benzoyl chloride in pyridine at 0 °C and recrystallized from methylcyclohexane: mp 84.5–85.5 °C; NMR (CCl_4) δ 0.5–2.0 (m, 12 H), 5.4 (q, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.38; H, 5.11.

***anti*-7-Methyl-*exo*-2-bicyclo[4.1.0]heptanol.** Oxidation of a 70:30 anti:syn mixture of 7-methyl-*endo*-2-bicyclo[4.1.0]heptanols with chromium trioxide in acetone-water at −10° followed by workup and distillation afforded a 78% yield of a 70:30 anti:syn mixture of 7-methyl-2-bicyclo[4.1.0]heptanones: bp 78–82 °C (10 mm); NMR (neat) δ 1.0–1.1 (m, 3 H, CCH_3), 1.1–2.1 (br m, 9 H); IR (neat) 1680 cm^{-1} (C=O str).

Reduction of the isomeric mixture of 7-methyl-2-bicyclo[4.1.0]heptanones with lithium aluminum hydride in ether provided, after workup, an 80% yield of an isomeric mixture consisting of 56% *anti-exo*-, 17% *anti-endo*-, 26% *syn-endo*-, and 17% *syn-exo*-7-methyl-2-bicyclo[4.1.0]heptanols. A pure sample of the desired anti-exo isomer was collected by GLC on a 5 ft × 0.25 in., 10% Carbowax 20M–15% KOH on 60–80-mesh firebrick column run at 115 °C; NMR (CCl_4) δ 0.0–2.1 (br m, 12 H), 2.6 (s, 1 H, OH), 3.8 (t, 1 H, CHOH).

Anal. Calcd for $C_8H_{14}O$: C, 76.19; H, 11.11. Found: C, 75.86; H, 11.12.

***anti*-7-Methyl-*exo*-2-bicyclo[4.1.0]heptyl 3,5-Dinitrobenzoate.** This material was prepared in 50% yield by the reaction of *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol with 3,5-dinitrobenzoyl chloride in pyridine at 0 °C and recrystallized from methylcyclohexane: mp 76–77 °C; NMR (CCl_4) δ 0.3–2.1 (m, 12 H), 5.3 (m, 1 H, CHODNB), 9.0 (m, 3 H, aromatic).

Anal. Calcd for $C_{15}H_{16}N_2O_6$: C, 56.25; H, 5.00. Found: C, 56.15; H, 5.15.

General Procedures for Hydrolysis Kinetics and Products and for Product and 3,5-Dinitrobenzoate Stability Controls. The procedures followed were all analogous to those described earlier[3] from our laboratory in connection with another investigation. All runs were carried out in duplicate.

Acknowledgment. The authors wish to acknowledge support for this work in part by a Faculty Research Grant to E.C.F. from the Committee on Research of the University of California, Davis, and in part by a Chancellor's Patent Fund Grant to J.D.C.J.

Registry No. *endo*-2-Bicyclo[4.1.0]heptanol, 7432-49-7; 2-cyclohexen-1-ol, 822-67-3; methylene bromide, 74-95-3; *endo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 52688-97-8; 2-bicyclo[4.1.0]heptanone, 56579-71-6; *exo*-2-bicyclo[4.1.0]heptanol, 31022-87-4; *exo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 52688-98-9; 2-methylcyclohex-2-en-1-one, 1121-18-2; 2-chloro-2-methylcyclohexanone, 10409-46-8; 2-methylcyclohex-2-en-1-ol, 20461-30-7; 1-methyl-*endo*-2-bicyclo[4.1.0-heptanol, 13388-56-2; 1-methyl-*endo*-2-bicyclo[4.1.0]-heptyl 3,5-dinitrobenzoate, 71785-30-3; *endo*-2-methyl-2-bicyclo[4.1.0]heptanol, 67731-03-7; *exo*-2-methyl-2-bicyclo[4.1.0]heptanol, 67731-02-6; *endo*-2-methyl-2-bicyclo[4.1.0]-heptyl *p*-nitrobenzoate, 71766-61-5; *exo*-2-methyl-2-bicyclo[4.1.0]-heptyl *p*-nitrobenzoate, 71774-57-7; 3-methylcyclohex-2-en-1-one, 1193-18-6; 3-methylcyclohex-2-en-1-ol, 21378-21-2; 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 13388-57-3; 6-methyl-*endo*-2-bicyclo[4.1.0]heptanol 3,5-dinitrobenzoate, 71766-62-6; *anti*-7-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 62862-03-7; *syn*-7-methyl-*endo*-2-bicyclo[4.1.0]heptanol, 62862-02-6; *anti*-7-methyl-*endo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 71785-31-4; *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 67731-05-9; *syn*-7-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 71766-63-7; *anti*-7-methyl-2-bicyclo[4.1.0]heptanone, 71766-64-8; *syn*-7-methyl-2-bicyclo[4.1.0]heptanone, 71806-60-5; *anti*-7-methyl-*exo*-2-bicyclo[4.1.0]heptyl 3,5-dinitrobenzoate, 71785-27-8; 4-methylcyclohepten-4-ol, 71766-65-9; 1-methylcyclohepta-1,3-diene, 14947-22-9; 6-methyl-2-bicyclo[4.1.0]heptanone, 14845-41-1; 6-methyl-*exo*-2-bicyclo[4.1.0]heptanol, 67731-04-8; 6-methyl-*exo*-2-bicyclo[4.1.0]heptanol 3,5-dinitrobenzoate, 71766-66-0.

