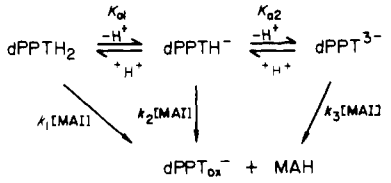
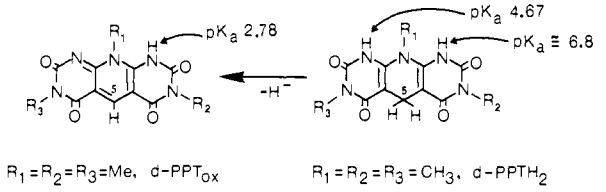
Scheme I

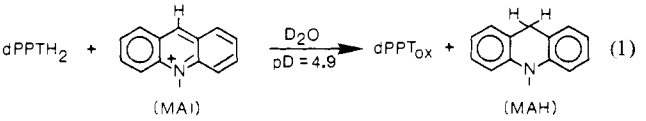


a very effective hydride equivalent reducing agent. Yoneda, Yamamoto, and Ono, however, have made the interesting ob-



servation that $dPPT_{ox}$ and its analogues (R_1, R_2, and R_3 phenyl substitutents) are very effective aerobic autorecycling catalysts for the oxidation of alcohols.[4] The expectation that $dPPT^{2-}$ should be a most effective organic reductant and the finding by Yoneda that $dPPT_{ox}$ and its analogues are good oxidants (at least in the autorecycling process) are explained by the results presented herein.

The reduction of *N*-methylacridinium iodide (MAI) by $dPPTH_2$ in D_2O was shown to yield (eq 1) *N*-methylacridan (MAH) devoid

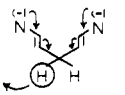


(1)

of deuterium substituent (by proton NMR). The kinetics of the reaction were followed in H_2O at 30 °C between pH 9.58 and −0.20 under pseudo-first-order conditions, with [MAI] in excess over $[dPPTH_2]_T = 7.5 \times 10^{-5}$ M by minimally 10-fold. The appearance of $dPPT_{ox}$ and $dPPT_{ox}^-$ was followed between 370 and 385 nm. Reactions followed the first-order rate law and the pseudo-first-order rate constants (k_{obsd}) were found to be independent of buffer concentration. Plots of k_{obsd} vs. [MAI] were found to be linear at each pH. The slopes of such plots provide the apparent second-order rate constant k_r. In Figure 1 there is plotted the log of k_r as a function of pH. The points of Figure 1 are experimental and the best fit line correlating the points was generated from eq 2 where $k_1 = 4.58 \times 10^{-1}$ M^{-1} s^{-1}, $k_2 = 4.70$

$$k_r = \frac{k_1 a_H^2 + k_2 K_{a1} a_H + k_3 K_{a1} K_{a2}}{K_{a1} K_{a2} + K_{a1} a_H + a_H^2} \qquad (2)$$

$\times 10^2$ M^{-1} s^{-1}, $k_3 = 1.30 \times 10^6$ M^{-1} s^{-1}, $pK_{a1} = 4.57$, and $pK_{a2} = 7.20$. Equation 2 may be derived for Scheme I. The kinetic pK_{app} values (i.e., 4.57 and 7.20) may be compared to the tritrimetric pK_{a1} and pK_{a2} values for stepwise dissociation of $dPPTH_2$ (i.e., 4.67 an 6.5–7.0, this study). From the values of k_1, k_2, and k_3 it may be seen that dissociation of a proton from $dPPTH_2$ to provide $dPPTH^-$ increases the rate of hydride transfer to *N*-methylacridinium cation by 1×10^3 while dissociation of $dPPTH^-$ to give $dPPT^{2-}$ provides an additional rate increase of 2.8×10^3. Thus, the rate for *N*-methylacridinium ion reduction is increased by ca. three-million fold on complete dissociation of $dPPTH_2$ to give $dPPT^{2-}$. Various *N*-alkylpyridine-substituted nicotinamides reduce *N*-methylacridinium ion with second-order rate constants ranging from 4×10^1 to 2×10^3,[5] so that they are kinetically more effective reductants of MAI than is $dPPTH_2$ by minimally $\sim 10^3$ while the most reactive *N*-alkylnicotinamides are kinetically comparable to $dPPT^-$. The species $dPPT^{2-}$ owes its very large hydride transfer potential to the dienamine anion portion of its structure. We find that $dPPT^{2-}$ reduces *m*-hydroxybenzaldehyde



to benzyl alcohol (pH 7.0) via hydride transfer and that undissociated $dPPT_{ox}$ is a mild oxidant capable of the "autorecycling" conversion of cyclohexanol to cyclohexanone. The latter observation was previously described by Yoneda and co-workers for certain phenyl-substituted $dPPT_{ox}$ molecules.[4]

Acknowledgment. This work was supported by a grant from the National Institutes of Health.

