2 H), 3.62 (q, 2 H), 4.1 (m, 4 H).

γ-Ethoxybutyrolactone 2. A mixture of 53.3 g (0.2 mol) of diethyl formylsuccinate diethyl acetal and 34 g (~ 0.48 mol) of potassium hydroxide pellets, dissolved in 420 mL of 95% ethanol, was refluxed for 2 h. The alcohol was then evaporated under reduced pressure. The residual potassium salt was dissolved in 70 mL of water. The aqueous phase was washed two times with 40 mL of ether to eliminate neutral byproducts, acidified with 10 N H_2SO_4, and extracted three times with ether. The pooled ether extracts were washed twice with saturated brine (see note), dried over $MgSO_4$, and evaporated.

The residue was placed in a Claisen flask fitted with a short Vigreux column and the distillation was performed under reduced pressure, by use of a water pump. At 100–110 °C the decarboxylation and the ethanol elimination began, allowing only a moderate vacuum. Finally the lactone distilled at 102–103 °C (14 mmHg); yield 19.3 g, 74%.

Note: If washing of the combined ethereal layers was omitted, traces of sulfuric acid present in the mixture caused the formation of ethyl β-formylpropionate (5–10%, bp 83–85 °C (12 mmHg) ν(C=O) 1725 cm^{-1}, ν(C–H) in CHO 1720 cm^{-1}). IR (CCl_4): ν(CO) 5.6 μm. 250-MHz ^1H NMR (CCl_4/Me_4Si): **2**, ABX_3 system, δ 1.12 (t, 3 H), 3.64 (2 H, AB $\Delta\nu$(AB) >50 Hz); δ 2.0 (m, 1 H), 2.25 (m, 2 H), 2.50 (m, 1 H), 5.34 (m, 1 H).

One-Pot Procedure for the Preparation of γ-Ethoxybutyrolactone (2). The isolation of diethyl formylsuccinate diethyl acetal can be omitted. Initially the procedure is as indicated for the synthesis of diethyl formylsuccinate diethyl acetal, starting on a 0.2-mol scale. When all the ethyl formate has distilled, the distillate is allowed to cool and 34 g (~0.48 mol) of potassium hydroxide pellets in 420 mL of 95% ethanol is added. The mixture is refluxed for 2 h. The procedure then continues as indicated for the γ-ethoxybutyrolactone. The yield is 18.7 g (72%).

Succinic Semialdehyde (1). To 6.5 g (0.05 mol) of γ-ethoxybutyrolactone was added 13 mL of distilled water. After this solution was heated to boiling, a rapid stream of steam was passed through the mixture for 1–2 min. The solution was transferred to a distillation flask fitted with a short column and the water was first distilled under reduced pressure. After a high vacuum was obtained, the succinic semialdehyde distilled as a white viscous oil at 91–92 °C (0.05 mmHg). The yield was 3.3 g (65%).

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Registry No. **1a**, 692-29-5; **1b**, 50768-69-9; **2**, 932-85-4; **4a**, 5472-38-8; **4b**, 14273-44-0; **6**, 70145-29-8; **7**, 70145-30-1; **8**, 70145-31-2; sodium ethanolate, 141-52-6; diethyl succinate, 123-25-1; ethyl formate, 109-94-4.

Stereoselective Synthesis of Alkenes and Alkenyl Sulfides from Alkenyl Halides Using Palladium and Ruthenium Catalysts

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Alkenyl halides react with organolithium compounds, such as alkyl, aryl, and heterocyclic lithiums, in the presence of zerovalent palladium compounds to form alkenes stereoselectively under both stoichiometric and catalytic conditions. Alkenyl halides also are easily converted to the corresponding alkenyl sulfides stereoselectively upon treatment with thiolate anions in the presence of the same palladium catalyst. These reactions occur readily at 80 °C and the yields are generally good to excellent.

The difficulty of nucleophilic substitution at an sp^2 carbon atom by conventional organic techniques is overcome by using transition metals.[1] Carbon–carbon bond formation by cross-coupling of alkenyl halides with either Grignard reagents or organolithium compounds is one of the attractive and important pathways for the synthesis of alkenes. The stoichiometric process for synthesis of alkenes by the reaction of alkenyl halides with organocuprates[2] has been replaced by catalytic processes.[3] Iron,[4,5] nickel,[6,7] and copper catalysts[8] are most efficient for cross-coupling between alkenyl halides and Grignard reagents. The scope of the nickel-catalyzed reaction has been verified by many successful applications,[9] and its mechanism has been clarified.[10] However, the nickel catalysts are unfortunately not applicable to the reaction

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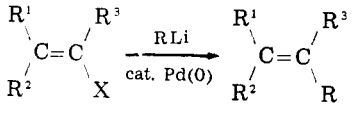
Table I. Stoichiometric Alkylation, Arylation, and Vinylation[a]

halides[b]	RM	product	yield,[d] %	isomeric purity,[e] %
(Z)-PhCH=CHBr	MeLi	1	88	99
(Z)-PhCH=CHBr	BuLi	2	66	99
(Z)-PhCH=CHBr	p-MeC$_6$H$_4$Li	3	98	99
(Z)-PhCH=CHBr	19	4	93	99
(Z)-PhCH=CHBr	20	5	90	98
(Z)-PhCH=CHBr	21	6	96	100
(E)-PhCH=CHBr	MeLi	7	98	100
(E)-PhCH=CHBr	MeMgBr	7	99	100
(E)-PhCH=CHBr	BuLi	8	55	100
(E)-PhCH=CHBr	p-MeC$_6$H$_4$Li	9	98	100
(E)-PhCH=CHBr	CH$_2$=CHMgBr	10	91	99.5
(E)-PhCH=CHBr	19	11	92	99
(E)-PhCH=CHBr	20	12	92	99
(E)-PhCH=CHBr	21	13	92	100
(E)-PhCH=CHBr	22	14	82	100
(Z)-PhCH=CHCl	MeLi	1	90	100
(Z)-PhCH=CHCl	p-MeC$_6$H$_4$Li	3	92	100
(Z)-BuCH=CHBr[c]	BuLi	15	63	99.5
(Z)-BuCH=CHBr[c]	p-MeC$_6$H$_4$Li	16	81	99
(E)-Ph(Me)C=CHBr	MeLi	18	89	99

[a] All reactions were carried out with 1 mmol of halide, 1 mmol of Pd(PPh$_3$)$_4$, and 1 mmol of organolithium compound (Grignard reagent) in benzene-ether at room temperature. [b] Oxidative addition was carried out at room temperature for 2 h. [c] Oxidative addition was carried out in reflux benzene for 3 h, but the halide was still recovered in 10-20% yield. [d] All yields are based on relative GLC peak area, corrected for the sensitivity of the detector, using mainly naphthalene as reference. [e] The isomeric purity was determined by relative GLC areas with those of the corresponding stereoisomers.

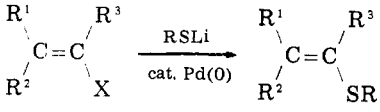
with organolithium compounds.

It has been reported that zerovalent palladium is an effective catalyst for stereoselective cross-coupling of alkenyl halides with Grignard reagents.[11,12] Importantly, by using the palladium catalyst, alkenyl halides undergo cross-coupling with organolithium compounds stereoselectively, to give alkenes whose isomeric purity is higher than those obtained from the nickel-catalyzed reaction of Grignard reagents (eq 1). Since organolithium compounds



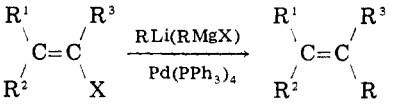
(1)

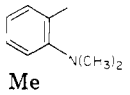
are versatile reagents and have advantages which include the ready formation by direct metalation of hydrocarbons,[13] the palladium-catalyzed reaction with organolithium compounds will open a wide range of synthetic procedures in addition to the reactions with alkenylaluminums[14] and -zirconiums,[15] acetylides,[16] and potassium cyanide.[17] Further, the efficiency of the palladium-catalyzed reaction will be enhanced by stereoselective synthesis of alkenyl sulfides upon treatment of thiolate anions, which are a typical example of soft carbanions (eq 2). Vinylic sulfides can be deprotonated and alkylated

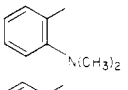
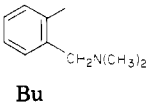


(2)

Chart I



	R^1	R^2	R^3	R
1	H	Ph	H	Me
2	H	Ph	H	Bu
3	H	Ph	H	p-MeC$_6$H$_4$
4	H	Ph	H	
5	H	Ph	H	
6	H	Ph	H	
7	Ph	H	H	Me
8	Ph	H	H	Bu
9	Ph	H	H	p-MeC$_6$H$_4$
10	Ph	H	H	CH$_2$=CH—

	R^1	R^2	R^3	R
11	Ph	H	H	
12	Ph	H	H	
13	Ph	H	H	
14	Ph	H	H	
15	H	Bu	H	Bu
16	H	Bu	H	p-MeC$_6$H$_4$
17	H	Bu	H	
18	Ph	Me	H	Me

α to sulfur, and they are synthetically equivalent to carbonyl compounds[18,19] and terminal acetylenes.[20] We report here full details of the palladium-catalyzed cross-coupling reaction of alkenyl halides with organolithium compounds, Grignard reagents, and lithium thiolates with respect to scope, limitation, and mechanism.

