were allowed to react for 5 min at 0 °C in 5 mL of CH_2Cl_2. Normal workup gave 180 mg of crude product that was purified by chromatography on silica gel (ether) to give 19 mg of recovered **10a** and 116 mg (63%, 72% based on recovered **10a**) of pure **11a**: NMR ($CDCl_3$) δ 5.40 (t, 1, J = 7 Hz) 4.92 (br s, 1), 4.83 (br s, 1), 4.12 (d, 2, J = 7 Hz), 3.51 (d, 2, J = 7 Hz), 2.80 (s, 2, OH), 1.66 (br s, 6), 1.3–2.5 (m, 5); IR (neat) 3320 (w), 2930, 1445, 1382, 1048, 1007, 898, 744 cm^{-1}. An analytical sample was prepared by evaporative distillation (90 °C, 0.25 torr). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.56; H, 11.05.

Reaction of linalool (10b) (150 mg, 1 mmol) **with paraformaldehyde** under identical conditions gave 184 mg of crude product. Chromatography on silica gel (1:1 hexane–ether and then ether) gave 33 mg of recovered **10b** and 91 mg (41%, 63% based on recovered **10b**) of **11b**: NMR ($CDCl_3$) δ 5.91 (ddd, 1, J = 10, 17, 1 Hz), 5.18 (dd, 1, J = 17, 1 Hz), 5.03 (dd, 1, J = 10, 1 Hz), 4.92 (br s, 1), 4.81 (br s, 1), 3.53 (d, 2, J = 7 Hz), 2.28 (br s, 2, OH), 1.9–2.4 (m, 1), 1.67 (s, 3), 1.46 (br s, 4), 1.25 (s, 3); IR (neat) 3360, 2935, 1648, 1460, 1417, 1377, 1127, 1055, 1007, 929, 900 cm^{-1}. An analytical sample was prepared by evaporative distillation (95 °C, 0.4 torr). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.53; H, 11.09.

Reaction of citral (10c)(150 mg, 1 mmol, *E–Z* mixture) **with paraformaldehyde** under identical conditions gave 171 mg of crude product. Chromatography on silica gel (1:1 hexane–ether and then ether) gave 35 mg of recovered citral, 20 mg of a mixture of citral and an unidentified compound, and 39 mg (21%) of a mixture of (*E*)- and (*Z*)-**11c**: NMR ($CDCl_3$) δ 10.02 (d, 1, J = 8 Hz, (*E*)-**11c**), 9.52 (d, 1, J = 8 Hz, (*Z*)-**11c**), 5.90 (d, 1, J = 8 Hz), 5.00 (br s, 1), 4.87 (br s, 1), 3.57 (d, 2, J = 7 Hz) 2.7–1.5 (m, 6), 2.17 (s, 3, (*E*)-**11c**), 1.98 (s, 3, (*Z*)-**11c**), 1.70 (s, 3); IR (neat) 3430, 2935, 2870, 1669, 1452, 1383, 1203, 1130, 1082, 1052, 920, 904, 742 cm^{-1}.

Reaction of geranylacetone (10d) (190 mg, 1 mmol) **with paraformaldehyde** under identical conditions gave 213 mg of crude product. Chromatography on silica gel (1:1 hexane–ether) gave 24 mg of recovered **10d** and 163 mg (73%, 85% based on recovered **11d**) of pure **11d**: ^1H NMR ($CDCl_3$) δ 5.09 (t, 1, J = 6 Hz), 4.94 (br s, 1), 4.84 (br s, 1), 3.53 (d, 2, J = 7 Hz), 2.12 (s, 3), 1.68 (s, 3), 1.60 (s, 3), 1.23–2.64 (m, 10); ^{13}C NMR ($CDCl_3$) δ 208.5, 144.8, 135.9, 122.5, 113.2, 63.9, 49.2, 43.5, 36.9, 29.6, 27.3, 22.2, 18.7, 15.7; IR (neat) 3430, 2930, 1712, 1648, 1447, 1364, 1169, 1051, 900 cm^{-1}. An analytical sample was prepared by evaporative distillation (112 °C, 0.15 torr). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.84; H, 10.90.

Reaction of 6-methyl-5-hepten-2-one (12) (126 mg, 1 mmol) **with paraformaldehyde** as described above for 5 min at 0 °C gave 135 mg of crude product. Chromatography on silica gel (9:1 hexane–ether) gave 5 mg of **14**, followed by 23 mg of recovered **12**. Elution with ether gave 52 mg (38%, 51% based on recovered **12**) of **13** as a 60:40 mixture of ketone and hemiketal forms.

The data for **14** follow: NMR ($CDCl_3$) δ 4.77 (br s, 1), 4.72 (br s, 1), 3.3–3.9 (m, 2), 1.2–2.5 (m, 5 with br s at δ 1.56), 1.72 (br s, 3), 1.20 (s, 6).

The data for **13** follow: NMR ($CDCl_3$) δ 4.6–5.0 (m, 2), 3.3–4.0 (m, 0.4 × 2, hemiketal form), 3.54 (d, 0.6 × 2, J = 7 Hz, ketone form), 1.2–2.9 (m, 0.6 × 5 + 0.4 × 7), 2.41 (t, 0.6 × 2, J = 8 Hz, ketone form), 2.12 (s, 0.6 × 3, ketone form) 1.67 (s, 3), 1.41 (s, 0.4 × 3, hemiketal form); IR (neat) 3200–3650, 3075, 2935, 2870, 1717, 1647, 1454, 1377, 1221, 1179, 1136, 1100, 1086, 1053, 980 cm^{-1}.

The identical reaction was carried out for 5 min at 0 °C and then 1 h at 25 °C to give 124 mg of crude product. Chromatography on silica gel (ether) gave 44 mg of recovered **12** followed by 52 mg (33%, 51% based on recovered **12**) of pure **15**: NMR ($CDCl_3$) δ 4.87 (br s, 1), 4.82 (br s, 1), 3.84 (dd, 1, J = 7, 11 Hz), 3.64 (dd, 1, J = 6, 11 Hz), 2.20 (br s, 2), 1.96 (br s, 2, OH), 1.24 (s, 3), 1.2–2.4 (m, 5); IR (neat) 3350, 3075, 2930, 2870, 1651, 1445, 1379, 1128, 1056, 1033, 920, 940 cm^{-1}.

Acknowledgment. We are grateful to the National Institutes of Health for financial support. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support. C.P.C.-M. gratefully acknowledges fellowship support from CONICIT (Venezuela).

Registry No. **1**, 616-12-6; **2**, 922-62-3; **3a**, 77103-98-1; **3b**, 90369-32-7; **3c**, 90369-33-8; **3d**, 90369-34-9; **3e**, 90369-35-0; **4a**, 90369-36-1; **4b**, 90369-37-2; **4c**, 90369-38-3; **4d**, 90369-39-4; **4e**, 90369-40-7; **5a**, 90388-39-9; **5b**, 90369-41-8; **5c**, 90369-42-9; **5d**, 90369-43-0; **5e**, 90369-44-1; **6b**, 90369-45-2; **6c**, 90369-46-3; **6d**, 90369-47-4; **6e**, 90369-48-5; **7b**, 90369-49-6; **7c**, 90369-50-9; **7d**, 90369-51-0; **7e**, 90369-52-1; **8b**, 90369-53-2; **8c**, 90369-54-3; **8e**, 90369-29-2; **9** (isomer 1), 90369-29-2; **9** (isomer 2), 90369-56-5; **11a**, 90369-26-9; **11b**, 90369-23-6; **11c** (isomer 1), 90369-24-7; **11c** (isomer 2), 90369-57-6; **11d**, 90369-25-8; **13** (isomer 1), 90369-27-0; **13** (isomer 2), 90369-28-1; **14**, 90369-31-6; **15**, 90369-30-5; Me_2AlCl, 1184-58-3; HCO_2H, 50-00-0; methylenecyclohexane, 1192-37-6; geraniol, 106-24-1; linalool, 78-70-6; citral, 5392-40-5; geranylacetone, 689-67-8; 6-methyl-5-hepten-2-one, 110-93-0; 2-phenylpropionaldehyde, 93-53-8; toluene, 108-88-3; paraformaldehyde, 30525-89-4; paraldehyde, 123-63-7; acetaldehyde, 75-07-0; propionaldehyde, 123-38-6; isobutyraldehyde, 78-84-2; 3-methoxypropionaldehyde, 2806-84-0.

Selectivity and Catalysis in Ene Reactions of Diethyl Oxomalonate

Mary F. Salomon, Simon N. Pardo, and Robert G. Salomon*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

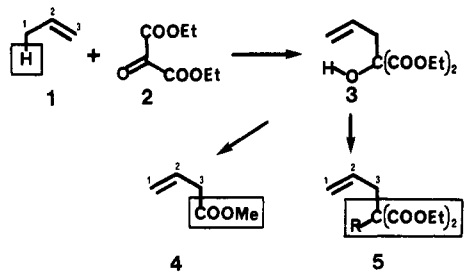
Received December 23, 1983

Stereoselectivity, regioselectivity, and structural selectivity of the thermal ene reactions of diethyl oxomalonate are strongly determined by steric approach control. For a series of 1-arylcyclopentenes thermal ene reactions only show a small enhancement of rate by electron-donating substituents ($\rho = -1.2 \pm 0.2$). Lewis acid catalysis is described which allows ene reactions of diethyl oxomalonate under thermally mild conditions. Furthermore, catalysis by $SnCl_4$ profoundly modifies the selectivity of the ene reactions which show a strong enhancement of rate by electron-donating substituents ($\rho = -3.9 \pm 0.3$) for a series of 1-arylcyclopentenes. Structural selectivity can be dramatically reversed by catalysts since the influence of electronic factors is amplified by Lewis acids, and steric approach control becomes less important.

