(s, 1 H), 1.65 (m, 2 H), 1.30 (m, 6 H), 0.87 (m, 3 H); IR 1745 (s), 1680 (s), 1652 (s), 1609 (s); MS, *m/e* 281 (CI); exact mass calcd for $C_{15}H_{20}O_5$ 280.1311, found 280.1311.

5-Bromo-3,4-dimethoxy-6-(phenylethynyl)-1-oxocyclohexa-2,4-dien-6-yl Succinate (34). Treatment of **4b** (1.3 g, 3.7 mmol) with the lithium salt of phenylacetylene was accomplished as described above at −78 °C in THF. The reaction was quenched by the addition of 0.75 g (7.5 mmol) of succinic anhydride and 2.5 mL of HMPA at −78 °C. The mixture was allowed to warm to ambient temperature and the THF was then removed in vacuo. To the residue were added 50 mL of water and 5 mL of concentrated hydrochloric acid. Immediately, this was extracted several times with diethyl ether. After removal of the solvent the residue was purified by flash column chromatography (ethyl acetate/hexane, 6:4) to give 1.71 g (76%) of **32** as pale orange crystals: mp 118–120 °C; ^{1}H NMR 2.76 (m, 4 H), 3.76 (s, 3 H), 3.87 (s, 3 H), 5.67 (s, 1 H), 7.26–7.34 (m, 5 H), 8.69 (br s, 1 H); IR 3500–2400, 2235, 1770, 1730.

Anal. Calcd for $C_{20}H_{17}BrO_7$: C, 53.47; H, 3.81. Found: C, 53.21; H, 3.80.

Hydrolysis of 34. A mixture containing 0.9 g (2 mmol) of **34** and 0.18 g (2.1 mmol) of sodium bicarbonate in 100 mL of water was stirred at ambient temperature. After 2 min, orange crystals of the quinone **6b** began to precipitate. After 10 min, the mixture was extracted with diethyl ether to give 0.45 g (71%) of **6b** after flash chromatography.

3-Bromo-2-hydroxy-4,5-dimethoxy-2-(2-phenyloxiran-1-yl)-3,5-cyclohexadien-1-one (35). A solution of 1.77 g (5 mmol) of **25** and 2.0 g (10.3 mmol) of *m*-chloroperbenzoic acid in 50 mL of dichloromethane was stirred at ambient temperature for 12 h. The reaction mixture was then washed with aqueous sodium bicarbonate. The organic layer was dried ($MgSO_4$) and concentrated, and the residue was subjected to flash column chromatography (ethyl acetate/hexane, 6:4) to give 0.48 g (26%) of **35** as colorless crystals: mp 128–129 °C; ^{1}H NMR 3.52 (s, 3 H), 3.59 (s, 1 H), 3.66 (d, 1 H, J = 4.21 Hz), 3.69 (s, 3 H), 4.08 (d, 1 H, J = 4.2 Hz), 4.81 (s, 1 H), 7.28 (s, 5 H); IR 3390, 1680, 1660, 1590; MS (CI), *m/e* (relative intensity) 367/369 (M^+ + 1, 21.5/22.0).

Anal. Calcd for $C_{16}H_{15}BrO_5$: C, 52.33; H, 4.12. Found: C, 52.16; H, 4.15.

3-Bromo-4,5-dimethoxy-2-(2-phenyloxiran-1-yl)-1-oxocyclohexa-3,5-dienyl Succinate (36). A solution of 0.25 g (0.68 mmol) of **35** in 30 mL of anhydrous THF was treated with 40 mg (0.83 mmol) of sodium hydride at 0 °C. Succinic anhydride, 80 mg (0.8 mmol), in 15 mL of THF was then added. After 3 days under nitrogen 1 mL of concentrated hydrochloric acid, 50 mL of water, and 50 mL of dichloromethane were added. The resulting mixture was extracted with dichloromethane, and the organic solution was dried ($MgSO_4$) and concentrated in vacuo. The residue was subjected to flash chromatography (ethyl acetate/hexane, 6:4) to give 0.21 g (66%) of **36** as colorless crystals: mp 178–179 °C; ^{1}H NMR (Me_2SO-d_6) 2.45 (m, 4 H), 3.49 (s, 3 H), 3.59 (s, 3 H), 3.72 (d, 1 H, J = 4.0 Hz), 3.84 (d, 1 H, J = 4.0 Hz), 4.93 (s, 1 H), 7.12 (br s, 1 H), 7.25–7.31 (m, 5 H); IR 3440, 1750, 1670, 1645, 1575; MS (CI), *m/e* (relative intensity) 367/369 [(M^+ + 1) − HO_2C − $(CH_2)_2CO_2H$, 6.8/7.6].

This compound slowly decomposed upon standing. As a result, satisfactory C, H analysis was not obtained.

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Oxidative Coupling of Carboxylic Acid Dianions: The Total Synthesis of (±)-Hinokinin and (±)-Fomentaric Acid[1]

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The oxidative coupling of carboxylic acid dianion derivatives provides the key intermediates needed for efficient syntheses of the symmetrical lignan hinokinin (**9**) and the unsymmetrical fungal metabolite fomentaric acid (**22**). Racemic hinokinin (**9**), a target chosen to test the facility of dianion oxidative coupling in the presence of electron-rich aromatic rings, is prepared in an overall conversion of 61% from 3,4-(methylenedioxy)hydrocinnamic acid. Racemic fomentaric acid (**22**), a trisubstituted succinic acid derivative, results from a straightforward two-step sequence that proceeds in an overall yield of 40% from eicosanoic acid. Preliminary studies demonstrate the utility of oxidative coupling in the synthesis of novel surfactant prototypes.

Valuable, but underutilized, methodology for the formation of carbon–carbon bonds involves the oxidative coupling of electron-rich systems.[2] The suitability of numerous carbanionic species to serve as substrates for oxidation makes accessible an almost unlimited variety of products.[3] In essence, coupling reactions provide an inherently convergent strategy for the assembly of complex molecular targets.[4]

Oxidative coupling reactions may be conveniently subdivided (Scheme I) into three separate classes: type I,[5] type II,[5] and type III.[6] This classification is based upon the similarity or difference of groups attached to the coupling carbons. The focus of this paper is on the application of type I and type II coupling to the synthesis of selected natural products.