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Remarkable Optical Induction in the Reduction of α-Keto Esters with *B*-(3-Pinanyl)-9-borabicyclo[3.3.1]nonane. Synthesis of α-Hydroxy Esters of 100% Optical Purity

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The asymmetric synthesis of chiral α-hydroxy esters is an objective of considerable current importance and activity of organic chemists.[1] Optical purities in the range of 90% ee are no longer exceptional. We now report a simple procedure to achieve the reduction of α-keto esters in optical purities approaching 100%.

Recently we reported an improved procedure for the asymmetric reduction of prochiral ketones with the chiral trialkylborane *B*-(3-pinanyl)-9-borabicyclo[3.3.1]nonane (**1**; Alpine-Borane, Midland's reagent).[2,3] In our procedure we utilized either the neat reagent or highly concentrated (~2 M) solution instead of the relatively dilute solutions employed by the original workers.[4] This led to vastly improved optical induction by greatly increasing the rate of reduction by the desirable bimolecular process in comparison to the rate of dissociation of the reagent into the undersirable 9-borabicyclo[3.3.1]nonane and α-pinene.[5] Another means of increasing the rate of reduction is by substituting the electron-withdrawing groups on the carbonyl compound.[4a] While

(1) (a) For a summary of earlier work, see: Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice Hall: Englewood Cliffs, NJ, 1971; Sections 2 and 5. (b) Ojima, I.; Kogure, T.; Kumagai, M. *J. Org. Chem.* **1977**, *42*, 1671 and references cited therein. (c) Ojima, I.; Kogure, T. *J. Chem. Soc., Chem. Commun.* **1977**, 428. (d) Ojima, I.; Miyazawa, Y.; Kumagai, M. *Ibid.* **1976**, 927. (e) Ridley, D. D.; Stralow, M. *Ibid.* **1975**, 400. (f) Terashime, S.; Jew, S. *Tetrahedron Lett.* **1977**, 1005. (g) Meyers, A. I.; Slade, J. *Synth. Commun.* **1976**, *6*, 601. (h) Eliel, E. L.; Koskimies, J. K.; Lohri, B. *J. Am Chem Soc.* **1978**, *100*, 1614. (i) Kaneko, T.; Turner, D. L.; Newcomb, M.; Bergbreiter, D. E. *Tetrahedron Lett.* **1979**, 103. (j) Abenhaim, D.; Boireau, G.; Sabouralt, B. *Ibid.* **1980**, 3043. (k) Mori, K.; Akao, H. *Tetrahedron* **1980**, *36*, 91. (l) Hirschbein, B. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 4458.

(2) (a) Brown, H. C.; Pai, G. G. *J. Org. Chem.* **1982**, *47*, 1606; (b) *Ibid.* **1983**, *48*, 1784.

(3) The reagent is now sold by Aldrich Chemical Co. under the trade name Alpine-Borane.

(4) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352. (b) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *Ibid.* **1980**, *102*, 867.

(5) Midland and co-workers have overcome this problem recently by carrying out the reduction under extremely high hydrostatic pressure (5000 atm). They were able to achieve the reduction of acetophenone with 100% ee.

0002-7863/84/1506-1531$01.50/0

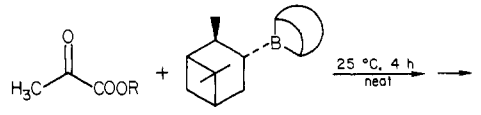
Table I. Reduction of α-Keto Esters with *B*-(3-Pinanyl)-9-borabicyclo[3.3.1]nonane (40% Excess) from 92% ee (+)-α-Pinene

