Enecarboxylation with Diethyl Oxomalonate as an Enophilic Equivalent of Carbon Dioxide. A Synthesis of Allylcarboxylic Acids[1]

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

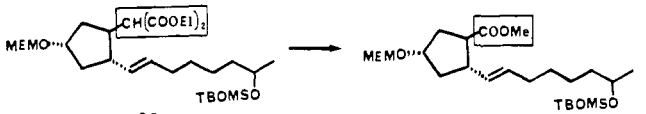
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received October 21, 1983*

Abstract: Allylcarboxylic acids are prepared from alkenes by a two-stage process which is synthetically equivalent to an ene reaction of carbon dioxide: (1) ene reaction with diethyl oxomalonate to afford an α-hydroxylmalonic ester and (2) oxidative bisdecarboxylation of the derived α-hydroxymalonic acid. The oxidative bisdecarboxylation of α-hydroxymalonic acids can sometimes be achieved with sodium periodate. However, occasionally decarboxylation is only partial, leading to pyruvic rather than carboxylic acids. While the bisdecarboxylations with periodate have previously been "buffered with a little pyridine", the latter is now shown to inhibit the reaction. In fact the pyruvate:carboxylate ratio can be a sensitive function of the amount of pyridine present in the reaction mixture, and the oxidative decarboxylation can be controlled to yield almost exclusively carboxylic or pyruvic acid. An effective new reagent, ceric ammonium nitrate in aqueous acetonitrile, was discovered for oxidative bisdecarboxylation of α-hydroxymalonic acids. Fortunately this reagent provides good to excellent yields of allylcarboxylic acids in many cases for which sodium periodate proved unsatisfactory.

Ene reactions are valuable for converting alkenes, which are readily available, into more functionally complex derivatives.[2] Allylic carboxylation of alkenes (enecarboxylation) by ene reactions of carbon dioxide is unknown, although the corresponding retro-ene decarboxylation of allylcarboxylic acids is well-known.[3] The ability of the carbonyl group to participate in ene reactions depends on the nature of the substituents on the carbonyl carbon, and in general electron-withdrawing groups enhance reactivity.[2] Since oxidative bisdecarboxylation of α-hydroxymalonic (tartronic) acids with periodate generates carboxylic acids,[4] we envisioned an enecarboxylation process which employs diethyl oxomalonate as an enophilic[5] equivalent of carbon dioxide (Scheme I). We now report that this protocol succeeds admirably in many cases. Moreover, we discovered that cerium(IV) oxidatively bisdecarboxylates the tartronic acid intermediates (**4** → **5**), providing good yields in many cases for which the periodate oxidation is unsatisfactory.

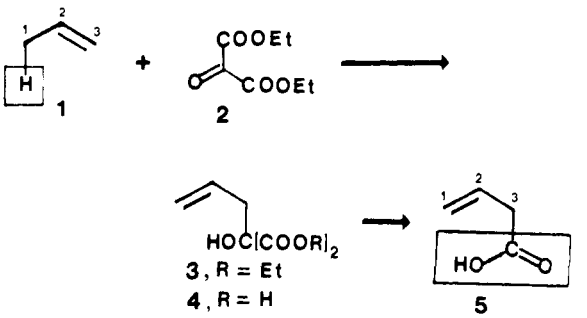
Results

The malonic ester unit can be converted into a carbomethoxyl group by α-hydroxylation and subsequent oxidative bisdecarboxylation of the derived tartronic acid (as for **4** → **5**) followed by esterification. In applying this strategy to the synthesis of the (±)-brefeldin A precursor **30** from malonic ester **29**, the

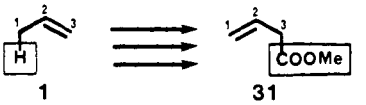


key oxidative bisdecarboxylation was performed with "aqueous sodium periodate buffered with a little pyridine".[4] We adopted

Scheme I

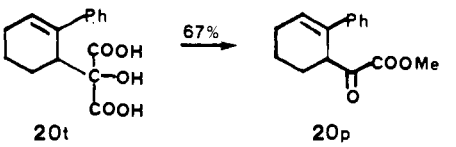


these reaction conditions for developing a process which achieves allylic carbomethoxylation (**1** → **31**) via ene reactions of diethyl



oxomalonate (**2**). A wide variety of ene adducts (**6b–28b**) were prepared by thermal or Lewis acid catalyzed ene reactions of **2** (Table I). The ene adducts were saponified by vigorous stirring with an aqueous 20% KOH solution at 20 °C. The diacids from the saponification were oxidatively bisdecarboxylated with aqueous sodium periodate buffered with a little pyridine to afford allylcarboxylic acids, which were characterized by ^{1}H NMR and elemental analysis after conversion to the corresponding methyl esters.

While this protocol succeeds admirably in many cases (Table I), in a few cases pyruvic esters were obtained instead of the expected carboxylic esters. Thus, under standard conditions (see Experimental Section), tartronic acid **20t** affords pyruvic ester **20p**. Both **13t** and **19t** gave mixtures of pyruvic esters **13p** and



19p and carboxylic esters **13c** and **19c**. Most importantly, we noticed that the pyruvate:carboxylate ratio is a sensitive function of the amount of pyridine present in the reaction mixture (Figure 1). Rather than being a beneficial "buffer", we find that in some cases, such as tartronic acid **24t**, pyridine suppresses oxidative bisdecarboxylation. In fact, the oxidative decarboxylation of **19t**

(1) For a preliminary report on this work see: Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2473.

(2) 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.

(3) (a) Arnold, R. T.; Elmer, O. C.; Dodson, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 4359. (b) House, H. O.; Müller, H. C. *J. Org. Chem.* **1962**, *27*, 4436. (c) Bigley, D. B. *J. Chem. Soc.* **1964**, 3897. (d) Bigley, D. B.; Thurman, J. C. *Ibid.* **1965**, 6202; (e) *J. Chem. Soc. B* **1966**, 1076. (f) *Ibid.* **1967**, 941; (g) *Ibid.* **1968**, 436. (h) Bigley, D. G.; May, R. W. *Ibid.* **1967**, 557.

