.5	*a*		
8.0	3.1	54.4	42.6	*a*		
16.0	1.1	89.3	4.8	8.8		
24.0	0.5	91.6	1.9	8.9	trace	trace
48.0	...	73.8	...	7.1	15.0	2.3
72.0	...	68.5	...	7.3	18.8	5.4

[a] Hidden by unreacted **38**.

to **56**, which in the absence of alkene reacts with $EtAlCl_2$ to give **57a** and **57b**. Malonate **57** reacts with **38** to give **58** which undergoes a Dieckmann cyclization to give **59**. The results in Table III indicate the relative amounts of products observed by GC. To accurately reflect product ratios **58** should be included. Unfortunately this dimer was not observed on the GC trace due its low volatility and high polarity. The disubstituted diester **46** rearranges rapidly to **48a** which reacts with $EtAlCl_2$ to give **60a** and **60b**.

Intramolecular Reactions. Lewis acid catalyzed cation–olefin cyclization reactions of cyclopropyl ketones to alkenes with give zwitterions which collapse to cyclopropyl ketones are well-known.[9-11] Therefore, we expected doubly activated cyclopropanes to be very effective initiators for cation–olefin cyclizations. Knoevenagel condensation[22] of aldehydes **61** and **65** with diethyl malonate gives **62** and **66**. Reaction with dimethylsulfoxonium methylide[21] gives **63** and **67** as a ca. 1:1 mixture of diastereomers. Treatment of **63** and **67** with $EtAlCl_2$ gives **64** and **68** in 70% and 73% yield, respectively. In both cases only two of the four possible diastereomers were formed. Unfortunately the available data do not permit assignment of stereochemistry.



Conclusion

The results described above indicate that treatment of 1,1-di-, tri-, and tetrasubstituted alkenes with diethyl cyclopropane-1,1-dicarboxylate (**1**) and 2 equiv of $EtAlCl_2$ gives zwitterions which collapse to cyclopentanedicarboxylates in good to excellent yield. This reaction thus provides a general procedure for the annelation of cyclopentanes to alkenes and a particularly valuable route for the synthesis of spirocyclic systems. The intermediate zwitterions undergo the 1,2-hydride and -methyl shifts characteristic of carbocations, although these side reactions are generally minor. Diethyl 2-methylcyclopropane-1,1-dicarboxylate (**38**) reacts similarly with alkenes at the more substituted carbon to give 3-methyl-1,1-cyclopentanedicarboxylates. Diethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate (**46**) rearranges to diethyl isobutylidenemalonate which reacts with alkenes and is reduced by $EtAlCl_2$. The intramolecular Lewis acid induced addition of alkenes to cyclopropanedicarboxylate esters occur analogously. We are continuing to explore these reactions, especially with enol ethers, and are exploiting them in total synthesis.

Experimental Section

Materials and Methods. NMR spectra were recorded on Varian EM-390 and XL-300 spectrometers in $CDCl_3$. IR spectra were obtained on a Perkin-Elmer 683 spectrometer. GC chromatography was performed on 10% XF-1150 on Chromosorb PNAW 60/80 columns. Analytical studies were carried out on a 6 ft × $^1/_4$ in. column while preparative work was performed by using a 7 ft × $^3/_8$ in. column. Combustion analyses were performed by Galbraith Laboratories, Inc. MPLC refers to medium-pressure liquid chromatography on a Merck Lobar silica gel column.

Dichloromethane and 1,2-dichloroethane were dried by distillation from calcium hydride. Diethyl ether and THF were dried by distillation from sodium benzophenone ketyl. $EtAlCl_2$ was obtained from Texas Alkyls, Inc., as a solution in hexane. Diethyl cyclopropane-1,1-dicarboxylate was obtained from the Aldrich Chemical Co. and used without further purification. Alkenes, unless otherwise noted, were commercial products used without further purification. 3-Methylmethylenecyclohexane,[23] 4-methylmethylenecyclohexane,[23] 4-*tert*-butylmethylenecyclohexane,[23] 1,4,4-trimethylcyclohexene,[24] and 2-methyl-1-propenyl trimethylsilyl ether[25] were prepared by the literature procedures. Diethyl 2-methylcyclopropane-1,1-dicarboxylate (**38**) and diethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate (**46**) were prepared by the procedure of Landor and Punja[21] in 48% and 63% yields, respectively.

All air-sensitive reactions were run under nitrogen in flame-dried glassware with magnetic stirring. Reagents were added via oven-dried syringes through septa.

Diethyl Spiro[4.5]decane-1,1-dicarboxylate (3). $EtAlCl_2$ (2.32 mL of a 1.44 M hexane solution, 3.34 mmol) was added slowly via syringe to methylenecyclohexane (0.20 mL, 160 mg, 1.66 mmol) and **1** (0.29 mL, 306 mg, 1.64 mmol) in 5 mL of dry 1,2-dichloroethane at 0 °C. The reaction mixture was stirred for 5 min at 0 °C, then warmed to room temperature, and stirred for an additional 48 h before quenching by the slow dropwise addition of 10 mL of water followed by 6 mL of 1.5 M aqueous HCl. The resulting mixture was diluted with 5 mL of dichloromethane and stirred vigorously until all precipated aluminum hydroxide had redissolved. The layers were separated, the aqueous phase was extracted with dichloromethane (3 × 20 mL), and the combined organic phases were dried ($MgSO_4$). Filtration and concentration in vacuo gave 486 mg of a clear viscous oil, which contained traces of 1,2-dichloroethane. Evaporative distillation (90 °C, 1.25–1.75 torr) gave 453 mg (98%) of **3** as a colorless oil: ^1H NMR δ 4.15 (dq, 2, J = 10.8, 7.0 Hz, OEt), 4.13 (dq, 2, J = 10.8, 7.0 Hz, OEt), 2.16–2.24 (m, 2, C_2H), 1.86–1.93 (m, 2, C_4H), 1.66–1.77 (m, 2, C_3H), 1.06–1.64 (m br, 10, $C_{6-10}H$), 1.23 (t, 6, J = 7.0 Hz, OEt); ^{13}C NMR δ 171.4 (C=O), 67.9 (C_1), 60.6 (OEt), 49.5 (C_5), 32.2 (C_4), 32.1 (C_2), 31.5 ($C_{6,10}$), 26.0 (C_8), 23.1 ($C_{7,9}$), 19.8 (C_3), 14.0 (OEt); assignments for C_2–C_4 and respective protons are based on single-frequency $^{13}C\{^1H\}$ decoupling experiments; IR (neat) 1725 cm^{-1}; t_R 11.5 min (180 °C, 35 mL/min). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.23; H, 9.04.

Diethyl 8-Methylspiro[4.5]decane-1,1-dicarboxylate (6). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 4-methylmethylenecyclohexane (0.20 mL, 157 mg, 1.42 mmol), and

(22) Cope, A. C.; Hoyle, K. E.; Heyl, D. *J. Am. Chem. Soc.* **1941**, *63*, 1843.

(23) Senda, Y.; Kamiyama, S.; Imaizumi, S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 530.

(24) Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535.

(25) Mukaiyama, T.; Banno, K.; Narasaka, K. *J. Am. Chem. Soc.* **1974**, *96*, 7503.

