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Reductive Dimerization of Alkylidenemalonates Using Samarium(II) Diiodide and ^{1}H-NMR Behavior of the Dimers, 2,3-Diaryl-1,1,4,4-butanetetracarboxylates

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Alkylidenemalonates were readily dimerized in the presence of SmI_2 to give 2,3-disubstituted 1,1,4,4-butanetetracarboxylates as mixtures of *meso* and racemic isomers in moderate to good yields. The structure of the less polar isomer of tetraethyl 2,3-diphenyl-1,1,4,4-butanetetracarboxylate was determined by X-ray crystallographic analysis to be the *meso* form. Characteristic ^{1}H-NMR behavior of the *meso* and racemic isomers is also discussed.

Key words samarium diiodide; alkylidenemalonate; reductive dimerization; 1,1,4,4-butanetetracarboxylate; X-ray crystallographic analysis; MOPAC calculation

Kagan and co-workers reported the first use of samarium diiodide (SmI_2) in synthetic organic chemistry[1] in 1977, and recently it has become very important as a one-electron reducing agent because of its easy handling and wide utility.[2] Many synthetic applications of this reagent have been developed, and we have also reported several new reactions.[3] In the literature, dimerization of various substrates such as acid chlorides, ketones or aldehydes, α,β-unsaturated esters or amides, imines, and isocyanates by SmI_2 have been reported.[3] We previously reported reductive dimerization of 2-substituted-1,1-cyclopropanedicarboxylates with SmI_2, giving 3,4-disubstituted 1,1,6,6-hexanetetracarboxylates in refluxing tetrahydrofuran (THF).[3a] The current paper deals with the reductive dimerization of alkylidenemalonates (**1a**—**l**) using SmI_2 and the characteristic ^{1}H-NMR behavior of the *meso* and racemic dimers (**2a**—**j**).

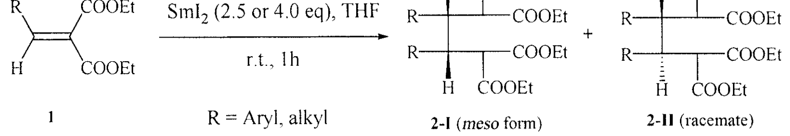
Diethyl benzylidenemalonate (**1a**, R=Ph) was treated with four equivalents of SmI_2 in THF at room temperature for 1 h.[4] Silica gel column chromatography of the product mixture afforded two compounds [**2a**-I (less polar) and **2a**-II (polar)].[5] The common formula $C_{28}H_{34}O_8$ for **2a**-I and **2a**-II was obtained from the electron impact ionization high-resolution MS (HRMS), and indicates that **2a**-I and **2a**-II are diastereomeric dimers of **1a**. The stereochemistry of the less polar dimer (**2a**-I) was clarified to be *meso* by X-ray crystallographic analysis as shown in Fig. 1,[6] therefore, the polar dimer (**2a**-II) was concluded to be the racemate. The stereochemistries of these products were also confirmed by HPLC analysis on chiral stationary phases.[3a,7] Thus, under common HPLC conditions [Column: CHIRALCEL OD, 4.6 mm i.d.× 25 cm (DAICEL Chemical Industries), eluent: hexane/2-propanol=90/10 by volume, flow: 0.5 ml/min, detection: UV 254 nm], the *meso* compound (**2a**-I) showed only a single peak (t_R=9.5 min) whereas the racemic compound (**2a**-II) showed two peaks (t_R=9.8 and 11.4 min) with approximately the same magnitude.

Characteristic differences in the ^{1}H-NMR spectra of **2a**-I and **2a**-II were observed. In the *meso* form (**2a**-I), the methyl proton signals of the ethoxy groups were observed at 0.91 (6H) and 1.11 ppm (6H) (Δ0.2 ppm).[8] These signals are at somewhat higher magnetic field compared to ordinarily observed positions (1.3—1.4 ppm). The upfield shift can be explained from the X-ray stereostructure, in which all ethoxy groups are located in the shielded area of the benzene rings, as shown in Fig. 1.

On the other hand, in the racemate (**2a**-II), the methyl proton signals of the ethoxy groups were observed at 0.79 (6H) and 1.42 ppm (6H) (Δ0.63 ppm).[8] In this case, one of the ethoxy protons seems to be shifted to higher magnetic field from the ordinarily observed position, and the others are located in the ordinary position. These results suggest that one of the two ethoxy groups in the racemic compound (**2a**-II) is shielded by the benzene rings, while the other is not effected by the benzene rings. In order to confirm this assumption, we performed a semiempirical molecular orbital calculation for **2a**-II. The most stable structure for **2a**-II was calculated by the MOPAC PM3 method,[9] and the obtained structure is shown in Fig. 2. The calculated result is highly consistent with the above-mentioned assumption.

