Diastereoselectivity and Reaction Pathway of the Reactions of Benzaldehyde with Allylic Iodides in the Presence of Sn or Pb

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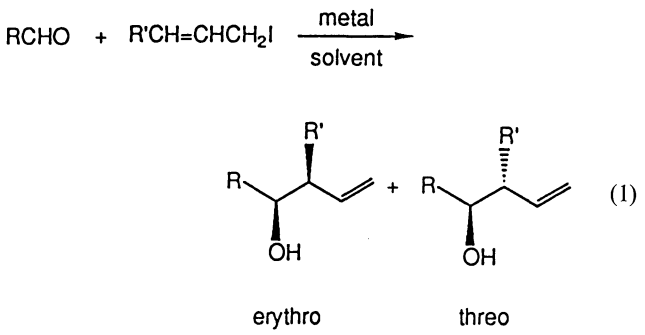
The relative reactivity and stereoselectivity were determined in the Sn- or Pb-promoted reactions of substituted benzaldehydes with 3-iodo-1-propene and 1-iodo-2-butene. The reactivity data suggested that the reactions go through a direct nucleophilic addition mechanism. No indication of the occurrence of electron transfer was obtained by the dehalogenation probe experiment. The diastereoselectivity was low in the Sn/THF system but was high in Pb/DMF. Large solvent effects were observed in the *erythro* selectivity for the Sn-promoted reaction; *erythro* : *threo* ratio was 31 : 69 in CH_2Cl_2 and 84 : 16 in HMPA.

Nucleophilic alkylations and allylations of carbonyl compounds with organometallics are one of the most useful reactions in organic synthesis. In general, two types of reactions are possible in such nucleophilic additions; the reaction of organometallic reagent on the one hand and the use of alkyl or allyl halide plus metal on the other. Although the latter type of reaction (often called Barbier-type, Eq. 1) has the advantage of simple manipulation, stereoselectivity is low in many cases. For example, the Barbier-type addition of 1-bromo-2-butene to benzaldehyde in the presence of Sn, Zn, or Mg gave nearly 1 : 1 mixture of the diastereomers.[1,2]



Mechanistically there also remain several points to be clarified in the Barbier-type reaction; (1) Does the reaction occur on the metal surface or in solution? (2) What is the true reacting reagent? (3) Does electron transfer occur from the metal or an organometallic reagent formed in situ to a carbonyl compound? (4) What does the transition state look like?

We report in this article the experimental results which resolve some of the mechanistic questions and give a clue to improve the stereoselectivity of the reaction.

Results and Discussion

The two reaction systems were initially chosen in the present study; Sn in THF and Pb in DMF. This is

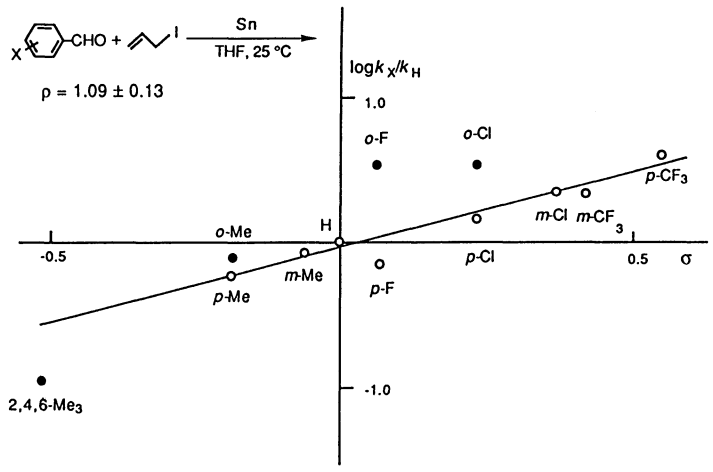


Fig. 1. Variations of reactivity with σ values for the Sn-promoted Barbier reactions of substituted benzaldehydes with 3-iodo-1-propene at 25 °C in THF.