1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 48 h. Normal workup and evaporative distillation (98 °C, 0.75 torr) gave 311.4 mg (74%) of **6** as a colorless oil: ^{1}H NMR δ 4.00–4.20 (m, 4, OEt), 2.12–2.22 (m, 2, C_2H), 1.78–1.89 (m, 2, C_4H), 1.61–1.75 (m, 2, C_3H), 1.30–1.60 (m, 6), 1.19 (t, 6, J = 7.1 Hz, OEt), 0.82–1.05 (m, 3), 0.80 (d, 3, J = 6.7 Hz, C_8CH_3); ^{13}C NMR δ 171.3 (C=O), 67.6 (C_1), 60.5 (OEt), 49.0 (C_5), 32.3 (C_8), 32.2 (C_4), 32.1 (C2), 31.7 ($C_{7,9}$), 31.4 ($C_{6,10}$), 22.4 (C_8CH_3), 19.7 (C_3), 14.0 (OEt) assignments for C_2 and C_4 are based on single-frequency ^{13}C{^{1}H} decoupling experiments; IR (neat) 1730 cm^{-1}; t_R 12.0 min (180 °C, 30 mL/min). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.65; H, 9.49.

Diethyl 8-*tert*-Butylspiro[4.5]decane-1,1-dicarboxylate (7). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 4-*tert*-butylmethylenecyclohexane (0.20 mL, 160 mg, 1.66 mmol) and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 60 h. Normal workup and evaporative distillation (115 °C, 0.75 torr) gave 381.7 mg (79%) of **7** as a clear colorless oil: ^{1}H NMR δ 4.13 (q, 4, J = 7.1 Hz, OEt), 2.12–2.28 (m, 2, C_2H), 1.78–1.90 (m, 2, C_4H), 1.63–1.77 (m, 2, C_3H), 1.48–1.62 (m, 6), 1.22 (t, 6, J = 7.1 Hz, OEt), 0.96–1.16 (m, 3), 0.80 (s, 9, CMe_3); ^{13}C NMR δ 171.4 (C=O), 67.6 (C_1), 60.6 (OEt), 49.2 (C_5), 47.7 (C_8), 32.3, 32.2, 31.9, 27.5 (CCH_3), 23.8 ($C_{7,9}$), 19.7 (C_3), 14.1 (OEt), the quaternary *tert*-butyl carbon resonance was not observed; IR (neat) 1728 cm^{-1}; t_R 15.1 min (180 °C, 37 mL/min). Anal. Calcd for $C_{20}H_{34}O_4$: C, 70.97; H, 10.12. Found: C, 70.61; H, 10.46.

Diethyl 7-Methylspiro[4.5]decane-1,1-dicarboxylate (8). $EtAlCl_2$ (0.37 mL of a 1.44 M hexane solution, 0.55 mmol), 3-methylmethylenecyclohexane (30 mg, 0.27 mmol) and 1 (50 mg, 0.27 mmol) were reacted as described above for 90 h. Normal workup gave 55.8 mg (69%) of crude product. Analytical GC indicated one major component (73% pure). An analytical sample of the major component **8** (50% yield) was prepared by preparative GC: ^{1}H NMR δ 4.08–4.21 (m, 4, OEt), 2.18–2.27 (m, 2, C_2H), 1.85–1.92 (m, 2, C_4H), 1.67–1.78 (m, 2, C_3H), 1.23 (t, 6, J = 7.0 Hz, OEt), 1.20–1.66 (m, 9), 0.83 (d, 3, J = 6.4 Hz); ^{13}C NMR 171.39 (C=O), 171.35 (C=O), 67.8 (C_1), 60.6 (OEt), 50.0 (C_5), 40.4 (C_6), 34.8 (C_8), 32.9, 32.1, 31.0 (C_2, C_4, or C_{10}), 29.2 (C_7), 23.1 (C_7CH_3), 22.9 (C_9), 19.9 (C_3), 14.1 (OEt); IR 1725 cm^{-1}; t_R 10.6 min (180 °C, 64 mL/min).

Diethyl 4-Methylspiro[4.5]decane-1,1-dicarboxylate (9). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), ethylidenecyclohexane (0.19 mL, 156 mg, 1.42 mmol), and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 50 h. Normal workup gave 418.7 mg (100%) of crude product. Analytical GC indicated one major component (87%) and at least five minor components. The major component **9** (87% yield) was isolated via preparative GC: ^{1}H NMR δ 4.00–4.22 (m, 4, OEt), 1.27 (t, 3, J = 7.0 Hz, OEt), 1.16 (t, 3, J = 7.0 Hz, OEt), 1.04 (d, 3, J = 6.8 Hz, C_4CH_3), 0.95–2.48 (m, 15); ^{13}C NMR δ 171.4 (C=O), 171.1 (C=O), 68.7 (C_1), 60.6 (OEt), 60.5 (OEt), 50.0 (C_5), 39.0 (C_4), 34.5, 31.5, 30.9 (C_2, C_6, C_{10}), 27.2, 25.5 (C_3, C_8), 23.7, 22.6 (C_7, C_9), 18.2 (C_4CH_3), 14.0 (OEt), 13.9 (OEt); IR (neat) 1729 cm^{-1}; t_R 15.5 min (180 °C, 58 mL/min). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 67.50, 67.28; H, 9.68, 9.45.

Diethyl 6-Methylbicyclo[4.3.0]nonane-7,7-dicarboxylate (10). $EtAlCl_2$ (1.97 mL of a 1.44 M hexane solution, 2.84 mmol), 1-methylcyclohexene (0.17 mL, 138.5 mg, 1.44 mmol), and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 5 days. Normal workup and evaporative distillation (98 °C, 1.25 torr) gave 261 mg (65%) of **10** as a clear colorless oil: ^{1}H NMR δ 4.01–4.23 (m, 4, OEt), 2.33–2.51 (m, 2, C_8H), 1.95–2.07 (m, 1), 1.66–1.79 (m, 2), 1.22 (t, 3, J = 7.0 Hz, OEt), 1.20 (s, 3, C_6CH_3), 1.19 (t, 3, J = 7.0 Hz, OEt), 1.03–1.55 (m, 8); ^{13}C NMR δ 172.4 (C=O), 171.0 (C=O), 68.9 (C_7), 60.8 (OEt), 60.7 (OEt), 46.3 (C_6), 42.4 (C_1), 30.3, 29.7 (C_5 and C_8), 24.7, 23.9 (C_2 and C_9), 21.7, 19.8 (C_3 and C_4), 18.7 (C_6CH_3), 14.1 (OEt); IR (neat) 1728 cm^{-1}; t_R 13.6 min (180 °C, 35 mL/min). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.06; H, 9.28. Found: C, 68.18; H, 9.15.

A singlet at δ 0.77 in the ^{1}H NMR spectrum indicates that ca. 5% of the product with a trans ring fusion is present.

Diethyl 6-Methyl-3-isopropylbicyclo[4.3.0]nonane-7,7-dicarboxylate (11). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 1-menthene (0.24 mL, 196.3 mg, 1.42 mmol), and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 6 days. Normal workup gave 469.5 mg (100%) of a thick viscous oil. Analytical GC showed one major component (87%) and five minor components. The major component **11** (87% yield) was isolated by preparative GC: ^{1}H NMR δ 4.09–4.25 (m, 4, OEt), 2.39–2.55 (m, 2), 1.97–2.10 (m, 1), 1.27 (t, 3, J = 7.0 Hz, OEt), 1.23 (t, 3, J = 7.0 Hz, OEt), 1.21 (s, 3, C_6CH_3), 0.87 (d, 6, J = 6.5 Hz, $CH(CH_3)_2$), 0.79–1.89 (m, 10); ^{13}C NMR δ 172.4 (C=O), 171.0 (C=O), 68.8 (C_7), 60.7 (OEt), 60.6 (OEt), 46.3 (C_6), 43.1 (C_1), 37.1 (C_3), 32.7 ($CH(CH_3)_2$), 30.30, 30.26, 27.8, 25.5, 25.1, 19.9 ($CH(CH_3)_2$), 19.8 ($CH(CH_3)_2$), 18.8 (C_6CH_3), 14.1 (OEt); IR (neat) 1735 cm^{-1}; t_R 20.7 min (180 °C, 64 mL/min). Anal. Calcd for $C_{19}H_{32}O_4$: C, 70.34; H, 9.94. Found: C, 70.40; H, 10.20.