To examine the generality of the present dimerization, several alkylidenemalonates (**1b**—**l**) were prepared and subjected to the dimerization conditions to give the corresponding diastereomeric mixtures of **2b**—**l** (see Experimental).

The diastereomers of **2b**—**g** were easily separated by silica gel column chromatography or preparative TLC (PTLC) to the less polar compound (I) and the polar compound (II).



1 R = Aryl, alkyl **2-I** (*meso* form) **2-II** (racemate)

Chart 1

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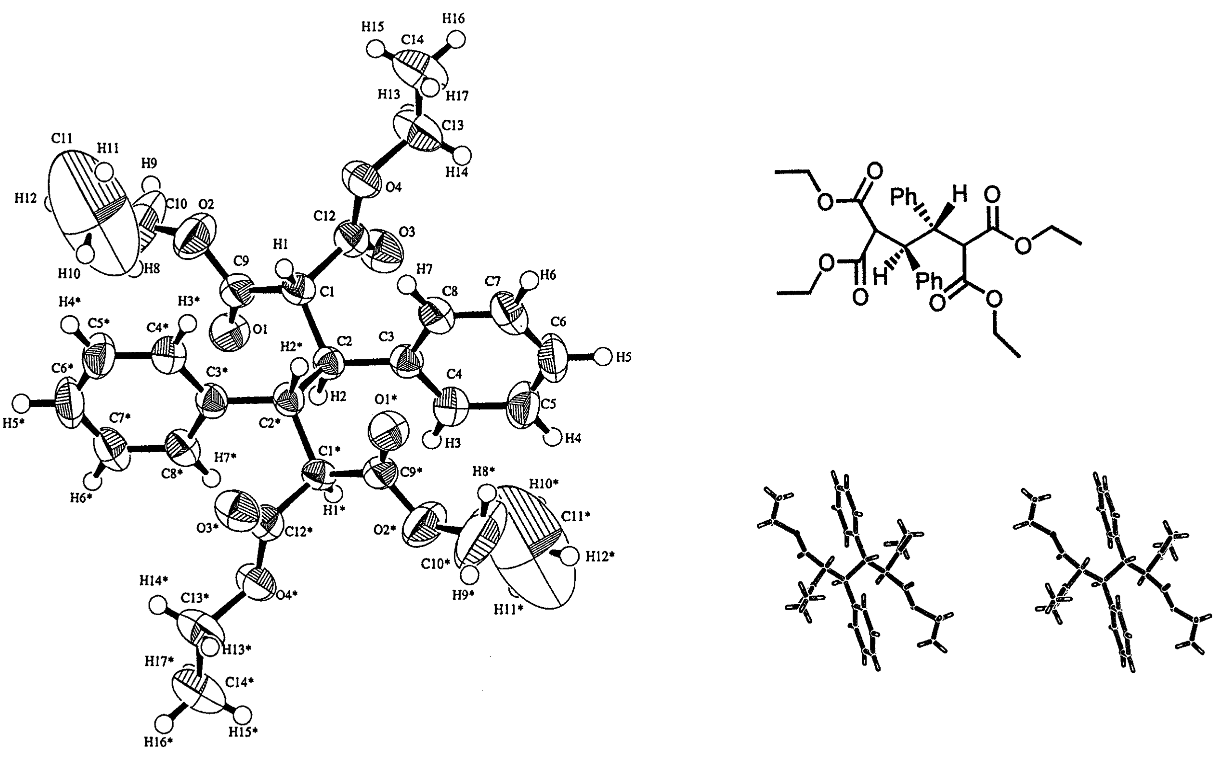
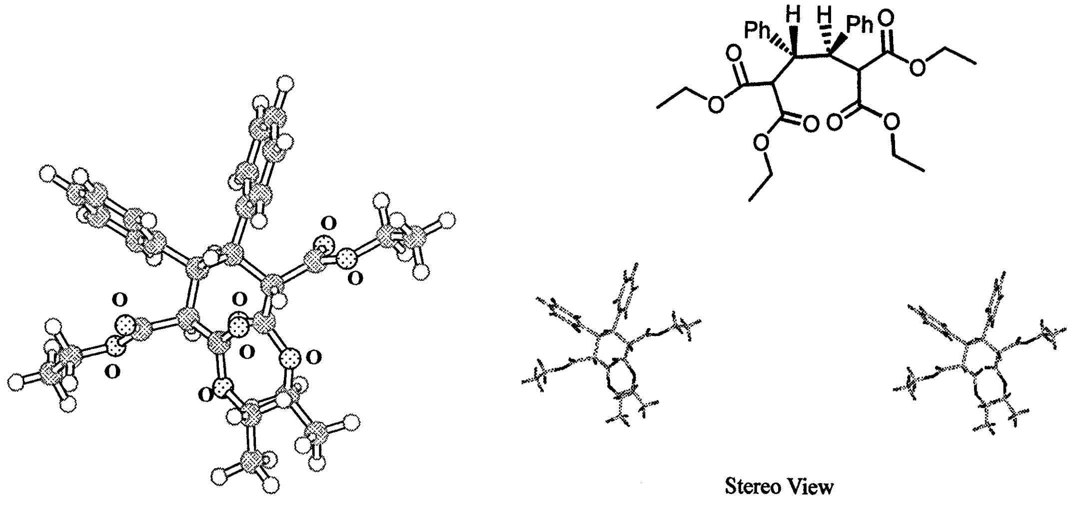


