(19) H. Friege and M. Klessinger, *J. Chem. Res. (S)*, 208 (1977).
(20) N. L. Owen and R. E. Hester, *Spectrochim. Acta, Part A*, **25**, 343 (1969).
(21) J. Aroney, R. J. W. Lefoer, P. K. Pierens, and M. G. N. The, *J. Chem. Soc. B*, 666 (1969).
(22) J. Naggy and P. Hencsei, *Acta Chim. Acad. Sci. Hung., Tomus*, **71**, 83 (1972).
(23) A. L. McCellan, "Tables of Experimental Dipole Moments", Freeman and Co., London, 1963.
(24) V. A. Granzhan, S. F. Manole, and S. K. Laktionova, *Izv. Akad. Nauk Mold. SSR, Ser. Biol. Khim. Nauk*, **4**, 72 (1972).
(25) L. M. DiBello, H. M. McDevitt, and D. M. Roberti, *J. Phys. Chem.*, **72**, 1405 (1968).
(26) (a) D. M. Roberti and C. P. Smyth, *J. Am. Chem. Soc.*, **82**, 2106 (1960); (b) W. E. Vaughan and C. P. Smyth, *J. Phys. Chem.*, **65**, 98 (1961); (c) E. L. Grubb and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 4873 (1961).
(27) G. Klages and Z. Zentek, *Z. Naturforsch. A.* **16**, 1016 (1961).
(28) (a) J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963); (b) R. W. Crecely, K. W. McCracken, and J. H. Goldstein, *Tetrahedron*, **25**, 877 (1969); (c) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **44**, 2855 (1966); see also, F. Effenberger, P. Fischer, W. W. Schoeller, and W. D. Stohrer, *Tetrahedron*, **34**, 2409 (1978).
(29) A. Zweig, *J. Phys. Chem.*, **67**, 506 (1963); A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Am. Chem. Soc.*, **85**, 3933 (1963).
(30) (a) A. I. Kitaigorodsky, "Molecular Crystals and Molecules", Academic Press, New York, 1973. (b) The packing coefficients of the *o*-dimethoxy-substituted aromatics showed no consistent difference between the planar and nonplanar structures, probably owing to the size of the alkaloids to which these groups are attached. Our procedure is more selective since the immediate environment of the methoxy substituent can be studied; however, unlike the packing coefficient defined by Kitaigorodsky, which is dependent only on the unit cell volume, our results vary with the unit cell geometries. In our work, the unit spherical volume was centered 2.5 Å along the $C_{aromatic}$–O axis and having a radius of 5.0 Å. The Bondi intersection volume of neighboring molecules was then computed in a manner similar to Kitaigorodsky's method.
(31) L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).
(32) E(barrier) = $34.99q_\pi + 0.677$, $r = 0.974$.
(33) ΔE(barrier) = $24.17q_\pi - 0.003$, $r = 0.999$.
(34) U. Braun, G. Braun, P. Jacob III, D. E. Nichols, and A. T. Shulgin in ref 7, pp 27–37.
(35) L. N. Domelsmith, L. L. Munchausen, and K. N. Houk, *J. Am. Chem. Soc.*, **99**, 4311 (1977).
(36) A. Veillard in "Quantum Mechanics of Molecular Conformations", B. Pullman, Ed., Wiley-Interscience, New York, 1976, Chapter 1, and references cited therein.
(37) P. Kollman, W. Trager, and S. Rothenburg, *J. Am. Chem. Soc.*, **95**, 458 (1973).

