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Lithium Aluminum Hydride Reduction of 1-Aryl-3-halopropenes, 1-Aryl-3-halobutenes, and (9-Anthryl)arylmethyl Halides. Nucleophilic Substitution vs. Single Electron Transfer

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Lithium aluminum hydride reduction of ambident 1-aryl-3-halopropenes (**1a–g**), 1-aryl-3-halobutenes (**4a–g**), and (9-anthryl)arylmethyl halides (**7a–i**) was undertaken systematically. The reactivity of the halides and the regiochemistry of the reduction products were significantly influenced by various factors including the donor power of ethereal solvents, the substituent steric and electronic effects of the halides, the leaving groups, and the additive 12-crown-4. The reduction of 9-(α-bromo-3-chlorobenzyl)anthracene (**7i**) in tetrahydrofuran or diglyme afforded dimers **10–12** together with reduction products **8** and **9**, with the ratio of alkylation products **8–9** vs. dimerization products **10–12** being around 2:1. When the reduction of **7i** with lithium aluminum deuteride (LAD) was performed in the presence of 2 molar equiv of tributyltin hydride, however, a mixture of reduction products **8e** and **9e** was exclusively obtained, the d_1 content being around 65%. In contrast, LAD reduction of 1-(3-chlorophenyl)-3-bromopropene (**1g**) and 1-(3-chlorophenyl)-3-bromobutene (**4g**) in the presence or absence of tributyltin hydride lead to the formation of only monodeuterated reduction products. On the basis of these results, the mechanism of reduction of these halides **1**, **4**, and **7** is discussed.

Main group metal hydrides have been extensively used as reducing agents for a variety of organic substrates.[1] Among them, lithium aluminum hydride (LAH)[2] and lithium triethylborohydride (LTB)[3] are the reagents of choise of rapid reduction of alkyl halides. However, the detailed mechanism of this important, well-studied LAH reduction is less certain. LAH reductions of alkyl and aralkyl halides are generally considered to proceed by the S_N2 displacement pathway.[2,4] Certain systems have been, however, proposed to undergo reduction involving prior ionization.[5] Alternatively, Ashby and his co-workers[6] have recently revealed that LAH reduction of secondary and tertiary alkyl halides would involve radical intermediates.[7,8] Thus, a delicate balance may exist between these mechanistic alternatives, and a minor change of reaction conditions would alter the extent of each process. As an approach to obtain further insight into the mechanism of this important reaction, systematic investigation of LAH reduction of (*E*)-1-aryl-3-halopropenes (**1a–g**), (*E*)-1-aryl-3-halobutenes (**4a–g**), and (9-anthryl)arylmethyl halides (**7a–i**) was therefore undertaken.

Table I. LAH Reduction of (*E*)-1-Phenyl-3-halopropenes (1a–g)[a]

substrate	solvent	reductn prod[b] % yield	reductn prod[b] 2/3
1a	EE	30	54:46
1b	EE	10	100:0
1c	EE	8	100:0
1d	EE	5	100:0
1e	EE	88	100:0
1f	EE	75	100:0
1g	EE	70	100:0
1a	THF	30	91:9
1b	THF	21	100:0
1c	THF	15	100:0
1d	THF	25	100:0
1e	THF	70	100:0
1f	THF	66	100:0
1g	THF	73	100:0
1a	DG	60	100:0
1b	DG	54	100:0
1c	DG	48	100:0
1d	DG	50	100:0

[a] The reaction of 10 molar equiv of LAH at 20 °C for 5 min. [b] The yield and composition of the reduction products **2** and **3** were determined by GLC.

Results and Discussion

Reaction of 1-Aryl-3-halopropenes and 1-Aryl-3-halobutenes with LAH. Reaction of (*E*)-1-aryl-3-chloropropenes (**1a–d**; the substituent = *p*-OMe, *p*-Me, H, *m*-Cl) with 10 molar equiv of LAH was undertaken in diethyl ether (EE), tetrahydrofuran (THF), and 2-methoxyethyl ether (DG) at 20 °C for 5 min, and the products were analyzed by GLC (eq 1 and Table I). (*E*)-1-Arylpropenes (**2a–d**) derived from attack at the α-position were exlusively obtained; the exception was the reductions of *p*-methoxy compound **1a** in EE and in THF, in which two reduction products **2a** (attack at C-α) and **3a** (attack at C-γ) were produced in the ratios 54:46 and 91:9, respectively. The bromides **1e–g** also gave exclusively the α-attack products **2b–d**. Treatment of **1d** or **1g** with lithium aluminum deuteride lead to the formation of 1-(*m*-chlorophenyl)-propene-*3-d* (Table V). In connection with

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(1) (a) Pinder, A. R. *Synthesis* **1980**, 425. (b) House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: New York, 1970. (c) Pinzy, J. S. "Synthetic Reagents"; Wiley: New York, 1974. (d) Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.

(2) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1982**, *47*, 276.

(3) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1983**, *48*, 3085.

(4) (a) Eliel, E. L. *J. Am. Chem. Soc.* **1949**, *71*, 3970. (b) Malter, D. J.; Wotiz, J. H.; Hollingsworth, C. A. *Ibid.* **1956**, *78*, 1311. (c) Parry, R. J.; Kunitani, H. G. *Ibid.* **1976**, *98*, 4024. (d) Levine, S. G.; Gopalakrishnan, B. *Tetrahedron Lett.* **1979**, 699.

