chloride (0.5 mL) was added, and the mixture was warmed on a steam bath for 5 min to ensure a homogeneous solution and then left at room temperature overnight. Water and methylene chloride were added, and the organic layer was removed, washed with dilute hydrochloric acid and then water, dried ($MgSO_4$), and evaporated to give **22b** as a viscous oil (20 mg, 23%): IR (Nujol) λ_{max} 1680, 1620, 1575, 1460, 1415, 1380, 1320, 1240, 1210, 1190, 1120, 1100, 790, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (s, 2 H, Ar H), 3.91 (s, 6 H, OCH_3), 6.14 (s, 1 H), 7.12 (m, 4 H, Ar H), 10.51 (s, 1 H, CHO); MS, m/z (relative intensity) 270 (M^+, 91), 269 (100), 241, 240, 239 (36.5), 226, 225, 224, 223, 213, 212, 211, 210, 198, 197, 196, 195, 184, 183, 182, 181, 169, 168, 167, 155, 154, 153, 139 (19); HRMS, calcd for $C_{16}H_{14}O_4$ m/z 270.0891, found m/z 270.0867.

1,3-Dimethoxy-4-(hydroxymethyl)-9*H*-xanthene (23b). To a solution of 1,3-dimethoxy-4-formylxanthene (**22b**: 33 mg) in a mixture of THF (5 mL) and ethanol (5 mL) was added sodium borohydride and the reaction mixture was stirred overnight. The excess sodium borohydride was destroyed by 20% acetic acid, and the solvents were removed in vacuo. The residue was extracted with ethyl acetate, and the extract was washed with sodium bicarbonate solution and water, then dried ($MgSO_4$), and evaporated. The crude product was purified by preparative TLC on silica gel plates using 10% EtOAc in methylene chloride as the eluent, to afford **23b** as an oil (29 mg, 87%): ^1H NMR ($CDCl_3$) δ 2.35 (t, 1 H, OH), 3.87 (s, 6 H, OCH_3), 4.84 (d, 2 H, CH_2OH), 6.20 (s, 1 H, Ar H), 7.06-7.25 (m, 4 H, Ar H); MS, m/z (relative intensity) 272 (M^+), 271 (100), 241 (83), 139 (28); HRMS, calcd for $C_{16}H_{14}O_4$ m/z 272.1048, found m/z 272.1036.

1,3-Dimethoxy-2-methyl-9*H*-xanthene (30). (a) Methylation of 18b. A suspension of **18b** in ether was treated with excess ethereal diazomethane at 0 °C. The mixture was allowed to stand at room temperature for 24 h. Evaporation of the solvent and trituation of the residue with ether gave a solid (0.03 g, 27%); mp 204-207 °C, which when recrystallized from methylene chloride-methanol gave the pure **30**: mp 208-209 °C; ^1H NMR ($CDCl_3$) δ 2.16 (s, 3 H, Ar CH_3), 3.81 (s, 6 H, OCH_3), 3.95 (s, 2 H, $ArCH_2Ar$), 6.54 (s, 1 H, Ar H), 6.89-7.24 (m, 4 H, Ar H); MS, m/z (relative intensity) 256 (M^+, 1.7), 240 (15), 226 (28), 225 (100), 211 (18), 210 (28), 182 (15), 181 (17), 67 (15); HRMS, calcd for $C_{16}H_{16}O_3$ m/z 256.1099, found m/z 256.1159.

(b) Hydrogenolysis of 29. 1,3-Dimethoxy-2-hydroxymethylxanthene (**29**; 10 mg) dissolved in ethyl acetate (5 mL) was hydrogenated over a 10% Pd-C catalyst for 2 h. The catalyst was removed by filtration and the solvent by evaporation. This afforded **24**, which was purified by preparative TLC (10% EtOAc in methylene chloride) to give a material (6 mg, 60%) mp and mixed mp 208-209 °C, identical in all spectroscopic properties with the sample prepared by method a.

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Stereo- and Regiochemistry in Palladium-Catalyzed Nucleophilic Substitution of Optically Active (*E*)- and (*Z*)-Allyl Acetates

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Optically active (*E*)- and (*Z*)-allyl acetates, 3-acetoxy-1-phenyl-1-butene (**1**) and its regioisomer, 1-acetoxy-1-phenyl-2-butene (**2**), were allowed to react with sodium dimethyl malonate, sodium acetylacetonate, and sodium methyl acetoacetate in the presence of a palladium catalyst. The reaction of (*E*)-acetates proceeded with retention of configuration and that of (*Z*)-acetates proceeded with inversion accompanied by geometrical isomerization from *Z* to *E*. The stereochemistry observed in the reaction with phenylzinc bromide was opposite to that with the soft nucleophiles.

Palladium-catalyzed allylation of nucleophiles is recognized to be useful for organic synthesis, and increasing attention has recently been paid to the reaction mechanism.[1] Stereochemical studies on the allylation with diastereomeric allylic substrates[2] and the intramolecular allylation[3] have shown that the reaction of soft nucleophiles represented by sodium dimethyl malonate proceeds with retention of configuration and that of hard nucleophiles proceeds with inversion of configuration. Here we report stereo- and regiochemical results obtained for the reaction of a set of regioisomeric optically active (*E*)- and (*Z*)-allyl acetates.