Chiral Trialkylborane Reducing Agents. Preparation of 1-Deuterio Primary Alcohols of High Enantiomeric Purity

M. Mark Midland,*[1] Sue Greer,[2] Alfonso Tramontano, and Stephen A. Zderic

Contribution from the Department of Chemistry, University of California, Riverside, California 92521. *Received September 11, 1978*

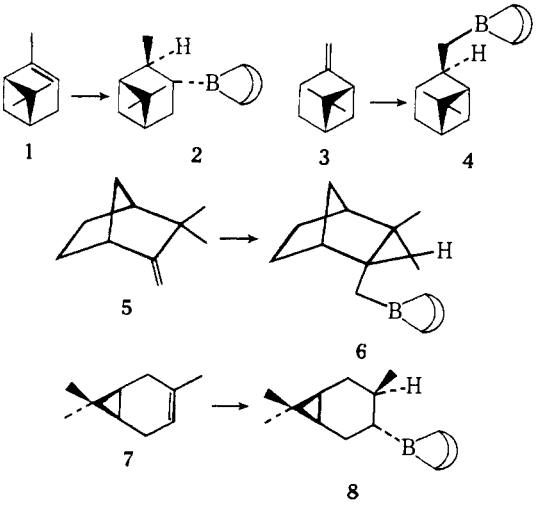
Abstract: *B*-3-Pinanyl-9-borabicyclo[3.3.1]nonane (3-pinanyl-9-BBN, prepared from (+)-α-pinene and 9-BBN) is an effective chemical reagent for the asymmetric reduction of 1-deuterio aldehydes to chiral 1-deuterio primary alcohols. For example, benzaldehyde-*1-d* is reduced to pure (*S*)-(+)-benzyl-*1-d* alcohol. A deuterated reagent prepared from α-pinene and 9-BBN-*9-d* was found to reduce a variety of aromatic, aliphatic, and α,β-unsaturated aldehydes to the corresponding chiral primary 1-deuterio alcohols. In each case a large excess of the *R* enantiomer is formed. Steric factors seem to have little effect on the extent of asymmetric induction, but electron-donating para substituents on benzaldehyde slightly decrease the enantioselectivity of the reduction. A number of other chiral-9-BBN derivatives were investigated. A model is proposed to account for the high asymmetric inductions.

We have previously shown that certain *B*-alkyl-9-borabicyclo[3.3.1]nonane (9-BBN) compounds reduce aldehydes under exceptionally mild conditions.[3] Thus the sluggish reaction originally reported by Mikhailov[4] can be made into a useful technique for the selective reduction of aldehydes.[5] Using the chiral reagent derived from α-pinene and 9-BBN, we have shown that benzaldehyde-*1-d* may be reduced to chiral benzyl-*1-d* alcohol of exceptionally high enantiomeric purity.[6] Such optically active primary 1-deuterio alcohols have been used extensively for mechanistic studies of chemical and biochemical processes,[7] However, previous techniques for their preparation are tedious or inefficient.[8] Herein we establish the organoborane route as an effective general method for the preparation of diverse 1-deuterio primary alcohols of high enantiomeric purity.

Results and Discussion

In the initial experiments the readily prepared[9] benzaldehyde-*1-d* was reduced by the *B*-alkyl-9-BBN reagents derived from (+)-α-pinene (**1**), (−)-β-pinene (**3**), (−)-camphene (**5**), and (+)-3-carene (**7**) (Scheme I). The optical purity of the resulting benzyl alcohol was determined using the chiral NMR shift reagent tris[(3-heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III),[8d] Eu(hfc)$_3$. The results are given in Table I, Since both enantiomers of α-pinene are

Scheme I



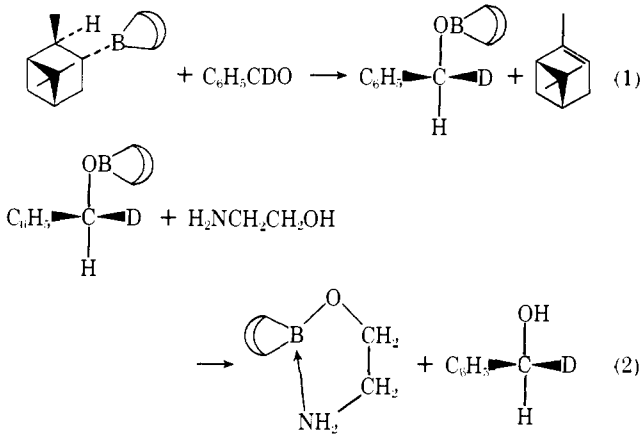
readily available in high optical purity[10] and since the corresponding borane, **2**, gave the best results, it was chosen for further studies.