Lewis Acid Induced Cyclizations of Ethylenetricarboxylates

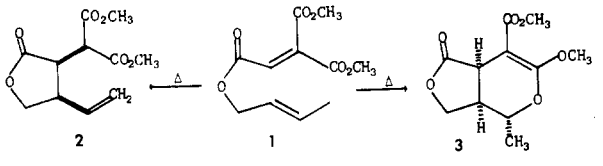
Barry B. Snider* and David M. Roush

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

Received June 11, 1979

Treatment of allylic dimethyl ethylenetricarboxylates (**1**, **5**) with ferric chloride gives high yields of β-chloroalkyl γ-lactones (**4**, **6**) with stereospecific trans addition of carbon and chlorine to the double bond. With the cyclohexenyl triester **13**, only one of eight possible diastereomers is formed. Trimethyl ethylenetricarboxylate (**24**) adds to alkenes in the presence of ferric chloride in a cis fashion to give γ-lactones **26**, **28**, **30**, and **32**, arising from zwitterion formation followed by rapid attack of the carbonyl oxygen on the cation.

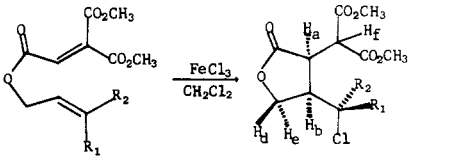
We are interested in developing intramolecular ene reactions[1] of unsaturated esters of allylic alcohols as a route to β-alkenyl-α-methylene lactones such as alantolactone.[2] We recently reported that acyclic allylic dimethyl ethylenetricarboxylates such as **1** react at 130 °C to give mixtures



2 **1** **3**

of the expected ene adduct **2** and a Diels–Alder adduct **3** which may be of value in iridoid synthesis.[3] Unfortunately, with the cyclohexenyl analogue **13** no reaction occurs prior to slow decomposition at 200 °C. Since the ene adducts of cycloalkenyl esters are needed to produce the desired fused α-methylene lactones we decided to investigate the effect of Lewis acids on this reaction.

Treatment of *trans*-2-butenyl triester **1** with ferric chloride in methylene chloride for 30 min at 25 °C gives an 85% yield of the chlorolactone **4**. The *cis*-2-butenyl



1, R_1 = H, R_2 = CH_3
5, R_1 = CH_3, R_2 = H
7, R_1, R_2 = CH_3
9, R_1 = H, R_2 = Ph

4, R_1 = H_c, R_2 = CH_3
6, R_1 = CH_3, R_2 = H_c
8, R_1, R_2 = CH_3
10, R_1 = H_c, R_2 = Ph
11, R_1 = Ph, R_2 = H_c

(1) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476.
(2) For a synthesis of alantolactone see: Marshall, J. A.; Cohen, N. *J. Am. Chem. Soc.* **1965**, *87*, 2773.
(3) Snider, B. B.; Roush, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023.

0022-3263/79/1944-4229$01.00/0

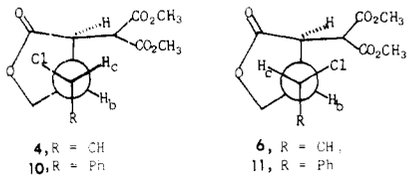
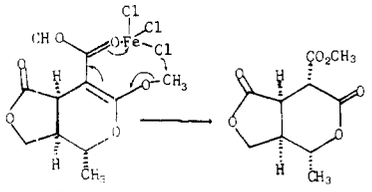


Figure 1. Preferred conformation of chlorolactones.

