H), 7.99 (s, 1 H), and 8.13 ppm (s, 1 H); ^{13}C NMR 24.51, 51.60, 52.12, 59.10, 119.26, 119.33, 119.62, 120.00, 120.17, 120.33, 126.42, 128.04, 132.26, 136.83, 138.34, 138.58, 176.43, 177.62; IR (KBr) 3400 (br, s), 3380 (m), 3210 (m), 3047 (m), 2942 (w), 1680 (vs), 1440 (vs), 1285 (vs), 1140 (s) cm^{-1}; MS (CI) 421 (P, 1), 323 (5), 295 (16), 294 (13), 114 (12), 112 (71), 111 (12), 55 (12), 43 (100); MS (CI) calcd for $C_{27}H_{21}N_2O_3$ (P + H) 421.1530, found 421.1541.

Reaction of 20. The procedure of Regitz[16] was used to prepare 10-diaza-9-anthrone (**20**) from 9-anthrone and *p*-toluenesulfonyl azide[17] in 90% yield. Bright red **20** (mp >300 °C) has ^{1}H NMR δ 7.33 (d, 2 H, J = 8 Hz), 7.41 (t, 2 H, J = 8 Hz), 7.70 (t, 2 H, J = 8 Hz), and 8.54 ppm (d, 2 H, J = 8 Hz).

A solution of **20** (126 mg, 0.594 mmol) and NMM (68 mg, 0.613 mmol) in 7 mL of pyridine was reduced in the usual manner with 15 mg of 10% Pd/C catalyst. After 1 h of vigorous stirring with H_2, and 5 h of additional stirring, the mixture was worked up in the usual manner. The deazotized cycloadduct **21** was estimated by NMR to have been formed in 45% yield, along with *N*-methylsuccinimide and 9-anthrone. An essentially quantitative yield of **21** was formed when this procedure was carried out by stepwise reduction–cycloaddition. The product **21** was identical with material prepared by direct reaction of anthrone with NMM, as recently described.[2]

Reaction of 22. The procedure of Clar was used to prepare 10-methylene-9-anthrone[18] (**22**) from 9-anthrone and aqueous formaldehyde. Compound **22** was obtained in 91% yield as colorless crystals: mp 146.5–147 °C (lit.[19] mp 145–147.5 °C); ^{1}H NMR δ 6.34 (s, 2 H), 7.54 (t, 2 H, J = 7 Hz), 7.65 (t, 2 H, J = 8 Hz), 8.01 (d, 2 H, J = 8 Hz), and 8.35 ppm (d, 2 H, J = 7 Hz).

A mixture of **22** (212 mg, 1.02 mmol), NMM (126 mg, 1.14 mmol), and 10 mg of 10% Pd/C in 10 mL of pyridine was hydrogenated for 40 min, stirred an additional 30 min, and then worked up in the usual manner. Analysis of the crude residue by NMR showed no absorptions anticipated for cycloadduct; instead, major amounts of *N*-methylsuccinimide and 10-methyl-9-anthrone (**23**) were formed. The latter was identical with **23** that had been independently prepared by methylation of anthrone and also by reduction of **22**: 10-methyl-9-anthrone (**23**) has mp 64–66 °C (lit.[19] mp 64.5–66.5 °C); ^{1}H NMR δ 1.59 (d, 3 H, J = 7.5 Hz), 4.30 (q, 1 H, J = 7.5 Hz), 7.44 (t, 2 H, J = 7.5 Hz), 7.50 (d, 2 H, J = 7.5 Hz), 7.62 (t, 2 H, J = 7.5 Hz), and 8.31 ppm (d, 2 H, J = 7.5 Hz).

Double Retro-Aldol Reaction of 4 in MeOD. A solution of 321 mg (1.0 mmol) of cycloadduct **4** in a solvent consisting of 7 mL each of MeOD and THF was treated with 1 mL of isopropylamine. After 24 h at room temperature, the solution was separated from the yellow needles of anthrquinone which had precipitated, and the solvent was removed under vacuum, with care to retain the relatively volatile *N*-methylsuccinimide. The ^{1}H NMR spectrum of the residue showed a singlet at 3.00 ppm (N-Me; relative area = 3) and a broadened triplet-like absorption at 2.72 ppm (relative area = 2.1, compared to 4.0 for the undeuterated *N*-methylsuccinimide methylene absorption), signifying formation of the dideuterio compound with high efficiency.

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Supplementary Material Available: ^{1}H NMR spectra of **4**, **6**, **8a** + **8b**, **10**, and **13–18** and ^{13}C NMR spectra of **4**, **6**, **8a** + **8b**, **13–16**, and **18** (67 pages). Ordering information is given on any current masthead page.

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Pentaalkylstiboranes. 1. Synthesis of Homobenzylic Alcohols, Homoallylic Alcohols, Ethyl 5-Aryl-5-hydroxypent-2-enoates, and β-Hydroxypropionic Acid Derivatives via Pentaalkylstiboranes†

Yao-Zeng Huang* and Yi Liao

Laboratories of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, China

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Although pentaalkylstiboranes have long been known, their applications in organic synthesis have not been exploited. It has been found that quaternary stibonium salts $(n\text{-}Bu_3SbCH_2E]^+X^-$ (E = Ph, CH=CH_2, CH=$CHCO_2Et$, CO_2Et, CN; X = Br, I, BPh_4) on treatment with RLi (R = *n*-Bu, *t*-Bu, Ph) afford pentaalkylstiboranes, $n\text{-}Bu_3Sb(R)CH_2E$, which react with aromatic aldehydes to give, after subsequent hydrolysis, homobenzylic alcohols, homoallylic alcohols, ethyl 5-aryl-5-hydroxypent-2-enoates, ethyl β-aryl-β-hydroxypropionates, and β-aryl-β-hydroxypropionitriles, respectively, in good to excellent yields. The reaction is chemoselective for aldehydes.