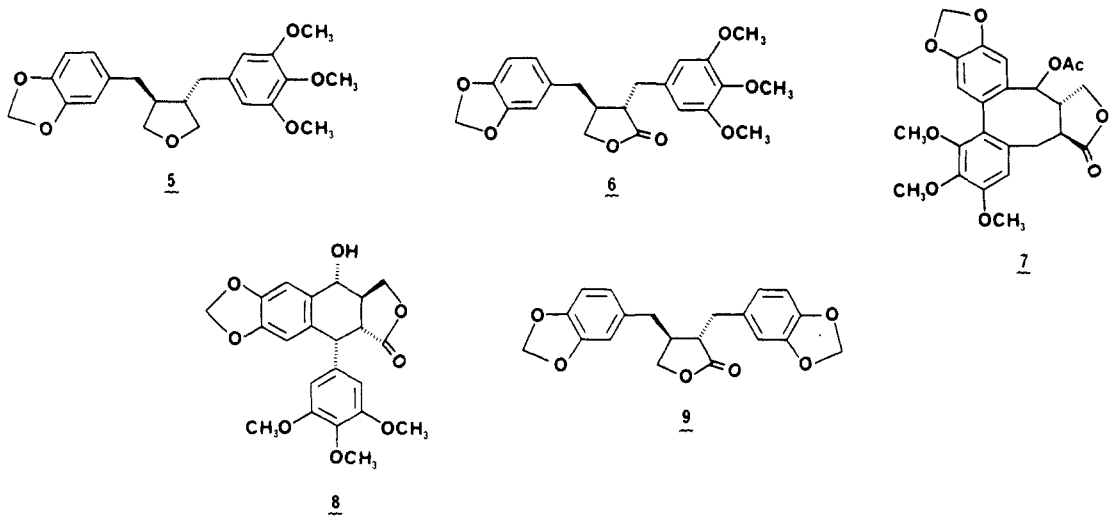
Carboxylic acid dianions are easily prepared, versatile, strongly nucleophilic intermediates.[7] Building upon initial studies published by Ivanoff[8] and by Morton,[9] carboxylic acid dianions have been shown to exhibit considerable

(1) Dedicated to Prof. George Büchi on the occasion of his 65th birthday.

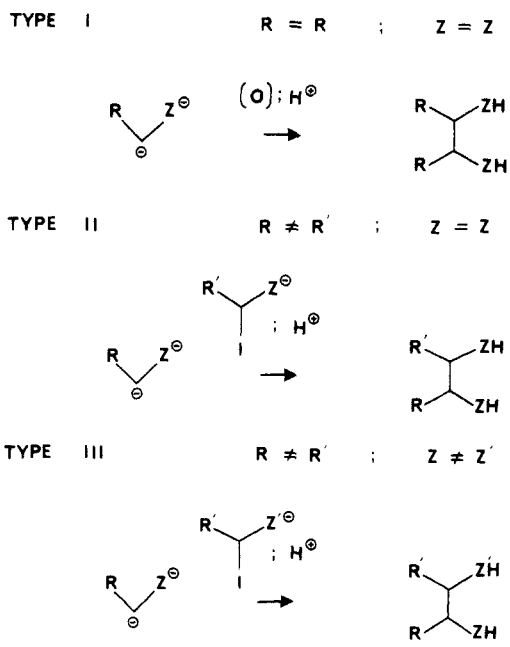
(2) See, for instance: (a) Eglinton, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 225. (b) Cadiot, P.; Chodkiewicz, W. In *Acetylenes*; Viehe, H. G., Ed.; Marcell Dekker, Inc.: New York, 1969; pp 597–647. (c) Taylor, W. L.; Battersby, A. R., Eds. *Oxidative Coupling of Phenols*; Marcell Dekker: New York, 1967. (d) Hampton, K. G.; Christie, J. J. *J. Org. Chem.* **1975**, *40*, 3887. (e), Paquette, L. A.; Snow, R. A.; Muthard, J. L.; Cynkowski, T. *J. Am. Chem. Soc.* **1978**, *100*, 1600. (f) Frazier, R. H., Jr.; Harlow, R. L. *J. Org. Chem.* **1980**, *45*, 5408. (g) Kobayashi, Y.; Taguchi, T.; Morikawa, T. *Tetrahedron Lett.* **1978**, 3555. (h) Ito, Y.; Konoike, T.; Saegusa, T. *J. Am. Chem. Soc.* **1975**, *97*, 649. (i) Ito, Y.; Konoike, T.; Harada, T.; Saegusa, T. *Ibid.* **1977**, *99*, 1487. (j) Kaiser, E. M. *J. Am. Chem. Soc.* **1967**, *89*, 3659. (h) Kauffmann, T. *Angew Chem. Int. Ed. Engl.* **1974**, *13*, 291. (l) Maryanoff, C. A.; Maryanoff, B. E.; Tang, R.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 5839. (m) Vijh, A. K.; Conway, B. E. *Chem. Rev.* **1967**, *67*, 623. (n) Weedon, B. C. L. *Q. Rev. Chem. Soc.* **1952**, *6* 380. (o) Weedon, B. C. L. *Adv. Org. Chem.* **1960**, *1*, 1. (p) Kofron, W. G.; Hauser, C. R. *J. Org. Chem.* **1970**, *35*, 2085. (q) Rathke, M. W.; Lindert, A. *J. Am. Chem. Soc.* **1971**, *93*, 4605. (r) Brocksom, T. J.; Petragnani, N.; Rodriques, R.; LaScala Teixeira, H. *Synthesis* **1975**, 396. (s) Chung, S. K.; Dunn, L. B., Jr. *J. Org. Chem.* **1983**, *48*, 1125. (t) Kobayashi, Y.; Taguchi, T.; Morikawa, T.; Tokuno, E.; Sekiguchi, S. *Chem. Pharm. Bull.* **1980**, *28*, 262.

0022-3263/87/1952-2549$01.50/0

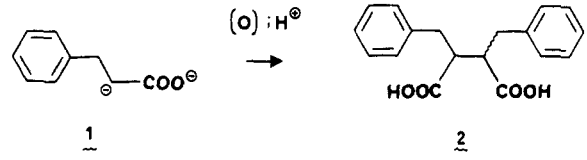
Chart I



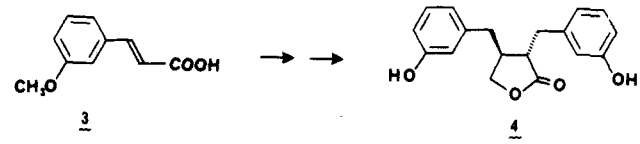
Scheme I



Scheme II



Scheme III



reactivity in type I and type II transformations.[5] Facile generation of these dianions employs a procedure modified after that of Krapcho.[10] Because each carboxylic acid system displays slightly different behavior, optimal dianion titer is best ascertained through preliminary alkylation experiments wherein the dianion is quenched by a reactive halide.

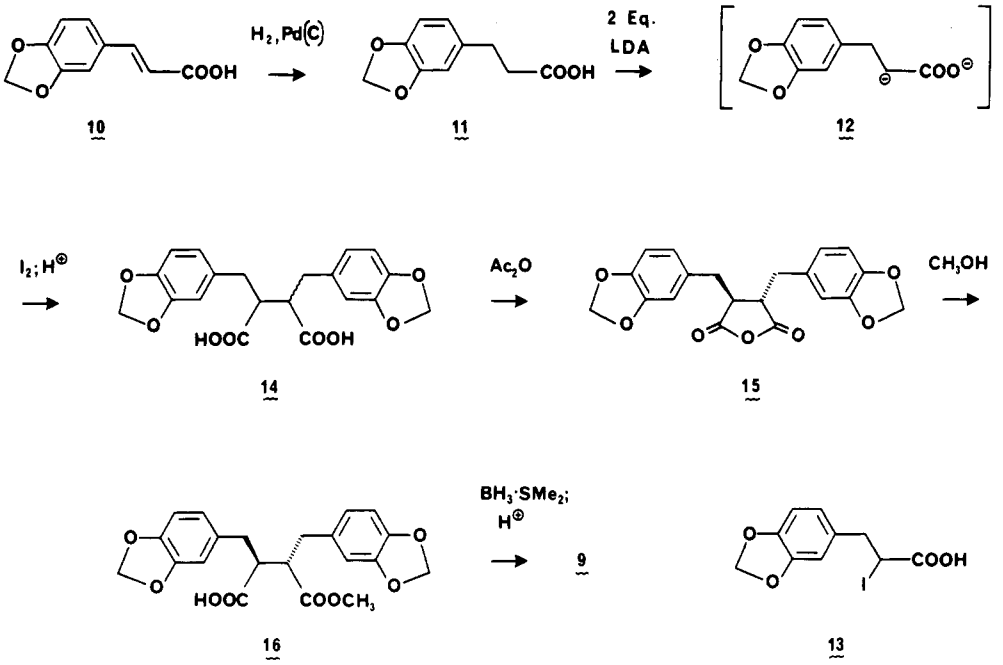
Several observations have been made regarding carboxylic acid dianion coupling:[5] (1) existing evidence suggests an electron-transfer mechanism; (2) dianion generation conditions are critical; (3) self-condensation between a carboxylic acid dianion and the corresponding carboxylate monoanion is insignificant; (4) molecular iodine serves as an excellent oxidant for the dianion; (5) hindered dianion systems couple to form bis(quaternary) adducts in moderate to good (25–75%) yields; and (6) the coupled succinic acid products contain an excess of the *threo* diastereoisomer.