In refluxing tetrahydrofuran (THF), the 3-pinanyl-9-BBN

0002-7863/79/1501-2352$01.00/0

(**2**) rapidly reduces benzaldehyde-*1-d* to (*S*)-(+)-benzyl-*1-d* alcohol of 88% enantiomeric excess (e.e.), When a slight excess of **2** is used, the reaction is over within 2 h even at room temperature; the enantiomeric purity of the alcohol is slightly increased to 90% e.e. Since the starting α-pinene was only 92% optically pure, the results represent an essentially quantitative asymmetric induction. In fact, *using optically pure* (+)-*α-pinene we cannot detect any of the R enantiomer by NMR*,

The process is operationally simple and can be done on a large scale, To facilitate isolation of the product and to minimize contamination by chiral impurities, the excess organoborane is destroyed by adding acetaldehyde. The pinene which is liberated during the reaction (eq 1) may then be removed



under vacuum. This process avoids the production of a second chiral alcohol, which may be difficult to separate from the product, following an oxidative workup,[11] The addition of 1 mol of 2-aminoethanol then precipitates the 9-BBN as an adduct[12] and liberates the benzyl alcohol (eq 2). (Alternatively, the cyclooctylborane may be oxidized and the product separated from the 1,5-cyclooctanediol.[12]) However, even using this process the rotation of the alcohol is often too high, although the alcohol appears to be pure by NMR. Further purification by conventional means such as careful distillation, liquid chromatography, VPC, or recrystallization of a derivative is required to obtain a product of acceptable optical purity.

We have observed that tertiary β hydrogens preferentially react in the presence of secondary or primary β hydrogens.[3] In fact, α-pinene is the only detected elimination product from reagent **2.** Thus the hydrogen added via the hydroboration process is the reducing hydrogen. Indeed, the organoborane resulting from deuteroboration of α-pinene with 9-BBN-*9-d* quantitatively transfers deuterium (based on the deuterium content on the 9-BBN-*9-d*) to benzaldehyde.

The availability of a deuterated reagent allows one to reduce a variety of aldehydes without the necessity of preparing diverse 1-deuterated aldehydes. The results are presented in Table II. The asymmetric inductions observed are consistently high regardless of the structure of the aldehyde. Thus a tertiary butyl group (entry 3) has about the same effect as a straight-chain alkyl group (entries 1 and 2). The reduction is more efficient with electron-donating substituents. Interestingly, this increase in selectivity is accompanied by an increase in the rate of reduction. Thus *p*-nitrobenzaldehyde is reduced exceptionally rapidly at room temperature, while *p*-dimethylaminobenzaldehyde requires 8 h at reflux to ensure completion. The effect of the para substituent on the rate of reduction is consistent with a hydride transfer to the carbonyl carbon in the cyclic transition state.[3] The increase in enantioselectivity with increasing rate of reduction is surprising. However, this change in selectivity reflects only a small change in the difference in

Table I. Reduction of Benzaldehyde-*1-d* with Chiral *B*-Alkyl-9-BBN Reagents

reagent	config of product	% e.e.[a]	reagent	config of product	% e.e.[a]
2	*S*	90	**6**	*R*	75
4	*S*	47	**8**	*S*	61

[a] Percent e.e. refers to the percent enantiomeric excess as determined by Eu(hfc)$_3$. No correction has been made for the enantiomeric purity of the starting terpenes.