The utility of ene reactions for carbon skeletal construction inheres not only in the efficiency of directly replacing an allylic C–H bond with a C–C bond but also in the regio- and stereospecificity of the operation. Thus, for example, we recently exploited ene reactions of diethyl oxomalonate (**2**) as a key step in new methods for the

0022-3263/84/1949-2446$01.50/0

Scheme I



synthesis of carboxylic esters 4[1] or malonic esters 5[2] from alkenes 1 (Scheme I). The constraints of a pericyclic mechanism ensure that ene reactions[3] of diethyl oxomalonate occur with allylic transposition of the C=C bond, substituting an α-hydroxymalonyl group for allylic hydrogen (1 → 3). However, for alkenes that possess nonequivalent allylic hydrogens or more than one C=C bond, the synthetic utility of the new methods depends on the feasibility of achieving one of several possible ene reactions. Therefore, the selectivity of diethyl oxomalonate ene reactions as well as the effect of catalysts on relative reaction rates and selectivity was explored. Relative reaction rates were determined by free-energy correlation studies with substituted arylcyclopentenes. Structural selectivity was determined by intramolecular competitions with selected dienes.

Results

Thermal Ene Reactions. Mono-, di-, and trisubstituted olefins listed in Table I afforded ene adducts upon heating with 1 equiv of diethyl oxomalonate at 80–185 °C for 1–340 h. Only a single adduct of better than 90% purity was isolated by simple short path distillation of crude product formed by the ene reactions of every olefin in Table I with the exception of 2-methylmethylenecyclohexane (**23a**), which gave regioisomeric adducts **23b** and **23b'**, and the terminal alkenes **11a–13a** and **42a–44a**, which gave both *E* and *Z* isomers. The structures of most ene adducts were readily established from their ^{1}H NMR spectra (see Experimental Section). However, the stereochemistries of the adducts **35b**, **37b**, and **38b** were determined by ^{1}H NMR spectral analysis of the corresponding allylcarboxylic esters **35c**, **37c**, and **38c** (vide infra).

To measure quantitatively the electronic effects that may contribute to the selectivities observed, a linear free-energy correlation study[5] was performed. Relative reactivities toward diethyl oxomalonate were determined for a series of 1-arylcyclopentenes **25a–31a** in pairwise intermolecular competitive reactions. Mixtures containing two olefins in equimolar amounts and 10 mol % of diethyl oxomalonate (relative to total olefin) were heated at 180 °C for 48 h. Product ratios were measured by analytical gas chromatography. Relative reaction rates, presumed to equal these product ratios, are presented in Table II and Figure 1.

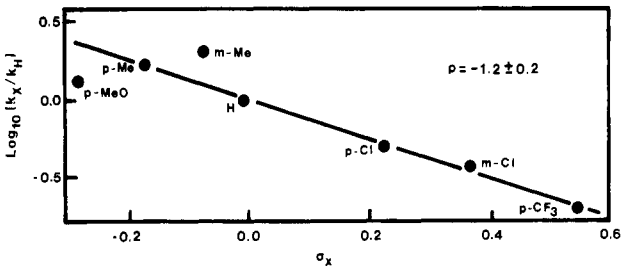


Figure 1. Substituent effects on thermal ene reactions of diethyl oxomalonate with 1-arylcyclopentenes.

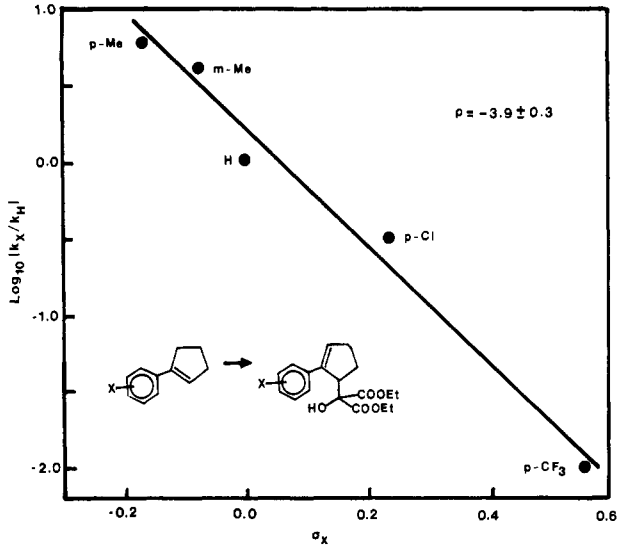


Figure 2. Substituent effects on $SnCl_4$-catalyzed ene reactions of diethyl oxomalonate with 1-arylcyclopentenes.

Catalyzed Ene Reactions. Catalysis by Lewis acids is known for ene reactions of numerous eneophiles.[3a,c] Generally, catalysis allows these reactions to be conducted under milder, more synthetically attractive reaction conditions. Furthermore, we hypothesized that catalysis might alter relative olefin reactivities (vide infra). Therefore, the possibility of catalysis for ene reactions of diethyl oxomalonate was explored. Indeed, various Lewis acids promote these reactions at or below room temperature (Table I). Olefins with mono (**43a**), geminal di (**10a**, **20a**, **45a**), vicinal di (**38a**), and trisubstitution (**16a**, **17a**, **24a–33a**, **44a**) were observed to undergo ene reactions catalyzed by $SnCl_4$, $ZnCl_2$, or $Hg(OCOCF_3)_2$. The relative reactivity of the olefins as a function of structure was determined by intramolecular competitions using dienes (**34a–45a**) containing two differently substituted C=C bonds.

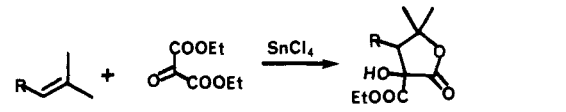
Reactions were performed by adding the required amount of catalyst to an equimolar solution of olefin and enophile in dry benzene at 0 °C. The reaction mixture was stirred up to 1 week at room temperature depending on the structure of the olefin and catalyst. In every case only a single ene adduct of better than 90% purity was isolated, after aqueous workup to remove catalyst, by simple short-path distillation. The structures of these ene adducts were established by their ^{1}H NMR spectra (see Experimental Section).

Relative rates for the $SnCl_4$-catalyzed ene reactions of diethyl oxomalonate were determined for a series of 1-arylcyclopentenes. To an equimolar amount of 1-phenylcyclopentene and substituted 1-arylcyclopentene dissolved in dry benzene was added 10 mol% (relative to total olefin) of diethyl oxomalonate. The resulting mixture was cooled to 0 °C, 1 equiv (relative to oxomalonate) of tin tetrachloride was added, and the reaction mixture was

(1) For a preliminary report of this work, see: Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2473.
(2) Pardo, S. N.; Ghosh, S.; Salomon, R. G. *Tetrahedron Lett.* **1981**, *22*, 1885.
(3) For reviews, see: (a) Hoffman, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (b) Conia, J. M.; LePerchee, P. *Synthesis* **1975**, 1. (c) Snider, B. B. *Acc. Chem. Res.* **1980**, *13*, 426.
(4) Wells, R. R. "Linear Free Energy Relationships"; Academic Press: New York, 1968. Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Reinehart: New York, 1959; pp 220–230.
(5) (a) Achmatowicz, O.; Achmatowicz, O., Jr. *Rocz. Chem.* **1962**, *36*, 1791; *Chem. Abstr.* **1963**, *59*, 8610*b*. (b) Achmatowicz, O., Jr.; Szymoniak, J. *J. Org. Chem.* **1980**, *45*, 1228.

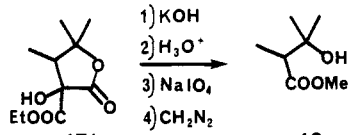
allowed to stand at room temperature overnight. Relative reaction rates were determined by analytical gas chromatography by measuring product ratios. The results are summarized in Table III and Figure 2.

The $SnCl_4$-catalyzed ene reactions of diethyl oxomalonate with acyclic trisubstituted olefins **16a**, **17a**, and **44a** were accompanied by the formation of lactone by-



16a, R = Et — **16ℓ**, R = Et
17a, R = Me — **17ℓ**, R = Me
44a, R = $(CH_2)_2CH{=}CH_2$ — **44ℓ**, R = $(CH_2)_2CH{=}CH_2$

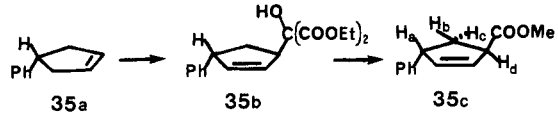
products **16l**, **17l**, and **44l**. ^1H NMR spectra of these lactones clearly show the presence of only one ethyl ester group, e.g., by the ratio of the OH proton at δ 3.9 to the ester CH_2 at δ 4.31–5. Although elemental analyses were only in fair agreement with the assigned structures, the latter were firmly established by oxidative bis-decarboxylation of **17l** to afford analytically pure methyl



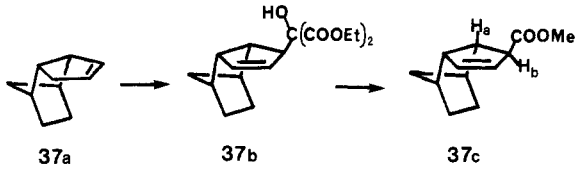
17ℓ — **46**

2,3-dimethyl-3-hydroxybutanoate (**46**) in 73% yield overall. The ratios of ene adducts to lactone byproducts are dependent on catalyst concentration and reaction time. Thus, the reaction of 2-methyl-2-butene (**17a**) with diethyl oxomalonate using 0.2 equiv of $SnCl_4$ at 0 °C for 5 min gives mainly ene adduct **17b**. When the reaction times are longer and 1.0 equiv of $SnCl_4$ catalyst is employed, the main volatile product is lactone byproduct which is isolated in about 30% yield by distillation.