Introduction

Few reports[1] concerning the application of organoantimony compounds in organic synthesis have appeared in the literature. Henry and Wittig[2] claimed that triphenylstibonium methylide, prepared from methyltriphenylstibonium iodide and phenyllithium, reacted with benzophenone to form acetaldehyde. However, Doleshall et al.[3] later reported a quite different result: that reaction of methyltriphenylstibonium iodide or tetraphenylborate with phenyllithium followed by introduction of benzophenone into the reaction mixtures gave a pentaorganylstiborane, methyltetraphenylstiborane, and unreacted benzophenone. On the other hand, Wittig and Laib[4] reported that $Me_2Sb(CH_2Ph)_2Br$ reacted with PhLi to yield $Me_2SbCH(CH_2Ph)Ph$, a product hypothesized to result from the rearrangement of an antimony ylide. The only successful Wittig-type process reported for an antimony ylide was the reaction of triphenylstibonium tetraphenylcyclopentadienylide, formed from triphenylstibine

† This paper is the 85th report of the synthetic application of elementoorganic compounds of group 15 and 16.

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and diazotetraphenylcyclopentadiene, and arylaldehydes to form fulvenes.[5]

Earlier, we reported a series of the trialkylstibine-mediated reactions[6] and the reduction of some organic compounds by tertiary stibines.[7] Almost all of these reports focused on the reactivity of tertiary stibines and antimony ylides. To our knowledge, scant attention has been paid to the use of pentaalkylstiboranes in organic synthesis,[8] although many, such as pentaethyl-,[9a] pentabutyl-,[9b] pentaallyl-,[9c] pentacyclopropyl-,[9d] pentaaryl-,[9e] and alkyltetraphenylstiborane,[3] have long been known. We have noticed that antimony has a greater tendency to form pentaalkyl derivatives than do phosphorus and arsenic. Our aim was thus to explore the scope of the reactivities of pentaalkylstiboranes (λ^5-stibanes).[8] We report here the first examples of the reactions of pentaalkylstiboranes and carbonyl compounds.

Results and Discussions

In a preliminary communication,[10] we reported the strong-base-mediated reactions of carbonyl compounds and benzyltrialkylstibonium bromides **1**. Reactions mediated by alkyllithiums gave homobenzylic alcohols, while those mediated by lithium diisopropylamide (LDA) gave mixtures of alkenes and epoxides.

Furthermore, we have found that many quaternary stibonium salts **1a–5**, after treatment with alkyl- or phenyllithium, reacted with aromatic aldehydes to give the corresponding alcohol derivatives (eq 1) rather than alkenes[11] or epoxides,[12] the products expected by analogy with the reaction of, for example, phosphorus ylides.

$$[n\text{-}Bu_3SbCH_2E]^+X^- \xrightarrow[3.\ H_2O]{1.\ R'Li;\ 2.\ RCHO} \quad \textbf{1–5}$$

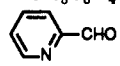
E = Ph, X = Br (**1a**); $Et_3SbCH_2Ph^+Br^-$ (**1b**)
E = CH=CH_2, X = Br (**2a**); X = I (**2b**)
E = CH=$CHCO_2Et$, X = Br (**3a**); X = BPh_4 (**3b**)
E = CO_2Me, X = Br (**4a**); X = BPh_4 (**4b**)
E = CO_2Et, X = BPh_4 (**4c**)
E = CN, X = Br (**5**).

$$\underset{\textbf{6–10}}{RCHCH_2E(OH)} + \underset{\textbf{11}}{n\text{-}Bu_3SbX(R')} \quad (1)$$

E = Ph (**6**)
E = CH=CH_2 (**7**)
E = CH=$CHCO_2Et$ (**8**)
E = CO_2R'' (**9**)
E = CN (**10**),

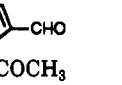
Stibonium bromides **1a–5** were readily prepared from trialkylstibines and alkyl bromides at room temperature. Anion exchange, by treatment of the bromides with $NaBPh_4$, gave the corresponding crystalline tetraphenylborates.

Table I. Synthesis of Homobenzylic Alcohols 6

entry	RCH=O	R'Li	product	yield (%)[a]
1	PhCHO	*n*-BuLi	**6a**	96
2	PhCHO	*t*-BuLi	**6a**	95
3	PhCHO	PhLi	**6a**	95
4	PhCHO	*n*-BuLi	**6a**	92[b]
5	4-ClC_6H_4CHO	*n*-BuLi	**6b**	98
6	PhCH=CHCHO	*t*-BuLi	**6c**	77
7	4-$CH_3C_6H_4CHO$	PhLi	**6d**	86
8		PhLi	**6e**	89

[a] Based on aldehyde. [b] $[Et_3SbCH_2Ph]^+Br^-$ (**1b**) was used in place of $[n\text{-}Bu_3SbCH_2Ph]^+Br^-$ (**1a**).

Table II. Synthesis of Homoallylic Alcohols 7

entry	R^1R^2C=O	R'Li	*T* (°C)/*t* (h)	product	yield (%)[a]
1	PhCHO	*t*-BuLi	−78–rt/3[c]	**7a**	90
2	PhCHO	*n*-BuLi	−78–rt/2	**7a**	91
3	PhCHO	PhLi	−40–rt/2	**7a**	90[b]
4	4-ClC_6H_4CHO	*n*-BuLi	−78–rt/2	**7b**	92
5	4-$CH_3C_6H_4CHO$	PhLi	−78–rt/2	**7c**	86
6	PhCH=CHCHO	PhLi	−40–rt/3	**7d**	68
7	citral	PhLi	−78–rt/2	**7e**	72
8		*n*-BuLi	−78–rt/2	**7f**	78
9	$PhCOCH_3$	PhLi	−78–rt/6	nd[d]	0

[a] Based on aldehyde. [b] *n*-$Bu_3Sb(CH_2CH{=}CH_2)^+I^-$ (**2b**) was used for this entry. In other entries, *n*-$Bu_3Sb(CH_2CH{=}CH_2)^+Br^-$ (**2a**) was used. [c] rt = room temperature. [d] nd = not detected.

