759 cm^{-1}; HRMS m/e calcd for $C_{20}H_{32}O$ 288.2454, found 288.2450.

9,9-Dimethyl-1,2,3,4-tetra-*n*-propylspiro[4.5]deca-1,3-dien-7-one (8): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 12 H), 1.24 (s, 6 H), 1.32–1.48 (m, 8 H), 1.66 (s, 2 H), 2.04–2.19 (m, 8 H), 2.27 (s, 2 H), 2.31 (s, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.18 (q), 14.67 (q), 23.08 (t), 23.57 (t), 27.95 (t), 28.47 (t), 31.36 (s), 31.52 (q), 36.52 (t), 42.48 (t), 51.78 (t), 56.36 (s), 138.54 (s), 147.34 (s), 214.55 (s); IR (neat) 2950, 2929, 2875, 1702, 1375, 1275, 1158, 759 cm^{-1}; HRMS m/e calcd for $C_{24}H_{40}O$ 344.3081, found 344.3079.

1,2,3,4-Tetramethylspiro[4.4]nona-1,3-dien-7-one (9): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 12 H), 1.91 (t, J = 8.4 Hz, 2 H), 2.17 (s, 2 H), 2.53 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 10.08 (q), 10.84 (q), 27.76 (t), 37.64 (t), 43.78 (t), 59.50 (s), 134.38 (s), 139.48 (s), 220.98 (s); IR (neat) 2975, 2929, 1732, 1389, 1144, 755 cm^{-1}; HRMS m/e calcd for $C_{13}H_{18}O$ 190.1358, found 190.1348.

1,2,3,4-Tetraethylspiro[4.4]nona-1,3-dien-7-one (10): ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (t, J = 7.5 Hz, 12 H), 2.01 (t, J = 8.4 Hz, 2 H), 2.04–2.27 (m, 10 H), 2.52 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.67 (q), 15.11 (q), 18.29 (t), 18.48 (t), 27.77 (t), 37.70 (t), 44.16 (t), 60.00 (s), 140.69 (s), 145.48 (s), 221.07 (s); IR (neat) 2969, 2935, 2876, 1721, 1459, 1402, 1379, 1158, 1059 cm^{-1}; HRMS m/e calcd for $C_{17}H_{26}O$ 246.1985, found 246.1989.

1,2,3,4-Tetra-*n*-propylspiro[4.4]nona-1,3-dien-7-one (11): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 12 H), 1.35–1.48 (m, 8 H), 1.98 (t, J = 8.4 Hz, 2 H), 2.03–2.20 (m, 8 H), 2.25 (s, 2 H), 2.49 (t, J = 8.4 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 14.23 (q), 14.56 (q), 14.60 (q), 14.66 (q), 23.20 (t), 23.73 (t), 27.89 (t), 27.98 (t), 28.15 (t), 37.70 (t), 44.33 (t), 60.00 (s), 139.56 (s), 144.52 (s), 221.02 (s); IR (neat): 2960, 2930, 2872, 1733, 1460, 1403, 1377, 1154 cm^{-1}; HRMS m/e calcd for $C_{21}H_{34}O$ 302.2611, found 302.2590.

1,2,3,4,6-Pentamethylspiro[4.4]nona-1,3-dien-7-one (12): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (d, J = 6.7 Hz, 3 H), 1.62 (s, 3 H), 1.62–1.73 (m, 1 H), 1.73 (s, 3 H), 1.75 (s, 3 H), 1.82 (s, 3 H), 2.03–2.15 (m, 1 H), 2.31 (q, J = 6.7 Hz, 1 H), 2.48–2.53 (m, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 7.04 (q), 8.90 (q), 10.48 (q), 11.13 (q), 11.95 (q), 25.23 (t), 35.61 (t), 49.48 (d), 63.54 (s), 135.84 (s), 135.90 (s), 135.98 (s), 137.88 (s), 221.35 (s); IR (neat) 2976, 2935, 2875, 1720, 1381, 1165, 758 cm^{-1}; HRMS m/e calcd for $C_{21}H_{34}O$ 302.2611, found 302.2606.