Results and Discussion

Reaction of optically active (*E*)- and (*Z*)-3-acetoxy-1-phenyl-1-butene (**1**) and 1-acetoxy-1-phenyl-2-butene (**2**) with sodium dimethyl malonate, sodium acetylacetonate, sodium methyl acetoacetate, and phenylzinc bromide was carried out in the presence of a phosphine/palladium catalyst. The results are summarized in Table I.

The allyl acetate with an *E* configuration, (*S*)-(*E*)-**1** ($[\alpha]^{20}_D$ -53.1° (*c* 1.2, CCl_4), 39% ee),[4] was allowed to react

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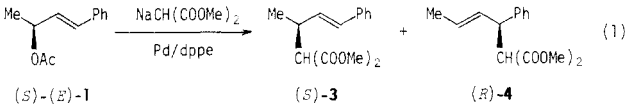
Table I. Palladium-Catalyzed Reaction of Optically Active Allyl Acetates 1 and 2 with Nucleophiles[a]

entry	acetate (% ee)	nucleophile	catalyst[c]	product (yield, %)[d]	$[\alpha]^{20}_D$, deg (c, $CHCl_3$)	% ee[b] (confign)
1	(S)-(E)-1 (39)	$NaCH(COOMe)_2$	Pd/dppe	3/4 (96) (92/8)	3 -25.2 (1.3)	37 (S)
					4 +12 (1.0)	30[e] (R)
2	(S)-(E)-1 (58)	$NaCH(COOMe)_2$	Pd/dppe	3/4 (97) (90/10)	3 -40.0 (0.5)	58 (S)
3	(S)-(E)-1 (68)	$NaCH(COOMe)_2$	$Pd(PPh_3)_4$	3/4 (4)		
4	(S)-(E)-2 (35)	$NaCH(COOMe)_2$	Pd/dppe	3/4 (100) (93/7)	3 -26.3 (1.4)	38 (S)
					4 +11 (0.2)	30[e] (R)
5	(R)-(Z)-1 (73)	$NaCH(COOMe)_2$	Pd/dppe	3/4 (100) (90/10)	3	73[e] (S)
6	(R)-(Z)-2 (61)	$NaCH(COOMe)_2$	Pd/dppe	3/4 (99) (90/10)	3 -41.7 (1.3)	61 (S)
7	(S)-(E)-1 (68)	$NaCH(COMe)_2$	Pd/dppe[f]	13 (82)	-91.0 (1.5)	69 (S)
8	(S)-(E)-1 (39)	$NaCH(COMe)_2$	Pd/dppe	13 (6)		
9	(S)-(E)-1 (39)	$NaCH(COMe)_2$	Pd/dppf	13 (82)	-47.7 (0.9)	36 (S)
10	(R)-(Z)-2 (58)	$NaCH(COMe)_2$	Pd/dppe[f]	13 (79)	-71.3 (1.5)	54 (S)
11	(S)-(E)-1 (39)	NaCH(COMe)COOMe	Pd/dppe	14[g] (42)	-32.3 (0.7)	37 (S)
12	(S)-(E)-1 (68)	PhZnBr	$Pd(PPh_3)_4$[h]	16 (95)	+23.1 (2.2)[i]	44 (R)
13	(R)-(Z)-2 (61)	PhZnBr	$Pd(PPh_3)_4$[h]	16 (78)	+16.1 (1.4)[i]	30 (R)

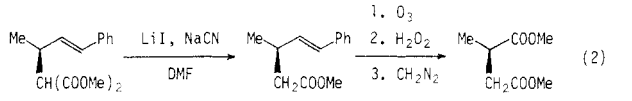
[a] Acetate/nucleophile/catalyst = 1/1.2/0.01. The reaction was carried out in THF at room temperature for 20–40 h unless otherwise noted. [b] Calculated on the basis of values for the optically pure compounds (see Experimental Section): (S)-3, $[\alpha]^{20}_D$ -68.9° (chloroform); (S)-13, $[\alpha]^{20}_D$ -132° (chloroform); (S)-14, $[\alpha]^{20}_D$ -87.5° (chloroform); (R)-16, $[\alpha]^{20}_D$ +52.9° (benzene), ref 11. [c] Pd/dppe and Pd/dppf are catalysts prepared in situ by mixing Bis(μ-chloro)bis(π-allyl)dipalladium with 1,2-bis(diphenylphosphino)ethane and 1,1′-bis(diphenylphosphino)ferrocene, respectively (Pd/P = 1/2). [d] Isolated yield by preparative TLC. [e] Determined by ^1H NMR analysis using $Eu(dcm)_3$. [f] Reaction at reflux in THF for 6 h. [g] A 1:1 mixture of diastereoisomers. [h] Reaction in the presence of 5 mol % of the catalyst. [i] $[\alpha]^{20}D$ (benzene).

with sodium dimethyl malonate in THF in the presence of 1 mol % of the palladium catalyst, generated in situ by mixing bis(μ-chloro)bis(π-allyl)dipalladium and 1,2-bis(diphenylphosphino)ethane (dppe) (Pd/P = 1/2), at room temperature for 20 h (eq 1). Aqueous workup followed