α-keto ester	reaction conditions: temp, °C	time, h	yield,[a] %	optically active α-hydroxy ester: optical rotation	% ee: obsd	% ee: corr	abs config
methyl pyruvate	25	4	64	$[\alpha]^{23}_D$ −7.16° (neat, *l* = 1)	79[b]	86	*S*
ethyl pyruvate	25	4	81	$[\alpha]^{23}_D$ −8.83° (neat, *l* = 1)	76[c]	83	*S*
ethyl pyruvate	0	24	81	$[\alpha]^{23}_D$ −9.43° (neat, *l* = 1)	82[c]	89	*S*
isopropyl pyruvate	25	4	72	$[\alpha]^{23}_D$ −8.664° (neat, *l* = 1)	72[d]	78	*S*
tert-butyl pyruvate	25	4	98	$[\alpha]^{23}_D$ −8.08° (neat, *l* = 1)	85[e]	92	*S*
tert-butyl pyruvate	0	24	98	$[\alpha]^{23}_D$ −8.76° (neat, *l* = 1)	92[e]	100	*S*
tert-butyl 2-oxobutyrate	0	24	71	$[\alpha]^{23}_D$ −3.4° (*c* 2.0, CCl_4)	92[d]	100	*S*
ethyl 2-oxopentanoate	25	4	77	$[\alpha]^{23}_D$ −4.44° (neat, *l* = 1)	88[f]	96	*S*
tert-butyl 2-oxopentanoate	0	24	79	$[\alpha]^{23}_D$ −3.46° (neat, *l* = 1)	92[d]	100	*S*
ethyl 4-methyl-2-oxopentanoate	25	20	50	$[\alpha]^{23}_D$ −5.30° (neat, *l* = 1)	75[g]	82	*S*
tert-butyl 4-methyl-2-oxopentanoate	0	24	72	$[\alpha]^{23}_D$ −7.88° (*c* 7.88, CCl_4)	92[h]	100	*S*
methyl benzoylformate	25	24	95	$[\alpha]^{23}_D$ −144.9° (*c* 0.7, $CHCl_3$)	83[i]	90	*R*
isopropyl benzoylformate	25	48	91	$[\alpha]^{27}_D$ −98.9° (*c* 1.0, $CHCl_3$)	88[d,j]	96	*R*
tert-butyl benzoylformate	25	48	89	$[\alpha]^{27}_D$ −119.1° (*c* 1.05, CCl_4)	92[d,j]	100	*R*

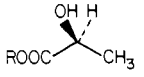
[a] Isolated yield of ~98% pure material. [b] Based on $[\alpha]^{25}_D$ −4.54° (neat, *l* = 0.5).[9] [c] Based on $[\alpha]_D$ −11.5° (neat, *l* = 1).[14] [d] By ^{19}F NMR of MTPA esters. [e] Based on $[\alpha]^{20}_D$ +9.48° (neat, *l* = 1).[15] [f] Based on $[\alpha]^{20}_D$ −5.05° (neat, *l* = 1).[16] [g] Based on $[\alpha]^{25}_D$ −7.06° (neat, *l* = 1).[17] [h] By ^1H NMR in the presence of chiral shift reagent Eu(hfc)$_3$. [i] Based on $[\alpha]^{25}_D$ −174.2° (*c* 0.58, $CHCl_3$).[18] [j] By conversion to styrene glycol.[8]

exploring the effect of various electron-withdrawing substituents, we discovered that the α-keto esters are reduced to the corresponding α-hydroxy esters rapidly by Alpine-Borane.[2a]

The first compound of this class we studied was ethyl pyruvate (**2**, R = C_2H_5; eq 1). The compound underwent a rapid reduction



2, R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9 1



(*S*)-3, R = CH_3 (79% ee), C_2H_5 (76% ee), *i*-C_3H_7 (72% ee), *t*-C_4H_9 (86% ee)

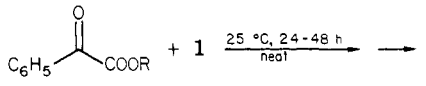
(<4 h) to ethyl lactate at 25 °C with an optical induction of 82% ee (corrected). We achieved a somewhat modest improvement in optical induction (89% ee) by conducting the reaction at 0 °C. Considering the synthetic importance of α-hydroxy esters, a further improvement, preferably close to 100% ee, was clearly desirable.

It seems logical to assume that the extent of asymmetric induction depends on the steric inequality of the two groups attached to the carbonyl functionality. The reduction of ethyl pyruvate [with Alpine-Borane derived from (+)-α-pinene] afforded ethyl lactate of *S* configuration. This means that, according to the model proposed by Midland for these reductions,[4] the ester group is bulkier than the methyl group. Thus, increasing the steric bulk of the ester moiety should lead to an increase in optical induction.