(4) For a recent example see: Corey, E. J.; Wollenberg, R. H. *Tetrahedron Lett.* **1976**, 4705.

(5) For studies on the ene reactions of oxomalonic esters see: (a) Achmatowicz, O.; Achmatowicz, O., Jr. *Rocz. Chem.* **1962**, *36*, 1971. *Chem. Abstr.* **1963**, *59*, 8610b. (b) Achmatowicz, O., Jr.; Szymoniak, J. *J. Org. Chem.* **1980**, *45*, 1228. (c) Salomon, M. F.; Pardo, S. N.; Salomon, R. G. *Ibid.*, in press.

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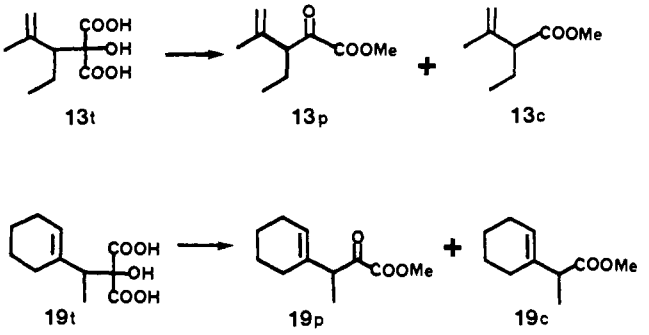
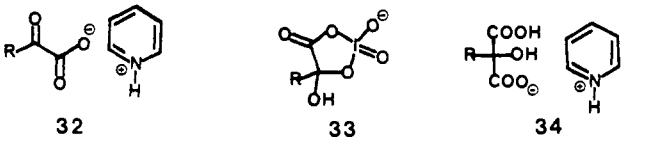
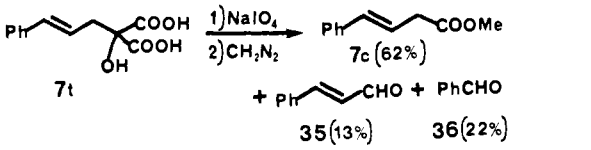


followed by esterification can be controlled to yield almost exclusively carboxylic ester **19c** or pyruvic ester **19p**. In the absence of pyridine, the carboxylate **19c** is virtually the sole product. Even miniscule amounts of pyridine diminish the yield of **19c** owing to isolation instead of the corresponding pyruvic ester **19p**. With 62 mol % of pyridine relative to hydroxymalonic acid **19t**, the yield of pyruvic ester **19p** nearly equals the yield of carboxylic ester **19c**. It is tempting to speculate that the pyridinium salt **32** is reluctant to form the requisite cyclic periodate intermediate **33** but that α-hydroxymalonic acid **19t** is not rendered similarly unreactive toward periodate by conversion to a pyridinium salt, **34**.[6] Whatever the mechanistic basis, the effect of pyridine on

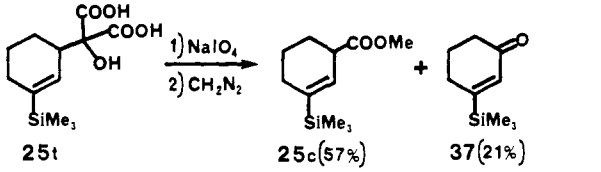


such oxidative bisdecarboxylations is pertinent to synthetic applications. With excess pyridine present (3 mol relative to **19t**, 0.1 mol relative to periodate), pyruvate **19p** is favored over **19c** by 9:1.

Noncarboxylic acid byproducts were isolated and characterized from the oxidative bisdecarboxylations of **7t** and **25t**. Thus, all of the starting tartronic acid **7t** not converted to carboxylic ester **7c** is accounted for by the coproduction of cinnamaldehyde (**35**) and benzaldehyde (**36**). The cyclohexenone **37** is produced in



21% yield in addition to the desired ester **25c** upon treatment of tartronic acid **25t** with $NaIO_4$ followed by CH_2N_2. Of course



these byproducts are readily removed from the desired carboxylic acid by extraction of the latter into aqueous base.

Clearly, sodium periodate is not always effective for oxidative bisdecarboxylation of allyltartronic acids. Thus, the tartronic acids derived from ene adducts **9a**, **10a**, **26a**, and **27a** failed to give more than traces (<5% yields) of allylcarboxylic acids under the standard conditions. This failure prompted a search for an alternative reagent. An effective new reagent, ceric ammonium nitrate in aqueous acetonitrile, was discovered. It is especially

(6) The rates of formation and decomposition of cyclic periodate intermediates to products are known to be sensitive functions of pH. See: Bunton, C. A. In "Oxidation in Organic Chemistry"; Wiberg, K. B., Ed.; Academic Press: New York, 1965; Part A, pp 367–88. Also see: Fleury, P.; Courtois, J. *C. R. Hebd. Seances Acad. Sci.* **1946**, *223*, 633. Sprinson, D. B.; Chargaff, E. *J. Biol. Chem.* **1946**, *164*, 433.

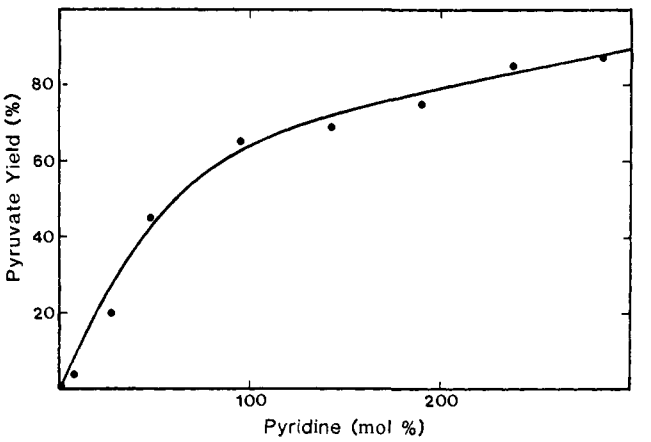
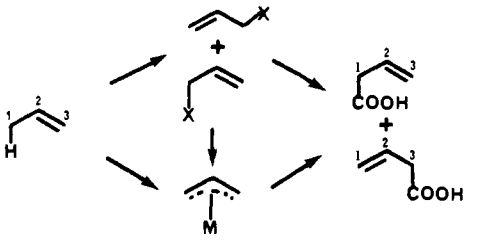
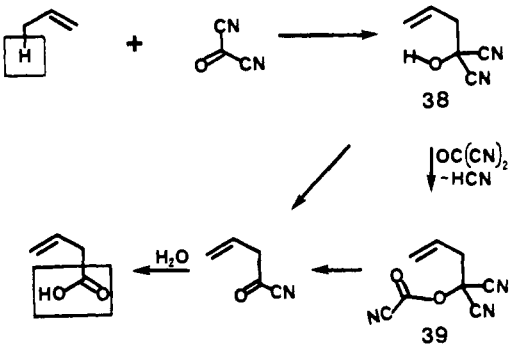