ORTEP Drawing

Stereo View

Fig. 1. X-Ray Structure of **2a**-I (Less Polar Compound; *meso* Form)



Stereo View

Fig. 2. The Stucture of **2a**-II (Polar Compound; Racemic Form) Obtained by MOPAC (PM3) Calculation

Stereochemistries of these compounds were determined on the basis of analogy in ^{1}H-NMR spectra and HPLC analysis on chiral stationary phases with **2a**-I and **2a**-II. Diastereomers of the products (**2h**—**l**) could not be separated by column chromatography, but the diastereomeric ratios of **2h**—**j** were easily estimated on the basis of their ^{1}H-NMR spectra. On the other hand, the diastereomeric ratios of **2k** and **2l**, which had aliphatic substituents on the 2- and 3-positions of butanetetracarboxylate, could not be estimated on the basis of their ^{1}H-NMR spectra because of complicated signal patterns.

In conclusion, we found that alkylidenemalonates (**1a**—**l**) were dimerized to *meso* and racemate mixtures of 2,3-disubstituted 1,1,4,4-butanetetracarboxylates (**2a**—**l**) in the presence of SmI$_2$ in THF, and the dimeric products (**2a**—**j**) having aromatic substituents on the 2- and 3-positions of butanetetracarboxylate showed characteristic patterns in their ^{1}H-NMR spectra. These results should be useful to determine the stereochemistry of 2,3-diaryl-1,1,4,4-butanetetracarboxylic acids and related compounds.

Experimental

Melting points were measured with a Yanaco MP micro-melting point apparatus and are uncorrected. ^{1}H-NMR spectra were measured on a Varian XL-300 (300 MHz) or a JEOL EX-270 (270 MHz) in CDCl$_3$ with tetramethylsilane as an internal standard and chemical shifts are reported in ppm. IR spectra were taken with a Shimadzu IR-435 spectrophotometer in CHCl$_3$. Shimadzu GCMS-QP 1000 and JEOL JMS-SX 102A QQ spectrometers were used for low-resolution MS and HRMS except for **2k** and **2l**. FAB-MS were measured with a JEOL JMS-SX 102A QQ spectrometer. Silica gel chromatography [Silica gel 60 (grade 7734, 60—230 mesh, Merck)] and PTLC [Silica gel 60 PF$_{254}$ (Nacalai Tesque Inc.)] were used. HPLC analyses were carried out on a Shimadzu HPLC instrument at 25 °C. As a chiral stationary phase, a CHIRALCELL OD column [4.6 mm i.d.×25 cm (DAICEL Chemical Industries)] was used. The eluent ratio (hexane : 2-propanol, volumes), flow rate (ml/min), and retention time(s) (t_R, min) are shown in parentheses. A UV detector (wavelength, 254 nm) was used for detection of peaks.

Reductive Dimerization of Diethyl Benzylidenemalonate (1a) Using SmI$_2$ (General Procedure) To a suspension of samarium metal (360 mg, 2.40 mmol) in THF (0.5 ml) was added dropwise a solution of 1,2-diiodoethane (564 mg, 2.00 mmol) in THF (1.5 ml) at room temperature under an N$_2$ atmosphere, and the mixture was stirred for 1 h. A solution of **1a** (124 mg, 0.50 mmol) in THF (1 ml) was added dropwise to the blue suspension of SmI$_2$ at room temperature and the whole was stirred for an additional 1 h. After acidification with 3% HCl under ice-cooling, the mixture was extracted with diethyl ether (10 ml×3). The combined organic layers were washed successively with water, saturated Na$_2$S$_2$O$_3$ solution, water, and brine followed by drying over MgSO$_4$, and evaporated under reduced pressure. The crude residue was chromatographed on silica gel (ethyl acetate : *n*-hexane=1 : 5) to give a less polar compound (**2a**-I, 35 mg, 28%) and a polar compound (**2a**-II, 36 mg, 29%).