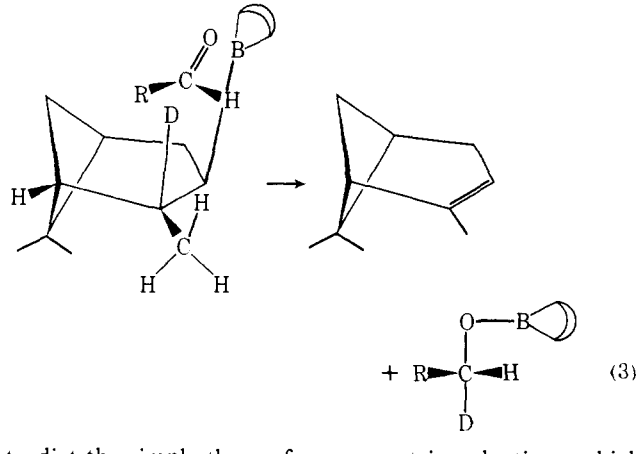
Table II. Reduction of Aldehydes with Deuterated *B*-3-Pinanyl-9-BBN

product	% e.e.[a]	corrected for % D[b]	corrected for % e.e. of pinene[c]
1. $CH_3CH_2CH_2CHDOH$	83	101	101[d]
2. $CH_3(CH_2)_4CHDOH$	64	83	89
3. $(CH_3)_3CCHDOH$	70	91	98
4. $C_6H_5CH{=}CHCHDOH$	60	78	84
5. $(CH_3)_2C{=}CHCH_2CH_2$-$CCH_3{=}CHCHDOH$	58	75	81
6. C_6H_5CHDOH	70	91	98
7. *p*-ClC_6H_4CHDOH	87	94	101
8. *p*-$O_2NC_6H_4CHDOH$	86	93	100
9. *p*-$CH_3C_6H_4CHDOH$	76	83	89
10. *p*-$CH_3OC_6H_4CHDOH$	70	76	82
11. *p*-$(CH_3)_2NC_6H_4CHDOH$	61	66	71

[a] As observed by measuring the area of the carbinyl proton signals in the presence of Eu(hfc)$_3$. The percent e.e. as measured by this method is low since undeuterated product contributes to both the peaks. [b] Entry 1 is corrected for 90% deuteration, entries 2-6 for 87% deuteration, and entries 7-11 for 96% deuteration. The difference in percent deuteration represents different samples of 9-BBN-*9-d*. [c] The (+)-α-pinene was 93% e.e. [d] The α-pinene was 100% e.e.

energies of activation leading to the two diastereomeric transition states. Subtle changes in conformation or electronic repulsion or attraction could account for the difference. Alternatively, a dehydroboration-reduction process[3] could be competing with the cyclic process in the case of the slower reductions.

The absolute configuration for the major product of reduction by deuterated **2** is the *R* enantiomer. This assignment is based on the greater shift observed for the carbinyl proton of the *R* enantiomer in the presence of Eu(hfc)$_3$.[8d] The aldehyde therefore must approach the borane with the R group over the pinane ring and the aldehydic hydrogen over the methyl group, as depicted in eq 3, This model seems to con-



tradict the simple theory for asymmetric reductions, which postulates that there is a dovetailing of a small and large group

on the ketone, respectively, with a large and small group on the reducing agent,[13] However, models suggest the R group is situated over the bridgehead hydrogen of the pinanyl ring and that the bridgehead hydrogen is held away from the R group. The pinanyl methyl group on the other hand is freely rotating, and its hydrogens would interfere if the R group were to approach from this side. This invariant result combined with the use of optically active shift reagents could be very useful in assigning the absolute configuration to chiral primary 1-deuterio alcohols.

The approach of the aldehyde with the R group toward the bridgehead hydrogen or large ring is also seen in organoboranes **4** and **8.** One may again postulate that the hydrogen on the bridgehead of **4** or on the carane ring of **8** is held back by the ring structure and thus gives the least resistance to the phenyl group. Organoborane **6** is the only one which follows the simple theory for asymmetric reductions. Benzaldehyde approaches the organoborane with the phenyl group away from the large geminal dimethyl group.