Successful type I oxidative dimerization of phenylpropionic acid dianion **1** to yield succinic acid derivative **2** (Scheme II) constitutes an efficient way to construct the basic lignan skeletal framework.[5] A practical application of this methodology (Scheme III) is the synthesis[11] (in 50% overall yield) of enterolactone **4**, a cytotoxic metabolite isolated from the human gastrointestinal tract.[12]

Since biologically active lignans often possess highly oxygenated aromatic rings,[13] an important question to be resolved concerns the compatibility of electron-rich aromatic systems with the oxidative coupling reagent, I_2. To test the suitability of oxidative coupling for substrates possessing an electron-donating methylenedioxy moiety, a structural unit that occurs in a variety of lignans (e.g. **5**,[14] **6**,[15] **7**,[16] and **8**[17]), we chose the symmetrical lignan

(3) Fuhrhop, J.; Penzlin, G. *Organic Synthesis: Concepts, Methods, Starting Materials*; Verlag Chemie: Weinheim, 1984.
(4) Warren, S. *Organic Synthesis: The Disconnection Approach*; Wiley: New York, 1982.
(5) Belletire, J. L.; Spletzer, E. G.; Pinhas, A. R. *Tetrahedron Lett.* **1984**, *25*, 5969.
(6) Belletire, J. L.; Spletzer, E. G. *Tetrahedron Lett.* **1986**, *27*, 131.
(7) Petragnani, N.; Yonashiro, M. *Synthesis* **1982**, 521.
(8) (a) Ivanoff, D.; Spassoff, A. *Bull. Soc. Chim. Fr., Mem.* **1931**, *49*, 19; (b) **1932**, *51*, 619.
(9) Morton, A. A.; Fallwell, F., Jr.; Palmer, L. *J. Am. Chem. Soc.* **1938**, *60*, 1426.
(10) Krapcho, A. P.; Kashdan, D. S.; Jahngen, E. G. E.; Lovey, A. J. *J. Org. Chem.* **1977**, *42*, 1189.
(11) Belletire, J. L.; Fremont, S. L. *Tetrahedron Lett.* **1986**, *27*, 127.
(12) (a) Stitch, S. R.; Toumba, J. K.; Groen, M. B.; Funke, C. W.; Leemhuis, J.; Vink, J.; Woods, G. F. *Nature (London)* **1980**, *287*, 738. (b) Setchell, K. D. R.; Lawson, A. M.; Mitchell, F. L.; Aldercreutz, H.; Kirk, D. N.; Axelson, M. *Ibid.* **1980**, 287, 740. (c) Setchell, K. D. R.; Borriello, S. P.; Gordon, H.; Lawson, A. M.; Harkness, R.; Morgan, D. M. L.; Kirk, D. N.; Aldercreutz, H.; Anderson, L. C.; Axelson, M. *Lancet* **1981**, *ii*, 4. (d) Axelson, M.; Sjövall, J.; Gustafsson, B. E.; Setchell, K. D. R. *Nature (London)* **1982**, *298*, 659. (e) Cooley, G.; Farrant, R. D.; Kirk, D. N.; Patel, S.; Wynn, S.; Buckingham, M. J.; Hawkes, G. E.; Hursthouse, M. B.; Galas, A. M. R.; Lawson, A. M.; Setchell, K. D. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 489.
(13) Rao, C. B. S. *Chemistry of Lignans*; Andhra University Press: Andhra Pradesh, 1978.
(14) (a) Cole, J. R.; Bianchi, E.; Trumbell, E. R. *J. Pharm. Sci.* **1969**, *58*, 175. (b) Trumbell, E. R.; Cole, J. R. *Ibid.* **1969**, *58*, 176.
(15) McDoniel, P. B.; Cole, J. R. *J. Pharm. Sci.* **1972**, *61*, 1992.

Scheme IV



hinokinin (**9**) as a suitable synthetic target (Chart I).

Hinokinin. Hinokinin is a widely distributed lignan whose structure was firmly established by Haworth.[18] Previously published hinokinin syntheses include the Stobbe condensation sequence of Haworth[19] and the butenolide-based route of Asano.[20]

Our reservations as to whether or not oxidation of dianion **12** would be accompanied by concomitant reaction at the 3,4-(methylenedioxy)benzyl system proved unfounded. Satisfactory conditions for dianion formation were established by optimizing the conditions for low-temperature alkylation of dianion **12** with iodomethane. Treatment (Scheme IV) of dianion **12** with molecular iodine gives diacid **14**, which is contaminated only by trace amounts of hydrocinnamic acid **11**, cinnamic acid **10**, and **13**, the 2-iodo derivative of **11**.

The recrystallized mixture of *erythro* and *threo* diastereoisomeric diacids **14** has a sharp melting point (190–191 °C) that is significantly lower than the reported[19] melting point (201 °C dec) of the pure *threo* (±)-isomer. Upon prolonged treatment with acetic anhydride, our initial diacid isomeric mixture affords the desired *threo* (±)-anhydride **15** uncontaminated with the *erythro* isomer. This sample of racemic anhydride has the same melting point as that reported by Haworth (160–161 °C) for his material. Since Haworth had converted **15** to hinokinin,[19] these results alone represent a formal relay synthesis of hinokinin.

Using a variant to Haworth's route, we have transformed our sample of **15** to racemic hinokinin. Crude diacid **14**, without purification, can be subjected to anhydride formation, methanolysis, borane reduction, and acidification.

Table I. ^{13}C Chemical Shifts of Natural[21] and Synthetic Hinokinin (δ Values Downfield from Me_4Si)

natural	synthetic	natural	synthetic	natural	synthetic
177.9	178.4	121.8	122.2	100.6	101.0
147.4	147.8	121.1	121.5	70.7	71.1
147.4	147.8	109.0	109.4	46.1	46.4
146.0	146.4	108.4	108.8	41.0	41.3
145.8	146.3	107.8	108.3	37.9	38.3
131.2	131.6	107.8	108.2	34.4	34.8
131.0	131.4				

All reactions in this sequence proceed smoothly and essentially as a "one-pot" sequence punctuated only by removal of volatiles. A final flash chromatography gives analytically pure (±)-hinokinin in an overall yield from 3,4-(methylenedioxy)cinnamic acid (**10**) of 61%.