6-Methyl-1,2,3,4-tetraethylspiro[4.4]nona-1,3-dien-7-one (13): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (d, J = 6.8 Hz, 3 H), 0.98–1.11 (m, 12 H), 1.49–1.62 (m, 1 H), 1.76–1.84 (m, 1 H), 2.14–2.62 (m, 11 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 6.98 (q), 14.78 (q), 14.83 (q), 17.24 (t), 18.11 (t), 18.80 (t), 19.37 (t), 25.33 (t), 35.97 (t), 49.48 (d), 63.96 (s), 142.36 (s), 142.53 (s), 143.39 (s), 221.76 (s); IR (neat) 2976, 2939, 2878, 1723, 1457, 1372, 1137, 757 cm^{-1}; HRMS m/e calcd for $C_{18}H_{28}O$ 260.2141, found 260.2148.

6-Methyl-1,2,3,4-tetra-*n*-propylspiro[4.4]nona-1,3-dien-7-one (14): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.57 (d, J = 7.0 Hz, 3 H), 0.88–0.99 (m, 12 H), 1.36–1.48 (m, 9 H), 1.71–1.79 (m, 1 H), 2.07–2.06 (m, 11 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 7.14 (q), 14.24 (q), 14.53 (q), 14.70 (q), 23.25 (t), 23.53 (t), 23.62 (t), 25.55 (t), 27.23 (t), 27.70 (t), 28.31 (t), 29.22 (t), 36.03 (t), 49.53 (d), 64.00 (s), 141.10 (s), 141.40 (s), 141.70 (s), 142.50 (s), 221.67 (s); IR (neat) 2963, 2876, 1726, 1458, 1375, 1176, 1083, 761 cm^{-1}; HRMS m/e calcd for $C_{22}H_{36}O$ 316.2627, found 316.2759.

6-Deuterio-6-methyl-1,2,3,4-tetraethylspiro[4.4]nona-1,3-dien-7-one (13-*d*): ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.56 (s, 3 H), 0.98–1.11 (m, 12 H), 1.49–1.62 (m, 1 H), 1.76–1.84 (m, 1 H), 2.14–2.62 (m, 10 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 6.81 (q), 14.69 (q), 14.76 (q), 17.18 (t), 18.05 (t), 18.74 (t), 19.31 (t), 25.27 (t), 35.93 (t), 48.91 (t, J_{C-D} = 18.5 Hz), 63.84 (s), 142.30 (s), 142.48 (s), 143.31 (s), 221.91 (s); MS m/e 261 ($C_{18}DH_{27}O$).

Compound 5: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (t, J = 6.7 Hz), 1.70 (s, 6 H), 1.71–1.79 (m, 4 H), 2.10 (s, 2 H), 2.10–2.18 (m, 2 H), 2.22–2.30 (m, 4 H), 2.43 (t, J = 6.8 Hz, 2 H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 10.99 (q), 22.90 (t), 23.62 (t), 23.85 (t), 29.86 (t), 40.52 (t), 45.74 (t), 59.33 (s), 134.95 (s), 139.50 (s), 214.00 (s); IR (neat) 2960, 2939, 2879, 1710, 1458, 1366, 1101, 760 cm^{-1}; HRMS m/e calcd for $C_{16}H_{22}O$ 230.1672, found 230.1678.

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Registry No. 1, 140110-75-4; 2, 140110-76-5; 3, 140110-77-6; 4, 140110-78-7; 5, 140110-79-8; 6, 140110-80-1; 7, 140110-81-2; 8, 140110-82-3; 9, 140110-83-4; 10, 140110-84-5; 11, 140110-85-6; 12, 140110-86-7; 13, 140110-87-8; 13-*d*, 140110-88-9; 14, 140110-89-0; PhC_2Ph, 501-65-5; $NiBr_2$, 13462-88-9; Zn, 7440-66-6; $NiBr_2$·PPh_3, 25802-21-5; $NiBr_2$·$2PPh_3$, 14126-37-5; $NiBr_2$·$4PPh_3$, 140110-90-3; $NiBr_2$·$6PPh_3$, 140110-91-4; $Pd(OAc)_2$, 301-04-2; $PdCl_2(PhCN)_2$, 14220-64-5; $PdCl_2(CH_3CN)_2$, 14592-56-4; $PdCl_2$·PPh_3, 116694-43-0; Mg, 7439-95-4; $SnCl_2$, 7772-99-8; 3-iodo-2-cyclohexen-1-ol, 56671-82-0; 5,5-dimethyl-3-iodo-2-cyclohexen-1-one, 56671-85-3; 3-iodo-2-cyclopenten-1-one, 61765-46-6; 3-iodo-2-methyl-2-cyclopenten-1-one, 56778-49-5; 2-butyne, 503-17-3; 3-hexyne, 928-49-4; 4-octyne, 1942-45-6; 2,8-decadiyne, 29518-82-9; 3-bromo-2-cyclohexen-1-one, 56671-81-9.