Figure 1. Effect of pyridine on the relative yield of pyruvate in the oxidative decarboxylation of **19t** (0.13 mmol) with excess $NaIO_4$ (3.7 mmol).

Scheme II



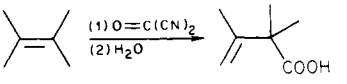
Scheme III



gratifying that this alternative reagent provides good to excellent yields of allylcarboxylic acids in oxidative decarboxylations of the tartronic acids **9a**, **10a**, **26a**, and **27a** for which $NaIO_4$ proved unsatisfactory.

Discussion

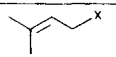
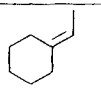
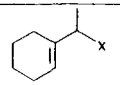
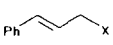
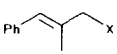
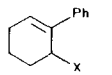
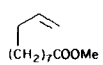
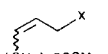
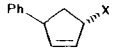
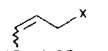
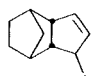
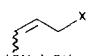
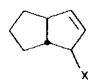
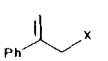
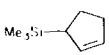
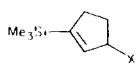
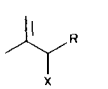
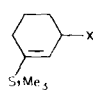
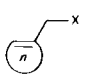
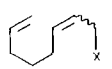
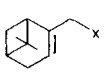
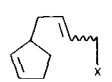
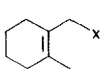
Synthetic methods which achieved stepwise substitution of a carboxyl group for allylic hydrogen by oxidation or metalation followed by C–C bond formation can result in retention or migration of the C=C bond (Scheme II). Ene reactions allow allylic functionalization with complete and predictable migration of the C=C bond. Direct enecarboxylation of olefins via ene reactions of carbon dioxide remain unknown. Enecarboxylation of tetramethylethylene was achieved by a stepwise process involving reaction with carbonyl cyanide followed by hydrolysis of an intermediate.[7]



Many additional examples of this process were reported subsequently, and these reactions are now considered to involve an initial ene reaction of carbonyl cyanide (Scheme III).[8] The carbonyl

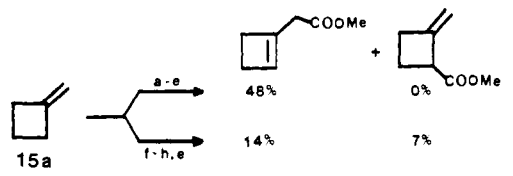
(7) Malachowski, R.; Jurkiewicz, L. *Rocz. Chem.* **1950**, *24*, 88; *Chem. Abstr.* **1954**, *48*, 3914c.

Table I. Synthesis of Allylcarboxylic Esters via Ene Reactions of Diethyl Oxomalonate

starting olefin			ene reaction		oxidation	starting olefin		ene reaction		oxidation
no.	compd	products[a]	conditions	yield, %	(Ce^{4+}, IO_4^-)[b]		products[a]	conditions	yield, %	(Ce^{4+}, IO_4^-)[b]
6a			72 h/180 °C	**6b** (83)	**6c** (..., 49)	**19a** 		48 h/180 °C 12 h/23 °C/0.2 equiv of $SnCl_4$	**19b** (49) **19b** (69)	**19c** (..., 78[i])
7a			48 h/160 °C	**7b** (80)	7c (83, 62[c])					
8a			12 h/23 °C/1.0 equiv of $SnCl_4$	**8b** (75)	**8c** (..., 87)	**20a** 		12 h/23 °C/1.0 equiv of $SnCl_4$ 72 h/185 °C	**20b** (59) **20b** (30)	**20p** (..., 67[j])
9a			72 h/165 °C	**9b** (63)	9c (87, <5)	**21a** 		48 h/150 °C	**21b** (19)	**21c** (81, 97)
10a			6 h/180 °C	**10b** (94) R = Ac	**10c** (60, <5) R = H	**22a** 		72 h/175 °C	**22b** (93)	**22c** (33, 65)
11a			24 h/165 °C	**11b** (86)	11c (76, 25[d])	**23a** 		72 h/185 °C 12 h/23 °C/1.0 equiv of $SnCl_4$	**23b** (87) **23b** (86)	**23c** (..., 62)
12a			48 h/160 °C	**12b** (86)	**12c** (64, 94)	**24a** 		144 h/145 °C	**24b** (49)	**24c** (84, 76)
13a, R = Et **14a**, R = Me			5 min/0 °C/0.2 equiv of $SnCl_4$	**13b** (50) **14b** (59)	**13c** (..., 88[e]) **14c** (..., 87)	**25a** 		72 h/165 °C	**25b** (60)	**25c** (..., 57[k])
15a, $n = 4$ **16a**, $n = 7$			170 h/80 °C 3 h/145 °C	**15b** (63) **16b** (87)	**15c** (98, 96) **16c** (45, 65)	**26a** 		24 h/145 °C	**26b** (60)	**26c** (87, <5)
17a			1 h/145 °C 5 h/23 °C/0.2 equiv of $Hg(OTf)_2$	**17b** (96) **17b** (90)	**17c** (..., 65)	**27a** 		12 h/23 °C/1.0 equiv of $SnCl_4$ 24 h/165 °C	**27b** (84) **27b** (77)	**27c** (68, <5)
18a			3 h/160 °C	**18b'** (30)	*f*	**28a**		5 min/0 °C/0.2 equiv of $SnCl_4$	(40)	**28c** (..., 68)
				18b (35)	**18c** (80,[g] 80[h])			[24 h/180 °C]	[75]	**28c'** (..., 57)