(1)

by preparative TLC on silica gel gave 96% yield of the allylated products consisting of dimethyl [1-((E)-styryl)-ethyl]malonate (3) and its regioisomer, dimethyl [1-phenyl-2(E)-butenyl]malonate (4), in a ratio of 92:8. The regioisomers 3 and 4 which could be isolated by preparative GLC were found to be an S isomer of 37% ee ($[\alpha]^{20}_D$ -25.2° (c 1.3, chloroform))[5] and an R isomer of 30% ee ($[\alpha]^{20}_D$ +12° (c 1.0, chloroform)), respectively (entry 1 in Table I). The configurations of 3 and 4 were determined by converting them into known (+)-(R)-dimethyl methylsuccinate[6] (6) and (-)-(R)-methyl 3-phenylhexanoate[7] (8), respectively, by a sequence of reactions shown in eq 2 and 3. Tetrakis(triphenylphosphine)palladium(0), which has



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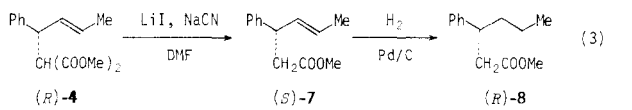
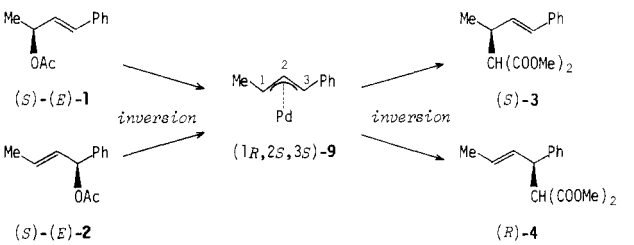


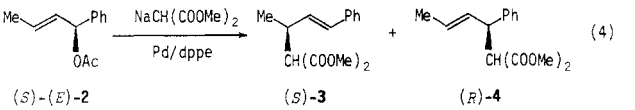
(3)

been used conventionally for many of the palladium-catalyzed allylation reactions,[1] was less active than the palladium/dppe catalyst to give only 4% yield of the products under the present reaction conditions (entry 3).

Scheme I



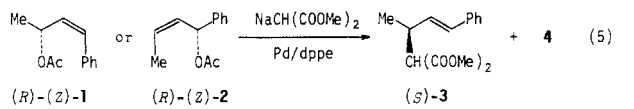
Reaction of the regioisomeric acetate (S)-(E)-2 ($[\alpha]^{20}_D$ +0.11° (c 9.2, CCl_4), 35% ee) catalyzed by the palladium/dppe complex in a similar manner to that of (E)-1 gave (S)-3 ($[\alpha]^{20}_D$ -26° (c 1.4, chloroform), 38% ee) and (R)-4 ($[\alpha]^{20}_D$ +11° (c 0.2, chloroform), 30% ee) in a ratio of 93:7 (entry 4) (eq 4).



(4)

Thus, it has been observed that the ratio of the regioisomeric products 3 and 4 was essentially the same regardless of whether one started with the acetate 1 or its regioisomer 2, and both of the products 3 and 4 were formed with the stereochemistry of retention (or syn). These results can be visualized by the mechanism involving π-allylpalladium complex (1R,2S,3S)-9 as a key intermediate (Scheme I). The π-allylpalladium 9 is formed by oxidative addition of the allyl acetate (S)-(E)-1 or (S)-(E)-2 to palladium(0) with inversion[4] and undergoes nucleophilic attack of malonate anion with inversion[4,5] to produce (S)-3 and (R)-4 with net retention. The stereochemistry, net retention resulting from double inversion, confirms that reported by use of diastereomeric systems.[2a-h]

The reaction of (Z)-acetates was also carried out (eq 5).



(5)

The alkylation products 3 and 4 which have an E configuration were also formed in a quantitative yield, none of the Z isomers being detected in the products. The ratio of the regioisomers 3 and 4 was 90:10, almost the same as

(4) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.
(5) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 107.
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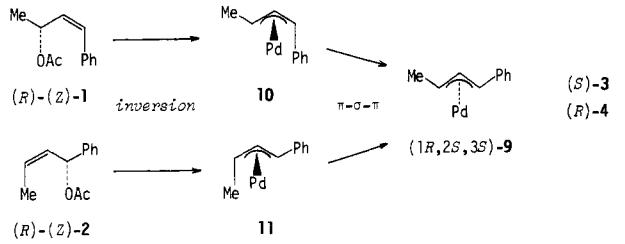
(7) West, B. D.; Preis, S.; Schroeder, C. H.; Link, K. P. *J. Am. Chem. Soc.* **1961**, *83*, 2676.

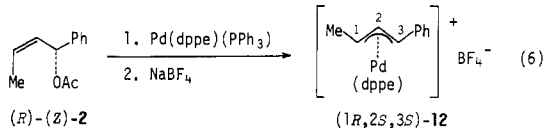
Scheme II



that observed with (*E*)-acetates. The stereochemistry was inversion as shown in the result that (*S*)-**3** of 73% ee and 61% ee was obtained from (*R*)-(*Z*)-**1** ($[\alpha]^{20}_D$ −75.3° (*c* 0.5, CCl_4), 73% ee) and (*R*)-(*Z*)-**2** ($[\alpha]^{20}_D$ −32.2° (*c* 1.5, CCl_4), 61% ee), respectively (entries 5 and 6).