Tetraethyl *meso*-2,3-Diphenylbutane-1,1,4,4-tetracarboxylate (**2a**-I): Colorless prisms (from hexane), mp 88.0—90.0 °C. ^{1}H-NMR δ: 0.91 (6H, t, J=7.1 Hz), 1.11 (6H, t, J=7.2 Hz), 3.67 (2H, dd, J=2.2, 6.0 Hz), 3.82 (4H, q, J=7.1 Hz), 3.89 (2H, dq, J=10.7, 7.2 Hz), 3.93 (2H, dq, J=10.7, 7.2 Hz), 4.09 (2H, dd, J=2.3, 6.0 Hz), 7.15—7.35 (10H, m). IR cm^{-1}: 1741, 1722. MS *m/z*: 498 (0.5, M$^+$), 135 (100). HRMS *m/z*: 498.2249 (Calcd for $C_{28}H_{34}O_8$: 498.2253). *Anal.* Calcd for $C_{28}H_{34}O_8$: C, 67.45; H, 6.87. Found: C, 67.86; H, 7.05. HPLC (90 : 10; 0.5; 9.5).

Tetraethyl *rac*-2,3-Diphenylbutane-1,1,4,4-tetracarboxylate (**2a**-II): Colorless oil. ^{1}H-NMR δ: 0.79 (6H, t, J=7.1 Hz), 1.42 (6H, t, J=7.1 Hz), 3.74 (2H, dq, J=10.8, 7.1 Hz), 3.77 (2H, d, J=11.9 Hz), 3.81 (2H, dq, J=10.8, 7.1 Hz), 3.90 (2H, d, J=11.9 Hz), 4.37 (2H, dq, J=10.8, 7.1 Hz), 4.45 (2H, dq, J=10.8, 7.1 Hz), 7.10—7.40 (10H, m). IR cm^{-1}: 1747, 1723. MS *m/z*: 498 (6.3, M$^+$), 338 (100). HRMS *m/z*: 498.2247 (Calcd for $C_{28}H_{34}O_8$: 498.2253). HPLC (90 : 10; 0.5; 9. 8, 11.4).

Compounds (**2b**—**l**) were prepared by the above-mentioned procedure. Two and half equivalents of SmI$_2$ were used except for the cases of **1b**, **1i**, and **1j** (4.0 eq).

Tetraethyl *meso*-2,3-Bis(4-methylphenyl)butane-1,1,4,4-tetracarboxylate (**2b**-I): Yield; 43%. Colorless needles (from hexane), mp 109.0—110.0 °C. ^{1}H-NMR δ: 0.95 (6H, t, J=7.1 Hz), 1.10 (6H, t, J=7.1 Hz), 2.30 (6H, s), 3.64 (2H, dd, J=2.2, 5.8 Hz), 3.81 (2H, dq, J=10.7, 7.1 Hz), 3.85 (2H, dq, J=10.7, 7.1 Hz), 3.88 (2H, dq, J=10.7, 7.1 Hz), 3.93 (2H, dq, J=10.7, 7.1 Hz), 4.02 (2H, dd, J=2.2, 5.7 Hz), 7.11 (4H, d, J=8.1 Hz), 7.16 (4H, d, J=8.1 Hz). IR cm^{-1}: 1740, 1722. MS *m/z*: 526 (0.3, M$^+$), 149 (100). *Anal.* Calcd for $C_{30}H_{38}O_8$: C, 68.42; H, 7.27. Found: C, 68.33; H, 7.25. HPLC (95 : 5; 0.5; 12.3).

Tetraethyl *rac*-2,3-Bis(4-methylphenyl)butane-1,1,4,4-tetracarboxylate (**2b**-II): Yield; 37%. Colorless crystals (from hexane), mp 106.5—107.5 °C. ^{1}H-NMR δ: 0.81 (6H, t, J=7.1 Hz), 1.41 (6H, t, J=7.1 Hz), 2.29 (6H, s), 3.68 (2H, d, J=11.8 Hz), 3.75 (2H, dq, J=10.7, 7.1 Hz), 3.81 (2H, dq, J= 10.7, 7.1 Hz), 3.84 (2H, d, J=11.8 Hz), 4.35 (2H, dq, J=10.8, 7.1 Hz), 4.43 (2H, dq, J=10.7, 7.1 Hz), 6.90—7.05 (8H, m). IR cm^{-1}: 1750, 1724. MS *m/z*: 526 (0.5, M$^+$), 149 (100). HRMS *m/z*: 526.2569 (Calcd for $C_{30}H_{38}O_8$: 526.2566). HPLC (95 : 5; 0.5; 9.8, 13.4).