(5) (a) Paquette, L. A.; Storm, P. C. *J. Org. Chem.* **1970**, *35*, 3390. (b) Story, P. R.; Saunders, M. *J. Am. Chem. Soc.* **1962**, *84*, 4876. (c) Corriu, R. J. P.; Fernandez, J. M.; Guerin, C. *Tetrahedron Lett.* **1978**, 3391.

(6) (a) Ashby, E. C.; Goel, A. E.; DePriest, R. N.; *Tetrahedron Lett.* **1981**, *22*, 3729. (b) Ashby, E. C.; DePriest, R. N.; Goel, A. B. *Ibid.* **1981**, *22*, 1763. (c) Ashby, E. C.; Goel, A. B. *Ibid.* **1981**, *22*, 1879. (d) Ashby, E. C.; DePriest, R. N.; Pham, T. N. *Ibid.* **1983**, *24*, 2825.

(7) Aryl, vinyl, bridgehead, and cyclopropyl halides that are generally considered to be inert toward an S_N2 process are reduced to hydrocarbons by LAH.[8] For these substances, a mechanism involving single electron transfer would contribute to a considerable extent.[8d–g]

(8) (a) Jefford, C. W.; Kirkpatrick, D.; Delay, F. *J. Am. Chem. Soc.* **1972**, *94*, 8905. (b) Krishnamurthy, S.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 849. (c) Jefford, C. W.; Burger, U.; Leffler, M.; Kabengelo, M. *Tetrahedron Lett.* **1973**, 2483. (d) Chung, S. K.; Chung, F. *Ibid* **1979**, 2473. (e) Chung, S. K. *J. Org. Chem.* **1980**, *45*, 3513. (f) Chung, S. K.; Filmore, K. L. *J. Chem. Soc., Chem. Commun.* **1983**, 358. (g) Beckwith, A. L. J.; Goh, S. H. *Ibid.* **1983**, 905.

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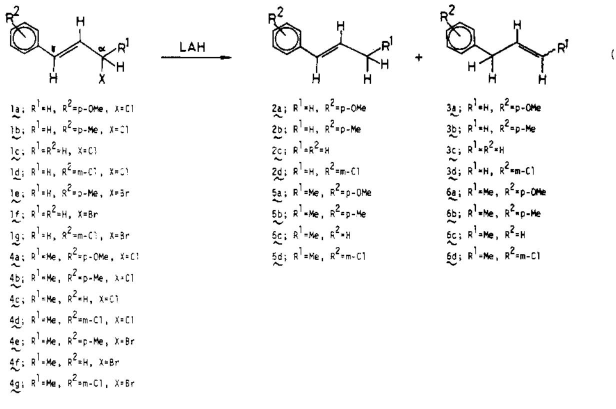


(1)

1a; R^1=H, R^2=p-OMe, X=Cl
1b; R^1=H, R^2=p-Me, X=Cl
1c; R^1=R^2=H, X=Cl
1d; R^1=H, R^2=m-Cl, X=Cl
1e; R^1=H, R^2=p-Me, X=Br
1f; R^1=R^2=H, X=Br
1g; R^1=H, R^2=m-Cl, X=Br
4a; R^1=Me, R^2=p-OMe, X=Cl
4b; R^1=Me, R^2=p-Me, X=Cl
4c; R^1=Me, R^2=H, X=Cl
4d; R^1=Me, R^2=m-Cl, X=Cl
4e; R^1=Me, R^2=p-Me, X=Br
4f; R^1=Me, R^2=H, X=Br
4g; R^1=Me, R^2=m-Cl, X=Br

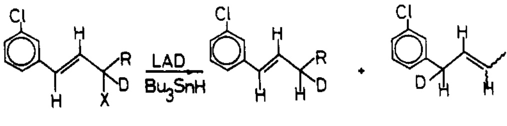
2a; R^1=H, R^2=p-OMe
2b; R^1=H, R^2=p-Me
2c; R^1=R^2=H
2d; R^1=H, R^2=m-Cl
5a; R^1=Me, R^2=p-OMe
5b; R^1=Me, R^2=p-Me
5c; R^1=Me, R^2=H
5d; R^1=Me, R^2=m-Cl

3a; R^1=H, R^2=p-OMe
3b; R^1=H, R^2=p-Me
3c; R^1=R^2=H
3d; R^1=H, R^2=m-Cl
6a; R^1=Me, R^2=p-OMe
6b; R^1=Me, R^2=p-Me
6c; R^1=Me, R^2=H
6d; R^1=Me, R^2=m-Cl

this high regioselectivity in the LAH reduction, it would be worth noting that reduction of **1a–d** with lithium triethylborohydride (LTB), the so-called Superhydride (Aldrich), also provided exclusively the α-attack products **2a–d** (Table VI). In the LAH reduction, the reactivity of **1a–d**, judged by the yield of reduced products **2a–d**, increased with increase in donor power of the solvents: EE < THF < DG. The same trend has been observed for simple primary alkyl halides.[9] The accepted mechanistic rationale for this trend is that in EE the lithium cation is poorly solvated, and in direct contrast, the lithium cation is strongly solvated in THF or DG, forming solvent-separated ion pairs, thereby dramatically enhancing the nucleophilicity of the tetrahydroaluminate,[9,10] resulting in rapid reduction in the latter solvents.[9] The fact that LAH reduction of (*Z*)-1-phenyl-3-chloropropene afforded exclusively (*Z*)-1-phenylpropene (eq 2) is not inconsistent with the LAH reduction of 1-aryl-3-chloropropenes being most likely to proceed by the S_N2 pathways.