Scheme I

$$\underset{\textbf{1a}}{n\text{-}Bu_3SbCH_2Ph^+Br^-} \xrightarrow{n\text{-BuLi}} \underset{\textbf{12}}{n\text{-}Bu_4SbCH_2Ph\ Li^+Br^-} \rightleftharpoons$$

$$[n\text{-}Bu_4Sb^{\delta+}\cdots CH_2^{\delta-}(Ph)(Li^+)]\ Br^- \quad \textbf{12'}$$

Although some quaternary stibonium salts with electron-withdrawing substituents condensed directly with carbonyl compounds when heated,[13] benzyltri-*n*-butylstibonium bromide (**1a**) did not react with carbonyl compounds in the absence of alkyl- or phenyllithium, even at 150 °C. A novel RLi-promoted condensation of **1a** and aromatic aldehydes did occur, however, and afforded homobenzylic alcohols. Neither benzophenone nor acetophenone reacted under the same conditions. Aliphatic aldehydes afforded complicated products. The results are shown in Table I.

Lithium reagents such as *n*-BuLi, *t*-BuLi, and PhLi promoted the reaction effectively. An alkyllithium is not only a strong base but also a strong nucleophile. The antimony atom of the stibonium salt is an electrophile with a large atom radius, so the alkyllithium can attack antimony atom preferentially and displace the anion X^-, instead of abstracting a proton and forming an antimony ylide, as occurs in the case of the phosphonium or arsonium analogues. A pentaalkylstiborane (**12**) thus may be formed, as shown in Scheme I. This species may become polarized in the presence of Li^+ to form **12'**, which by nucleophilic addition to aldehydes can afford, after hydrolysis, homobenzylic alcohol.

In fact, when benzyltri-*n*-butylstibonium bromide (**1a**) was treated with *n*-BuLi, we did isolate an intermediate,

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Table III. Synthesis of Ethyl 5-Aryl-5-hydroxypent-2-enoates 8

entry	R	time (h)	product	yield (%)[a]
1	C_6H_5	4	**8a**	81
2	4-ClC_6H_4	2	**8b**	98
3	4-BrC_6H_4	2	**8c**	95
4	4-FC_6H_4	4	**8d**	55
5	4-$CH_3C_6H_4$	4	**8e**	90
6	4-$NO_2C_6H_4$	2	**8f**	65

[a] Based on aldehyde.

Table IV. Synthesis of β-Hydroxypropionic Esters 9

entry	$R^1R^2C{=}O$	time (h)	product	yield (%)[a]
1	PhCHO	2	PhCH(OH)-CH_2CO_2Me (**9a**)	96[b]
2	PhCHO	2	PhCH(OH)-CH_2CO_2Et (**9b**)	97
3	4-ClC_6H_4CHO	2	*p*-$ClC_6H_4CH(OH)$-CH_2CO_2Et (**9c**)	95
4	4-$CH_3C_6H_4$-CHO	2	*p*-$CH_3C_6H_4CH(OH)$-CH_2CO_2Et (**9d**)	93
5	4-$CH_3OC_6H_4$-CHO	4	*p*-$CH_3OC_6H_4CH(OH)$-CH_2CO_2Et (**9e**)	93
6	$PhCOCH_3$	6	$PhC(CH_3)(OH)$-CH_2CO_2Et (**9f**)	0

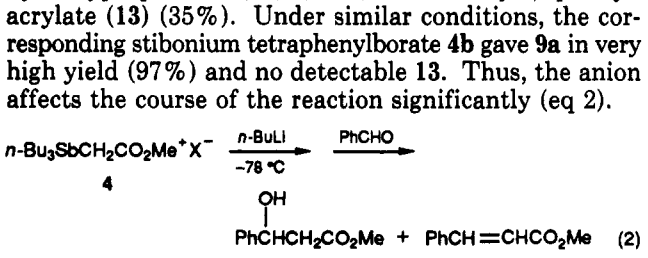
[a] Based on aldehyde. [b] *n*-$Bu_3Sb(CH_2CO_2Me)^+BPh_4^-$ was used instead of *n*-$Bu_3Sb(CO_2Et)^+BPh_4$.

n-Bu_4SbCH_2Ph (**12**), which was stable only under nitrogen but which could be characterized by mass spectrometry. If the reaction was stopped at this stage (−78 °C) and was allowed to reach room temperature, addition of benzaldehyde still gave the product alcohol. Thus, it appears that pentaalkylstiborane **12** is a likely intermediate.

Allyltri-*n*-butylstibonium bromide (**2a**), under the mediation of phenyl- or alkyllithium, reacted with aromatic aldehydes to give homoallylic alcohols **7** in good to excellent yields. The same products could also be prepared by tri-*n*-butylstibine-promoted reaction of carbonyl compounds with allyl bromide at 80–110 °C.[13] The former reaction also may involve a pentaalkylstiborane intermediate such as **12**. The results are shown in Table II.

Of great interest is the *n*-BuLi-mediated synthesis of ethyl 5-aryl-5-hydroxypent-2-enoates **8** in high yields from stibonium salt **3b** and aldehydes (eq 1). The results are shown in Table III. These compounds are usually prepared via the Reformatsky reaction and are often obtained in only low yields.[14] Our procedure seems to be a promising alternative method for preparing these compounds.

[(Methoxycarbonyl)methyl]tributylstibonium bromide (**4a**), after treatment with *n*-BuLi in tetrahydrofuran at −78 °C, reacted with benzaldehyde to give in good yield, after hydrolysis, a mixture of methyl β-phenyl-β-hydroxypropionate (**9a**) (65%) and methyl β-phenylacrylate (**13**) (35%). Under similar conditions, the corresponding stibonium tetraphenylborate **4b** gave **9a** in very high yield (97%) and no detectable **13**. Thus, the anion affects the course of the reaction significantly (eq 2).