Results and Discussion

Stoichiometric Alkylation and Arylation of Alkenyl Halides Using Palladium(0) Compounds. It is well-known that Pd[P(C$_6$H$_5$)$_3$]$_{4-n}$ reacts readily with a

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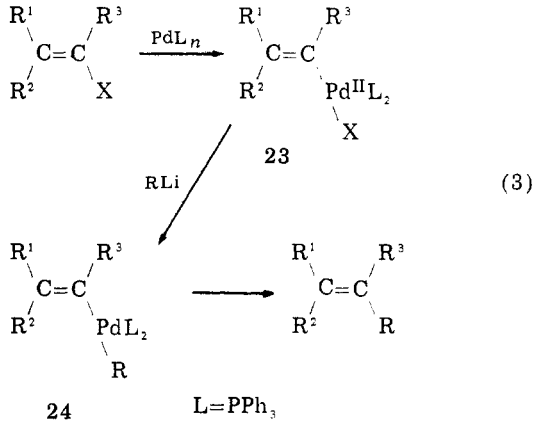
variety of organic halides to form oxidative addition products of the type $[P(C_6H_5)_3]_2PdXR$.[21-23] Alkenyl halides were allowed to react with tetrakis(triphenylphosphine)palladium until completion of the oxidative addition. Subsequent addition of organolithium compounds gave the desired cross-coupling products in high yields. For example, methylation of (*Z*)- and (*E*)-β-bromostyrenes gave (*Z*)- and (*E*)-propenylbenzenes in 90 and 88% yield, respectively. The GLC analysis of the products showed that the isomeric purity is over 99%, indicating that the cross-coupling reactions proceed stereospecifically. Grignard reagents undergo similar alkylation. There is no discrepancy between arylvinyl bromides and arylvinyl chlorides. The reactivity of alkylvinyl halides is low in comparison with that of arylvinyl halides because of the electron-donating effect of the alkyl group. The oxidative addition of palladium toward para-substituted aryl halides is enhanced with an electron-withdrawing group.[21] Even when reacted at benzene reflux for 3 h, 1-bromo-1-hexene was still recovered in a 10–20% yield.

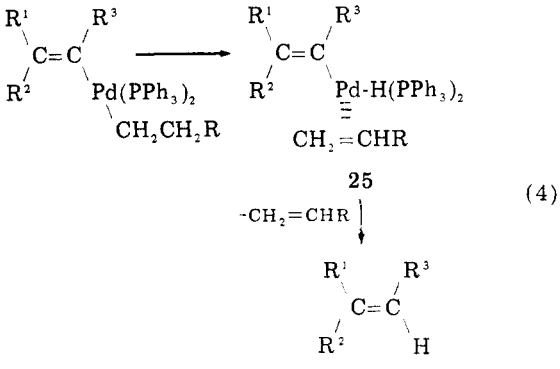
The stereoselective syntheses of di- and trisubstituted alkenes are summarized in Table I. All products were analyzed by GLC, isolated, and characterized by NMR, IR, and mass spectral data or comparison with the authentic samples. Noticeable was the lower yield of butylation products **2**, **8**, and **15** (see Table I). In addition to alkyl-, aryl-, and vinyllithiums, prepared by the metal–halogen exchange reaction of a halide, the use of organolithium compounds prepared directly from hydrocarbons by the metal–hydrogen exchange reactions increases the value of this method. The reactions of (*Z*)- and (*E*)-β-bromostyrenes with 2-furyllithium (**19**) in benzene in the presence of tetrakis(triphenylphosphine)palladium gave (*Z*)- and (*E*)-2-furylstyrenes in 93 and 92% yield, respectively, in a stereospecific manner. The similar reactions with 2-thienyl- (**20**), 2-(*N*,*N*-dimethylamino)phenyl- (**21**), and 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (**22**) also gave the corresponding substituted alkenes in high yields as shown in Table I. Although alkylation and arylation of alkenyl halides are accomplished by using nickel[6,7] and iron catalysts,[4,5] they are limited to the reaction with Grignard reagents and are not applicable to organolithium compounds.

The alkylation of alkenyl halides can be rationalized by assuming the oxidative addition of alkenyl halides to zerovalent palladium to give **23**, substitution with an organolithium compound, and reductive coupling to give alkenes (eq 3).[6,10,21-24] The stereochemistry obtained shows that the oxidative addition takes place stereoselectively, as expected from the stereochemistry at the trigonal carbon atom of alkenyl halides on nucleophilic substitution by $Pt(PPh_3)_3$ and $Pd(PPh_3)_3$.[25] In support of the substitution of the halide on palladium with the alkyl moiety of an alkyllithium compound, the reactions of bromostyrene with butyllithium afforded styrene in 10–30% yields. This is attributable to the facile β elimination of an alkene from



(3)

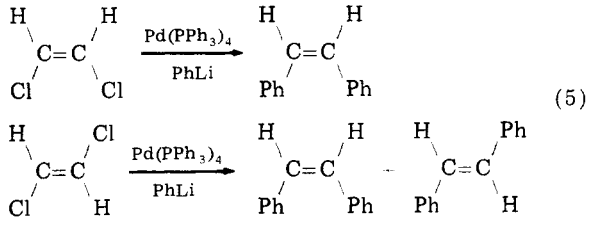
24 (R = C_4H_9), producing hydride complex **25**, which undergoes reductive coupling to give styrene (eq 4).[24] This



(4)

may be a major factor for decreasing the yield of the butylation products **2**, **8**, and **15**.

An attempt at the stereoselective diarylation of 1,2-dichloroethylenes with an aryllithium failed. The stereochemistry of the arylation is noticeable. For example, phenylation of (*Z*)-1,2-dichloroethylene with 2 equiv of phenyllithium in the presence of tetrakis(triphenylphosphine)palladium at room temperature gave (*Z*)-stilbene in 18% yield, while that of (*E*)-1,2-dichloroethylene gave a mixture of (*Z*)- and (*E*)-stilbenes in 19 and 28% yield, respectively (eq 5). Another product was biphenyl.



(5)

Naturally, without palladium, 1,2-dichloroethylene did not undergo the diphenylation. Since the oxidative addition of 1,2-dichloroethylene to zerovalent palladium does not occur at room temperature,[21] phenyllithium may be responsible, at least in part, for the oxidative addition by weakening the carbon–chlorine bond. Twice stereoselective cross-coupling of phenyllithium to (*E*)-1,2-dichloroethylene would give (*E*)-stilbene. The formation of (*Z*)-stilbene may be rationalized by assuming the oxidative addition to palladium, substitution with phenyllithium, β elimination of palladium–chloride species **26**,[26] cis addition of the phenylpalladium to acetylene,[27] nucleophilic

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Table II. Catalytic Alkylation, Arylation, and Vinylation

halide	RM[a]	condition[b]	product	yield,[c] %	isomeric purity,[d] %
(Z)-PhCH=CHBr	MeMgBr	A	1	99	99
(Z)-PhCH=CHBr	MeLi	B	1	90	99
(Z)-PhCH=CHBr	BuLi	B	2	62	99
(Z)-PhCH=CHBr	19	B	4	85	98
(Z)-PhCH=CHBr	20	A	5	94	98
(Z)-PhCH=CHBr	21	B	6	87	100
(E)-PhCH=CHBr	MeMgBr	A	7	99	99
(E)-PhCH=CHBr	p-MeC_6H_4MgBr[e]	A	9	85	99
(E)-PhCH=CHBr	CH_2=CHMgBr	A	10	81	99
(E)-PhCH=CHBr	MeLi	B	7	88	99
(E)-PhCH=CHBr	BuLi	B	8	46	99
(E)-PhCH=CHBr	19	B	11	85	98
(E)-PhCH=CHBr	20	A	12	83	99
(E)-PhCH=CHBr	21	A	13	75	100
(E)-PhCH=CHBr	22	A	14	60	99
(Z)-BuCH=CHBr	BuLi	B	15	40	99
(Z)-BuCH=CHBr	19	B	17	34	99

[a] One equivalent of organometallic compound was used. [b] All reactions were run in benzene: condition A, 1.0 mmol of alkenyl halides and 0.029 mmol of $Pd(PPh_3)_4$ were used at room temperature; condition B, 2.0 mmol of alkenyl halides and 0.10 mmol of palladium catalyst were used at benzene reflux for 2 h. [c] GLC yields based on alkenyl halides. [d] Determined by GLC analysis. [e] Five equivalents of p-MeC_6H_4MgBr was used.

attack of the second phenyllithium, and reductive coupling as shown in Scheme I, although more information is needed before a firm mechanistic conclusion can be drawn.