(2)

The reaction of relatively more ionizable but sterically more congested (at C-α) (*E*)-1-aryl-3-halobutenes (**4a–g**; the substituent = *p*-OMe, *p*-Me, H, *m*-Cl) in EE, THF, or DG gave the corresponding mixture of two reduction products **5** (attack at C-α) and **6** (attack at C-γ) (eq 1 and Table III).[11,12] . The data in Table II revealed the following. (a) The **5**:**6** ratio was influenced by both the substituent-electronic effects and the donor power of the solvents, the ratio being increased with the increase of electron-withdrawing ability of the substituent R^2 and with the increase of donor power of the solvents (Figure 1). In connection with this solvent effect on the product regiochemistry, LTB reduction of **4a–d** was found to result in predominant formation of α-attack products **5a–d** (Table VI). (b) The reaction of **4a–d** in EE was significantly faster than that in THF, this trend being the reverse of that for chloride **1**. (c) Leaving group effects exerted a small but significant influence on the product regiochemistry, the relatively higher proportion of α-attack product being observed for bromides **4e–g**.[13] (d) Lithium aluminum deuteride (LAD) reduction of chloride **1d** and bromide **1g** in the presence or absence of tributyltin hydride, a good

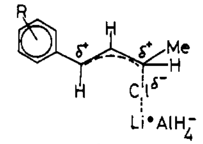


(3)

R = H or Me, X = Cl or Br

hydrogen atom donor to organic free radicals,[14,15] lead to the exlcusive formation of monodeuterated products (Table V). This result would imply that a process involving the 1-phenylbutenyl radical is not important in the LAH reduction of halides **4** (see the later discussion).

It is interesting to note that the nucleophilicity of tetrahydroaluminate in THF is expected to be significantly larger than that in EE and, nevertheless, the LAH reduction of chloride **4** in the former solvent is considerably slower than that in the latter one. To understand this apparently complicated fact, LAH reduction of **4** was undertaken in the presence of 12-crown-4, a good chelating agent toward lithium cation (Table IV). Treatment of chloride **4c** with LAH (1 molar equiv) in the presence of 12-crown-4 (2 molar equiv) in EE at 20 °C for 1 h afforded a mixture of **5c** and **6c** in only 4% yield, the **5c**/**6c** ratio being 80:20. In marked contrast, the reaction in the absence of 12-crown-4 provided a mixture of **5c** and **6c** in 40% yield, the ratio being 65:35. Chlorides **4a,b,d** also exerted the same trend, i.e., the decrease of reactivity and the increase of **5**:**6** ratio by addition of 12-crown-4 (Figure 1). These results would be interpreted as follows. In EE having a relatively poor donating power, lithium cation provides some external assistance to the cleavage of the C–Cl bond:[5,9] The additive 12-crown-4 decreases this assistance, as do THF and DG. A charge-developed species **13** would be produced by the lithium cation coordination,



13

which in turn leads to the formation of two reduction products **5** and **6**, the ratio being influenced by the relative charge densities of C-α and C-γ.[16] Maybe in harmony with this, the substituent-dependent **5**/**6** ratios obtained from the reactions of **4a–d** with LAH in EE are noted to be much the same as those from the $NaBH_4$ reductions of **4a–d** in aqueous DG, which are considered to proceed by prior ionization (Table VII).[17]

For the less ionizable chlorides **1b–d** addition of 12-crown-4 gave rise to the increased rate of reduction to a small but significant extent (Table IV). This result is in harmony with our former conclusion that the reactions of these chlorides **1b–d** are more likely to proceed by S_N2 pathways: Probably the complexation of lithium cation by 12-crown-4 increases the nucleophilicity of LAH and,

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[9] Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550.

[10] Ashby, E. C.; Dobbs, F. R.; Hopkins, H. R. Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3158.

[11] An increase in steric bulk at the site of the leaving group in a conjugated allylic system leads to substitution with rearrangement.[12]

[12] Bordwell, F. G.; Wiley, P. F.; Mecca, F. G. *J. Am. Chem. Soc.* **1975**, *97*, 132 and the references therein.

[13] Hirabe, T.; Nojima, M.; Kusabayashi, S. *J. Org. Chem.* **1984**, *49*, 4084.

[14] Kuivila[16a] and Ashby[6d] have shown that dicyclohexylphosphine is an efficient agent for trapping alkyl radicals produced by the reaction of R_3SnNa with alkyl halides and LAH reduction of alkyl iodides, respectively. Since Sn–H bond energy (70 kcal/mol) is significantly lower than P–H bond energy (77 kcal/mol),[16b] tributyltin hydride is expected to trap more efficiently the organic free radicals produced by SET pathways.

[15] (a) Smith, G. F.; Kuivila, H. G.; Simon, R.; Sultan, L. *J. Am. Chem. Soc.* **1981**, *103*, 833. (b) Sakurai, H. "Organic Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 25.