[a] For ene reactions X = C(OH)(COOEt)$_2$; for oxidation reactions followed by treatment with CH_2N_2 in ether, X = COOMe. [b] From left to right, yields of methyl allylcarboxylic ester after oxidation with Ce(IV) or periodate, respectively, followed by methylation with diazomethane. [c] Cinnamaldehyde (13%) and benzaldehyde (22%) byproducts also isolated. [d] Octanal and decenal byproducts also isolated. [e] Combined yield of carboxylic and pyruvic esters; ratio varies; see text. [f] See text. [g] Yield based on **18b** contained in a 1:1 mixture with **18b'**; product contains less than 15% methyl 2-methylcyclohexenylethanoate. [h] Yield based on **18b** contained in a 1:1 mixture with **18b'**; product contains less than 9% methyl 2-methylcyclohexenylethanoate. [i] Yield of **19c** contains only traces of the pyruvate **19p**; see text. [j] Yield of pyruvate ester. [k] Byproduct 3-(trimethylsilyl)cyclohex-2-en-1-one (21%) also isolated.

Scheme IV[a]

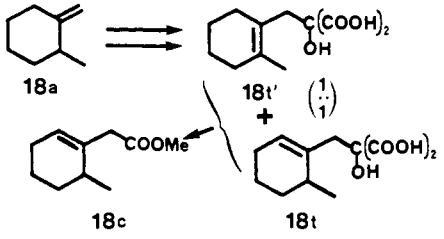


[a] (a) $OC(COOEt)_2$, 80 °C, 6 days; (b) KOH, H_2O; (c) HCl; (d) $NaIO_4$, H_2O, pyridine; (e) CH_2N_2, Et_2O; (f) BuLi; TMEDA, −78 °C; (g) CO_2; (h) H_3O^+.

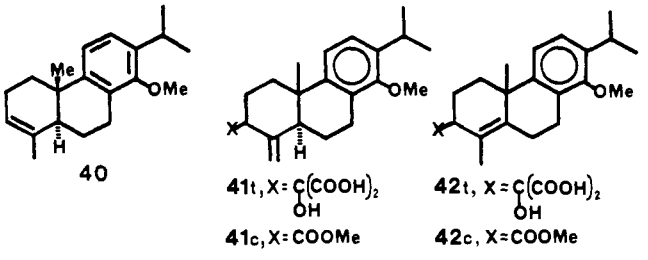
cyanide route for enecarboxylation is mild and effective. However, this reagent is highly toxic and less readily available than diethyl oxomalonate. These problems are exacerbated by the proclivity of the initial adduct **38** to react with a second equivalent of carbonyl cyanide to give **39** with the evolution of HCN.

We now have demonstrated the feasibility of a stepwise process which exploits diethyl oxomalonate as an enophilic equivalent of carbon dioxide. Allylic carboxylation of methylenecyclobutane (**15a**) provides a noteworthy contrast between the ene approach and a metalation–carboxylation procedure.[9] The overall conversion via ene reaction of diethyl oxomalonate provides transposed allylcarboxylic acid regiospecifically (Scheme IV).

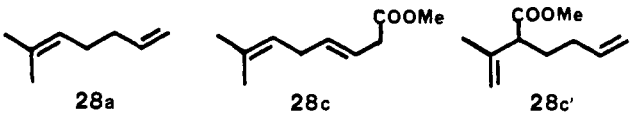
The regioselective enecarboxylation achievable with olefin **18a** is not the result of a regioselective ene reaction. Rather, nonselective reaction of diethyl oxomalonate generates a 1:1 mixture of isomeric adducts. However, treatment of the derived tartronic acids, **18t'** and **18t**, with periodate or cerium(IV) affords nearly pure **18c** in 80% yield based on **18t** contained in the mixture.



Apparently, the **18t'**, which contains a tetrasubstituted C=C bond is selectively destroyed presumably by conversion into nonacidic byproducts. Similar results were recently encountered during a total synthesis of the anticancer dieterpene triptolide.[10] Thus, a 1:3 mixture of tartronic acids **41t** and **42t**, respectively, was obtained in 91% yield from olefin **40**. Owing to selective destruction of **42t**, periodate oxidation of this mixture afforded a 1:1 mixture of **41c** and **42c**. That is, the oxidative decarboxylations of **41t** and **42t** proceeded in 92% and 31% yield, respectively.



The stereoselectivity, regioselectivity, and structural selectivity achievable in ene reactions of diethyl oxomalonate can be important for practical synthetic applications of the new enecarboxylation method.[10,11] Of course C–C bond formation predictably occurs at the vinyl terminus of the allylic system. However, for alkenes that possess nonequivalent allylic hydrogens or more than one C=C bond, the synthetic utility of the new method depends on the feasibility of achieving one of several possible ene reactions. Allylic carboxylation of olefins **21a–23a** is regio- and stereoselective (Table I). Only a single isomeric tartronic ester is produced in the ene reaction of each olefin with diethyl oxomalonate,[5c] and these adducts provide the isomerically pure allylcarboxylic esters **21c–23c**, respectively. With trisubstituted olefins **13a**, **14a**, **19a**, and **20a**, C—C bond formation occurs regioselectively at the least substituted terminus of the C=C bond. Owing to the extraordinary sensitivity of thermal ene reactions of diethyl oxomalonate (**2**) to steric approach control,[5c] high structural selectivity is achieved in the enecarboxylations of dienes **27a** and **28a**. Thus, in spite of the expected[1] electronic preference for reaction of the more electron rich C=C bond, a strong preference is observed for thermal ene reactions to occur at the less electron rich monosubstituted C=C bond instead of the more electron rich di- or trisubstituted C=C bonds of **27a** or **28a**, respectively. Only **27b** is produced from **27a** whereas **28a** affords an 11:1 mixture of **28b** and **28b'**, respectively. The excellent control which characterizes our method for allylic functionalization is epitomized by the two different structurally specific enencarboxylations possible with diene **28a** (Table I). Structurally selective enecarboxylation at the trisubstituted C=C bond in **28a** to produce ester **28c'** can be achieved by Lewis acid