The spectroscopic data for our synthetic (±)-hinokinin (**9**) are in accord with expected values. As in the case of enterolactone **4**,[11] (±)-**9** initially was obtained as a viscous syrup. Asano also reports[20] synthesis of (±)-hinokinin as a colorless oil. After considerable effort, our (±)-hinokinin sample was induced to crystallize. Recrystallization from methanol gives beautiful needles whose melting point (83–84 °C) differs from that reported[19] by Haworth (108 °C). Presumably, this is due to the presence of a polymorphic crystal habit. Nevertheless, our synthetic (±)-hinokinin provides a satisfactory combustion analysis and an exact mass molecular ion. Furthermore, the ^{13}C NMR spectrum of our preparation agrees within experimental error (Table I) with that published[21] for naturally occurring hinokinin.

Fomentaric Acid. Type II coupling provides an effective methodology for the synthesis of highly substituted, unsymmetrical succinic acids. Fomentaric acid, a metabolite isolated from the Indian wood-rotting fungus *Fomes fomentarius* (L.) Fr. and assigned structure **22**,[22] is a convenient natural product target to test the efficacy of type II coupling. Singh and Rangaswami describe[22] an

(16) Becker, D.; Hughes, L. R.; Raphael, R. A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1674 and references cited within.
(17) Van der Eycken, J.; De Clercq, P.; Vandewalle, M. *Tetrahedron Lett.* **1985**, *26*, 3871.
(18) Haworth, R. D.; Wilson, L. *J. Chem. Soc.* **1950**, 71. In order to discount the possibility that our sample of synthetic hinokinin had somehow undergone a spontaneous resolution during the time required for crystallization, we examined our material in a polarimeter. At a concentration of 100 mg of synthetic hinokinin in 3 mL of $CHCl_3$, we observe an optical rotation = 0° within experimental error.
(19) Haworth, R. D.; Woodcock, D. *J. Chem. Soc.* **1938**, 1985.
(20) Asano, Y.; Kamikawa, T.; Tokoroyama, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3232.
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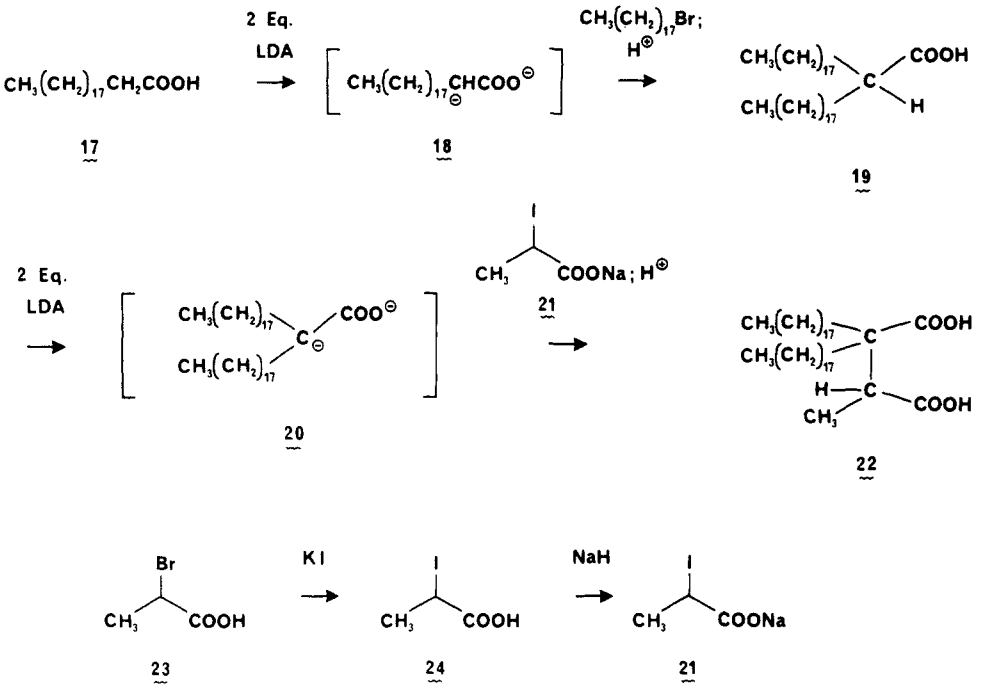
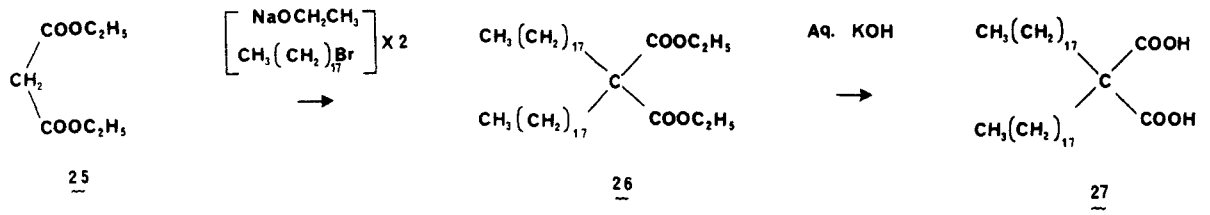
(22) Singh, P.; Rangaswami, S. *Tetrahedron Lett.* **1967**, 149. Initially, these authors claimed an optical rotation for material prepared from racemic precursors, see: Singh, P.; Rangaswami, S. *Tetrahedron Lett.* **1967**, 2128.

Scheme V



Scheme VI



apparently successful malonate ester dialkylation/hydrolysis/decarboxylation approach to fomentaric acid.

Because our type II coupling strategy for fomentaric acid (Scheme V) envisioned reaction of dianion **20** with sodium 2-iodopropionate **21**, practical procedures for the preparation of precursor acids **19** and **24** were essential.

Preliminary experiments (Scheme VI) involving the synthesis of **19** were patterned after the work of Adam and Dyer.[23] Using their procedure, we could obtain only a 10–20% yield of **26**. This is consistent with earlier publications that note that dialkylation of malonate anion with long-chain alkyl halides often proceeds in only modest yield.[24] Furthermore, we have found that saponification of **26** is extremely slow. Both phenomena are probably the result of a number of factors including chain entanglement, steric congestion, solvation, and micelle effects. Although reactions of long-chain carboxylic acid dianions are often sluggish for similar reasons,[25] careful control of dianion generation and alkylation does provide a useful approach to **19**.

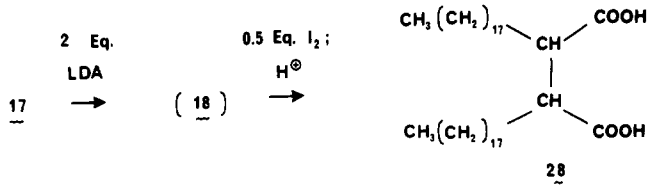
Treatment of eicosanoic acid (**17**) with 2 equiv of LDA produces, at room temperature, a suspension of the sparingly soluble lithium carboxylate monoanion. Even in the presence of excess LDA, conversion of this precipitated salt to a reasonably concentrated solution of dianion **18** does not occur. While the use of HMPA to solubilize dianions of long-chain carboxylic acids has been reported,[26] addition of HMPA to the LDA/eicosanoic acid mixture failed to increase the titer of **18**. Fortunately, suitable dianion generation may be obtained simply by heating the LDA/eicosanoic acid mixture to 50 °C for several hours[27] prior to addition of the alkyl halide. In a model study addition of benzyl chloride to **18** gives the corresponding benzylated derivative in ca. 80% yield. Reaction of a similarly prepared solution of dianion **18** with octadecyl bromide affords satisfactory (ca. 70%) yields of **19**. For optimal results, it is necessary during workup to carry out a vigorous and exhaustive partitioning of the crude gel-like reaction mixture between aqueous acid and organic solvent.