[16] Ogata, F.; Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1981**, *103*, 1145.

[17] Bell, H. M.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 1473. In harmony with this, the reaction of (*Z*)-1-phenyl-3-chloropropene with $NaBH_4$ in aqueous DG gave an equimolar mixture of (*E*)- and (*Z*)-1-phenylpropene, together with 3-phenylpropene.

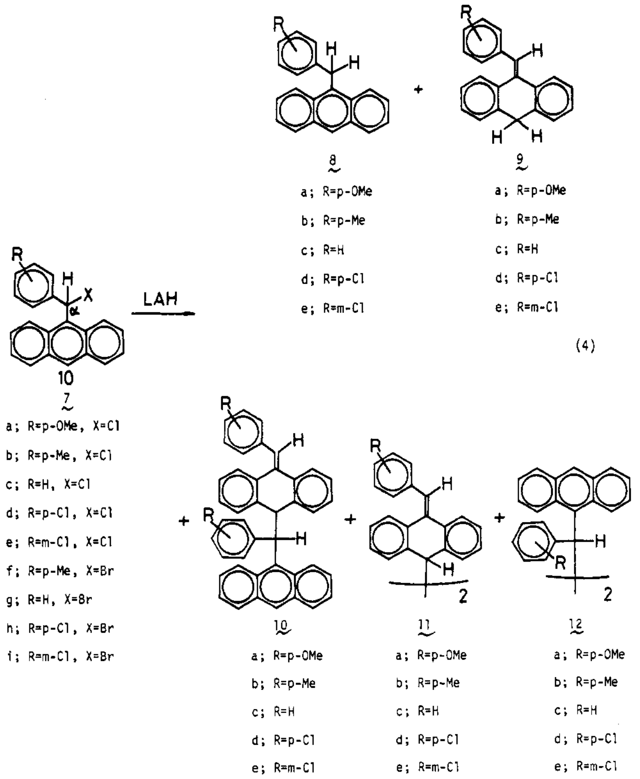
Table II. LAH Reduction of (*E*)-1-Phenyl-3-halobutenes (4a–g)[a]

substrate	solvent	reductn prod[b] % yield	reductn prod[b] 5/6
4a	EE	65	51:49
4b	EE	54	57:43
4c	EE	24	68:32
4d	EE	17	69:31
4e	EE	78	72:28
4f	EE	80	85:15
4g	EE	85	100:0
4a	THF	25	58:42
4b	THF	9	62:38
4c	THF	2	78:22
4d	THF	5	89:11
4e	THF	64	80:20
4f	THF	68	96:4
4g	THF	79	100:0
4a	DG	13	58:42
4b	DG	10	86:14
4c	DG	11	97:3
4d	DG	20	100:0

[a] The reaction with 10 molar equiv of LAH at 20 °C for 5 min. [b] The yield and composition of the reduction products **5** and **6** were determined by GLC. The errors of **5**/**6** ratios were of the order of 2%. The E/Z ratio of **6** was around 95:5.

consequently, increases the rate of the reduction. The reduction of para-methoxy compound **1a** in EE was, however, significantly slowed down by addition of 12-crown-4, suggesting that in the case of relatively more ionizable **1a**, lithium cation assistance to the C–Cl bond cleavage is more important.

Reaction of (9-Anthryl)arylmethyl Halides with LAH. Treatment of (9-anthryl)arylmethyl chlorides (**7a–e**; the substituent = *p*-OMe, *p*-Me, H, *p*-Cl, *m*-Cl) with LAH in EE, THF, or DG gave the corresponding mixture of two reduction products **8** (reduction at C-α) and **9** (reduction at C-10) (eq 4 and Table III). The data revealed the following. (a) The reaction in EE gave mainly the anthracene derivative **8**. The **8**:**9** ratio decreased with the increase of electron-withdrawing ability of the substituent. (b) In the reaction in THF, the plots of **8**:**9** ratio vs. σ gave a U-shaped line with a minimum of the ratio at the unsubstituted one **7c**. The same trend was observed for the reaction in DG. (c) For the reaction in EE, the reactivity of the chlorides **7a–e** increased as the substituent became increasingly electron donating. In contrast, curvature of Hammett plots was observed for the reaction in DG. (d) LAD reduction of chloride **7e** in the presence or absence of tributyltin hydride lead to the exclusive formation of monodeuterated products **8e**-*α*-*d* and **9**-*10*-*d* (Table V).



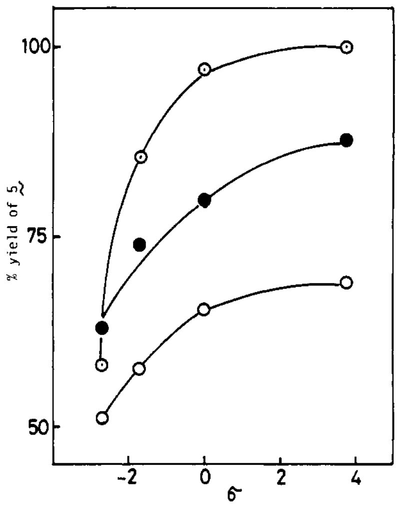


Figure 1. Plot of % yield of **5** vs. σ constant for the reaction of **4a–d** with LAH in an appropriate solvent: (○) EE, (●) EE in the presence of 12-crown-4, (⊙) DG.