The oxidative addition of (*Z*)-acetates to the palladium(0) must proceed with inversion, in the same manner as that of (*E*)-acetates, to form π-allylpalladium complexes **10** and **11** where one of the phenyl and methyl groups is located at an anti position with respect to the central hydrogen (Scheme II). The π-allylpalladium complexes undergo the isomerization of the substituent from anti to syn by way of σ-allylpalladium intermediates. It has been reported that the 1,3-disubstituted π-allylpalladium complexes have a strong tendency to adopt both substituents syn.[8] This π−σ−π rearrangement moves the palladium from front side to back side to give the π-allylpalladium **9** which has the same configuration as that from (*E*)-acetates (*S*)-(*E*)-**1** and (*S*)-(*E*)-**2**. Nucleophilic attack of the malonate anion with inversion which is slow compared with the π−σ−π rearrangement completes the catalytic reaction of (*Z*)-acetates with inversion of configuration accompanied by *Z* to *E* isomerization.[9]

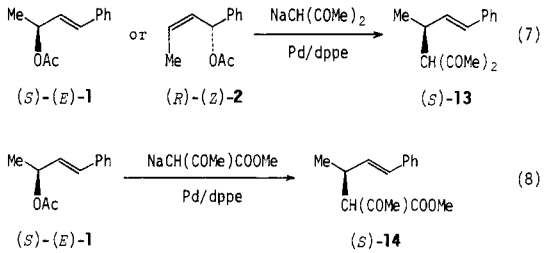
Reaction of (*R*)-(*Z*)-**2** (67% ee) with a palladium(0) complex Pd(dppe)(PPh_3)[4] in ether followed by treatment of the reaction mixture with sodium tetrafluoroborate gave 39% yield of cationic π-allylpalladium complex (1*R*,2*S*,3*S*)-**12** ($[\alpha]^{20}_D$ +32.6° (*c* 1.1, chloroform), 27% ee)[4] which has both methyl and phenyl groups at syn positions (eq 6). This result supports the mechanism involving the



(6)

π−σ−π rearrangement shown in Scheme II. The loss of enantiomeric purity during the oxidative addition may be attributable to attack of palladium(0) on the π-allyl moiety of initially formed π-allylpalladium with 1*R*,2*S*,3*S* configuration from the side opposite to palladium which produces the enantiomeric π-allylpalladium complex, or to attack of acetate anion on the π-allyl from the same side as palladium which generates (*R*)-(*E*)-**1**.[2b]

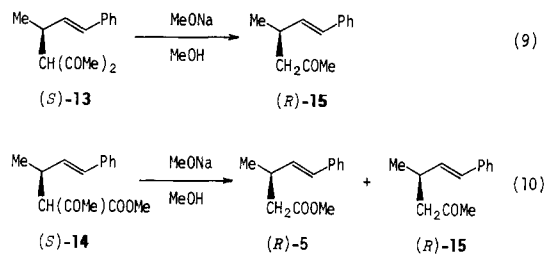
Alkylation with sodium acetylacetonate gave similar results to that with sodium malonate except that [1-((*E*)-styryl)ethyl]acetylacetone (**13**) was formed regioselectively (eq 7). The stereochemistry was retention in the reaction of (*E*)-acetate (entries 7 and 9) and inversion accompanied by the *Z* to *E* isomerization in the reaction



(7)

(8)

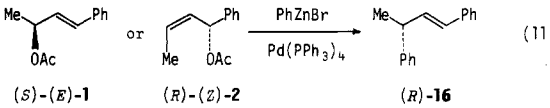
of (*Z*)-acetate (entry 10). The retention of configuration was also observed in the reaction of (*S*)-(*E*)-**1** with sodium methyl acetoacetate which gave (*S*)-methyl [1-((*E*)-styryl)ethyl]acetoacetate (**14**) regioselectively (entry 11) (eq 8). It is noted that sodium acetylacetonate and sodium methyl acetoacetate were less reactive than sodium malonate and a higher temperature (reflux in THF) was required to obtain a good yield of the allylation products (entry 8). The palladium complex containing 1,1′-bis(diphenylphosphino)ferrocene (dppf)[10] as a ligand was found to be more active than the palladium–dppe to catalyze the reaction of sodium acetylacetonate at room temperature (entry 9). The configuration and enantiomeric purity of the products **13** and **14** were determined by comparison of the rotation data of [1-((*E*)-styryl)ethyl]acetone (**15**) obtained from **13** and **14** with those of methyl [1-((*E*)-styryl)ethyl]acetate (**5**) obtained from **14** and **3** (eq 9 and 10) (see Experimental Section).



(9)

(10)

Reaction of phenylzinc bromide proceeded with opposite stereochemistry to that of sodium dimethyl malonate and of sodium acetylacetonate, as is to be expected from the results reported in the phenylation of a diastereomeric allyl acetate.[2j] Thus, the acetates (*S*)-(*E*)-**1** (68% ee) and (*R*)-(*Z*)-**2** (61% ee) gave, in the presence of 5 mol % of tetrakis(triphenylphosphine)palladium(0) as a catalyst, (*R*)-(*E*)-1,3-diphenyl-1-butene (**16**)[5,11] of 44% ee and 30% ee, respectively (entries 12 and 13) (eq 11). The opposite



(11)

stereochemistry may be accounted for by retention of configuration at the final step[5] in the catalytic cycle, where phenylzinc bromide attacks the palladium atom in π-allylpalladium intermediate (1*R*,2*S*,3*S*)-**9** to form the palladium–phenyl bond and reductive elimination gives the product (*R*)-**16**.[2i-k,12]

Experimental Section

Optical rotations were measured with a Perkin-Elmer 241 polarimeter. ^1H NMR spectra were obtained on a JEOL MH-100 or JEOL JNM-GX-400 spectrometer in carbon tetrachloride solution containing Me_4Si as an internal standard. A Varian

(8) (a) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc.* **1971**, *93*, 2642. (b) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3407. (c) Mackenzie, P. B.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1985**, *107*, 2046. (d) Hayashi, T.; Konishi, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1983**, 736.

