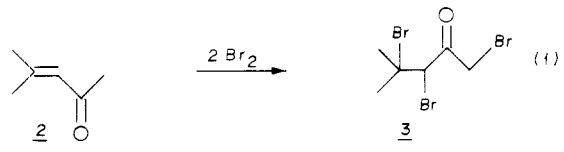
amounts of ethyl 4-methyl-2,4-pentadienoate as a minor product in the reaction with sodium ethoxide in ethanol. Since pentadienoates have been used as intermediates in the syntheses of functionalized cyclic compounds, for example, through reactions with enamines,[3] maleic anhydride,[4] and ammonia,[5] and since the specific compound obtained has been prepared previously via the expensive modified Wittig procedure of reacting 2-methylacrolein with triethyl phosphonoacetate,[6] we felt it worth investigating the formation of the byproduct.

We initially suspected that the byproduct must have come from excess bromination of mesityl oxide which would produce tribromo ketones as an impurity in our dibromo ketone (3,4-dibromo-4-methyl-2-pentanone). Therefore we reacted the mesityl oxide (neat) with 2 mol of bromine and obtained a product with an NMR spectrum coherent with that expected for 1,3,4-tribromo-4-methyl-2-pentanone (eq 1), containing the 3,4-dibromo ketone[2] as a 10% impurity.



(1)

2 3

Reaction of the tribromo ketone with 3 equiv of sodium ethoxide (1 N in absolute ethanol) for 2 h at 0 °C led to the formation of ethyl *trans*-methyl-2,4-pentadienoate (88% according to gas chromatography) (eq 2). We were able to isolate the dienoate in 57% yield from the reaction mixture.

(2)

3 1

The reaction should occurr via a Favorskii rearrangement similar to that observed by us for 3,4-dibromo-4-methyl-2-pentanone[2] and by Wagner and Moore for 3,4-dibromo-3-methyl-2-pentanone.[7] It is probable that this reaction can be generalized and we are proceeding with our studies of it.

Experimental Section

NMR spectra were obtained by Antonio Ribeiro Jorge on a Varian XL-100 with chemical shifts expressed as values downfield from a tetramethylsilane internal standard. IR spectra were recorded with a Perkin-Elmer 467 spectrophotometer from liquid films between NaCl plates.

GLC was done on a Perkin-Elmer 900 instrument with an H_2 flame detector, using an aluminum column (1/8 in. × 10 ft) packed with 10% Carbowax 20M at a column temperature of 80 °C.

1,3,4-Tribromo-4-methyl-2-pentanone (3). In a 100-mL round-bottomed flask was placed 4.9 g (0.05 mol) of mesityl oxide and to the flask was attached an addition funnel with a pressure-equalizing sidearm, protected by a drying tube containing calcium chloride and containing bromine (16 g, 0.10 mol). The reaction vessel was immersed in an ice bath and the bromine was added dropwise over a period of 30 min. The resultant liquid exhibited the following spectrum: NMR (CCl_4) δ 2.0 (6 H, s), 4.2 (2 H, s), 5.1 (1 H, s), as well as an impurity peak corresponding to 3,4-dibromo-4-methyl-2-pentanone at δ 2.4 (7% of the area of the peak at δ 2.0). This product was used in the second reaction as quickly as possible because our own experience[2] and that of others[8,9] show that the α,β-dibromo ketones are highly unstable in contact with air.

Ethyl 4-Methyl-2,4-pentadienoate (1). A solution of 1 N sodium ethoxide was prepared by reacting sodium (3.45 g, 0.15 mol) with 150 mL of absolute ethanol in a 300-mL flask. To this solution was added 1,3,4-tribromo-4-methyl-2-pentanone (3; 16.9 g, 0.05 mol) dropwise in 10 min, while the reaction vessel was maintained in an ice bath and the mixture was subjected to magnetic stirring. The solution was stirred for 2 h and then added to ice water (200 mL), which was extracted with *n*-hexane (5 × 10 mL). The extract was dried over sodium sulfate and analyzed by GLC, showing 88% of the desired ester (the other 12% is the products observed in the analogous reaction of the dibromo ketone[2]).