It is possible that an initial complex between the organoborane and the carbonyl oxygen may play a role in the stereochemical outcome of the reaction. Indirect evidence for such a complex is that a slight yellow to reddish-orange color develops upon addition of the aldehyde to the organoborane.[14] We reasoned that the best chance for observing such a complex would occur with a nonreducing, sterically unhindered organoborane and with a benzaldehyde containing an electron-donating para substituent. Addition of 1 mol of *B*-methyl-9-BBN to 1 mol of *p*-dimethylaminobenzaldehyde gave an intense reddish-orange color. The aldehydic proton absorption was shifted from δ 9.70 to 9.45 ppm, Excess organoborane caused a maximum shift to 9.00 ppm. The dimethylamino group was shifted only slightly upfield, indicating that the borane is not complexing significantly to the nitrogen. The aldehydic proton of benzaldehyde was also shifted in the presence of *B*-methyl-9-BBN, but only 0.07 ppm upfield. These results are consistent with a stabilization of the positive charge on the carbonyl carbon in the complex by the electron-donating group. The importance of this complex in the mechanism of the reduction remains to be seen. Attempts to detect a complex with **2,** which also gives a reddish-orange color, failed. Only reduction products could be observed.

The reduction of aldehydes with *B*-3-pinanyl-9-BBN provides an efficient route to chiral primary alcohols with an enantiomeric purity which approaches that of enzymes. The reaction consistently gives a predictable absolute configuration. Either the *R* or the *S* product is available by using either (−)- or (+)-α-pinene or by using the deuterated organoborane reagent. Finally, the reagent may be used to prepare chiral tritium-labeled alcohols.[15]

Experimental Section

All operations involving air-sensitive reagents were performed under a dry nitrogen atmosphere using syringe techniques.[16] All glassware was dried at 135 °C for at least 4 h, assembled hot, and cooled while being purged with nitrogen. ^{1}H NMR were obtained on a Varian EM-390 (90 MHz) instrument. The VPC analysis of reactions was carried out on a Hewlett-Packard 5732TCD chromatograph using 6 ft × $\frac{1}{8}$ in. SE-30, DC-710, or XE-60 columns as needed. Optical rotations were measured on a Rudolph Model 451 visual polarimeter. Areas of the carbinyl proton signal in the presence of Eu(hfc)$_3$ were determined by cutting and weighing expanded spectra.

THF was distilled under nitrogen from benzophenone ketyl and stored under a positive nitrogen pressure. Liquid aldehydes were distilled before use. Solid aldehydes were dissolved in a minimum amount of THF and added by syringe. Benzaldehyde-*1-d* was prepared according to the literature.[9] Solid 9-BBN was prepared by the method of Brown[17] and dissolved in THF to make a 0.5 M solution. 9-BBN-*9-d* (87–90% D) was obtained from Aldrich Chemical Co. or solid 9-BBN-*9-d* (98% D) was prepared using borane-d_3 (Alfa) and 1,5-cyclooctadiene.[18] α-Pinene ($[\alpha]^{22}_D$ +46.6° (neat, *l* = 1)) and β-pinene ($[\alpha]^{22}_D$ −21.0° (neat, *l* = 1)) were obtained from Aldrich Chemical Co. Δ^3-Carene, $[\alpha]^{25}_D$ +15.4° (neat, *l* = 1), was a gift of International Flavors and Fragrances. These olefins were distilled under vacuum from a small quantity of lithium aluminum hydride prior to use. Camphene ($[\alpha]^{25}_D$ −108° (*c* 5, benzene), lit.[19] $[\alpha]_D$ −117°) was prepared according to a literature procedure from *l*-borneol.[19]

