

Palladium(II)-Induced Alkylation of Styrenes. Kinetics, Stereochemistry, and Mechanism

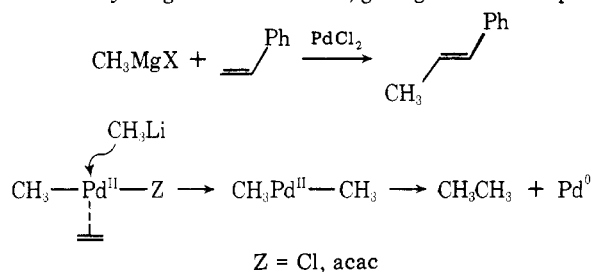
Shun-Ichi Murahashi,* Masaaki Yamamura, and Nobuaki Mita

Department of Chemistry, Faculty of Engineering Science, Osaka University, Machikaneyama, Toyonaka, Osaka, Japan 560

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Reaction of styrene with methyl lithium in the presence of Pd(II) complexes gave an anti-Markownikoff product, β -methylstyrene, whose yield increases in the order Cl (3%) < OAc (75%) < acac (90%). A competitive method has been used to measure the relative reactivities of this reaction toward a series of styrenes. The data correlate well ($\gamma = 0.98$) with the Hammett σ constants yielding a ρ value of $+2.68 \pm 0.189$, indicating that in the transition state there is considerable negative charge at the benzylic carbon atom, resulting from nucleophilic attack of methyl moiety. *cis*- and *trans*- β -deuteriostyrenes can be converted into *trans*- β -methylstyrene and *cis*- β -deuterio-*trans*- β -methylstyrene, respectively, with inversion of configuration. The kinetic and stereochemical results demonstrate that methylation of styrene proceeds via a *cis* addition of methylpalladium species followed by a *cis* elimination of hydridopalladium species. In contrast to this, reaction of styrene with a softer carbanion, diethyl sodiomalonate, afforded a Markownikoff product, α -methyl benzylidenemalonate. Nucleophilic attack of the carbanion toward the α position of palladium-coordinated styrene directly on the side remote from palladium seems to occur.

Palladium alkyls, which are prepared in situ by the exchange reaction of the corresponding metal alkyl compounds with palladium salts, has been reported to react with olefins to give alkyl olefins.¹ Direct alkylation of olefins by Grignard reagents in the presence of palladium chloride was attempted, but its yield was extremely poor (less than 5%).² This low yield can be rationalized by assuming that the reaction of methylpalladium species with styrene proceeds slower than that with excess methylmagnesium bromide, giving ethane and palla-

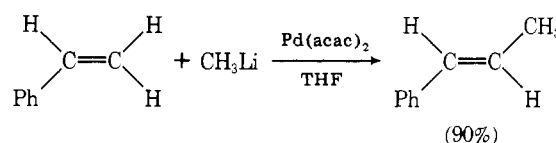


dium metal. If this is the case, retardation of the latter reaction³ and promotion of the former⁴ can accomplish a palladium-induced direct alkylation of olefins with Grignard reagents or alkyllithium compounds. Increasing the electron density on palladium would satisfy these conditions. Indeed, we have found that the reaction of styrenes with methyl lithium affords methylstyrenes in high yields upon using a palladium complex bearing more basic ligands. Thus, styrene can be converted into β -methylstyrene in 90% yield on treatment with methyl lithium in the presence of palladium acetylacetonate.

Studies on the palladium(II)-induced reaction of nucleophiles such as hydroxide,⁵ acetate,⁶ chloride,⁷ amide,⁸ methoxide,⁹ and methoxycarbonyl¹⁰ with olefins have been extensively investigated, and hence considerable understanding has been obtained. On the other hand, concerning the reaction of carbanionoids with a simple olefin, studies have focused on arylpalladium species,¹¹⁻¹³ although the reaction of carbanionoid with preformed olefin complexes which have a second olefinic group has been reported.¹⁴ We report here the results of kinetics and stereochemical studies of palladium(II)-induced methylation of styrene giving β -methylstyrene and discuss the mechanism in relation to the reaction of styrene with a softer carbanion such as diethylmalonate anion, giving a Markownikoff-type product.