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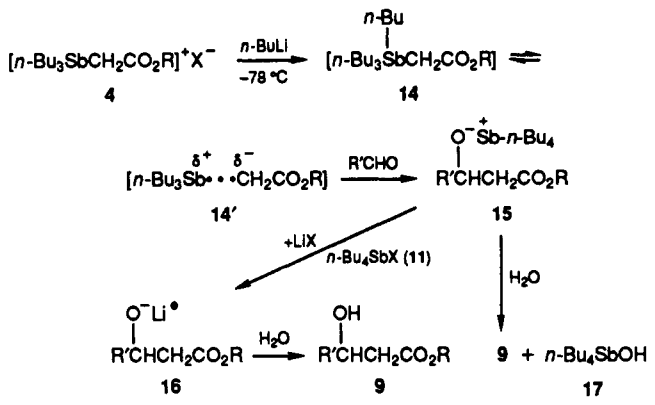
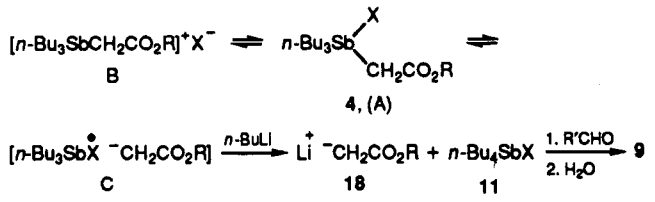
Scheme II



Scheme III



Stibonium salt **4c** reacted with aromatic aldehydes to give ethyl β-aryl-β-hydroxypropionates **9** in excellent yield. The reaction was also chemoselective for aldehydes: ketones did not react under the same conditions. The results are shown in Table IV.

β-Hydroxycarboxylic esters are useful in organic synthesis and are usually prepared via the Reformatsky reaction.[16] The approach described here is a novel alternative method for the synthesis of these compounds.

We hypothesize that this alkyllithium-mediated reaction proceeds by a pathway different from that of Wittig reactions. It may also involve a pentaalkylstiborane intermediate (**14**) as shown in Scheme II. Species **14** could be polarized as in **14′** by the influence of the electron-withdrawing alkoxycarbonyl group. The anion formed from the cleavage of the antimony–carbon bond of intermediate **14** could then attack the aldehyde to form intermediate **15**. Hydrolysis of **15** would give rise to **9**. Alternatively, reaction of **15** with LiX could lead to the stable stibonium salt **11** and intermediate **16**, the latter yielding **9** on hydrolysis.

The effects of the counter ion are unclear. When the anion of the stibonium salt is bromide, the *n*-BuLi-mediated reaction afforded some of the olefin derivatives. Olefin formation may proceed by a pathway involving an antimony ylide.[10] When the anion is tetraphenylborate, the strong electrophilicity of the cation and the steric hindrance of anion may permit the reaction to proceed exclusively by nucleophilic attack of alkyllithium on antimony, so the reaction gives the β-hydroxypropionic ester as the sole product.

Another possibility (Scheme III) has also been considered for this *n*-BuLi-mediated reaction. Compound **4** may exist as a hybrid of three structures: salt form B, pentacovalent form A, and ion pair form C. Compound **4** in C form could react with *n*-BuLi to give [(alkoxycarbonyl)methyl]lithium **18** and *n*-Bu_4SbX **11**. Species **18** could then react with aldehyde to afford product **9**. Although we have no bond strength data that show that the Sb–X

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Table V. Synthesis of β-Aryl-β-hydroxypropionitriles 10

entry	RCHO	condtns: time (h)	product (yield, %)[a] RCH(OH)-CH_2CN	RCH=CHCN
1	C_6H_4CHO	2	**10a** (95)	**19a** (3)
2	4-ClC_6H_4CHO	2	**10b** (92)	**19b** (6)
3	4-$CH_3OC_6H_4CHO$	2	**10c** (85)	**19c** (12)
4	3,4-$(CH_3O)_2C_6H_3CHO$	3	**10d** (80)	**19d** (18)
5	3,4-$(CH_2O_2)C_6H_3CHO$	3	**10e** (82)	**19e** (15)

[a] Based on aldehyde.

bond is weaker than the Sb–C bond, the fast atom bombardment mass spectrum (FABMS) of **4** shows that cleavage of the Sb–X bond appears to be more facile than cleavage of the Sb–C bond. The presence of a strong base peak for $Bu_3SbCH_2CO_2R^+$ and the absence of a Bu_3SbX^+ peak suggest that form B makes the greatest contribution to the hybrid. In fact, the FABMS of all the quaternary stibonium salts $Bu_3SbCH_2E^+X^-$ **1a–5** showed $Bu_3SbCH_2E^+$ as the base peak and no Bu_3SbX^+ peak.[15] Obviously, a strong nucleophile such as alkyl- or phenyllithium can attack the antimony atom of the salt, displacing X and forming a pentaalkylstiborane. Therefore, we hypothesize that the reaction proceeds mainly through a pentaalkylstiborane intermediate.

Finally, our method can also be applied to the synthesis of β-aryl-β-hydroxypropionitriles **10**, starting from (cyanomethyl)tributylstibonium bromide (**5**). Besides the expected β-hydroxypropionitriles **10**, α,β-unsaturated nitriles were also produced as minor products. The latter may have been formed by dehydration of **10**. The results are shown in Table V. We hypothesize that the intermediate in this instance is also a pentaalkylstiborane.

In conclusion, quaternary stibonium salts *n*-$Bu_3SbCH_2E^+X^-$ (E = Ph, $CH{=}CH_2$, $CH{=}CHCO_2Et$, CO_2Et, CN; X = Br, I, BPh_4) on treatment with RLi (R = *n*-Bu, *t*-Bu, Ph) afforded pentaalkylstiboranes *n*-$Bu_3Sb(R)CH_2E$. These reacted with aromatic aldehydes to give, after subsequent hydrolysis, homobenzylic alcohols, homoallylic alcohols, ethyl 5-aryl-5-hydroxypent-5-enoates, ethyl β-aryl-β-hydroxypropionates, and β-aryl-β-hydroxypropionitriles, respectively, in good to excellent yields. This reaction allows the chemoselective functionalization of aldehydes, since aromatic ketones are unreactive under similar conditions.

Experimental Section

Proton magnetic resonance (^1H NMR) spectra were recorded on a Varian 360L instrument in CCl_4 solution unless indicated otherwise. Infrared spectra were recorded of neat liquid films unless indicated otherwise. All reactions were carried out under nitrogen. All solvents were dried by standard methods and redistilled before use. Boiling and melting points are uncorrected. Tri-*n*-butylstibine,[17] triethylstibine,[18] ethyl 4-bromobut-2-enoate,[19] bromoacetonitrile,[20] and ethereal PhLi[21] were prepared according to literature methods.