Stereoselective Ene Reactions. Ene reactions of olefins **35a**, **37a**, and **38a** with diethyl oxomalonate (**2**) are regio- and stereoselective. Only a single isomeric tartronic



35a — **35b** — **35c**



37a — **37b** — **37c**

38a — **38b**

ester is produced in the ene reaction of each olefin with diethyl oxomalonate. The structures of ene adducts **35b** and **37b** were determined indirectly by conversion[1] to the corresponding carboxylic esters **35c** and **37c**. The structure of **35c** was assigned by analysis of its ^1H NMR spectrum, which has characteristic resonances of δ 2.02 (ddd, 1 H, J = 5, 9, 13 Hz), 2.75 (ddd, 1 H, J = 4, 9, 13 Hz), and 3.70 (s, 3 H). The resonances at δ 2.02 and 2.75 correspond to protons H_c and H_b, respectively. Analysis of the H_c resonance at δ 2.02 shows that there exist three coupling constants: J = 13 Hz, characteristic of geminally coupled protons, corresponding to J_{bc}; J = 9 Hz, characteristic of a syn coupling, corresponding to J_{dc}, and J = 5 Hz, characteristic of an anti coupling, corresponding to J_{ac}. Similar analysis of the resonances due to H_b lead to the conclusion that the phenyl and carbomethoxy groups are anti with respect to each other. Moreover, the presence of only one signal for the methyl ester group at δ 3.70 supports the conclusion that only one isomer has been formed. In the case of **37c**, from the analysis of the resonances at δ 2.77 (dt, 1 H, J = 11, 4 Hz) and 3.18 (dd, 1 H, J = 11, 4 Hz) for protons H_a and H_b, respectively, an anti relationship of these protons is evident from the anti vicinal coupling J_{ab} = 4 Hz. Only one signal was observed for the ester methyl at δ 3.70, which supports the conclusion that only one isomer was formed. The structure of **38b** is presumed by analogy to be the exo ene adduct **38b**.

Discussion

Regio- and Stereocontrol in Thermal Ene Reactions. Our interest in ene reactions of diethyl oxomalonate was sparked by the control inherent in such reactions. Control of the sites of C–C bond formation and C–H bond cleavage is important for synthetic exploitation of allylic activation in carbon skeletal construction. As noted above, ene reactions are constrained by a pericyclic mechanism to occur with allylic transposition of the C=C bond during replacement of an allylic hydrogen with a bond to the enophile.

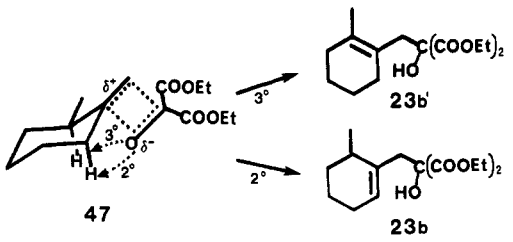
For olefins in which all allylic hydrogens are equivalent (**6a–15a**, **18a**, **19a**, **21a**, **22a**, **34a**, **35a**, and **42a**) only a single constitutional isomer of monoadduct with eneophile is expected. For ene adducts in which geometric isomerism of the product olefin is possible (**9b–13b** and **42b**, **44b**), cis–trans isomers were often detected, and it is assumed that generation of geometric isomer mixtures is general. Previous studies on the thermal ene reactions of diethyl oxomalonate have generally been limited to olefins whose allylic hydrogens are all equivalent.[5]

We now find that ene reactions of diethyl oxomalonate often proceed with synthetically valuable stereo and regioselectivity with olefins incorporating nonequivalent allylic hydrogens. Thus, for cases in which epimeric products could be generated, i.e., adducts **35b**, **37b**, and **38b**, only one isomer is formed. That is, C–C bond formation in ene reactions of olefins **35a**, **37a**, and **38a** with diethyl oxomalonate is stereoselective. Clearly, the stereochemical course of these ene reactions is dictated by steric approach control.

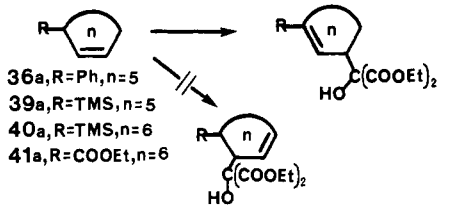
For olefins possessing a variety of nonequivalent allylic hydrogens, C–H bond cleavage need not be regioselective. Nevertheless, a high degree of regioselectivity is often observed in the thermal ene reactions diethyl oxomalonate. In the cases of olefins **37a** and **38a**, the preference observed for formation of **37b** and **38b**, respectively, may be the result of the strain that would be present in the new C=C bonds of the alternative ene adducts **37b′** and **38b′**, re-

37b′ — **38b′**

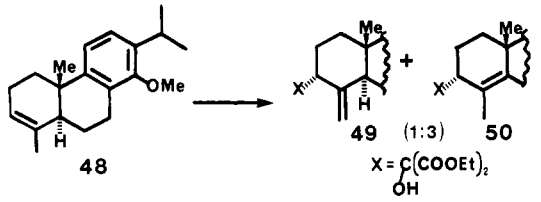
spectively. On the other hand it is not likely that the preference results from an inherent difference in the reactivity of 2° and 3° allylic hydrogens. Thus, olefin **23a** affords nearly equal yields of adduct **23b** via 2° C–H cleavage and **23b′** via 3° C–H cleavage. Assuming a transition state resembling a $2\pi + 2\pi$ charge-transfer complex[6] **47**, transfer of either the 3° or 2° allylic axial



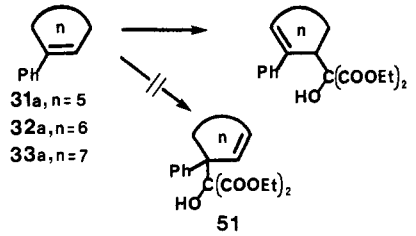
hydrogen occurs with similar ease. In contrast, there is a stong preference for cleavage of the 3° allylic C–H for cycloalkenes **36a**, and **39a–41a** where the allylic carbon bears a phenyl (e.g., **36a**), trimethylsilyl (e.g., **39a** and **40a**), or carbethoxyl substituent (e.g., **41a**).



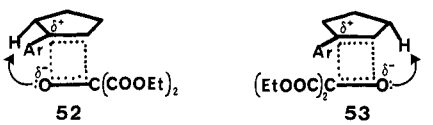
With trisubstituted olefins **16a**, **17a**, and **24a**, C=C bond formation is found to occur regioselectively at the least substituted terminus of the C=C bonds. A similar result was reported recently for the ene reaction of diethyl oxomalonate with the cyclic trisubstituted alkene **48**. A 91%



yield of adducts consisting of a 1:3 mixture of **49** and **50** was obtained.[7] This regioselectivity for C—C bond formation at the least substituted terminus of the C=C bond was also found for the 1-phenylcycloalkenes **31a–33a**.

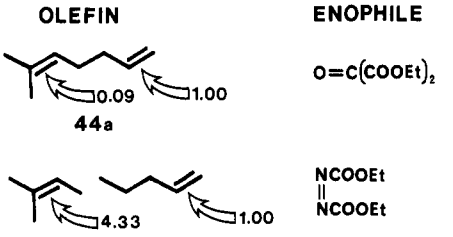


Adducts of structure **51** were never observed. A small accelerating effect of electron-donating substituents (ρ = -1.2 ± 0.2) was detected for thermal ene reactions of diethyl oxomalonate with a series of arylcyclopentenes **25a–31a**. This effect would be expected if the transition state resembled a $2\pi + 2\pi$ charge-transfer complex[6] of either structure **52** or **53**. That only **52** is important is the

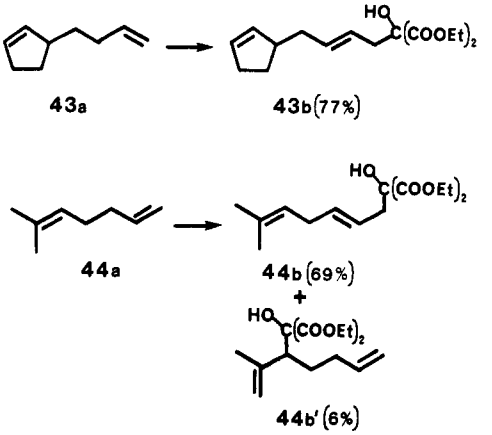


reasonable consequence of steric hinderance to the juxtaposition of the aryl and carbethoxyl substituents required in **53**.

Chart I



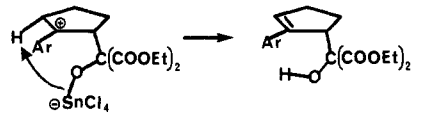
In fact, the thermal ene reactions of diethyl oxomalonate are extraordinarily sensitive to steric approach control. This is evident from the structural selectivity of its ene reactions with the dienes **43a** and **44a**. Thus, in spite of the expected *electronic* preference for reaction of the more electron rich C=C bond, a strong preference is observed for thermal ene reaction of diethyl oxomalonate to occur with the less electron rich monosubstituted C=C bond instead of the more electron rich di- or trisubstituted C=C of **43a** or **44a**, respectively. Only **43b** is produced from **43a**



whereas **44a** affords an 11:1 mixture of **44b** and **44b'**, respectively. This *extraordinarily high sensitivity of thermal ene reactions of diethyl oxomalonate to steric approach control* contrasts sharply with the behavior of diethyl azodicarboxylate as enophile.[8] Thus, the relative reactivities of mono- and trisubstituted C=C bonds of **44a** toward diethyl oxomalonate are 1.00 to 0.09. This contrasts sharply with the relative reactivities of 1-pentene and 2-methyl-2-butene (1.00 to 4.33) toward diethyl azodicarboxylate (Chart I).

Catalyzed Ene Reactions. As expected, in the presence of Lewis Acids, ene reactions of diethyl oxomalonate proceed at or below room temperature, with reaction times as short as a few minutes. More importantly, the electrophilicity of this enophile is dramatically enhanced by Lewis acids. Consequently, control of selectivity is more electronically determined and less dependent on steric effects than that for the corresponding thermal ene reactions. Thus, a large accelerating effect of electron-donating substituents ($\rho = -3.9 \pm 0.3$) is observed for $SnCl_4$–catalyzed ene reactions of diethyl oxomalonate with a series of arylcyclopentenes **26a–31a**. This ρ value is reminiscent of those observed for solvolytic reactions in which benzylic cation intermediates are considered important, e.g., hydrolysis of cumyl chloride ($\rho = -4.48 \pm 0.12$).[4] This might suggest a fully developed dipolar *intermediate* of structure **54**. Such dipolar intermediates are implicated by kinetic isotope effect studies for the ene-like reactions of the acetic anhydride–zinc chloride complex[9] which acts as a synthetic

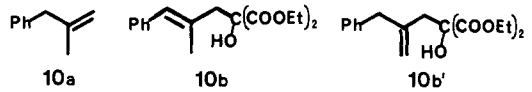
(6) (a) Achmatowicz, O., Jr.; Szymoniak, J. *J. Org. Chem.* **1980**, *45*, 4774. (b) Kwart, H.; Brechbiel, M. W. *Ibid.* **1982**, *47*, 3355. (c) Also see: Papadopoulos, M.; Jenner, G. *Tetrahedron Lett.* **1981**, *22*, 2773.
(7) Garver, L. C.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1982**, *104*, 867.
(8) Thaler, W. A.; Franzus, B. *J. Org. Chem.* **1964**, *29*, 2226.
(9) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848.