Benzyl-*1-d* Alcohol (from 2). A dry, 1000-mL flask equipped with a side arm covered with a rubber stopple, a reflux condenser, and a magnetic stirrer bar was flushed with nitrogen. The flask was charged with 25 g (0.205 mol) of solid 9-BBN. Then 400 mL of dry THF was added by a double-ended needle. This was followed by 35 mL of α-pinene (0.22 mol). The mixture was stirred at a gentle reflux for 2 h. The flask was then cooled to room temperature and 19 mL of benzaldehyde-*1-d* (0.185 mol, 99% deuterated) was added by syringe. The solution became slightly yellow. After 10 min the solution was refluxed for 1 h to ensure completion of the reaction. Then the mixture was cooled to room temperature and 5 mL of acetaldehyde was added. The THF was removed with a water aspirator. The pinene was then removed on a vacuum pump (0.05 mm, 2 h) with the flask surrounded by a warm water bath (40 °C). Nitrogen was admitted to the flask and 150 mL of anhydrous diethyl ether added. The solution was cooled to 0 °C and 12.4 mL (0.205 mol) of 2-aminoethanol added. A white precipitate formed and was removed by filtration. The precipitate was washed with 2 × 20 mL of ether. The ether solution was washed with water, then dried ($MgSO_4$), and removed under vacuum. The resulting liquid was distilled through a 10-cm Vigreux column to give 16.5 g of benzyl-α-*d* alcohol (81.6%): bp 110 °C (30 mm); $[\alpha]^{25}_D$ +1.56 ± 0.05° (neat, *l* = 1), n^{25}_D 1.5318 (lit.[8a] $[\alpha]^{24}_D$ +1.58°, n^{20}_D 1.5350). The compound appeared to be pure by VPC and ^{1}H NMR: (CCl_4) δ 2.0 (s, 1, H), 4.6 (t, 1 H, J_{HCD} = 1.8 Hz), 7.33 (s, 5 H). Examination in the presence of Eu(hfc)$_3$ indicated a mixture of 6% *R* and 94% *S* enantiomers. The alcohol may be further purified as the phthalate ester to give a product with a rotation of $[\alpha]^{25}_D$ +1.39 ± 0.05° (88% e.e.). Repetition of the reaction at room temperature (2 h) produced alcohol of 5% *R* and 95% *S* composition.

Benzyl-*1-d* Alcohol (from 4, 6, and 8). Olefins **3, 5,** or **7** (5 mmol) were hydroborated with 9-BBN (4.5 mmol) for 2 h at reflux in THF and then cooled to room temperature. Benzaldehyde-*1-d* (4 mmol) was then added to each flask and the solution stirred overnight at room temperature and then refluxed for 1 h to assure completion. (Reduction of benzaldehyde was usually complete after 2 h at room temperature as judged by VPC analysis.) The cooled solution was then treated with 0.5 mL of acetaldehyde and stirred for 15 min. The reaction was worked up as above by removing the solvent on an aspirator, heating under vacuum to remove olefin, and adding ether (10 mL) and then 2-aminoethanol (0.33 mL). The solid was removed and washed with ether, and the ether was washed with saturated sodium chloride solution. After drying with magnesium sulfate, and concentrating the solution, the residue was distilled by Kugelrohr. The alcohol was then analyzed by NMR using Eu(hfc)$_3$. The results are reported in Table I.

Reductions with Deuterated 2. The following procedure is representative: α-pinene, 2.5 mmol, and 9-BBN-*9-d*, 2.0 mmol, in 4 mL of tetrahydrofuran were refluxed for 4 h in a dry, nitrogen-flushed, round-bottomed flask. The solution was cooled to room temperature and freshly distilled hexanal, 2.5 mmol, was added. The solution was stirred overnight at room temperature. The solvent was removed by water aspirator and then the oily residue heated to 40 °C at 0.05 mm to remove the α-pinene and excess aldehyde. The flask was filled with nitrogen and the liquid dissolved in 4 mL of anhydrous ether and cooled to 0 °C. Then ethanolamine, 2.5 mmol, was added and the mixture stirred for 15 min. The white precipitate was removed by filtration and the ether washed with 10 mL of saturated sodium chloride solution. The ether layer was dried ($MgSO_4$) and concentrated and the product distilled by Kugelrohr (50 °C, 30 mm). The sample was then analyzed by NMR in the presence of Eu(hfc)$_3$. Since undeuterated material contributes equally to the area of both the *R* and *S* signals, the percent e.e. was corrected for deuterium incorporation using the following equations: % e.e. (corrected) = % e.e. (measured) $(1 + X)/(1 - X)$, where % e.e. (measured) is determined from the peak areas and X is the fraction of undeuterated alcohol.