(9) The π−σ−π isomerization during the allylation has been reported in the intramolecular system (ref 3b) and in the asymmetric allylation (ref 8c).

(10) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(11) Hayashi, T.; Konishi, M.; Fukushima, M.; Mise, T.; Kagotani, M.;Tajika, M.; Kumada, M. *J. Am. Chem. Soc.* **1982**, *104*, 180.

(12) Numata, S.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *131*, 301.

Aerograph Model 920, equipped with a 10-ft column packed with Silicone DC 550 (30% on Celite) was used for isolation of the products.

Preparation of Optically Active Allyl Acetates. Optically active allyl acetates (*E*)-**1**, (*E*)-**2**, (*Z*)-**1**, and (*Z*)-**2** were obtained by acetylation of the corresponding allyl alcohols. (*S*)-(*E*)-3-Hydroxy-1-phenyl-1-butene was prepared by asymmetric reduction of benzalacetone according to the reported procedure.[13] (*S*)-(*E*)-1-Hydroxy-1-phenyl-2-butene ($[\alpha]^{20}_D$ +12.5° (*c* 2.1, chloroform), 35% ee) and (*R*)-(*Z*)-3-hydroxy-1-phenyl-1-butene ($[\alpha]^{20}_D$ +9.7° (*c* 1.0, chloroform), 73% ee) were prepared by MCPBA oxidation of (*S*)-(*Z*)-1-phenyl-3-(trimethylsilyl)-1-butene and (*R*)-(*E*)-1-phenyl-1-(trimethylsilyl)-2-butene, respectively.[14] (*R*)-(*Z*)-1-Hydroxy-1-phenyl-2-butene ($[\alpha]^{20}_D$ −101° (*c* 1.6, chloroform), 61% ee) was prepared by oxidation (MCPBA, KHF_2, DMF) of (*R*)-(*Z*)-1-(triethoxysilyl)-1-phenyl-2-butene which was obtained by asymmetric hydrosilylation of 1-phenylbutadiene with trichlorosilane in the presence of a chiral (ferrocenylphosphine)palladium catalyst.[15]

A typical procedure for the acetylation of the allyl alcohols is as follows. To a solution of 3.50 g (23.6 mmol) of (*S*)-(*E*)-3-hydroxy-1-phenyl-1-butene (39% ee) in 15 mL of THF was added successively 2.6 mL (28 mmol) of acetic anhydride, 4.1 mL (30 mmol) of triethylamine, and 10 mg of 4-(*N*,*N*-dimethylamino)-pyridine at 0 °C. The mixture was stirred at ambient temperature for 16 h. Ether was added and the solution was washed four times with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Distillation (89 °C (0.8 mmHg)) of the residue gave 4.13 g (92%) of (*S*)-(*E*)-**1**. (*S*)-(*E*)-**1** (39% ee): $[\alpha]^{20}_D$ −53.1° (*c* 1.2, CCl_4); ^1H NMR δ 1.38 (d, *J* = 6 Hz, 3 H), 2.00 (s, 3 H), 5.44 (quintet), *J* = 6 Hz, 1 H), 6.08 (dd, *J* = 6 and 16 Hz, 1 H), 6.54 (d, *J* = 16 Hz, 1 H), 7.08–7.44 (m, 5 H).

(*S*)-(*E*)-**2** (35% ee): $[\alpha]^{20}_D$ +0.11° (*c* 9.2, CCl_4); ^1H NMR δ 1.73 (d, *J* = 5 Hz, 3 H), 2.00 (s, 3 H), 5.43–5.88 (m, 2 H), 6.15 (d, *J* = 5 Hz, 1 H), 7.02–7.58 (m, 5 H).

(*R*)-(*Z*)-**1** (73% ee): $[\alpha]^{20}_D$ −75.3° (*c* 0.5, CCl_4); ^1H NMR δ 1.26 (d, *J* = 6 Hz, 3 H), 1.92 (s, 3 H), 5.35–5.82 (m, 2 H), 6.36 (d, *J* = 11 Hz, 1 H), 6.96–7.34 (m 5 H).

(*R*)-(*Z*)-**2** (61% ee): $[\alpha]^{20}_D$ −32.2° (*c* 1.5, CCl_4); ^1H NMR δ 1.83 (d, *J* = 5 Hz, 3 H), 2.03 (s, 3 H), 5.46–5.88 (m, 2 H), 6.58 (d, *J* = 8 Hz, 1 H), 7.16–7.48 (m, 5 H).

Palladium-Catalyzed Alkylation of Optically Active Allyl Acetates 1 and 2. The reaction conditions and data obtained are listed in Table I. Detailed precedures for the reaction of (*S*)-(*E*)-**1** with sodium dimethyl malonate in the presence of palladium/dppe catalyst are described below. All other reactions were carried out in essentially the same manner.

