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Novel Homologation Reaction of Arylzincates Bearing a Leaving Group at the Ortho and Meta Positions

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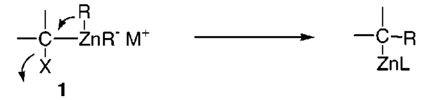
Arylzincates bearing a leaving group at the ortho, meta, and para positions were generated by iodine/zinc exchange reaction of the corresponding iodoaryl sulfonates with Bu_3ZnLi, and their reactivity was investigated via product analysis after hydrolysis and treatment with iodine. Zincates derived from *o*-iodophenyl triflates and tosylate underwent homologation reaction to give *o*-butylphenylzinc species. *o*-Benzyne as an intermediate of the reaction was demonstrated by the lack of regioselectivity for trisubstituted zincates. Zincates derived from *m*-iodophenyl triflates also underwent homologation leading to *m*-butylphenylzinc species. Similar product ratios observed in the reactions of regioisomeric trisubstituted iodophenyl triflates as well as the formation of radical reaction byproducts suggested the involvement of *m*-benzyne intermediate. *p*-(Trifluoromethanesulfonyloxy)phenylzincate was thermally stable at room temperature; generation of *p*-benzyne was not observed.

Homologation of organometallics is becoming of increasing importance in organic synthesis because subsequent bond formation of the resulting organometallics leads to the convergent construction of complex carbon frameworks by a one-pot procedure.[1] Recent reports from this laboratory revealed that organozincates **1** and **2** bearing leaving groups at the α- and γ-position, respectively, undergo 1,2-migration at low temperatures to give the corresponding homologated organozinc reagents (eqs 1 and 2).[2] More recently, we have shown that facile 1,2-migration is also observed for arylzincates **3**, bearing a leaving group at the benzylic position, despite the initial formation of dearomatized organozinc species **4** (eq 3).[3]



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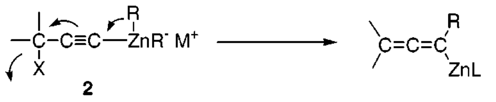

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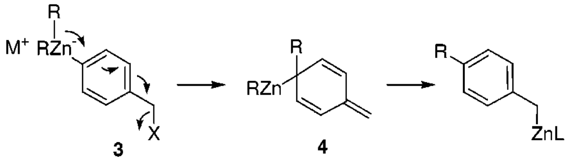
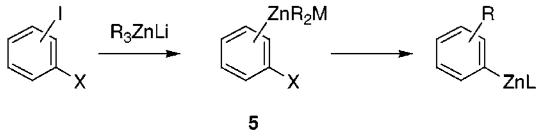


(3)

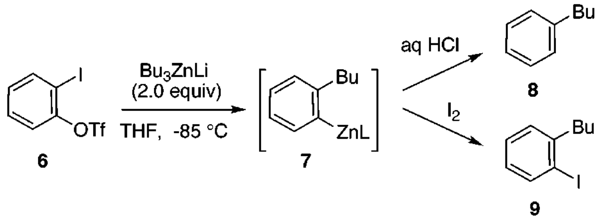
To clarify the scope of 1,2-migration of organozincates, we investigated the reactivity of phenylzincates **5** bearing a leaving group directly at the benzene ring (eq 4). Phenylzincates **5** (R = Bu) were generated from the corresponding iodoarenes by iodine/zinc exchange[4,2] with Bu_3ZnLi, and their reactions were studied on the basis of product analysis after hydrolysis and treatment with iodine. We wish to report herein the results of the study that revealed that arylzincates bearing a leaving group at the ortho and meta position undergo a novel homologation reaction not through a pathway involving 1,2-migration.



(4)

Results and Discussion

2-Iodophenyl triflate (**6**) was treated with Bu_3ZnLi (2.0 equiv) in THF at −85 °C for 0.5 h. Hydrolysis of the resulting mixture with aqueous HCl−THF gave butylbenzene (**8**) in 62% yield[5] (eq 5). On the other hand, iodination product **9** was obtained in 68% yield by treatment of the same reaction mixture with I_2, demonstrating the generation of 2-butylphenylzinc species **7**.