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Stereochemistry of the Dicarbonylation of Olefins Using Styrene as the Model Compound

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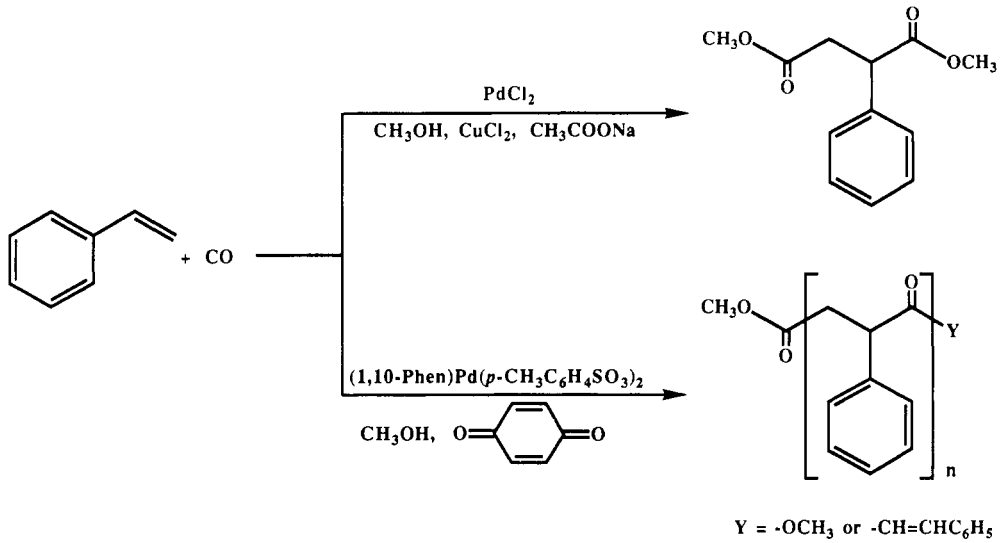
Summary: The dicarbonylation reaction of *trans*-β-deuteriostyrene to dimethyl 2-phenylbutanedioate and dimethyl 2,5-diphenyl-4-oxoheptanedioate using Pd(CF$_3$COO)$_2$/2,2′-bipyridine as the catalyst precursor in the presence of 1,4-benzoquinone (i.e., under conditions suitable for the formation of syndiotactic poly(1-phenyl-3-oxotrimethylene)) takes place stereospecifically in a syn fashion. The same stereochemical outcome was found for the dicarbonylation of the same substrate to dimethyl 2-phenylbutanedioate in the presence of (Diop)Pd(CF$_3$COO)$_2$.

The dicarbonylation of olefinic substrates is of interest due to the nature of the products that can be obtained, namely succinic acid derivatives[1] and (2-substituted) poly(1-oxotrimethylenes)[2-4] (compare Scheme I for styrene). The first reaction is carried out in methanol using