54

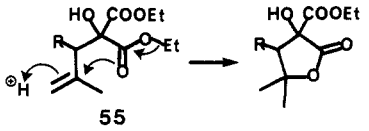
equivalent of an acetylium ion enophile.[10] However, the generality of such a stepwise mechanism for $SnCl_4$-catalyzed ene reactions of diethyl oxomalonate (**2**) was recently challenged by kinetic isotope effect studies for the $SnCl_4$-catalyzed reaction of **2** with **10a**.[11]

We reported synthetically valuable regioselectivity for the $SnCl_4$-catalyzed ene reaction of **10a** which affords a single adduct **10b** and no **10b′**. It is now apparent that



10a **10b** **10b′**

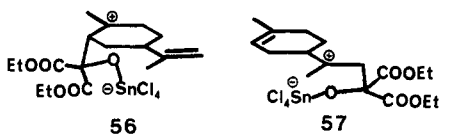
this selectivity does not result from an inherent difference in the reactivity of the primary and secondary allylic hydrogens. Rather, it is the result of equilibration of the initial reaction product mixtures. Thus, if the reaction is conducted under milder conditions, 0.2 equiv of $SnCl_4$ for 2–3 min instead of 1.0 equiv of $SnCl_4$ for 12 h, a 1:1 mixture of **10b** and **10b′** is obtained.[11] Protonation of **10b′** undoubtedly is the first step in the rearrangement to **10b**. Protonation of the initial product as in **55** is undoubtedly



55

responsible for generation of lactone byproducts in the $SnCl_4$-catalyzed ene reactions of trisubstituted olfeins **16a**, **17a**, and **44a**.

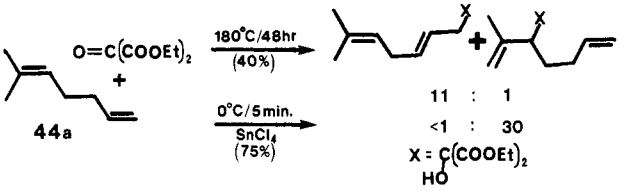
Attack at the more electron rich trisubstituted C=C bond in diene **45a** might be favored electronically for Zn^{2+}-catalyzed reaction with diethyl oxomalonate. However, to the extent that the reaction resembles a stepwise process, this electronic preference would disappear since attack at either C=C bond can lead to a 3° carbocationic intermediate **56** or **57**. Electronic effects thus being equal,



56 57

attack at the geminally disubstituted C=C bond is less sterically congested than a reaction involving **56**. Similarly selective ene reactions of limonene (**45a**) were observed previously. These include thermal reactions with acrylonitrile, 3-buten-2-one and methyl propiolate,[12] as well as Lewis acid catalyzed reactions with formaldehyde[13] and 3-buten-2-one.[12]

Most importantly, Lewis acid catalysis allows synthetically valuable control of reactivity. This is vividly illustrated by a comparison of the thermal and $SnCl_4$-catalyzed reactions of diene **44a** with diethyl oxomalonate (**2**). The preference for attack at the monosubstituted C=C bond in the thermal reaction is reversed by $SnCl_4$ to a preference for attack at the trisubstituted C=C bond.



Experimental Section

Melting points were measured with a Thomas-Hoover capillary melting point apparatus and are not corrected. Proton magnetic resonance spectra were recorded with a Varian A60A or EM 360A spectrometer with tetramethylsilane as internal standard and $CDCl_3$ as solvent. Analytical gas chromatography was performed with a Varian Aerograph Series 1400, using a 5 ft × $^1/_8$ in. column of 10% Apiezon N on 80/100 Chromosorb W at 225 °C. Preparative gas chromatography was carried out with a Varian Aerograph Model 90P using columns of 6, 3, 2, or 7 ft × 0.25 in. of 10% DC710 on 60/80 Chromosorb W. Elemental analyses were performed by Chemalytics, Inc., Tempe, Az.

Thermal Ene Reactions of Diethyl Oxomalonate; General Procedure. A Pyrex tube was charged with equimolar amounts of the olefin and diethyl oxomalonate,[15] sealed and kept at the temperature and for the time indicated in the tables (vide supra). The products were distilled. Products thus obtained were generally at least 90% pure. Samples for analysis were further purified by preparative gas–liquid-phase chromatography.

Tin Tetrachloride Catalyzed Ene Reactions of Diethyl Oxomalonate. Ene adducts were synthesized according to the following procedures. **Method A**: A dry three-necked flask fitted with addition funnel, magnetic stirrer, and nitrogen inlet was charged with a solution of alkene (3 mmol) and diethyl oxomalonate (0.52 g, 3 mmol) in dry benzene (25 mL). The mixture was cooled with an ice bath, and tin tetrachloride (0.79 g, 3 mmol) was added with a syringe. The resulting mixture was stirred at ambient temperature overnight. The reaction mixture was carefully poured into 10% HCl (20 mL) and extracted with ether (2 × 10 mL). The combined organic extracts were washed with water (2 × 5 mL) and saturated $NaHCO_3$ (3 × 5 mL) and dried over $MgSO_4$. After rotary evaporation of the solvent, the crude ene adduct was distilled under reduced pressure.

Method B: as described in method A, except for the amount of tin tetrachloride (0.16 g, 0.6 mmol) and reaction conditions (5 min at 0 °C).

Diethyl 2-(3-methyl-2-buten-1-yl)-2-hydroxypropane-1,3-dioate (6b): from 3-methyl 1-butene; bp 110–115 °C (3 mm); ^{1}H NMR δ 1.25 (t, J = 7 Hz, 6 H), 1.42–1.80 (m, 6 H), 2.76 (br d, J = 7 Hz, 2 H), 3.03 (br s, 1 H), 4.26 (t, J = 7 Hz, 4 H), 4.86–5.32 (m, 1 H). Anal. Calcd for $C_{12}H_{20}O_5$: C, 63.36; H, 8.51. Found: C, 63.18; H, 8.47.

Diethyl 2-(2-cyclohexylideneethyl)-2-hydroxypropane-1,3-dioate (7b): from vinylcyclohexane; bp 125–130 °C (0.2 mm); ^{1}H NMR δ 1.26 (t, J = 7 Hz, 6 H), 1.5 (br s, 6 H), 2.10 (br, s, 4 H), 2.73 (d, J = 7 Hz, 2 H), 3.65 (s, 1 H), 4.21 (q, J = 7 Hz, 4 H), 4.96 (t, J = 7 Hz, 1 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.52; H, 8.27.

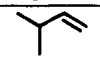
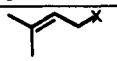
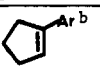
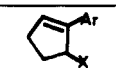
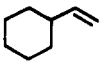
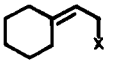
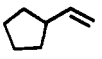
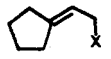
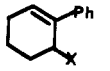
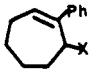
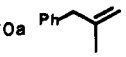
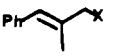
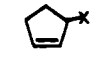
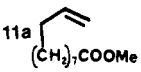
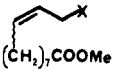
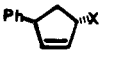
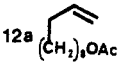
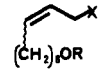
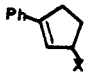
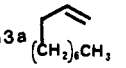
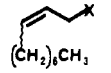
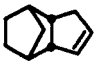
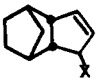
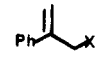
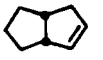
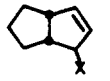
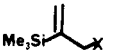
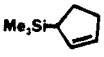
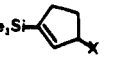
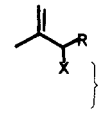
Diethyl 2-(2-cyclopentylideneethyl)-2-hydroxypropane-1,3-dioate (8b): from vinylcyclopentane; bp 116–120 °C (0.6 mm); ^{1}H NMR δ 1.31 (t, J = 7 Hz, 6 H), 1.65–2.11 (m, 2 H), 2.13–2.55 (m, 4 H), 2.95 (s, 1 H), 3.78 (s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.56 (br s, 1 H). Anal. Calcd for $C_{14}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.97; H. 7.76.

Diethyl 2-hydroxy-2-(3-phenyl-2-propenyl)propane-1,3-dioate (9b): from 2-propenylbenzene; bp 130–135 °C (0.05 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 6 H), 2.98 (d, J = 6 Hz, 2 H), 3.93 (br s, 1 H), 4.30 (q, J = 7 Hz, 4 H), 6.20 (dt, J = 16, 6 Hz, 1 H), 6.63 (d, J = 16 Hz, 1 H), 7.37 (br s, 5 H). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.73; H, 7.01.

Diethyl 2-hydroxy-2-(2-methyl-3-phenyl-2-propenyl)-propane-1,3-dioate (10b): from 2-benzylpropene; bp 147–153 °C (0.25 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 6 H), 1.90 (d, J = 1.5 Hz, 3 H), 2.96 (s, 2 H), 3.91 (s, 1 H), 4.27 (q, J = 7 Hz, 4 H),

(10) Hoffman, H. M. R.; Tsushima, T. *J. Am. Chem. Soc.* **1977**, *99*, 6008.
(11) (a) Stephenson, L. M.; Orfanopoulos, M. *J. Org. Chem.* **1981**, *46*, 2200. (b) Also see: Brechbiel, M.; Kwart, H. *Ibid.* **1982**, *47*, 5409.
(12) Mehta, G.; Reddy, A. V. *Tetrahedron Lett.* **1979**, 2625.
(13) Bloomquist, A. T.; Himics, R. J. *J. Org. Chem.* **1968**, *33*, 1156.
(14) Conversions of the α-hydroxymalonic esters into the corresponding methyl esters were performed as described previously: Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem Soc.*, in press.
(15) Prepared and purified as described previously: Pardo, S. N.; Salomon, R. G. *J. Org. Chem.* **1981**, *46*, 2598.