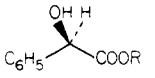
On the basis of this hypothesis, we prepared the isopropyl and the *tert*-butyl esters of pyruvic acid and studied their reduction with Alpine-Borane. The reductions were carried out at 25 °C, using a 40% excess of neat Alpine-Borane prepared from 92% ee (+)-α-pinene. Even though the isopropyl derivative did not show any improvement, we were gratified to note that the *tert*-butyl derivative did. The *tert*-butyl lactate was isolated in 98% chemical yield and 85% ee (92% correcting for the optical purity of α-pinene; **3**, R = *t*-C_4H_9; eq 1). *The extent of optical induction was readily upgraded to 92% ee (100% ee corrected) by lowering the reaction temperature to 0* °C.

Alkyl groups of moderate steric requirements are readily accommodated. Thus, the replacement of the methyl group of pyruvic esters by ethyl, *n*-propyl, and isobutyl, as in 2-oxobutyrate, 2-oxopentanoate, and 4-methyl-2-oxopentanoate, gave 75–88% ee for the ethyl esters (82–96% ee after correcting for the optical purity of α-pinene) and values of 92% ee for the corresponding *tert*-butyl esters (100% ee after correcting for the optical purity of the α-pinene). On the other hand, the reduction fails for derivatives containing branches α to the carbonyl group, such as methyl 3-methyl-2-oxobutyrate. The reduction of this ester was so slow, 8 days at 25 °C with only 10% ee, that we did not undertake to prepare and examine the *tert*-butyl ester.

Next, we undertook to examine the reaction using aromatic α-keto esters. In this case the theory would predict that the *tert*-butyl ester should give less optical induction than the corresponding methyl ester since the phenyl group is bulkier than the ester group. To our great surprise, we discovered that this was not the case. In reality, *tert*-butyl mandelate (**5**) was obtained in 89% chemical yield and 92% ee (100% ee corrected) at 25 °C (eq 2, R = *t*-C_4H_9).



4, R = CH_3, *i*-C_3H_7, *t*-C_4H_9



(2)

(*R*)-5, R = CH_3 (83% ee), *i*-C_3H_7 (88% ee), *t*-C_4H_9 (92% ee)

The quantitative optical induction realized with the *tert*-butyl esters in both aliphatic and aromatic systems is a mystery. In the aliphatic series, one can argue that the enhanced optical induction is due to the larger steric bulk of the *t*-butyl ester group (eq 1). But this argument does not explain the results realized in the aromatic series where the phenyl group must be bulkier than the ester group, as evidenced by the formation of products with the *R* configuration (eq 2). It appears that the *tert*-butyl ester moiety must possess a special quality that renders it especially valuable in controlling the course of the reduction.

We wish to emphasize that the validity of the procedure used to extrapolate the results to 100% ee α-pinene has been previously tested and confirmed.[2b] Moreover, we have now achieved a simple procedure for upgrading both (+)- and (−)-α-pinene to essentially 100% ee material.[6] α-Pinene of 97–98% ee has recently become available from Aldrich.

In conclusion, the present development provides an extremely efficient synthesis of both enantiomers of chiral α-hydroxy esters and the host of derivatives into which they are readily transformed,

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such as α-halo esters (both isomers without loss of optical activity),[7] glycols,[8] epoxides,[9] amino acids,[10] etc. Their importance in natural product synthesis is well documented by their application for the synthesis of several chiral pheromones.[11]