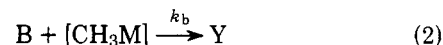
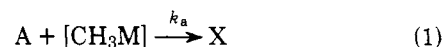
Results and Discussion

Reaction of Styrenes with Methyl lithium in the Presence of Pd(II) Salts. Reaction of styrene and methyl lithium



in the presence of a palladium(II) complex in THF at room temperature gave β -methylstyrene. Among various palladium(II) complexes palladium acetylacetonate gave the best yield of β -methylstyrene. The yields are dependent on the basicity of anionic ligands of the palladium complexes and increase in the order Cl (3%) < OAc (75%) < acac (90%).¹⁵ The excess methyl lithium was required to neutralize the HX (or HPdX). Addition of phosphines or phosphites as an additional ligand retarded the reaction completely, and the starting materials were recovered. This is consistent with the fact that triphenylphosphine, for example, has a higher dissociation energy from palladium than olefins by 10 kcal/mol.¹⁶

The results of the reaction of substituted styrenes summarized in Table I show the tendency that styrenes bearing a strong electron-withdrawing substituent are converted into β -methylstyrene in a higher yield. For quantitative treatment of the substituted effect, rate-constant ratios were determined by a competitive method in which two olefins were allowed to compete for a limited amount of methylating reagent. For a system in which a methylating reagent adds irreversibly in a single stage to competing olefins A and B to form intermediates X and Y, respectively, which are quantitatively converted into products by β -elimination of hydridopalladium species, the reaction can be represented as



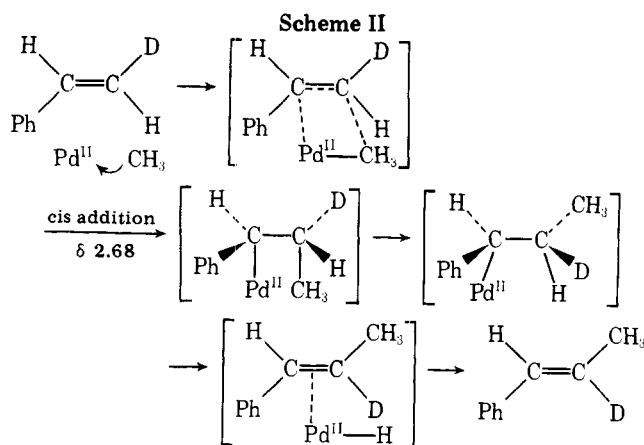
The rate constant ratio (k_{rel}) is given by

$$k_{\text{rel}} = \frac{k_b}{k_a} = \frac{\log [B^0]/[B]}{\log [A^0]/[A]} \quad (3)$$

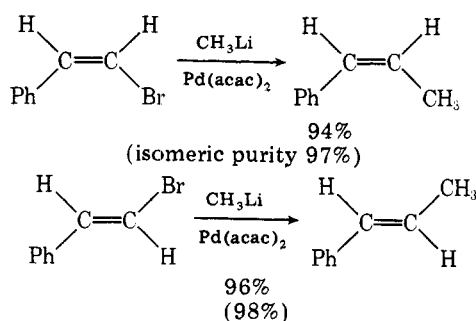
where $[A^0]$ and $[A]$ represent respectively the initial and final concentrations of olefin A, and similarly for B. In experiments, when the extent of reaction is low, eq 3 reduces to

$$k_{\text{rel}} = \frac{[Y][A]}{[X][B]} \quad (4)$$

The validity of this equation depends on maintaining an essentially constant ratio of the olefins under the reaction conditions. This point was confirmed by removal of aliquots from