Table I. Ene Reactions of Diethyl Oxomalonate

starting olefin	products[a]	conditions	yields, %	starting olefin	products[a]	conditions	yields, %
6a 		72h/180°C	**6b**(83)	**25a-31a** 		12h/23°C 1.0equiv. $SnCl_4$ 48h/165°C	**25b-31b** (52-89)[c] **31b**(65)
7a 		72h/180°C	**7b**(78)	**31a**, Ar = Ph			
8a 		72h/180°C	**8b**(90)	**32a** 		12h/23°C 1.0equiv. $SnCl_4$ 72h/185°C	**32b**(59) **32b**(30)
9a 		48h/160°	**9b**(80)	**33a** 		12h/23°C 1.0equiv. $SnCl_4$	**33b**(72)
10a 		12h/23°C/ 1.0 equiv. $SnCl_4$	**10b**(75)	**34a** 		72h/180°C	**34b**(58)
11a 		72h/165°C	**11b**(63)	**35a** 		48h/150°	**35b**(19)
12a 		6h/180°C	**12b**(94) R=Ac	**36a** 		72h/145°C	**36b**(41)
13a 		24h/165°	**13b**(86)	**37a** 		72h/175°C	**37b**(93)
14a 		48h/160°	**14b**(86)	**38a** 		72h/185°C 12h/23°C 1.0equiv. $SnCl_4$	**38b**(87) **38b**(86)
15a 		48h/180°C	**15b**(55)	**39a** 		144h/145°C	**39b**(49)
16a, R = Et **17a**, R = Me		5 min/0°C/ 0.2equiv. $SnCl_4$	**16b**(50) **17b**(59)	**40a** 		72h/165°C	**40b**(60)
18a, n = 4		170h/80°C	**18b**(63)	**41a**		340h/165°C	**41b**(35)
19a, n = 5		12h/170°C	**19b**(90)				
21a, n = 6		3h/145°C	**21b**(91)	**42a**		24h/145°C	**42b**(60)
22a, n = 7		3h/145°C	**22b**(87)	**43a**		12h/23°C 1.0equiv. $SnCl_4$	**43b**(84)
20a		1h/145°C	**20b**(96)			24h/165°C	**43b**(77)
		5h/23°C/ 0.2equiv. $Hg(OTf)_2$	**20b**(90)	**44a**		5min/0°C 0.2equiv. $SnCl_4$	(40)
23a		3h/160°C	**23b'**(30)		3 : 97 [92 **44b** : 8 **44b'**]	[24h/180°]	[75]
			23b(35)				
24a		48h/180°C	**24b**(49)	**45a**		170h/23°C 0.2equiv. $ZnCl_2$	**45b**(67)
		12h/23°C/ 0.2equiv. $SnCl_4$	**24b**(69)				

[a] X = C(OH)(COOEt)$_2$. [b] Various 1-arylcyclopentenes, see text. [c] [Ar, yield (%)]: *p*-MeOPh (83), *p*-MePh (83), *m*-MePH (86), *p*-ClPh (69), *m*-ClPh (57), *p*-F_3CPh (52), Ph (71).

H), 6.42 (br s, 1 H), 7.1–7.5 (5 H). Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.53; H, 7.37.

Diethyl 2-(10-carbomethoxy-2-decenyl)-2-hydroxypropane-1,3-dioate (11b): from methyl 10-undecenoate; bp 155–170 °C (0.04 mm); ^{1}H NMR δ 1.32 (t, J = 7 Hz, 6 H), 1.0–1.80 (buried m, 10 H), 1.80–2.15 (m, 2 H), 2.15–2.50 (m, 2 H), 2.73 (d, J = 6 Hz, 2 H), 3.72 (s, 3 H), 3.85 (br s, 1 H), 4.30 (q, J = 7 Hz, 4 H), 5.35–5.68 (m, 2 H). Anal. Calcd for $C_{19}H_{32}O_7$: C, 61.27; H, 8.66. Found: C, 61.35; H, 8.59.

Diethyl 2-(11-acetoxy-2-undecenyl)-2-hydroxypropane-1,3-dioate (12b): from 11-acetoxyundec-1-ene; bp 190–205 °C (0.2 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 6 H), 1.17–1.77 (buried m, 14 H), 1.97 (s. 3 H), 2.68 (br d, J = 5 Hz, 2 H), 3.8 (br s, 1 H), 3.92–4.22 (buried m, 2 H), 4.25 (q, J = 7 Hz, 4 H), 5.30–5.47 (m, 1 H), 5.47–5.62 (m, 1 H). Anal. Calcd for $C_{20}H_{34}O_7$: C, 62.15; H, 8.87. Found: C, 62.08; H, 8.90.

Diethyl 2-hydroxy-2-(2-decenyl)propane-1,3-dioate (13b): from 1-decene; bp 140–155 °C (0.2 mm); ^{1}H NMR δ 0.88 (br t,

Table II. Relative Reaction Rates for Thermal Reaction of Diethyl Oxomalonate with Arylcyclopentenes

olefin	k_X/k_H	log (k_H/k_O)	σ_X
1-(*p*-methoxyphenyl)cyclopentene (**25a**)	1.34	0.13	−0.27
1-(*p*-methylphenyl)cyclopentene (**26a**)	1.62	0.21	−0.17
1-(*m*-methylphenyl)cyclopentene (**27a**)	2.04	0.31	−0.07
1-(*p*-chlorophenyl)cyclopentene (**28a**)	0.53	−0.28	0.23
1-(*m*-chlorophenyl)cyclopentene (**29a**)	0.372	−0.43	0.37
1-[*p*-(trifluoromethyl)phenyl]cyclopentene (**30a**)	0.185	−0.73	0.55
1-phenylcyclopentene (**31a**)	1.00	0.00	0.00

Table III. Relative Reaction Rates for the $SnCl_4$-Catalyzed Reaction of Arylcyclopentenes with Diethyl Oxomalonate

olefin	k_X/k_H	log (k_X/k_H)	δ_X
1-(*p*-methylphenyl)cyclopentene (**26a**)	5.88	0.77	−0.17
1-(*m*-methylphenyl)cyclopentene (**27a**)	4.52	0.66	−0.07
1-(*p*-chlorophenyl)cyclopentene (**28a**)	0.27	−0.57	0.23
1-[*p*-(trifluoromethyl)phenyl]cyclopentene (**30a**)	0.009[a]	−2.05	0.55
1-phenylcyclopentene (**31a**)	1.00	0.00	0.00

[a] Determined indirectly from $k_{p\text{-}CF_3}/k_{p\text{-}Cl}$.

J = Hz, 3 H), 1.27 (t, J = 7 Hz, 6 H), 1.08–1.45 (buried m, 10 H), 1.75–2.17 (m, 2 H), 2.72 (d, J = 5 Hz, 2 H), 3.73 (br s, 1 H), 4.23 (q, J = 7 Hz, 4 H), 5.30–5.45 (m, 1 H), 5.45–5.58 (m, 1 H). Anal. Calcd for $C_{17}H_{30}O_5$: C, 64.94; H, 9.62. Found: C, 64.87; H, 9.68.

Diethyl 2-hydroxy-2-(2-phenyl-2-propenyl)propane-1,3-dioate (14b): from (1-methylethenyl)benzene; bp 139–141 °C (0.05 mm) (reported 145–147 °C/0.6 mm);[5a] ^{1}H NMR δ 1.16 (t, J = 7 Hz, 6 H), 3.30 (br s, 2 H), 3.77 (br s, 1 H), 4.02 (q, J = 7 Hz, 2 H), 4.05 (q, J = 7 Hz, 2 H), 5.30 (br s, 1 H), 5.38 (d, J = 1.5 Hz, 1 H), 7.37 (s, 5 H). Anal. Calcd for $C_{16}H_{20}O_5$: C, 65.74; H, 6.90. Found: C, 65.73; H, 7.01.

Diethyl 2-hydroxy-2-[2-(trimethylsilyl)-2-propenyl]propane-1,3-dioate (15b): from 2-propenyltrimethylsilane; bp 86–95 °C (0.15 mm); ^{1}H NMR δ 0.08 (s, 9 H), 1.28 (t, J = 7 Hz, 6 H), 2.93 (s, 2 H), 3.75 (br s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.39–5.65 (m, 1 H), 5.65–5.92 (m, 2 H). Anal. Calcd for $C_{13}H_{24}O_5Si$: C, 54.14; H, 8.39. Found: C, 54.31; H, 8.04.

Diethyl 2-hydroxy-2-(2-methyl-1-penten-3-yl)propane-1,3-dioate (16b): from 2-methyl-2-pentene; 154–157 °C (15 mm); ^{1}H NMR δ 0.83 (t, 3 H, J = 7 Hz), 1.10–1.95 (buried m, 2 H), 1.26 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 1.71 (s, 3 H), 3.00 (q, J = 4.7 Hz, 1 H), 3.71 (s, 1 H), 4.22 (q, J = 7 Hz, 2 H), 4.29 (q, J = 7 Hz, 2 H), 4.88 (br s, 2 H). Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.73; H, 8.35.

Diethyl 2-hydroxy-2-(2-methyl-1-buten-3-yl)propane-1,3-dioate (17b): from 2-methyl-2-butene; bp 96–100 °C (2 mm); ^{1}H NMR δ 1.11 (d, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 1.76 (br s, 3 H), 3.28 (q, J = 7 Hz, 1 H), 3.75 (br s, 1 H), 4.26 (q, J = 7 Hz, 2 H), 4.33 (q, J = 7 Hz, 2 H), 4.83 (m, 1 H), 4.92 (br s, 1 H). Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.90; H, 8.24.