Tetraethyl *meso*-2,3-Bis(4-ethylphenyl)butane-1,1,4,4-tetracarboxylate (**2c**-I): Yield; 49%. Colorless needles (from hexane), mp 93.0—94.5 °C. ^{1}H-NMR δ: 0.91 (6H, t, J=7.2 Hz), 1.08 (6H, t, J=7.1 Hz), 1.19 (6H, t, J=7.5 Hz), 2.59 (4H, q, J=7.5 Hz), 3.65 (2H, dd, J=2.0, 5.7 Hz), 3.84 (4H, dq, J=10.5, 7.1 Hz), 3.89 (4H, dq, J=10.5, 7.1 Hz), 4.04 (2H, dd, J=2.1, 5.6 Hz), 7.08 (4H, d, J=7.9 Hz), 7.21(4H, d, J=8.1 Hz). IR cm^{-1}: 1739, 1720. MS *m/z*: 554 (0.4, M$^+$), 163 (100). *Anal.* Calcd for $C_{32}H_{42}O_8$: C, 69.29; H, 7.63. Found: C, 69.43; H, 7.63. HPLC (95 : 5; 1.0; 5.2).

Tetraethyl *rac*-2,3-Bis(4-ethylphenyl)butane-1,1,4,4-tetracarboxylate (**2c**-II): Yield; 39%. Colorless oil. ^{1}H-NMR δ: 0.77 (6H, t, J=7.2 Hz), 1.20 (6H, t, J=7.6 Hz), 1.41 (6H, t, J=7.1 Hz), 2.59 (4H, q, J=7.6 Hz), 3.69 (2H, d, J=11.9 Hz), 3.74 (4H, dq, J=10.6, 7.1 Hz), 3.81 (4H, dq, J=10.6, 7.1 Hz), 4.35 (4H, dq, J=10.7, 7.1 Hz), 4.41 (4H, dq, J=10.7, 7.1 Hz), 6.2—6.8 (4H, br), 6.98 (4H, d, J=6.1 Hz). IR cm^{-1}: 1747, 1721. MS *m/z*: 554 (1.6, M$^+$), 394 (100). HRMS m/z: 554.2887 (Calcd for $C_{32}H_{42}O_8$: 554.2879). HPLC (95 : 5; 1.0; 5.4, 10.4).

Tetraethyl *meso*-2,3-Bis(4-isopropylphenyl)butane-1,1,4,4-tetracarboxylate (**2d**-I): Yield; 40%. Colorless needles (from hexane), mp 103.5—105.0 °C. ^{1}H-NMR δ: 0.87 (6H, t, J=7.1 Hz), 1.05 (6H, t, J=7.1 Hz), 1.21 (12H, d, J=6.9 Hz), 2.85 (2H, septet, J=7.5 Hz), 3.65 (2H, dd, J=2.1, 5.7 Hz), 3.78 (4H, dq, J=10.6, 7.1 Hz), 3.86 (4H, dq, J=10.7, 7.2 Hz), 4.04 (2H, dd, J=2.2, 5.6 Hz), 7.10 (4H, d, J=8.3 Hz), 7.24 (4H, d, J=8.3 Hz). IR cm^{-1}: 1739, 1720. MS *m/z*: 582 (0.4, M$^+$), 422 (100). *Anal.* Calcd for $C_{34}H_{46}O_8$: C, 70.08; H, 7.96. Found: C, 70.03; H, 8.08. HPLC (90 : 10; 0.5; 6.9).

Tetraethyl *rac*-2,3-Bis(4-isopropylphenyl)butane-1,1,4,4-tetracarboxylate (**2d**-II): Yield; 40%. Colorless needles (from hexane), mp 98.0—100.5 °C. ^{1}H-NMR δ: 0.72 (6H, t, J=7.1 Hz), 1.207 (6H, t, J=6.9 Hz), 1.214 (6H, d, J=6.9 Hz), 1.41 (6H, t, J=7.1 Hz), 2.84 (2H, septet, J=6.9 Hz), 3.70 (2H, d, J=11.1 Hz), 3.74 (4H, dq, J=11.2, 7.1 Hz), 3.81 (4H, dq, J=10.9, 7.1 Hz), 3.87 (2H, d, J=11.6 Hz), 4.35 (4H, dq, J=10.7, 7.1 Hz), 4.44 (4H, dq, J=10.7, 7.1 Hz), 6.3—6.9 (4H, br), 7.01 (4H, d, J=7.4 Hz). IR cm^{-1}: 1745, 1720. MS *m/z*: 582 (1.6, M$^+$), 177 (100). *Anal.* Calcd for $C_{34}H_{46}O_8$: C, 70.08; H, 7.96. Found: C, 70.16; H, 8.14. HPLC (90 : 10; 0.5; 7.8, 12.5).