The extract was stripped in the presence of crystals of *p*-hydroquinone and then distilled in a short-path head to yield 4.0 g (57%): bp 71–72 °C (17 mm) [lit.[6] 81–83 bp °C (17 mm)]; IR 1720, 1640, 1601, 970, 905 cm^{-1}; NMR ($CDCl_3$) δ 1.30 (3 H, t, J = 7 Hz), 1.86 (3 H, s), 4.20 (2 H, q, J = 7 Hz), 5.18 (2 H, br s), 5.75 (1 H, d, J = 13 Hz), 6.45 (1 H, d, J = 13 Hz) (agrees with the literature spectra[6]); mass spectrum (Varian CH 5-DF, 70 eV), m/e 140 (M^+), 67 (base), other peaks greater than 60% of base 95, 43, 41, and 39.

Acknowledgment. We thank the Núcleo de Pesquisas de Produtos Naturais for the NMR spectra. Support was given by the following Brazilian agencies: FINEP, CNPq, and CEPG (UFRJ).

Registry No. 1, 35227-70-4; 2, 141-79-7; 3, 74563-05-6.

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Decarboxylative Iodination: A Convenient Synthesis of Bridgehead Iodides

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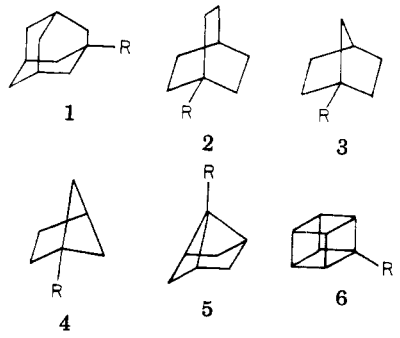
As part of a program of study of bridgehead-substituted derivatives of polycyclic hydrocarbons, we required the series of bridgehead iodides 1–6 (R = I). Of these, 1–3



1 2 3 4 5 6

have previously been synthesized, whereas 4–6 are, as yet, unknown.

1-Iodoadamantane[1-4] and 1-iodobicyclo[2.2.2]octane,[3,5,6]

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Table I. Decarboxylative Iodination of Bridgehead Acids 2-6 (R = COOH)

substrate	product	% yield[a]
2, R = COOH	2, R = I	55 (55)
3, R = COOH	3, R = I	58 (58)
4, R = COOH	4, R = I	54 (65)
5, R = COOH	5, R = I	45 (50)
6, R = COOH	6, R = I	40 (53)

[a] Isolated yields. Numbers in parentheses refer to yields based on recovered acid.

both of which possess a certain degree of flexibility, have normally been obtained via methods which involve cationic-type intermediates. These methods have been found to be inappropriate for the synthesis of the more rigid bicyclo[2.2.1]heptane system and presumably would also not be applicable to the synthesis of the iodides **4–6** (R = I). 1-Iodobicyclo[2.2.1]heptane (**3**, R = I) has invariably been prepared by treating 1-lithiobicyclo[2.2.1]heptane with elemental iodine, as first described by Lansbury and co-workers.[6] Two isolated procedures have been reported for bridgehead iodination of molecules possessing the bicyclo[2.2.1]heptane skeleton. The 1,4-diiodo derivative has been obtained by aluminum iodide catalyzed halogen exchange of the corresponding dichloride,[7] and 1-iodocamphane has been synthesized by (i) photochemically induced decomposition of the corresponding iodooxalyl ester[8] and (ii) oxidation of the corresponding carbazate with iodine–pyridine.[9]

In view of the ready accessibility of many bridgehead carboxylic acids, particularly highly constrained systems via a Favorskii-type ring contraction,[10] we set out to develop a general route to bridgehead iodides using the carboxylic acids **1–6** (R = COOH) as typical substrates.