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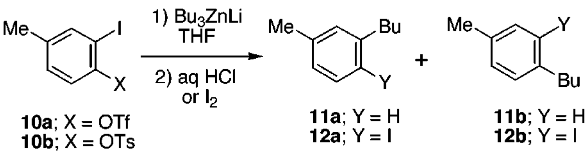

(6)

Under similar conditions at −85 °C, 4-methyl-2-iodophenyl triflate (**10a**) gave a mixture of the butylation

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(1) (a) Knochel, P. In*Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 865. (b) Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1988**, *110*, 4718. (c) Lipshutz, B. H.; Wood, M. R. *J. Am. Chem. Soc.* **1994**, *116*, 11689. (d) Marek, I.; Normant, J.-F. *Chem. Rev.* **1996**, *96*, 3241.

(2) (a) Harada, T.; Hara, D.; Hattori, K.; Oku, A. *Tetrahedron Lett.* **1988**, *29*, 3821−3824. (b) Harada, T.; Katsuhira, T.; Osada, A.; Iwazaki, K.; Maejima, R.; Oku, A. *J. Am. Chem. Soc.* **1996**, *118*, 11377 and references therein. (c) Harada, T.; Oku, A. In *Organozinc Reagents. A Practical Approach*; Knochel, P., Jones, P., Eds.; Oxford University Press: Oxford, 1999; p 101.

(3) (a) Harada, T.; Kaneko, T.; Fujiwara, T.; Oku, A. *J. Org. Chem.* **1997**, *62*, 8966. (b) Harada, T.; Kaneko, T.; Fujiwara, T.; Oku, A. *Tetrahedron* **1998**, *54*, 9317.

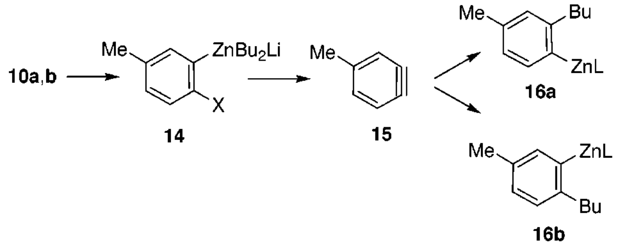
10.1021/jo990937m CCC: $18.00

Table 1. Reaction of Iodophenyl Sulfonates 10a,b with Bu$_3$ZnLi[a]

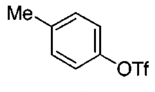
entry	substrate	electrophile	conditions	products	ratio[b]	yield (%)
1	**10a**	aq HCl	−85 °C, 0.5 h	**11a**, **11b**	1.1:1	65
2	**10b**	aq HCl	−85 °C, 0.5 h	**13**		87
3	**10b**	aq HCl	0 °C, 1 h	**11a**, **11b**	1.1:1	63
4	**10a**	I$_2$	−85 °C, 0.5 h	**12a**, **12b**	1.3:1	55
5	**10b**	I$_2$	0 °C, 1 h	**12a**, **12b**	1.3:1	66

[a] All reactions were carried out by adding substrate to a THF solution of Bu$_3$ZnLi (2.0 equiv) at −85 °C. [b] Determined by GC analysis.

Scheme 1



products **11a** and **11b** nonselectively (eq 6, entry 1 in Table 1). Arylzincate derived from tosylate **10b** was less reactive at −85 °C and afforded 4-methylphenyl tosylate (**13**) (entry 2). At 0 °C, nonselective formation of **11a** and **11b** (1.1:1, 63%) was observed also from **10b** (entry 3). Generation of the corresponding arylzinc species **16a**,**b** (Scheme 1) was verified by the formation of iodoarenes **12a** and **12b** in I$_2$ trapping experiments (entries 4 and 5). Arylzincate **14**, produced by iodine/zinc exchange reaction, would undergo 1,2-migration to give **16a**. The lack of regioselectivity observed indicates that such concerted pathway is energetically less favorable than a stepwise pathways involving *o*-benzyne[6–7] as an intermediate. Thus, arylzincate **14** undergoes β elimination to generate *o*-benzyne **15**. Subsequent nonselective carbometalation by Bu$_2$Zn and/or Bu$_3$ZnLi gives a mixture of **16a** and **16b**.