A singlet at δ 0.80 in the ^{1}H NMR spectrum indicates that ca. 15% of a product with a trans-ring fusion is present.

Diethyl 2,6-Dimethylbicyclo[4.3.0]nonane-7,7-dicarboxylate (12–14). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 1,3-dimethylcyclohexene (0.19 mL, 156.5 mg, 1.42 mmol), and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 4 days. Normal workup gave 401.7 mg (95%) of a pale yellow oil. GC analysis showed two peaks in a 1.5:1 ratio. Analysis of the ^{13}C NMR spectrum indicated that at least three different compounds were present. The peaks were then separated via preparative GC.

The spectral data for the major product **12** follow: ^{1}H NMR δ 4.16 (q, 2, J = 7.1 Hz, OEt), 4.07–4.16 (m, 2, OEt), 2.32–2.45 (m, 2), 2.00–2.12 (m, 1), 1.69–1.90 (m, 3), 1.24 (t, 3, J = 7.1 Hz, OEt), 1.21 (t, 3, J = 7.1 Hz, OEt), 1.10–1.68 (m, 6), 0.82 (d, 3, J = 6.3 Hz, C_2CH_3), 0.80 (s, 3, C_6CH_3); ^{13}C NMR δ 172.1 (C=O), 171.4 (C=O), 67.4 (C_7), 60.8 (OEt), 60.3 (OEt), 51.3 (C_1), 47.7 (C_6), 35.0, 33.4, 31.7 (C_2), 30.1, 24.6, 22.0, 20.5, 15.9, 14.1 (OEt); IR (neat) 1730 cm^{-1}; t_R 13.9 min (180 °C, 52 mL/min). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89, H, 9.52. Found: C, 67.33, 67.29; H, 9.22, 9.41.

The minor peak, t_R 15.3 min (180 °C, 52 mL/min), was an approximately 1:1 mixture of the two products **13** and **14** with a cis-ring fusion. Only partial separation of these two products could be accomplished by capillary GC. Assignment of peaks in the NMR spectra to a particular compound was not attempted: ^{1}H NMR δ 1.29 (s, 3, C_6CH_3), 1.22 (s, 3, C_6CH_3), 1.02 (d, 3, J = 6.5 Hz, C_2CH_3), 0.82 (d, 3, J = 6.5 Hz, C_2CH_3); ^{13}C NMR δ 172.3 (C=O), 172.1 (C=O), 171.9 (C=O), 171.2 (C=O), 69.1, 68.5, 60.5 (OEt), 49.4, 48.4, 47.1, 46.0, 43.6, 30.6, 29.8, 29.0, 28.0, 26.5, 22.0, 20.5, 18.6, 15.8, 14.0.

Diethyl 3,3,6-Trimethylbicyclo[4.3.0]nonane-7,7-dicarboxylate (15 and 16). $EtAlCl_2$ (1.13 mL of a 1.44 M hexane solution, 1.63 mmol), 1,4,4-trimethylcyclohexene (101.8 mg, 0.82 mmol) and 1 (0.144 mL, 152.7 mg, 0.82 mmol) were reacted as described above for 4 days. Normal workup and evaporative distillation gave 193.4 mg (76%) of a colorless oil shown to be a 2:1 mixture of **15** and **16** and two minor components. Adducts **15** and **16** were isolated by preparative GC.

The spectral data for **15** follow: ^{1}H NMR δ 4.10–4.26 (m, 4 OEt), 2.40–2.55 (m, 2), 1.85–2.05 (m, 2), 1.70–1.84 (m, 1), 1.28 (t, 3, J = 7.1 Hz), 1.24 (t, 3, J = 7.1 Hz), 1.20 (s, 3), 1.10–1.60 (m, 6), 0.96 (s, 3), 0.89 (s, 3); ^{13}C NMR δ 172.0 (C=O), 171.1 (C=O), 68.7 (C_7), 60.7 (OEt), 60.6 (OEt), 46.0 (C_6), 42.5, 37.5, 34.4, 34.1, 30.9, 29.4 (C_3), 27.3, 27.2, 27.0, 19.8, 14.1 (OEt); t_R 9.3 min (180 °C 50 mL/min).

The spectral data for **16** follow: ^{1}H NMR δ 4.09–4.16 (4, m, OEt), 2.40–2.52 (m, 2), 2.10 (ddd, 1, J = 14.8, 9.5, 6.7 Hz), 1.92 (ddd, 1, J = 4.5, 13.2, 13.2 Hz), 1.60–1.70 (m, 2), 1.27 (t, 3, J = 7.1 Hz, OEt), 1.24 (t, 3, J = 7.1 Hz, OEt), 0.94 (s, 3), 0.93 (s, 3), 0.83–1.43 (m, 5), 0.76 (s, 3); ^{13}C NMR δ 172.2 (C=O), 171.4 (C=O), 66.5 (C_7), 60.8 (OEt), 60.7 (OEt), 47.4 (C_6), 39.9, 39.1, 35.0, 33.0, 31.0 (C_3), 30.7, 29.4, 26.1, 26.0, 14.5, 14.1 (OEt); t_R 8.1 min (180 °C, 50 mL/min).

Diethyl 1-Methylbicyclo[3.3.0]octane-2,2-dicarboxylate (17). $EtAlCl_2$ (1.97 mL of a 1.44 M hexane solution, 2.84 mmol), 1-methylcyclopentene (0.15 mL, 118.3 mg, 1.44 mmol), and 1 (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 5 days. Normal workup and evaporative distillation (90 °C, 1.50 torr) gave 292.3 mg (77%) of **17** as a clear colorless oil: ^{1}H NMR δ 4.16 (q, 2, J = 7.1 Hz, OEt), 4.04–4.22 (m, 2, OEt), 2.37 (m, 2, C_3H), 1.84–2.38 (m, 5), 1.50–1.70 (m, 2), 1.22–1.46 (m, 2), 1.24 (t, 3, J = 7.1 Hz, OEt) 1.21 (t, 3, J = 7.1 Hz, OEt), 1.20 (s, 3, C_1Me); ^{13}C NMR δ 172.9, 171.7, 67.8 (C_2), 60.7, 60.6, 56.1 (C_1), 50.4 (C_5), 38.2 (C_8), 33.8, 32.8 (C_3, C_6), 30.1 (C_4), 24.6 (C_7), 23.0 (C_1 Me), 14.0; IR (neat) 1738, 1725 cm^{-1}; t_R 7.7 min (180 °C, 34 mL/min). Anal.

Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.48; H, 9.14.

Diethyl 2,2,3-Trimethylcyclopentane-1,1-dicarboxylate (18). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 2-methyl-2-butene (0.15 mL, 98.2 mg, 1.44 mmol), and **1** (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 42 h. Normal workup gave 314.3 mg (86%) of a 30:1 mixture of **18** and **19** as a clear oil. Pure samples were prepared by preparative GC.

The spectral data for **18** follow: ^1H NMR δ 4.00–4.20 (m, 4, OEt), 2.20–2.40 (m, 2, C_5H), 1.78–2.05 (m, 2), 1.15–1.34 (m, 1), 1.20 (t, 3, J = 7.0 Hz, OEt), 1.16 (t, 3, J = 7.1 Hz, OEt), 1.11 (s, 3, C_2CH_3), 0.79 (d, 3, J = 6.8 Hz, C_3CH_3), 0.69 (s, 3, C_2CH_3); ^{13}C NMR δ 172.2, 171.0, 67.4 (C_1), 60.6, 60.5, 47.0 (C_2), 41.7 (C_5), 30.5, 29.2 (C_3, C_4), 21.9 (C_2 *trans*-CH_3), 18.3 (C_2 *cis*-CH_3), 13.9 (C_3CH_3), 13.8; IR (neat) 1730 cm^{-1}; t_R 3.2 min (180 °C, 35 mL/min).