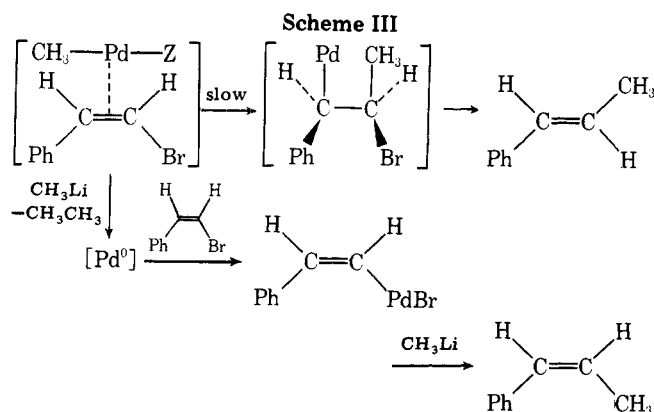


tion-elimination mechanism, the bromo group can be substituted by methyl group with inversion of configuration, since elimination of bromopalladium species occurs more readily than that of hydridopalladium species.²⁶ The results are, however, opposite to the expected one, and the bromo group was substituted by methyl group with retention of configuration. Thus, reaction of *cis*- β -bromostyrene with methyl lithium in the presence of Pd(acac)₂ gave *cis*- β -methylstyrene in 94% yield along with *trans*- β -methylstyrene (3%). Similarly, reaction of *trans*- β -bromostyrene afforded *trans*- β -methylstyrene in 96% yield in addition to 2% of *cis*- β -methylstyrene.



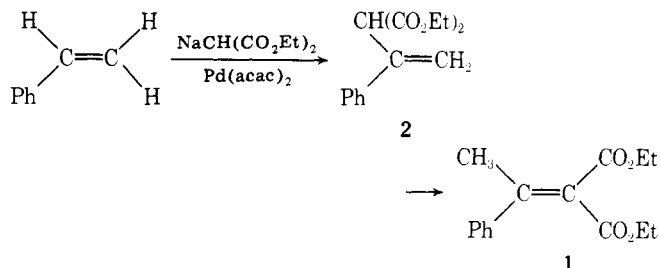
These results can be rationalized by assuming that the addition of the methylpalladium species toward β -bromostyrene is simply retarded by steric effects,²⁷ and hence nucleophilic attack of methyl lithium toward the methylpalladium species occurs, producing zerovalent palladium species,³ which then catalyzes methylation of the vinyl halides with methyl lithium by the oxidative addition-reductive elimination mechanism.²⁸ Therefore, it should be noted that the stereochemistry of the methylation of styrenes depends upon the valency of palladium.

Reaction of Styrene with Diethyl Sodiomalonnate in the Presence of Palladium(II) Acetylacetonate. Reaction of styrene with diethyl sodiomalonate in the presence of Pd(acac)₂ was investigated. Although reactions of such soft carbanions with olefin complexes have been reported, they are

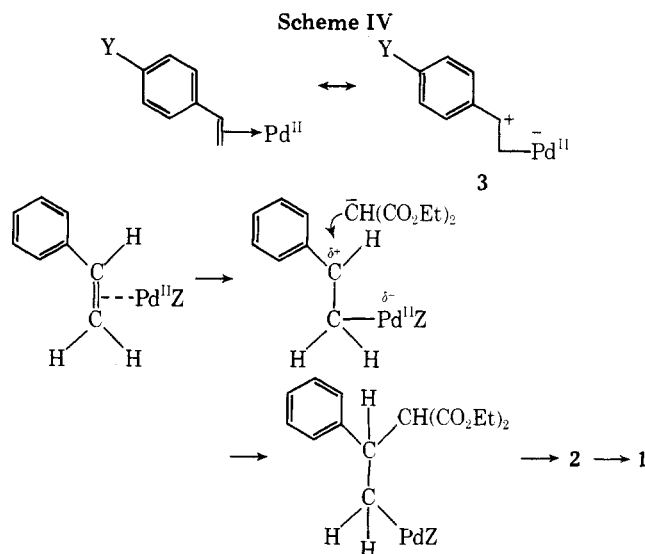


limited to olefin complexes that are part of a chelating ligand containing a second olefinic group.¹⁴

A mixture of styrene and Pd(acac)₂ was allowed to react with $\frac{2}{3}$ molar equiv of diethyl sodiomalonate in THF at reflux for 5 h. Quenching with an 1 N acetic acid solution followed by usual workup gave an 18% yield of diethyl α -methylbenzylidenemalonate (1), probably derived from the initial product 2 by base-induced 1,3-hydride shift, along with di-