Efficient preparation of 2-iodopropionic acid (**24**) involves a Finkelstein reaction[28] performed upon commercially available 2-bromopropionic acid. Careful purification gives pure **24** as an off-white, light-sensitive solid. A fluffy suspension of sodium 2-iodopropionate (**21**) results from deprotonation of **24** with NaH. An alternative approach to 2-iodopropionic acid involving the reaction between propionic acid dianion and excess I_2 succeeds, but only in modest (ca. 40%) yield.

Formation of fomentaric acid (**22**) by type II coupling is straightforward. Simple addition of a precooled (0 °C)

(23) Adam, N. K.; Dyer, J. W. W. *J. Chem. Soc.* **1925**, *127*, 70.
(24) For a review of ester alkylation reactions, see: Cope, A. C.; Holmes, H. L.; House, H. O. *Org. React. (N.Y.)* **1975**, *9*, 107.
(25) (a) Staudinger, H.; Bier, G.; Lorentz, G. *Makromol. Chem.* **1949**, *3*, 251. (b) Deutsch, E. University of Cincinnati, personal communication, 1985. (c) Creger, P. L. *J. Am. Chem. Soc.* **1967**, *89*, 2500. (d) Pfeffer, P. E.; Silbert, L. S. *J. Org. Chem.* **1970**, *35*, 262.
(26) Pfeffer, P. E.; Silbert, L. S.; Chirinko, J. M., Jr. *J. Org. Chem.* **1972**, *37*, 451 and references cited within.
(27) THF/LDA/carboxylic acid mixtures even can withstand being kept at gentle reflux for short periods. However, treatment at 50 °C seems most satisfactory (see ref 10).
(28) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 381.

Scheme VII



solution of dianion **20** to a precooled (0 °C) suspension of sodium 2-iodopropionate followed by prolonged stirring at room temperature and workup yields crude fomentaric acid admixed with ca. 20% **19** and ca. 20% **24**. Flash chromatography provides, in addition to pure fomentaric acid, starting material **19** in sufficient purity for reuse. Ignoring recovered **19**, the yield of **22** is at least 56%; however, on the basis of recovered **19**, the yield of **22** is in excess of 70%. Recrystallization of **22** from the minimum volume of ethyl acetate gives analytically pure racemic fomentaric acid whose combustion analysis and spectroscopic data are completely in accord with structure **22**.

The successful preparation of fomentaric acid by oxidative coupling suggests that this methodology might have utility for the synthesis of novel surfactants.[29] To test this hypothesis, type I coupling of eicosanoic acid dianion **18** was examined (Scheme VII). Highly crystalline diacid **28**, obtained as a mixture of diasteroisomers, is isolated in 79% yield. Even dianion **20** affords (Scheme VIII) coupling product **29** in modest (29%) chromatographed yield. Confirming observations made with other bis(quaternary) coupling products,[30] tetraalkylated succinic acid **29** readily dehydrates to form anhydride **30**.

Thus, oxidative coupling provides a useful and efficient means for establishing the crucial carbon–carbon bond in the total synthesis of two different natural products. Further exploitation of this technique, including the use of type III coupling for the preparation of biologically active lignan **6**,[31] is actively underway.

Experimental Section

Materials and General Procedures. Melting points were determined with a Mel-Temp melting point apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. ^{1}H NMR spectra were recorded on IBM Instruments NR-80 (80 MHz) and Nicolet NT-300 (300 MHz) spectrometers with Me_4Si as internal standard. ^{13}C NMR spectra were recorded on the Nicolet spectrometer at 75 MHz with Me_4Si as internal standard; the multiplicity was determined by the off-resonance proton decoupling. Infrared spectra were recorded with a Perkin-Elmer Model 559 grating spectrophotometer. Mass spectra were determined with a Kratos MS-801 DS55 spectrometer. All reactions were run under dry N_2 unless otherwise specified. Glassware for the dianion reactions was assembled hot from a 115 °C oven, purged with N_2, and then flame-dried under vacuum. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately before use. Diisopropylamine was distilled from barium oxide immediately prior to use. Ligroine, chloroform, and ethyl acetate were distilled before use.

2,3-Bis[(1,3-benzodioxol-5-yl)methyl]butanedioic Acid (14). To a solution of diisopropylamine (1.14 mL, 8.2 mmol) in 40 mL of THF at −25 °C was added *n*-butyllithium (1.55 M, 5.30 mL, 8.2 mmol). The mixture was stirred below −20 °C for 10 min and then at room temperature for 20 min. The LDA solution was then cooled to −78 °C and to it was added 3,4-(methylenedioxy)-hydrocinnamic acid (0.776 g, 4.0 mmol) in 22 mL of THF over 3 min. The clear greenish yellow solution was stirred below −50 °C for 1 h, at 0 °C for 2.5 h, and at room temperature for 1.5 h. The dianion solution was then cooled to −62 °C and to it was added I_2 (0.509 g, 2.0 mmol) in 10 mL of THF over 1 min. The resulting clear deep yellow mixture was allowed to warm up to room temperature over 21 h. The THF was evaporated and the resulting brownish froth was acidified with 20 mL of 1 N HCl and extracted 2× with 75 mL of EtOAc. The combined organic layers were washed with 20 mL of $NaHSO_3$ solution, 2× with 20 mL of H_2O, and 1× with 30 mL of brine, dried over $MgSO_4$, and filtered. The volatiles were evaporated to give a pale yellow solid (0.792 g, over theory). For hinokinin: the crude diacid was carried on in the synthesis as is. An analytical sample of diacid **14** was prepared by recrystallization of the crude solid from EtOAc to afford an off-white powder: mp 190–191 °C; ^{1}H NMR ($CDCl_3$/Me_2SO-d_6) δ 6.72–6.56 (m, 6 H), 5.905 (s, 4 H), 3.10–2.80 (m, 6 H); ^{13}C NMR ($CDCl_3$/Me_2SO-d_6) δ 174.775 (s), 147.202 (s), 145.693 (s), 132.738 (s), 121.804 (d), 109.172 (d), 107.812 (d), 100.603 (t), 47.838 (d); 34.718 (t); IR (KBr) 3260–2240 (s, br), 1700 (s), 1485 (s), 1440 (s), 1240 (s), 1185 (s), 1030 (s), 925 (s), 810 (s) cm^{-1}; MS, *m/e* (relative intensity) 368 (M^+ − 18) 192, 176, 135 (100), 105, 77; exact mass (M^+ − 18) calcd 368.0896, found 368.0873.