The spectral data for **19** are identical with those of an authentic sample (vide infra): t_R 2.6 min (180 °C, 35 mL/min).

1-Bromo-2,3-dimethylbutane was prepared from 2,3-dimethylbutan-1-ol and PBr_5 in 60% yield by the procedure of Tsuda et al.:[19] ^1H NMR δ 3.44 (dd, 1, J = 4.1, 9.9 Hz, C_1H), 3.33 (dd, 1, J = 6.8, 9.9 Hz, C_1H), 1.58–1.80 (m, 2, $C_{2,3}H$), 0.97 (d, 3, J = 6.8 Hz), 0.92 (d, 3, J = 6.8 Hz), 0.86 (d, 3, J = 6.8 Hz); ^{13}C NMR δ 41.2, 40.0, 30.6, 20.4, 18.0, 15.0.

Diethyl (2,3-Dimethylbutyl)malonate (19). 1-Bromo-2,3-dimethylbutane (0.59 mL, 701.6 mg, 4.25 mmol) was added slowly to a solution of Na (100 mg, 4.35 mmol) and diethyl malonate (0.73 mL, 696.7 mg, 4.35 mmol) in 10 mL of anhydrous ethanol. The reaction mixture was heated at reflux for 16 h, and 8 mL of ethanol was removed via simple distillation. The mixture was cooled to 20 °C and quenched by the addition of 10 mL of water and 5 mL of hexane. The layers were separated, and the aqueous phase was extracted with hexane (3 × 10 mL). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo to give 869 mg of **19** (86%) as a yellow oil. An analytical sample was prepared by preparative GC: ^1H NMR δ 4.12–4.25 (m, 4, OEt), 3.40 (dd, 1, J = 9.5, 5.8 Hz, C_1H) 2.00 (ddd, 1, J = 4.6, 9.9, 14.0 Hz), 1.63 (ddd, 1, J = 6.0, 9.3, 14.0 Hz), 1.57 (m, 1), 1.32 (m, 1), 1.27 (t, 3, J = 7.1 Hz, OEt), 1.26 (t, 3, J = 7.1 Hz, OEt), 0.87 (d, 3, J = 6.8 Hz, C_3CH_3), 0.83 (d, 6, J = 6.8 Hz, $CH(CH_3)_2$); ^{13}C NMR δ 169.9 (C=O), 169.7 (C=O), 61.3 (OEt), 61.2 (OEt), 50.4 (C_1), 36.3, 33.1, 31.9, 19.8, 17.8, 14.9, 14.1 (OEt).

Diethyl 2,3-Dimethyl-2-ethylcyclopentane-1,1-dicarboxylate (20 and 21). $EtAlCl_2$ (2.30 mL of a 1.44 M hexane solution, 3.32 mmol), (*Z*)-3-methyl-2-pentene (0.20 mL, 140 mg, 1.66 mmol), and **1** (0.29 mL, 309 mg, 1.66 mmol) were reacted for 60 h. Normal workup gave 345.3 mg of a clear colorless oil. Analytical GC and ^{13}C NMR spectroscopy showed the product to be a 4:1 mixture of cyclopentane diastereomers with a trace of a faster eluting impurity which is probably diethyl 2,3-dimethylpentylmalonate. The yield of the cyclopentane adducts **20** and **21** is 73%. IR (neat): 1729 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 64.08, 63.95; H, 9.34, 9.43.

The spectral data for the major isomer **20** determined from the mixture follow: ^1H NMR δ 4.07–4.18 (m, 4, OEt) 1.85–2.32 (m, 3), 1.50–1.66 (m, 2), 1.23 (t, 3, J = 7.0 Hz, OEt), 1.22 (t, 3, J = 7.0 Hz, OEt), 0.90 (t, 3, J = 6.9 Hz, CCH_2CH_3), 0.89 (d, 3, J = 6.9 Hz, C_3CH_3), 0.87 (s, 3, C_2CH_3); ^{13}C NMR δ 172.3 (C=O), 171.1 (C=O), 68.1 (C_1), 60.6 (OEt), 60.4 (OEt), 49.7 (C_2), 41.1, 31.4, 30.1, 29.7 (CCH_2CH_3), 15.7 (C_2CH_3), 15.1 (C_3CH_3), 13.9 (OEt), 9.5 (CCH_2CH_3); t_R 4.1 min (180 °C, 50 mL/min).

The spectral data for the minor isomer **21** determined from the mixture follow: ^1H NMR δ 1.10 (s, 3, C_2CH_3), 0.81 (t, 3, J = 6.7 Hz, CCH_2CH_3); ^{13}C NMR δ 172.2 (C=O), 171.8 (C=O), 67.7 (C_1), 61.3, (OEt), 61.1 (OEt), 49.6 (C_2), 42.9, 31.2, 29.9, 25.1 (CCH_2CH_3), 21.0 (C_2CH_3), 14.9 (C_3CH_3), 13.9 (OEt), 10.2 (CCH_2CH_3); t_R 4.1 min (180 °C, 50 mL/min).

A similar reaction carried out with (*E*)-3-methyl-2-pentene gave an identical mixture of products.

Diethyl 2,2,3,3-Tetramethylcyclopentane-1,1-dicarboxylate (22). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), 2,3-dimethyl-2-butene (0.17 mL, 121 mg, 1.44 mmol), and **1** (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 48 h. Normal workup gave 304.9 mg (79%) of crude product as a pale yellow oil. GC analysis showed the crude reaction product to be a mixture of **22** and diethyl 2,3,3-trimethylbutylmalonate (**23**) in a 12:1 ratio. The yield of **22** is 73%. Analytical samples were obtained by preparative GC.

The spectral data for **22** follow: ^1H NMR δ 4.11 (q, 4, J = 7.1 Hz, OEt), 2.29–2.38 (m, 2, C_5H), 1.52–1.61 (m, 2, C_4H), 1.21 (t, 6, J = 7.1 Hz, OEt), 1.03 (s, 6, C_2CH_3), 0.91 (s, 6, C_3CH_3); ^{13}C NMR δ 171.8, 66.9, 60.8, 49.4, 44.7, 37.9, 30.6, 25.9, 21.9, 14.0; IR (neat) 1733 cm^{-1}; t_R 4.0 min (180 °C, 35 mL/min). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.55; H, 9.91.

The spectral data for **23** follow: ^1H NMR δ 4.07–4.29 (m, 4, OEt), 3.37 (dd, 1, J = 11.2, 4.1 Hz, C_2H), 2.19 (ddd, 1, J = 13.4, 11.2, 2.3 Hz, Bu_1H), 1.41 (ddd, 1, J = 13.4, 11.2, 4.1 Hz, Bu_1H), 1.26 (t, 3, J = 7.1 Hz, OEt), 1.24 (t, 3, J = 7.1 Hz, OEt), 1.09 (dqd, 1, J = 11.2, 6.9, 2.3 Hz, Bu_2H), 0.84 (s, 9, $C(CH_3)_3$), 0.82 (d, 3, J = 6.9 Hz, Bu_2CH_3); ^{13}C NMR δ 170.0, 169.8, 61.3, 61.1, 51.0, 40.4, 33.0, 31.2, 27.1, 14.1, 13.8; t_R 3.0 min (180 °C, 35 mL/min).