Tetraethyl *meso*-2,3-Bis(4-*tert*-butylphenyl)butane-1,1,4,4-tetracarboxylate (**2e**-I): Yield; 45%. Colorless prisms (from hexane), mp 120.0—122.0 °C. ^{1}H-NMR δ: 0.86 (6H, t, J=7.1 Hz), 1.03 (6H, t, J=7.2 Hz), 1.28 (18H, s), 3.65 (2H, dd, J=2.1, 5.6 Hz), 3.76 (4H, dq, J=10.8, 7.1 Hz), 3.84 (4H, dq, J=10.7, 7.1 Hz), 4.04 (2H, dd, J=2.1, 5.6 Hz), 7.26 (8H, s). IR cm^{-1}: 1740, 1719. MS *m/z*: 610 (0.6, M$^+$), 450 (100). *Anal.* Calcd for $C_{36}H_{50}O_8$: C, 70.79; H, 8.25. Found: C, 70.89; H, 8.42. HPLC (90 : 10; 0.5; 7.3).

Tetraethyl *rac*-2,3-Bis(4-*tert*-butylphenyl)butane-1,1,4,4-tetracarboxylate (**2e**-II): Yield; 38%. Colorless needles (from hexane), mp 118.0—119.5 °C. ^{1}H-NMR δ: 0.69 (6H, t, J=7.1 Hz), 1.28 (18H, s), 1.42 (6H, t, J=7.1 Hz), 3.70 (2H, d, J=11.9 Hz), 3.73 (4H, dq, J=10.8, 7.1 Hz), 3.80 (4H, dq, J=10.8, 7.1 Hz), 3.88 (2H, d, J=11.5 Hz), 4.36 (4H, dq, J=10.8, 7.1 Hz), 4.44 (4H, dq, J=10.8, 7.1 Hz), 6.3—7.0 (4H, br), 7.16 (4H, d, J=8.1 Hz). IR cm^{-1}: 1747, 1720. MS *m/z*: 610 (1.5, M$^+$), 450 (100). *Anal.* Calcd for $C_{36}H_{50}O_8$: C, 70.79; H, 8.25. Found: C, 70.76; H, 8.41. HPLC (90 : 10; 0.5; 7.8, 11.8).

Tetraethyl *meso*-2,3-Bis(4-isobutylphenyl)butane-1,1,4,4-tetracarboxylate (**2f**-I): Yield; 47%. Colorless prisms (from hexane), mp 78.0—81.5 °C. ^{1}H-NMR δ: 0.87 (12H, d, J=6.8 Hz), 0.91 (6H, t, J=7.1 Hz), 1.09 (6H, t, J=7.1 Hz), 1.82 (2H, nonet, J=6.7 Hz), 2.42 (4H, d, J=7.3 Hz), 3.65 (2H, dd, J=2.1, 5.9 Hz), 3.81 (4H, q, J=7.1 Hz), 3.89 (4H, q, J=7.1 Hz), 4.05 (2H, dd, J=2.1, 5.9 Hz), 7.10 (4H, d, J=8.1 Hz), 7.19 (4H, d, J=8.1 Hz). IR cm^{-1}: 1740, 1719. MS *m/z*: 610 (0.4, M$^+$), 450 (100). *Anal.* Calcd for $C_{36}H_{50}O_8$: C, 70.79; H, 8.25. Found: C, 71.05; H, 8.28. HPLC (90 : 10; 0.5; 7.5).

Tetraethyl *rac*-2,3-Bis(4-isobutylphenyl)butane-1,1,4,4-tetracarboxylate (**2f**-II): Yield; 37%. Colorless oil. ^{1}H-NMR δ: 0.77 (6H, t, J=7.1 Hz), 0.84 (6H, d, J=6.4 Hz), 0.85 (6H, d, J=6.4 Hz), 1.42 (6H, t, J=7.2 Hz), 1.80 (2H, nonet, J=6.7 Hz), 2.37 (2H, dd, J=7.2, 18.5 Hz), 2.44 (2H, dd, J=7.2, 18.5 Hz), 3.74 (2H, d, J=11.9 Hz), 3.74 (2H, dq, J=10.8, 7.1 Hz), 3.81 (2H, dq, J=10.7, 7.1 Hz), 3.81 (2H, d, J=11.9 Hz), 4.35 (2H, dq, J=10.7, 7.1 Hz), 4.44 (2H, dq, J=10.9, 7.1 Hz), 6.0—7.2 (8H, m). IR cm^{-1}: 1738, 1721. MS *m/z*: 610 (1.7, M$^+$), 450 (100). HRMS *m/z*: 610.3499 (Calcd for $C_{36}H_{50}O_8$: 610.3505). HPLC (90 : 10; 0.5; 7.5, 10.8).