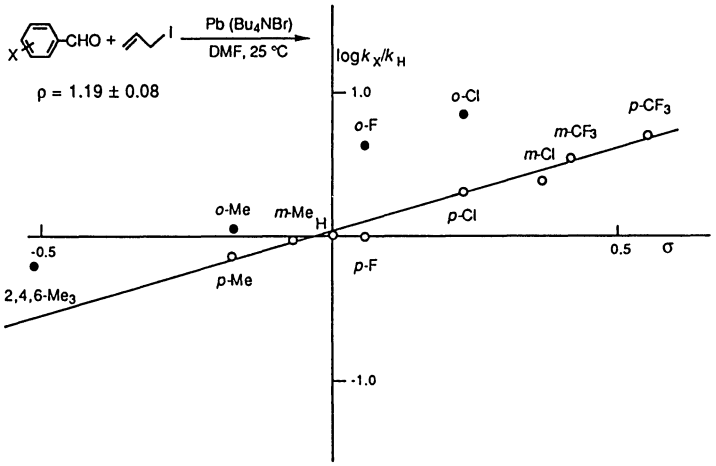


Fig. 2. Variations of reactivity with σ values for the Pb-promoted Barbier reactions of substituted benzaldehydes with 3-iodo-1-propene at 25 °C in DMF.

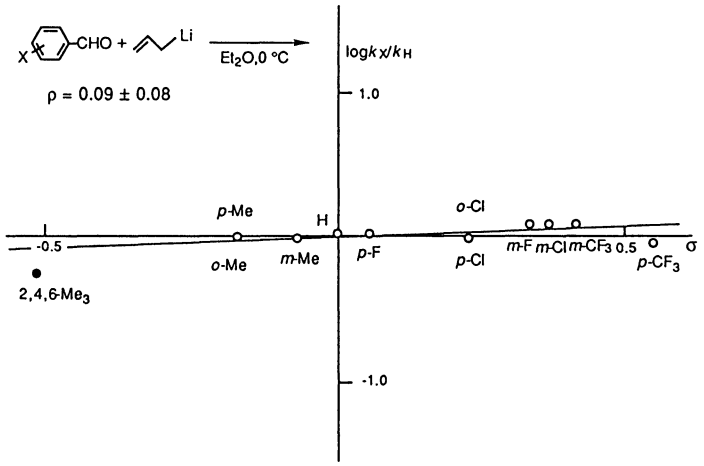
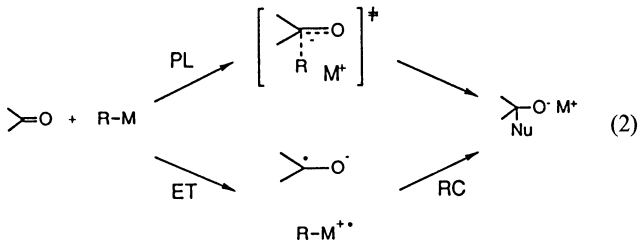


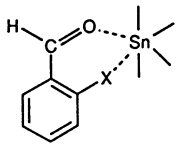
Fig. 3. Variations of reactivity with σ values for the reactions of substituted benzaldehydes with allyllithium at 0 °C in ether.

because Sn is one of the most commonly used metals in the Barbier-type reactions,[1,3,4] while the Pb-promoted reaction is rather new and no data have been reported on the diastereoselectivity.[5] Furthermore, it would be expected to observe some differences between the two group 14 metals.

The relative reactivities in the Barbier-type reactions of substituted benzaldehydes with 3-iodo-1-propene in the presence of Sn powder (in THF) or a Pb plate (in DMF) were determined at 25 °C by the competition experiments.[6] The substituent effects in the reactions with allyllithium were also measured for comparison in a similar manner at 0 °C in ether. In Figs. 1—3 are shown the Hammett plots of these reactions. Since the σ constants of the ortho substituents were not determined, the $\log(k_X/k_H)$ values for the ortho derivatives were plotted against the corresponding para-substituent constants and indicated by closed circles. Although the points for the *p*-F substituent deviated downward,[7] other *m*- and *p*-substituents gave reasonably good straight lines, from which the ρ values were calculated.