***trans*-(±)-3,4-Bis[(1,3-benzodioxol-5-yl)methyl]dihydro-2,5-furandione (15).** To the crude diacid (0.792 g, ca. 2.0 mmol) was added Ac_2O (50 mL), and the resulting mixture was refluxed at 160 °C for 48 h. The Ac_2O was then distilled off at reduced pressure to give a dusty brownish yellow solid (0.74 g, theory). For hinokinin: the crude anhydride was carried on in the synthesis as is. An analytical sample of the anhydride was prepared by flash chromatography (20 g of silica gel, $CHCl_3$) followed by recrystallization from EtOAc/ligroin and drying under vacuum: mp 160–161 °C (lit.[19] mp 160–161 °C); ^{1}H NMR ($CDCl_3$) δ 6.70 (dd, *J* = 1.2, 7.2 Hz, 2 H), 6.48 (s, 2 H), 6.465 (dd, *J* = 7.2, 1.2 Hz, 2 H), 5.941 (dd, *J* = 1.2, 7.2 Hz, 4 H), 3.11–3.09 (m, 2 H), 2.90–2.80 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 172.290 (s), 148.218 (s), 147.058 (s), 129.355 (s), 122.431 (d), 109.360 (d), 108.583 (d), 101.264 (t), 46.138 (d), 35.155 (t); IR (KBr) 2980 (w), 2910 (m), 2860 (w), 1850 (s), 1780 (s), 1600 (m), 1495 (s), 1445 (s), 1370 (m), 1325 (m), 1250 (s), 1030 (s), 925 (s) cm^{-1}; MS, *m/e* (relative intensity) 368 (M+), 176, 135 (100); exact mass (M^+) calcd 368.0896, found 368.0893.

***(R*,R*)*-(±)-2,3-Bis[(1,3-benzodioxol-5-yl)methyl]butanedioic Acid Monomethyl Ester (16).** To the crude anhydride (0.74 g, ca. 2 mmol) was added methanol (50 mL). The mixture was refluxed at 75 °C for 48 h. The methanol was then evaporated, leaving a viscous brown syrup (0.89 g, ca. 2 mmol). For hinokinin: the crude acid ester was carried on in the synthesis as is. An analytical sample of the acid ester was prepared by crystallization from EtOAc: mp 169–170 °C; ^{1}H NMR ($CDCl_3$/Me_2SO-d_6) δ 6.9–6.3 (m, 6 H), 5.918 (s, 4 H), 3.601 (s, 3 H), 3.1–2.7 (m, 6 H); ^{13}C NMR δ ($CDCl_3$/Me_2SO-d_6) 174.777 (s), 173.577 (s), 147.364 (s), 145.907 (s), 132.479 (s), 121.907 (d), 109.120 (d), 107.902 (d), 100.708 (t), 51.437 (q), 47.898 (d), 34.976 (t); IR (KBr) 3500–2400 (br, m), 1725 (s), 1695 (s), 1490 (s), 1440 (s), 1375 (m), 1240 (s), 1195 (s), 1030 (s), 920 (m), 860 (m), 820 (m), 810 (m) cm^{-1}; MS, *m/e* (relative intensity) 400 (M^+), 368, 192, 176, 135 (100), 105, 77; exact mass (M^+) calcd 400.1158, found 400.1172. Anal. Calcd for $C_{21}H_{20}O_8$: C, 63.00; H, 5.03. Found: C, 63.11; H, 5.16.

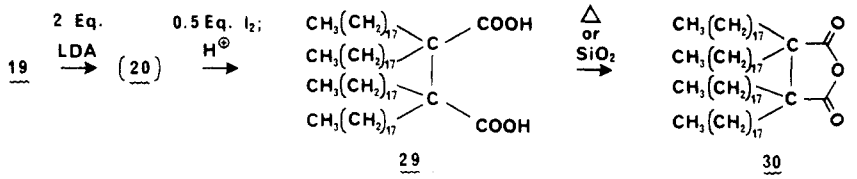
***trans*-(±)-3,4-Bis[(1,3-benzodioxol-5-yl)methyl]dihydro-2(3*H*)-furanone (Hinokinin, 9).** To a solution of the acid ester **16** (0.90 g, ca. 2 mmol) in 50 mL of THF at −50 °C was added BH_3·SMe_2 (8 mL; 2.0 M in Et_2O, 16 mmol) over 1 min. The mixture was stirred below 0 °C for 0.5 h and then at 0 °C for 1.25 h. At this point, evolution of gas was noted from the solution. After being stirred for an additional 1.25 h at room temperature, the mixture was acidified *carefully* with 9 mL of 6 N HCl over 45 min and then stirred at room temperature for 1 h. The solvents were removed under reduced pressure, and the residue was placed under vacuum for 12 h. The crude hinokinin (0.709 g) was purified by flash chromatography (20 g of silica gel, $CHCl_3$) to yield 0.426 g (1.202 mmol, 60.2% overall) of racemic hinokinin as a pale yellow oil. A sample of hinokinin was coaxed into crystallizing after a 6-month trituration with MeOH. An analytical sample was

(29) Rosen, M. J. *CHEMTECH* May, 1985, 292 and references cited within.

(30) Belletire, J. L.; Conroy, G. M., University of Cincinnati, 1986.

(31) Preliminary experiments involving a sequence using type III coupling between the appropriate acylsulfonamide dianion and 2-iodo carboxylate salt, reduction with BH_3·SMe_2, and treatment with aqueous acid has produced material, which, by TLC, ^{1}H NMR, and mass spectroscopy (M^+), behaves in a manner consistent with **6**. Optimization of conditions, stereochemical analysis, and complete characterization are in progress. Belletire, J. L.; Fry, D. F., University of Cincinnati, 1986.

Scheme VIII



prepared by recrystallization from MeOH: mp 83–84 °C (lit.[19] mp 108 °C, lit.[20] oil); ^{1}H NMR ($CDCl_3$) δ 6.75–6.66 (m, 2 H), 6.65–6.56 (m, 2 H), 6.50–6.42 (m, 2 H), 5.925 (br s, 4 H), 4.118 (dd, J = 6.9, 9.1 Hz, 1 H), 3.850 (dd, J = 6.9, 9.1 Hz, 1 H), 2.978 (dd, J = 4.9, 13.9 Hz, 1 H), 2.826 (dd, J = 4.9, 13.9 Hz, 1 H), 2.64–2.39 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 178.391 (s), 147.847 (s), 146.441 (s), 146.309 (s), 131.652 (s), 131.396 (s), 122.205 (d), 121.525 (d), 109.424 (d), 108.810 (d), 108.293 (d), 108.277 (d), 101.007 (t), 71.101 (t), 46.427 (d), 41.252 (d), 38.274 (t), 34.777 (t); IR ($CDCl_3$) 2890 (m), 1770 (s), 1610 (w), 1505 (s), 1495 (s), 1370 (m), 1250 (s), 1190 (m), 1050 (s), 935 (s), 815 (m) cm^{-1}; MS, m/e (relative intensity) 354 (M^+), 218, 192, 162, 135 (100), 105, 83; exact exact (M^+) calcd 354.1103, found 354.1121. Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 67.70; H, 5.44.