Diethyl 3,3-Dimethyl-2-hydroxycyclopentane-1,1-dicarboxylate (24). $EtAlCl_2$ (2.00 mL of a 1.44 M hexane solution, 2.88 mmol), silyl enol ether **31** (225 mg, 1.56 mmol), and **1** (0.25 mL, 264 mg, 1.42 mmol) were reacted as described above for 60 h. Normal workup gave 375.2 mg of crude product. MPLC (5:1 hexane/ethyl acetate) gave 177.8 mg (48%) of pure **24**: ^1H NMR δ 4.15–4.30 (m, 4, OEt), 4.21 (d, 1, J = 9.0 Hz, C_2H), 3.66 (d, 1, J = 9.0 Hz, O*H*), 2.14–2.43 (m, 2), 1.40–1.55 (m, 2), 1.27 (t, 3, J = 7.1 Hz, OEt), 1.26 (t, 3, J = 7.1 Hz, OEt), 1.07 (s, 3, C_3 methyl), 0.92 (s, 3, C_3 methyl); ^{13}C NMR δ 171.9, 85.0, 62.1, 61.7, 61.6, 42.1, 36.7, 30.1, 27.9, 21.1, 14.0; IR (neat) 1728 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.44; H, 8.58. Found: C, 58.73; H, 7.92.

Diethyl 3-Methylspiro[4.5]decane-1,1-dicarboxylate (39). Reaction of $EtAlCl_2$ (2.00 mL of a 1.44 M solution in hexane, 2.88 mmol), methylenecyclohexane (138 mg, 1.43 mmol), and **38** (282 mg, 1.41 mmol) in 5 mL of dry 1,2-dichloroethane at room temperature for 60 h followed by normal workup and evaporative distillation (110 °C, 1.25–2.0 torr) gave 320 mg (76.5%) of pure **39**: ^1H NMR δ 4.20–4.02 (m, 4), 2.41 (dd, 1, J = 8.8, 14.1 Hz, H_2), 2.15–2.29 (m, 1, H_3), 2.11 (dd, 1, J = 12.6, 9.2 Hz, H_4), 1.82 (dd, 1, J = 7.6, 14.0 Hz, H_2), 1.65–1.25 (m, 11), 1.21 (t, 3, J = 7.3 Hz), 1.20 (t, 3, J = 7.3 Hz), 0.98 (d, 3, J = 6.5 Hz); ^{13}C NMR δ 171.7, 171.1, 68.4 (C_1), 60.6, 60.5, 49.9 (C_5), 41.0, 40.6 (C_2, C_4), 32.6, 31.5 (C_6, C_{10}), 28.7 (C_3), 26.6 (C_8), 23.0 (C_7), 23.0 (C_9), 22.0 (Me), 14.0, 14.0; IR 1722 cm^{-1}; t_R 8.4 min (180 °C). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.88; H, 9.52. Found: C, 68.94; H, 9.54.

Diethyl 1,4-Dimethylbicyclo[3.3.0]octane-2,2-dicarboxylate (40 and 41). Reaction of $EtAlCl_2$ (2.00 mL of a 1.44 M solution in hexane, 2.88 mmol), 1-methylcyclopentene (117 mg, 1.43 mmol), and **38** (282 mg, 1.41 mmol) in 5 mL of dry 1,2-dichloroethane at room temperature for 60 h followed by normal workup gave 343 mg (87%) of crude product which was shown by GC and NMR analysis to consist of **41** (18%), **40** (54%), and two minor components (15%).

The spectral data for **41** follow: ^1H NMR δ 4.21–4.09 (m, 4), 2.69 (dd, 1, J = 10.6, 14.6 Hz, H_3), 1.96–1.89 (m, 1), 1.82–1.62 (m, 6), 1.61–1.42 (m, 2), 1.25 (t, 3, J = 7.4 Hz), 1.24 (t, 3, J = 7.1 Hz), 1.09 (s, 3), 1.02 (d, 3, J = 6.6 Hz); ^{13}C NMR δ 171.6, 171.5, 67.0 (C_2), 60.9, 60.5, 59.3 (C_5), 57.5 (C_1), 43.8 (C_3), 40.3 (C_8), 37.3 (C_4), 35.9 (C_6), 22.7 (C_7), 21.6 (1-Me), 19.5 (4-Me), 14.0, 14.0; IR 1723 cm^{-1}; t_R 5.8 min (180 °C). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 66.58; H, 9.47.

The spectral data for **40** follow: ^1H NMR δ 4.21–4.04 (m, 4), 2.51 (dddq, 1, J = 10.9, 9.6, 8.1, 7.0 Hz), 2.18 (m, 1), 1.97 (dd, 1, J = 13.0, 7.0 Hz), 1.95 (dd, 1, J = 13.0, 11.0 Hz), 1.75–1.30 (m, 7), 1.28 (s, 3), 1.24 (t, 3, J = 7.3 Hz), 1.21 (t, 3, J = 7.1 Hz), 0.89 (d, 3, J = 7.0 Hz); ^{13}C NMR δ 173.3, 173.3, 66.5 (C_2), 60.7, 60.6, 55.9 (C_1), 53.6 (C_5), 41.0 (C_3), 39.9 (C_8), 31.7 (C_4), 27.9 (C_6), 25.4 (C_7), 24.1 (1-Me), 15.3 (4-Me), 14.1, 14.1; IR 1725 cm^{-1}; t_R 6.5 min (180 °C). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.05; H, 9.28. Found: C, 67.53; H, 9.44.

Diethyl 2,2,3,4-Tetramethylcyclopentane-1,1-dicarboxylate (42 and 43). Reaction of $EtAlCl_2$ (2.00 mL of a 1.44 M solution in hexane, 2.88 mmol), 2-methyl-2-butene (100 mg, 1.43 mmol), and **38** (282 mg, 1.41 mmol) in 5 mL of dry 1,2-dichloroethane at room temperature for 60 h followed by normal workup gave 316 mg (83%) of crude product which was shown by NMR and GC analysis to consist of **43** (11%), **42** (54%), and diethyl 2,3-dimethylbutylmalonate (**19**) (13%).

The spectral data for **43** follow: ^1H NMR δ 4.21–4.03 (m, 4), 2.73 (m, 1), 1.97 (m, 1), 1.74–1.57 (m, 2), 1.26 (t, 3, J = 7.0 Hz), 1.22 (t, 3, J = 7.4 Hz), 1.15 (s, 3), 1.00 (d, 3, J = 6.5 Hz), 0.82 (d, 3, J = 6.8 Hz), 0.76 (s, 3); ^{13}C NMR δ 169.9, 169.6, 66.0 (C_1), 60.7,

60.7, 49.4 (C_5), 48.0 (C_2), 39.6 (C_3), 36.8 (C_4), 22.4 (2-Me), 19.6 (2-Me), 18.9 (4-Me), 14.0, 14.0, 12.1 (3-Me); IR 1730 cm^{-1}; t_R 3.4 min (180 °C). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.73. Found: C, 66.64; H, 9.96.

The spectral data for **42** follow: ^1H NMR δ 4.21–4.03 (m, 4), 2.47 (m, 3), 2.05–1.87 (m, 1), 1.25 (t, 3, J = 7.0 Hz), 1.21 (t, 3, J = 7.1 Hz), 1.14 (s, 3), 0.91 (d, 3, J = 6.9 Hz), 0.79 (d, 3, J = 7.6 Hz), 0.78 (s, 3); ^{13}C NMR δ 171.9, 171.1, 66.9 (C_1), 60.7, 60.6, 47.5 (C_2), 43.0 (C_5), 41.1 (C_3), 31.7 (C_4), 23.3 (2-Me), 20.3 (2-Me), 18.4 (4-Me), 14.1, 14.1, 10.0 (3-Me); IR 1730 cm^{-1}; t_R 4.2 min (180 °C). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.73. Found: C, 66.56; H, 9.84.

Diethyl 2,2,3,3,4-Pentamethylcyclopentane-1,1-dicarboxylate (44). Reaction of $EtAlCl_2$ (2.00 mL of a 1.44 M solution in hexane, 2.88 mmol), 2,3-dimethyl-2-butene (120 mg, 1.43 mmol), and **38** (282 mg, 1.41 mmol) in 5 mL of dry 1,2-dichloroethane at room temperature for 48 h followed by normal workup gave 304 mg (75%) of crude product which was shown by GC and NMR analysis to consist of **44** (57%) and diethyl 3,4,4-trimethylbutylmalonate (**23**) (11%).