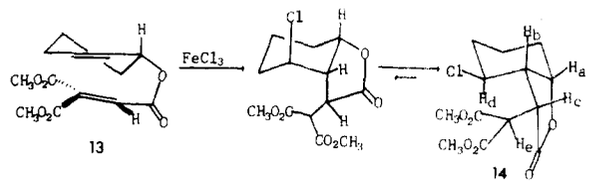
triester **5** gives a 75% yield of the chlorolactone **6**. Use of aluminum chloride gives lower yields of chlorolactone contaminated with ca. 10% of **2**. Triesters **1** and **5** each give only a single lactone. The substituents appear to be cis in both cases since J_{H_a,H_b} = 8 and 6.7 Hz for **4** and **6**, respectively.[4] These lactones therefore differ in configuration at the exocyclic carbon, and the coupling constants, J_{H_b,H_c} = 3.0 and 5.5 Hz for **4** and **6**, permit a structural assignment. Since the most stable conformation is expected to be that with the methyl group antiperiplanar to the large group as shown in Figure 1, **6** should have a larger value for J_{H_b,H_c} than **4**.[5,6]

This reaction produces only one of four possible diasteriomers. Clean trans addition to the double bond occurs. A plausible mechanism for this reaction involves chelation of the malonate to the Lewis acid, inducing electrophilic addition to the double bond followed by nucleophilic attack of chloride. The formation of the cis-substituted lactone may be favored by minimization of charge separation in the intermediate. The stereochemistry of the ene and Diels–Alder adducts is also cis. However, adducts **2** and **3** cannot be intermediates in chlorolactone formation since reaction proceeding through **2** would involve loss of stereochemistry at the exocyclic carbon, and **3** is demethylated to the lactone **12** with anhydrous ferric chloride in methylene chloride.

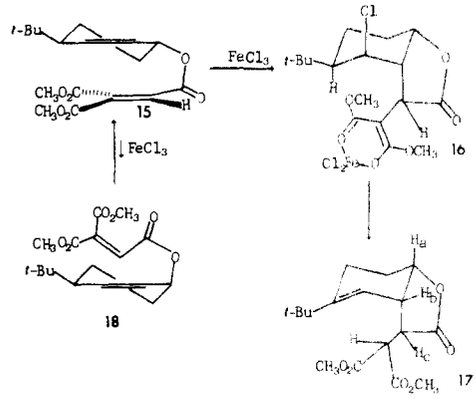


Substrates in which a more stable carbonium ion can be formed behave differently. Apparently, the more stable tertiary and benzylic carbonium ions exist long enough to lose stereochemistry or to transfer a hydrogen to give the ene adduct. Treatment of the prenyl triester **7** with aluminum chloride gives 11% of chlorolactone **8** and 29% of the isomeric ene adducts.[3] Treatment of the cinnamyl triester **9** with ferric chloride gives 58% of a 60:40 mixture of **10** and **11**. Stereochemistry is lost on the side chain since both isomers **10** and **11** have the substituents cis, J_{H_a,H_b} = 7 Hz. The major isomer, **10**, is clearly the isomer resulting from trans addition to the double bond since J_{H_b,H_c} (5.3 Hz) is smaller than that for the minor isomer, J_{H_b,H_c} = 9.0 Hz (see Figure 1).

Treatment of the cyclohexenyl triester **13** with ferric chloride gives only one of eight possible diasteriomers, **14**, in 67% yield. The spectral data are consistent with those of the expected structure in which the lactone is cis fused, trans addition to the double bond has occurred, and the substituents in the α and β positions of the lactone are cis. The lactone **14** is expected to be more stable with the highly substituted carbon and chlorine in the equatorial

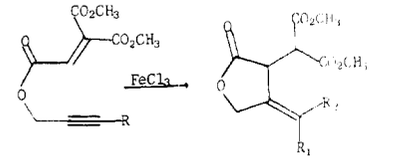


positions. The reaction of *trans*-4-*tert*-butylcyclohexenyl triester **15**[7] gives the "ene" adduct **17** in 85% yield. Pre-



sumably chlorolactone **16** is formed, which unlike **14** does not ring flip and therefore can easily eliminate hydrogen chloride. The stereochemistry can be assigned to **17** on the basis of $J_{Ha,Hb}$ = 8.0 Hz and $J_{Hb,Hc}$ = 8.0 Hz and is consistent with the proposed mechanism. *cis*-4-*tert*-Butylcyclohexenyl triester **18** also gives **17**, presumably by isomerization to **15** prior to reaction. *cis*- and *trans*-4-*tert*-butylcyclohexenol interconvert under acidic conditions.[7] If **15** and **18** also interconvert, exclusive reaction through **15** would be expected since axial attack on the cyclohexene of **18** would lead to a bridged ring system.

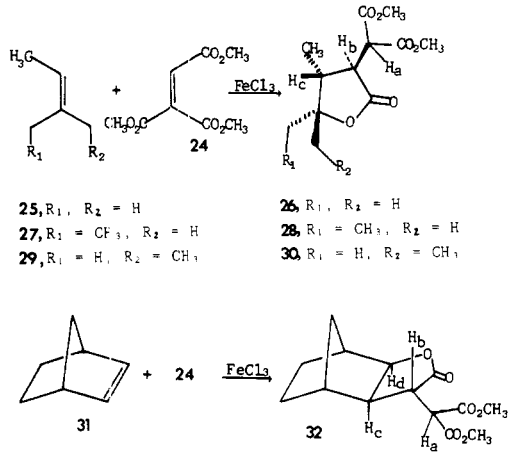
Propargylic triesters are also suitable substrates for this reaction. Treatment of the butynyl triester **19** with ferric



chloride gives a single adduct in 94% yield which is assigned structure **20** on mechanistic grounds, since Friedel–Crafts acylation of acetylenes proceeds via trans addition.[8] Treatment of the phenylpropargyl triester **21** with ferric chloride gives a 95% yield of **22** and **23** as a 55:45 mixture. As is the case with the cinnamyl triester **9**, the stabilizing effect of the phenyl permits the formation of a cationic intermediate which loses stereochemistry.