2-Octadecyleicosanoic Acid (19). To a solution of diisopropylamine (1.15 mL, 8.2 mmol) in 50 mL of THF at −25 °C was added n-butyllithium (5.12 mL, 1.6 M, 8.2 mmol). The mixture was stirred below −20 °C for 5 min and then at room temperature for 25 min. The clear, pale yellow LDA solution was then cooled to 0 °C and eicosanoic acid (1.25 g, 4.0 mmol) in 20 mL THF was added over 3.5 min. The resulting white heterogeneous solution was stirred at 0 °C for 30 min, at room temperature for 30 min, and then at 50 °C for 2.0 h. This resulted in a pale yellow slightly cloudy solution. After cooling the dianion solution to room temperature over 30 min, 1-octadecylbromide (1.33 g, 4.0 mmol) in 11 mL of THF was added over 1.5 min. The mixture was stirred at room temperature for 30 min, then at 50 °C for 20 h, and then cooled to room temperature. The solvents were removed under reduced pressure, and the residue was acidified with 50 mL of a 1:1 6 N HCl/brine solution and extracted 3× with 2:1 Et_2O/$CHCl_3$ (1 × 150 mL, 2 × 75 mL). The initial extraction may require up to 30 min of vigorous shaking to dissolve the suspended solids. The combined organic layers were washed with 25 mL of brine, dried over $MgSO_4$, and filtered, and the solvents were evaporated to give a powdery white solid. This was purified by flash chromatography (40 g of silica gel, ligroin to remove starting bromide, followed by 1:1 $CHCl_3$/ligroine to remove alkylated product, and $CHCl_3$ to remove starting acid). By this technique, 1.617 g of product (71.5%) was recovered, along with 0.284 g of starting material. An analytical sample of 2-octadecyleicosanoic acid was prepared by recrystallization from EtOAc: mp 81–83 °C (lit.[23] mp 81–82 °C); ^{1}H NMR ($CDCl_3$) δ 2.45–2.25 (m, 1 H), 1.70–1.50 (m, 4 H), 1.253 (br s, 64 H), 0.880 (t, J = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 182.129 (s), 45.649 (d), 32.257 (t), 31.939 (t), 29.716(t), 29.504 (t), 29.378 (t), 27.416 (t), 22.706 (t), 14.106 (q); IR ($CHCl_3$) 2930 (s), 2855 (s), 1705 (m), 1465 (m) cm^{-1}; MS, m/e (relative intensity) 564, 318, 312, 283, 269, 213, 184, 171, 129, 97, 73 (100); exact mass (M^+) calcd 564.5849, found 564.5843.

2-Iodopropionic Acid (24). To acetone (200 mL) was added KI (60.0 g, 0.364 mol) and 2 bromopropionic acid (34.0 g, .222 mol). The resulting mixture was heated at reflux for 20 h and cooled to room temperature, the acetone was removed at reduced pressure, and the reaction mixture residue was diluted with $CHCl_3$ and water. The chloroform layer was separated, washed with water and $NaHSO_3$ solution, dried over $MgSO_4$, and filtered, and the volatiles were removed to give an amber liquid. Kugelrohr distillation (95–105 °C (1.3 × 10^3 Pa)) followed by recrystallization from ligroin afforded an off-white solid (33.2 g, 74.8%): mp 42–43 °C (lit.[32] mp 45.5 °C); ^{1}H NMR ($CDCl_3$) δ 10.62 (br s, 1 H), 4.53 (q, J = 7 Hz, 1 H), 2.0 (d, J = 7 Hz, 3 H); IR ($CHCl_3$) 2900 (br), 1700 cm^{-1}.

3-Methyl-2,2-dioctadecylbutanedioic Acid (Fomentaric Acid, 22). To diisopropylamine (0.57 mL, 4.1 mmol) in 25 mL of THF at −25 °C was added n-butyllithium (2.56 mL, 1.6 M, 4.1 mmol). The mixture was kept under −20 °C for 5 min and then stirred at room temperature for 25 min. The LDA solution was then cooled to 0 °C and 2-octadecyleicosanoic acid (1.13 g, 2.0 mmol) in 10 mL of THF was added over 3 min. The resulting pale yellow heterogeneous solution was stirred at 0 °C for 0.5 h, room temperature for 0.5 h, and 50 °C for 3 h. After being cooled to room temperature over 0.5 h, the dianion solution was cooled to 0 °C.

In a separate flask, sodium 2-iodopropionate was prepared by adding 2-iodopropionic acid (0.40 g, 2.0 mmol) in 10 mL of THF to a suspension of a 3× ligroin-washed 50% NaH/oil dispersion (0.130 g, 2.5 mmol) in 30 mL of THF at 0 °C over 5 min. The resulting fluffy-white suspension was stirred at 0 °C for 35 min.

The dianion solution (at 0 °C) was added to the carboxylate (also at 0 °C) via cannula over 45 min. The hazy pale yellow solution was allowed to warm up to room temperature over 18 h. The THF was then evaporated, yielding a pale yellow syrup. The syrup was acidified with 50 mL of 1:1 4 N HCl/brine and this aqueous solution was extracted 3× with 75 mL of 2:1 Et_2O/$CHCl_3$, then washed 1× with 25 mL of brine. After drying over $MgSO_4$, filtering, and evaporation of solvents, a waxy reddish yellow solid remained. This was purified by flash chromatography (10 g of silica gel, 3:1 ligroin/$CHCl_3$ to remove starting materials, EtOAc to remove fomentaric acid). The yield was 0.383 g (0.678 mmol) of starting material and 0.716 g (1.12 mmol, 56.1%) of racemic fomentaric acid. An analytical sample of fomentaric acid was prepared by recrystallization from EtOAc: mp 79.5–80.5 °C (lit.[22] mp 78–80 °C)[33]; ^{1}H NMR ($CDCl_3$) δ 2.848 (q, J = 6.9 Hz, 1 H), 1.80–1.50 (m, ca. 7 H), 1.50–1.25 (br s, ca. 66 H), 0.879 (t, J = 6.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 182.500, 181.442, 50.138, 45.097, 34.231, 31.961, 31.667, 30.412, 30.218, 29.745, 29.492, 24.048, 22.715, 14.141, 12.298; IR (CCl_4) 2910 (s), 2825 (m), 1710 (s), 1465 (m) cm^{-1}; MS, m/e (relative intensity) 618 ($M^+ - H_2O$), 590, 573, 572, 366, 347, 337 (100), 308, 280, 97; exact mass ($M^+ - H_2O$) calcd 618.5954, found 618.5936. Anal. Calcd for $C_{41}H_{80}O_4$: C, 77.30; H, 12.66. Found: C, 77.42; H, 12.53.