The spectral data for **44** follow: ^1H NMR δ 4.20–4.00 (m, 4), 2.78 (dd, 1, J = 8.0, 14.3 Hz), 1.94 (m, 1), 1.58 (dd, 1, J = 11.7, 14.3 Hz), 1.26 (s, 3), 1.24 (t, 3, J = 7.4 Hz), 1.23 (t, 3, J = 7.0 Hz), 0.84 (s, 3), 0.83 (d, 3, J = 7.4 Hz), 0.78 (s, 3), 0.74 (s, 3); ^{13}C NMR δ 172.1, 171.6, 64.7 (C_1), 60.8, 60.3, 50.4 (C_2), 46.4 (C_5), 40.2 (C_3), 39.8 (C_4), 24.1, 23.2, 20.0, 18.9, 14.2, 14.0, 13.9; IR 1730 cm^{-1}; t_R 5.05 min (180 °C). Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.92. Found: C, 67.15; H, 10.13.

Diethyl 8-Isopropylbicyclo[4.3.0]nonane-7,7-dicarboxylate (51a). Reaction of $EtAlCl_2$ (2.14 mL of a 1.44 M solution in hexane, 3.08 mmol), methylenecyclohexane (147 mg, 1.53 mmol), and **46** (323 mg, 1.51 mmol) in 6 mL of dry 1,2-dichloroethane at room temperature for 72 h followed by normal workup gave 380 mg of crude product which was shown by NMR and GC analysis to consist of **51a** (28%) and numerous minor unidentified components. A pure sample of **51a** was isolated by preparative GC: ^1H NMR δ 4.26–3.99 (m, 4), 2.86 (ddd, 1, J = 7.0, 7.0, 9.5 Hz, H_8), 2.72–2.59 (m, 1), 2.48–2.38 (m, 1), 1.86 (dqq, 1, J = 7.0, 7.0, 7.0 Hz), 1.72 (ddd, 1, J = 10.0, 10.0, 13.0 Hz), 1.64–1.27 (m, 6), 1.22 (t, 3, J = 6.9 Hz), 1.21 (t, 3, J = 7.4 Hz), 1.19–1.02 (m, 3), 0.94 (d, 3, J = 6.8 Hz), 0.75 (d, 3, J = 6.6 Hz); ^{13}C NMR δ 171.2, 169.8, 67.6, 60.8, 60.7, 48.3, 46.8, 36.5, 28.9, 28.7, 26.8, 24.7, 24.3, 23.9, 20.5, 19.0, 14.1, 13.9; t_R 9.8 min (180 °C).

Diethyl 8-Methylbicyclo[4.3.0]nonane-7,7-dicarboxylate (51b). Reaction of $EtAlCl_2$ (1.73 mL of a 1.44 M solution in hexane, 2.49 mmol), methylenecyclohexane (119 mg, 1.24 mmol), and diethyl ethylidenemalonate (**48**) (225 mg, 1.21 mmol) in 5 mL of dry 1,2-dichloroethane at room temperature for 24 h followed by normal workup gave 310 mg of crude product which was shown by NMR and GC analysis to consist of **51b** (27%) and a mixture of unidentifiable minor products. A pure sample of **51b** was isolated by preparative GC: ^1H NMR δ 4.26–4.03 (m, 4), 3.08 (ddq, 1, J = 5.8, 10.5, 6.9 Hz, H_8), 2.81–2.68 (m, 1), 2.52–2.40 (m, 1), 1.98 (ddd, 1, J = 13.0, 10.5, 10.5 Hz, H_9), 1.67–1.25 (m, 7), 1.22 (t, 3, J = 7.1 Hz), 1.21 (t, 3, J = 6.9 Hz), 1.20–1.00 (m, 2), 0.98 (d, 3, J = 6.9 Hz); ^{13}C NMR δ 68.5 (C_7), 60.7, 60.5, 46.1 (C_6), 36.6, 36.3 (C_1, C_8), 35.5 (C_9), 26.7 (C_5), 24.7, 24.1 (C_2, C_3), 20.6 (C_4), 18.3 (Me), 14.1; t_R 9.2 min (180 °C).

Diethyl 2,2,4,4,6-Pentamethylcyclohexane-1,1-dicarboxylate (52). Reaction of $EtAlCl_2$ (1.87 mL of a 1.44 M solution in hexane, 2.69 mmol), isobutylene (250 mg, ≈5 mmol), and diethyl ethylidenemalonate (**48**) (234 mg, 1.26 mmol) in 2 mL of dry 1,2-dichloroethane at room temperature in a sealed tube for 60 h followed by normal workup gave 382 mg of crude product which was shown by NMR and GC analysis to consist of **52** (55%) and three minor components. A pure sample of **52** was isolated by preparative GC: ^1H NMR δ 4.24–4.03 (m, 4), 2.56 (ddq, 1, J = 11.8, 4.8, 6.7 Hz), 2.13 (d, 1, J = 12.9 Hz), 1.26 (t, 3, J = 7.4 Hz), 1.23 (t, 3, J = 7.4 Hz), 1.22–1.03 (m, 3), 1.15 (s, 3), 1.00 (s, 3), 0.96 (s, 3), 0.91 (d, 3, J = 6.7 Hz), 0.89 (s, 3); ^{13}C NMR δ 70.9, 60.4, 60.0, 50.8, 43.3, 36.9, 34.6, 29.6, 28.9, 28.0, 27.8, 19.7, 14.1, 14.1, 11.1; t_R 4.65 min (170 °C).

Reaction of Diethyl Cyclopropane-1,1-dicarboxylate (1) with $EtAlCl_2$. A solution of **1** (0.25 mL, 263.7 mg, 1.42 mmol) in 5 mL of 1,2-dichloroethane was reacted with $EtAlCl_2$ (2.38 mL of a 1.44 M hexane solution, 3.43 mmol) for 74 h. Following normal workup, analytical GC showed a 6:1 ratio of starting material **1** to diethyl 2-chloroethylmalonate (**53**). Chloride **53** was isolated by preparative GC: ^1H NMR δ 4.15–4.26 (m, 4, OEt), 3.65 (t, 1, J = 6.7 Hz, C_2H), 3.60 (t, 2, J = 6.7 Hz, Et_2H), 2.36 (q, 2, J = 6.7 Hz, Et_1H), 1.28 (t, 6, J = 7.1 Hz, OEt); t_R 5.1 min (180 °C, 46 mL/min).

Reaction of Diethyl 2-Methylcyclopropane-1,1-dicarboxylate (38) with $EtAlCl_2$. A solution of cyclopropane **38** (250 mg, 1.25 mmol) in 10 mL of dry 1,2-dichloroethane was treated with $EtAlCl_2$ (1.75 mL of a 1.44 M hexane solution, 2.50 mmol) at 20 °C. The progress of the reaction was monitored for 72 h by GC. The results are shown in Table III.

The reaction was repeated and quenched after 14 min. Normal workup and preparative GC purification allowed the isolation and identification of diethyl 2-chloropropylmalonate (**54**): ^1H NMR δ 4.18–4.24 (m, 4, OEt), 4.00–4.10 (m, 1, Pr_2H), 3.65 (dd, 1, J = 4.5, 9.7 Hz, C_2H), 2.10–2.42 (m, 2, Pr_1H), 1.55 (d, 3, J = 6.4 Hz, Pr_3H), 1.28 (t, 3, J = 7.1 Hz, OEt), 1.27 (t, 3, J = 7.1 Hz, OEt); IR (neat) 1733 cm^{-1}; t_R 4.1 min (180 °C, 49 mL/min).