Diethyl 2-(1-cyclobutenyl)-2-hydroxypropane-1,3-dioate (18b): from methylenecyclobutane at 80 °C for 2 weeks; bp 90–105 °C (0.25 mm); ^{1}H NMR δ 1.28 (t, J = 7 Hz, 6 H), 2.42 (br s, 4 H), 2.78 (br s, 2 H), 3.78 (br s, 1 H), 4.27 (q, J = 7 Hz, 4 H), 5.85 (br s, 1 H). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.05; H, 7.49. Found: C, 58.94; H, 7.44.

Diethyl 2-(1-cyclopentenyl)-2-hydroxypropane-1,3-dioate (19b): from methylenecyclopentane; bp 116–120 °C (0.6 mm); ^{1}H NMR δ 1.31 (t, J = 7 Hz, 6 H), 1.65–2.11 (m, 2 H), 2.13–2.55 (m, 4 H), 2.95 (s, 2 H), 3.78 (s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.56 (br s, 1 H). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 60.74; H, 7.82.

Diethyl 2-[(6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl]-2-hydroxypropane-1,3-dioate (20b): from β-pinene; bp 115–120 °C (0.1 mm); ^{1}H NMR δ 0.82 (s, 3 H), 1.25 (s, 3 H), 1.30 (t, J = 7 Hz, 6 H), 1.55–2.47 (m, 6 H), 2.80 (br s, 2 H), 3.68 (br s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.30–5.53 (m, 1 H). Anal. Calcd for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.59; H, 8.47.

Diethyl 2-(1-cyclohexenylmethyl)-2-hydroxypropane-1,3-dioate (21b): from methylenecyclohexane; bp 107–110 °C (0.15 mm); ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.5–1.8 (m, 4 H), 1.85–2.25 (4 H), 2.75 (s, 2 H), 3.85 (s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.65 (br s, 1 H). Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.27; H, 8.22.

Diethyl 2-(1-cycloheptenylmethyl)-2-hydroxypropane-1,3-dioate (22b): from methylenecycloheptane; bp 115–130 °C (0.1 mm); ^{1}H NMR δ 1.28 (t, J = 7 Hz, 6 H), 1.40–1.70 (m, 6 H), 1.87–2.32 (m, 4 H), 2.72 (br s, 2 H), 3.67 (br s, 1 H), 4.23 (q, J = 7 Hz, 4 H), 5.65 (br t, 1 H, J = 6 Hz). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.57 H, 8.55.

Ene Reaction of 2-Methyl-1-methylenecyclohexane with Diethyl Oxomalonate. A mixture of ene adducts was obtained; bp 105–118 °C (0.03 mm). The two isomeric adducts were separable by preparative GLPC on a 3 ft × $^1/_4$ in. column packed with 10% DC710 on 60/80 Chromosorb W. At 218 °C the relative retention times of the isomers were 1.00 and 1.15 in 51% and 49% relative yields, respectively. The isomer of relative retention time 1.00 is **diethyl 2-hydroxy-2-[(3-methylcyclohex-1-en-2-yl)methyl]propane-1,3-dioate (23b)**: ^{1}H NMR δ 1.02 (d, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 6 H), 1.17–2.33 (m, 7 H), 2.67–2.92 (m, 2 H), 3.70 (br s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.47–5.67 (m, 1 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.39; H, 8.51.

The isomer of relative retention time 1.15 is **diethyl 2-hydroxy-2-[(2-methylcyclohex-1-en-1-yl)methyl]propane-1,3-dioate (23b)**: ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.45–1.75 (m, 4 H), 1.67 (br s, 3 H), 1.75–2.22 (m, 4 H), 2.92 (br s, 2 H), 3.62 (br s, 1 H), 4.28 (q, J = 7 Hz, 4 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.28; H, 8.42.

Diethyl 2-(1-cyclohex-1-enylethyl)-2-hydroxypropane-1,3-dioate (24b): from ethylidenecyclohexane; bp 135–141 °C (3 mm); ^{1}H NMR δ 1.09 (d, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.45–1.75 (m, 4 H), 1.80–2.20 (4 H), 3.11 (q, J = 7 Hz, 1 H), 3.70 (s, 1 H), 4.24 (q, J = 7 Hz, 2 H), 4.29 (q, J = 7 Hz, 2 H), 5.62 (br s, 1 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.55, H, 8.39.

Diethyl 2-hydroxy-2-[2-(*p*-methoxyphenyl)cyclopenten-3-yl]propane-1,3-dioate (25b): from 1-(*p*-methoxyphenyl)-cyclopentene; mp 113–115 °C; ^{1}H NMR δ 1.10 (t, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 1.70–2.90 (m, 5 H), 3.84 (s, 3 H), 3.4–4.4 (3 H), 4.35 (q, J = 7 Hz, 2 H), 6.01 (br s, 1 H), 6.83–7.11 (m, 2 H), 7.21–7.50 (m, 2 H). Anal. Calcd for $C_{19}H_{24}O_6$: C, 65.50; H, 6.94. Found: C, 65.53, H, 7.02.

Diethyl 2-hydroxy-2-[2-(*p*-methylphenyl)cyclopenten-3-yl]propane-1,3-dioate (26b): from 1-(*p*-methylphenyl)cyclopentene; 95–96 °C; ^{1}H NMR δ 1.03 (t, J = 7 Hz, 3 H), 1.27 (t, J = 7 Hz, 3 H), 1.8–2.7 (4 H), 2.32 (s, 3 H), 3.1–4.4 (4 H), 4.30 (q, J = 7 Hz, 2 H), 6.05 (br s, 1 H), 7.00–7.50 (m, 4 H). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.66; H, 7.28. Found: C, 69.33; H, 7.21.

Diethyl 2-hydroxy-2-[2-(*m*-methylphenyl)cyclopenten-3-yl]propane-1,3-dioate (27b): from 1-(*m*-methylphenyl)cyclopentene; bp 190–195 °C (0.3 mm); ^{1}H NMR δ 1.03 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 1.73–2.66 (m, 7 H), 3.1–4.3 (4 H), 4.27 (q, J = 7 Hz, 2 H), 6.00 (br s, 1 H), 6.90–7.83 (m, 4 H). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.55; H, 7.28. Found: C, 68.86; H, 6.80.

Diethyl 2-[2-(*p*-chlorophenyl)cyclopenten-3-yl]-2-hydroxypropane-1,3-dioate (28b): from 1-(*p*-chlorophenyl)-cyclopentene; mp 121–122.5 °C; ^{1}H NMR δ 1.08 (t, J = 7 Hz, 3 H), 1.39 (t, J = 7 Hz, 3 H), 1.66–2.76 (4 H), 3.3–4.4 (4 H), 4.34 (q, J = 7 Hz, 2 H), 6.05 (br s, 1 H), 7.26 (s, 4 H). Anal. Calcd for $C_{18}H_{21}O_5Cl$: C, 61.27; H, 5.99; Cl, 10.04. Found: C, 61.46; H, 6.04; Cl, 10.32.

Diethyl 2-[2-(*m*-chlorophenyl)cyclopenten-3-yl]-2-hydroxypropane-1,3-dioate (29b): from 1-(*m*-chlorophenyl)-cyclopentene; mp 79–80 °C; ^{1}H NMR δ 1.11 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.9–2.8 (4 H), 3.3–4.4 (4 H), 4.32 (q, J = 7 Hz, 2 H), 6.10 (br s, 1 H), 7.05–7.50 (m, 4 H). Anal. Calcd for $C_{18}H_{21}O_5Cl$: C, 61.27; H, 5.99. Found: C, 61.60; H, 6.20.

Diethyl 2-hydroxy-2-[2-[*p*-(trifluoromethyl)phenyl]-cyclopenten-3-yl]propane-1,3-dioate (30b): from 1-[*p*-(trifluoromethyl)phenyl]cyclopentene; mp 129–131 °C; ^{1}H NMR δ

1.03 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 3 H), 1.8–2.7 (4 H), 3.2–4.4 (4 H), 4.32 (q, J = 7 Hz, 2 H), 6.15 (br s, 1 H), 7.50 (s, 4 H). Anal. Calcd for $C_{19}H_{21}O_5F_3$: C, 59.06; H, 5.47. Found: C, 58.96; H, 5.54.

Diethyl 2-hydroxy-2-(2-phenylcyclopenten-3-yl)propane-1,3-dioate (31b): from 1-phenylcyclopentene; mp 81–82 °C; ^{1}H NMR δ 1.04 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.9–2.8 (4 H), 3.1–4.4 (4 H), 4.28 (q, J = 7 Hz, 2 H), 6.0 (br s, 1 H), 7.30 (s, 5 H). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 68.40; H, 6.97.

Diethyl 2-hydroxy-2-(2-phenyl-1-cyclohexen-3-yl)-propane-1,3-dioate (32b): from 1-phenylcyclohexene; bp 177–180 °C (0.5 mm); ^{1}H NMR δ 1.00 (t, J = 7 Hz, 3 H), 1.28 (t, J = 7 Hz, 3 H), 1.48–2.02 (m, 4 H), 2.02–2.38 (m, 2 H), 2.83–3.92 (m, 3 H), 4.08–4.55 (m, 3 H), 5.01 (br t, J = 3 Hz, 1 H), 7.23 (s, 5 H). Anal. Calcd for $C_{19}H_{24}O_5$: C, 68.65; H, 7.28. Found: C, 68.47; H, 7.21.

Diethyl 2-hydroxy-2-(2-phenylcyclohepten-3-yl)propane-1,3-dioate (33b): from 1-phenylcycloheptene; 183–185 °C (0.4 mm); ^{1}H NMR δ 0.81 (t, J = 7 Hz, 3 H), 1.26 (t, J = 7 Hz, 3 H), 1.4–4.2 (12 H), 4.26 (q, J = 7 Hz, 2 H), (5.94 dd, J = 6, 9 Hz, 1 H), 7.23 (s, 5 H). Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.49; H, 7.81.