Table III. LAH Reduction of (9-Anthryl)arylmethyl Halides (7a–i)[a]

substrate	solvent	reductn prod[b] % yield	reductn prod[b] 8/9	dimers[b] % yield	dimers[b] 10/11
7a	EE	95	100:0		
7b	EE	95	90:10		
7c	EE	49	79:21		
7d	EE	33	74:26		
7e	EE	11	71:29		
7f[c]	EE	93	79:21		
7g[c]	EE	92	68:32		
7h[c]	EE	79	66:34		
7i[c]	EE	76	61:39		
7a	THF	95	68:32		
7b	THF	63	27:73		
7c	THF	26	26:74		
7d	THF	19	46:54		
7e	THF	16	69:31		
7f[c]	THF	87	31:69	5	45:55
7g[c]	THF	87	29:71	13	43:57
7h[c]	THF	77	49:51	20	40:60
7i[c]	THF	55	72:28	25	40:60
7a	DG	76	68:32		
7b	DG	44	50:50		
7c	DG	28	43:57		
7d	DG	63	85:15		
7e	DG	70	95:5		
7f	DG	73	47:53		
7g	DG	53	40:60	14	49:51
7h	DG	68	73:27	19	53:47
7i	DG	69	92:8	29	50:50

[a] The reaction with 10 molar equiv of LAH at 20 °C for 10 min unless otherwise noted. [b] The isolated yield. The product composition was determined by ^1H NMR spectroscopy. The errors were of the order of 2%. Dimer **12** was also obtained; its proportion in dimeric products was ca. 5%. [c] The reaction for 5 min.

Addition of 12-crown-4 exerted a notable effect on the LAH reduction of chlorides **7a–e** in EE (Table IV and Figure 2). (a) The reactivity was significantly decreased

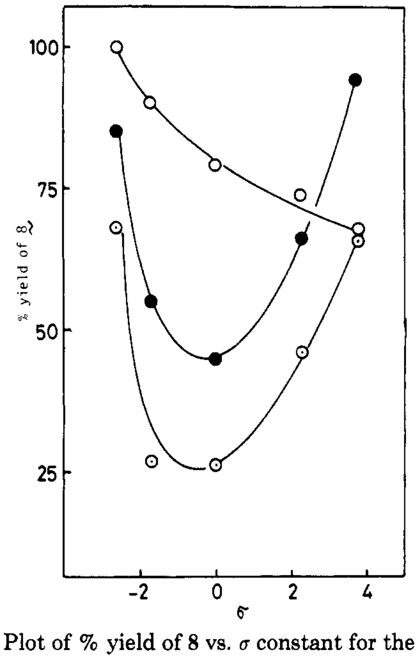


Figure 2. Plot of % yield of 8 vs. σ constant for the reaction of **7a–e** with LAH in an appropriate solvent; (○) EE, (●) EE in the presence of 12-crown-4, (⊙) THF.

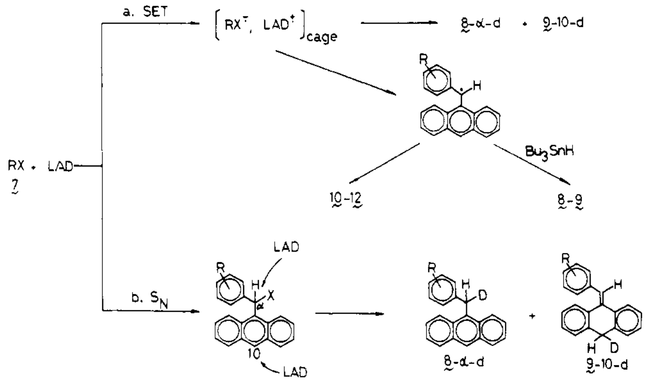
Table IV. LAH Reduction in the Presence of 12-Crown-4[a]

substrate	12-crown-4, molar equiv	reductn prod % yield	 S_N/S_N'[b]
1a	none	40	82:18
1b	none	7	100:0
1c	none	6	100:0
1d	none	6	100:0
1a	2	15	100:0
1b	2	14	100:0
1c	2	14	100:0
1d	2	15	100:0
4a	none	80	51:49
4b	none	61	62:38
4c	none	40	65:35
4d	none	10	67:33
4a	2	6	63:37
4b	2	4	74:26
4c	2	4	80:20
4d	2	4	88:12
7a	none	95	100:0
7b	none	95	93:7
7c	none	84	89:11
7d	none	80	86:14
7e	none	30	80:20
7a	2	30	85:15
7b	2	15	55:45
7c	2	7	45:55
7d	2	7	66:34
7e	2	7	96:4

[a] The reaction with equimolar amounts of LAH in EE at 20 °C for 1 h. [b] The **2**/**3** ratio for **1**, **5**/**6** for **4**, and **8**/**9** ratio for **7**. The errors were of the order of 2%.

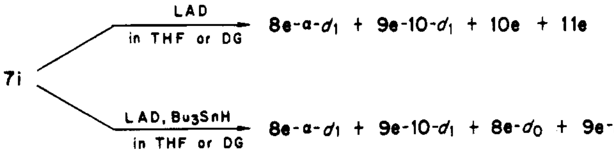
by the addition of 12-crown-4, suggesting that the 12-crown-4 decreases lithium cation assistance to the C–Cl bond cleavage in EE to a significant extent. (b) The plots of **8**:**9** ratio vs. σ showed a U-shaped line, the unsubstituted chloride **7c** exerting the smallest value. This trend was the same as that observed for the reaction in THF or DG.