Bis(μ-chloro)bis(π-allyl)dipalladium (2.2 mg, 0.006 mmol) and 1,2-bis(diphenylphosphino)ethane (dppe) (5.3 mg, 0.013 mmol) were placed in a 50-mL two-necked flask equipped with a serum cap and a three-way stopcock. The flask was filled with argon or nitrogen after evacuation and to it were added through the serum cap with a syringe 5 mL of THF and 234 mg (1.23 mmol) of (*S*)-(*E*)-**1** (39% ee). The solution was stirred at 0 °C for 5 min, and a solution of sodium dimethyl malonate was added at 0 °C, which was prepared in a second flask by slow addition of 0.23 mL (2.0 mmol) of dimethyl malonate to a suspension of 72 mg (1.5 mmol) of 50% sodium hydride in mineral oil in 10 mL of THF at 0 °C. The mixture was kept stirring at room temperature for 20 h, hydrolyzed with 30 mL of water, and extracted with ether (20 mL × 4). The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Preparative TLC on silica gel (chloroform) of the residue gave 310 mg (96%) of the allylated products. The ^1H NMR and GLC analysis showed that dimethyl [1-((*E*)-styryl)ethyl]malonate (**3**) and its regioisomer, dimethyl [1-phenyl-2-(*E*)-butenyl]malonate (**4**) are present in a ratio of 92:8. The isomers **3** and **4** were separated by preparative GLC (Silicone DC 550, 30% on Celite). **3**: $[\alpha]^{20}_D$ −25.2° (*c* 1.3, chloroform); ^1H NMR δ 1.13 (d, *J* = 7 Hz, 3 H), 2.80–3.26 (m, 1 H), 3.21 (d, *J* = 8 Hz, 1 H), 3.58 (s, 3 H), 3.64 (s, 3 H), 6.02 (dd, *J* = 8 and 16 Hz, 1 H), 6.33 (d, *J* = 16 Hz, 1 H), 6.90–7.30 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.64; H, 7.04. **4**: $[\alpha]^{20}_D$ +12° (*c* 1.0, chloroform); ^1H NMR (400 MHz) δ 1.63 (d, *J* = 5 Hz, 3 H), 3.48 (s, 3 H), 3.73 (s, 3 H), 3.82 (d, *J* = 11 Hz, 1 H), 4.04 (dd, *J* = 7 and 11 Hz, 1 H), 5.56 (dq, *J* = 15 and 5 Hz, 1 H), 5.61 (dd, *J* = 15 and 7 Hz, 1 H), 7.18–7.36 (m, 5 H). Enantiomeric purity of **4** was determined to be 30% by ^1H NMR analysis in the presence of a chiral shift reagent tris[*d*,*d*-dicampholylmethanato]europium(III) [Eu(dcm)$_3$],[16] where one of the OCH_3 singlets (δ 3.48) was used for the determination. The singlet of the major enantiomer appeared at a higher field than that of the minor one.

Reaction of the acetate **1** or **2** with sodium acetylacetonate, sodium methyl acetoacetate, or phenylzinc bromide proceeded regioselectively to give [1-((*E*)-styryl)ethyl]acetylacetone (**13**), methyl [1-((*E*)-styryl)ethyl]acetoacetate (**14**), or (*E*)-1,3-diphenyl-1-butene (**16**), respectively. These products were isolated by preparative TLC on silica gel. The preparation of sodium acetylacetonate and sodium methyl acetoacetate was carried out in a similar manner to that of sodium dimethyl malonate, and phenylzinc bromide was prepared by mixing phenylmagnesium bromide with an excess of zinc bromide in THF. **13**: ^1H NMR δ 1.05 (d, *J* = 7 Hz, 3 H), 2.03 (s, 3 H), 2.12 (s, 3 H), 2.92–3.36 (m, 1 H), 3.54 (d, *J* = 12 Hz, 1 H), 5.90 (dd, *J* = 8 and 15 Hz, 1 H), 6.36 (d, *J* = 15 Hz, 1 H), 6.96–7.40 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 78.16; H, 8.03. **14** (a 1:1 mixture of diastereoisomers): ^1H NMR δ 1.10, 1.12 (d, *J* = 6 Hz, 3 H), 2.10, 2.16 (s, 3 H), 2.88–3.24 (m, 1 H), 3.28, 3.31 (d, *J* = 9 Hz, 1 H), 3.60, 3.69 (s, 3 H), 5.94, 5.97 (dd, *J* = 9 and 15 Hz, 1 H), 6.35 (d, *J* = 15 Hz, 1 H), 6.92–7.34 (m, 5 H). Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 73.03; H, 7.48.

Decarbomethoxylation of Dimethyl [1-((*E*)-Styryl)-ethyl]malonate (3). The procedure reported by Trost[17] was followed. A solution of 153 mg (0.582 mmol) of **3** ($[\alpha]^{20}_D$ −54.4° (*c* 1.2, chloroform)), 28 mg (0.60 mmol) of sodium cyanide, and 99 mg (0.60 mmol) of lithium iodide dihydrate in 10 mL of DMF was heated at 120 °C for 15 h. After cooling, the reaction mixture was diluted with ether and washed successively with water, 10% HCl, and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by preparative TLC on silica gel (hexane/ethyl acetate = 3/1) of the residue gave 84 mg (71%) of methyl [1-((*E*)-styryl)-ethyl]acetate (**5**) ($[\alpha]^{20}_D$ −49.2° (*c* 1.3, CCl_4)). Enantiomeric purity was determined to be 79% by ^1H NMR analysis in the presence of Eu(dcm)$_3$.[16] The OCH_3 singlet of the major enantiomer appeared at a lower field than that of the minor one. The maximum specific rotation of **5** is calculated to be $[\alpha]^{20}_D$ 62.2°. **5**: ^1H NMR δ 1.16 (d, *J* = 7 Hz, 3 H), 2.11–2.50 (m, 2 H), 2.82 (septet, *J* = 7 Hz, 1 H), 3.61 (s, 3 H), 6.03 (dd, *J* = 7 and 16 Hz, 1 H), 6.36 (d, *J* = 16 Hz, 1 H), 7.03–7.31 (m, 5 H). Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.50; H, 8.04.