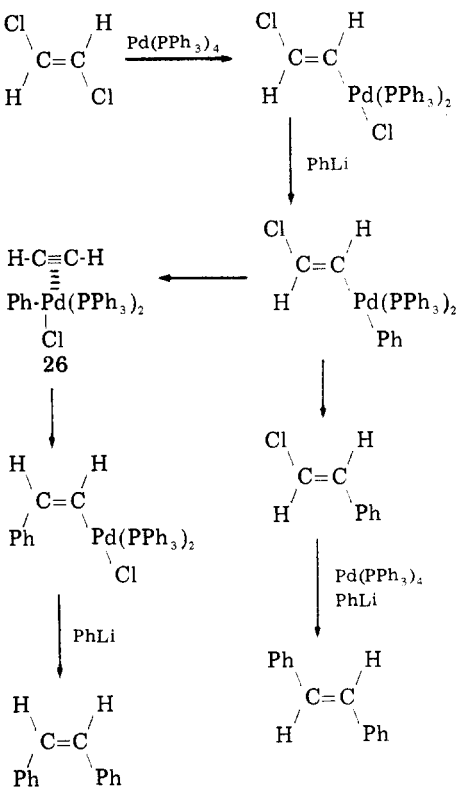
Catalytic Alkylation and Arylation of Alkenyl Halides. (A) Palladium Catalyst. While the alkylation and arylation of vinyl halides provide an efficient method for synthesis of olefins, they suffer from requiring the use of a stoichiometric amount of palladium(0) complex. Consequently, the development of a catalytic cycle to carry out this reaction is desirable. Grignard reagents undergo palladium-catalyzed cross-coupling reaction with alkenyl halides as well as with aryl halides[28] as shown in Table II. For example, the methylation of (Z)- and (E)-β-bromostyrenes with 1 equiv of methylmagnesium bromide gave (Z)- and (E)-propenylbenzenes stereoselectively in quantitative yields. The isomeric purity of alkenes thus obtained is higher than that obtained with a nickel catalyst.[9]

Catalytic alkylation of alkenyl halides with organolithium compounds does not occur under the reaction conditions employed for Grignard reagents. For example, methylation of β-bromostyrene with methyllithium at room temperature produced a stoichiometric amount of propenylbenzene based on palladium. The major product was phenylacetylene. This result is ascribed to the fact that the second oxidative addition of β-bromostyrene to the recycled palladium(0) catalyst or the reductive coupling of the intermediate (methyl-β-styryl)palladium is slower than the lithiation of the vinyllic hydrogen with methyllithium to give carbenoid **28**, which undergoes E2cB elimination[29] or Fritsch-Butlenberg-Wiechell-type rearrangement[30] to produce phenylacetylide (eq 6). In

$$\underset{\mathbf{27}}{RCHC{=}HBr} \xrightarrow{RLi} \underset{\mathbf{28}}{RCH{=}LiBr} \rightarrow RC{\equiv}CLi \quad (6)$$

order to overcome this difficulty, we allowed an organolithium compound to react gradually with the oxidative addition product **23** so that the competitive, direct metalation of alkenyl halides with the organolithium compound would be retarded. Actually, as shown in Table II, when a diluted benzene solution of an alkyllithium compound was added dropwise to a mixture of an alkenyl halide and palladium catalyst at benzene reflux over a period of 2 h, the alkylation product was obtained in high yield. It is noteworthy that, for butylation, high yields are not always obtained unless a modified palladium catalyst is used (see Table III). Organolithium compounds have the advantage of ready formation by direct lithiation of acidic hydrocarbons with butyllithium. When the acidity of the parent hydrocarbon of an organolithium compound is equivalent to or higher than that of the alkenyl halides, the alkylation takes place under the conditions employed for the stoichiometric alkylation reaction. However, in order to be completed, the alkylation should be carried out

Scheme I



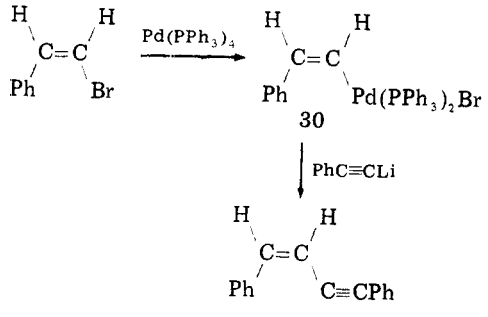
(28) (a) A. Sekiya and N. Ishikawa, *J. Organomet. Chem.*, 118, 349 (1976); (b) *ibid.*, 125, 281 (1977).
(29) G. Köbrich, H. Trapp, and I. Hornke, *Chem. Ber.*, 100, 961 (1967).
(30) M. Schlosser and V. Ladenberger, *Chem. Ber.*, 100, 3877, 3901 (1967).

Table III. Palladium Catalysts for Alkylation and Furylation[a]

halide	Li compd	catalyst	product	yield,[b] %
(Z)-PhCH=CHBr	MeLi	$Pd(PPh_3)_4$	1	90
(Z)-PhCH=CHBr	MeLi	$PdCl_2(PPh_3)_2$	1	95
(Z)-PhCH=CHBr	BuLi	$Pd(PPh_3)_4$	2	62
(Z)-PhCH=CHBr	BuLi	$PdCl_2(PPh_3)_2$	2	73
(Z)-PhCH=CHBr	BuLi	$PdCl_2$-PPh_3	2	82
(Z)-PhCH=CHBr	BuLi	$PdCl_2$-PBu_3	2	14
(Z)-PhCH=CHBr	19	$Pd(PPh_3)_4$	4	85
(Z)-PhCH=CHBr	19	$PdCl_2(PPh_3)_2$-BuLi	4	88
(Z)-PhCH=CHBr	19	$PdCl_2$-PPh_3-BuLi	4	75
(Z)-PhCH=CHBr	19	$PdCl_2$-PPh_3-K	4	92
(Z)-BuCH=CHBr	19	$Pd(PPh_3)_4$	17	34
(Z)-BuCH=CHBr	19	$PdCl_2(PPh_3)_2$-BuLi	17	48
(Z)-BuCH=CHBr	19	$PdCl_2$-PPh_3-K	17	68

[a] A mixture of alkenyl halide (2.0 mmol) and palladium catalyst (0.10 mmol) was reacted at benzene reflux; then the organolithium compound was added at reflux for 2 h. [b] GLC yield based on palladium.

under the conditions which are employed for the reaction of alkyllithium compounds whose parent hydrocarbon is less acidic. Actually, for example, when 2-furyllithium was added to the mixture of (Z)-β-bromostyrene and palladium catalyst at benzene reflux for 20 min, the desired (Z)-2-styrylfuran (4) was contaminated with the formation of 10–20% (Z)-1,4-diphenyl-1-buten-3-yne (29). This is due to the competitive reaction between lithium phenylacetylide and the alkenylpalladium 30 (eq 7).[16] The



(7)

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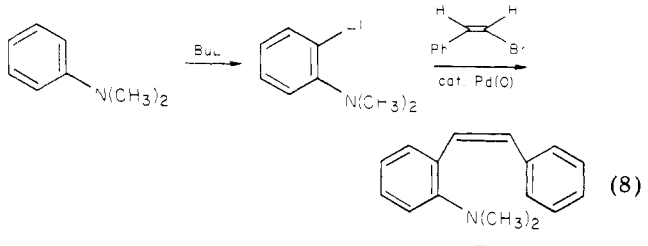
reaction of (Z)-β-bromostyrene with 2-(N,N-dimethylamino)phenyllithium, prepared readily upon treatment of N,N-dimethylaniline with butyllithium, in the presence of zerovalent palladium catalyst produced (Z)-β-(2-(N,N-dimethylamino)phenyl)styrene (6) in 89% yield (eq 8).



(8)

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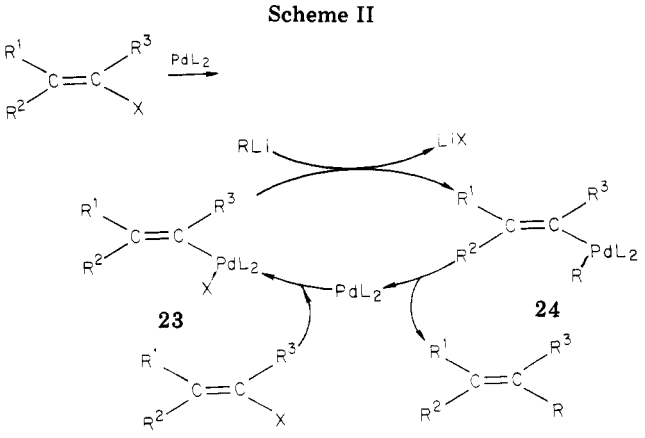
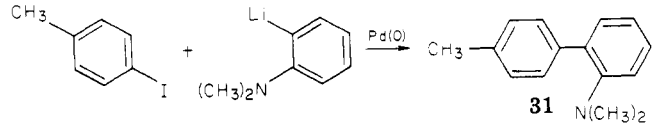
Other examples of stereoselective alkylation of alkenyl halides with organolithium compounds, which include 2-furyl-, 2-thienyl-, and 2-(N,N-dimethylaminomethyl)-phenyllithiums are summarized in Table II. In the alkylation with organolithium compounds, palladium catalyst turns over 30 times; it does likewise in the reaction with Grignard reagents. Other palladium catalysts were prepared, and their efficiency was examined with respect to the reactions of (Z)-β-bromostyrene and (Z)-1-bromo-1-hexene. As shown in Table III, for the butylation, the modified palladium catalysts which were prepared by reducing a mixture of palladium chloride and 4 equiv of triphenylphosphine increased the yield markedly. The product yields were dependent upon the ligand used, and