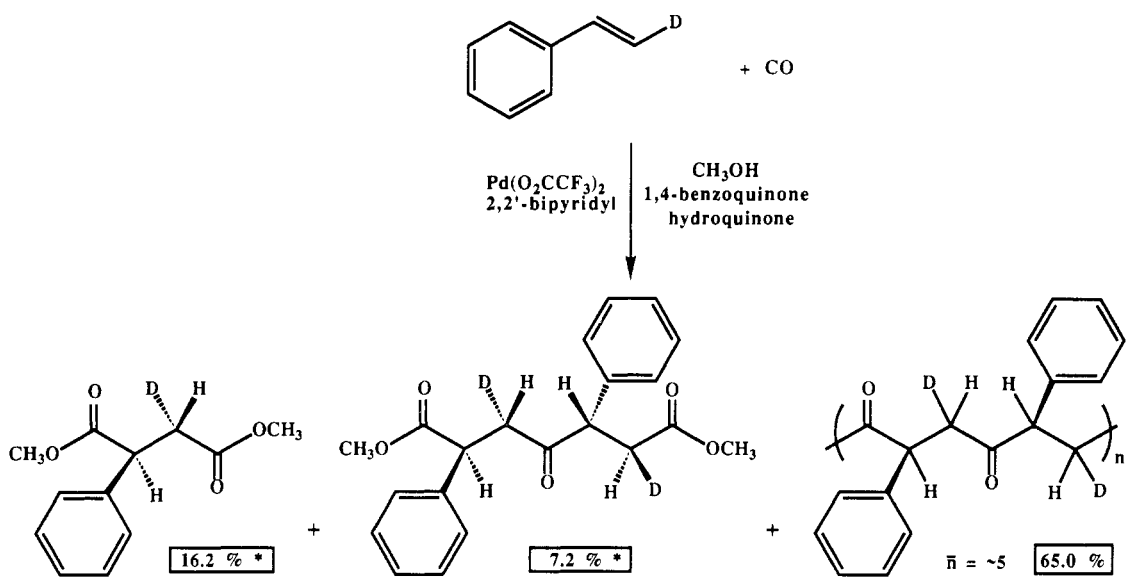
(1) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810.
(2) Drent, E. Eur. Pat. Appl. 229,408, 1986; *Chem. Abstr.* **1991**, *108*, 6617.
(3) Corradini, P.; De Rosa, C.; Panunzi, A.; Petrucci, G.; Pino, P. *Chimia* **1976**, *44*, 52.
(4) Barsacchi, M.; Consiglio, G.; Medici, L.; Petrucci, G.; Suter, U. W. *Angew. Chem.* **1991**, *103*, 992.