Ozonolysis of Methyl [1-((*E*)-Styryl)ethyl]acetate (5). (*R*)-Dimethyl Methylsuccinate (6). Ozone was introduced into an ethyl acetate solution (12 mL) of 83.3 mg (0.408 mmol) of **5** ($[\alpha]^{20}_D$ −49.2° (*c* 1.3, CCl_4), 79% ee) at −78 °C, until the color of the solution changed to blue. After warming the solution up to room temperature, H_2O_2 (30%, 1.2 mL) and H_2O (1.2 mL) were added and the mixture was heated at 60 °C for 9.5 h. Addition of 2 N NaOH (1.7 mL) followed by usual workup gave 40.5 mg of a 1:1 mixture of (*R*)-(+)-methylsuccinic acid and benzoic acid. Optical rotation of the mixture was $[\alpha]^{21}_D$ +3.5° (*c* 2.0, ethanol) (lit.[6] (*S*)-acid: $[\alpha]^{24.2}_D$ −15.0° (*c* 1.89, ethanol)). To a solution of the mixture in ether (10 mL) was added excess diazomethane in ether at −10 °C, and the solution was stirred at room temperature for 1 h. Excess acetic acid was added at 0 °C and the solution was washed successively twice with saturated sodium bicarbonate solution and water and dried over anhydrous magnesium sulfate. After evaporation of the solvent, preparative TLC on silica gel (chloroform) of the residue gave 27.2 mg (42% based on **5**) of (*R*)-(+)-dimethyl methylsuccinate (**6**) ($[\alpha]^{21}_D$ +2.0° (*c* 0.6, chloroform); lit.[6] (*R*)-**6**, $[\alpha]^{29}_D$ +4.1° (*c* 4.1, chloroform)).

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Decarbomethoxylation of Dimethyl [1-Phenyl-2(*E*)-butenyl]malonate (4). Decarbomethoxylation of **4** (71.6 mg, 0.273 mmol, $[\alpha]^{20}_D$ +12° (*c* 1.0, chloroform), 30% ee), in a similar manner to that of **3**, gave 31.4 mg (56%) of methyl [1-phenyl-2-(*E*)-butenyl]acetate (**7**). $[\alpha]^{20}_D$ +1.1° (*c* 0.9, chloroform). ^{1}H NMR δ 1.64 (d, *J* = 5 Hz, 3 H), 2.58 (d, *J* = 8 Hz, 2 H), 3.54 (s, 3 H), 3.60–3.92 (m, 1 H), 5.12–5.80 (m, 2 H), 7.00–7.52 (m, 5 H).

Hydrogenation of Methyl [1-Phenyl-2(*E*)-butenyl]acetate (7). A solution of 31.4 mg (0.154 mmol) of **7** ($[\alpha]^{20}_D$ +1.1° (*c* 0.9, chloroform)) in 1.5 mL of benzene and 7 mg of Pd/C (10% Pd) were placed in a stainless micro autoclave, and magnetically stirred with hydrogen at 130 atm for 21 h. The reaction mixture was passed through a short silica gel column and evaporated to give 31.1 mg (98%) of methyl 3-phenylhexanoate (**8**). ($[\alpha]^{24}_D$ −3.8° (*c* 0.9, chloroform); lit.[7] (*S*)-**8**, $[\alpha]^{24}_D$ +13.4° (neat)).

Decarbomethoxylation and Deacetylation of Methyl [1-((*E*)-Styryl)ethyl]acetoacetate (14). A solution of 398 mg (1.62 mmol) of **14** ($[\alpha]^{20}_D$ −69.1° (*c* 0.95, chloroform)) and 40 mg (0.75 mmol) of sodium methoxide in 10 mL of methanol was refluxed for 22 h. Water was added and the mixture was extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Preparative TLC on silica gel (hexane/ethyl acetate = 5/1) gave 94 mg (29%) of methyl [1-((*E*)-styryl)ethyl]acetate (**5**) ($[\alpha]^{20}_D$ −49.0° (*c* 0.99, CCl_4), 35 mg (12%) of [1-((*E*)-styryl)-ethyl]acetone (**15**) ($[\alpha]^{20}_D$ −57.3° (*c* 0.78, CCl_4)), and 145 mg (36%) of recovered **14**. The ester **5** obtained here is 79% ee *R* according to its maximum specific rotation $[\alpha]^{20}_D$ +62.2° (CCl_4) *R*-(−), and therefore the maximum specific rotation of the ketone **15** is calculated to be $[\alpha]^{20}_D$ 72.5° (CCl_4) *R*-(−) since **15** should have the same configuration and enantiomeric purity as **5**. **15**: ^{1}H NMR δ 1.10 (d, *J* = 7 Hz, 3 H), 2.04 (s, 3 H), 2.41 (m, 2 H), 2.83 (septet, *J* = 7 Hz, 1 H), 5.96 (dd, *J* = 7 and 15 Hz, 1 H), 6.28 (d, *J* = 15 Hz, 1 H), 6.94–7.36 (m, 5 H). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.07; H, 8.67.