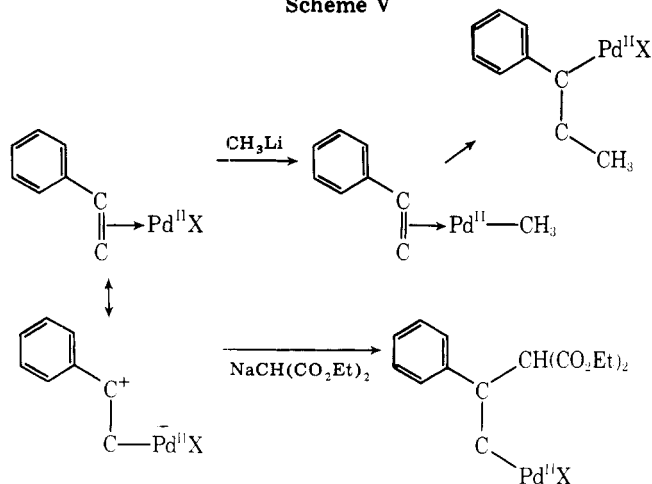


ethyl *trans*-styrylmalonate (4%). In the absence of the palladium complex, the starting materials were recovered. In contrast to the β -carbon attack of methyl moiety in the reaction of methyl lithium, diethylmalonate anion attacks at the α position of styrene, indicating that direct attack of diethylmalonate anion toward the α carbon of styrene coordinating to palladium occurs slowly, probably because nucleophilic attack toward palladium(II) of olefin-palladium complexes is retarded. Powell showed that from ¹³C NMR studies of a series of *para*-substituted styrene-palladium(II) complexes there is a significant ionic contribution to the styrene-palladium bond in palladium-styrene complexes,^{18,19} and electron donor Y groups would increase the contribution of canonical form 3 to the overall styrene-Pd bonding, i.e., the equilibrium position of Pd to the styrene C=C bond lies closer to the β carbon for electron donor Y groups. Moreover, x-ray study of [(PhCH=CH₂)PdCl₂]₂ showed the terminal olefinic carbon C _{β} to be closer to the coordination plane than C _{α} .²⁹ This consideration was again confirmed by the fact that when *p*-methoxystyrene was reacted under the same reaction condition, diethyl *p*-methoxybenzylidenemalonate was obtained in 23% yield without losing regioselectivity. A stronger electron-donating group increases the contribution of canonical form 3, leading to the attack of diethylmalonate anion toward the α carbon of *p*-methoxystyrene. Therefore, diethylmalonate anion can attack the α position of styrenes directly on the side remote from palladium^{6,8,9} as shown in Scheme IV.³⁰



In conclusion, addition of nucleophiles and palladium(II) across double bonds can have either *cis* or *trans* stereochemistry on the nature of nucleophiles; diethylmalonate anion

Scheme V



attacks the α position of coordinated styrene directly, while methyl carbanion initially coordinates to palladium, giving methylpalladium species which subsequently attacks the β position in a *cis* fashion. The most important factor is probably the ability of the nucleophile to coordinate to palladium(II) prior to addition across the double bond. It should be noted that alkylation of π -allylpalladium complexes occurs readily with soft carbanions such as anions of diethylmalonate³¹ and methyl 2-phenylsulfinylacetate,³² and enamines,³³ while alkylation does not with harder anions such as methyl-lithium. Further, in the former reaction nucleophilic attack occurs directly at carbon on the face of the π -allyl unit opposite to that of the palladium.³⁴

Experimental Section

General Comments. All reactions were carried out under nitrogen atmosphere. Infrared spectra were recorded using a Hitachi 215 grating spectrometer. The proton magnetic resonance spectra were recorded in solution either with JNM-MH-60 or HNMR-4H-100 spectrometers (internal Me₄Si).

Materials. Palladium complexes [Pd(acac)₂,³⁵ Pd(OAc)₂,³⁶ PdCl₂(PhCN)₂,³⁷ and PdCl₂(PPh₃)₂³⁸] were prepared by literature procedures. Methylolithium was prepared from methyl iodide and lithium in ether and titrated by Watson and Eastham's method.³⁹ Substituted styrenes were made from the reactions of the corresponding aldehydes with methylmagnesium bromide followed by dehydration with iodide.