The following experimental procedure is typical. An oven-dried, 50-mL, round-bottom flask equipped with a septum-capped side arm, magnetic stirring bar, and stopcock adaptor was cooled to room temperature in a stream of nitrogen. The flask was charged with 2.5 g of solid 9-BBN (20 mmol), and 3.5 mL (22 mmol) of (+)-α-pinene ($[\alpha]^{25}_D$ +47.3°, 92% ee, distilled from $LiAlH_4$) were added to the flask. The hydroboration was completed by heating the flask to 65 °C for 5 h.[3] The flask was cooled to room temperature and 2.16 g (15 mmol) of *tert*-butyl pyruvate (prepared according to the general procedure[12] from pyruvoyl chloride[13]) was injected into the flask. The reaction was complete in 4–5 h, as indicated by ^1H NMR. Acetaldehyde (0.5 mL) was added to destroy the excess reagent, and the liberated α-pinene was pumped off at 40 °C (0.01 mm). The residue was dissolved in 30 mL of dry ether and cooled to 0 °C, and 1.32 mL (22 mmol) of ethanolamine was added to displace the 9-BBN moiety. The white solid was separated by filtration and washed twice with dry ether. From the combined filtrate, ether was removed by distillation at atmospheric pressure and the product distilled in a Kügelrohr oven at 100 °C (20 mm), yield 2.14 g (98%). GC analysis on both Carbowax 20M and SE-30 columns showed a single peak and traces of ethanol. ^1H NMR ($CDCl_3$) δ 1.37 (d, J = 7 Hz, 3 H), 1.48 (s, 9 H), 2.3 (broad, 1 H, exchanges with D_2O), 4.12 (q, J = 7 Hz, 1 H). The compound was further purified by preparative GC on a Carbowax column at 75 °C, isothermal, and the rotation taken: $[\alpha]^{23}_D$ −8.08° (neat), 85% ee, $[\alpha]^{23}_D$ −4.92° (c 5.02, CCl_4). Repeating the reaction at 0 °C (24 h) gave the distilled product again in 98% yield. The specific rotation in this case was $[\alpha]^{23}_D$ −8.76° (neat), 92.4% ee; $[\alpha]^{23}_D$ −5.36° (c 5.04, CCl_4). Our experimental results are summarized in Table I.

In other cases, no attempt was made to optimize the chemical yields. It is probable that with such efforts comparable yields could be realized.

Acknowledgment. Originally, we were also examining the reduction of acyl cyanides. However, we learned from M. M. Midland that he and his co-workers had also noted the facile reduction of these two groups of compounds, the keto esters and acyl cyanides. To minimize the overlap, we have restricted our study to the keto esters, and he is examining the acyl cyanides. His results will be reported shortly. We thank David N. Whittern for his assistance in obtaining ^{19}F spectra of MTPA esters on the Varian XL-200 Spectrometer (NSF Grant CHE-8004246). The financial support of the National Institutes of Health, GM 10937-20, is gratefully acknowledged.

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An Alternate Path to Reductive Elimination for Group 4B Metals: Mechanism of Cyclopropane Formation from Titanacyclobutanes

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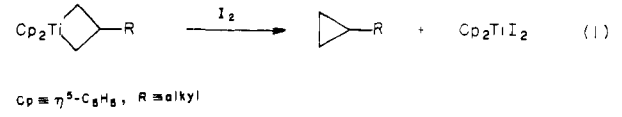
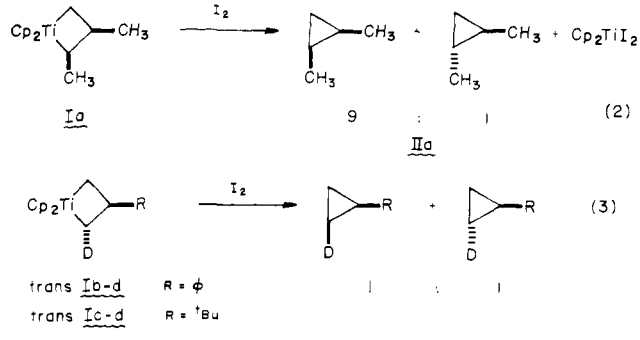
Reductive elimination of alkanes from dialkylmetal complexes is a key step in numerous catalytic reactions. In many cases, this reaction is accelerated by prior oxidation of the metal complex.[1,2] We now report a clean example of alkane elimination from an early transition-metal dialkyl and describe the stereochemistry of formation and reaction of an observed intermediate.

The readily available titanacyclobutanes[3] provide the complexes required for such a study since treatment of these with iodine produces cyclopropanes cleanly and in good yield (eq 1).[4]



Initial sterochemical studies of these iodinations were puzzling. *cis*-2,3-Dimethyltitanacyclobutane (Ia) gave mostly retention, favoring the less stable dimethylcyclopropane (IIa, 9:1 cis/trans).[5] In contrast, *trans*-2-deuterio-3-phenyltitanacyclobutane (*trans*-Ib-*d*), which was expected to show even greater stereospecificity, gave an essentially nonstereospecific mixture of deuterated phenylcyclopropanes (IIb) under similar conditions (eq 2 and 3).[6]



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