As shown in Fig. 3, an extremely small ρ value was observed for the allyllithium addition. This is not unexpected since similar small ρ values have been reported for related addition reactions of various organolithium reagents and allylmagnesium bromide to benzaldehyde or benzophenone.[6,8,9] These reactions have been concluded on the basis of the kinetic isotope effect and other criteria to proceed through the rate-determining electron transfer mechanism (ET rate determining, in Eq. 2), and therefore the reaction of allyllithium with benzaldehyde is also likely to go through electron transfer from the lithium reagent to benzaldehyde. On the other hand, the two Barbier-type reactions showed significantly large positive ρ values (Figs. 1 and 2), which are good indication that the reactions





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Structure 1.

have considerable nucleophilic character (PL in Eq. 2). Although the substituent effects themselves do not exclude the possibility that the reactions go through fast electron transfer followed by a subsequent slow radical coupling process (RC rate determining), such mechanism is very unlikely because the dehalogenation probe, a new criterion for the occurrence of electron transfer from a reagent to aromatic carbonyl compounds,[10] was found to be negative. In this probe experiment, *o*-bromo- or *o*-iodobenzophenone is treated with a reagent. If electron transfer occurred, the halobenzophenone ketyl thus formed would undergo dehalogenation to yield benzophenone and other dehalogenated products, and therefore the detection of such products can be evidence for the occurrence of electron transfer. The usefulness of the criterion was confirmed for the Grignard reaction recently.[10]

The polar nucleophilic character of the Barbier-type reactions is consistent with the reactivity difference between benzaldehyde and benzophenone. In the Sn-promoted Barbier-type reaction, benzaldehyde proceeded completely at 25 °C within 1 h while benzophenone did not yield the product at all under the same reaction conditions; the larger reactivity of aldehyde compared to ketone is a well-known characteristic for nucleophilic addition reactions of carbonyl compounds. In contrast, allylmagnesium bromide was found to react with benzaldehyde and benzophenone in similar rates, $k_{BP}/k_{BA}=0.76\pm0.07$, which is consistent with the rate-determining electron transfer mechanism since the reduction potential for the two substrates is quite similar ($E_{red}=1.84$ and 1.80 V vs. SCE, respectively).

It is noticeable in Fig. 1 that the points for ortho substituents deviate upward in the Sn promoted Barbier-type reactions. We have previously observed similar deviations for *o*-halogen substituents in the reaction of benzaldehyde with $Bu_3SnCH_2CH{=}CH_2$;[9] since the *o*-halogen substituents not only accelerate the reaction but also increase the *erythro* selectivity in the $Bu_3SnCH_2CH{=}CH_2$ reaction, the *o*-halogen effects could be attributed to a chelating interaction between the halogen atom and the attacking tin reagent in the acyclic transition state.[9] In contrast to this, the *o*-halogen substituent effects on reactivity in the present Barbier-type reactions are not accompanied by the change in the stereoselectivity of the product (vide infra). The reason for this difference is not clear at present, but one possibility is that the halogen atom interacts, together with the carbonyl oxygen, with the acidic tin atom of $I_2Sn(CH_2CH{=}CH_2)_2$ in situ formed in the Barbier-type reaction as shown in **1**; such chelation makes the aldehyde more electron-deficient and then more reactive toward another molecule of nucleophile.

The evidence of the in situ formation of the organotin reagent was obtained in two ways. First, the addition of benzaldehyde to the supernatant solution prepared from 1-iodo-2-butene and tin powder afforded the expected products in high yields with the same *erythro*:*threo* ratio as observed under the usual Barbier conditions. Second, the supernatant solution from the mixture of 3-iodo-1-propene and tin powder in [$^2H_8$]THF gave an NMR spectrum which is consistent with $I_2Sn(CH_2CH{=}CH_2)_2$.[4b] These results eliminate the possibility of electron transfer from the metal to the aldehyde or the halide[11] at least for the Sn-promoted Barbier reaction.