Our approach was based on that employed by Barton and colleagues[11] for the synthesis of a number of primary and secondary acyclic iodides. Their procedure, which involves irradiation of a mixture of the carboxylic acid and *tert*-butyl hypoiodite in benzene, was thought[11] to proceed by an initial rapid exchange giving the acyl hypoiodite (eq 1) followed by homolytic decomposition of the latter to the

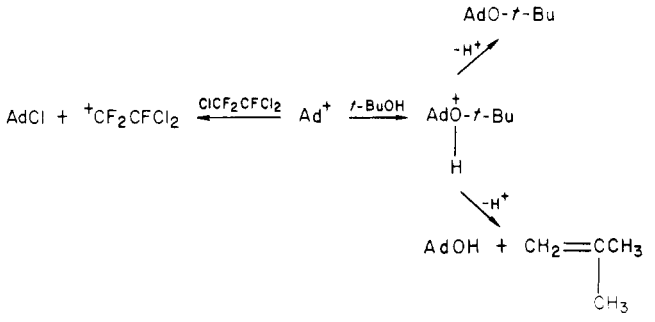
$$\mathrm{RCOOH} + t\text{-BuOI} \rightleftharpoons \mathrm{RCOOI} + t\text{-BuOH} \quad (1)$$

$$\mathrm{RCOOI} \xrightarrow{h\nu} \mathrm{RI} + \mathrm{CO_2} \quad (2)$$

iodide (eq 2). Application of this method to caged molecules was limited to apocamphanecarboxylic acid, which, however, was converted into 1-iodoapocamphane in good yield.

We have found the following modified procedure to be a convenient method of synthesis of the iodides **2–6** (R = I). Preparation of *tert*-butyl hypoiodite is best accomplished[12] by treatment of *tert*-butyl hypochlorite with mercuric iodide in 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113). This solvent is inexpensive and is sufficiently low boiling to be separated without difficulty from the more highly volatile of the iodides, e.g., **4** (R = I). After being filtered to remove mercuric chloride, the violet-colored solution of the hypoiodite is added to a solution of the carboxylic acid in Freon 113 and the stirred mixture held at 35–40 °C for 30 min while being illuminated with a 200-W tungsten lamp. A simple workup permits isolation of the iodides cleanly and in moderate to good yield (Table I).

Scheme I



When the progress of the reaction was monitored by measurement of the rate of evolution of carbon dioxide, the following qualitative order of reactivity was observed: **1 > 2 > 3 > 4 ~ 5 > 6** (R = COOH). It seems likely that the rate of iodination is controlled by the ease of decomposition of the acyloxy radical ($\mathrm{RCO_2\cdot} \rightarrow \mathrm{R\cdot} + \mathrm{CO_2}$). Thus the sequence of reactivity observed is in accord with the relative order of stability of the corresponding bridgehead radicals—at least as far as those derived from **1–3**, for which data are available,[13] are concerned. In fact, some starting material was always recovered from the reaction involving the acids **4–6** (R = COOH). Use of 5 equiv of *tert*-butyl hypoiodite minimized the quantity of carboxylic acid recovered, suggesting that, besides the anticipated loss of *tert*-butyl hypoiodite due to photochemical decomposition, some of the reagent is consumed by those acyloxy radicals which lose carbon dioxide less readily (eq 3). Presumably some of the acyloxy radicals may also interact with the *tert*-butyl alcohol present to give the carboxylic acid (eq 4).

$$\mathrm{RCO_2\cdot} + t\text{-BuOI} \rightarrow \mathrm{RCO_2I} + t\text{-BuO}\cdot \quad (3)$$

$$\mathrm{RCO_2\cdot} + t\text{-BuOH} \rightarrow \mathrm{RCO_2H} + \cdot\mathrm{CH_2C(CH_3)_2OH} \quad (4)$$

It is apparent from Table I that this procedure provides a convenient entry into a variety of bridgehead iodides, including those which are significantly strained. Interestingly, it proved to be unsatisfactory for the synthesis of 1-iodoadamantane from adamantane-1-carboxylic acid. The product obtained from **1** (R = COOH) under the conditions specified above consisted of a 6:1:2 mixture of 1-chloroadamantane, 1-adamantanol, and 1-*tert*-butoxyadamantane, with very little (ca. 5%) of the iodide **1** (R = I) being detected.