2,3-Octadecylbutanedioic Acid (28). To a solution of diisopropylamine (1.15 mL, 8.2 mmol) in 50 mL of THF at −25 °C was added n-butyllithium (5.12 mL, 1.6 M, 8.2 mmol). The mixture was stirred below −20 °C for 5 min and then at room temperature for 25 min. After cooling the LDA solution to 0 °C, eicosanoic acid (1.25 g, 4.0 mmol) in 20 mL of THF was added over 3 min. The resulting white suspension was stirred at 0 °C for 30 min, at room temperature for 30 min, and then at 50 °C for 2.0 h. The dianion solution was cooled to room temperature over 30 min, and I_2 (0.508 g, 2.0 mmol) in 10 mL of THF was added over 2.5 min. The resulting pale yellow opalescent solution was stirred at room temperature for 20 h. The solvents were evaporated, the residue was acidified with 75 mL of a 2:1 1 N HCl/brine solution, and the aqueous solution was extracted 3× with 75 mL of 2:1 Et_2O/$CHCl_3$. The combined organic layers were washed 1× with 1:1 bisulfite/brine solution and 1× with 2:1 brine/H_2O, dried over $MgSO_4$, and filtered, and the solvents were removed to yield a yellow solid. Recrystallization from EtOAc yielded 0.991 g (79.5%) of diacid: mp 125–132 °C (mixture of *erythro* and *threo* stereoisomers); ^{1}H NMR ($CDCl_3$/Me_2SO-d_6) δ 2.60–2.55 (br s, 2 H), 1.5–1.6 (br s, 4 H), 1.40–1.15 (br s, 64 H), 0.876 (t, J = 6.5 Hz, 6 H); ^{13}C NMR ($CDCl_3$/Me_2SO-d_6) δ 177.149 (s), 46.745 (d), 31.884 (t), 29.665 (t), 29.447 (t), 29.321 (t), 29.188 (t), 27.149 (t), 22.655 (t), 14.113 (q); IR (Nujol mull) 1690 (br)

(32) Abderhalden, E.; Guggenheim, M. *Chem. Ber.* **1908**, *41*, 2852.

(33) The mp reported by Singh and Rangaswami is that of a sample of fomentaric acid that had been purified by a procedure involving Fisher esterification, chromatography, and saponification. Their material had an optical rotation of 0°. It is possible that racemization occurred during saponification. If so, the identical mp for natural and (racemic) synthetic material is explained.

cm^{-1}; exact mass ($M^+ - 18$) calcd 604.5797, found 604.5786. Anal. Calcd for $C_{40}H_{78}O_4$: C, 77.11; H, 12.62. Found: C, 76.84; H, 12.72.

Dihydro-3,3,4,4-tetraoctadecyl-2,5-furandione (30). To a solution of diisopropylamine (0.57 mL, 4.1 mmol) in 25 mL THF at −25 °C was added *n*-butyllithium (2.56 mL, 1.6 M, 4.1 mmol). The mixture was stirred below −20 °C for 5 min and then at room temperature 25 min and then cooled to 0 °C. 2-Octadecyleicosanoic acid (1.13 g, 2.0 mmol) in 12 mL of THF was added over 3 min, and the resulting pale yellow heterogeneous solution was stirred at 0 °C for 30 min and at room temperature for 30 min. After being stirred at 50 °C for 3 h, the clear yellow dianion solution was cooled to room temperature over 30 min and then to 0 °C. I_2 (0.254 g, 1.0 mmol) in 9 mL of THF was added over 1.5 min, resulting in a clear pale yellow solution. The mixture was allowed to stir for 18 h while being warmed to room temperature. The solvents were then evaporated, and the residue was acidified with 50 mL of 1:1 4 N HCl/brine. The aqueous solution was extracted 3× with 75 mL of 2:1 $Et_2O/CHCl_3$, and the combined organic layers were washed 1× with brine. After drying over $MgSO_4$ and filtering, the solvents were evaporated, leaving a waxy yellow solid. This was purified by flash chromatography (12 g of silica gel; 3:1 ligroin/$CHCl_3$ to remove starting materials, followed by EtOAc to remove diacid). Starting material (0.552 g) was recovered, as well as 0.330 g (29.3%) of diacid. A second chromatography (15 g of silica gel, 3:1 ligroin, then $CHCl_3$) performed on the semipure diacid afforded 0.112 g of anhydride. The waxy anhydride was unsuitable for recrystallization. However, material isolated by chromatography gave a satisfactory combustion analysis: mp 53–54 °C; ^1H NMR ($CDCl_3$) δ 1.653 (t, J = 6.6 Hz, 8 H), 1.257 (br s, 128 H), 0.880 (t, J = 6.6 Hz, 12 H); ^{13}C NMR ($CDCl_3$) δ 175.560 (s), 54.746 (s), 31.969 (t), 30.157 (t), 29.696 (t), 29.362 (t), 24.438 (t), 22.720 (t), 14.101 (q); IR (CCl_4) 2920 (s), 2860 (s), 1780 (s), 1460 (m), 940 (m) cm^{-1}. Anal. Calcd for $C_{76}H_{148}O_3$: C, 82.24; H, 13.44. Found: C, 82.52; H, 13.17.

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Catalytic Reactions of Metalloporphyrins. 3.[1] Catalytic Modification of Hydroboration–Oxidation of Olefin with Rhodium(III) Porphyrin as Catalyst[2]

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(Octaethylporphyrinato)- or (tetraphenylporphyrinato)rhodium(III) chloride catalyzes the anti-Markovnikov "hydration" of olefin with $NaBH_4$ and O_2 in THF. 1,5-Cyclooctadiene gives rise to cyclooctanol and 1,5-cyclooctanediol (in a ratio of approximately 1:2), and acetylenes are converted directly to alcohols under similar conditions. The initial step in the catalytic reaction of olefin is the hydride and borane transfers from BH_4^- respectively to Rh^{III} porphyrin and olefin to give hydridorhodium (RhH) porphyrin and alkylborane. The RhH species undergoes oxidation with O_2 back to Rh^{III} with concomitant oxidation of alkylborane with *retention of configuration*. This coupled oxidation of alkylborane is in competition with its nonstereospecific autoxidation without assistance of Rh–H. The present system provides a catalytic modification of hydroboration–oxidation of olefin in the presence of oxygen, as illustrated by the one-pot conversion of 1-methylcyclohexene to (*E*)-2-methylcyclohexanol with 100% regioselectivity and up to 97% stereoselectivity.

Our recent study indicates that the combination of $NaBH_4$, O_2, and rhodium(III) porphyrin as catalyst constitutes a highly efficient, catalytic modification of synthetic reactions of borane in the presence of oxygen.[3] The reduction of ketone with this catalytic system involves (1) the rate-determining complexation of BH_4^- with Rh^{III} porphyrin (eq 1, where and hereafter OEP ligand is omitted), (2) rapid borane transfer from the adduct to ketone to give dialkoxyborane and hydridorhodium species (eq 2), and (3) oxidation of hydridorhodium species with O_2 back to Rh^{III} with concomitant "hydrolysis" of dialkoxyborane to alcohol (eq 3).

$$Rh^{III} + BH_4^- \rightarrow Rh^{III}BH_4^- \quad (1)$$

$$Rh^{III}BH_4^- + 2{>}C{=}O \rightarrow HB{\leftarrow}(OCH)_2 + RhH \quad (2)$$

$$HB{\leftarrow}(OCH)_2 + RhH + O_2 \rightarrow Rh^{III} + 2HO{-}CH + BO_2^- \quad (3)$$

The essential reaction of the ternary system of $NaBH_4$, O_2, and rhodium porphyrin can be regarded as borane generation with concomitant reduction of O_2 upon metal-controlled, two-electron aerial oxidation of BH_4^- (eq 4).

$$BH_4^- + O_2 \xrightarrow{\text{Rh porphyrin}} \text{"}BH_3\text{"} + \text{"}HO_2^-\text{"} \quad (4)$$

In the present work we have taken up olefins and acety-

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(3) Aoyama, Y.; Fujisawa, T.; Watanabe, T.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.* **1986**, *108*, 943.

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