Scheme I



The reaction of bromides **7f–i** with LAH in THF gave dimers **10b–e**, **11b–e**, and **12b–e**, together with reduction products **8b–e** and **9b–e**. The substituent-independent **10**:**11** ratios were all around 1:1[18,19] (the dimers **12b–e** were produced in only small amounts and, therefore, their yields were not counted). The yields of dimers increased with the increase of electron-withdrawing ability of the substituents. The substituent-dependent **8**:**9** ratio was, however, very similar to the corresponding **8**:**9** ratio obtained from the reaction of chlorides **7b–e**. The reaction of DG also gave dimers **10–12**, along with reduction products **8** and **9**. From the reaction in EE, however, only reduction products **8** and **9** were obtained.

To understand the reactions of bromides **7f–i** in THF or DG, the reaction of **7i** with LAD was undertaken in the presence or absence of tributyltin hydride (eq 5). LAD



(5)

reduction of **7i** in the absence of tributyltin hydride gave, together with dimeric products **10e** and **11e** (25% yield), reduction products **8e** and **9e** (55% yield) with a d_1 content of 100%, whereas LAD reduction in the presence of 2 molar equiv of tributyltin hydride yielded exclusively reduction products **8e** and **9e** with a d_1 content of around 65% (Table V). The similar trend was observed for the reaction of **7i** in DG. These results lead us to deduce that in the reaction of **7i** with LAH in THF or DG, radical species **14** are really produced (Scheme I).[20,21] In the absence of tributyltin hydride, (9-anthryl)arylmethyl radicals **14** dimerize to yield dimers **10–12**, while in the presence of tributyltin hydride the radicals **14** are effectively captured to yield reduction products **8** and **9**.

For the formation of the monodeuterated products **8**-α-*d* and **9**-10-*d*, however, two different mechanisms, i.e., SET and S_N, are possible (Scheme I). Although circumstantial, the following facts would suggest that the latter process rather than the former one is more important. (a) The yield of the monodeuterated products **8**-α-*d* and **9**-10-*d* is not significantly affected by the presence of tributyltin hydride.[14,15] (b) The substituent electronic effects exert a remarkable effect on the **8**/**9** ratio. This is in marked contrast to the fact that the reaction of halides **7a–e** with Grignard reagents, which is most likely to proceed by a mechanism involving SET,[22] affords the substituent-in-

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[18] The reaction of **7a,f,g,h** with silver in THF gave the substituent-independent mixture of dimers **10** and **11** (**10**:**11** = ca. 1:1).[19]

[19] (a) Takagi, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* 1982, *104*, 1636. (b) Takagi, M.; Nojima, M.; Kusabayashi, S. *Ibid.* 1983, *105*, 4676.

[20] The increase of solvent polarity,[21a] leaving group ability,[19,21b] and electron-withdrawing ability of the substituent[19] have been found to pronounce the contribution of SET processes.

[21] (a) Panek, E.-J. *J. Am. Chem. Soc.* 1973, *95*, 8460. (b) Zieger, H. E.; Angres, I.; Mathisen, D. J. *Ibid.* 1976, *98*, 2580.

Table V. LAD Reduction in the Presence or Absence of Tributyltin Hydride[a]

				reductn prod			dimers	
substrate	Bu_3SnH, molar equiv	solvent	reactn time, min	% yield	S_N/S_N'[b]	d_1 content	% yield	10/11
1d	5	THF	60	48	100:0	100		
1g	none	THF	60	73	100:0	100		
1g	5	THF	60	75	100:0	100		
4d	5	THF	60	18	100:0	100		
4g	none	THF	60	72	100:0	100		
4g	5	THF	60	70	100:0	100		
7e	none	THF	10	16	69:31	100		
7e	2	THF	10	15	70:30	95		
7i	none	THF	5	55	72:28	100	25	40:60
7i	2	THF	5	82	90:10	65		
7i	none	DG	5	68	92:8	100	30	50:50
7i	2	DG	5	90	91:9	67		

[a] The reaction with 10 molar equiv of LAD at 20 °C. [b] The **2**/**3** ratio for **1**, **5**/**6** for **4**, and **8**/**9** ratio for **7**.

Table VI. Reaction of Allylic Chlorides with Lithium Triethylborohydride in THF[a]

		reductn prod	
substrate	reactn time, min	% yield	S_N/S_N'[b]
1a	5	88	100:0
1b	5	83	100:0
1c	5	63	100:0
1d	5	67	100:0
4a	60	36	72:28
4b	60	24	94:6
4c	60	22	96:4
4d	60	26	90:10
7a	60	83	41:59
7b	60	68	18:82
7c	60	70	11:59
7d	60	56	18:82
7e	60	50	16:84

[a] The reaction with 5 molar equiv of lithium triethylborohydride in THF at 20 °C. [b] The **2**/**3** ratio for **1**, **5**/**6** for **4**, and **8**/**9** ratio for **7**.