0276-7333/92/2311-1975$03.00/0

Scheme I



Scheme II



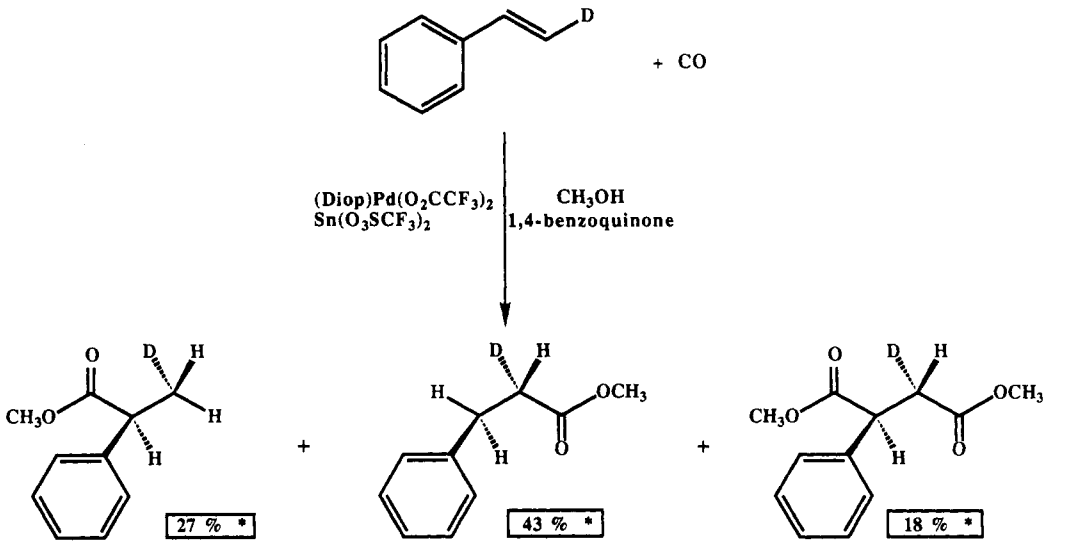
* only one enantiomer is shown

$PdCl_2$ as the catalyst precursor in the presence of $CuCl_2$ as reoxidant and a base such as sodium acetate.[1] The copolymerization of olefins with carbon monoxide requires palladium-containing catalytic systems modified by phosphorus or nitrogen ligands and weakly coordinating or noncoordinating anions.[5] In the case of styrene as the substrate the carbonylation to syndiotactic poly(1-oxo-2-phenyltrimethylene) requires nitrogen ligands such as 2,2′-bipyridyl and 1,10-phenanthroline.[2,3] The stereochemistry of the first reaction was found to involve a syn addition of the two carbomethoxy groups to the double bond.[6] No information whatsoever exists on the stereochemistry of the copolymerization of styrene and other olefins with carbon monoxide. The only data related to this aspect refer to the oligomerization of norbornene with carbon monoxide catalyzed by $Pd(PPh_3)_4$ in the presence of sodium carbonate and β-bromostyrene.[7] On the basis of ^{13}C NMR spectra a cis-exo stereochemistry was assigned to the recovered oligomers. Recent data seem to imply that the mechanism of copolymerization of olefins with carbon monoxide does not correspond[8] to an alternate insertion of the two monomer units into a metal–alkyl and into a metal–acyl bond, respectively.[9] Therefore, an unambiguous determination of the stereochemical aspects of the dicarbonylation reaction appeared necessary.

In the course of our studies on the copolymerization of styrene with carbon monoxide catalyzed by (1,10-phen)-$Pd(p\text{-}CH_3C_6H_4SO_3)_2$ (1,10-phen is 1,10-phenanthroline) or the system formed "in situ" from $Pd(CF_3COO)_2$/2,2′-bipyridine, in the presence of 1,4-benzoquinone it appeared that an increase of the concentration of this last component could cause a shift of the chemoselectivity of the reaction toward the formation of low-molecular-weight compounds.[4] Further investigation showed that this effect was due to the presence of excess 1,4-hydroquinone, which is probably formed during the reaction. In fact, a carbonylation re-

(5) (a) Drent, E. *Pure Appl. Chem.* **1990**, *62*, 661. (b) Drent, E.; van Broekhoven, J. A. M.; Doyle, M. J. *J. Organomet. Chem.* **1991**, *417*, 235.
(6) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1806.
(7) Roberto, D.; Catellani, M.; Chiusoli, G. P. *Tetrahedron Lett.* **1988**, *29*, 2115.
(8) Van Doorn, J. A.; Wong, P. K.; Sudmeier, O. Eur. Pat. Appl. 376,364, 1989; *Chem. Abstr.* **1991**, *114*, 24797. Drent, E. Eur. Pat. Appl. 399,617, 1989; *Chem. Abstr.* **1991**, *114*, 165108.
(9) Lai, T.-W.; Sen, A. *Organometallics* **1984**, *3*, 866.

Scheme III



* only one enantiomer is shown

action carried out using a styrene to hydroquinone molar ratio of ~0.5 allowed us to isolate dimethyl 2-phenylbutanedioate (17%), methyl *p*-hydroxyphenyl 2-phenylbutanedioate (4%), and dimethyl 2,5-diphenyl-4-oxoheptanedioate (9%) in addition to 65% of oligomeric materials (compare Scheme II). The products were separated by column chromatography and fully characterized by mass and ^1H and ^{13}C NMR spectroscopy. The presence of methyl *p*-hydroxyphenyl 2-phenylbutanedioate, in spite of the low concentration of hydroquinone with respect to methanol, seems to indicate that the alcoholysis of the involved acyl intermediates by phenols is more rapid than that by alcohols. This kind of reaction seems therefore important for the regulation of the molecular weight of the products in this carbonylation reaction.

The same experiment was then carried out using diastereomerically pure *trans*-β-deuteriostyrene (isotopic purity 91%) in the presence of a catalyst formed in situ from $Pd(CF_3COO)_2$/2,2′-bipyridine. Selectivities similar (Scheme II) to those in the previously described experiment were obtained. NMR characterization of dimethyl 2-phenylbutanedioate showed labeling on only one of the two diastereotopic hydrogen atoms in position 3, in a quantity corresponding to the isotopic purity of the starting material. The *ul* nature of the diastereomer formed was determined by comparison with the same compound obtained from the same substrate using $PdCl_2$ as the catalyst precursor in the presence of $CuCl_2$, as previously described,[1] which is known to take place through a syn addition.[6] Furthermore, NMR analysis of dimethyl 2,5-diphenyl-4-oxoheptanedioate again shows labeling on only one of the two diastereotopic hydrogen atoms for both methylene groups in positions 3 and 6. The assignment of the same relative stereochemistry with respect to the phenyl-substituted carbon atoms to this compound (both *ul*) is based on the fact that the same proton for the two units is labeled, namely the one having a 5.6-Hz coupling constant with the benzylic hydrogen atom. From this fact a double syn addition is apparent. Unfortunately, no information can be derived from the NMR spectrum of the copolymer formed, due to the broadness of the bands. The reported results, however, strongly suggest the same type of stereochemistry also for the copolymerization process.

