2-Butyryl-1,4-naphthohydroquinone (4). The butyrate ester, 50 g (0.166 mol), was mixed with 60.0 g (0.45 mol) of anhydrous aluminum chloride to produce a brilliant yellow mixture which was added in small amounts with stirring to a 1-L beaker suspended in an oil bath heated to 115 °C. Heating was continued for 0.5 h after the last addition. The glossy solid produced by the reaction was ground to a fine powder which was added to 1.2 L of ice containing 60 mL of concentrated HCl. The mixture was extracted with diethyl ether. The ether solution then dried over $MgSO_4$ and evaporated to give 32 g of crude butyrylnaphthalenediol monobutyrate which was refluxed for 3 h in 350 mL of anhydrous methanol containing 5% dry hydrogen chloride. Water was added and the resultant mixture refluxed for another 3 h, poured onto cold ice water, and extracted with ether. The ether solution was dried ($MgSO_4$) and evaporated to give a mixture of the desired hydroquinone and its 4-methyl ether. The hydroquinone was separated by fractional crystallization from chloroform to give 25.1 g (50%) of yellow crystals: mp 147–148.5 °C (lit.[5] mp 147–148 °C); IR (KBr) 3315, 1630 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 1.01 (t, 3 H), 1.75 (2 H, m), 3.02 (2 H, t), 7.20 (1 H, s), 7.90 (4 H, m), 8.70 (1 H, s), 13.23 (1 H, s), the last two resonances disappear upon addition of D_2O; mass spectrum, *m/e* 250, 229, 196, 186, 158, 131, 104, 102, 101, 76, 75, 51, 43.

2-Butyryl-1,4-naphthoquinone (1). The hydroquinone 4 (11.0 g, 0.048 mol) and 43.4 g of silver carbonate (adsorbed on Celite, assuming 1 mm of silver carbonate per 0.57 g of reagent is 0.076 mol of silver carbonate) was stirred at reflux under N_2 for 2 h in 1.5 L of dichloromethane. The mixture was filtered and washed three times with 100 mL of dichloromethane. The solvent was evaporated and the residue was recrystallized several times from petroleum ether (30–60 °C) to give 5.05 g (46%) of yellow needles: mp 54.5–55.5 °C (Lit.[5] mp 55–56 °C); IR(neat) 1695, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1./0 (3 H, t), 1.80 (2 H, m), 2.95 (3 H, t), 7.10 (1 H, s), 8.05 (4 H, m).

2,4-Dicarbethoxy-1-propyl-9,10-anthraquinone (2). To a solution containing 2.80 g (0.015 mol) of diethyl glutaconate and 1.89 g (0.008 mol) of 2-butyryl-1,4-naphthoquinone dissolved in 30 mL of methanol was added 10 mL of concentrated ammonium hydroxide. The reaction mixture turned brown. After 10 min, 100 mL of water was added and the mixture extracted three times with 100 mL of ether. The aqueous layer was acidified with dilute H_2SO_4 and extracted three times with 100 mL of ether. The ether solutions were dried ($MgSO_4$), filtered, and evaporated. A brown residue resulted from the basic extract which crystallized slowly on standing. This material was recrystallized from acetone to give 1.05 g (33%) of the light yellow anthraquinone: mp 77.5–79 °C; IR (KBr) 1730, 1670 cm^{-1}; mass spectrum, *m/e* 394, 365, 349; ^1H NMR (CCl_4) δ 1.1 (3 H, t), 1.4 (6 H, t), 1.6 (2 H, m), 3.35 (2 H, t), 4.45 (4 H, q), 7.75–8.1 (5 H, m); ^{13}C NMR ($CDCl_3$) 14.0 (q), 14.6 (q, 24.5 (t), 33.3 (t), 62.0 (t), 126–147 (aromatic carbons), 167.0 (s), 169.0 (s), 169.0 (s), 182.5 (s), 184 (s). Anal. Calcd for $C_{23}H_{22}O_6$: C, 70.02; H, 5.63; Found: C, 70.23; H, 5.78.

Registry No. 1, 65781-70-6; 2, 74007-41-3; 3, 40036-53-1; 4, 72827-02-2; 1,4-naphthoquinone, 130-15-4; butyric anhydride, 106-31-0; diethyl glutaconate, 2049-67-4.