Deacetylation of [1-((*E*)-Styryl)ethyl]acetylacetone (13). A solution of 332 mg (1.44 mmol) of **13** ($[\alpha]^{20}_D$ −101° (*c* 1.0, chloroform)) and 35 mg (0.65 mmol) of sodium methoxide in 10 mL of methanol was refluxed for 16 h. Water was added and the mixture was extracted with ether. The ether extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Preparative TLC on silica gel (hexane/ethyl acetate = 5/1) gave 218 mg (80%) of [1-((*E*)-styryl)ethyl]acetone (**15**) ($[\alpha]^{20}_D$ −55.3° (*c* 0.97, CCl_4), 76% ee *R*). The maximum specific rotation of the acetylacetone **13** is calculated to be $[\alpha]^{20}_D$ 132° (chloroform), *S*-(−).

Oxidative Addition of the Allyl Acetate (*R*)-(*Z*)-2 to Palladium(0). To a mixture of 63 mg (0.11 mmol) of dichloro[bis(diphenylphosphino)ethane]palladium(II) and 29 mg (0.11 mmol) of triphenylphosphine in 3 mL of ether was added at room temperature 0.44 mL (0.22 mmol) of diisobutylaluminum hydride (0.5 M) in hexane. After the mixture was stirred for 20 min, 101 mg (0.53 mmol) of (*R*)-(*Z*)-**2** ($[\alpha]^{20}_D$ −35.4° (CCl_4), 67% ee) was added at 0 °C. The mixture was stirred at 0 °C for 21 h, and 15.4 mg (0.14 mmol) of sodium tetrafluoroborate was added. After 1 h, the mixture was hydrolyzed with 10 mL of water and extracted 3 times with chloroform. The chloroform extracts were washed with water, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. Preparative TLC on silica gel (hexane/ethyl acetate = 1/4; R_f 0.1–0.2) of the residue gave 31 mg (39%) of the cationic π-allylpalladium complex (1*R*,2*S*,3*S*)-**12**[4] ($[\alpha]^{20}_D$ +32.6° (*c* 1.1, chloroform), 27% ee).

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Registry No. (*S*)-(*E*)-**1**, 88154-75-0; (*R*)-(*Z*)-**1**, 100017-26-3; (*S*)-(*E*)-**1** (alcohol), 81176-43-4; (*R*)-(*Z*)-**1** (alcohol), 92075-80-4; (*S*)-(*E*)-**2**, 100017-27-4; (*R*)-(*Z*)-**2**, 100017-28-5; (*S*)-(*E*)-**2** (alcohol), 92075-81-5; (*R*)-(*Z*)-**2** (alcohol), 100017-30-9; (*R*)-(*Z*)-**2** (1-triethoxysilyl deriv), 99903-35-2; (*S*)-**3**, 88057-04-9; (*R*)-**4**, 100017-29-6; (*R*)-**5**, 99903-36-3; (*R*)-**6**, 22644-27-5; (*S*)-**7**, 99903-37-4; (*R*)-**8**, 99903-38-5; (1*R*,2*S*,3*S*)-**12**, 88083-20-9; (*S*)-**13**, 99903-32-9; (*S*,*R*)-**14**, 99903-33-0; (*S*,*S*)-**14**, 99903-34-1; (*R*)-**15**, 100017-31-0; (*R*)-**16**, 79767-68-3; $NaCH(COMe)_2$, 15435-71-9; $NaCH(CO_2Me)COMe$, 50321-58-9; PhZnBr, 38111-44-3; $NaCH(CO_2Me)_2$, 18424-76-5; $Pd(PPh_3)_4$, 14221-01-3; PhCH=CHCOMe, 122-57-6; (*S*)-(*Z*)-$MeCH(SiMe_3)CH$=CHPh, 88133-09-9; (*R*)-(*E*)-MeCH=CHCH-$(SiMe_3)$Ph, 82570-93-2; H_2C=CHCH=CHPh, 30733-89-2; (*R*)-$HO_2CCH(Me)CH_2CO_2H$, 3641-51-8; bis(μ-chloro)bis(π-allyl)dipalladium, 12012-95-2; bis(diphenylphosphino)ethane, 1663-45-2; 1,1′-bis(diphenylphosphino)ferrocene, 12150-46-8; 4-(*N*,*N*-dimethylamino)pyridine, 1122-58-3; dichloro[bis(diphenylphosphino)ethane]palladium(II), 19978-61-1.

Studies in Sugar Chemistry. 2.[1] A Simple Method for O-Deacylation of Polyacylated Sugars

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Total solvolytic O-deacylation of polyacylated sugars is readily accomplished upon stirring for 15 min–6 h a solution of a sugar in methanol in the presence of a catalytic amount of cyanide. The reaction proceeds in high yields, under neutral conditions, at room temperature. The overall rate of the reaction, readily followed by observing the changes in the ^{1}H 300-MHz NMR spectra, is greatly influenced by the substituent at the anomeric position in the order of 1-OH > 1-OAc ≫ 1-OR.

Synthetic studies in sugar chemistry most frequently require the introduction of O-protective groups and their subsequent removal. Successful deprotection constitutes a critical step in the synthesis of desired products.[2] The selective removal of protecting groups in carbohydrates has been reviewed.[3]

A facile, room-temperature, rapid, under neutral conditions, virtually quantitative method for cyanide-catalyzed removal of acetate (and benzoate) groups at all positions

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