In the Pb-mediated reaction in DMF, not only the *o*-halogen substituents but 2,4,6-Me_3 substituents appear to accelerate the reaction. This is totally unexpected and we have no rationalization for this phenomenon. However, further study revealed that the results can be attributed to DMF rather than Pb (vide infra).

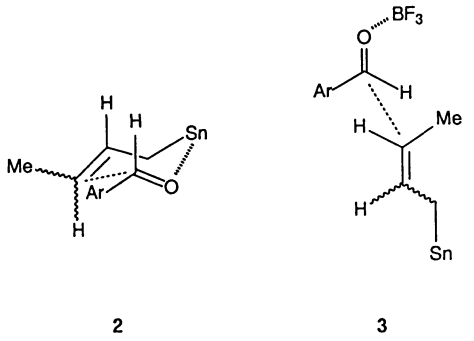
Table 1 summarizes the *erythro*:*threo* ratios in the Barbier-type reactions of substituted benzaldehydes with 1-iodo-2-butene. It can be seen that the selectivity is low in the Sn-promoted reaction, consistent with the earlier report,[1] and is essentially independent of the substituents used. These results can be rationalized by considering a cyclic six-membered ring transition state (Chart 1, **2**) as usually assumed for the Barbier-type reactions.[12] In such a transition state, the *erythro*:*threo* ratio should basically be governed by the

Table 1. *Erythro*: *Threo* Ratios in the Barbier-Type Additions of Substituted Benzaldehydes with 1-Iodo-2-butene[a]

Substituent	Sn/THF	Pb/DMF
H	52:48	91:9
o-Cl	54:46	95:5
p-Cl	54:46	92:8
o-Me	56:44	95:5
p-Me	55:45	93:7
2,4,6-Me_3	51:49	78:22

a) Reactions were carried out at 25 °C. Figures are the averages of more than two runs, and the reproducibility is ±2%.

E: Z ratio of the butenyl unit of the in situ formed tin reagent[13] and the ratio would be independent of the substituent. This is in sharp contrast to the reaction with $Bu_3SnCH_2CH{=}CHCH_3$, which is considered to go through an acyclic transition state (Chart 1, **3**); here the *erythro*: *threo* ratio is independent the E: Z ratio of the reagent[14] but is influenced by the *o*-substituent of benzaldehyde.[10]



2 **3**

Chart 1.

On the other hand, the Pb-promoted reaction showed fairly high *erythro* selectivity. The results may suggest that this Barbier-type reaction would be of practical use in the diastereoselective synthesis. The difference in the diastereoselectivity between the Sn- and Pb-promoted reactions must be attributed to either the metal (Sn vs. Pb) or the solvent used (THF vs. DMF) or both. Since the Pb-promoted reaction proceeded only in DMF while the Sn-promoted reaction was found to proceed in various solvents, the latter reaction was carried out in DMF to clarify this point.

The substituent effects on reactivity in the Sn-promoted reaction in DMF were measured as in THF and illustrated in Fig. 4. The Hammett plots showed a quite similar pattern to those obtained for the Pb-promoted reaction in DMF. Apparently, the differ-

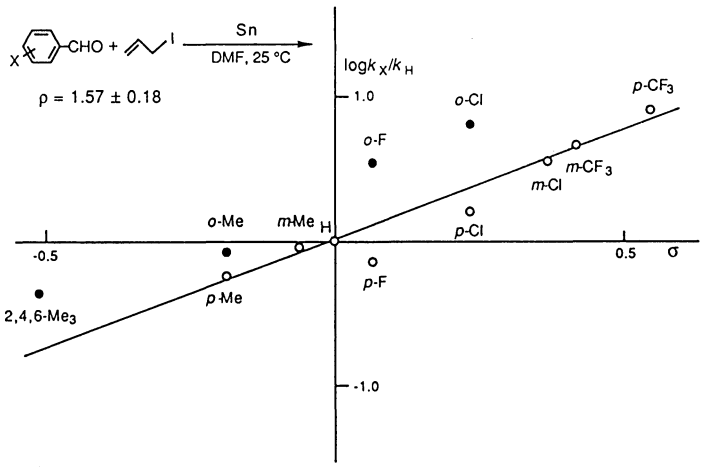


Fig. 4. Variations of reactivity with σ values for the Sn-promoted Barbier reactions of substituted benzaldehydes with 3-iodo-1-propene at 25 °C in DMF.