Preparation of Trialkylstibonium Halides. General Procedure. Benzyltributylstibonium Bromide (1a). Tributylstibine (590 mg, 2 mmol) and benzyl bromide (376 mg, 2.2 mmol) were stirred at room temperature for 8 h to afford **1a** as a solid. Compound **1a** was washed with light petroleum ether (0.5 mL) at −40 °C under N_2 and was dried under vacuum to give 882 mg (95%) as a hygroscopic solid: ^1H NMR δ 0.87 (t, 9 H, *J* = 5 Hz), 1.03–2.10 (m, 12 H), 2.23–2.70 (m, 6 H), 4.03 (s, 2 H), 7.10 (m, 5 H); FABMS *m/e* (rel intensity) 383, 385 (100). Anal. Calcd for $C_{19}H_{34}SbBr$: C, 49.17; H, 7.38; Br, 17.22. Found: C, 48.78; H, 7.51; Br, 16.50.

Benzyltriethylstibonium bromide (1b): white solid after washing with CCl_4; mp 149–151 °C; ^1H NMR ($CDCl_3$) δ 1.36 (t, 9 H, *J* = 8 Hz), 2.43 (q, 6 H, *J* = 8 Hz), 3.88 (s, 2 H), 7.33 (s, 5 H); FABMS *m/z* (rel intensity) 299, 301 (100). Anal. Calcd for $C_{13}H_{22}BrSb$: C, 41.09; H, 5.83; Br, 21.03. Found: C, 39.89; H, 5.90; Br, 20.59.

All other stibonium halides (**2a–5**) were generated from tri-*n*-butylstibine and the appropriate halide in the manner described above and were used in situ without further purification. Anion exchange via $NaBPh_4$ gave the corresponding crystalline [(ethoxycarbonyl)allyl]tributylstibonium tetraphenylborate (**3b**), [(methoxycarbonyl)methyl]tributylstibonium tetraphenylborate (**4b**), and [(ethoxycarbonyl)methyl]tributylstibonium tetraphenylborate (**4c**).[15,22]

3b: mp 120–122 °C; ^1H NMR ($CDCl_3$) δ 0.70–1.50 (m, 30 H), 1.77 (d, 2 H, J_1 = 9 Hz), 4.20 (q, 2 H, J_2 = 7.0 Hz), 5.67 (d, 1 H, J_3 = 16 Hz), 6.40 (dt, 1 H, J_3 = 16 Hz, J_1 = 9 Hz), 7.00 (m, 12 H), 7.50 (m, 8 H); IR (KCl) 1720 (s), 1640 (m), 1580 (m), 1480 (m) cm^{-1}; FABMS *m/z* (rel intensity) 405, 407 (100). Anal. Calcd for $C_{42}H_{56}BO_2Sb$: C, 69.54; H, 7.74. Found: C, 69.95; H, 7.78.

4b: mp 152–4 °C; ^1H NMR ($CDCl_3$) δ 0.83 (t, 9 H, *J* = 4.5 Hz), 0.95–1.76 (m, 18 H), 2.00 (s, 2 H), 3.57 (s, 3 H), 6.92 (m, 12 H), 7.45 (m, 8 H); IR (KCl) 1720 (s) cm^{-1}; FABMS *m/z* (rel intensity) 365 (100). Anal. Calcd for $C_{39}H_{52}BO_2Sb$: C, 68.34; H, 7.65. Found: C, 68.77; H, 7.92.

Synthesis of Homobenzylic Alcohols 6 and Homoallylic Alcohols 7. Typical Procedure. Compound **1a** (2.2 mmol) in tetrahydrofuran (THF) (4 mL) was treated with *n*-BuLi (2.2 mmol, in hexane) at −78 °C. After 0.5 h, benzaldehyde (212 mg, 2 mmol) in THF (1 mL) was added dropwise, and the solution was allowed to reach room temperature with continuous stirring. The reaction mixture was then chromatographed on a 1:1 alumina–silica gel column (petroleum ether/ethyl acetate, 4:1), giving 380 mg (96%) of 1,2-diphenylethanol (**6a**): mp 63 °C (lit.[23] mp 67 °C); ^1H NMR δ 2.00 (s, 1 H, OH), 2.81 (d, 2 H, *J* = 6.2 Hz), 4.62 (t, 1 H, *J* = 6.2 Hz), 7.10 (s, 5 H), 7.08 (s, 5 H); IR (KCl) 3400 (s) cm^{-1}.

1-(4-Chlorophenyl)-2-phenylethanol (6b): mp 49–50 °C (lit.[24] mp 52.5–53.5 °C); ^1H NMR δ 2.13 (s, 1 H, OH), 2.81 (d, 2 H, *J* = 6 Hz), 4.66 (t, 1 H, *J* = 6 Hz), 7.06 (s, 5 H), 7.15 (s, 4 H); IR (KCl) 3360 (s) cm^{-1}; EIMS *m/z* (rel intensity) 232 (M^+, 3).

1,4-Diphenylbut-1-en-3-ol (6c): mp 62 °C (lit.[25] mp 65–6 °C); ^1H NMR δ 1.69 (s, 1 H), 2.81 (d, 2 H, J_1 = 6 Hz), 4.39 (dt, 1 H, J_1 = 6 Hz, J_2 = 5 Hz), 6.15 (dd, 1 H, J_3 = 15.8 Hz, J_2 = 5 Hz), 6.56 (d, 1 H, J_3 = 15.8 Hz), 7.22 (br s, 10 H); IR (KCl) 3400 (vs) cm^{-1}; EIMS *m/z* (rel intensity) 223 (M^+ − 1, 2).

1-(4-Methylphenyl)-2-phenylethanol (6d): oil (lit.[26] mp 107–8 °C); ^1H NMR δ 1.80 (s, 1 H, OH), 2.30 (s, 3 H), 2.85 (d, 2 H, *J* = 6.2 Hz), 4.66 (t, 1 H, *J* = 6.2 Hz), 7.02 (s, 4 H), 7.07 (s, 5 H); IR 3300 (s) cm^{-1}.