Reaction of Styrenes with Methylolithium in the Presence of a Palladium(II) Salt. To a solution of styrene (0.312 g, 3.0 mmol) and palladium(II) salt (1.0 mmol) in dry THF (15 mL) was added a solution of methylolithium in ether (1.6 mL, 2.0 mmol) at 0 °C under nitrogen atmosphere. The mixture was allowed to warm to room temperature and stirred for 8 h. The reaction mixture was treated with water (1.0 mL) and filtered off. Extraction with ether, drying (MgSO₄), and concentration gave products to which internal standard (naphthalene) was added. GLC analyses (Carbowax 20M, 130 °C) gave the results summarized in Table I. When an additional ligand (2.0 mmol) such as PPh₃, P(*n*-Bu)₃, and P(OPh)₃ was added under the reaction condition, none of β -methylstyrenes was obtained, and the starting materials were recovered.

Characterization of the Products. In the first set of experiments product samples were isolated by preparative GLC; in the second set, yield determination was accomplished by GLC. The products were as follows. *trans*- β -Methylstyrene: 90% yield; IR (liquid film) 687, 734, 960 cm⁻¹; NMR (CCl₄) δ 1.83 (d, 3 H, *J* = 5.0 Hz), 5.37 (d-q, H, *J* = 16.0 and 5.0 Hz), 6.33 (d, H, *J* = 16 Hz), 7.03–7.40 (m, 5 H). *trans*- β -Methyl-*p*-chlorostyrene: 99% yield; IR 680, 780, 960 cm⁻¹; NMR δ 1.82 (d, 3 H, *J* = 5.0 Hz), 5.87 (d-q, H, *J* = 15.8, 5.0 Hz), 6.27 (d, H, *J* = 15.8 Hz), 7.02 (s, 2 H), 7.23 (s, 2 H). *trans*- β -Methyl-*m*-chlorostyrene: 80% yield; IR 680, 760, 960 cm⁻¹; NMR δ 1.88 (d, 3 H, *J* = 5.0 Hz), 6.10–6.35 (m, 2 H), 7.12–7.35 (m, 4 H). *trans*- β -Methyl-*p*-methylstyrene: 60% yield; IR 690, 770, 960 cm⁻¹; NMR δ 1.85 (d, 3 H, *J* = 5.2 Hz), 2.30 (s, 3 H), 6.02 (d-q, H, *J* = 14.8, 5.2 Hz), 6.35 (d, H, *J* = 14.8 Hz), 6.97–7.27 (m, 5 H). *trans*- β -Methyl-*p*-methoxystyrene: 15% yield; IR 780, 960, 1040, 1250 cm⁻¹; NMR δ 1.83 (d, 3 H, *J* = 5.5 Hz), 3.72 (s, 3 H), 6.03 (d-q, H, *J* = 15.2, 5.5 Hz), 6.30 (d, H, *J* = 15.2 Hz), 6.70 (d, 2 H, *J* = 7.0 Hz), 7.15 (d, 2 H, *J* = 7.0 Hz).

General Comments Concerning the Competitive Experiments.

The competing olefins were selected so that an adequate separation of the olefins, internal standard, and adduct peaks would be obtained on the final chromatogram. A solution of the competing olefins (6.0 mmol of each) and Pd(acac)₂ (1.0 mmol) in dry THF (15 mL) was stirred under nitrogen atmosphere at 25 °C for 10 min. A solution of methylolithium (2.0 mmol) in ether (1.6 mL) was added. After quenching with water (1.0 mL) the mixture was carefully extracted with ether. To the ethereal solution a measured amount of biphenyl was added as an internal standard, and the mixture was analyzed by GLC (Carbowax 20M). The methylated styrenes, which it was necessary to prepare separately, were amenable to direct analysis by GLC. Aliquots from the reaction mixture of styrene vs. *p*-chlorostyrene were removed at 10, 30, 60, 120, and 180 min. The relative ratio of styrenes and products was observed not to change with time. The relative rate constants thus obtained were analyzed, the data being fit to the best straight line for σ and σ^+ constants using a least-squares program. The following value of ρ were obtained: using σ constant 2.69 \pm 0.189 (γ = 0.98); using σ^+ constants 1.51 \pm 0.237 (γ = 0.92).