Table 2. Solvent Dependence of the *Erythro*: *Threo* Ratio in the Sn-Promoted Barbier Reaction

Solvent	DN[a]	Time/h	*Erythro*: *Threo*[b]
HMPA	38.8	1	84:16 (81)
DMF	26.6	1	84:16 (100)
NH_2CHO	24.7	1	66:34 (100)
THF	20.1	1	52:48 (100)
CH_3CN	14.1	5	54:46 (55)
C_6H_6	0.1	12	34:66 (60)
CH_2ClCH_2Cl	0.0	12	35:65 (60)
CH_2Cl_2		5	31:69 (72)
Hexane		24	40:60 (62)
THF+0.1 equiv[c] NMPA		1	64:36 (84)
THF+0.5 equiv[c] HMPA		1	79:21 (99)
THF+1.0 equiv[c] HMPA		1	80:20 (99)
C_6H_6+1.0 equiv[c] HMPA		1	76:24 (92)
CH_2Cl_2+1.0 equiv[c] HMPA		1	78:22 (100)

a) V. Gutmann, "The Donor–Acceptor Approach to the Molecular Interaction," Plenum, New York (1978). b) Reproducibility is in most cases ±2%. The figures in parentheses are absolute yields determined by GC. c) Molar equivalent of HMPA to 1-iodo-2-butene.

ence in the solvent is much more important than the difference in the metal. Then the *erythro*: *threo* ratio was determined for the Sn-promoted reaction of parent benzaldehyde with 1-iodo-2-butene in various solvents. As shown in Table 2, the stereoselectivity was found highly dependent on the solvent. Interestingly the use of a solvent of larger donor number (DN) gave a higher *erythro* selectivity. Furthermore, the addition of 0.5 or 1.0 equiv of HMPA to solvents of small DN not only accelerates the reaction but enhances the *erythro* selectivity close to the value observed in HMPA. These results suggest the occurrence of some donor–acceptor interaction between HMPA and the reagent or the substrate at the transition state.

It was reported that in the reaction of aldehyde with chloroorganotin reagents, in situ prepared by the reaction between $Bu_3SnCH_2CH{=}CHCH_3$ and Bu_2SnCl_2, the *erythro*: *threo* ratio of the product is related to the *Z*: *E* ratio of the reagents.[13] The present results might be then rationalized by assuming that the *Z*: *E* ratio of $I_2Sn(CH_2CH{=}CHCH_3)_2$ is high in a solvent of large DN. Alternatively and more likely, the molecule of high lone-pair donating ability such as HMPA or DMF may interact with the tin reagent and prevent the otherwise important interaction between the reagent and the aldehyde oxygen in the transition state. Consequently, the reaction becomes to proceed via an acyclic transition state and affords high *erythro* selectivity as in the case of $Bu_3SnCH_2CH{=}CHCH_3$.[14] In any event, the present findings may provide a clue to improving the stereoselectivity of the Barbier-type reactions.

The present experimental results may be summarized as follows. (1) The Barbier-type reaction does not occur on the metal surface but in solution. (2) The reaction appears to go through the direct polar addition mechanism. No evidence was obtained for the occurrence of electron transfer during the reaction. (3) The diastereoselectivity is highly dependent on the solvent used. The dependence may be rationalized by the switching of the transition state from cyclic for the reaction in the solvent of low DN to acyclic for the reaction in the solvent of high DN. The origin of ortho-substituent effect on the reactivity in DMF is not clear, and further study is needed to clarify this point.