Intermolecular reactions of trimethyl ethylenetricarboxylate (**24**)[9] were briefly investigated. With 2-methyl-2-butene (**25**) and ferric chloride, **26** is formed in 77% yield. The coupling constant, J_{H_b,H_c} = 12 Hz, allows the assignment of stereochemistry.[4] With norbornene (**21**) and ferric chloride, **32** is formed in 91% yield. The formation of the *exo*-γ-butyrolactone is known to be favored

(4) Savastianoff, D.; Pfau, M. *Bull. Soc. Chem. Fr.* **1967**, 4162.
(5) Stapp, P. S.; Weinberg, D. S. *J. Org. Chem.* **1969**, *34*, 3592.
(6) Gaudemer, A. *Stereochem: Fundam. Methods* **1977**, *3*, 62–73.
(7) *cis*- and *trans*-4-*tert*-Butyl-2-cyclohexen-1-ol were prepared by the procedure of: Barilli, P. L.; Bellucci, G.; Berti, G.; Golfarini, M.; Marioni, F.; Scartoni, V. *Gazz. Chim. Ital.* **1974**, *104*, 197.
(8) Martens, H.; Janssen, F.; Moormaert, G. *Tetrahedron* **1975**, *31*, 177.
(9) Ouali, M. S.; Vaultier, M.; Carrié, R. *Synthesis* **1978**, 626.



under equilibrating conditions.[10] The stereochemistry of the malonate side chain is determined from $J_{Hb,Hc}$ = 4.5 Hz.[4] With cyclohexene or *trans*-2-butene a complex mixture of products is obtained.

The intermolecular reactions may proceed as shown for 2-methyl-2-butene in Figure 2. The tertiary or norbornyl chloride may be formed reversibly in these reactions. The stereochemistry is consistent with the least hindered approach of **24** to the alkene. Cis addition to the alkene will occur if attack of the carbomethoxy group on the cation is rapid relative to rotation about the single bond. This was tested with 3-methyl-2-pentenes. At 25 °C, (*Z*)-3-methyl-2-pentene (**27**) gives a 59% yield of a ~90:10 mixture of **28** and **30** while (*E*)-3-methyl-2-pentene (**29**) gives a 55% yield of a ~10:90 mixture of **28** and **30**. At −15 °C the stereoselectivity is >95:5. The stereochemistry of the products is easily determined from the chemical shift of the quaternary methyl group. The methyl of **30** is shielded by the cis methyl group and absorbs at δ 1.24. The methyl of **28** absorbs at δ 1.39. An identical difference has been observed in α- and β-reolones, natural products with similarly substituted γ-lactones.[11]

The Lewis acid induced reactions of ethylenetricarboxylates are useful in producing a variety of highly substituted γ-lactones stereospecifically. The intermolecular additions proceed in a cis fashion with a high degree of selectivity.[12] Studies of the chemistry of these adducts and their uses in synthesis are in progress.

Experimental Section

NMR spectra were recorded on a Varian A60, a Varian XL-100 or a Perkin-Elmer R32 spectrometer. The mass spectra were obtained with an AEI-MS9 mass spectrometer. Infrared spectra were obtained on a Perkin-Elmer 283 spectrometer. All melting points and boiling points are uncorrected. Methylene chloride was dried by distillation from calcium hydride. Aluminum chloride was sublimed before use. Anhydrous ferric chloride was used without further purification. Microanalyses were performed by Galbraith Laboratories.

All ethylene tricarboxylates were prepared as previously described.[3,9]

Reaction of 1-(*trans*-2-Buten-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (1) with Ferric Chloride. To a solution of 0.170 g (0.70 mmol) of butenyl triester **1** in 3 mL of CH_2Cl_2 was added 0.20 g (1.2 mmol) of ferric chloride. After being stirred for 0.5 h, the reaction mixture was poured into 25 mL of water and extracted with three portions of ether. The combined organic layers were washed twice with water and once with brine and dried.