Scheme II



triphenylphosphine gave the best result. Highly reactive palladium slurry which was prepared by reducing palladium chloride with potassium in the presence of 2 equiv of triphenylphosphine[31] gave the highest yield of the furylation products of both (Z)-β-bromostyrene and (Z)-1-bromo-1-hexene among the catalysts examined. Consequently, for large-scale alkylation of alkenyl halides with organolithium compounds, active palladium slurry and the homogeneous palladium catalysts, prepared by the reduction of dichlorobis(triphenylphosphine)palladium with potassium and methyllithium,[32] would be convenient catalysts. Using the latter catalyst, we prepared compound 6 in a 90% isolated yield. The palladium-catalyzed alkylation of aryl halides with organolithium compounds proceeds efficiently without the difficulty observed in the reactions of alkenyl halides. For example, the reaction of p-iodotoluene with 2-(N,N-dimethylamino)phenyllithium in the presence of palladium catalyst, prepared from palladium chloride–triphenylphosphine–methyllithium, gave 2-(N,N-dimethylamino)-4′-methylbiphenyl (31) in 90% yield (eq 9).



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(9)

The catalytic alkylations can be rationalized by assuming Scheme II. Oxidative addition of an alkenyl halide to

(31) R. D. Rieke, W. J. Wolf, N. Kujundžić, and A. V. Kavaliunas, J. Am. Chem. Soc., 99, 4159 (1977), and references therein.
(32) S.-I. Murahashi, M. Yamamura, and N. Mita, J. Org. Chem., 42, 2870 (1977).

Table IV. Alkylation and Arylation of (*E*)-β-Bromostyrene[a]

RM	catalyst	*T*, °C	product	convrsn, %	yield,[d,e] %
MeMgBr	$RuCl_2(PPh_3)_3$[b]	25	1	72	34
MeMgBr	$RuCl_2(PPh_3)_3$[b]	80	1	100	88
MeLi	$RuCl_2(PPh_3)_3$[b]	80	1	100	54
MeMgBr	$RuCl_3$-PBu_3-K[c]	25	1	60	50
MeMgBr	$RuCl_2(PPh_3)_4$-K[c]	25	1	100	91
MeMgBr	$RuCl_2(PPh_3)_4$-PPh_3-Na/Hg[c]	25	1	94	86
PhMgCl	$RuCl_2(PPh_3)_3$[b]	80	(*E*)-stilbene	100	62
C_4H_9MgBr	$RuCl_2(PPh_3)_3$[b]	80	2	50	46

[a] (*E*)-β-Bromostyrene (1 equiv), RM (5 equiv), and Ru catalyst (0.1 equiv) were reacted. [b] Benzene solvent. [c] THF solvent. [d] GLC yield based on (*E*)-β-bromostyrene. [e] Isomeric purity is over 96%.

Table V. Preparation of Sulfides[a]

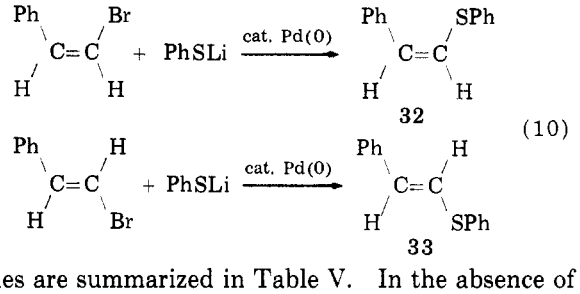
halide	thiolate	sulfides	yields, %	isomeric purity, %
(*Z*)-PhCH=CHBr	PhSLi	(*Z*)-PhCH=CHSPh	95	100
(*Z*)-PhCH=CHBr	PhSNa	(*Z*)-PhCH=CHSPh	99	100
(*Z*)-PhCH=CHBr	EtSLi	(*Z*)-PhCH=CHSEt	93	100
(*E*)-PhCH=CHBr	PhSLi	(*E*)-PhCH=CHSPh	95	100
(*Z*)-BuCH=CHBr	PhSLi	(*E*)-PhCH=CHSPh	98	100

[a] The reaction was carried out in benzene in the presence of 0.05 equiv of $Pd(PPh_3)_4$ at reflux.

zerovalent palladium (palladium metal or PdL_2) produces an alkenylpalladium (**23**), which begins a catalytic reduction–oxidation cycle.

(B) **Ruthenium Catalyst.** It is clear that palladium(0) complexes are highly efficient catalysts for cross-coupling between alkenyl halides and organolithium compounds or Grignard reagents. For further extension and improvement of the reaction, we examined the efficiency of some ruthenium catalysts, with which specific affinity for oxygen and nitrogen atoms is expected.[33] As a model, the reaction of β-bromostyrene with Grignard reagents has been tested. Ruthenium–hydride complexes such as dihydridotetrakis(triphenylphosphine)ruthenium and chlorohydridotris(triphenylphosphine)ruthenium give styrene as a reduction product predominantly. The nonhydride complex dichlorotris(triphenylphosphine)ruthenium gives the desired propenylbenzene in moderate yields as shown in Table IV. However, the reaction requires 80 °C, probably due to the slow oxidative addition of β-bromostyrene to the divalent ruthenium catalyst. To overcome this difficulty, zero- or univalent ruthenium catalysts were prepared by the reduction of dichlorotetrakis(triphenylphosphine)ruthenium with potassium or sodium amalgam. When this catalyst is used, the cross-coupling reaction takes place efficiently. Nevertheless some disadvantageous points have been found in comparison with the palladium catalysts. It may be of value in comparing the catalytic system to point them out. (1) The use of 1 equiv of methylmagnesium bromide gave only a 13% yield of propenylbenzene, and 5 equiv of methylmagnesium bromide was required to get over a 90% yield. (2) The stereochemistry is nonselective. Thus, (*Z*)-β-bromostyrene was converted to a mixture of (*Z*)- and (*E*)-propenylbenzene in a ratio of 1:2. Under even milder conditions (−78 to +25 °C), the *Z*/*E* ratio was 3:2, indicating that the vinylic carbon–ruthenium bond is labile in contrast to a stable vinylic carbon–palladium bond[25] and gives alkenyl radicals which undergo facile configurational inversion.[34] (3) Grignard reagents having a β-hydrogen undergo reduction predominantly. The reaction of (*E*)-β-bromostyrene with butylmagnesium bromide gave ethylbenzene (54%) and 1-hexenylbenzene (46%). The ruthenium–hydride complex, derived from the β elimination of butyl–ruthenium complexes, is a key intermediate for the formation of ethylbenzene. (4) Methylation with 5 equiv of methyllithium in the presence of $RuCl_2(PPh_3)_3$ gave only 54% propenylbenzene. This low yield may be due to the formation of complicated methyl–ruthenium compounds.[35]

Palladium–Catalyzed Sulfenylation of Alkenyl Halide. The reaction of alkenyl halides with a lithium benzenethiolate in the presence of the palladium catalyst at 80 °C gave the corresponding alkenyl sulfide in an excellent yield, in a stereospecific manner. The sulfenylation of (*Z*)- and (*E*)-β-bromostyrene with lithium or sodium benzenethiolates gave (*Z*)- and (*E*)-(2-phenylethenylthio)benzene (**32**, **33**) in 95% yields, respectively (eq 10). Other results of the preparation of alkenyl



(10)

sulfides are summarized in Table V. In the absence of palladium catalyst the sulfenylation does not occur with thiolates and only occurs upon treatment with copper methanethiolate at 200 °C.[36] The isomeric purity of the products was over 99.5%. Proton NMR coupling constants of 9.5–10.5 Hz for the vinylic protons in 1-alkenyl sulfides confirmed the *Z* stereochemistry of these alkenes, whereas those of 16 Hz confirmed *E* stereochemistry. The sulfenylation of (*Z*)-1-bromo-1-hexene proceeds smoothly to give (*Z*)-1-phenylthiohexene (**34**) in 90% yield, indicating that the oxidative addition of palladium of (*Z*)-1-bromo-1-hexene is again assisted by benzenethiolate anions as suggested for the phenylation of 1,2-dichloroethylene. Sulfenylation with sodium thiolates also gave excellent yields of sulfides. Ruthenium catalyst did not give sat-