1-(2-Pyridyl)-2-phenylethanol (6e): mp 115–8 °C (lit.[27] mp 119–121 °C); ^1H NMR δ 2.96 (d, 2 H, *J* = 6 Hz), 3.80 (br s, 1 H), 4.80 (t, 1 H, *J* = 6 Hz), 7.07 (s, 5 H), 7.40 (m, 2 H), 8.40 (m, 1 H); IR (KCl) 3350 (vs) cm^{-1}; EIMS *m/z* (rel intensity) 200 (M^+ + 1, 62), 119 (M^+, 3.4).

1-Phenylbut-3-en-1-ol (7a): oil (lit.[28] bp 228–9 °C); ^1H NMR δ 2.32 (dd, 2 H, J_1 = J_2 = 6.3 Hz), 2.94 (br s, 1 H), 4.47 (t, 1 H, J_1 = 6.3 Hz), 4.74–5.15 (m, 2 H), 5.32–6.02 (m, 1 H), 7.19 (s, 5 H); IR 3350 (vs), 1640 (s) cm^{-1}.

1-(4-Chlorophenyl)but-3-en-1-ol (7b): oil; ^1H NMR δ 2.30 (dd, 2 H, J_1 = J_2 = 7.0 Hz), 2.50 (s, 1 H), 4.44 (t, 1 H, J_2 = 7.0

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Hz), 4.72–5.19 (m, 2 H), 5.30–6.07 (m, 1 H), 7.15 (s, 4 H); IR 3320 (vs), 1640 (m) cm^{-1}. Anal. Calcd for $C_{10}H_{11}ClO$: C, 65.76; H, 6.07; Cl, 19.41. Found: C, 65.54; H, 5.93; Cl, 19.80.

1-(4-Methylphenyl)but-3-en-1-ol (7c): oil (lit.[29] bp 194 °C/160 mmHg); ^1H NMR δ 2.10 (s, OH), 2.25 (s, 3 H), 2.35 (dd, 2 H, $J_1 = J_2 = 6$ Hz), 4.50 (t, 1 H, $J_1 = 6$ Hz), 4.70–5.20 (m, 2 H), 5.30–6.10 (m, 1 H), 7.03 (m, 4 H); IR 3400 (s), 1640 (s) cm^{-1}.

1-Phenylhexa-1,5(*E*)-dien-3-ol (7a): bp 105 °C/1 mmHg (lit.[30] bp 110–1 °C/1 mmHg); ^1H NMR δ 2.21 (dd, 1 H, $J_1 = J_2 = 6.0$ Hz), 2.80 (s, OH), 4.10 (dt, 1 H, $J_2 = J_3 = 6.0$ Hz), 4.73–5.15 (m, 2 H), 5.35–6.00 (m, 1 H), 5.95 (dd, 1 H, $J_3 = 6.0$ Hz, $J_4 = 16.0$ Hz), 6.40 (d, 1 H, $J_4 = 16.0$ Hz), 7.10 (s, 5 H); IR 3350 (s), 1640 (m) cm^{-1}.

6,10-Dimethylundeca-1,5,9-trien-4-ol (7e): bp 85–7 °C/3–4 mmHg (lit.[31] bp 80–2 °C/1 mmHg); ^1H NMR δ 1.23 (s, 1 H, OH), 1.59 (s, 3 H), 1.65 (s, 6 H), 1.90–2.40 (m, 6 H), 4.20 (m, 1 H), 4.66–6.10 (m, 5 H); IR 3350 (vs), 1660 (m), 1640 (m) cm^{-1}.

1-(2-Furfuryl)but-3-en-1-ol (7f): bp 98 °C/20 mmHg (lit.[32] bp 87–93 °C/3 mmHg); ^1H NMR δ 2.50 (dd, 2 H, $J_1 = J_2 = 6.2$ Hz), 2.55 (s, 1 H), 4.56 (t, 1 H, $J = 6.0$ Hz), 4.81–5.24 (m, 2 H), 5.38–5.98 (m, 1 H), 6.14 (m, 2 H), 7.24 (s, 1 H); IR 3320 (s), 1662 (m), 1640 (m) cm^{-1}.

Isolation of Intermediate 12. (To a solution of **1a** (3 mmol) in THF (4 mL) was added by syringe *n*-BuLi (3 mmol, 1.6 M in pentane) at −78 °C under N_2. After the mixture was stirred for 0.5 h, the solvent was removed by distillation and the residue was distilled under vacuum to give 844 mg (64%) of **12**: bp 72 °C/1 mmHg; ^1H NMR δ 0.90 (t, 12 H, $J = 5$ Hz), 1.15–1.90 (br s, 24 H), 2.83 (s, 2 H), 7.10 (s, 5 H); EIMS m/z (rel intensity) 383 (0.43), 381 (M^+ − Bu, 1.60), 351 (82.24), 349 ($M^+ - CH_2Ph$, 84.94), 294 (5.50), 292 (Bu_3Sb^+, 6.30), 237 (1.01), 235 (Bu_2Sb^+, 1.83), 182 (28.86), 181 (18.70), 179 (29.68), 177 (15.30), 91 ($PhCH_2^+$, 100); FABMS m/z (rel intensity) 351 (100), 349 (Bu_4Sb^+, 100), 294 (10.4), 292 (Bu_3Sb^+, 10.1), 181 (8.1), 179 (14.2), 177 (6.3). A detectable molecular ion was not observed in the high resolution mass spectrum.

Synthesis of Ethyl 5-Hydroxy-5-arylpent-2-enoates 8. Typical Procedure. The reaction was carried out as above, using stibonium tetraphenylborate **4c** and benzaldehyde. The reaction mixture was then chromatographed on a 1:1 alumina–silica gel column (ethyl acetate). The eluant was evaporated, and to the residue was added CCl_4(10 mL). After 0.5 h, the white solid suspended in solution was collected by filtration and was identified as tetrabutylstibonium tetraphenylborate (**11**, R′ = *n*-Bu) (yield, 64%). The filtrate was concentrated to give 360 mg (81%) of product **8a**, which was purified by chromatography on silica gel or by distillation. Compound **11**: mp 184–6 °C; ^1H NMR ($CDCl_3$) δ 0.88 (br s, 12 H), 1.05–1.65 (m, 24 H), 6.97 (m, 12 H), 7.51 (m, 8 H); IR (KCl) 1580 (s), 1480 (s), 705 (vs), 605 (s) cm^{-1}; FABMS m/z (rel intensity) 349 (100). Anal. Calcd for $C_{40}H_{56}BSb$: C, 71.77; H, 8.43. Found: C, 71.93; H, 8.49.