In belief that the anomalous behavior of adamantane-1-carboxylic acid arose as a result of the instability of the derived iodide, we exposed the latter to the conditions of the reaction and observed that it was converted into a mixture[14] of products similar to that obtained above. Furthermore, when the attempted iodination of adamantane-1-carboxylic acid was interrupted at about 50% completion, 1-iodoadamantane was found to be present in

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moderate proportion (22%), together with 1-chloro- (3%) and 1-*tert*-butoxyadamantane (6%). It is noteworthy that iodoadamatane proved to be reasonably stable under thermal conditions; in Freon 113 at 40 °C, without illumination, it was found to undergo decomposition quite slowly.

Accordingly it seems likely that iodoadamantane is indeed formed but that under the conditions it suffers homolytic fission of the carbon–iodine bond. Electron transfer from the adamantyl radical to the iodine atom generates the adamantyl cation (eq 5) which abstracts a

$$\mathrm{AdI} \rightleftarrows \mathrm{Ad}\cdot + \mathrm{I}\cdot \rightleftarrows \mathrm{Ad}^{+}\mathrm{I}^{-} \qquad (5)$$

chlorine anion from the solvent to give 1-chloroadamantane or, alternatively, reacts with *tert*-butyl alcohol to produce the *tert*-butyl ether and the alcohol (Scheme I).[15] The pathway depicted in Scheme I was suggested by Kropp and his colleagues,[16] and by Perkins and Pincock,[17] to explain the effects of high-energy ultraviolet irradiation of both 1-iodoadamantane[16,17] and 1-iodonorbornane.[16] Photochemically induced decomposition of the latter dissolved in *tert*-butyl alcohol was shown[16] to afford a mixture of 1-norbornanol and 1-*tert*-butoxynorbornane. Evidently, of the iodides **1**–**6** (R = I) only iodoadamantane is sufficiently labile to be affected by the longer wavelength, lower energy radiation employed in this work.

It is noteworthy that Barton's group did not isolate *tert*-butyl iodide when a mixture of pivalic acid and *tert*-butyl hypoiodite was irradiated; nor did they specify what product was actually obtained.[11] On the basis of the results of the present work, it is highly probable that *tert*-butyl iodide is formed but then suffers the same fate as **1** (R = I), giving products derived from the *tert*-butyl cation. Convincing evidence for this proposal can be found in the investigation by Tanner and Gidley[12] of the iodination of hydrocarbons promoted by *tert*-butyl hypoiodite under ultraviolet irradiation. These authors report that primary and secondary alkyl iodides can generally be obtained in low to moderate yield but that *tert*-butyl iodide is unstable toward the reagent.

Finally, it is of interest to compare the yields obtained by this procedure with those of other bridgehead decarboxylative halogenations. Thus the bromides **2**–**6** (R = Br) have been prepared from the corresponding carboxylic acids via the Cristol–Firth modification of the Hunsdiecker reaction, and in all cases[18] the yields of bromides (70–80%) are consistently higher than those of the iodides. On the other hand, bridgehead halodecarboxylation promoted by lead tetraacetate in the presence of lithium halide (Cl^-, Br^-, I^-)[19] has been reported in only a few instances. The acid **2** (R = COOH) and apocamphanecarboxylic acid, for example, have been converted by the Kochi procedure[19] into the corresponding chlorides; unfortunately, yields were not recorded.[20] However, a modification employing *N*-chlorosucciniminide as the halogen carrier in a dipolar aprotic solvent has been shown[21] to give an excellent yield (95%) of 1-chlorobicyclo[2.2.2]octane from **2** (R = COOH).