Stereochemistry of the Reactions of β -Deuteriostyrenes. *cis*- and *trans*- β -deuteriostyrenes were prepared from the corresponding β -bromostyrenes by Yoshino's method.⁴⁰ Pure samples were collected by preparative GLC and the deuterium contents were checked by NMR spectrum. *trans*- β -Deuteriostyrene: NMR (CCl₄) δ 5.67 (d, H, *J* = 17.5 Hz), 6.63 (d-t, H, *J* = 17.5 and 1.2 Hz), 7.07–7.47 (m, 5 H). *cis*- β -Deuteriostyrene: NMR δ 5.17 (d, H, *J* = 10.7 Hz), 6.63 (d-t, H, *J* = 10.7 and 2.6 Hz), 7.07–7.47 (m, 5 H). *trans*- β -Deuteriostyrene was reacted by the same method as described above in the reaction of styrenes with methylolithium in the presence of Pd(acac)₂. The β -methylstyrene fraction was collected by preparative GLC (Carbowax 20M, 130 °C) and subjected to measurement of NMR spectra. Careful analysis of the spectra showed that *trans*- β -deuterio- β -methylstyrene was obtained exclusively and its deuterium content was 0.90 \pm 0.08: NMR δ 1.81 (t, 3 H, *J* = 0.2 Hz), 6.20 (t, *J*_{HD} = 4.0 Hz), 7.10 (m, 5 H). Similarly, the reaction of *cis*- β -deuteriostyrene gave *trans*- β -methylstyrene, whose deuterium content was 0.08 \pm 0.06. Therefore, the stereochemistry of the reaction is inversion of configuration.

Reaction of β -Bromostyrene with Methylolithium in the Presence of Pd(acac)₂. A solution of Pd(acac)₂ (0.304 g, 1.0 mmol) and *cis*- β -bromostyrene⁴¹ (0.552 g, 3.0 mmol) in dry THF (15 mL) was treated with a solution of methylolithium (6.0 mmol) in ether (2.4 mL) similarly as described above. The GLC analysis (Carbowax 20M, internal standard method using biphenyl) showed that *cis*- β -methylstyrene⁴² were obtained (0.110 g, 94%) along with *trans*- β -methylstyrene (0.04 g, 4%). *cis*- β -Methylstyrene: IR 690, 1644 cm⁻¹; NMR (CCl₄) δ 1.87 (d-d, 3 H), 4.77 (m, H), 6.05 (d-q, H, *J* = 11 and 2 Hz), 7.68 (m, 5 H). Similar reaction of *trans*- β -bromostyrene⁴³ gave *trans*- and *cis*- β -methylstyrene in 96 and 2% yields, respectively.

Reaction of Styrene with Diethyl Sodiomalonate in the Presence of Pd(acac)₂. To 0.305 g (1.0 mmol) of Pd(acac)₂ in 50 mL of freshly distilled dry THF was added 0.312 g (3.0 mmol) of styrene and the solution was stirred for 20 min. To this solution was added a THF solution of diethyl sodiomalonate, which was prepared upon treatment of diethyl malonate (0.320 g, 2.0 mmol) with sodium hydride (50% in Bayol, 0.096 g) in THF (5 mL). The mixture was stirred at reflux for 12 h, cooled, quenched with aqueous acetic acid solution (2 N), filtered off, and extracted with ether. The ether solution was washed with a solution of sodium hydrogen carbonate, dried over MgSO₄, and concentrated with a rotary evaporator. The bulb-to-bulb distillation (bath temperature 187–190 °C, 2 mmHg) gave oily products, which subsequently chromatographed on a 20 \times 20 cm Merck silica gel F 254 preparative layer plate in benzene. A band (*R*_f 0.58) was eluted to afford diethyl α -methylbenzylidenemalonate (1): *m/e* 262; IR (liquid film) 1625, 1720 cm⁻¹; NMR (CCl₄) δ 0.88 (t, 3 H, *J* = 6.5 Hz), 1.31 (t, 3 H, *J* = 6.5 Hz), 2.42 (s, 3 H), 3.86 (q, 2 H), 4.23 (q, 2 H), 7.26 (s, 5 H). Anal. Calcd for C₁₅H₁₈O₄: C, 68.68; H, 6.92. Found: C, 68.93; H, 7.07. A band (*R*_f 0.61) gave diethyl *trans*-styrylmalonate: *m/e* 262; IR (liquid film) 1725 cm⁻¹; NMR (CDCl₃) δ 1.27 (t, 6 H, *J* = 8 Hz), 4.12 (d, H, *J* = 4 Hz), 4.18 (q, 4 H, *J* = 8 Hz), 6.31 (d-d, *J* = 16 and 4 Hz), 6.54 (d, *J* = 16 Hz), 7.16–7.40 (m, 5 H). The authentic sample was prepared by the reaction of ethoxymethylenemalonate with benzylmagnesium bromide in ether at reflux followed by separation with silica gel chromatography. Nabar et al.⁴⁴ reported that this reaction gave diethyl phenethylidenemalonate; however, the structure should be assigned to be the isomerized product, diethyl *trans*-styrylmalonate, from the NMR spectrum. Treatment of a solution of diethyl *trans*-styrylmalonate in THF with sodium hydride followed by quenching with water gave the recovered ester. The accurate yields of the reaction products were determined by GLC analyses (SE-30, 10%, 1m, column temperature 100–230 °C).