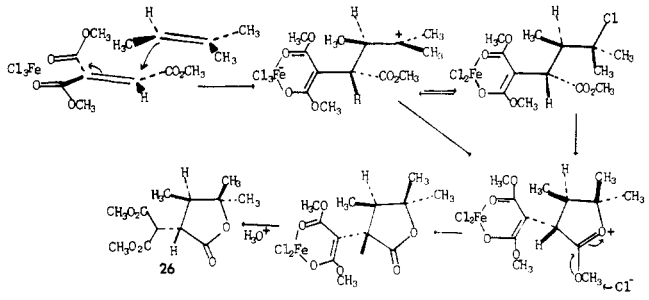


Figure 2. Possible mechanism for the reaction of trimethyl ethylenetricarboxylate (**24**) with alkenes.

The solvent was removed in vacuo, and the residual dark oil was filtered through ca. 0.5 g of Florisil (eluting with methylene chloride) to give 0.166 g (85%) of **4** as a pale yellow oil: IR (neat) 1780, 1745, 1430, 1190, 1160 cm^{-1}; NMR ($CDCl_3$) δ 1.50 (3 H, d, J = 7 Hz), 3.06 (1 H, m, H_b), 3.18 (1 H, d of d, J = 4, 8 Hz, H_a), 3.76 (3 H, s), 3.80 (3 H, s), 4.08 (1 H, d, J = 4 Hz, H_f), 4.30 (1 H, d of q, J = 3, 7 Hz, H_c), 4.2–4.5 (2 H, m, H_d, H_e). Anal. Calcd for $C_{11}H_{15}ClO_6$: C, 47.41; H, 5.43; Cl, 12.72. Found: C, 47.11; H, 5.35; Cl, 12.93.

Treatment of 0.388 g (1.6 mmol) of **1** with 0.22 g (1.6 mmol) of aluminum chloride in 8 mL of methylene chloride for 1 h followed by normal workup gave 0.33 g (85%) of crude product. Chromatography on silica (eluting with 70:30 hexane:ethyl acetate) gave 50 mg (13%) of ene adduct **2** and 177 mg (46%) of chloride **4**.

Reaction of 1-(*cis*-2-Buten-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (5) with Ferric Chloride. Treatment of 0.100 g (0.41 mmol) of **5** with 0.100 g (0.62 mmol) of ferric chloride in 3 mL of methylene chloride followed by workup and purification as previously described gave 0.085 g (74%) of chloride **6**: IR (neat) 1780, 1745, 1435, 1200, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (3 H, d, J = 7.0 Hz), 2.91 (1 H, d of d of d of d, J = 5.3, 5.5, 6.7, 8.3 Hz, H_b), 3.14 (1 H, d of d, J = 4.0, 6.7 Hz, H_a), 3.80 (3 H, s), 3.82 (3 H, s), 4.11 (1 H, d, J = 4 Hz, H_f), 4.18 (1 H, d of d, J = 5.3, −9.3 Hz, H_d), 4.19 (1 H, d of q, J = 5.5, 7.0 Hz, H_c), 4.55 (1 H, d of d, J = 8.3, −9.3 Hz, H_e); mass spectrum, m/e 280, 278 (M^+), 249, 247, 243, 242, 215; mol wt calcd for $C_{11}H_{15}ClO_6$ m/e 278.0557, found m/e 278.0556.

Treatment of 0.332 g (1.37 mmol) of **5** with 0.183 g of aluminum chloride in 5 mL of methylene chloride gave, after chromatography on silica, 27 mg (8%) of **2** and 86 mg (32%) of **6**.

Reaction of Diels–Alder Adduct 3 with Ferric Chloride. To a solution of 24.5 mg (0.10 mmol) of **3**[3] in 1 mL of methylene chloride was added an excess (25 mg, 0.15 mmol) of ferric chloride. After 0.5 h the reaction was worked up in the usual manner to yield 21 mg of crude bis lactone **12**, which was identified by NMR spectral comparison with an authentic sample.[3]

Reaction of 1-(3-Methyl-2-buten-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (7) with Aluminum Chloride. Treatment of 0.112 g (0.44 mmol) of triester **7** with 0.107 g (0.80 mmol) of aluminum chloride in 5 mL of methylene chloride as previously described, followed by chromatography on silica gel, gave 33 mg (29%) of ene adduct and 14 mg (11%) of chlorolactone **8**: IR (neat) 1775, 1740, 1435, 1195, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.54 (3 H, s), 1.56 (3 H, s), 2.75 (1 H, d of d of d, J = 4.5, 5.7, 8.5 Hz, H_b), 3.20 (1 H, d of d, J = 4.2, 5.7 Hz, H_a), 3.80 (6 H, s), 4.01 (1 H, d, J = 4.2 Hz, H_f), 4.37 (1 H, d of d, J = 4.5, −9.5 Hz, H_d), 4.59 (1 H, d of d, J = 8.5, −9.5 Hz, H_e); mass spectrum, m/e 277 (M − CH_3), 261 (M − OCH_3), 257 (M − Cl), 256, 215, 132, 125, 121, 103.