Table VII. Reaction of Allylic Halides with Sodium Borohydride in Aqueous Diglyme[a]

		reductn prod	
substrate	reactn time, min	% yield	S_N/S_N'[b]
1a	60	98	43:57
1b	60	87	62:38
1c	60	33	81:29
1g	60	30	98:2
4a	60	93	48:52[c]
4b	60	95	60:40[c]
4c	60	95	60:40[c]
4d	60	97	71:29[c]
7a	30	81	100:0[d]
7b	30	81	45:55[d]
7c	30	86	42:58[d]
7d	30	96	33:67[d]
7e	30	86	33:67[d]

[a] The reaction with 5 molar equiv of sodium borohydride in aqueous diglyme at 20 °C. [b] The **2**/**3** ratio for **1**, **5**/**6** ratio for **4**, and **8**/**9** ratio for **7**. [c] The *E*/*Z* ratio of **6** was around 94:6. [d] Taken from the data in ref 16.

dependent mixture of reduction products **8** and **9** (the **8**/**9** ratio = ca. 3:2), along with the substituent-independent mixture of two alkylation products and also the substituent-independent mixture of dimers **10** and **11**.[19]

Conclusion

The systematic investigation for LAH reduction of 1-aryl-3-halopropenes (**1a–g**), 1-aryl-3-halobutenes (**4a–g**), and (9-anthryl)arylmethyl halides (**7a–i**) leads to the following conclusions. (a) LAH reductions of halides **1a–g**, **4a–g**, and **7a–e** in EE, THF, or DG are most likely to proceed by S_N pathways, as are the reductions of bromides **7f–i** in EE. (b) In the reduction of relatively more ionizable halides **4a–g** and **7a–i** in EE, lithium cation assistance to the cleavage of the carbon–halogen bond is important. (c) In the reaction of bromides **7f–i** with LAH in THF or DG, (9-anthryl)arylmethyl radicals **14** are produced in a significant amount, which dimerize to give dimers **10–12**. As the process leading to reduction products **8** and **9**, however, S_N rather than SET seems to be more important.

Experimental Section

^1H NMR spectra were obtained with a JNM-PS-100 spectrometer. Mass spectral data were obtained with a Hitachi RMU-6H spectrometer and infrared spectra with a Hitachi 215 spectrometer. GLC analysis was carried out on a Hitachi 164 gas chromatograph. The following columns were used: 20% SE-30 on Aeropak 30, 3 ft × 0.125 in.; 20% PEG-20M on Aeropak 30, 6 ft × 0.125 in.

Materials. Halides **1a–d**,[23] **1e–g**,[24] **4a–b**,[25] **4c–d**,[24] **4e–g**,[24] **7a–i**,[16] and (*Z*)-1-phenyl-3-chloropropene[26] were prepared by the reported methods. Solvent, EE, THF, and diglyme were purified by the standard methods.[27] LAH and LAD were from Wako Chem. Co. and lithium triethylborohydride, 1 M solution in THF, was from Aldrich. 12-Crown-4 was distilled from LAH under N_2.

Preparation of Standardized Solutions of LAH or LAD in EE, THF, or DG. The method developed by Krishnamurthy and Brown[2] was used to prepare the standardized solutions of LAH or LAD: the EE solution (ca. 0.5 M in LAH or LAD), the THF solution (ca. 1.0 M in LAH or LAD), the DG solution (ca. 1.0 M in LAH or LAD).[28]

Reaction of 1-(4-Methoxyphenyl)-3-chloropropene with LAH in EE. In a 100-mL flask, equipped with a magnetic stirrer and maintained under N_2, was added a solution of **1a** (3 mmol) in EE (20 mL) by a syringe. Then the standardized EE solution of LAH (30 mmol) was added in one portion at 20 °C, and the mixture was kept with stirring for 5 min under a slow stream of nitrogen. The mixture was poured into ice-cold HCl and extracted with ether. The crude products were treated with boiling methanol for 2 h to convert the unreacted chloride **1a** to the corresponding methyl ether.[29] Then the yield and composition of the reduction products **2a** and **3a** were determined by GLC. The two reduction

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products were separated by column chromatography on silica gel.

The physical properties of the products **2a–e**[30] and **3a–e**[31] were identical with those of the reported ones.

Reaction of 1-Phenyl-3-chlorobutene with LAH in THF. To a solution of **4c** (3 mmol) in THF (20 mL) was added a solution of LAH (30 mmol)) in THF (30 mL) in one portion, and the reaction was continued at 20 °C for 5 min. After conventional workup, the products were analyzed by GLC.

The physical properties of **5a–e**,[32] **6a**,[33] and **6b–e**[13,34] were identical with those of the authentic samples prepared by the reported methods.

Reaction of (9-Anthryl)benzyl Chloride with LAH in the Presence of 12-Crown-4. To a solution of **7c** (1 mmol) and freshly distilled 12-crown-4 (2 mmol) in EE (20 mL) was added a solution of LAH (1 mmol) in EE, and the mixture was kept with stirring at 20 °C for 1 h under a nitrogen atmosphere. After conventional workup, the crude products were treated with boiling methanol–benzene (30 mL, 1:1 v/v) for 2 h. Then the products were isolated by column chromatography on silica gel. The first fraction contained **8c** and **9c** (7% yield), the ratio being 45:55. The second fraction was (9-anthryl)benzyl methyl ether[1]6 (90% yield).