***p*-Nitrobenzyl-*1-d* Alcohol.** The following modified procedure for the isolation of product was used: the reduction was performed at room temperature for 3 h. After destroying excess organoborane with ac-

etaldehyde, the solvent was removed under vacuum at room temperature. The residue was dissolved in a small quantity of ether and 1 mol of 2-aminoethanol was added. The solution was filtered and the ether concentrated under vacuum (but not to dryness) (a drop or two of methanol will redissolve any precipitate). The product was eluted with ether from a silica gel column, concentrated by rotary evaporator, and distilled by Kugelrohr at 0.01 mmHg, 110 °C, yield 46%. (We have previously isolated this alcohol in 76% on a larger scale using *B*-siamyl-9-BBN.[5])

***p*-Dimethylaminobenzyl-*1-d* Alcohol.** The following modified procedure was used: The reaction was refluxed in THF for 8 h. The solution was then cooled to room temperature and treated with 2 mL of water, stirred for 15 min, and then extracted with 2 × 30 mL of acidified water (concentrated HCl added dropwise until the solution had a pH of 1). The aqueous solution extracts were combined, made basic to pH paper (with 3 N sodium hydroxide solution), and extracted with 2 × 20 mL of ether (saturating the water with potassium carbonate after the first extraction). The combined extracts were dried over magnesium sulfate, filtered, and concentrated under vacuum to yield the product (60%). Using *B*-siamyl-9-BBN on a larger scale, we have isolated the alcohol in 92% yield.[5]

Organoborane–Aldehyde Complex. *p*-Dimethylaminobenzaldehyde, 0.25 mmol, in 0.5 mL of THF was added to a nitrogen-flushed NMR tube. *B*-Methyl-9-BBN[20] (0.25 mmol) was added and the solution immediately became reddish orange. The aldehyde proton shifted from 9.70 to 9.45 ppm. Addition of excess *B*-methyl-9-BBN (3 mmol of borane to 0.1 mmol of aldehyde) caused an additional shift to a maximum value of 9.00 ppm.

Acknowledgments. We wish to thank the Research Corporation and the National Institutes of Health for support of this research.

References and Notes

(1) Alfred P. Sloan Foundation Fellow, 1978–1980.
(2) National Science Foundation–Undergraduate Research Participant, 1977.
(3) M. M. Midland, A. Tramontano, and S. A. Zderic, *J. Organomet. Chem.*, **134**, C17 (1977); **156**, 203 (1978).
(4) (a) B. M. Mikhailov, Yu N. Bubnov, and V. G. Kiselev, *J. Gen. Chem. USSR*, **36**, 65 (1966); see also, (b) J. D. Buhler, Ph.D. Thesis, Purdue University, 1973.
(5) M. M. Midland and A. Tramontano, *J. Org. Chem.*, **43**, 1470 (1978).
(6) M. M. Midland, A. Tramontano, and S. A. Zderic, *J. Am. Chem. Soc.*, **99**, 5211 (1977).
(7) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127–244 (1969); L. Verbit, *Prog. Phys. Org. Chem.*, **7**, 51–127 (1970); K. S. Y. Lau, P. K. Wong, and J. K. Stille, *J. Am. Chem. Soc.*, **98**, 5832 (1976); E. Caspi and C. R. Eck, *J. Org. Chem.*, **42**, 767 (1977), and references therein.
(8) For examples, see: (a) V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Am. Chem. Soc.*, **88**, 3595 (1966); (b) K. R. Varma and E. Caspi, *Tetrahedron*, **24**, 6365 (1968); (c) S. Wolfe and A. Rauk, *Can. J. Chem.*, **44**, 2591 (1966); (d) C. J. Reich, G. R. Sullivan, and H. S. Mosher, *Tetrahedron Lett.*, 1505 (1973); (e) A. Streitwieser, Jr., J. R. Wolfe, Jr., and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959); (f) H. Gerlach, *Helv. Chim. Acta*, **49**, 2481 (1966).
(9) A. W. Burgstahler, D. E. Walker, Jr., J. P. Kuebrick, and R. L. Schowen, *J. Org. Chem.*, **37**, 1272 (1972); also see T. Chancellor, M. Quill, D. E. Bergbreiter, and M. Newcomb, *ibid.*, **43**, 1245 (1978); D. Seebeck, B. W. Erickson, and G. Singh, *ibid.*, **31**, 4303 (1966).
(10) (+)-α-Pinene of 100% optical purity may be prepared by equilibration of diisopinocampheylborane: H. C. Brown and N. M. Yoon, *Isr. J. Chem.*, **15**, 12 (1976/1977). (−)-α-Pinene may be prepared by isomerization of (−)-β-pinene: W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc. C*, 41 (1966); C. A. Brown, *Synthesis*, 754 (1978). Both (+)- and (−)-α-pinene of 85–90% optical purity are available from a number of commercial sources.
(11) The optical rotation of isopinocampheol is $[\alpha]^{23}_{D}$ −35.1° (c 10, benzene); see Brown and Yoon, ref 10. An impurity of 0.1% isopinocampheol in the deuterated alcohol will add about 0.3–0.4° to the rotation.
(12) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **42**, 1197 (1977).
(13) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1970, p 164.
(14) Mikhailov also reported a yellow color during his reduction,[4a] but he was unable to detect a complex by IR.
(15) R. J. Parry and D. A. Trainor, *J. Am. Chem. Soc.*, **100**, 5243 (1978).
(16) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley, New York, 1975, Chapter 9.
(17) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974).
(18) M. M. Midland and S. Greer, *Synthesis*, 845 (1978).
(19) W. Huckel, C. M. Jennewein, H. J. Kern, and O. Vogt, *Justus Liebigs Ann. Chem.*, **719**, 157 (1968).
(20) Reference 16, p 172.