Reaction of 1-Cinnamyl 2,2-Dimethyl Ethylenetricarboxylate (9) with Ferric Chloride. Treatment of 0.132 g (0.43 mmol) of **9** with 0.12 g (0.74 mmol) of ferric chloride gave, after chromatography, 85 mg (58%) of a 60:40 mixture of **10** and **11**. The spectral data for **10** are as follows: IR (neat) 1775, 1730, 1435, 1280, 1200, 1170 cm^{-1}; NMR (CCl_4) δ 3.2 (1 H, m), 3.16 (1 H, d of d, J = 4, 7 Hz, H_a), 3.40 (1 H, d, J = 3.8 Hz, H_f), 3.76 (3

(10) Sauers, R. R.; Sonnet, P. E. *Tetrahedron* **1964**, *20*, 1029.
(11) Bukrewa, T. V.; Kir'yalov, N. P.; Gindin, V. A. *Chem. Nat. Prod.* **1977**, *13*, 25.
(12) For other syntheses of lactones from alkenes see: (a) Das Gupta, T. K.; Felix, D.; Kempe, V. M.; Eschenmoser, A. *Helv. Chim. Acta* **1972**, *55*, 2198. (b) Boldt, P.; Thielecke, W.; Etzemuller, J. *Chem. Ber.* **1969**, *102*, 4157. (c) Mori, Y.; Tsujo, J. *Tetrahedron* **1972**, *28*, 29. (d) Hudrlik, P. F.; Takacs, J. M.; Chou, D. T.-W.; Rudnick, L. R. *J. Org. Chem.* **1979**, *44*, 786. (e) Singh, R. K.; Danishevsky, S. *Ibid.* **1976**, *41*, 1668.

H, s), 3.78 (3 H, s), 4.30 (2 H, m, H_d, H_e), 5.12 (1 H, d, J = 5.3 Hz, H_c), 7.35 (5 H, m). The data for **11** are as follows: NMR (CCl_4) δ 3.2 (1 H, m), 3.16 (1 H, d of d, J = 3.3, 7 Hz, H_a), 3.71 (3 H, s), 3.78 (3 H, s), 4.00 (1 H, d, J = 3.3 Hz, H_f), 4.30 (2 H, m, H_d, H_e), 4.94 (1 H, d, J = 9 Hz, H_c), 7.35 (5 H, m); mass spectrum, m/e 340 (M^+), 309 (M - OCH_3), 305, 304, 273, 245, 244; mol wt calcd for $C_{16}H_{17}ClO_6$ m/e 340.0713, found m/e 340.0717.

Reaction of 1-(2-Cyclohexen-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (13) with Ferric Chloride. Treatment of 0.112 g (0.42 mmol) of triester **13** in 5 mL of methylene chloride with 0.120 g (0.74 mmol) of ferric chloride for 30 min followed by normal workup yielded 0.104 g (82%) of crude product which was purified on 10 g of silica gel (eluting with 1:1 petroleum ether:ether) to yield 86 mg (67%) of pure **14**: IR (neat) 1780, 1749, 1435, 1250, 1195, 1165 cm^{-1}; NMR ($CDCl_3$) δ 1.5–1.9 (4 H, m), 1.9–2.2 (2 H, m), 2.78 (1 H, d of d of d, J = 5.8, 6.6, 8.8 Hz, H_b), 3.26 (1 H, d of d, J = 5.1, 8.8 Hz, H_c), 3.79 (3 H, s), 3.81 (3 H, s), 3.98 (1 H, d, J = 5.1 Hz, H_e), 4.18 (1 H, d of d of d, J = 3.7, 5.8, 6.0 Hz, H_d), 4.85 (1 H, d of d of d, $J \approx$ 6.5, 6.5, 6.5 Hz, H_a); mass spectrum, m/e 306, 304 (M^+), 275, 273, 269, 268. Anal. Calcd for $C_{13}H_{17}ClO_6$: C, 51.24; H, 5.62. Found: C, 51.51; H, 5.64.

Reaction of 1-(*trans*-4-*tert*-Butyl-2-cyclohexen-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (15) with Ferric Chloride. Treatment of 0.133 g (0.41 mmol) of **15** in 5 mL of methylene chloride with 0.120 g (0.74 mmol) of ferric chloride followed by normal workup gave 0.125 g (94%) of crude **17**. Purification by column chromatography (10 g of silica gel, eluting with 75:25 hexane:ethyl acetate) gave 0.113 g (85%) of pure lactone **17**: IR (neat) 1770, 1740, 1435, 1195, 1160 cm^{-1}; NMR ($CDCl_3$) δ 1.04 (9 H, s), 1.7–2.2 (4 H, m), 2.97 (1 H, d of d, J = 5.8, 8.0 Hz, H_c), 3.18 (1 H, d of d of d, J = 3.7, 8.0, 8.0 Hz, H_b), 3.80 (3 H, s), 3.82 (3 H, s), 3.94 (1 H, d, J = 5.8 Hz), 4.74 (1 H, d of d of d, J = 5.0, 8.0, 8.0 Hz, H_a), 5.33 (1 H, d of t, J = 3.7, 1 Hz). Anal. Calcd for $C_{17}H_{24}O_6$: C, 62.95; H, 7.46. Found: C, 62.83; H, 7.63.