Diethyl 2-(cyclopenten-1-yl)-2-hydroxypropane-1,3-dioate (34b): from cyclopentene; bp 110–115 °C (0.7 mm); ^{1}H NMR δ 1.26 (t, J = 7 Hz, 6 H), 1.4–3.0 (4 H), 3.56 (s, 1 H), 3.4–3.9 (buried, 1 H), 4.23 (q, J = 7 Hz, 4 H), 5.31–5.63 (m, 1 H), 5.75–5.98 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.34; H, 7.46.

Diethyl 2-hydroxy-2-(*trans*-5-phenyl-1-cyclopenten-3-yl)propane-1,3-dioate (35b): from 4-phenylcyclopentene; bp 145–155 °C (0.1 mm); ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.75–2.62 (m, 2 H), 3.58 (br s, 1 H), 4.33 (q, J = 7 Hz, 4 H), 4.08–4.58 (buried m, 2 H), 5.67–5.87 (m, 1 H), 5.92–6.10 (m, 1 H), 7.20–7.50 (m, 5 H). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 68.10; H, 6.86.

Methyl *trans*-5-phenyl-1-cyclopentene-3-carboxylate (35c): from diethyl 2-hydroxy-2-(*trans*-5-phenyl-1-cyclopenten-3-yl)-propane-1,3-dioate (**35b**)[14]; ^{1}H NMR δ 2.02 (ddd, J = 5, 9, 13 Hz, 1 H), 2.75 (ddd, J = 4, 9, 13 Hz), 3.70 (s, 3 H), 3.63–3.92 (buried m, 1 H) 3.92–4.33 (m, 1 H), 5.93 (s, 2 H), 7.07–7.50 (m, 5 H). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.34; H, 6.82.

Diethyl 2-hydroxy-2-(1-phenylcyclopenten-3-yl)propane-1,3-dioate (36b): from 3-phenylcyclopentene; bp 160–170 °C (0.2 mm); ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.7–2.42 (m, 2 H), 2.58–3.03 (m, 2 H), 3.7 (s, 1 H), 3.67–4.07 (m, 1 H), 4.32 (q, J = 7 Hz, 4 H), 6.02 (br d, J = 2 Hz, 1 H), 7.22–7.55 (m, 5 H). Anal. Calcd for $C_{18}H_{22}O_5$: C, 67.91; H, 6.97. Found: C, 67.90; H, 7.20.

Diethyl 2-(3α,4,5,6,7,7α-hexahydro-4,7-methanoinden-1-yl)-2-hydroxypropane-1,3-dioate (37b): from 3α,4,5,6,7,7α-hexahydro-4,7-methanoindene; bp 125–140 °C (0.01 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 6 H), 1.08–1.53 (buried m, 6 H), 2.00–2.50 (m, 3 H), 2.78–3.20 (m, 1 H), 3.30–3.58 (m, 1 H), 3.57 (br s, 1 H), 4.27 (q, J = 7 Hz, 4 H), 5.30–5.55 (m, 1 H), 5.60–5.88 (m, 1 H). Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.85. Found: C, 66.22; H, 7.78.

Methyl 3α,4,5,6,7,7α-hexahydro-4,7-methanoindene-1-*exo*-carboxylate (37c): from diethyl 2-(3α,4,5,6,7,7α-hexahydro-4,7-methanoinden-1-yl)-2-hydroxypropane-1,3-dioate (**37b**)[14]; ^{1}H NMR δ 1.23 (br s, 4 H), 1.45 (br s, 2 H), 2.30 (br s, 2 H), 2.77 (dt, J = 11, 4 Hz, 1 H), 3.18 (dd, J = 11, 4 Hz, 1 H), 3.33–3.53 (m, 1 H), 3.70 (s, 3 H), 5.73 (br s, 2 H). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.35.

Diethyl 2-(*cis*-bicyclo[3.3.0]oct-2-en-4-yl)-2-hydroxypropane-1,3-dioate (38b): from *cis*-bicyclo[3.3.0]oct-2-ene; bp 130–133 °C (0.15 mm); ^{1}H NMR δ 1.33 (t, J = 7 Hz, 6 H), 1.30–2.00 (6 H), 2.30–2.80 (1 H), 2.95–3.43 (2 H), 3.60 (br s, 1 H), 4.31 (q, J = 7 Hz, 2 H), 4.34 (q, J = 7 Hz, 2 H), 5.26–5.65 (m, 1 H), 5.65–5.93 (m, 1 H). Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.87; H, 7.91.

Diethyl 2-hydroxy-2-[1-(trimethylsilyl)-1-cyclopenten-3-yl]propane-1,3-dioate (39b): from 3-(trimethylsilyl)cyclopentene; bp 100–110 °C (0.2 mm); ^{1}H NMR δ 0.0 (s, 9 H), 1.22 (t, J = 7 Hz, 6 H), 1.47–2.1 (m, 2 H), 2.1–2.55 (m, 2 H), 3.53 (br s, 1 H), 4.25 (q, J = 7 Hz, 4 H), 3.46–4.47 (buried m, 1 H), 5.7 (br q, J = 2 Hz, 1 H). Anal. Calcd for $C_{15}H_{26}O_5Si$: C, 57.29; H, 8.33. Found: C, 57.56; H, 8.14.

Diethyl 2-hydroxy-2-[1-(trimethylsilyl)-1-cyclohexen-3-yl]propane-1,3-dioate (40b): from 3-(trimethylsilyl)cyclohexene; bp 94–109 °C (0.03 mm); ^{1}H NMR δ 0.0 (s, 9 H), 1.25 (t, J = 7 Hz, 6 H), 1.33–2.17 (m, 6 H), 2.88–3.25 (m, 1 H), 3.62 (s, 1 H), 4.26 (q, J = 7 Hz, 4 H), 5.62–5.74 (m, 1 H). Anal. Calcd for $C_{16}H_{28}O_5Si$: C, 58.50; H, 8.59. Found: C, 58.73; H, 8.42.

Diethyl 2-[1-(ethoxycarbonyl)cyclohex-1-en-3-yl]-2-hydroxypropane-1,3-dioate (41b): from ethyl cyclohex-2-enecarboxylate; bp 165–175 °C (0.1 mm); ^{1}H NMR δ 1.28 (t, J = 7 Hz, 3 H), 1.32 (t, J = 7 Hz, 6 H), 1.5–2.05 (m, 4 H), 2.08–2.43 (m, 2 H), 3.1–3.45 (m, 1 H), 3.8 (br s, 1 H), 4.22 (q, J = 7 Hz, 2 H), 4.33 (q, J = 7 Hz, 4 H), 6.8 (br s, 1 H). Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.52; H, 7.37. Found: C, 58.53; H, 7.35.

Diethyl 2-(octa-2,7-dienyl)-2-hydroxypropane-1,3-dioate (42b): from 1,7-octadiene; bp 118–120 °C (0.15 mm); ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.33–1.77 (m, 2 H), 1.80–2.33 (m, 4 H), 2.73 (br d, J = 6 Hz, 2 H), 3.77 (br s, 1 H), 4.32 (q, J = 7 Hz, 4 H), 4.83–5.27 (m, 2 H), 5.43–6.17 (m, 3 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.46; H, 8.51.

Diethyl 2-hydroxy-2-(4-cyclopenten-3-ylbut-2-enyl)-propane-1,3-dioate (43b): from 3-butenylcyclopent-2-ene; bp 125–132 °C (0.15 mm); ^{1}H NMR δ 1.30 (t, J = 7 Hz, 6 H), 1.92–2.47 (m, 6 H), 2.77 (br d, J = 5 Hz, 2 H), 2.67–2.92 (m, 1 H), 3.75 (s, 1 H), 4.28 (q, J = 7 Hz, 4 H), 5.37–5.67 (m, 2 H), 5.73 (br s, 2 H). Anal. Calcd for $C_{16}H_{24}O_5$: C, 64.85; H, 8.16. Found: C, 64.85; H, 8.19.

Diethyl 2-hydroxy-2-(6-methylhepta-2,5-dienyl)propane-1,3-dioate (44b): from 6-methyl-1,5-heptadiene; bp 107–111 °C (0.15 mm); ^{1}H NMR δ 1.28 (t, J = 7 Hz, 6 H), 1.60 (br s, 3 H), 1.68 (br s, 3 H), 2.50–2.95 (m, 4 H), 3.70 (br s, 1 H), 4.26 (q, J = 7 Hz, 4 H), 5.18 (t, J = 7 Hz, 1 H), 5.46 (m, 2 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.50; H, 8.25.

Diethyl 2-hydroxy-2-(2-methylhepta-1,6-dien-3-yl)-propane-1,3-dioate (44b′): from 6-methyl-1,5-heptadiene; bp 170–174 °C (15 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.5–2.3 (4 H), 1.73 (br s, 3 H), 2.87–3.35 (1 H), 3.80 (br s, 1 H), 4.23 (q, J = 7 Hz, 2 H), 4.29 (q, J = 7 Hz, 2 H), 4.6–5.3 (4 H), 5.3–6.1 (m, 1 H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36, H, 8.51. Found: C, 63.51; H, 8.55.

Diethyl 2-hydroxy-2-[2-(4-methyl-3-cyclohexen-1-yl)-prop-2-enyl]propane-1,3-dioate (45b): from 1-methyl-4-(2-methylethenyl)cyclohexene; bp 145–160 °C (0.2 mm); ^{1}H NMR δ 1.27 (t, J = 7 Hz, 6 H), 1.63 (br s, 3 H), 1.55–2.42 (buried m, 7 H), 2.83 (s, 2 H), 3.78 (br s, 1 H) 4.25 (q, J = 7 Hz, 4 H), 4.90 (br s, 2 H), 5.40 (br s, 1 H). Anal. Calcd for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.99; H, 8.24.