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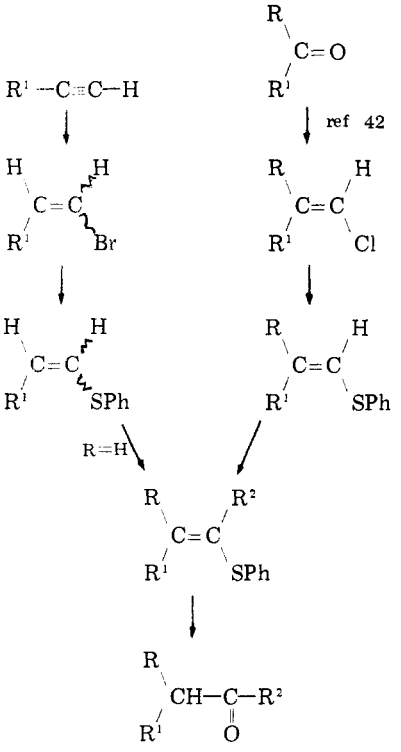
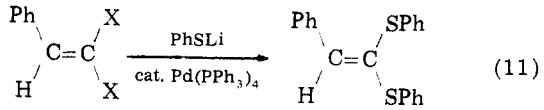
Scheme III



isfactory results. The similar palladium-catalyzed sulfenylation of aryl bromides and iodides to aryl sulfides is less successful.[37]

Since alkenyl sulfides are valuable synthetic precursors of carbonyl compounds[18,19] and acetylenes,[20] various methods for their syntheses have been explored. The major methods, which include Wittig-type reactions,[38] dehydration of β-hydroxy thioacetals,[39] and dehydrochlorination of β-chloro sulfides,[40] use carbonyl compounds as starting compounds. Quite recently, Posner reported the two-step synthesis of alkenyl sulfides from alkenyl halides.[41] Thus, 1-alkenylmagnesium bromides react stereoselectively with methyl sulfinate esters to produce alkenyl sulfoxides, which are reduced to the alkenyl sulfides upon treatment with ethylmagnesium bromide–cuprous iodide. In analogy to Posner's process, our one-step process from alkenyl halides would afford a convenient method for the synthesis of carbonyl compounds from acetylenes or carbonyl compounds as depicted in Scheme III, since alkenyl sulfides can be deprotonated and alkylated α to sulfur, and they are synthetically equivalent to carbonyl compounds.[42]

Ketene thioacetals have been received considerable attention in recent years as important synthetic intermediates,[43] and various methods for their synthesis have been reported.[44] For further extension of the sulfenylation of 1-haloalkenes, the synthesis of ketene thioacetals by disulfenylation of 1,1-dihaloalkenes was attempted. Although ketene diacetals are an exclusive product, the conversion of dihaloalkenes was quite low under the reaction conditions employed for the sulfenylation of haloalkenes. For example, treatment of 1,1-dichloro- and 1,1-dibromo-2-phenylethylene with benzenethiolate gave 1,1-diphenylthio-2-phenylethylene each in 96% yield, although the conversion of dihalides is 10–20% (eq 11).



X = Cl, Br

In summary, the palladium-catalyzed reactions of alkenyl halides with various organolithium compounds provide an efficient method for stereoselective synthesis of alkenes. Alkenyl sulfides can be also conveniently prepared by the similar palladium-catalyzed reaction of alkenyl halides with thiolate anions. These new methods are marked improvements over existing methods in certain cases and should find application in the synthesis of complex molecules.

Experimental Section

General. All reactions were carried out under an argon atmosphere. All melting points are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. The NMR spectra were obtained on JNM-4H-60 and HNM-4H-100 spectrometers, and chemical shifts are reported in δ values downfield from the internal standard tetramethylsilane. Mass spectra were taken on a Hitachi RSM-4 mass spectrometer. GLC was carried out with a Jeol-20K by using a 1-m analytical column packed with Carbowax 20M on Celite or a 1-m column packed with Apiezon L.

Materials. All solvents were distilled over benzophenone ketyl and stored under an argon atmosphere. THF was refluxed over $LiAlH_4$ and distilled under argon at atmospheric pressure. (*Z*)-β-Bromostyrene,[45] (*E*)-β-bromostyrene,[46] (*Z*)-β-chlorostyrene,[47] (*Z*)-1-bromo-1-hexene,[48] and (*E*)-α-methyl-β-bromostyrene[49] were all prepared by standard methods. Dichlorobis(triphenylphosphine)palladium,[50] tetrakis(triphenylphosphine)palladium,[51] dichlorotris(triphenylphosphine)ruthenium,[52] dichlorotetrakis(triphenylphosphine)ruthenium,[52] chlorohydridotris(triphenylphosphine)ruthenium,[53] and dihydridotetrakis(triphenylphosphine)ruthenium[54] were prepared by literature procedures. Butyllithium in hexane was commercially available (Mitsuwa Chemical Co.). Methyllithium and *p*-tolyllithium were prepared by the reaction of lithium with methyl iodide and *p*-tolyl bromide, respectively, in ether and titrated by Watson and Eastham's method.[55] 2-Furyllithium,[56] 2-thienyllithium,[57] 2-(*N*,*N*-dimethylamino)phenyllithium,[58] and 2-(*N*,*N*-dimethylaminomethyl)phenyllithium[59] were prepared from furan, thiophene,

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(54) R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. C. Yuen, *J. Organomet. Chem.*, **54**, 259 (1973).
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N,N-dimethylaniline, and (*N,N*-dimethylaminomethyl)benzene, respectively, by direct lithiation with butyllithium by known methods. The structural assignment of (*Z*)-propenylbenzene (**1**),[32] (*E*)-propenylbenzene (**7**),[32] (*E*)-4-methylstilbene(**9**),[60] and (*E*)-1-phenylbutadiene (**10**)[61] was made by comparison of their spectral data with those reported.

General Procedure for Stoichiometric Alkylation and Arylation of Alkenyl Halides with Organolithium Compounds. In a 25-mL round-bottomed flask containing a magnetic stirring bar was placed 1.16 g of tetrakis(triphenylphosphine)-palladium (1.0 mmol) and 1.0 mmol of the alkenyl halide and benzene (10 mL). A water-cooled condenser was placed on the flask, and the mixture was stirred magnetically at the appropriate temperature for the required length of time, during which time a green color changed to milky white. To the mixture a solution of 1.0 mmol of the organolithium compound in ether (1 mL) was added. The mixture became yellow after constant stirring for 1 h. The reaction mixture was quenched with 10 mL of 1 M HCl and extracted with three 30-mL portions of ether. The combined ether extracts were washed with water and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator. Products were separated by preparative TLC and GLC. The GLC yield was determined by using Carbowax 20 M, using an appropriate internal standard.

(*Z*)-4-Methylstilbene (3): NMR (CCl_4) δ 2.23 (s, 3, CH_3), 6.43 (s, 2, CH=CH), 6.90–7.17 (m, 9, ArH); IR (neat) 1600, 805, 743, 700 cm^{-1}; mass spectrum *m/e* 194.

(*Z*)-1-Tolyl-1-hexene (16): NMR (CCl_4) δ 0.90 (t, J = 5.8 Hz, 3, CH_3), 1.13–1.60 (m, 4, CH_2CH_2), 1.90–2.58 (m, 2, $C{=}CCH_2$), 2.33 (s, 3, CH_3), 5.55 (dt, J = 10.5, 6.8 Hz, 1, C=CHC), 6.33 (dt, J = 10.5, 1.5 Hz, 1, ArCH=C), 7.00–7.22 (m, 4, ArH); IR (neat) 831, 735 cm^{-1}.

(*E*)-2-Phenyl-2-butene (18): NMR (CCl_4) δ 1.75 (d, J = 7.0 Hz, 3, $C{=}CCH_3$), 1.97 (s, 3, $Ph(CH_3)C{=}C$), 5.73 (q, 1, C=CH), 7.17 (m, 5, ArH); IR (neat) 1645, 1598, 830, 750, 690 cm^{-1}.

Phenylation of 1,2-Dichloroethylene. To a suspension of (*Z*)- or (*E*)-1,2-dichloroethylene (1.0 mmol) and $Pd(PPh_3)_4$ (1.0 mmol) in benzene (5 mL) was added a solution of phenyllithium (2.0 mmol) in ether (3.2 mL) at room temperature. After 2 h of continuous stirring, the reaction mixture was worked up as described above. GLC analysis using dibenzyl as an internal standard showed that from (*Z*)-1,2-dichloroethylene, (*Z*)-stilbene and biphenyl were obtained in 18 and 80% yields, while from the *E* isomer, (*Z*)- and (*E*)-stilbenes and biphenyl were obtained in 19, 28, 40% yields, respectively.

General Procedure for the Catalytic Reactions of β-Bromostyrene with Grignard Reagents (Condition A). In a one-necked flask was placed $Pd(PPh_3)_4$ (35 mg, 0.029 mmol). A solution of 1 mmol of β-bromostyrene in benzene (10 mL) was added, and the mixture was stirred for 30 min. The appropriate amount of Grignard reagent in ether was added to the flask via syringe, and the solution was stirred at room temperature overnight. The reaction mixture was quenched with water and extracted with two 30-mL portions of ether. The ether extract was washed with water, dried ($MgSO_4$), and concentrated. The products were analyzed by GLC, using an internal standard.