Reaction of 1-(*cis*-4-*tert*-Butyl-2-cyclohexen-1-yl) 2,2-Dimethyl Ethylenetricarboxylate (18) with Ferric Chloride. The reaction was done in the same manner as that for the trans triester **15** by using 0.134 g (0.41 mmol) of **18** and 0.20 g (1.2 mmol) of ferric chloride to give 0.118 g (88%) of crude material which was identical with the product derived from **15**.

Reaction of 1-(2-Butynyl) 2,2-Dimethyl Ethylenetricarboxylate (19) with Ferric Chloride. Treatment of 0.238 g (0.99 mmol) of triester **19** in 5 mL of methylene chloride with 0.26 g (1.6 mmol) of ferric chloride for 1 h followed by normal workup yielded 0.257 g (94%) of crude crystalline **20**. A portion was recrystallized from carbon tetrachloride (mp 101.5–102.0 °C): IR ($CHCl_3$) 1780, 1750, 1435, 1165 cm^{-1}; NMR ($CDCl_3$) δ 2.24 (3 H, m), 3.82 (3 H, s), 3.84 (3 H, s), 3.95 (1 H, m), 4.07 (1 H, d, J = 4 Hz), 4.85 (2 H, m). Anal. Calcd for $C_{11}H_{13}ClO_6$: C, 47.75; H, 4.74; Cl, 12.81. Found: C, 47.48; H, 4.79; Cl, 13.12.

Reaction of 1-(3-Phenyl-2-propynyl) 2,2-Dimethyl Ethylenetricarboxylate (21) with Ferric Chloride. Treatment of 0.190 g (0.62 mmol) of **21** in 3 mL of methylene chloride with 0.15 g (0.93 mmol) of ferric chloride followed by normal workup yielded 0.23 g of crude product. Purification on 10 g of silica gel (eluting with 80:20 hexane:ethyl acetate) yielded 0.200 g (95%) of **22** and **23** as a 55:45 mixture of isomers: IR (neat) 1780, 1740, 1435, 1260, 1230 cm^{-1}; NMR (CCl_4) δ 3.11 (1 H, d, J = 4 Hz, major isomer), 3.67 (3 H, s, major isomer), 3.70 (3 H, s, major isomer), 3.84 (3 H, s, minor isomer), 3.87 (3 H, s, minor isomer), 3.6–4.2 (2 H, minor isomer; 1 H, major isomer), 4.90 (2 H, AB d, major isomer), 5.10 (2 H, AB d, minor isomer), 7.4 (5 H, m); mass spectrum, m/e 340, 338 (M^+), 307, 302, 263, 211; mol wt calcd for $C_{16}H_{15}ClO_6$ m/e 338.0557, found m/e 338.0554.

Reaction of Trimethyl Ethylenetricarboxylate (24) with 2-Methyl-2-butene (25). To a solution of 0.141 g (0.79 mmol) of trimethyl ethylenetricarboxylate (**24**) and 0.066 g (0.95 mmol) of 2-methyl-2-butene (**25**) in 5 mL of methylene chloride was added 0.113 g (0.70 mmol) of ferric chloride. After 0.5 h the reaction was worked up in the usual manner. Column chromatography on 10 g of silica gel (eluting with 60:40 petroleum ether:ether) yielded 0.147 g (77%) of **26** which was greater than 95% pure by NMR. A portion was recrystallized from hexane:chloroform (mp 95.5–96.0 °C): IR ($CHCl_3$) 1775, 1750, 1435, 1260 cm^{-1}; NMR ($CDCl_3$) δ 1.01 (3 H, d, J = 6.7 Hz), 1.24 (3 H, s), 1.44 (3 H, s), 2.48 (1 H, d of q, J = 6.7, 12.0 Hz, H_c), 3.04 (1 H, d of d, J = 5.2, 12.0 Hz, H_b), 3.80 (3 H, s), 3.82 (3 H, s), 3.91 (1 H, d, J = 5.2 Hz, H_a). Anal. Calcd for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02. Found: C, 55.68; H, 7.01.