The reaction was repeated and quenched after 74 h. Products **57b**, **59a**, and **59b** were isolated by preparative GC and identified by ^1H NMR spectroscopy.

The spectral data for diethyl 1-ethylpropylmalonate (**57b**) follow: ^1H NMR δ 4.19 (q, 4, J = 7.1 Hz, OEt), 3.40 (d, 1, J = 8.1 Hz, C_2H), 2.00–2.10 (m, 1, Pr_1H), 1.31–1.50 (m, 4, CH(CH_2CH_3)$_2$), 1.27 (t, 6, J = 7.1 Hz, OEt), 0.89 (t, 6, J = 7.4 Hz, CH(CH_2CH_3)$_2$); ^{13}C NMR δ 169.1, 61.1, 55.1, 40.8, 22.9, 14.1, 10.8; t_R 2.5 min (180 °C, 46 mL/min).

The spectral data for triethyl 4-methyl-2-oxo-3-propylcyclopentane-1,1,3-tricarboxylate (**59a**) follow: ^1H NMR δ 4.19 (q, 2, J = 7.1 Hz, OEt), 4.19 (q, 2, J = 7.1 Hz, OEt), 4.13 (q, 2, J = 7.1 Hz, OEt), 1.80–2.48 (m, 6), 1.26 (t, 3, J = 7.1 Hz, OEt), 1.25 (t, 3, J = 7.1 Hz, OEt), 1.20–1.40 (m, 1), 0.95 (d, 3, J = 6.8 Hz, C_4CH_3), 0.91 (t, 3, J = 7.2 Hz, CH_2CH_3); ^{13}C NMR δ 61.9, 60.8, 60.3, 36.6, 36.1, 33.2, 28.2, 21.1, 18.0, 14.5, 14.2; t_R 19.1 min (180 °C, 46 mL/min).

The spectral data for triethyl 3-(1-ethylpropyl)-4-methyl-2-oxocyclopentane-1,1,3-tricarboxylate (**59b**) follow: ^1H NMR δ 4.13–4.23 (m, 4, OEt), 4.12 (q, 2, J = 7.0 Hz, OEt), 1.27 (t, 6, J = 7.0 Hz, OEt), 1.25 (t, 3, J = 7.0 Hz, OEt), 1.00–2.50 (m, 6), 0.80–0.98 (m, 9); ^{13}C NMR δ 169.8 (C=O), 61.6 (OEt), 49.0, 42.1, 31.4 (C_2), 14.0 (OEt); t_R 25.3 min (180 °C, 46 mL/min).

Reaction of Diethyl 2,2-Dimethylcyclopropane-1,1-dicarboxylate (46) with $EtAlCl_2$. A solution of **46** (256 mg, 1.19 mmol) in 5 mL of 1,2-dichloroethane was reacted with $EtAlCl_2$ (2.08 mL of a 1.44 M hexane solution, 2.99 mmol) for 74 h. Following normal workup, analytical GC showed a 3–4:1 ratio of the two products **60a** and **60b** which were isolated by preparative GC. The uncertainty is due to impurities present in the starting material (only 80% pure) which have nearly identical retention times to the major product **60a**.

The spectral data for diethyl isobutylmalonate (**60a**) follow: ^1H NMR δ 4.20 (q, 4, J = 7.1 Hz, OEt), 3.41 (t, 1, J = 7.5 Hz, C_2H), 1.80 (t, 1, J = 7.5 Hz, Pr_1H), 1.50–1.63 (m, 1, Pr_2H), 1.27 (t, 6, J = 7.1 Hz, OEt), 0.92 (d, 6, J = 6.6 Hz, CH(CH_3)$_2$); ^{13}C NMR δ 169.7 (C=O), 61.3 (OEt), 50.3, 37.5, 26.1, 22.2, 14.1 (OEt); t_R 1.97 min (180 °C, 46 mL/min).

The spectral data for diethyl (1-ethyl-2-methylpropyl)malonate (**60b**) follow: ^1H NMR δ 4.21 (q, 2, J = 7.1 Hz, OEt), 4.18 (q, 2, J = 7.1 Hz, OEt), 3.42 (d, 1, J = 7.9 Hz, C_2H), 1.22–1.32 (m, 6, OEt), 1.13–2.10 (m, 4), 0.93 (d, 3, J = 6.9 Hz, CH(CH_3)$_2$), 0.92 (t, 3, J = 7.5 Hz, CH_2CH_3), 0.87 (d, 3, J = 6.8 Hz, CH(CH_3)$_2$); ^{13}C NMR 169.6 (C=O), 169.4 (C=O), 61.2 (OEt), 60.8 (OEt), 54.7, 45.7, 29.5, 23.1, 21.4, 20.3, 18.6, 14.1 (OEt); t_R 2.75 min (180 °C, 46 mL/min).

Preparation of Diethyl (2,6-Dimethyl-5-heptenylidene)malonate (62). Condensation of 2,6-dimethyl-5-heptenal (**61**) with diethyl malonate in the presence of piperidine and acetic acid according to the method of Cope et al.[22] gave **62** (87%): ^1H NMR δ 6.71 (d, 1, J = 10.3 Hz, C_2H), 5.02 (m, 1, C_6H), 4.00–4.40 (m, 4, OEt), 1.67 (s, 3, C_8H), 1.53 (s, 3, C_7CH_3), 1.05 (d, 3, J = 6.4 Hz, C_3CH_3), 0.90–2.70 (m, 11); IR (neat) 1728, 1645 cm^{-1}.

Preparation of Diethyl (3,7-Dimethyl-6-octenylidene)malonate (66). Condensation of citronellal (**65**) with diethyl malonate in the presence of piperidine and acetic acid according to the method of Cope et al.[22] gave **66** (58%): ^1H NMR δ 6.99

(t, 1, J = 7.5 Hz, C_2H), 5.10 (m, 1, C_7H), 4.10–4.40 (m, 4, OEt), 1.68 (s, 3), 1.60 (s, 3), 0.92 (d, 3, J = 6.2 Hz, C_4CH_3), 0.80–2.50 (m, 13); IR (neat) 1728, 1643 cm^{-1}.

Preparation of Diethyl 2-(1,5-Dimethyl-4-hexenyl)cyclopropane-1,1-dicarboxylate (63). Treatment of **62** with trimethylsulfoxonium iodide in the presence of NaH in DMF according to the method of Landor and Punja[21] afforded cyclopropane **63** (53%) as a mixture of diastereomers: ^1H NMR δ 4.95–5.09 (m, 1, C_7H), 4.05–4.29 (m, 4, OEt), 1.65 (s, 3, C_9H), 1.57 (s, 3, C_8CH_3), 0.70–2.30 (m, 17). IR (neat) 1727 cm^{-1}.

Preparation of Diethyl 2-(2,6-Dimethyl-5-heptenyl)-cyclopropane-1,1-dicarboxylate (67). Treatment of **66** with trimethylsulfoxonium iodide in the presence of NaH in DMF according to the method of Landor and Punja[21] afforded cyclopropane **67** (70%) as a mixture of diastereomers: ^1H NMR δ 5.06 (m, 1, C_8H), 4.00–4.35 (m, 4, OEt), 1.68 (s, 3), 1.60 (s, 3), 1.15–1.40 (m, 6, OEt), 0.76–2.30 (m, 13); IR (neat) 1725 cm^{-1}.