catalysis of the ene reaction with $SnCl_4$. This contrasts sharply with the conversion of **28a** to the isomeric ester **28c** via *thermal* ene reaction of **28a** with diethyl oxomalonate. Clearly, Lewis acid catalysis not only allows ene reactions under thermally mild conditions but also drastically alters the reactivity of diethyl oxomalonate since the influence of electronic factors is amplified by Lewis acids, and steric approach control becomes less important. Further improvements in the synthetic utility of the new enecarboxylation method can be anticipated from modifications of the enophile structure.[12] While our understanding of the factors that favor high yields in oxidative bisdecarboxylation of tartronic acids remains incomplete, the discoviery that cerium(IV) is often effective for oxidative bisdecarboxylations where periodate fails is a major breakthrough for the development of a generally useful new method for enecarboxylation.

Experimental Section

General. 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 and preparative gas chromatography was performed with a Varian Aerograph Model 90P using columns of 7, 6, 3, or 2 ft × 0.25 in. of 10% Dow Corning (DC) 710 silicone oil on 60/80 mesh Chromosorb W. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ.

Enecarboxylations. Two representative procedures are presented. The first, a synthesis of methyl 3-methyl-4-phenyl-3-butenoate (**8c**) from 2-benzylpropene (**8a**), illustrates a Lewis acid catalyzed ene reaction of diethyl oxomalonate (**2**) followed by oxidative bisdecarboxylation of the derived tartronic acid with sodium periodate. The second procedure, a synthesis of dimethyl dodec-3-enedioate (**9c**) from methyl 10-undecenoate (**9a**), illustrates a thermal ene reaction of diethyl oxomalonate (**2**) followed by oxidative bisdecarboxylation of the derived tartronic acid with ceric ammonium nitrate.

Methyl 3-Methyl-4-phenyl-3-butenoate (8c). A solution of 2-benzylpropene (1.32 g, 10 mmol) and diethyl oxomalonate (1.74 g, 1.52 mL, 10 mmol) in benzene (15 mL) was cooled in an ice–water bath under nitrogen and treated with $SnCl_4$ (2.6 g, 1.17 mL, 10 mmol). The resulting solution was then warmed to 23 °C. After 12 h the reaction mixture was poured into aqueous 10% HCl (150 mL) and extracted with

(8) (a) Achmatoicz, O.; Leplawy, M.; Zamojski, A. *Bull. Acad. Pol. Sci., Cl. 3* **1955**, *3*, 539. (b) Achmatowicz, O.; Werner-Zamojka, F. *Ibid.* **1957**, *5*, 923. (c) Achmatowicz, O.; Belniak, K. *Rocz. Chem.* **1965**, *39*, 1685; *Chem. Abstr.* **196**, *64*, 17474f.

(9) Wilson, S. R.; Phillips, L. R. *Tetrahedron Lett.* **1975**, 3047.

(10) Garver, L. C.; van Tamelen, E. E. *J. Am. Chem. Soc.* **1982**, *104*, 867.

(11) Pearlman, B. A.; McNamara, J. M.; Hasan, I.; Hatakeyama, S.; Sekizaki, H.; Kishi, Y. *J. Am. Chem. Soc.* **1981**, *103*, 4248.

(12) Indantrione recently was reported to be a somewhat more reactive substitute for diethyl oxomalonate for enecarboxylation: Gill, G. B.; Kirollos, K. S. *Tetrahedron Lett.* **1982**, *23*, 1399.

diethyl ether (150 mL). The extract was washed with water (2 × 50 mL) and saturated aqueous $NaHCO_3$ (2 × 25 mL) and then dried ($MgSO_4$). Rotary evaporation of the solvent and distillation of the residual oil under reduced pressure afforded **diethyl hydroxy(2-methyl-3-phenyl-2-propen-1-yl)propanedioate (8b)** (2.3 g, 75% yield): bp 147–153 °C (0.25 torr); ^1H 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), 6.42 (br s, 1 H), 7.1–7.5 (5 H). For analysis, a small sample was purified further by gas chromatography on a 3 ft × 0.25 in. column of 10% DC 710 silicone oil at 220 °C. Anal. Calcd for $C_{17}H_{22}O_5$: C, 66.65; H, 7.24. Found: C, 66.53; H, 7.37. This tartronic ester (2.0 g, 6.5 mmol) was stirred vigorously with aqueous 10% KOH (30 mL) at 23 °C for 18 h. The resulting homogeneous solution was acidified to pH 3 by addition of concentrated HCl, saturated with NaCl, and then extracted with ether (2 × 40 mL). Rotary evaporation of the solvent afforded the tartronic acid (1.6 g, 98% yield) which was used in the next step without further purification. The tartronic acid (1.6 g, 6.4 mmol) was vigorously stirred with aqueous 0.25 M $NaIO_4$ (64 mL) containing pyridine (64 μL). After vigorous magnetic stirring at 22 °C for 1 h, the reaction mixture was acidified to pH 3 by addition of concentrated HCl, saturated with NaCl, and then extracted with ether (2 × 100 mL). The combined extracts were washed with saturated aqueous NaCl (2 × 50 mL) and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The resulting allylcarboxylic acid was methylated with a solution of CH_2N_2 in ether. Rotary evaporation of solvent gave **methyl 3-methyl-4-phenyl-3-butenoate (8c)** (1.06 g, 87% yield) which was at least 95% pure by ^1H NMR analysis: ^1H NMR δ 1.95 (d, J = 2 Hz, 3 H), 3.16 (s, 2 H), 3.70 (s, 3 H), 6.31 (br s, 1 H), 7.21 (s, 5 H). For analysis, a small sample was purified further by gas chromatography on a 4 ft × 0.25 in. column of 10% DC 710 silicone oil at 200 °C. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.77; H, 7.40.