Experimental

Materials. Substituted benzaldehydes were commercially available and purified by distillation. THF was distilled from $LiAlH_4$ and benzophenone/Na successively. Dichloromethane was distilled from CaH_2. Other solvents were fractionally distilled and dried over MS 4A. 1-Iodo-2-butene was prepared from the reaction of 1-bromo-2-butene and NaI in acetone. Commercial tin powder (Mitsuwa, 200 mesh, >99% purity) and lead plate (Nakarai, 0.5×100×900 mm, 99% purity) were purified according to the literature.[5,15] Allyllithium was prepared from allyltriphenyltin and phenyllithium as described in the literature[16] and standardized.[17] Allylmagnesium bromide was prepared from allyl bromide and doubly sublimed Mg (Ventron).

Reactions. The Barbier-type reactions were carried out under stirring at 25 °C under the dry nitrogen atmosphere. The general procedure for the Pb-promoted reaction is similar to that in the literature[5] except for the addition of Me_3SiCl. Since the added Me_3SiCl showed an only moderate effect on the reactivity, all the Pb-promoted reactions were carried out without Me_3SiCl. The reactions with allyllithium and allylmagnesium bromide were run as described previously.[6] All reactions gave the expected addition products exclusively. The material balance was confirmed for the unsubstituted benzaldehyde and found excellent (100.0±0.1%). The products were isolated and characterized by ^1H NMR (Bruker-360, $CDCl_3$) and IR. The ^1H NMR chemical shifts of the products are as follows:

Substituted 1-Phenyl-3-buten-1-ol; H, δ=2.29 (1H, s), 2.46—2.50 (2H, m), 4.68 (1H, dd, *J*=6.0, 7.0 Hz), 5.09—5.16 (2H, m), 5.72—5.80 (1H, m), 7.22—7.34 (5H, m); ***o*-Me**, 2.06 (1H, s), 2.32 (3H, s), 2.40—2.50 (2H, m), 4.95 (1H, dd, *J*=4.6, 8.1 Hz), 5.12—5.20 (2H, m), 5.79—5.90 (1H, m), 7.10—7.45 (4H, m); ***m*-Me**, 2.00 (1H, s), 2.36 (3H, s), 2.50—2.54 (2H, m), 4.67—4.72 (1H, m), 5.12—5.20 (2H, m), 5.78—5.86 (1H, m), 7.08—7.26 (4H, m); ***p*-Me**, 1.97 (1H, s), 2.34 (3H, s), 2.48—2.53 (2H, m), 4.70 (1H, t, *J*=6.4 Hz), 5.11—5.19 (2H, m), 5.75—5.87 (1H, m), 7.16 (2H, d, *J*=7.7 Hz), 7.25 (2H, d, *J*=8.1 Hz); **2,4,6-Me$_3$**, 1.80 (1H, s), 2.24 (3H, s), 2.41 (6H, s), 2.46—2.76 (2H, m), 5.11—5.20 (3H, m), 5.79—5.91 (3H, m), 6.82 (2H, s); ***o*-Cl**, 2.18 (1H, s), 2.35—2.68 (2H, m), 5.17—5.22 (3H, m), 5.82—5.93 (1H, m), 7.18—7.58 (4H, m); ***m*-Cl**, 2.05 (1H, s), 2.44—2.56 (2H, m), 4.71—4.74 (1H, m), 5.18 (2H, dd, *J*=10.7, 15.8 Hz), 5.74—5.85 (1H, m), 7.21—7.38 (4H, m); ***p*-Cl**, 2.05 (1H, s), 2.43—2.51 (2H, m), 4.72 (1H, dd, *J*=5.3, 7.7 Hz), 5.16 (2H, dd, *J*=10.7, 15.8 Hz), 5.72—5.84 (1H, m), 7.28—7.33 (4H, m); ***o*-F**, 2.09 (1H, d, *J*=3.7 Hz), 2.47—2.62 (2H, m), 5.06—5.08 (1H, m), 5.14—5.20 (2H, m), 5.77—5.87 (1H, m), 6.99—7.50 (4H, m); ***p*-F**, 2.04 (1H, s), 2.46—2.52 (2H, m), 4.72 (1H, dd, *J*=5.6, 7.4 Hz), 5.16 (2H, dd, *J*=10.7, 17.4 Hz), 5.73—5.83 (1H, m), 7.01—7.06 (2H, m), 7.31—7.35 (2H, m); ***m*-CF$_3$**, 2.10 (1H, d, *J*=3.2 Hz), 2.43—2.56 (2H, m), 4.76—4.82 (1H, m), 5.16—5.22 (2H, m), 5.74—5.86 (1H, m), 7.36—7.64 (4H, m); ***p*-CF$_3$**, 2.10 (1H, s), 2.43—2.59 (2H, m), 4.76—4.83 (1H, m), 5.16—5.21 (2H, m), 5.74—5.86 (1H, m), 7.48 (2H, d, *J*=8.4 Hz), 7.61 (2H, d, *J*=8.4 Hz):