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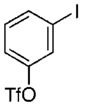
In comparison with arylzincates derived from *o*-iodophenyl triflates, those derived from *m*- and *p*-iodophenyl triflates were found to be considerably more stable. Thus, treatment of 3- and 4-iodophenyl triflate **17** and **18** with Bu$_3$ZnLi (2.0 equiv) in THF at −85 °C for 0.5 h and hydrolysis of the resulting mixture gave phenyl triflate in 95% and 93% yield, respectively. An arylzincate derived from **18** was stable even at room temperature, affording phenyl triflate (85%) in the reaction at room temperature for 20 h. On the other hand, at the temperature above 0 °C, a zincate derived from **17** was unstable undergoing novel butylation reaction (eq 7, Table 2).



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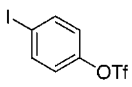

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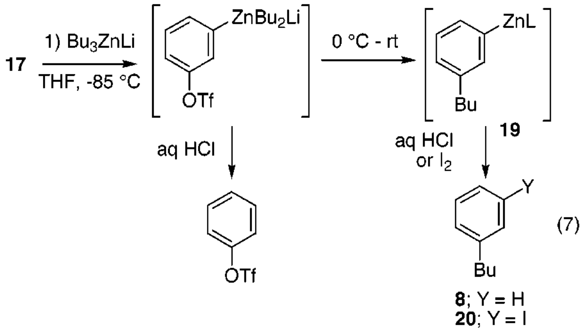
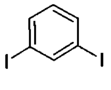
Table 2. Reaction of 3-Iodophenyl Triflate (17) with Bu$_3$ZnLi[a]

entry	Bu$_3$ZnLi (equiv)	concn (M)[b]	time (h)	GC yield (%) of **8**
1	1.2	0.3	5	24
2	2.0	0.3	1	47
3[c]	2.0	0.3	7	39
4[d]	2.0	0.3	2	35
5	3.0	0.3	2	53
6	2.0	0.6	1	53
7	3.0	0.6	1	60

[a] Unless otherwise noted, reactions were carried out at room temperature in THF. [b] Concentration of Bu$_3$ZnLi. [c] The reaction was performed at 0 °C. [d] Et$_2$O was used as a solvent.



Thus, hydrolysis of the reaction mixture of **17** and Bu$_3$ZnLi (2.0 equiv) after being stirred for 1 h at room temperature afforded butylbenzene (**8**) in 47% yield (entry 2). Lower reaction temperature or Et$_2$O as a solvent did not give better results (entries 3 and 4). The yield of **8** was improved by the use of the excess zincate (entry 5 vs entries 1 and 2) and by carrying out the reaction at higher concentration (entries 6 and 7). The reaction of **17** with 3.0 equiv of the zincate at 0.6 M in THF gave **8** in 60% yield (entry 7). It should be noted that the reaction of **17** with butyllithium gave a complex mixture even at −85 °C. The formation of 3-butylphenylzinc species **19** was verified by the formation of iodoarene **20** (56%) in the I$_2$ trapping experiment (eq 7). In this reaction, *m*-diiodobenzene (**21**) (15%) and tetrahydrofuran derivative **22** (6%) were also obtained as byproducts.



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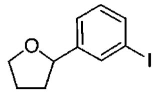

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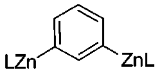

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To clarify the regiochemistry of butylation, the reaction of isomeric iodo(methoxy)phenyl triflates **24a** and **24b** were examined (eqs 8 and 9). The reaction of **24a** with Bu$_3$ZnLi (3 equiv, 0.6 M) at room temperature for 8 h gave *p*-isomer **25a** as a major butylation product together with a minor formation of *o*-isomer **25b** (**25a**:**25b** = 6.6:1, 17% combined yield). The butylation reaction was relatively slow and triflate **26a** was also obtained in 24%. Under similar conditions, **24b** also afforded a mixture of **25a** and **25b** (8.1:1) in 13% combined yield as well as triflate **26b** (40% yield).

It is difficult to rationalize similar product ratios (**25a**:**25b**) observed for the reactions of isomeric triflates **24a** and **24b** by a direct alkylation pathway from the corresponding arylzincate intermediates **27a**,**b**. The