Dimethyl Dodec-3-enedioate (9c). A homogeneous mixture of methyl 10-undecenoate (2.00 g, 10 mmol) and diethyl oxomalonate (1.74 g, 1.52 mL, 10 mmol) was sealed in a glass tube and heated in the oven of a gas chromatograph at 165 °C for 3 days. Distillation of the resulting oil under reduced pressure afforded **diethyl (10-carbomethoxy-2-decenyl)-hydroxypropanedioate (9b)** (2.36 g, 63% yield): bp 155–170 °C (0.04 torr); ^1H 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). For analysis, a small sample was purified further by gas chromatography on a 3 ft × 0.25 in. column of 10% DC 710 silicone oil at 220 °C. Anal. Calcd for $C_{19}H_{32}O_7$: C, 61.27; H, 8.66. Found: C, 61.35; H, 8.59. This tartronic ester (2.1 g, 5.6 mmol) was stirred vigorously with aqueous 10% KOH (30 mL) at 22 °C for 18 h. The resulting homogeneous solution was acidified to pH 3 by addition of concentrated HCl, saturated with NaCl, and then extracted with ether (2 × 40 mL). Rotary evaporation of the solvent afforded the tartronic acid (1.7 g, 96% yield), which was used in the next step without further purification. The tartronic acid (1.7 g, 5.4 mmol) was stirred vigorously at 22 °C for 1 h with an aqueous 1.0 M solution of ceric ammonium nitrate (27 mL) and acetonitrile (80 mL). The reaction mixture was then diluted with water (500 mL) and extracted with ether (3 × 300 mL). The organic extracts were washed serially with saturated aqueous NaCl (2 × 200 mL) and dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The resulting allylcarboxylic acid was methylated with a solution of CH_2N_2 in ether. Rotary evaporation of solvent gave **dimethyl dodec-3-enedioate (9c)** (1.2 g, 87% yield) which was at least 95% pure by ^1H NMR analysis: ^1H NMR δ 1.20–1.82 (m, 10 H), 1.82–2.17 (m, 2 H), 2.33 (t, J = 7 Hz, 2 H), 2.97–3.20 (m, 2 H), 3.70 (s, 6 H), 5.47–5.72 (m, 2 H). For analysis, a small sample was purified further by gas chromatography on a 6 ft × 0.25 in. column of DC 710 silicone oil at 200 °C. Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.28; H, 9.20.

Other enecarboxylations, reported in Table I, were performed similarly. The ene reactions were performed under specific conditions listed in Table I. Details of these ene reactions are reported elsewhere.[5c] The oxidative bisdecarboxylations with periodate or cerium(IV) were conducted exactly as described above for preparation of **8c** and **9c**, respectively. Characterization of the enecarboxylation products is given below.

Methyl 4-methyl-3-pentenoate (6c) was prepared from diethyl (3-methyl-2-buten-1-yl)hydroxypropanedioate (**6b**): ^1H NMR δ 1.50–2.32 (m, 6 H), 2.90–3.31 (m, 1 H), 3.70 (s, 3 H), 4.80–5.25 (m, 1 H). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.75; H, 9.62.

Methyl 4-phenyl-3-butenoate (7c) was prepared from diethyl hydroxy(3-phenyl-2-propenyl)propanedioate (**7b**): ^1H NMR δ 3.23 (d, J = 6 Hz, 2 H), 3.70 (s, 3 H), 6.16 (dt, J = 15, 6 Hz, 1 H), 6.56 (d, J = 15 Hz, 1 H), 7.30 (br s, 5 H). This ester was reported previously.[14]

Methyl 12-hydroxydodec-3-enoate (10c) was prepared from diethyl (11-acetoxy-2-undecenyl)hydroxypropanedioate (**10b**): ^1H NMR δ 1.17–1.75 (m, 12 H), 1.55 (br s, 1 H), 1.87–2.20 (m, 2 H), 3.05 (br d, J = 5 Hz, 2 H), 3.67 (partly buried t, J = 7 Hz, 2 H), 3.73 (s, 3 H), 5.47–5.72 (m, 2 H). Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.49; H, 10.70.

Methyl undec-3-enoate (11c) was prepared from diethyl hydroxy(2-decenyl)propanedioate (**11b**): ^1H NMR δ 0.87 (br t, J = 7 Hz, 3 H), 1.23 (br s, 10 H), 1.75–2.17 (m, 2 H), 3.00 (d, J = 5 Hz, 2 H), 3.63 (s, 3 H), 5.36–5.63 (m, 2 H). Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.51; H, 10.98.

Methyl 3-phenylbut-3-enoate (12c) was prepared from diethyl hydroxy(2-phenyl-2-propenyl)propanedioate (**12b**): ^1H NMR δ 3.52 (d, J = 1 Hz, 2 H), 3.65 (s, 3 H), 5.25 (t, J = 1 Hz, 1 H); 5.57 (s, 1 H); 7.25–7.67 (m, 5 H). This ester was reported previously.

Methyl 2-ethyl-3-methylbut-3-enoate (13c) was prepared from diethyl hydroxy(2-methyl-1-penten-3-yl)propanedioate (**13b**): ^1H NMR δ 0.88 (t, J = 7 Hz, 3 H), 1.2–2.2 (5 H), 2.96 (t, J = 7 Hz, 1 H), 3.70 (s, 3 H), 4.88–5.02 (m, 2 H). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 66.87; H, 9.52.

Methyl 3-ethyl-2-oxo-4-methylpent-4-enoate (13p) was prepared from diethyl hydroxy(2-methyl-1-penten-3-yl)propanedioate (**13b**): ^1H NMR δ 0.88 (t, J = 7 Hz, 3 H), 1.3–2.1 (5 H), 3.78 (buried t, J = 7 Hz, 1 H), 3.85 (s, 3 H), 4.83 (br s, 1 H), 5.03 (m, 1 H). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.41; H, 8.21.

Methyl 2,3-dimethylbut-3-enoate (14c) was prepared from diethyl hydroxy(2-methyl-1-buten-3-yl)propanedioate (**14b**): ^1H NMR δ 1.28 (d, J = 7 Hz, 3 H), 1.76 (br s, 3 H), 3.20 (q, J = 7.5 Hz, 1 H), 3.70 (s, 3 H), 6.56 (br s, 2 H). Anal. Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.48; H, 9.65.