Dicarbonylation of styrene can also be achieved with similar palladium-containing catalytic systems modified by diphosphines. In this case dicarbonylation competes with monocarbonylation of the substrate. By using $(Diop)Pd(CF_3COO)_2$ in the presence of $Sn(CF_3SO_3)_2$ in methanol at room temperature and under 400 bar of carbon monoxide, an 18% yield of dimethyl 2-phenylbutanedioate, together with 27% of methyl 2-phenylpropanoate and 43% of methyl 3-phenylpropanoate, is obtained (Scheme III). The recovered dimethyl 2-phenylbutanedioate was again the *ul* diastereomer, showing that also this catalyst precursor promotes double carbonylation in a syn fashion. The possibility for synthesis of dimethyl 2-phenylbutanedioate in a very stereospecific manner with ligand-modified catalysts suggests a new kind of enantioselective synthesis of succinic acid derivatives, which has indeed been realized.[10]

Experimental Section

Starting Materials. $Sn(O_3SCF_3)_2$, 2,2′-bipyridyl, and hydroquinone were purchased from Fluka. 1,4-Benzoquinone and $Pd(O_2CCF_3)_2$ were purchased from Aldrich. Methanol was dried according to normal procedures and distilled under nitrogen. $Pd(Diop)(O_2CCF_3)_2$ was synthesized by following literature procedures for analogous compounds.

General Procedures. The NMR spectra were measured on a Bruker AM 300 WB or a Bruker AC 200 spectrometer with tetramethylsilane as the internal standard. Gas chromatographic analyses were carried out on a Shimadzu 8A GC instrument with flame ionization detector using a 10 m (0.20 mm i.d.) cross-linked methyl silicone capillary column or on a Hewlett-Packard 5890 II GC instrument with flame ionization detector using a 25 m (0.32 mm i.d.) cross-linked methyl silicone capillary column. Helium was used as the carrier gas.

Preparation of *trans*-β-Deuteriostyrene. The deuterated styrene was prepared according to the procedure of ref 11. NMR analysis and mass spectroscopy indicated an isotopic purity of 91%. MS: isotopic composition d_0 9%, d_1 91%.

Carbonylation of Styrene in the Presence of $Pd(O_2CCF_3)_2$ and 2,2′-Bipyridyl. A nitrogen-filled 250-mL stainless steel autoclave was charged with 0.11 mmol of $Pd(O_2CCF_3)_2$, 0.15 mmol

(10) Nefkens, S. C. A.; Consiglio, G. Manuscript in preparation. For some literature related to optically active succinic acid derivatives see: Jendralla, H. *Tetrahedron Lett.* **1991**, *32*, 3671.

(11) (a) Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616. (b) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834.

of 2,2′-bipyridyl, 0.028 mol of 1,4-benzoquinone, 0.012 mol of hydroquinone, 0.022 mol of styrene, and 50 mL of methanol. The autoclave was sealed and pressurized with CO to 40 bar at room temperature. The autoclave was then placed in an oil bath at 70 °C, and the contents were mechanically stirred for 20 h. After reaction the copolymer was removed by filtration, washed with methanol, dissolved in warm CH_2Cl_2, and precipitated with methanol. Gas chromatographic analysis of the reaction mixture showed an 82% conversion of styrene. Product distribution: 17.0% dimethyl 2-phenylbutanedioate, 9.0% dimethyl 2,5-diphenyl-4-oxoheptanedioate, 4% 1-*p*-hydroxyphenyl 4-methyl phenylbutanedioate, 65% copolymer, and 5.0% other (high-boiling) products.