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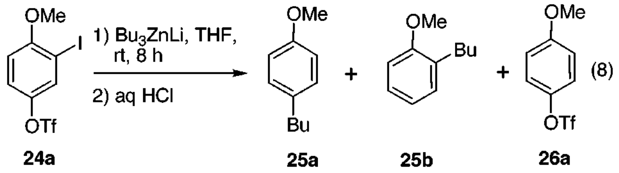
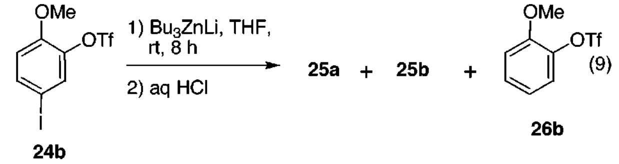
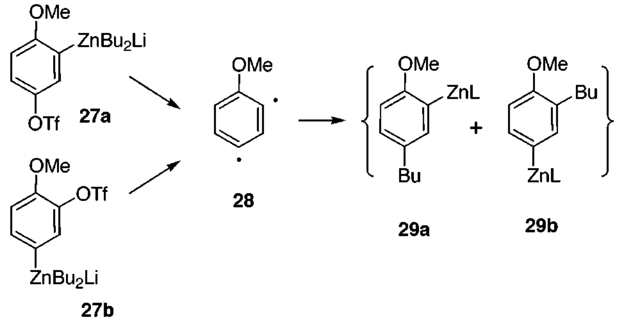
(5) The yield was determined by GC.





Scheme 2



result rather implies a stepwise pathway, which may involve a common intermediate derived from **27a** and **27b**. *m*-Benzyne[9] is a σ,σ-biradical intermediate possessing a singlet ground state with a singlet−triplet gap of 21 kcal/mol,[10] whose chemistry has been less studied than that of *o*- and *p*-benzynes.[11] Recent gas-phase study using Fourier transform ion cyclotron resonance mass spectrometry showed that *m*-benzyne undergoes both addition reactions, characteristic of *o*-benzyne, and radical reactions, characteristic of *p*-benzyne.[12] One possible explanation for the result of the reaction of **24a**,**b** could be the involvement of *m*-benzyne as an intermediate (Scheme 2). Thus, both zincates **27a** and **27b** would undergo elimination to give *m*-benzyne **28**, which may undergo regioselective carbometalation by Bu_2Zn and/or Bu_3ZnLi to form *p*-butylphenylzinc **29a** preferentially over *o*-butyl isomer **29b** probably due to the steric reason. Diiodobenzene **21** and tetrahydrofuran derivative **22** were produced as byproducts in the reaction of parent 3-iodophenyl triflate (**17**) followed by I_2 trap. The formation of **21** implies the generation of dimetal species **23**. The radical-type reactivity of *m*-benzyne[12] may allow iodine abstraction from iodobutane, which was produced in the initial iodine/zinc exchange of Bu_3ZnLi. Dimetalation of the resulting diiodobenzene by Bu_3ZnLi may lead to generation of **23**. Formation of **22** can be rationalized by the reaction of **23** with 2-iodotetrahydrofuran, which might be formed through a pathway involving hydrogen abstraction of tetrahydrofuran by *m*-benzyne and iodine abstraction of the resulting radical from iodobutane.

Conclusion

We have described the results of the study on the reactivity of arylzincates bearing a leaving group at the ortho, meta, and para position. The arylzincates were prepared by iodine/zinc exchange reaction of the corresponding iodoaryl sulfonates with Bu_3ZnLi. Zincates derived from *o*- and *m*-iodoaryl sulfonates were found to undergo homologation to give the corresponding butylphenylzinc species while a zincate derived from a para derivative was stable. The lack in regioselectivity observed for trisubstituted zincates demonstrated that *o*-benzyne is an intermediate for the reaction of *o*-iodo derivatives. Based on a similar product rations in the reactions of regioisomeric trisubstituted zincates as well as the formation of radical reaction byproducts, we proposed a pathway involving *m*-benzyne as an intermediate for the reaction of *m*-iodo derivatives.

Experimental Section

NMR spectra were recorded in $CDCl_3$. All commercially available reagents were used without further purification unless otherwise noted. THF was distilled from sodium benzophenone ketyl. Commercial anhydrous $ZnCl_2$ was dried in *vacuo* at 100 °C for 10 h over P_2O_5. All reactions were performed under argon. Reactions at −85 °C were performed with a Neslab Cryo Cool immersion cooler. Organic extracts were dried over Na_2SO_4. Flash chromatography was conducted on silica gel (Wakogel C-300).