Experimental Section

NMR spectra were recorded on a Varian A60-D spectrometer or on a JEOLCO FX90Q instrument and mass spectra on an AEI MS-30 spectrometer. Infrared spectra were measured with a Perkin-Elmer 237 grating spectrophotometer. GLC analyses were performed on a Varian 1740 instrument, using 10 ft × 0.25 in. stainless steel columns packed with 5% SE-30 on Chromosorb W or 5% Carbowax 20M on Chromosorb G. Solvents and reagents were purified by standard techniques. Adamantane-1-carboxylic acid,[22] bicyclo[2.2.2]octane-1-carboxylic acid,[23] bicyclo[2.2.1]-heptane-1-carboxylic acid,[24] bicyclo[2.1.1]hexane-1-carboxylic acid,[18c] tricyclo[3.1.1.$0^{3,6}$]heptane-6-carboxylic acid[25] and cubanecarboxylic acid[26] were prepared according to the published procedures.

General Procedure for Decarboxylative Iodination. *tert*-Butyl hypochlorite[27] (3.8 g, 35 mmol) was added with stirring to a solution of mercuric iodide (7.95 g, 17.5 mmol) in Freon 113 (25 mL) held at 0 °C under an atmosphere of nitrogen. The progress of the halogen exchange was monitored by removing aliquots periodically, adding a drop of benzene, and analyzing the signals present in the NMR spectrum at δ 5.96 (*t*-BuOCl) and 6.06 (*t*-BuOI) upfield from benzene. After 1 h the peak due to the hypochlorite had disappeared completely, and the mixture was then filtered to remove mercuric chloride. The filtrate was added to a solution of the carboxylic acid (7 mmol) in Freon 113 (5 mL) and the resulting solution was stirred at 40 °C while being irradiated with a 200-W tungsten lamp. When the evolution of carbon dioxide had ceased, the purple solution was washed successfully with 10% sodium thiosulfate solution (2 × 30 mL), 10% sodium hydrogen carbonate solution (2 × 20 mL), and water (1 × 10 mL). The organic layer was dried ($MgSO_4$) and the solvent distilled through a 15-cm column packed with glass helices. The residue was either distilled or sublimed under vacuum.

1-Iodobicyclo[2.2.2]octane (2, R = I) and 1-iodobicyclo-[2.2.1]heptane (3, R = I) had physical constants and spectral properties in agreement with those of authentic specimens prepared by published procedures.

1-Iodobicyclo[2.1.1]hexane (4, R = I). Distillation of the product obtained from treatment of the acid **4** (R = COOH) under the conditions described above gave the iodide **4** (R = I): bp 60 °C (10 torr); n^{21}_{D} 1.5430; ^{1}H NMR ($CDCl_3$) δ 1.52–1.87 (m, 4 H), 2.05 (m, 4 H), 2.51 (m, 1 H); mass spectrum, *m/e* 208.

Anal. Calcd for C_6H_9I: C, 34.62; H, 4.36. Found: C, 34.96; H, 4.50.

6-Iodotricyclo[3.1.1.$0^{3,6}$]heptane (5, R = I). Similar treatment of the acid **5** (R = COOH) gave the iodide **5** (R = I): bp 75 °C (10 torr); n^{25}_{D} 1.5535; ^{1}H NMR ($CDCl_3$) δ 2.35 (m, 3 H), 2.97 (m, 6 H); mass spectrum, *m/e* 220.

Anal. Calcd for C_7H_9I: C, 37.89; H, 4.12. Found: C, 38.21; H, 4.18.

Iodocubane (6, R = I). Sublimation of the product obtained from similar treatment of the acid **6** (R = COOH) yielded the iodide **6** (R = I): mp 31 °C; ^{1}H NMR ($CDCl_3$) δ 4.25 (m); mass spectrum, *m/e* 230.

Anal. Calcd for C_8H_7I: C, 41.77; H, 3.07. Found: C, 42.06; H, 3.13.