The physical properties of **8a–e** and **9a–e** have been previously described.[16]

Reaction of 9-(α-Bromo-3-chlorobenzyl)anthracene with LAD in the Presence or Absence of Tributyltin Hydride. A solution of **7i** (1 mmol) in THF (20 mL) was treated with LAD (10 mmol) at 20 °C for 5 min under a nitrogen atmosphere. The crude products were chromatographed on silica gel. Elution with 15:85 benzene–hexane gave a mixture of **8e** and **9e** in a ratio of 72:28 (55% yield). Elution with 1:1 benzene–hexane afforded a mixture of dimers **10e** and **11e** in a ratio of 2:3 (25% yield). The reduction products were separated from each other by elaborate column chromatography on silica gel. The mass and ^{1}H NMR analyses confirmed that the reduction products were **8e**-α-d_1 and **9**-*10*-d_1. **8e**-α-*d*: mp 102–103 °C; ^{1}H NMR δ 4.95 (1 H); MS, *m/e* 313 and 315 (M$^+$).[16] **9e**-*10*-*d*: mp 94–96 °C; ^{1}H NMR δ 3.97 (1 H); MS, *m/e* 313 and 315 (M$^+$).[16]

The physical properties of dimers **10a–e** and **11a–e** have been previously reported.[16]

To a solution of LAD (10 mmol) and tributyltin hydride (2 mmol) in THF (20 mL) was added **7i** (1 mmol) in THF (20 mL) in one portion, and the mixture was kept with stirring at 20 °C for 5 min under a nitrogen atmosphere. After workup, the products were column chromatographed on silica gel. The reduction products **8e** and **9e** were obtained in 82% yield, the **8e**/**9e** ratio being 90:10. By elaborate column chromatography on silica gel and recrystallization, 9-(3-chlorobenzyl)anthracene (**8e**) was isolated in a pure state. The characteristic signal at δ 4.95 in ^{1}H NMR spectrum indicated that the d_1 content of **8e** is around 65%. This analysis for d_1 content was in good agreement with that by mass spectroscopy.

LAD Reduction of 1-(3-Chlorophenyl)-3-bromopropene (1g) and 1-(3-Chlorophenyl)-3-bromobutene (4g) in the Presence of Tributyltin Hydride. Treatment of **1g** (1 mmol) with LAD (10 mmol) in the presence of tributyltin hydride (5 mmol) in THF at 20 °C for 1 h, followed by column chromatography on silica gel, afforded 1-(3-chlorophenyl)propene-*3*-d_1 (75% yield): an oil; ^{1}H NMR δ 1.75–1.90 (m, 2 H), 5.98–6.40 (m, 2 H), 7.00–7.32 (m, 4 H); MS, *m/e* 153 and 155 (M$^+$).

Treatment of **4g** (1 mmol) with LAD (10 mmol) in the presence of tributyltin hydride (5 mmol) in THF at 20 °C for 1 h, followed by column chromatography on silica gel afforded 1-(3-chlorophenyl)butene-*3*-d_1 (80% yield): an oil; ^{1}H NMR δ 1.08 (d, J = 7.0 Hz, 3 H), 2.00–2.34 (m, 1 H), 6.00–6.35 (m, 2 H), 7.00–7.34 (m, 4 H); MS, *m/e* 167 and 169 (M$^+$).

Reaction of 4c with Lithium Triethylborohydride (LTB) in THF. To a solution of **4c** (2 mmol) in THF (20 mL) was added a solution of LTB (10 mmol) in THF in one portion, and the mixture was kept with stirring at 20 °C for 1 h. By column chromatography on silica gel, 1-phenyl-1-butene (**5c**) was isoalted in 22% yield.

Reaction of 1c with NaBH$_4$ in Aqueous Diglyme. To a solution of sodium borohydride (0.5 g, 13 mmol) in 70% aqueous diglyme (10 mL) was added **1c** (2 mmol), and the mixture was kept at 20 °C for 1 h. The products were analyzed as described previously.

Registry No. **1a**, 94607-41-7; **1b**, 96000-21-4; **1c**, 21087-29-6; **1d**, 96000-22-5; **1e**, 52966-73-1; **1f**, 26146-77-0; **1g**, 52925-45-8; **4a**, 96000-23-6; **4b**, 96000-24-7; **4c**, 91861-50-6; **4d**, 96000-25-8; **4e**, 96000-26-9; **4f**, 91861-49-3; **4g**, 96000-27-0; **7a**, 77032-88-3; **7b**, 77032-89-4; **7c**, 72948-51-7; **7d**, 77032-90-7; **7e**, 77032-91-8; **7f**, 77032-92-9; **7g**, 77032-93-0; **7h**, 77032-94-1; **7i**, 96000-28-1; **8e**, 77033-24-0; **8e**-α-*d*, 96000-29-2; **9e**, 75128-85-7; **9e**-*10*-*d*, 96000-30-5; NaBH$_4$, 16940-66-2; LAH, 16853-85-3; LTB, 22560-16-3; 12-crown-4, 294-93-9; tributyltin hydride, 688-73-3; 1-(3-chlorophenyl)propene-*3*-*d*, 96000-31-6; 1-(3-chlorophenyl)butene-*3*-*d*, 96000-32-7.

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