2-Iodo-4-methylphenol[14] and 5-iodo-2-methoxyphenol[15] were prepared according to the literature procedures. The following aryl triflates were prepared from the corresponding phenols by the standard procedure.[16]

2-Iodophenyl trifluorometanesulfonate (6): 85% yield; ^{1}H NMR (300 MHz) δ 7.10 (1H, dt, $J = 1.5, 7.8$ Hz), 7.32 (1H, dd, $J = 1.2, 8.1$ Hz), 7.42 (1H, dt, $J = 1.5, 8.1$ Hz), 7.91 (1H, dd, $J = 1.5, 8.1$ Hz); ^{13}C NMR (125.8 MHz) δ 89.05, 118.69 (q, $J = 321$ Hz), 122.04, 129.60, 130.05, 140.77, 150.22; IR (liquid film) 1425, 1215, 890, 765 cm^{-1}. Anal. Calcd for $C_7H_4O_3F_3SI$: C, 23.88; H, 1.15. Found: C, 23.57; H, 1.15.

2-Iodo-4-methylphenyl trifluorometanesulfonate (10b): 75% yield; ^{1}H NMR (500 MHz) δ 2.37 (s, 3H), 7.21 (2H, m), 7.74 (1H, br s); ^{13}C NMR (125.8 MHz) δ 20.39, 88.78, 118.70 (q, $J = 321$ Hz), 121.50, 130.61, 140.07, 140.96, 141.89, 148.18; IR (liquid film) 1440, 1225, 900 cm^{-1}. Anal. Calcd for $C_8H_6O_3F_3SI$: C, 26.25; H, 1.65. Found: C, 25.94; H, 1.59.

3-Iodophenyl trifluorometanesulfonate (17): 90% yield; ^{1}H NMR (300 MHz) δ 7.19 (1H, t, $J = 8.4$ Hz), 7.27 (1H, br d, $J =$ ca. 8.5 Hz), 7.63 (1H, t, $J = 2.1$ Hz), 7.74 (1H, br d, $J =$ ca. 8 Hz); ^{13}C NMR (125.8 MHz) δ 93.83, 115.00, 118.65 (q, $J = 321$ Hz), 120.82, 122.00, 130.42, 131.45, 137.66, 149.20; IR (liquid film) 1430, 1215, 995, 795 cm^{-1}. Anal. Calcd for $C_7H_4O_3F_3SI$: C, 23.88; H, 1.15. Found: C, 23.61; H, 1.17.

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4-Iodophenyl trifluorometanesulfonate (18): 67% yield; ^{1}H NMR (500 MHz) δ 7.06 and 7.81 (4H, AA′BB′, J = ca. 9 Hz); ^{13}C NMR (125.8 MHz) δ 93.15, 118.66 (q, J = 321 Hz), 123.30, 139.39, 149.37; IR (liquid film) 1435, 1220, 890, 830, 750 cm^{-1}. Anal. Calcd for $C_7H_4O_3F_3SI$: C, 23.88; H, 1.15. Found: C, 23.61; H, 1.14.

5-Iodo-2-methoxyphenyl trifluorometanesulfonate (24b): 90% yield; ^{1}H NMR (300 MHz) δ 3.90 (3H, s), 6.80 (1H, d, J = 8.7 Hz), 7.49 (1H, d, J = 2.1 Hz), 7.62 (1H, dd, J = 2.1, 8.7 Hz); ^{13}C NMR (125.8 MHz) δ 55.27, 80.72, 118.63 (q, J = 320 Hz), 131.06, 138.09, 138.75, 151.51; IR (liquid film) 1425, 1220, 905, 810 cm^{-1}. Anal. Calcd for $C_8H_6O_4F_3SI$: C, 25.15; H, 1.58. Found: C, 25.00; H, 1.64.

2-Iodo-4-methylphenyl *p*-Toluenesulfonate (10a). The tosylate was prepared in 85% yield by the reaction of the corresponding phenol with *p*-toluenesulfonyl chloride under the Schotten−Baumann conditions in benzene−aqueous NaOH. **10a:** mp 104−105 °C (recrystallized from benzene and hexane); ^{1}H NMR (500 MHz) δ 2.31 (3H, s), 2.48 (3H, 1), 7.14 (1H, br d, J = ca. 8.5 Hz), 7.20 (1H, d, J = 8.4 Hz), 7.35 and 7.83 (4H, AA′BB′, J = ca. 8.5 Hz), 7.60 (1H, br s); ^{13}C NMR (125.8 MHz) δ 20.31, 21.72, 89.91, 122.43, 128.80, 129.72, 130.09, 132.76, 138.53, 140.24, 145.59, 147.78; IR (KBr disk) 1385, 1185, 840, 690 cm^{-1}. Anal. Calcd for $C_{14}H_{13}O_4SI$: C, 43.31; H, 3.38. Found: C, 43.30; H, 3.34.