Tetraethyl *meso*-2,3-Bis(4-biphenyl)butane-1,1,4,4-tetracarboxylate (**2g**-I): Yield; 20%. Colorless prisms (from PhH–hexane), mp 160.5—162.0 °C. ^{1}H-NMR δ: 0.94 (6H, t, J=7.1 Hz), 1.10 (6H, t, J=7.1 Hz), 3.75 (2H, dd, J=2.1, 5.8 Hz), 3.86 (4H, q, J=7.1 Hz), 3.94 (4H, dq, J=3.5, 7.1 Hz), 4.18 (2H, dd, J=2.2, 5.8 Hz), 7.30—7.65 (18H, m). IR cm^{-1}: 1740, 1721. MS *m/z*: 650 (1.3, M$^+$), 325 (100). *Anal.* Calcd for $C_{40}H_{42}O_8$: C, 73.83; H, 6.51. Found: C, 73.88; H, 6.56. HPLC (90 : 10; 0.5; 12.5).

Tetraethyl *rac*-2,3-Bis(4-biphenyl)butane-1,1,4,4-tetracarboxylate (**2g**-II): Yield; 35%. Colorless needles (from PhH–hexane), mp 144.0—147.5 °C. ^{1}H-NMR δ: 0.82 (6H, t, J=7.1 Hz), 1.45 (6H, t, J=7.1 Hz), 3.82 (2H, d, J=11.7 Hz), 3.70—3.95 (4H, m), 3.99 (2H, d, J=11.7 Hz), 4.40 (2H, dq, J=10.7, 7.1 Hz), 4.48 (2H, dq, J=10.7, 7.1 Hz), 6.0—7.2 (2H, br), 7.3—7.6 (16H, m). IR cm^{-1}: 1746, 1722. MS *m/z*: 650 (3.3, M$^+$), 490 (100). *Anal.* Calcd for $C_{40}H_{42}O_8$: C, 73.83; H, 6.51. Found: C, 73.53; H, 6.52. HPLC (90 : 10; 0.5; 11.4, 24.0).

Mixture of Tetraethyl 2,3-Bis(4-methoxycarbonylphenyl)butane-1,1,4,4-tetracarboxylate (**2h**): Yield; 67%. *meso* form : racemate=7 : 6. Colorless needles (from AcOEt), mp 167.0—170.0 °C. ^{1}H-NMR δ: 0.84 (2.8H, t, J=7.0 Hz), 0.93 (3.2H, t, J=7.0 Hz), 1.15 (3.2H, t, J=7.1 Hz), 1.45 (2.8H, t, J=7.0 Hz), 3.65 (0.9H, d, J=7.4 Hz), 3.91 (6H, s), 3.00—4.20 (8.4H, m), 4.19 (0.9H, d, J=6.9 Hz), 4.38 (0.9H, dq, J=10.8, 7.1 Hz), 4.46 (0.9H, dq, J=10.8, 7.2 Hz), 6.0—7.2 (1.8H, br), 7.33 (2.2H, d, J=8.1 Hz), 7.86 (1.8H, br-s), 7.95 (2.2H, d, J=8.1 Hz). IR cm^{-1}: 1740, 1719. MS *m/z*: 614 (1.9, M$^+$), 193 (100). *Anal.* Calcd for $C_{32}H_{38}O_{12}$: C, 62.53; H, 6.23. Found: C, 62.62; H, 6.27.

Mixture of Tetraethyl 2,3-Bis(4-methoxyphenyl)butane-1,1,4,4-tetracarboxylate (**2i**): Yield; 77%. *meso* form : racemate=3 : 2. Colorless prisms (from AcOEt–hexane), mp 111.5—112.0 °C. ^{1}H-NMR δ: 0.84 (2.4H, t, J=7.1 Hz), 0.97 (3.6H, t, J=7.1 Hz), 1.11 (3.6H, t, J=7.1 Hz), 1.41 (2.4H, t, J=7.1 Hz), 3.60—4.05 (10H, m), 3.78 (6H, s), 4.36 (0.8H, dq, J=10.6, 7.1 Hz), 4.43 (0.8H, dq, J=10.6, 7.1 Hz), 6.65—6.75 (4.8H, m), 6.80 (1.6H, d, J=8.8 Hz), 7.22 (1.6H, d, J=8.8 Hz). IR cm^{-1}: 1745, 1722. MS *m/z*: 558 (1.0, M^{+}), 279 (100). *Anal.* Calcd for $C_{30}H_{38}O_{10}$: C, 64.50; H, 6.86. Found: C, 64.01; H, 6.86.

Mixture of Tetraethyl 2,3-Bis(3,4-methylenedioxyphenyl)butane-1,1,4,4-tetracarboxylate (**2j**): Yield; 77%. *meso* form : racemate=3 : 2. Colorless needles (from $CHCl_3$–hexane), mp 165.5—166.5 °C. ^{1}H-NMR δ: 0.88 (2.4H, t, J=7.1 Hz), 1.03 (3.6H, t, J=7.2 Hz), 1.14 (3.6H, t, J=7.2 Hz), 1.41 (2.4H, t, J=7.2 Hz), 3.50—4.10 (10.4H, m), 4.30—4.50 (1.6H, m), 5.9—6.0 (2.4H, m), 6.6—6.8 (3.2H, m), 6.93 (2.4H, s). IR cm^{-1}: 1745, 1723. MS *m/z*: 556 (6.8, M^{+}), 175 (100). *Anal.* Calcd for $C_{30}H_{34}O_{12}$: C, 61.65; H, 5.90. Found: C, 61.43; H, 5.84.