Reaction of Adamantane-1-carboxylic Acid under Iodination Conditions. A. The acid **1** (R = COOH) was treated with *tert*-butyl hypoiodite under the conditions specified above to give a product consisting of three components in the ratio 6:1:2. These were identified as 1-chloroadamantane (**1**, R = Cl), 1-adamantanol (**1**, R = OH), and 1-*tert*-butoxyadamantane (**1**, R = O-*t*-Bu), respectively, by comparison of their spectral properties with those of authentic specimens.

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B. When a similar reaction was interrupted after half the theoretical amount of carbon dioxide had been evolved, the product was shown to consist of a mixture of 1 (R = Cl), 1 (R = O-*t*-Bu), and 1 (R = I) in the ratio 1:2:7.

Irradiation of 1-Iodoadamantane (1, R = I). The iodide 1 (R = I) was irradiated with the 200-W lamp under the following conditions to give the products noted: (a) in Freon 113 alone, yielding 1 (R = Cl) almost quantitatively; (b) in Freon 113 containing *tert*-butyl alcohol to give a mixture of 1-chloroadamantane, 1-adamantanol, and 1-*tert*-butoxyadamantane.

Registry No. 1 (R = COOH), 828-51-3; 2 (R = COOH), 699-55-8; 2 (R = I), 931-98-6; 3 (R = COOH), 18720-30-4; 3 (R = I), 930-80-3; 4 (R = COOH), 64725-77-5; 4 (R = I), 74725-75-0; 5 (R = COOH), 53292-20-9; 5 (R = I), 74725-76-1; 6 (R = COOH), 53578-15-7; 6 (R = I), 74725-77-2; *t*-BuOI, 917-97-5.

Asymmetric Reductions with Chiral Alkoxy(acyloxy)borohydrides

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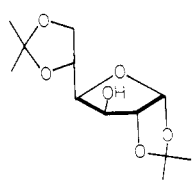
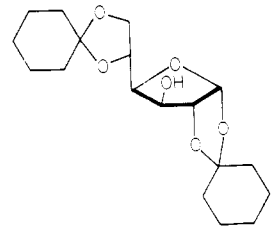
A number of modified lithium aluminum hydride reagents containing chiral ligands have been used to reduce unsymmetrical ketones asymmetrically.[1] Relatively little success, however, has been realized with chiral sodium borohydride derived systems.[2]

Recently, Yamazaki and co-workers described the asymmetric reduction of several ketones (but primarily propiophenone) with sodium borohydride in the presence of 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (DIPGF) alone[3] and also sodium borohydride plus Lewis acids and DIPGF.[4] In the latter report as high as 88% ee was claimed although more typical values in the range of 25–55% were reported for propiophenone reductions. Unfortunately, in both papers the percent enantiomeric excess values for ethylphenylcarbinol are considerably higher than they should be because a "maximum rotation" value for the carbinol was used that is only about 63% of the true value.[5]

Independently, we have been investigating some related borohydride reducing systems. This paper will describe one that employs $NaBH_4$, a carboxylic acid, and 1,2:5,6-di-*O*-cyclohexylidene-D-glucofuranose (DCHGF)[6] as ingredients. In THF solutions, variants of this system give percent enantiomeric excess values in the range of 35–50% for acetophenone and propiophenone reductions. These values are 2–3 times those obtained when the carboxylic acid is omitted from the recipe and are comparable to the true values obtained when $NaBH_4$ and Lewis acids are used with DIPGF.[4,5] Some of the features of this system have been explored, and the results suggest a hypothesis that may be helpful in the design of synthetic chiral borohydride modifiers.



DIPGF



DCHGF

Our general view of this process is that there is initial formation of an (acyloxy)borohydride,[7] which is soluble in THF. Addition of DCHGF or DIPGF (usually 2 equiv) results in the evolution of 1 equiv of dihydrogen over a period of 2–3 h, indicating addition of one hydroxy-monosaccharide unit to the (acyloxy)borohydride with formation of a mono-alkoxy(acyloxy) species. Then, somewhat more slowly, a second equivalent of dihydrogen is released as a bis[alkoxy(acyloxy)] intermediate is formed (Scheme I). Addition of 1 equiv of ketone along with the hydroxymonosaccharide or within the time period required for the release of the first equivalent of dihydrogen results in quantitative ketone reduction over a 48-h period and the production of an optically active carbinol.