Dimethyl 2-phenylbutanedioate[1] was isolated by vacuum distillation followed by column chromatography on silica using hexane–ether (3:1) as the solvent. White crystals were grown from a warm hexane solution. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.33–7.26 (m, 5 H, C_6H_5), 4.09 (dd, 1 H, CH, J = 5.2, J = 10.2 Hz), 3.67 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.21 (dd, 1 H, CH_2, J = 10.2, J = 17.0 Hz), 2.66 (dd, 1 H, CH_2, J = 5.2, J = 17.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.4 (1 C, $COOCH_3$), 172.2 (1 C, $COOCH_3$), 137.6, 128.9, 127.7, and 127.69 (6 C, C_6H_5), 52.4 (1 C, OCH_3), 51.9 (1 C, OCH_3), 47.0 (1 C, *C*H), 37.6 (1 C, CH_2).

Dimethyl 2,5-diphenyl-4-oxoheptanedioate was isolated by column chromatography on silica using hexane–ether (3:1) as the solvent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.24–7.00 (m, 10 H, C_6H_5), 3.61 (s, 3 H, OCH_3), 3.60 (s, 3 H, OCH_3); first styrene unit $CH_3OOCCH(C_6H_5)CH_2CO$–, δ 4.04 (dd, 1 H, $(C_6H_5)CH$, J = 5.6, J = 9.2 Hz), 3.32 (dd, 1 H, CH_2, J = 17.9, J = 9.2 Hz), 2.75 (dd, 1 H, CH_2, J = 17.9, J = 5.6 Hz); second styrene unit –COCH-$(C_6H_5)CH_2COOCH_3$, δ 4.25 (dd, 1 H, $(C_6H_5)CH$, J = 5.6, J = 9.1 Hz), 3.17 (dd, 1 H, CH_2, J = 16.9, J = 9.1 Hz), 2.54 (dd, 1 H, CH_2, J = 16.9, J = 5.6 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 206.3 (1 C, –*C*O–), 173.5 ($COOCH_3$), 172.1 ($COOCH_3$), 137.7, 136.8, and 129.1–127.3 (12 C, C_6H_5), 54.2 (1 C, *C*H), 52.3 (1 C, OCH_3), 51.8 (1 C, OCH_3), 46.2 (1 C, *C*H), 44.7 (1 C, CH_2), 36.7 (1 C, CH_2). MS (EI): m/e 354.2.

1-*p*-Hydroxyphenyl 4-methyl 2-phenylbutanedioate was isolated by column chromatography on silica using hexane–ether (3:1) as the solvent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.40–7.32 (m, 5 H, C_6H_5), 6.81–6.65 (m, 4 H, C_6H_4), 5.81 (s, broad, 1 H, OH), 4.29 (dd, 1 H, CH, J = 4.9, J = 10.6 Hz), 3.70 (s, 3 H, OCH_3), 3.29 (dd, 1 H, CH_2, J = 10.6, J = 17.1 Hz), 2.76 (dd, 1 H, CH_2, J = 4.9, J = 17.1 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 172.5 (1 C, *C*OOR), 172.3 (1 C, *C*OOR), 153.6 (1 C, –O(C_6H_4)OH), 143.9 (1 C, –O(C_6H_4)OH), 136.9, 129.1, 127.9, and 127.7 (6 C, C_6H_5), 122.1 and 115.9 (4 C, O(C_6H_4)OH), 52.1 (1 C, OCH_3), 47.2 (1 C, *C*H), 37.6 (1 C, CH_2). MS (EI): m/e 300.15.

Carbonylation of *trans*-β-Deuteriostyrene in the Presence of $Pd(O_2CCF_3)_2$ and 2,2′-Bipyridine. The reaction was carried out as described above for unlabeled styrene. Similar conversion and product distribution were obtained.

Dimethyl 3-Deuterio-2-phenylbutanedioate. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.35–7.25 (m, 5 H, C_6H_5), 4.09 (d, 1 H, CH, J = 10.1 Hz), 3.67 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.19 (dt, 1 H, CHD, J = 10.1, J_{HD} = 2.2 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 173.4 (1 C, $COOCH_3$), 171.9 (1 C, $COOCH_3$), 137.6, 128.9, 127.7, and 127.67 (6 C, C_6H_5), 52.3 (1 C, OCH_3), 51.8 (1 C, OCH_3), 47.0 (1 C, *C*H), 37.3 (t, 1 C, *C*HD, J_{CD} = 20.0 Hz). MS: isotopic composition d_0 10%, d_1 = 90% (calculated on the basis of the fragment at m/e 190, M – OCH_3).