Diethyl 2,2,6-Trimethylbicyclo[3.3.0]octane-3,3-dicarboxylate (64). $EtAlCl_2$ (0.56 mL of a 1.44 M hexane solution, 0.81 mmol) was added slowly via syringe to cyclopropane **63** (120 mg, 0.40 mmol) as a 2:1 mixture of diastereomers in 5 mL of dry 1,2-dichloroethane at 0 °C. The reaction mixture was stirred for 5 min. at 0 °C, then warmed to room temperature, and stirred for an additional 5 h before quenching by the slow dropwise addition of 10 mL of water followed by 10 mL of 1.5 M aqueous HCl. The resulting mixture was stirred vigorously overnight to dissolve the precipitated aluminum hydroxide, the layers were separated, and the aqueous phase was extracted with dichloromethane (4 × 15 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo to give 99.2 mg of a faintly yellow oil. Evaporative distillation (100 °C, 0.6 torr) gave 83.7 mg (70%) of **64** as a 2:1 mixture of diastereomers: IR (neat) 1730 cm^{-1}. Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.72; H, 9.45.

Attempted separation via preparative GC afforded only partial resolution of the two components. However, this allowed assignment of various peaks in the NMR spectra to the proper component. The following data was taken from mixtures which contained from 10 to 30% of the other isomer.

The spectral data for the major component **64a** follow: ^1H NMR δ 4.0–4.3 (m, 4, OEt), 2.36–2.48 (m, 4), 1.28 (t, 3, J = 7.0 Hz, OEt), 1.23 (s, 3, C_2CH_3), 1.23 (t, 3, J = 7.0 Hz, OEt), 0.92–1.89 (m, 5), 0.90 (d, 3, J = 6.9 Hz, C_6CH_3), 0.79 (s, 3, C_2CH_3); ^{13}C NMR δ 173.0, 171.2, 66.6, 60.7, 53.5, 47.1, 41.2, 40.6, 38.1, 34.9, 33.1, 25.3, 22.3 (imp), 20.0, 14.1, 12.4 (imp), 11.0; t_R 8.7 min (170 °C, 32 mL/min).

The spectral data for the minor component **64b** follow: ^1H NMR δ 4.0–4.3 (m, 4, OEt), 2.52 (dd, 1, J = 13.5, 8.4 Hz), 1.99 (dd, 1, J = 13.5, 11.0 Hz), 1.25 (t, 3, J = 7.1 Hz, OEt), 1.23 (t, 3, J = 6.9 Hz, OEt), 1.17 (s, 3, C_2CH_3), 1.10 (s, 3, C_2CH_3), 0.92–1.81 (m, 7), 0.86 (d, 3, J = 6.7 Hz, C_6CH_3); ^{13}C NMR δ 172.1, 65.6, 60.7, 60.5, 50.4, 48.1, 38.7, 35.5, 33.4, 32.9, 27.7, 26.4, 22.7, 21.5, 14.1; t_R 10.25 min (170 °C, 32 mL/min).

Diethyl 3,7,7-Trimethylbicyclo[4.3.0]nonane-8,8-dicarboxylate (68). $EtAlCl_3$ (1.93 mL of a 1.44 M hexane solution, 2.78 mmol) and a 1:1 mixture of diastereomers of cyclopropane **67** were reacted as described above for 72 h. Normal workup and evaporative distillation (100 °C, 0.6 torr) gave 315.6 mg (73%) of a 1:1 mixture of two of the four possible diastereomers of **68** as a clear colorless oil: IR (neat) 1733 cm^{-1}. Anal. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74. Found: C, 69.72; H, 9.67.

The components were partially separated via preparative GC. The following spectroscopic data was obtained from mixtures containing up to 15% of the other diastereomer.

The spectral data for **68a** follow: ^1H NMR δ 4.01–4.28 (m, 4, OEt), 2.70–2.83 (m, 1), 1.28 (t, 3, J = 7.0 Hz, OEt), 1.23 (s, 3, C_7CH_3), 1.23 (t, 3, J = 7.0 Hz, OEt), 0.90 (d, 3, J = 6.6 Hz, C_3CH_3), 0.79 (s, 3, C_7CH_3), 0.73–1.90 (m, 10); ^{13}C NMR δ 173.0, 171.3, 66.6, 60.7, 53.5, 47.1, 41.2, 40.6, 38.1, 34.9, 33.1, 25.3, 22.34, 22.26, 19.9, 14.1; t_R 16.3 min (170 °C, 30 mL/min).

The spectral data for **68b** follow: ^1H NMR δ 4.05–4.28 (m, 4, OEt), 2.53 (dd, 1, J = 13.3, 8.2 Hz), 2.32–2.47 (m, 2), 1.98 (dd, 1, J = 13.3, 10.8 Hz), 1.25 (t, 3, J = 7.0 Hz, OEt), 1.23 (t, 3, J = 7.0 Hz, OEt), 1.17 (s, 3, C_7CH_3), 1.10 (s, 3, C_7CH_3), 0.86 (d, 3, J = 6.1 Hz), 0.80–1.95 (m, 7); ^{13}C NMR δ 172, 171.7, 65.6, 60.7, 60.5, 50.4, 48.0, 38.6, 35.5, 33.4, 32.9, 27.7, 26.3, 22.7, 22.3, 21.4, 14.1; t_R 18.7 min (170 °C, 30 mL/min).

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Registry No. 1, 1559-02-0; **3**, 104643-45-0; **6**, 104643-46-1; **7**, 104643-47-2; **8**, 104643-48-3; **9**, 104643-49-4; *cis*-**10**, 104643-50-7; *trans*-**10**, 104643-85-8; **11** (isomer 1), 104643-51-8; **11** (isomer 2), 104643-86-9; **12**, 104643-52-9; **13**, 104643-53-0; **14**, 104643-54-1; **15**, 104643-55-2; **16**, 104643-56-3; **17**, 104643-57-4; **18**, 104643-58-5; **19**, 104643-59-6; **20**, 104643-60-9; **21**, 104643-61-0; **22**, 104643-62-1; **23**, 104643-63-2; **24**, 104643-64-3; **31**, 6651-34-9; **38**, 16783-17-8; **39**, 104643-65-4; **40**, 104643-66-5; **41**, 104643-67-6; **42**, 104643-68-7; **43**, 104643-69-8; **44**, 104663-69-6; **46**, 16783-05-4; **48b**, 1462-12-0; **51a**, 104643-70-1; **51b**, 104643-73-4; **52**, 104643-71-2; **53**, 18719-42-1; **54**, 104643-72-3; **57b**, 71691-56-0; **59a**, 104643-74-5; **59b**, 104643-75-6; **60a**, 10203-58-4; **60b**, 104643-76-7; **61**, 106-72-9; **62**, 104643-77-8; **63** (isomer 1), 104643-82-5; **63** (isomer 2), 104643-83-6; **64**, 104643-78-9; **65**, 106-23-0; **66**, 104643-79-0; **67** (isomer 1), 104643-80-3; **67** (isomer 2), 104643-84-7; **68**, 104643-81-4; $EtAlCl_2$, 563-43-9; $BrCH_2CH(CH_3)CH(CH_3)_2$, 30540-31-9; methylenecyclohexane, 1192-37-6; 4-methylmethylenecyclohexane, 2808-80-2; 4-*tert*-butylmethylenecyclohexane, 13294-73-0; 3-methylmethylenecyclohexane, 3101-50-6; ethylidenecyclohexane, 1003-64-1; 1-methylcyclohexene, 591-49-1; 1-menthene, 5502-88-5; 1,3-dimethylcyclohexene, 2808-76-6; 1,4,4-trimethylcyclohexene, 3419-71-4; 1-methylcyclopentene, 693-89-0; 2-methyl-2-butene, 513-35-9; 2,3-dimethylbutan-1-ol, 19550-30-2; diethyl malonate, 105-53-3; (*Z*)-3-methyl-2-pentene, 922-62-3; (*E*)-3-methyl-2-pentene, 616-12-6; 2,3-dimethyl-2-butene, 563-79-1; isobutylene, 115-11-7; trimethylsulfoxonium iodide, 1774-47-6.