General Procedure for Catalytic Alkylation of Alkenyl Halides with Organolithium Compounds (Condition B). In a 50-mL side-arm flask fitted with a reflux condenser, a magnetic stirring bar, and serum cap was placed 0.1 mmol of palladium catalyst. The flask was alternately evacuated and filled with argon on a vacuum line. A solution of an alkenyl halide (2.0 mmol) in 20 mL of benzene was added, and the mixture was stirred at reflux for 30 min. To the mixture was added a solution of an organolithium compound (2.40 mmol) in a mixed solvent (2 mL of hexane, ether, or THF and 10 mL of benzene), and the mixture was stirred at reflux for 2 h. After an additional 30 min of stirring at reflux, the mixture was allowed to cool to room temperature. The reaction mixture was quenched with 20 mL of a 0.2 M solution of HCl and extracted with three 10-mL portions of ether. The combined ether extracts were washed with water and dried over $MgSO_4$. After the solvent was removed the products were subjected to GLC analysis (Carbowax 20 M, 10%, 1 m or 2 m).

(*Z*)-1-Hexenylbenzene (2). (A) **Using $Pd(PPh_3)_4$.** The butylation was carried out under the reaction conditions in B. (*Z*)-1-Hexenylbenzene was obtained in 62% yield: NMR (CCl_4) δ 0.88 (t, J = 6.0 Hz, 3, CH_3), 1.10–1.63 (m, 4, CH_2CH_2), 2.02–2.55 (m, 2, $C{=}CCH_2$), 5.55 (dt, J = 11.5, 6.7 Hz, 1, PhC=CH), 6.33 (dt, J = 11.5, 1.5 Hz, 1, PhCH=C), 7.02–7.35 (m, 5, ArH); IR (neat) 1640, 1600, 765, 693 cm^{-1}; mass spectrum *m/e* 160.

(B) **Using $PdCl_2(PPh_3)_2$.** To a suspension of $PdCl_2(PPh_3)_2$ (0.070 g, 0.10 mmol) and (*Z*)-β-bromostyrene in 20 mL of benzene was added a solution of butyllithium in benzene (10 mL), with stirring at reflux for 2 h. The standard workup gave **2** in 73% yield, along with 19% of styrene.

(C) **Using $PdCl_2$–PPh_3.** A mixture of $PdCl_2$ (0.018 g, 0.10 mmol), triphenylphosphine (0.105 g, 0.40 mmol), and (*Z*)-β-bromostyrene in 20 mL of benzene was stirred at reflux for 30 min. To the resulting mixture was added a solution of butyllithium (2.40 mmol) in hexane (1.45 mL), and benzene (10 mL) was added with stirring at reflux for 2 h. After 30 min of continuous stirring, the reaction mixture was treated in the usual manner. The GLC analysis showed that **2** was obtained in 82% yield along with 16% styrene.

(D) **Using $PdCl_2$–PBu_3.** To a suspension of $PdCl_2$ (0.018 g, 0.10 mmol), tributylphosphine (0.081 g, 0.40 mmol), and (*Z*)-β-bromostyrene in 20 mL of benzene was added a mixture of butyllithium, hexane (1.45 mL), and benzene (10 mL), with stirring at reflux for 2 h. The standard treatment gave **2** in 14% yield along with styrene (4%).

(*E*)-1-Hexenylbenzene (8): NMR (CCl_4) δ 0.94 (t, J = 6.0 Hz, 3, CH_3), 1.13–1.63 (m, 4, CH_2CH_2), 2.03–2.43 (m, 2, $C{=}CCH_2$), 6.10 (dt, J = 15.4, 5.5 Hz, 1, PhC=CH), 6.37 (d, 1, PhCH=C), 7.10–7.37 (m, 5, ArH); IR (neat) 1660, 1600, 960, 740, 682 cm^{-1}; mass spectrum *m/e* 160.

(*Z*)-2-Styrylfuran (4). (A) **Using $Pd(PPh_3)_4$.** The reaction was carried out under the reaction conditions in B: NMR (CCl_4) δ 6.1–6.4 (m, 2, C=CH–CH=C), 6.27 (d, J = 12 Hz, 1, PhC=CH), 6.53 (d, 1, PhCH=C), 7.1–7.6 (m, 6, ArH, OCH=C); IR (neat) 1600, 920, 690 cm^{-1}; mass spectrum *m/e* 170.

(B) **Using $PdCl_2(PPh_3)_2$–BuLi.** To a suspension of $PdCl_2$-$(PPh_3)_2$ (0.070 g, 0.10 mmol) in 20 mL of benzene was added a solution of butyllithium (0.20 mmol) in hexane (0.12 mL). The mixture was stirred at reflux for 1 h, and (*Z*)-β-bromostyrene (0.366 g, 2.0 mmol) was added, with stirring at reflux for 1 h; subsequently a solution of 2.0 mmol of 2-furyllithium was added at reflux for 2 h. (*Z*)-2-Styrylfuran was obtained in 88% yield.

(C) **Using $PdCl_2$–PPh_3–BuLi.** A mixture of $PdCl_2$ (0.018 g, 0.10 mmol), triphenylphosphine (0.105 g, 0.40 mmol), and THF (5 mL) was heated at reflux for 30 min. To the resulting mixture was added a solution of butyllithium (0.20 mmol) in hexane (0.12 mL), using a syringe. After 1 h of additional stirring at reflux, (*Z*)-β-bromostyrene (2.0 mmol) was added at reflux, and then a solution of 2-furyllithium (2.0 mmol) in benzene (10 mL) was added at reflux for 2 h. After 1 h of continuous stirring at reflux, the mixture was treated in a usual manner. GLC analysis showed that **4** was obtained in 75% yield.

(D) **Using $PdCl_2$–PPh_3–K.** To a mixture of $PdCl_2$ (0.018 g, 0.10 mmol) and triphenylphosphine (0.105 g, 0.40 mmol) in THF (5 mL) was added potassium (8 mg, 0.21 mmol). The mixture was stirred at reflux for 2 h. To the resulting black slurry was added a solution of 2.0 mmol of (*Z*)-β-bromostyrene in benzene (20 mL). After 1 h of stirring at reflux, 2.0 mmol of 2-furyllithium was added at reflux for 2 h. (*Z*)-2-Styrylfuran was obtained in 92% yield.

The yield of (*Z*)-2-styrylfuran was dependent upon the rate of the addition of 2-furyllithium. For example, when a solution of 1.2 equiv of furyllithium in THF was added to a mixture of (*Z*)-β-bromostyrene (2.0 mmol) and palladium catalyst (0.10 mmol) at reflux for 20 min, the yield of (*Z*)-2-styrylfuran decreased to 10–50%. The side product was (*Z*)-1,4-diphenyl-1-buten-3-yne (**29**) (5–40% yield): NMR (CCl_4) δ 5.85 (d, J = 12 Hz, 1, PhC=CH), 6.63 (d, J = 12 Hz, 1, PhCH=C), 7.15–7.60 (m, 8, ArH), 7.70–8.80 (m, 2, ArH); IR (neat) 3070, 2200, 1600, 1030, 920, 780, 755, 690 cm^{-1}. Similarly, under the above reaction conditions, the reaction of (*E*)-β-bromostyrene produced a side product of (*E*)-1,4-diphenyl-1-buten-3-yne: NMR (CCl_4) δ 6.36 (d, J = 17 Hz, 1, PhC=CH), 7.06, (d, J = 17 Hz, 1, PhCH=C), 7.22–7.60

(60) Y. Fujiwara, I. Moritani, S. Danno, R. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, 91, 7166 (1969).
(61) A. I. Meyers and M. E. Ford, *J. Org. Chem.*, 41, 1735 (1976).

(m, 10, ArH); IR (Nujol mull) 1595, 950, 745, 690 cm^{-1}. Furthermore, the reaction of (*Z*)-1-bromohexene produced (*Z*)-5-undecen-7-yne: NMR (CCl_4) δ 0.95 (t, J = 7.5 Hz, 6, CH_3), 1.2–1.7 (m, 8, CH_2CH_2), 2.2–2.8 (m, 4, C=CCH_2, C≡CCH_2), 5.33 (d, J = 11.2 Hz, 1, C=CH–C≡C), 5.73 (dt, J = 11.2, 7.2 Hz, 1, BuCH=C); IR (neat) 3025, 2220, 1620, 1330, 1320, 1280, 1060, 730 cm^{-1}.

(*Z*)-2-(1-Hexenyl)furan (17): NMR (CCl_4) δ 0.95 (t, J = 7.5 Hz, 3, CH_3), 1.2–1.8 (m, 4, CH_2CH_2), 2.23–2.75 (m, 2, C=CCH_2), 5.59 (dt, J = 13, 7.5 Hz, 1, BuCH=C), 6.29 (d, J = 13 Hz, 1, BuC=CH), 6.30 (d, J = 3.6 Hz, 1, BuC=CC(O)CH), 6.31 (dd, J = 3.6, 2.0 Hz, 1, OC=CHC=C), 7.49 (d, J = 2.0 Hz, 1, OCH=CC); IR (neat) 3125, 930, 890, 730 cm^{-1}; mass spectrum m/e 150.

(*E*)-2-Styrylfuran (11): NMR (CCl_4) δ 6.1–6.4 (m, 2, CH=COC=CH), 6.66 (d, J = 18 Hz, 1, PhC=CH), 7.00 (d, J = 18 Hz, 1, PhCH=C), 7.1–7.5 (m, 6, ArH, furyl H); IR (neat) 1600, 930, 885, 690 cm^{-1}.