Several variations on the above general scheme were examined by using acetophenone and propiophenone. In preliminary reactions we allowed $NaBH_4$ to react with 1 equiv of some chiral carboxylic acids and carried out reductions without adding any DCHGF. Such reagents, presumably chiral (acyloxy)borohydrides gave only a few percent asymmetric synthesis. Similarly, using chiral $PhCH(OH)CH_2OH$ as a secondary modifier gave no asymmetric induction. $NaBH_4$ and DCHGF (2 equiv) alone (no initial modification with carboxylic acid) gave about 18% ee and quantitative reduction with both acetophenone and propiophenone. Quantitative reductions and substantial increases in the percent enantiomeric excess were realized when both carboxylic acid and DCHGF modification were used. Table I shows some results.

As expected, in view of the absence of any asymmetric induction with chiral acids alone, if a chiral acid is used along with DCHGF, the sugar derivative is the controlling influence. Thus, enantiomeric acids (runs 8 and 9 in Table I) gave the same direction and virtually the same degree of asymmetric reduction when used with DCHGF. Racemic 2-phenylbutanoic acid was often used as the acid component, but achiral lipophilic acids like 3-methylbutanoic (isovaleric) acid were equally effective.

An interesting difference was observed between 2-phenylbutanoic acid and (+)- or (−)-pinanecarboxylic acid. In reactions involving the former as a preliminary modifier, the reaction solution remained clear for about 20 h, and then a gelatinous precipitate formed. In contrast, reductions involving the pinanecarboxylic acid enantiomers remained homogeneous over the entire 48-h reaction period. We believe this is merely a reflection of the relative lipophilicities of the alkoxy(acyloxy) intermediates that are produced; but it reveals one consideration that might be applied to the choice of the acid modifier if completely

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(2) For examples and leading references see: (a) J. P. Masse and E. R. Parayre, *J. Chem. Soc., Chem. Commun.*, 438 (1976); (b) C. Innis and G. Lamaty, *Nouv. J. Chim.*, 1(6), 503 (1977); (c) T. Sugimoto, Y. Matsumura, S. Tanimoto, and M. Okano, *J. Chem. Soc., Chem. Commun.*, 926 (1978); (d) S. I. Goldgerg et al., *J. Am. Chem. Soc.*, **100**, 6768 (1978); (e) R. Kinishi, Y. Nakajima, J. Oda, and Y. Inouye, *Agric. Biol. Chem.*, **42**, 869 (1978); (f) S. Colonna and R. Fornasier, *J. Chem. Soc., Perkin Trans. 1*, 371 (1978).

(3) A. Hirao, H. Mochizuki, S. Nakahama, and N. Yamazaki, *J. Org. Chem.*, **44**, 1720 (1979).

(4) A. Hirao, S. Nakahama, D. Mochizuki, S. Itsuno, M. Ohowa, and N. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 807 (1979).

(5) In ref 3 and 4 a maximum rotation for ethylphenylcarbinol (erroneously called 3-phenylpropanol in ref 4) of $[\alpha]^{20}_D$ +34.8° (c 8, ether) was used. The correct value is $[\alpha]^{20}_D$ 55.54° in ether [P. A. Levene and L. Mikeska, *J. Biol. Chem.*, **70**, 355 (1926)]. Thus, to obtain true percent enantiomeric excess values one should multiply the reported values by 0.63.

(6) R. C. Hockett, R. E. Miller, and A. Scattergood, *J. Am. Chem. Soc.*, **71**, 3072 (1949).

(7) G. W. Gribble, "Eastman Organic Chemicals Bulletin", **No. 51**, Eastman Chemical Co., 1979, p 1.

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