Dimethyl 3,6-Dideuterio-2,5-diphenyl-4-oxoheptanedioate. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.24–7.00 (m, 10 H, C_6H_5), 3.62 (s, 3 H, OCH_3), 3.61 (s, 3 H, OCH_3); first styrene unit CH_3OOC-$CH(C_6H_5)CHDCO$–, δ 4.02 (d, 1 H, $(C_6H_5)CH$, J = 9.1 Hz), 3.27 (d, 1 H, CHD, J = 9.1 Hz); second styrene unit –$COC(C_6H_5)$-$HCHDCOOCH_3$, δ 4.22 (d, 1 H, $(C_6H_5)CH$, J = 9.0 Hz), 3.13 (d, 1 H, CHD, J = 9.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 206.3 (1 C, –*C*O–), 173.5 ($COOCH_3$), 172.1 ($COOCH_3$), 137.7, 136.8, and 129.1–127.3 (12 C, C_6H_5), 54.2 (1 C, *C*H), 52.3 (1 C, OCH_3), 51.8 (1 C, OCH_3), 46.2 (1 C, *C*H), 44.4 (t, 1 C, *C*HD, J_{CD} = 19.6 Hz), 36.9 (t, 1 C, *C*HD, J_{CD} = 20.0 Hz). MS: isotopic composition d_0 2%, d_1 20%, d_2 78% (calculated on the basis of the fragment at m/e 263, M – ($COOCH_3$, OCH_3)).

Carbonylation of *trans*-β-Deuteriostyrene in the Presence of $Pd(Diop)(O_2CCF_3)_2$. In a nitrogen-filled glovebox a suitable glass insert equipped with a magnetic stirrer was charged with 0.14 mmol of $Pd(Diop)(O_2CCF_3)_2$, 0.14 mmol of $Sn(O_3SCF_3)_2$, 35 mmol of 1,4-benzoquinone, 7 g of MeOH, and 1.8 g of *trans*-β-deuteriostyrene. The glass insert was placed in an 80-mL stainless steel autoclave, after which the autoclave was sealed and pressurized with CO to 350 bar at room temperature. The mixture was magnetically stirred at room temperature for 100 h, after which the pressure was vented.

Gas chromatographic analysis of the reaction mixture showed an almost complete conversion of the deuterated styrene (97%). Product distribution: 18% dimethyl 2-phenylbutanedioate, 27% methyl 2-phenylpropanoate,[12] 43% methyl 3-phenylpropanoate,[12] and 12% other products. The deuterated dimethyl 2-phenylbutanedioate was isolated by Kugelrohr distillation followed by column chromatography on silica, using chloroform as the solvent, and analyzed by NMR spectroscopy. The NMR spectrum was identical with that from the reaction described above.

Carbonylation of *trans*-β-Deuteriostyrene in the Presence of $PdCl_2$, $CuCl_2$, and NaOAc. The reaction was carried out as described in ref 1. The NMR spectra for the deuterated dimethyl 2-phenylbutanedioate are the same as described above.

Registry No. $Pd(O_2CCF_3)_2$, 42196-31-6; $PdCl_2$, 7647-10-1; $Pd(DIOP)(O_2CCF_3)_2$, 140360-60-7; 2,2′-bipyridine, 366-18-7; *trans*-β-deuteriostyrene, 6911-81-5; dimethyl 3-deuterio-2-phenylbutanedioate, 140360-53-8; dimethyl 3,6-dideuterio-2,5-diphenyl-4-oxoheptanedioate, 140360-54-9; methyl 3-deuterio-2-phenylpropanoate, 140360-55-0; methyl 2-deuterio-3-phenylpropanoate, 140360-56-1; 1,4-benzoquinone, 106-51-4; hydroquinone, 123-31-9; styrene, 100-42-5; dimethyl 2-phenylbutanedioate, 82079-51-4; dimethyl 2,5-diphenyl-4-oxoheptanedioate, 140360-57-2; 1-*p*-hydroxyphenyl 4-methyl phenylbutanedioate, 140360-58-3; carbon monoxide–styrene polymer, 52626-84-3; carbon monoxide–*trans*-β-deuteriostyrene polymer, 140360-59-4.

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(12) Hayashi, T.; Tanaka, M.; Ogata, I. *J. Mol. Catal.* **1984**, *26*, 17.