Linear Free Energy Correlation for the Relative Rates of Catalyzed Ene Reactions of Diethyl Oxomalonate with 1-Arylcyclopentenes. The relative reaction rates for the different 1-arylcyclopentenes with diethyl oxomalonate in the presence of tin tetrachloride were determined by competition reactions. The method is exemplified by the determination of $k_{p\text{-Cl}}/k_H$: To a solution of 1-(*p*-chlorophenyl)cyclopentene (53.60 mg, 0.3 mmol) and 1-phenylcyclopentene (43.76 mg, 0.3 mmol) in benzene (1 mL) was added diethyl oxomalonate (10 mg, 0.06 mmol). The reaction mixture was cooled with an ice bath, and tin tetrachloride (10 μL, 0.06 mmol) was added with a syringe. The resulting mixture was allowed to stand at ambient temperature overnight. The reaction mixture was worked up as described for the catalyzed ene reaction. The relative reaction rate, which is the same as the ratio of the products, was determined by analytical gas–liquid-phase chromatography, $k_{p\text{-Cl}}/k_H$ = 0.270. By the same procedure the following relative rates were measured: $k_{p\text{-CF}_3}/k_{p\text{-Cl}}$ = 0.033; $k_{p\text{-CH}_3}/k_H$ = 5.88; $k_{m\text{-CH}_3}/k_H$ = 4.52; also $k_{p\text{-CF}_3}/k_H$ was calculated as follows:

$$\frac{k_{p\text{-CF}_3}}{k_H} = \left(\frac{k_{p\text{-CF}_3}}{k_{p\text{-Cl}}}\right)\left(\frac{k_{p\text{-Cl}}}{k_H}\right) = (0.033)(0.270)$$

$$k_{p\text{-CF}_3}/k_H = 0.0089$$

Linear Free Energy Correlation for the Relative Rates of Thermal Ene Reactions of Diethyl Oxomalonate with 1-Arylcyclopentenes. As in the free energy study for the catalyzed ene reaction, the relative rates were determined by competition reactions. The procedure is illustrated by the mea-

surement of $k_{p\text{-Cl}}/k_H$: a Pyrex tube was charged with 1-(*p*-chlorophenyl)cyclopentene (53.60 mg, 0.3 mmol), 1-phenylcyclopentene (43.26 mg, 0.3 mmol), and diethyl oxamalonate (10 mg, 0.06 mmol). The tube was sealed and heated at 180 °C for 48 h. The reaction mixture was diluted with benzene and analyzed by analytical gas chromatography, $k_{p\text{-Cl}}/k_H = 0.527$. By the same method the following relative rates were determined: $k_{p\text{-CH}_3}/k_H = 1.62$; $k_{m\text{-CH}_3}/k_H = 2.04$; $k_{m\text{-Cl}}/k_H = 0.372$; $k_{p\text{-CF}_3}/k_H = 0.185$, and $k_{p\text{-OCH}_3}/k_H = 1.34$.

Lactone Byproducts from $SnCl_4$-Catalyzed Ene Reactions of Diethyl Oxomalonate. Byproducts which were only generated in trace amounts under the reaction conditions of method B (vide supra) became the major volatile products under the more vigorous conditions of method A. Samples isolated by distillation exhibited ^1H NMR spectra consistent with 3-carbethoxy-3-hydoxytetrahydro-2-furanone structures. Although elemental analyses suggested that these samples were not pure, chemical transformation of one of these byproducts into analytically pure methyl 2,3-dimethyl-3-hydroxybutanoate (vide infra) confirms the assigned structures.

4-(3-Butenyl)-3-carbethoxy-5,5-dimethyl-3-hydroxytetrahydro-2-furanone (44l): from 6-methyl-1,5-heptadiene; yield 15%; bp 124–126 °C (15 mm); ^1H NMR δ 0.7–1.11 (m, 2 H), 1.11–2.1 (m, 12 H), 2.41–2.95 (m, 2 H), 3.90 (br s, 1 H), 4.31 (q, J = 7 Hz, 2 H), 4.61–5.60 (m, 3 H). Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87. Found: C, 61.82; H, 7.56.

3-Carbethoxy-5,5-dimethyl-4-ethyl-3-hydroxytetrahydro-2-furanone (16l): from 2-methyl-2-pentene; yield 28%; bp 97–100 °C (0.25 mm); ^1H NMR δ 0.85 (t, J = 7 Hz, 3 H), 1.10–1.82 (m, 12 H), 2.32–2.75 (m, 1 H), 3.90 (br s, 1 H), 4.35 (q, J = 7 Hz, 2 H). Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 58.60; H, 7.84.

3-Carbethoxy-3-hydroxytetrahydro-4,5,5-trimethyl-2-furanone (17l): from 2-methyl-2-butene; yield 30%; bp 114–120 °C (2 mm); ^1H NMR δ 1.02 (d, J = 7 Hz, 3 H), 1.33 (t, J = 7 Hz, 3 H), 1.42 (s, 3 H), 1.51 (s, 3 H), 2.75 (q, J = 7 Hz, 1 H), 3.90 (br s, 1 H), 4.35 (q, J = 7 Hz, 2 H). Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 56.45; H, 7.80.

Methyl 2,3-Dimethyl-3-hydroxybutanoate. The byproduct, 3-carbethoxy-3-hydroxytetrahydro-4,5,5-trimethyl-2-furanone (17l), from $SnCl_4$-catalyzed ene reaction of diethyl oxomalonate with 2-methyl-2-butene was saponified with aqueous KOH, oxidatively decarboxylated with $NaIO_4$, and methylated with CH_2N_2 as described for analogous transformations of the corresponding one adduct[1] to afford the hydroxy ester in 73% yield overall: ^1H NMR δ 1.03 (d, J = 7 Hz, 3 H), 1.43 (s, 3 H), 1.51 (s, 3 H), 2.77 (q, J = 7 Hz, 1 H), 3.92 (s, 3 H), 4.01 (s, 1 H). Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.29; H, 9.71.

Zinc Chloride Catalyzed Ene Reactions of Diethyl Oxomalonate. Freshly fused zinc chloride (540 mg, 4 mmol, dried by heating in vacuo with a flame to the melting point) was placed in a dry 50-mL round-bottomed flash under nitrogen followed by anhydrous diethyl ether (30 mL, distilled from lithium aluminum hydride), the olefin (20 mmol), and diethyl oxomalonate (3 mL, 18.4 mmol). The solution was stirred at room temperature under nitrogen and monitored by NMR until no further reaction occurred (1–14 days). The mixture was washed with saturated aqueous sodium bicarbonate (30 mL), dried ($MgSO_4$), concentrated on the rotary evaporator, and distilled under high vacuum. The ene adduct was analyzed as in the thermal ene reaction above.

Mercuric Trifluoroacetate Catalyzed Ene Reactions of Diethyl Oxomalonate. Diethyl oxomalonate (3 mL, 18.4 mmol) and the olefin (20 mmol) were dissolved in anhydrous benzene (30 mL, distilled from potassium benzophenone ketyl) under nitrogen. Mercuric trifluoroacetate (1.70 g, 0.4 mmol) was added and the mixture stirred at room temperature until NMR indicated no more reaction was occurring (1–14 days). The product was worked up and analyzed as for the zinc chloride catalyzed reaction above.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. **2**, 609-09-6; **6a**, 563-45-1; **6b**, 90046-55-2; **7a**, 695-12-5; **7b**, 90046-56-3; **8a**, 3742-34-5; **8b**, 90046-57-4; **9a**, 300-57-2; (*E*)-**9b**, 77028-80-9; (*Z*)-**9b**, 90046-66-5; **10a**, 3290-53-7; (*E*)-**10b**, 77028-68-3; (*Z*)-**10b**, 77028-66-1; **11a**, 111-81-9; (*E*)-**11b**, 90046-58-5; (*Z*)-**11b**, 90046-85-8; **12a**, 112-19-6; (*E*)-**12b**, 90046-59-6; (*Z*)-**12b**, 90046-86-9; **13a**, 872-05-9; (*E*)-**13b**, 90046-60-9; (*Z*)-**13b**, 90046-87-0; **14a**, 98-83-9; **14b**, 78925-84-5; **15a**, 18163-07-0; **15b**, 90046-61-0; **16a**, 625-27-4; **16b**, 90046-62-1; **16l**, 90046-80-3; **17a**, 513-35-9; **17b**, 73961-93-0; **17l**, 90046-81-4; **18a**, 1120-56-5; **18b**, 90046-63-2; **19a**, 1528-30-9; **19b**, 78925-80-1; **20a**, 127-91-3; **20b**, 90046-65-4; **21a**, 1192-37-6; **21b**, 78925-81-2; **22a**, 2505-03-5; **22b**, 90046-64-3; **23a**, 2808-75-5; **23b**, 90046-68-7; **23b'**, 90046-67-6; **24a**, 1003-64-1; **24b**, 90046-69-8; **25a**, 709-12-6; **25b**, 73961-84-9; **26a**, 827-56-5; **26b**, 73961-87-2; **27a**, 37511-86-7; **27b**, 74012-80-9; **28a**, 2371-98-4; **28b**, 73961-85-0; **29a**, 2626-31-5; **29b**, 73961-88-3; **30a**, 38941-62-7; **30b**, 73961-86-1; **31a**, 825-54-7; **31b**, 73961-83-8; **32a**, 771-98-2; **32b**, 73961-82-7; **33a**, 25308-75-2; **33b**, 73961-81-6; **34a**, 142-29-0; **34b**, 90046-70-1; **35a**, 39599-89-8; **35b**, 90046-71-2; **35c**, 90046-83-6; **36a**, 37689-22-8; **36b**, 90046-72-3; **37a**, 2825-86-7; **37b**, 90046-73-4; **37c**, 90046-84-7; **38a**, 930-99-4; **38b**, 73961-80-5; **39a**, 14579-08-9; **39b**, 78925-83-4; **40a**, 40934-71-2; **40b**, 90046-74-5; **41a**, 55510-68-4; **41b**, 90046-75-6; **42a**, 3710-30-3; (*E*)-**42b**, 90046-76-7; (*Z*)-**42b**, 90046-88-1; **43a**, 73961-94-1; (*E*)-**43b**, 90046-77-8; (*Z*)-**43b**, 90046-89-2; **44a**, 7270-50-0; (*E*)-**44b**, 90046-78-9; (*Z*)-**44b**, 90046-90-5; **44b'**, 73961-90-7; **44l**, 90046-79-0; **45a**, 138-86-3; **45b**, 73961-91-8; **46**, 90046-82-5; $SnCl_4$, 7646-78-8; $ZnCl_2$, 7646-85-7; mercuric trifluoroacetate, 13257-51-7.