Reaction of Trimethyl Ethylenetricarboxylate (24) with Norbornene (31). To a solution of 0.264 g (1.31 mmol) of **24** and 0.152 g (1.61 mmol) of norbornene (**31**) in 5 mL of CH_2Cl_2 was added 0.30 g (1.8 mmol) of ferric chloride. After 1 h the reaction was worked up in the normal manner to yield 0.336 g (91%) of crystalline **32** which was 90% pure by NMR. A portion was recrystallized from hexane–chloroform for analysis (mp 99–100 °C): IR ($CHCl_3$) 1765, 1755, 1740, 1435, 1200 cm^{-1}; NMR ($CDCl_3$) δ 1.0–1.7 (6 H, br m), 2.18 (1 H, m), 2.33 (1 H, d of d, J = 4.5, 7.3 Hz, H_c), 2.51 (1 H, m), 2.72 (1 H, d of d, J = 4.5, 4.5 Hz, H_b), 3.79 (3 H, s), 3.82 (3 H, s), 4.02 (1 H, d, J = 4.5 Hz, H_a), 4.47 (1 H, br d, J = 7.3 Hz, H_d). Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.72; H, 6.35.

Reaction of (*Z*)-3-Methyl-2-pentene (27) with Trimethyl Ethylenetricarboxylate (24). To 0.132 g (0.72 mmol) of **24** and 0.07 g (0.8 mmol) of (*Z*)-3-methyl-2-pentene (**27**) in 5 mL of methylene chloride was added 0.141 g (1.2 mmol) of ferric chloride. The mixture was stirred for 1 h. Normal workup gave 0.145 g (82%) of crude product which was shown by NMR to be a 90:10 mixture of **28** and **30**. Purification on 10 g of silica gel (eluting with 4:1 hexane:ethyl acetate) yielded 28 mg of an unknown compound (R_f 0.23) and 105 mg (59%) of lactones **28** and **30** which crystallized on standing (R_f 0.11; mp 76-80°). The NMR spectrum showed the lactones to be a 90:10 mixture of **28** and **30**. An analytical sample was prepared by recrystallization from hexane:chloroform (mp 79–81 °C). The spectral data for **28** are as follows: IR (neat) 1775, 1750 (br), 1435 cm^{-1}; NMR (CCl_4) δ 0.97 (3 H, d, J = 7 Hz), 1.02 (3 H, t, J = 6.5 Hz), 1.39 (3 H, s), 1.3–1.8 (2 H, m), 2.47 (1 H, d of q, J = 12, 7 Hz), 2.88 (1 H, d of d, J = 5, 12 Hz), 3.75 (3 H, s), 3.76 (3 H, s), 3.78 (1 H, d, J = 5 Hz). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.57; H, 7.57.

The reaction was repeated at −15 °C by using 0.126 g (0.62 mmol) of **24**, 0.07 g (0.8 mmol) of **27**, and 0.12 g (0.64 mmol) of ferric chloride in 5 mL of methylene chloride to yield 0.133 g (79%) of crude lactones that contained a >95:5 mixture of **28** and **30**.

Reaction of (*E*)-3-Methyl-2-pentene (29) with Trimethyl Ethylenetricarboxylate (24). To 0.115 g (0.57 mmol) of **24** and 0.07 g (0.8 mmol) of (*E*)-3-methyl-2-pentene (**29**) in 3 mL of methylene chloride was added 0.10 g (0.62 mmol) of ferric chloride. The mixture was stirred for 1 h. Normal workup gave 0.12 g (78%) of crude product which was shown by NMR to be a 90:10 mixture of **30** and **28**. Column chromatography using 10 g of silica gel (eluting with 4:1 hexane:ethyl acetate) yielded 86 mg (55%) of a 9:1 mixture of lactones **30** and **28**. The spectral data for **30** are as follows: IR (neat) 1775, 1750 (br), 1435 cm^{-1}; NMR (CCl_4) δ 0.99 (3 H, d, J = 6.5 Hz), 1.02 (3 H, t, J = 7 Hz), 1.24 (3 H, s), 1.6–1.9 (2 H, m), 2.57 (1 H, d of q, J = 12, 6.5 Hz), 2.90 (1 H, d of d, J = 4.5, 12 Hz), 3.76 (3 H, s), 3.77 (3 H, s), 3.80 (1 H, d, J = 4.5 Hz). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.32; H, 7.18.

Acknowledgment. We wish to thank the National Institutes of Health for financial support.

Registry No. **1**, 71719-45-4; **2**, 71719-46-5; **3**, 71719-47-6; **4**, 71719-48-7; **5**, 71719-49-8; **6**, 71771-97-6; **7**, 71719-50-1; **8**, 71719-51-2; **9**, 71719-52-3; **10**, 71719-53-4; **11**, 71771-98-7; **12**, 71719-54-5; **13**, 71719-55-6; **14**, 71719-56-7; **15**, 71719-57-8; **17**, 71719-58-9; **18**, 71719-59-0; **19**, 71719-60-3; **20**, 71719-61-4; **21**, 71719-62-5; **22**, 71719-63-6; **23**, 71719-64-7; **24**, 51175-48-5; **25**, 513-35-9; **26**, 71719-65-8; **27**, 922-62-3; **28**, 71719-66-9; **29**, 616-12-6; **30**, 71719-67-0; **31**, 498-66-8; **32**, 71719-68-1.