Ethyl 5-hydroxy-5-phenylpent-2-enoate (8a): bp 148–151 °C/2 mmHg) (lit.[14] bp 143–145.5 °C/1 mmHg); ^1H NMR δ 1.13 (t, 3 H, $J_1 = 7.0$ Hz), 2.40 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.43 (br s, 1 H, OH), 3.95 (q, 2 H, $J_1 = 7.0$ Hz), 4.52 (t, 1 H, $J_2 = 6.0$ Hz), 5.65 (d, 1 H, $J_4 = 16$ Hz), 6.69 (dt, 1 H, $J_3 = 6.0$ Hz, $J_4 = 16$ Hz), 7.12 (s, 5 H); IR 3400 (vs), 1710 (vs), 1650 (s) cm^{-1}; EIMS m/z (rel intensity) 220 (M^+, 1.89), 203 (26.64), 143 (49.9).

Ethyl 5-hydroxy-5-(4-chlorophenyl)pent-2-enoate (8b): oil, ^1H NMR δ 1.26 (t, 3 H, $J_1 = 6.5$ Hz), 2.50 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.65 (br s, 1 H, OH), 4.10 (q, 2 H, $J_1 = 6.5$ Hz), 4.63 (t, 1 H, $J_2 = 6.0$ Hz), 5.79 (s, 1 H, $J_4 = 16$ Hz), 6.85 (dt, 1 H, $J_3 = 6.5$ Hz, $J_4 = 16$ Hz), 7.28 (s, 4 H); IR 3400 (vs), 1710 (vs), 1650 (s) cm^{-1}; EIMS m/z (rel intensity) 254 (M^+, 22), 237 (100). Anal. Calcd for $C_{13}H_{15}ClO_3$: C, 61.30; H, 5.94; Cl, 13.93. Found: C, 60.77; H, 6.03; Cl, 14.27.

Ethyl 5-hydroxy-5-(4-bromophenyl)pent-2-enoate (8c): oil; ^1H NMR δ 1.22 (t, 3 H, $J_1 = 7.0$ Hz), 2.47 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.62 (br s, 1 H, OH), 4.05 (q, 2 H, $J_1 = 7.0$ Hz), 4.61 (t 1 H, $J_2 = 6.0$ Hz), 5.76 (d, 1 H, $J_4 = 16$ Hz), 6.74 (dt, 1 H, $J_4 = 16$ Hz, $J_3 = 6.0$ Hz), 7.15 (d, 2 H, $J_5 = 9.0$ Hz), 7.45 (d, 2 H, $J_5 = 9.0$ Hz); IR 3400 (vs), 1710 (vs), 1660 (s) cm^{-1}; EIMS m/z (rel intensity) 301 (M^+ + 2, 3.2), 299 (M^+, 3.7), 2.83 (91.5), 281 (86.7). Anal. Calcd for $C_{13}H_{15}BrO_3$: C, 52.19; H, 5.05; Br, 26.71. Found: C, 51.71; H, 4.87; Br, 27.32.

Ethyl 5-hydroxy-5-(4-fluorophenyl)pent-2-enoate (8d): ^1H NMR δ 1.21 (t, 3 H, $J_1 = 7.0$ Hz), 2.45 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.46 (br s, OH), 4.04 (q, 2 H, $J_1 = 7.0$ Hz), 4.58 (t, 1 H, $J_2 = 6.0$ Hz), 5.81 (d, 1 H, $J_4 = 16.0$ Hz), 6.72–7.20 (m, 5 H); IR 3400 (vs), 1710 (vs), 1655 (s) cm^{-1}; EIMS m/z (rel intensity) 221 (3.88), 220 (3.38), 175 (6.10), 174 (6.70), 148 (18.22), 147 (9.79), 125 (100). Anal. Calcd for $C_{13}H_{15}FO_3$: C, 65.54; H, 5.35. Found: C, 64.97; H, 6.26.

Ethyl 5-hydroxy-5-(4-methylphenyl)pent-2-enoate (8e): oil; ^1H NMR δ 1.21 (t, 3 H, $J_1 = 7.0$ Hz), 2.32 (s, 3 H), 2.44 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.37 (br s, OH), 4.05 (q, 2 H, $J_1 = 7.0$ Hz), 4.55 (t, 1 H, $J_2 = 6.0$ Hz), 5.71 (d, 1 H, $J_4 = 16.0$ Hz), 6.73 (dt, 1 H, $J_4 = 16.0$ Hz, $J_3 = 6.0$ Hz), 7.08 (s, 4 H); IR 3400 (vs), 1710 (vs), 1655 (s) cm^{-1}; EIMS m/z (rel intensity) 234 (M^+, 0.2), 217 (M^+ − OH, 2), 143 (9.4), 121 (100). Anal. Calcd for $C_{14}H_{18}O_2$: C, 71.77; H, 7.74. Found: C, 72.15; H, 7.90.

Ethyl 5-hydroxy-5-(4-nitrophenyl)pent-2-enoate (8f): ^1H NMR δ ($CDCl_3$) 1.26 (t, 3 H, $J_1 = 7.0$ Hz), 2.64 (dd, 2 H, $J_2 = J_3 = 6.0$ Hz), 3.04 (br s, 1 H, OH), 4.16 (q, 2 H, $J_1 = 7.0$ Hz), 4.94 (t, 1 H, $J_3 = 6.0$ Hz), 5.89 (d, 1 H, $J_4 = 16$ Hz), 6.98 (dt, 1 H, $J_2 = 6.0$ Hz, $J_4 = 16.0$ Hz), 7.55 (d, 2 H, $J_5 = 9.0$ Hz), 8.28 (d, 2 H, $J_5 = 9.0$ Hz); IR (KCl) 3350 (vs), 1700 (vs), 1640 (s) cm^{-1}; EIMS m/z (rel intensity) 266 (M^+ + 1, 39), 247 (M^+ − OH, 40), 114 (100). Anal. Calcd for $C_{13}H_{15}NO_5$: C, 58.86; H, 5.70; N, 5.28. Found: C, 59.14; H, 5.73; N, 4.93.