1-Phenyl-2-methyl-3-buten-1-ol, Spectra were measured for the threo (*t*)-erythro (*e*) mixture; **H**, 0.89 (3H, *t*, d, *J*=7.0 Hz), 1.01 (1H, *t*, s), 2.18 (2H, *e*+*t*, m), 4.35 (1H, *t*, d, *J*=7.7 Hz), 4.59 (1H, *e*, d, *J*=5.6 Hz), 5.02—5.07 (2H, *e*, m), 5.15—5.21 (2H, *t*, m), 5.70—5.83 (2H, *e*+*t*, m), 7.24—7.35 (10H, *e*+*t*, m); ***o*-Me**, 0.91 (3H, ,*t*, d, *J*=7.0 Hz), 1.06 (3H, *e*, d, *J*=7.0 Hz), 1.85 (1H, *e* or *t*, s), 2.07 (1H, *e* or *t*, s), 2.31 (3H, *e*, s), 2.35 (3H, *t*, s), 2.50—2.57 (2H, *e*+*t*, m), 4.66 (1H, *t*, d, *J*=7.7 Hz), 4.83 (1H, *e*, d, *J*=5.6 Hz), 5.04 (2H, *e*, dd, *J*=10.5, 17.2 Hz), 5.18 (2H, *t*, dd, *J*=11.6, 17.2 Hz), 5.76—5.90 (2H, *e*+*t*, m), 7.10—7.45 (8H, *e*+*t*, m); ***p*-Me**, 0.85 (3H, *t*, d, *J*=6.7 Hz), 1.01 (3H, *e*, d, *J*=7.0 Hz), 1.98 (1H, *e* or *t*, s), 2.15 (1H, *e* or *t*, s), 2.33 (6H, *e*+*t*, s), 2.40—2.60 (2H, *e*+*t*, m), 4.31 (1H, *t*, d, *J*=7.7 Hz), 4.54 (1H, *e*, d, *J*=5.6 Hz), 5.03 (2H, *e*, dd, *J*=11.2, 16.1 Hz), 5.17 (2H, *t*, dd, *J*=10.5, 17.2 Hz), 5.69—5.86 (2H, *e*+*t*, m), 7.11—7.14 (8H, *e*+*t*, m); **2,4,6-Me$_3$**, 0.79 (3H, *t*, d, *J*=7.0 Hz), 1.26 (3H, *e*, d, *J*=6.7 Hz), 1.79 (1H, *e* or *t*, s), 1.96 (1H, *e* or *t*, s), 2.23 (3H, *e* or *t*, s), 2.24 (3H, *e* or *t*, s), 2.37 (6H, *e*, s), 2.41 (6H, *t*, s), 2.84 (2H, *e*+*t*, m), 4.75—5.27 (6H, *e*+*t*, m), 5.46—5.56 (1H, *e*, m), 5.83—5.93 (1H, *t*, m), 6.78 (2H, *e*,