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Stereochemistry in the Reduction of Vinyl Bromides with Lithium Aluminum Hydride

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Complex metal hydrides such as lithium aluminum hydride ($LiAlH_4$) and sodium borohydride ($NaBH_4$) have proven to be extremely versatile reagents for the reduction of a wide variety of organic functional groups.[1] Although they are generally believed to react as nucleophilic hydride donating species, the detailed mechanistic picture of the reduction is far from clear, especially in the reduction of aryl, vinyl, bridgehead, and cyclopropyl halides which are normally inert to the S_N processes.[2] In a recent report we have shown that $LiAlH_4$ reduction of aryl bromides proceeds most likely via a radical mechanism. We have further suggested that the metal hydride might serve not only as an efficient hydrogen atom donor to the radical intermediate but also as an electron-transfer reagent in the initial production of the radical.[3] As an extension of this mechanistic scheme, we have now examined the stereochemical outcomes in the $LiAlH_4$ reduction of vinyl bromides.

The energy barrier of the configurational inversion for the vinyl radical has been determined to be ca. 2 kcal/mol by kinetic ESR experiments,[4] and the value is comparable to 4.3 kcal/mol calculated by the semiempirical MINDO method.[5] On the other hand, the configurational stabilities of vinyl anions have long been established experi-

Table I

run	substr	molar ratio of $LiAlD_4$/ substr	conditions[a]	d_1/d_0[b]	ratio of 4a/4b[c]
1	1a (trans)	4.0	ether, rt	63/37	50/50
2[f]	1a	8.0	ether, rt	77/23	48/52
3[f]	1a	4.0	THF, rt	59/41	52/48
4	1a	4.0	THF, Δ	60/40	90/10
5	1a	4.0[d]	THF, Δ	5/95	
6	1a	1.05[e]	benzene, Δ	72/28	50/50
7	1a	5.0[e]	benzene, Δ	76/24	50/50
8	1a	2 mmol of 1a, 1 g of Zu-Cu	EtOD, Δ (10 mL)	72/28	95/5
9	1b (cis)	4.0	ether, rt	65/35	48/53
10	1b	4.0	THF, rt	55/45	50/50
11[f]	1b	4.0	THF, Δ	56/44	16/84
12	1b	4.0[d]	THF, Δ	2/98	

[a] Reactions were run under an Ar atmosphere at a 0.1 concentration of the substrate for periods well over half the reaction time; rt = room temperature. [b] Determined by mass spectral analysis on a Hewlett-Packard GC/MS data system, Model 5982-A, and corrected for the amount of natural abundance of M + 1. [c] Determined by NMR analysis and corrected for the amounts of styrene-d_0 present based on the ratios of d_1/d_0. [d] $LiAlH_4$ was used, and the reaction was quenched by addition of D_2O. [e] $(n\text{-}Bu)_3SnD$ was used. [f] Averaged values of d_1/d_0 and 4a/4b from two runs.

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(3) S. K. Chung and F. F. Chung, *Tetrahedron Lett.*, 2473 (1979). More recently we were able to identify O_2-trapped products of the radical intermediates in the $LiAlH_4$ reduction of *p*-bromoanisole and α-bromonaphthalene. $LiAlH_4$ reduction of aryl halides is not significantly inhibited by 5 molar % of tetraphenylhydrazine or 9,10-dihydroanthracene, thus suggesting that the free-radical chain process is not likely involved in these reactions.

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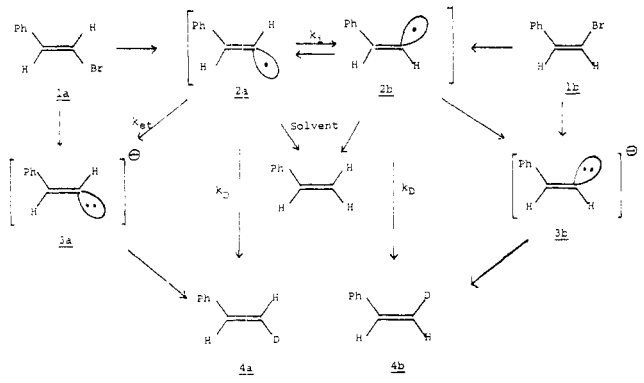
Scheme I



mentally,[6] again in accordance with the calculated inversion barrier of 31.1 kcal/mol.[5] On the basis of the reasonable assumption that the rate of inversion of configuration of the β-styrenyl radical would be similar to that established for the vinyl radical ($k_i \simeq 10^{8-10}$ s^{-1}),[7] it is expected that the reduction of β-bromostyrene (1) by $LiAlD_4$ would result in a loss of stereochemistry, if such radicals are involved as intermediates.