Methyl cyclobutenylethanoate (15c) was prepared from diethyl (cyclobuten-1-yl)hydroxypropanedioate (**15b**): ^1H NMR δ 2.28–2.67 (m, 4 H), 3.10 (br s, 2 H), 3.70 (s, 3 H), 5.92 (br s, 1 H). Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 67.35; H, 7.98.

Methyl cycloheptenylethanoate (16c) was prepared from diethyl [(1-cycloheptenyl)methyl]hydroxypropanedioate (**16b**): ^1H NMR δ 1.22–1.88 (m, 6 H), 1.88–2.30 (m, 4 H), 2.93 (s, 2 H), 3.65 (s, 3 H), 5.67 (t, J = 6 Hz, 1 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.51; H, 9.37.

Methyl 6,6-dimethylbicyclo[3.1.1]hept-2-en-2-ylethanoate (17c) was prepared from diethyl (6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-methylhydroxypropanedioate (**17b**): ^1H NMR δ 0.85 (s, 3 H), 1.28 (s, 3 H), 1.90–2.57 (m, 6 H), 3.03 (t, J = 1 Hz, 2 H), 3.70 (s, 3 H), 5.30–5.57 (m, 1 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.02; H, 9.14.

Methyl 3-methylcyclohexen-2-ylethanoate (18c) was prepared from a 1:1 mixture of diethyl hydroxy(3-methylcyclohex-1-en-2-ylmethyl)-propanedioate (**18b**) and diethyl hydroxy(2-methylcyclohex-1-en-1-ylmethyl)propanedioate (**18b'**): ^1H NMR δ 1.00 (d, J = 7 Hz, 3 H), 1.22–1.63 (m, 4 H), 1.67–2.38 (m, 3 H), 3.00 (br s, 2 H), 3.67 (s, 3 H), 5.38–5.63 (m, 1 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.95; H, 9.56.

Methyl 2-(1-cyclohexenyl)propanoate (19c) was prepared from diethyl [1-(1-cyclohexenyl)ethyl]hydroxypropanedioate (**19b**): ^1H NMR δ 1.24 (d, J = 7 Hz, 3 H), 1.4–1.8 (4 H), 1.8–2.3 (4 H), 3.08 (q, J = 7 Hz, 1 H), 3.70 (s, 3 H), 5.60 (br s, 1 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.23; H, 9.68.

Methyl 2-(1-cyclohexenyl)-2-oxobutanoate (19p) was prepared from diethyl [1-(1-cyclohexenyl)ethyl]hydroxypropanedioate (**19b**) in the presence of excess pyridine (see Discussion): ^1H NMR δ 1.20 (d, J = 7 Hz, 3 H), 1.33–1.75 (4 H), 1.83–2.20 (4 H), 3.50–3.95 (buried m, 1 H), 3.85 (s, 3 H), 5.58 (br s, 1 H). Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.22; H, 8.46.

Methyl 2-phenylcyclohexen-3-yloxoethanoate (20p) was prepared from diethyl hydroxy(2-phenyl-1-cyclohexen-3-yl)propanedioate (**20b**): ^1H NMR δ 1.3–2.5 (6 H), 3.75 (s, 3 H), 4.38–4.73 (m, 1 H), 6.32 (td, J = 4, 1 Hz, 1 H), 7.30 (s, 5 H). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.15; H, 6.98.

Methyl *trans*-5-phenyl-1-cyclopentene-3-carboxylate (21c) was prepared from diethyl hydroxy(*trans*-5-phenyl-1-cyclopenten-3-yl)propanedioate (**21b**): ^1H 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.

Methyl 3a,4,5,6,7,7a-hexahydro-4,7-methanoindene-1-*exo*-carboxylate (22c) was prepared from diethyl (3α,4,5,6,7,7α-hexahydro-4,7-methanoinden-1-yl)hydroxypropanedioate (**22b**): ^1H NMR δ 1.23 (br

(13) A detailed description of these reactions is reported elsewhere.[5c]

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Table II. Oxidative Decarboxylation of **19t** in the Presence of Pyridine

pyridine			products, %[b]	
			pyruvate	carboxylate
μL	mol	mol %[a]	**19p**	**19c**
0	0.00	0	<1	99
1	0.012	9	4	96
3	0.037	28	20	80
5	0.062	48	45	55
10	0.124	95	65	35
15	0.186	143	69	31
20	0.248	191	75	25
25	0.310	238	85	15
30	0.371	285	87	13

[a] Relative to starting hydroxymalonic acid **19t**. [b] Relative yields determined by ^{1}H NMR analysis of the reaction product mixture.

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.

Methyl *cis*-bicyclo[3.3.0]oct-3-ene-2-*exo*-carboxylate (23c) was prepared from diethyl *cis*-bicyclo[3.3.0]oct-2-en-4-yl)hydroxypropanedioate (**23b**): ^{1}H NMR δ 1.2-2.2 (6 H), 2.7-3.5 (3 H), 3.70 (s, 3 H), 5.45-5.91 (m, 2 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.05; H, 8.45.

Methyl 1-(trimethylsilyl)cyclopent-1-ene-3-carboxylate (24c) was prepared from diethyl hydroxy[1-(trimethylsilyl)-1-cyclopenten-3-yl]-propanedioate (**24b**): ^{1}H NMR δ 0.0 (s, 9 H), 1.83-2.83 (m, 4 H), 3.35-4.00 (buried m, 1 H), 3.68 (s, 3 H), 5.78-5.95 (m, 1 H). Anal. Calcd for $C_{10}H_{18}O_2Si$: C, 60.56; H, 9.15. Found: C, 60.78; H, 9.08.

Methyl 1-(trimethylsilyl)cyclohex-1-ene-3-carboxylate (25c) was prepared from diethyl hydroxy(1-(trimethylsilyl)-1-cyclohexen-3-yl)-propanedioate (**25b**): ^{1}H NMR δ 0.0 (s, 9 H), 1.52-2.20 (m, 6 H), 2.88-3.33 (m, 1 H), 3.65 (s, 3 H), 5.88-6.08 (m, 1 H). Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 61.67; H, 9.24.