3-Iodo-4-methoxyphenyl Trifluorometanesulfonate (24a). A mixture of *p*-methoxyphenyl triflate[16] (2.31 g, 9.00 mmol), iodine (1.83 g, 7.20 mmol), iodic acid (0.633 g, 3.6 mmol) in H_2SO_4 (10.4 mL, CCl_4 (1.8 mL), acetic acid (4.3 mL), and H_2O (2.2 mL) was heated under reflux for 2 days. The mixture was poured into water and extracted twice with ether. The organic layers were washed successively with water, aqueous $Na_2S_2O_3$, 10% aqueous NaOH, and brine, dried, and concentrated in vacuo. Purification of the residue by flash chromatography gave 3.15 g (92%) of **24a**: ^{1}H NMR (300 MHz) δ 3.90 (3H, s), 6.82 (1H, d, J = 9.0 Hz), 7.26 (1H, dd, J = 3.0, 9.0 Hz), 7.68 (1H, d, J = 3.0 Hz); ^{13}C NMR (125.8 MHz) δ 55.79, 85.60, 110.62, 118.63 (q, J = 321 Hz), 122.14, 132.01, 142.58, 157.99; IR (liquid film) 1420, 1220, 900, 820 cm^{-1}. Anal. Calcd for $C_8H_6O_4F_3SI$: C, 25.15; H, 1.58. Found: C, 25.05; H, 1.64.

Representative Procedure for the Reaction of Arenesulfonates with Bu_3ZnLi: Hydrolysis of the Reaction Mixture (Table 1, Entry 1). To a solution of $ZnCl_2$ (0.27 g, 2.0 mmol) in THF (6 mL) at 0 °C was added a solution of BuLi (6.0 mmol) (BuLi; 1.6 M in hexane, 3.75 mL). The mixture was stirred for 15 min at 0 °C. To the resulting solution of Bu_3ZnLi (2.0 mmol) at −85 °C was added a THF (1 mL) solution of triflate **10a** (0.39 g, 1.0 mmol), and the mixture was stirred for 30 min at this temperature. The reaction was quenched by the addition of aqueous HCl−THF. The mixture was poured into 1 N aqueous HCl and extracted twice with hexane. The organic layers were washed with aqueous $NaHCO_3$, dried, and concentrated in vacuo. Kugelrohr distillation (80−130 °C/20 mmHg) of the residue gave 0.185 g (65% combined yield) of a 1.1:1 mixture of 3-butyltoluene (**11a**)[17] and 4-butyltoluene (**11b**).[17]

For the reactions of **6**, **10b** (Table 1, entry 3), and **17** (Table 2), the yields of the product **8** were determined by capillary GC (OV-1, 30 m) analysis by using dodecane as an internal standard. For the reaction of **10b** (Table 1, entry 2), **18**, and **24a**,**b**, the crude products were purified by flash chromatography. The spectral data of products, **13**,[18] **25a**,[19] **25b**,[20] **26a**,[16] and **26b**[21] were in good accordance with reported values.

Representative Procedure for the Reaction of Arenesulfonates with Bu_3ZnLi: I_2 Trap (Eq 5). Triflate **6** (0.35 g, 1.0 mmol) was treated with Bu_3ZnLi (2.0 mmol) in THF (7 mL) at −85 °C for 30 min by a procedure similar to that described above. To the resulting mixture at −85 °C was added a THF (3 mL) solution of iodine (1.52 g, 6.0 mmol). After being stirred for 15 min, the mixture was poured into 1 N aqueous HCl and extracted twice with hexane. The organic layers were washed successively with aqueous $Na_2S_2O_3$ and aqeous $NaHCO_3$, dried, and concentrated in vacuo. Kugelrohr distillation (60−150 °C/0.5 mmHg) of the residue gave 0.185 g (68%) of 2-butyliodobenzene (**9**).[22]