The readily available *trans*- and *cis*-β-bromostyrenes (**1a** and **1b**) were reduced with $LiAlD_4$ under a variety of conditions, and the results are summarized in Table I. Styrene was obtained as the major product in all of the runs along with the starting material and some polymeric products. The percent of deuterium incorporation in sytrene (d_1/d_0) was determined by mass spectral analysis, and the rations of *trans*- and *cis*-β-deuteriostyrenes (**4a**/**4b**) were measured by NMR spectral analysis in the region of δ 5.0–6.0.[8]

The data clearly show a number of useful features. First, the reduction at room temperature (runs 1–3 and 9–10) proceeds with a virtually complete loss of stereochemistry regardless of the substrate geometry (trans or cis) or choice of the solvent (ether or THF). In a striking contrast, reduction at refluxing THF temperature (runs 4 and 11) proceeds with a predominant retention of the configuration. It is also interesting to compare these stereochemical results with $LiAlD_4$ with those of $(n\text{-Bu})_3SnD$ in refluxing benzene and Zn–Cu in refluxing EtOD—conditions known to proceed via radical intermediates[9] and electron-transfer processes,[10] respectively. Second, a significant amount of nonlabeled styrene (d_0) was produced in all the runs, indicating that the intermediate is capable of abstracting hydrogen from both the metal hydride and the solvents. The control experiments involving the substrate reduction with $LiAlH_4$ followed by D_2O workup (runs 5 and 12) demonstrate that the reduction was complete before the aqueous workup.

Although intervention of a β-styrenyl carbonium ion could result in the loss of stereochemistry, such a highly energetic species is very unlikely to be produced under the reaction conditions.[11] Another possible cause for the loss of stereochemistry, namely, elimination of HBr followed by reduction with $LiAlD_4$, could be readily excluded by the following control experiments. Phenylacetylene was never detected during the course of reduction by a careful GC analysis, nor was it reduced to styrene under the identical reaction conditions. It was also observed that the starting material did not undergo geometrical isomerization prior to the reduction. Therefore, it appears that the data obtained from $LiAlD_4$ reductions of **1a** and **1b** at room temperature may be best accommodated by a mechanistic picture involving the two rapidly interconverting radicals **2a** and **2b** as depicted Scheme I. The predominant retention of the stereochemistry in the $LiAlD_4$ reduction of **1a** and **1b** at refluxing THF temperature is unexpected. Although these results can be rationalized by the radical mechanistic scheme, with the assumption that the k_{et} step is markedly temperature dependent, it appears possible that entirely different reaction pathways, e.g., S_N2 displacement on bromine resulting in carbanion formation or stereospecific syn addition of $LiAlD_4$ followed by anti elimination of $LiAlD_3Br$ etc., might be operating under the elevated temperature conditions. In summary, the evidence seems to suggest the involvement of a radical mechanistic pathway in the metal hydride reduction of vinyl halides under certain conditions.

Experimental Section

Lithium aluminum hydride and deuteride were purchased from Ventron Corp. (Alfa Division). The NMR spectra were obtained on a Varian Associates Model T-60 or CFT-20 with Me_4Si as internal standard. Mass spectral analyses were done on a Hewlett-Packard GC/MS system, Model 5982-A. GC analyses were performed with an Antek Instruments Model 300 and a Varian Aerograph Model 2700 by using the following columns: 5 ft, 10% OV-101; 5 ft, 10% FFAP on Anakrom-SD, 60/70 mesh. The NMR measurement of β-deuteriostyrenes was carried out according to the established literature method.[8]

***trans*-β-Bromostyrene (1a)** was purchased from Aldrich Chemical Co. and purified according to a literature procedure,[8] and was at least 92% isomerically pure by GC analysis (FFAP column).

***cis*-β-Bromostyrene (1b)** was prepared from *trans*-cinnamic acid according to a literature procedure,[12] and was at least 90% isomerically pure by GC analysis (FFAP column).

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Registry No. **1a**, 588-72-7; **1b**, 588-73-8; $LiAlH_4$, 16853-85-3.

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Unequivocal Assignment of the Skeletal Structure of the Guanine–Glyoxal Adduct

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The reaction of guanine and its derivatives with various aldehydes has been shown to be useful in the base-selective modification of both DNA[1,2] and RNA.[2,3] Monocarbonyl

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