(*Z*)-β-(2-Thienyl)styrene (5). The reaction of (*Z*)-β-bromostyrene with 2-thienyllithium was carried out under similar conditions to the conditions of A except for the Grignard reagent. A 1.2-equiv amount of 2-thienyllithium, prepared by direct metalation of thiophene, was used. The styrene **5** was obtained in 94% yield: NMR (CCl_4) δ 6.32 (d, J = 12 Hz, 1, PhC=CH), 6.55 (d, J = 12 Hz, 1, PhCH=C), 6.7–7.0 (m, 2, CH=CSC=CH), 7.1–7.3 (m, 6, ArH, SCH=C); IR (neat) 3025, 1600, 1440, 685 cm^{-1}.

(*E*)-β-(2-Thienyl)styrene (12): NMR (CCl_4) δ 6.8–7.5 (m, 10); IR (neat) 3020, 1600, 1440, 940, 685 cm^{-1}.

(*Z*)-β-[2-(*N*,*N*-Dimethylamino)phenyl]styrene (6): NMR (CCl_4) δ 2.76 (s, 6, CH_3), 6.38 (d, J = 12 Hz, 1, PhC=CH), 6.63 (d, 1, PhCH=C), 6.5–7.3 (m, 9, ArH); IR (neat) 1600, 690 cm^{-1}.

Preparative-Scale Synthesis of (*Z*)-β-[2-(*N*,*N*-Dimethylamino)phenyl]styrene. Using $PdCl_2$–PPh_3–CH_3Li. A mixture of $PdCl_2$ (0.090 g, 0.50 mmol) and triphenylphosphine (0.525 g, 2.0 mmol) in benzene (100 mL) was stirred at reflux for 1 h. To the resulting solution was added a solution of methyllithium (1.1 mmol) in ether (1.0 mL), with stirring, and the mixture was heated at reflux for 1 h. To the resulting homogeneous solution was added (*Z*)-β-bromostyrene (9.15 g, 50 mmol) in one portion. A solution of 2-(*N*,*N*-dimethylamino)phenyllithium, which was prepared from *N*,*N*-dimethylaniline (6.05 g, 50 mmol) and butyllithium (50 mmol) in hexane (30 mL), was diluted with 300 mL of benzene and then added dropwise with stirring to the above solution at reflux over a period of 6 h. After 30 min of stirring at reflux, the resulting solution was allowed to cool to room temperature and quenched by adding 100 mL of water. The ether extract was washed with water and then saturated NaCl solution, after which it was dried over Na_2SO_4. Distillation gave **6** (8.1 g, 71%); bp 100–103 °C (0.05 mmHg).

(*E*)-β-[2-(*N*,*N*-Dimethylamino)phenyl]styrene (13): NMR (CCl_4) δ 2.56 (s, 6, CH_3), 6.6–7.5 (m, 11); IR (neat) 1580, 970 cm^{-1}.

(*E*)-β-[2-(*N*,*N*-Dimethylaminomethyl)phenyl]styrene (14): NMR (CCl_4) δ 2.30 (s, 6, CH_3), 3.53 (s, 2, CH_2N), 6.9–7.9 (m, 11); IR (Nujol) 1590, 960 cm^{-1}.

(*Z*)-5-Decene (15): NMR (CCl_4) δ 0.90 (t, J = 5.8 Hz, 6, CH_3), 1.07–1.63 (m, 8, CH_2CH_2), 1.67–2.25 (m, 4, CH_2C=CCH_2), 5.27 (t, J = 5.2 Hz, 2, CH=CH); IR (neat) 1655, 778 cm^{-1}; mass spectrum m/e 140.

2-(*N*,*N*-Dimethylamino)-4′-methylbiphenyl (31). A suspension of $PdCl_2$ (0.045 g, 0.25 mmol) and PPh_3 (0.271 g, 1.03 mmol) in benzene (30 mL) was stirred at reflux until the solution became a yellow homogeneous solution (10 min). To the solution was added an ethereal solution of methyllithium (0.35 mL, 0.60 mmol). The color of the solution changed to pale yellow. After 1 h of stirring at reflux, a solution of *p*-iodotoluene (1.090 g, 5.00 mmol) in benzene (10 mL) was added for 10 min; then, a solution of 2-(*N*,*N*-dimethylamino)phenyllithium (4.0 mL, 6.0 mmol) was diluted with benzene (50 mL) and added dropwise over a 2.5 h period. After 1.5 h of additional stirring, the reaction mixture was allowed to cool to room temperature and quenched by adding 40 mL of water. Ether extracts (three 30-mL portions) were combined, washed with water and saturated NaCl solution, and dried over Na_2SO_4. Bulb-to-bulb distillation (bath temperature 190–194 °C (1.5 mmHg)) gave **31** (0.978 g, 4.43 mmol) in 89% yield: NMR ($CDCl_3$) δ 2.35 (s, 3, CH_3Ar), 2.50 (s, 6, NCH_3), 6.75–7.30 (m, 4, ArH), 7.15 (d, J = 9.0 Hz, 2, ArH), 7.45 (d, 2, ArH); IR (neat) 1490, 1450, 945, 815, 760, 745 cm^{-1}; mass spectrum m/e 211.

Alkylation and Arylation of (*E*)-β-Bromostyrene with Ruthenium Catalyst. (A) **Using $RuCl_2(PPh_3)_3$.** Typically, to a solution of (*E*)-β-bromostyrene (20 mg, 0.11 mmol) and $RuCl_2(PPh_3)_3$ (9.6 mg, 0.010 mmol) in benzene (3 mL) was added a solution of methylmagnesium bromide (0.50 mmol), and the mixture was heated at reflux for 17 h. After the mixture was quenched with water, the ether extract was subjected to GLC analysis which showed that (*E*)-propenylbenzene was obtained in 88% yield.

(B) **Using $RuCl_3$–PBu_3–K.** A mixture of anhydrous $RuCl_3$ (219 mg, 1.1 mmol), potassium (119 mg, 3.0 mmol), PBu_3 (966 mg, 4.8 mmol), and THF (10 mL) was heated at reflux for 16 h. Using the resulting green solution as catalyst, we reacted (*E*)-β-bromostyrene (244 mg, 1.2 mmol) with methylmagnesium bromide (6 mmol) in the usual manner. The products consisted of styrene (12%), (*E*)-propenylbenzene (30%), (*Z*)-propenylbenzene (4%), and (*E*)-β-bromostyrene (40%).

(C) **Using $RuCl_2(PPh_3)_4$–K.** A mixture of $RuCl_2(PPh_3)_4$ (24 mg, 0.018 mmol), potassium (2.0 mg, 0.051 mmol), and THF (3 mL) was stirred at reflux for 17 h. To the resulting homogeneous pale brown solution was added (*E*)-β-bromostyrene (37 mg, 0.20 mmol), with stirring, and subsequently a solution of methylmagnesium bromide (1.0 mmol) in ether (1 mL). After 12 h of additional stirring, the mixture was treated in the usual way. (*E*)-Propenylbenzene was obtained in 91% yield. The isomeric purity is over 96%.

(D) **Using $RuCl_2(PPh_3)_4$–PPh_3–Na/Hg.** A mixture of $RuCl_2(PPh_3)_4$ (2.61 g, 2.14 mmol), triphenylphosphine (1.12 g, 428 mmol), sodium amalgam, prepared from mercury (4 mL) and sodium (0.46 g), and toluene (10 mL) was stirred for 12 h at room temperature. Recrystallization of the resulting brown solid with a mixture of pentane and ether gave 0.93 g of a pale green complex; mp 119–120 °C. Using the complex (14.6 mg) as a catalyst, we reacted (*E*)-β-bromostyrene (0.0207 g, 0.113 mmol) with methylmagnesium bromide (0.5 mmol). (*E*)-Propenylbenzene was obtained in 81% yield along with the recovered (*E*)-β-bromostyrene (6%).

(*Z*)-(2-Phenylethenylthio)benzene (32). In a 50-mL flask was placed $Pd(PPh_3)_4$ (34 mg, 0.03 mmol). A solution of (*Z*)-β-bromostyrene (0.345 g, 1.88 mmol) in benzene (10 mL) was added, and the mixture was stirred at reflux for 1 h. Under reflux was added a solution of lithium benzenethiolate (2.0 mmol) in THF (10 mL), prepared from thiophenol and butyllithium, dropwise with stirring for 20 min. After 1 h of additional stirring, the reaction mixture was quenched with water. An ethereal extract was treated in the usual fashion. The GLC analysis showed that (*Z*)-(2-phenylethenylthio)benzene was obtained in 95% yield, and its isomeric purity was 100%: NMR (CCl_4) δ 6.46 (d, J = 10.5 Hz, 1, C=CHSPh), 6.66 (d, 1, PhCH=C), 7.26–7.65 (m, 10, ArH); IR (neat) 3025, 1600, 1440, 1360, 1025, 845, 770, 740, 685 cm^{-1}.