using an internal standard of biphenyl. An unknown minor product was detected in GLC analysis.

When a mixture of Pd(OAc)₂ (5 mmol), styrene (50 mmol), and diethyl sodiomalonate (10 mmol) in THF was reacted under similar reaction conditions, 1 (21%), diethyl phenethylmalonate (4%), α -phenylnaphthalene (1.6%), and α -phenyltetralin⁴⁵ (1%) were obtained.

Reaction of *p*-Methoxystyrene with Diethyl Sodiomalonate in the Presence of Pd(acac)₂. The reaction of *p*-methoxystyrene (0.402 g, 3.0 mmol), Pd(acac)₂ (0.305 g, 1.0 mmol), and diethyl sodiomalonate (2.0 mmol) in THF was carried out and worked up under the same condition employed on the reaction of styrene. The oily product obtained from the bulb-to-bulb distillation (bath temperature 199–201 °C, 2 mmHg) was subjected to TLC. A band (*R*_f 0.560) was eluted with benzene to afford diethyl α -methyl(*p*-methoxybenzylidene)malonate: *m/e* 292; IR (liquid film) 1715 cm⁻¹; NMR (CCl₄) δ 0.96 (t, 3 H, *J* = 6.6 Hz), 1.30 (t, 3 H, *J* = 6.6 Hz), 2.40 (s, 3 H), 3.80 (s, 3 H), 3.93 (q, 2 H, *J* = 6.6 Hz), 4.24 (q, 2 H, *J* = 6.6 Hz), 6.92 (d, 2 H, *J* = 9 Hz), 7.28 (d, 2 H, *J* = 9 Hz). A band (*R*_f 0.625) gave a minor unknown product: mp 97.5–98.5 °C (recrystallized from petroleum ether); *m/e* 230; IR (Nujol mull) 1670 cm⁻¹; NMR (CDCl₃) δ 2.40 (s, 3 H), 2.61 (s, 3 H), 3.81 (s, 3 H), 6.72 (s, H), 6.95 (d, 2 H, *J* = 9 Hz), 7.61 (d, 2 H, *J* = 9 Hz).

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Registry No.—1, 5294-56-4; *trans*- β -methylstyrene, 873-66-5; *trans*- β -methyl-*p*-chlorostyrene, 1879-53-4; *trans*- β -methyl-*m*-chlorostyrene, 23204-80-0; *trans*- β -methyl-*p*-methylstyrene, 2077-30-7; *trans*- β -methyl-*p*-methoxystyrene, 4180-23-8; *trans*- β -deuteriostyrene, 6911-81-5; *cis*- β -deuteriostyrene, 21370-59-2; *trans*- β -deuterio- β -methylstyrene, 21370-50-3; *cis*- β -bromostyrene, 588-73-8; *cis*- β -methylstyrene, 766-90-5; diethyl sodiomalonate, 996-82-7.

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- (46) **Note Added in Proof.** A minor product (mp 97.5–98.0 °C) from the reaction of *p*-methoxystyrene with diethyl sodiomalonate was assigned to 1-[2-methyl-5-(*p*-methoxyphenyl)-3-furanyl]ethanone (4%), which can be formed by nucleophilic attack of acetylacetonate ligand of Pd(acac)₂ toward *p*-methoxystyrene. Similarly, a small amount of 1-(2-methyl-5-phenyl-3-franyl)ethanone, mp 57.5 °C, was detected among the products from the reaction of styrene with diethyl sodiomalonate in the presence of Pd(acac)₂.