Electron Transfer Processes. 18. Reaction of 2-Halo-2-nitropropanes and 2,2-Dinitropropane with Resonance-Stabilized Carbanions and 1-Alkynyllithiums[1]

Glen A. Russell,* Mikolaj Jawdosiuk, and Mieczyslaw Makosza

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received September 11, 1978*

Abstract: α-Substituted benzylic carbanions react with 2-X-2-nitropropane, where X = Cl, Br, or NO_2, to undergo dimerization with no evidence of formation of cross-coupling products. Lithium acetylenides (RC≡CLi, R = alkyl) react with 2-chloro-2-nitropropane or 2,2-dinitropropane to form the cross-coupled product ($RC{\equiv}CC(CH_3)_2NO_2$) by a process which does not involve a free radical chain mechanism. 2-Cyano-2-nitropropane reacts with lithium acetylenides in THF to form the cyanoacetylene (RC≡CCN).

2-Halo-2-nitropropanes, 2,2-dinitropropane, or 2-arylsulfonyl-2-nitropropane undergo a variety of reactions with carbanions. Substitution at carbon with loss of halide,[2] nitrite,[3] or arylsulfinate anions[4] can occur via a free radical chain process which has been labeled $S_{RN}1$ (Scheme I),[5]

This process has been observed with tertiary carbanions including anions derived from nitroalkanes, malonic esters, malononitriles, β-keto nitriles, cyanoacetic esters, β-keto esters, and β-diketones.[2-5]

A modified radical pathway leads to the dimerization of the carbanions (Scheme II).[6] The nitronate anion formed in

Scheme I

X = Cl, Br, NO_2, $ArSO_2$

$$[XC(R)_2NO_2]^{-\cdot} \rightarrow X^- + R_2\dot{C}NO_2$$

$$R_2\dot{C}NO_2 + {>}C:^- \rightarrow [O_2NC(R)_2C{<}]^{-\cdot}$$

$$[O_2NC(R)_2C{<}]^{-\cdot} + XC(R)_2NO_2 \rightleftharpoons O_2NC(R)_2C{<} + [XC(R)_2NO_2]^{-\cdot}$$

Scheme II can react further with the substituted nitroalkane via the $S_{RN}1$ process to yield the dimer of the nitroalkane ($R_2C(NO_2)C(NO_2)R_2$). Dehydrogenation of the dimerization

0002-7863/79/1501-2355$01.00/0