Methyl nona-3,8-dienoate (26c) was prepared from diethyl (octa-2,7-dienyl)hydroxypropanedioate (**26b**): ^{1}H NMR δ 1.17-1.75 (m, 2 H), 1.80-2.28 (m, 4 H), 3.00 (br d, J = 5 Hz, 2 H), 3.63 (s, 3 H), 4.77-5.18 (m, 2 H), 5.43-7.17 (m, 3 H). The corresponding ethyl ester was reported previously.[15]

Methyl 5-(cyclopenten-3-yl)pent-3-enoate (27c) was prepared from diethyl hydroxy[4-(cyclopenten-3-yl)but-3-enyl]propanedioate (**27b**): ^{1}H NMR δ 1.20-1.72 (m, 2 H), 1.78-2.87 (m, 5 H), 3.03 (br d, J = 5 Hz, 2 H), 3.73 (s, 3 H), 5.50-5.78 (m, 2 H), 5.75 (s, 2 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.79; H, 8.38.

Methyl 7-methylocta-3,6-dienoate (28c) was prepared from diethyl hydroxy(6-methylhepta-2,5-dienyl)propanedioate (**28b**): ^{1}H NMR δ 1.62 (br s, 3 H), 1.70 (br s, 3 H), 2.50-3.25 (m, 4 H), 3.70 (s, 3 H), 4.85-5.75 (m, 3 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.15; H, 9.62.

Methyl 2-(2-propenyl)hex-5-enoate (28c′) was prepared from diethyl hydroxy(2-methylhepta-1,6-dien-3-yl)propanedioate (**28b′**): ^{1}H NMR δ 1.5-2.3 (7 H), 3.09 (t, J = 7 Hz, 1 H) 3.70 (s, 3 H), 4.8-5.3 (4 H), 5.3-6.2 (H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.40; H, 9.43.

Effect of Pyridine on the Bisdecarboxylation of [1-(1-Cyclohexenyl]-ethyl)hydroxypropanedioic Acid with Sodium Periodate. The diacid **19t** (30 mg, 0.13 mmol) was oxidized with $NaIO_4$ (15 mL of 0.25 M) in the presence of various amounts of pyridine (1-30 μL). After methylation of the resulting acids with diazomethane, the relative ratio of products was determined by ^{1}H NMR using the resonance of the methyl ester group at δ 3.85 for methyl 3-(1-cyclohexenyl)-2-oxobutanoate (**19p**) and δ 3.70 for methyl 2-(1-cyclohexenyl)propanoate (**19c**). The results are presented in Table II.

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Registry No. 2, 609-09-6; **6a**, 563-45-1; **6b**, 90046-55-2; **6c**, 2258-65-3; **7a**, 300-57-2; **7b**, 90107-07-6; **7c**, 24891-74-5; **8a**, 3290-53-7; **8b**, 73961-89-4; **8t**, 90107-23-6; **8c**, 52386-62-6; **9a**, 111-81-9; **9b**, 90107-08-7; **9t**, 90107-24-7; **9c**, 90107-89-8; **10a**, 112-19-6; **10b**, 90107-10-1; **10c**, 90107-11-2; **11a**, 872-05-9; **11b**, 90107-12-3; **11c**, 64749-23-1; **12a**, 98-83-9; **12b**, 78925-84-5; **12c**, 3461-38-9; **13a**, 625-27-4; **13b**, 90046-62-1; **13t**, 90107-27-0; **13c**, 58544-19-7; **13p**, 90107-28-1; **14a**, 513-35-9; **14b**, 73961-93-0; **14c**, 49714-67-2; **15a**, 1120-56-5; **15b**, 90046-63-2; **15c**, 71092-57-4; **16a**, 2505-03-5; **16b**, 90107-13-4; **16c**, 61704-65-2; **17a**, 127-91-3; **17b**, 90046-65-4; **17c**, 90107-14-5; **18a**, 2808-75-5; **18b**, 90046-68-7; **18b′**, 90046-67-6; **18c**, 90107-15-6; **19a**, 1003-64-1; **19b**, 90046-69-8; **19t**, 90107-25-8; **19c**, 62184-70-7; **19p**, 90107-26-9; **20a**, 771-98-2; **20b**, 73961-82-7; **20t**, 90107-29-2; **20p**, 90107-16-7; **21a**, 39599-89-8; **21b**, 90046-71-2; **21c**, 90046-83-6; **22a**, 2825-86-7; **22b**, 90046-73-4; **22c**, 90046-84-7; **23a**, 930-99-4; **23b**, 73961-80-5; **23c**, 65656-67-9; **24a**, 14579-08-9; **24b**, 78925-83-4; **24c**, 90107-17-8; **25a**, 40934-71-2; **25b**, 90046-74-5; **25c**, 90107-18-9; **26a**, 3710-30-3; **26b**, 90107-19-0; **26c**, 30463-55-9; **27a**, 73961-94-1; **27b**, 78925-82-3; **27c**, 90107-20-3; **28a**, 7270-50-0; **28b**, 77028-79-6; **28b′**, 73961-90-7; **28c**, 90107-21-4; **28c′**, 90107-22-5; carbon dioxide, 124-38-9; ceric ammonium nitrate, 16774-21-3.

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Regiochemistry of Alkenylsilyl and Alkenyldisilanyl Radical Cyclizations

Thomas J. Barton* and Anthony Revis[1]

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011.
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Abstract: The silyl radicals produced by hydrogen abstraction from a butenylsilane, an allyldisilane, a pentenylsilane, a butenyldisilane, and a (butenyloxy)silane all cyclize in an endo fashion, in contrast to the analogous carbon-centered radicals.

Possibly the most frequency encountered radical rearrangement is the exo cyclization of 5-hexenyl radicals.[2] The somewhat surprising kinetic control of this reaction to afford the five-membered-ring exo radicals rather than the thermodynamically favored six-membered-ring endo radicals has been rationalized[3,4] as stereoelectronic control and generalized as the familiar Baldwin-Beckwith rules.[5,6]

(1) Dow Corning Predoctoral Minority Fellow, 1981-1983.
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