(*E*)-(2-Phenylethenylthio)benzene (33). $Pd(PPh_3)_4$ (82 mg, 0.07 mmol), (*E*)-β-bromostyrene (0.400 g, 2.19 mmol), and lithium benzenethiolate (2.23 mmol) were reacted in THF (10 mL). (*E*)-(2-Phenylethenylthio)benzene was obtained in 95% yield: NMR (CCl_4) δ 6.60 (d, J = 16 Hz, 1, C=CHSPh), 6.92 (d, 1, PhCH=C), 7.10–7.50 (m, 10, ArH); IR (neat) 3020, 1600, 1440, 1020, 940, 735, 685 cm^{-1}.

(*Z*)-1-Phenylthiohexene (34). $Pd(PPh_3)_4$ (0.207 g, 0.179 mmol) and 1-bromohexene (0.537 g, 3.30 mmol) in benzene (20 mL) were reacted at reflux for 1 h. The mixture was allowed to react with lithium benzenethiolate (3.30 mmol) in THF (22.5 mL) at reflux overnight. GLC showed that (*Z*)-1-phenylthiohexene was obtained in 98% yield, and its isomeric purity was 100%: NMR (CCl_4) δ 0.93 (t, J = 6 Hz, 3, CH_3), 1.1–1.7 (m, 4, CH_2CH_2), 2.1 (m, 2, C=CCH_2), 5.70 (dt, J = 9.5, 7.5 Hz, 1, BuCH=C), 6.14 (d, J = 9.5 Hz, 1, C=CHSPh), 7.0–7.4 (m, 5, ArH); IR (neat) 3070, 1590, 1440, 1030, 740, 690 cm^{-1}.

(*Z*)-(2-Ethylthioethenyl)benzene (35). To a solution of $Pd(PPh_3)_4$ (0.116 g, 0.10 mmol) in benzene (20 mL) was added (*Z*)-β-bromostyrene (0.366 g, 2.00 mmol). To the mixture was added, with stirring, a solution of lithium ethanethiolate (3.30 mL, 2.16 mmol), prepared from ethanethiol (0.132 g, 2.13 mmol) and a hexane solution of butyllithium (1.30 mL, 2.16 mmol) in THF (2 mL); the mixture was then diluted with 10 mL of benzene,

added dropwise at reflux over a 1.5 h period. After 1 h of additional stirring, the reaction mixture was cooled to room temperature and quenched with a 0.2 M HCl solution (20 mL). The standard treatment gave 93% of **35**: NMR ($CDCl_3$) δ 1.30 (t, J = 7.5 Hz, 3, CH_3), 2.78 (q, J = 7.5 Hz, 2, CH_2), 6.18 (d, J = 10.6 Hz, 1, PhC=CH), 6.45 (d, J = 10.6 Hz, 1, PhCH=C), 7.10–7.58 (m, 5 H, ArH); IR (neat) 1600, 1500, 1370, 1275, 850, 775, 720, 690 cm^{-1}; mass spectrum m/e 164.

1,1-Diphenylthio-2-phenylethylene. In a 100-mL, three-necked flask, fitted with a dropping funnel, a reflux condenser, a nitrogen inlet, and a magnetic stirring bar, was placed tetrakis(triphenylphosphine)palladium (0.117 g, 0.10 mmol). The flask was alternately evacuated and filled with argon on a vacuum line. A solution of an 1,1-dichloro-2-phenylethylene (0.371 g, 2.1 mmol) in 20 mL of benzene was added, and the mixture was stirred at reflux for 30 min. To the mixture was added dropwise a solution of lithium benzenethiolate, prepared from thiophenol (0.446 g, 4.0 mmol) and butyllithium (4.0 mmol), and then the mixture was diluted with 10 mL of benzene and refluxed for 1 h. After 4 h of stirring, the reaction mixture was cooled to room temperature and quenched by adding 0.2 M HCl (20 mL). The ether extract was washed, dried, and concentrated. The GLC analysis using an internal standard showed that 1,1-diphenylthio-2-phenylethylene[62] (**36**) was obtained in 96% yield (the conversion of the dihalide is 12%): NMR (CCl_4) δ 7.05 (s, 1, PhCH=C), 7.10–7.33 (m, 13, ArH), 7.42–7.70 (m, 2, ArH); IR (Nujol) 1585, 1480, 1440, 750, 740, 690 cm^{-1}; mass spectrum m/e 320. Even when the palladium catalyst, prepared from $PdCl_2$–PPh_3–CH_3Li, was used, the conversion of dichloride did not increase. The reaction of 1,1-dibromo-2-phenylethylene[60] under the same reaction conditions gave the ketene thioacetal in 96% yield. (The conversion of the dibromide was again only 10%.)

(62) A. J. Speziale, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 361.

Registry No. **1**, 766-90-5; **2**, 15325-54-9; **3**, 1657-45-0; **4**, 18138-87-9; **5**, 23516-73-6; **6**, 70197-43-2; **7**, 873-66-5; **8**, 6111-82-6; **9**, 1860-17-9; **10**, 16939-57-4; **11**, 21676-00-6; **12**, 26708-50-9; **13**, 70197-44-3; **14**, 52728-09-3; **15**, 7433-78-5; **16**, 56949-84-9; **17**, 70197-45-4; **18**, 768-00-3; **29**, 13343-78-7; **37**, 70197-46-5; **32**, 7214-56-4; **33**, 7214-53-1; **34**, 70197-34-1; **35**, 20890-79-3; **36**, 35550-81-3; (*Z*)-PhCH=CHBr, 588-73-8; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-PhCH=CHCl, 4604-28-8; (*Z*)-BuCH=CHBr, 13154-12-6; (*E*)-$Ph(CH_3)C$=CHBr, 16917-35-4; (*Z*)-1,2-dichloroethylene, 156-59-2; (*E*)-1,2-dichloroethylene, 156-60-5; (*Z*)-5-undecen-7-yne, 70197-33-0; 1,1-dichloro-2-phenylethylene, 698-88-4; (*Z*)-stilbene, 645-49-8; (*E*)-stilbene, 103-30-0; biphenyl, 92-52-4; MeLi, 917-54-4; BuLi, 109-72-8; *p*-MeC_6H_4Li, 2417-95-0; **19**, 2786-02-9; **20**, 2786-07-4; **21**, 22608-37-3; **22**, 27171-81-9; phenyllithium, 591-51-5; lithium benzenethiolate, 2973-86-6; lithium ethanethiolate, 30383-01-8; PhSNa, 930-69-8.

Supplementary Material Available: Analytical data of compounds **2–6**, **11–13**, **16**, **31**, **32**, and **34–36** (1 page). Ordering information is given on any current masthead page.

Hydroboration. 52. Monohaloborane–Methyl Sulfide Adducts as New Reagents for the Hydroboration of Alkenes. A Convenient Synthesis of Dialkylhaloboranes and Their Derivatives for Organic Synthesis[1]

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Reactions of alkenes with the recently discovered monochloroborane–methyl sulfide ($H_2BCl{\cdot}SMe_2$), monobromoborane–methyl sulfide ($H_2BBr{\cdot}SMe_2$), and monoiodoborane–methyl sulfide ($H_2BI{\cdot}SMe_2$) were investigated in detail in order to establish their usefulness as hydroborating agents. $H_2BCl{\cdot}SMe_2$ hydroborates alkenes rapidly and quantitatively at 25 °C. Simple distillation under low pressure affords pure R_2BCl. Similarly, the hydroboration of alkenes with $H_2BBr{\cdot}SMe_2$ followed by distillation affords pure R_2BBr in the case of hindered alkyl groups and the corresponding methyl sulfide complexes in the case of unhindered alkyl groups. Distillation of $R_2BBr{\cdot}SMe_2$ following the addition of 1 mol equiv of BBr_3 gives pure R_2BBr. The reactions of $H_2BI{\cdot}SMe_2$ are slower, but it reacts satisfactorily with alkenes in refluxing dichloromethane. Distillation affords dialkyliodoboranes almost free from SMe_2. These dialkylhaloboranes are readily converted into other dialkylboron derivatives by treatment with appropriate reagents. Such derivatives are useful as intermediates in organic synthesis.

We recently reported a detailed study of the hydroboration of alkenes with monochloroborane etherate, $H_2BCl{\cdot}OEt_2$ (MCBE).[3] This study revealed that MCBE is an excellent reagent for converting alkenes into dialkylchloroboranes. It provided for the first time a convenient general procedure for the synthesis of dialkylchloroboranes and their derivatives. Since then, such dialkylboron derivatives have been found to be excellent intermediates for a wide variety of synthetic applications.[4-7]

Unfortunately, monochloroborane etherate, although a superb hydroborating agent, suffers from some practical difficulties. The most convenient preparation of the reagent starts from lithium borohydride, a relatively expensive chemical. Moreover, the reagent can be prepared only as a dilute ether solution and, therefore, must be handled as such, since it disproportionates upon concentration. MCBE possesses only limited stability at room

(1) For preliminary reports on some aspects of the present study, see: (a) H. C. Brown and N. Ravindran, *J. Org. Chem.*, **42**, 2533 (1977); (b) H. C. Brown and N. Ravindran, *Synthesis*, 695 (1977).

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