2-Butyl-4-methyliodobenzene (12a) and 2-butyl-5-methyliodobenzene (12b): obtained as a mixture (**12a**:**12b** = 1.3:1) by Kugelrohr distillation (70−100 °C/0.3 mmHg); ^{1}H NMR (300 MHz) δ 0.95 (3H for **12b**, d, J = 7.2 Hz), 0.96 (3H for **12a**, d, J = 7.2 Hz), 1.4 (2H, m), 1.55 (2H, m), 2.26 (3H for **12b**, s), 2.27 (3H for **12a**, s), 2.66 (2H, t), 6.77 (1H for **12a**, dd, J = 2.4, 7.2 Hz), 7.02 (1H for **12a**, d, J = 2.4 Hz), 7.07 (2H for **12b**, br s), 7.64 (1H for **12b**, br s), 7.66 (1H for **12a**, d, J = 7.2 Hz); ^{13}C NMR (125.8 MHz) δ 13.97 (for **12a**,**b**), 20.25 (for **12a**), 20.89 (for **12b**), 22.40 (for **12b**), 22.49 (for **12a**), 32.52 (for **12a**,**b**), 39.98 (for **12a**), 40.41 (for **12b**), 96.47 (for **12b**), 100.49 (for **12a**), 128.49 (for **12b**), 128.89 (for **12a**), 129.02 (for **12b**), 130.25 (for **12a**), 137.28 (for **12a**), 138.09 (for **12b**), 139.07 (for **12a**), 139.76 (for **12b**), 142.23 (for **12b**), 145.06 (for **12a**). Anal. Calcd for $C_{11}H_{15}I$: C, 48.19; H, 5.51. Found: C, 47.88; H, 5.23.

Reaction of Triflate 17 with Bu_3ZnLi: I_2 Trap (Eq 7). Triflate **17** (1.06 g, 3.01 mmol) was treated with Bu_3ZnLi (6.0 mmol) in THF (21 mL) at −85 °C for 30 min by a procedure similar to that described above. The mixture was allowed to warm to room temperature during 0.5 h and stirred further for 1 h at room temperature. To the resulting mixture at −85 °C was added a THF (9 mL) solution of iodine (4.6 g, 18 mmol). After being stirred for 15 min, the mixture was poured into 1 N aqueous HCl and extracted twice with hexane. The organic layers were washed successively with aqueous $Na_2S_2O_3$ and aqueous $NaHCO_3$, dried, and concentrated in vacuo. Purification of the residue by flash chromatography (0.5−15% ethyl acetate/hexane) gave, in order of elution, a 3.8:1 mixture of **20** (56%) and **21**[23] (15%) (0.587 g) and **22** (48.4 mg, 6%). Separation of the mixture by a recycling preparative HPLC, equipped with a GPC column (JAIGEL-1H column, Japan Analytical Industry) using $CHCl_3$ as an eluent, afforded pure **20**. 3-Butyl-1-iodobenzene (**20**): ^{1}H NMR (300 MHz) δ 0.93 (3H, t, J = 7.2 Hz), 1.34 (2H, m), 1.58 (2H, m), 2.55 (2H, t, J = 7.8 Hz), 7.00 (1H, t, J = 7.8 Hz), 7.14 (1H, br d, J = ca. 8 Hz), 7.51 (1H, br d, J = ca. 8 Hz), 7.55 (1H, br s); ^{13}C NMR (125.8 MHz) δ 13.89, 22.25, 33.38, 35.19, 94.40, 127.66, 129.93, 134.61, 137.39, 145.30; IR (liquid film) 790, 695 cm^{-1}. Anal. Calcd for $C_{10}H_{13}I$: C, 46.18; H, 5.04. Found: C, 45.99; H, 4.91. (3-Iodophenyl)tetrahydrofuran (**22**): ^{1}H NMR (300 MHz) δ 1.77 (1H, m), 1.99 (2H, m), 2.32 (1H, m), 3.93 (1H, m), 4.08 (1H, m), 4.83 (1H, t, J = 7.2 Hz), 7.05 (1H, t, J = 7.8 Hz), 7.25 (1H, br d, J = ca. 8 Hz), 7.58 (1H, br d, J = ca. 8 Hz), 7.68 (1H, br s); ^{13}C NMR (125.8 MHz) δ 25.91, 34.63, 68.78, 79.75, 94.39, 124.85, 130.03, 134.55, 136.10, 145.99; IR (liquid film) 1070, 785, 735, 695 cm^{-1}. Anal. Calcd for $C_{10}H_{11}OI$: C, 43.82; H, 4.04. Found: C, 43.78; H, 4.01.

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