s), 6.80 (2H, *t*, s); ***o*-Cl**, 0.98 (3H, *e*, d, *J*=7.0 Hz), 1.02 (3H, *t*, d, *J*=6.7 Hz), 1.97 (1H, *e*, s), 2.14 (1H, *t*, s), 2.52—2.64 (1H, *t*, m), 2.66—2.77 (1H, *e*, m), 4.95—5.18 (6H, *e*+*t*, m), 5.78—5.89 (2H, *e*+*t*, m), 7.14 (8H, *e*+*t*, m); ***p*-Cl**, 0.86 (3H, *t*, d, *J*=7.0 Hz), 0.98 (3H, *e*, d, *J*=7.0 Hz), 2.06 (1H, *e*, s), 2.23 (1H, *t*, s), 2.36—2.47 (1H, *t*, m), 2.47—2.58 (1H, *e*, m), 4.33 (1H, *t*, d, *J*=7.7 Hz), 4.57 (1H, *e*, d, *J*=5.3 Hz), 5.05 (1H, *e*, dd, *J*=10.8, 17.2 Hz), 5.15—5.20 (6H, *t*, m), 5.67—5.79 (2H, *e*+*t*, m), 7.20—7.32 (8H, *e*+*t*, m).

Relative Reactivity. The relative reactivities of substituted benzaldehydes with allyllithium were determined as reported previously.[6] The reactivity ratios in the Barbier-type reactions were measured as follows. A pair of benzaldehydes (normally the parent and a substituted one, 0.2 mmol each), 3-iodo-1-propene (0.4 mmol), and naphthalene (internal standard, ca. 0.2 mmol) were placed in a flame-dried, serum-capped test tube and dissolved in 2 mL of dry THF. A half of the solution was transferred by means of a syringe into a test tube which contained Sn powder (0.1 mmol) and the mixture was stirred at 25 °C for 1 h. The solution was hydrolyzed, extracted with ether, dried over $MgSO_4$, and subjected to GC analysis (2-m glass column packed with 3% PEG-HT). The relative intensity of each reactant to that of the internal standard was compared to the corresponding relative intensity from the solution that was not mixed with Sn powder. The fraction of reaction was calculated for both reactants, and the reactivity ratio was computed according to Eq. 3. The Pb-promoted reaction was carried out in a similar manner

$$k_A/k_B = \log(1-f_A)/\log(1-f_B) \quad (3)$$

except that the reaction was initiated by adding 3-iodo-1-propene (0.2 mmol) and a Pb plate (0.5×5.0×5.0 mm) to a dry DMF solution which contained a pair of benzaldehydes (0.1 mmol each), Bu_4NBr (0.2 mmol), and naphthalene (0.1 mmol). Similar experiments were carried out for the 1 : 1 mixture of benzaldehyde and benzophenone, and their relative reactivities were measured.

Reactions with Supernatant Solution. In a flame-dried test tube were placed Sn powder (0.1 mmol), 3-iodo-1-propene (0.2 mmol) and [$^2H_8$]THF (1.0 mL), and the mixture was stirred at 25 °C for 1.5 h. The solid was eliminated by centrifugation, and the supernatant solution was transferred to an NMR tube and its spectrum was measured (Hitachi R-90H). In separate experiments, the supernatant solution prepared from 1-iodo-2-butene and Sn was mixed with benzaldehyde and the *erythro* : *threo* ratio was measured.

Dehalogenation Experiment. In a flame-dried test tube were placed *o*-bromobenzophenone (0.4 mmol), small amount of dibenzyl ether (internal standard), and dry THF (2 mL). To a half of the solution were added Sn powder (0.2 mmol) and 3-iodo-1-propene (0.2 mmol), and the mixture was stirred for 1 h at 25 °C. After the usual work-up, the organic layer was analyzed by GC (PEG-HT, 2 m), which showed that the reactant was recovered quantitatively.

Diastereomer Ratio. In a test tube were placed the parent or a substituted benzaldehyde (*o*-Me, *p*-Me, *o*-Cl, *p*-Cl, or 2,4,6-Me_3, 0.2 mmol) and dry THF (1 mL), and were added Sn powder (0.3 mmol) and 1-iodo-2-butene (0.6 mmol). The mixture was stirred at 25 °C for 1 h, hydrolyzed, extracted with ether, and dried over $MgSO_4$. The diastereomer ratio was determined by GC (capillary, CBP20, 25 m). For some reactions the ratio was also measured by NMR (Bruker-360) and the results obtained by GC and NMR were in perfect agreement.

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