Mixture of Tetraethyl 2,3-dimethylbutane-1,1,4,4-tetracarboxylate (**2k**): Yield; 69%. Unknown ratio. Colorless oil. ^{1}H-NMR δ: 0.90 (6H, d, J=6.8 Hz), 1.07 (6H, d, J=6.6 Hz), 1.26 (6H, t, J=7.1 Hz), 1.27 (6H, t, J=7.1 Hz), 1.28 (6H, t, J=7.1 Hz), 1.29 (6H, t, J=7.1 Hz), 2.30—2.45 (4H, m), 3.33 (2H, d, J=9.7 Hz), 3.48 (2H, d, J=6.4 Hz), 4.19 (4H, q, J=7.1 Hz), 4.20 (4H, q, J=7.1 Hz), 4.20 (4H, q, J=7.1 Hz), 4.23 (4H, q, J=7.1 Hz). IR cm^{-1}: 1740, 1722. FAB-MS m/z; 375.2026 (Calcd for $C_{18}H_{30}O_8$+H; 375.2019).

Mixture of Tetraethyl 2,3-Diisopropylbutane-1,1,4,4-tetracarboxylate (**2l**): Yield; 55%. Unknown ratio. Colorless oil. ^{1}H-NMR δ: 0.83, 0.93, 0.96, 1.01 (total 12H, each d, J=6.6 Hz), 1.271, 1.276 (total 12H, each t, J=7.2 Hz), 2.00—2.20 (2H, m), 2.30—2.45, 2.60—2.70 (total 2H, m), 3.56, 3.79 (total 2H, each d, J=4.8, 3.9 Hz), 4.10—4.30 (12H, m). IR cm^{-1}: 1730, 1720. FAB-MS *m/z*; 431.2649 (Calcd for $C_{22}H_{38}O_8$+H; 431.2645).

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References and Notes

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4) The dimerization reaction requires more than 2.0 eq of SmI_2.

5) Jiang and Zhang reported the reductive coupling of diethyl benzylidenemalonate in a SmI_2–hexamethylphosphoramide (HMPA)–THF–*tert*-BuOH system but did not discuss the stereochemistries of the products. [Jiang H.-J., Zhang Y.-M., *Youji Huaxue*, **17**, 242—246 (1997), CA, **127**: 81215*q*]. On the other hand, Inanaga *et al.* reported that α,β-unsaturatued esters were dimerized to hexanedioic acid ester derivatives (48—90%) by treatment with SmI_2 in a HMPA–THF system in the presence of a proton source, and that in the absence of HMPA, slow reduction of the double bond or no dimerization reaction was observed [Inanaga J., Handa Y., Tabuchi T., Otsubo K., Yamaguchi M., Hanamoto T., *Tetrahedron Lett.*, **32**, 6557—6558 (1991)]. In the present case, it was found that HMPA and a proton source were not always necessary for the coupling.

6) $C_{28}H_{34}O_8$; FW 498.57; monoclinic; C2/c (# 15); a=23.156 (3), b=5.696 (3), c=22.890 (2) Å, β=115.709(9)°; V=2720 (1) Å^3; Z=4; D_{calc}=1.217 g/cm^3; λ(Cu$K\alpha$)=1.54178 Å; μ(Cu$K\alpha$)=7.33 cm^{-1}; F(000)=1064.00; T=296 K; R=0.074 (R_{w}=0.137) for 1616 observations ($I>3.00\theta\sigma(I)$). Detailed X-ray crystallographic data are available from the Cambridge Crystallographic Data Centre.

7) Pappas S. P., Pappas B. C., Okamoto Y., Sakamoto H., *J. Org. Chem.*, **53**, 4404 (1988).

8) Elinson *et al.* observed similar tendencies in $C\underline{H}_3O$-signals [3.37 and 3.43 ppm (Δ0.06 ppm) for the *meso* compound; 3.30 and 3.94 ppm (Δ 0.64 ppm) for the racemic compound] of the diastereomers of tetramethyl 2,3-diphenylbutane-1,1,4,4-tetracarboxylate, which were prepared by a different method [Elinson M. N., Feducovich S. K., Znkharenkov A. A., Ugrak B. I., Nikishin G. I., Lindeman S. V., Struchkov J. T., *Tetrahedron*, **51**, 5035—5046 (1995)].

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