Synthesis of β-Hydroxy-β-arylpropionates 9 and -propionitriles 10. The compounds were prepared in a manner analogous to those given above.

Ethyl β-hydroxy-β-phenylpropionate (9b): bp 128 °C/4 Torr (lit.[33] bp 136 °C/6 Torr); ^1H NMR δ 1.26 (t, 3 H, $J_1 = 6.2$ Hz), 2.55 (d, 2 H, $J_2 = 6$ Hz), 3.46 (s, 1 H, OH), 4.12 (q, 2 H, $J_1 = 6.2$ Hz), 5.00 (t, 1 H, $J_2 = 6$ Hz), 7.23 (m, 5 H); IR 3500 (vs), 1710 (vs) cm^{-1}.

Ethyl β-hydroxy-β-(4-chlorophenyl)propionate (9c): oil;[33] ^1H NMR δ 1.23 (t, 3 H, $J_1 = 6.5$ Hz), 2.56 (d, 2 H, $J_1 = 6$ Hz), 3.80 (s, 1 H, OH), 4.08 (q, 2 H, $J_1 = 6.5$ Hz), 5.03 (t, 1 H, $J_2 = 6$ Hz), 7.28 (s, 4 H); IR 3510 (vs), 1725 (vs) cm^{-1}.

Ethyl β-hydroxy-β-(4-methylphenyl)propionate (9d): oil (lit.[33] bp 142 °C/8 Torr); ^1H NMR δ 1.20 (t, 3 H, $J_1 = 6.5$ Hz), 2.30 (s, 3 H), 2.53 (d, 2 H, $J_2 = 6.5$ Hz), 3.30 (s, 1 H), 4.04 (q, 2 H, $J_1 = 6.5$ Hz), 4.93 (t, 1 H, $J_2 = 6.5$ Hz), 7.06 (s, 5 H); IR 3500 (vs), 1725 (vs) cm^{-1}.

Ethyl β-hydroxy-β-(4-methoxyphenyl)propionate (9e): oil (lit.[33] bp 163 °C/7.5 Torr); ^1H NMR δ 1.20 (t, 3 H, $J_1 = 6.5$ Hz), 2.54 (d, 2 H, $J_2 = 6$ Hz), 3.15 (br s, 1 H, OH), 3.73 (s, 3 H), 4.08 (q, 2 H, $J_1 = 6.5$ Hz), 4.94 (t, 1 H, $J_2 = 6$ Hz), 6.76 (d, 1 H, $J_3 = 8$ Hz), 7.23 (d, 2 H, $J_3 = 8$ Hz); IR 3450 (s), 1720 (vs) cm^{-1}.

Methyl β-hydroxy-β-phenylpropionate (9a): bp 150 °C/15 Torr (lit.[34] bp 158–161 °C/17–18 Torr); ^1H NMR δ 2.52 (d, 2 H, $J = 6$ Hz), 3.57 (s, 5 H), 4.93 (t, 1 H, $J = 6$ Hz), 7.17 (s, 5 H); IR 3450 (vs), 1720 (vs) cm^{-1}.

β-Hydroxy-β-phenylpropionitrile (10a): bp 147–152 °C/1 mmHg (lit.[35] bp 154–5 °C/1 mmHg); ^1H NMR ($CDCl_3$) δ 2.76 (d, 2 H, $J = 6$ Hz), 3.57 (s, OH), 4.95 (t, 1 H, $J = 6$ Hz), 7.40 (s, 5 H); IR 3400 (vs), 2240 (w) cm^{-1}.

β-Hydroxy-β-(4-chlorophenyl)propionitrile (10b):[37] ^1H NMR δ 2.72 (d, 2 H, $J = 6$.Hz), 3.44 (s, 1 H), 4.95 (t, 1 H, $J = 6$ Hz), 7.45 (s, 4 H); IR 3450 (vs), 2240 (w) cm^{-1}.

β-Hydroxy-β-(4-methoxyphenyl)propionitrile (10c): oil (lit.[38] bp 173 °C/4 Torr); ^1H NMR δ 2.68 (d, 2 H, $J = 6.0$ Hz),

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3.50 (br s, OH), 3.79 (s, 3 H), 4.93 (t, 1 H, J = 6.0 Hz), 6.90 (d, 2 H, J = 8.5 Hz), 7.33 (d, 2 H, J = 8.5 Hz); IR 3400 (vs), 2260 (w) cm^{-1}.

β-Hydroxy-β-(3,4-dimethoxyphenyl)propionitrile (10d): oil; ^1H NMR δ 2.65 (d, 2 H, J = 6 Hz), 3.30 (s, OH), 3.79 (s, 6 H), 4.86 (t, 1 H, J = 6 Hz), 6.83 (m, 3 H); IR 3410 (vs), 2250 (w) cm^{-1}. The dehydration of **10d** was shown to give **19d**.

β-Hydroxy-β-[3,4-(methylenedioxy)phenyl]propionitrile (10e): oil (lit.[38] mp 80.5–81.0 °C); ^1H NMR δ 2.67 (d, 2 H, J = 6 Hz), 3.65 (s, OH), 4.90 (t, 1 H, J = 6 Hz), 5.95 (s, 2 H), 6.80 (m, 2 H); IR 3400 (vs), 2260 (w) cm^{-1}.

***trans*-3-(3,4-Dimethoxyphenyl)propenenitrile (19d)**: mp 88–90 °C (lit.[37] mp 91–2 °C); ^1H NMR δ 3.76 (s, 6 H), 5.56 (d, 1 H, J = 16 Hz), 6.80 (m, 3 H, Ar H), 7.06 (d, 1 H, J = 16 Hz); IR (KCl) 2200 (m), 1615 (m) cm^{-1}.

The physical constants of authentic **19a–e** were in agreement with those reported in the literature.[36,38]

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Enantioselective Total Synthesis of (+)- and (−)-Pyrrolidine 197B, a New Class of Alkaloid from the Dendrobatid Poison Frog: Assignment of the Absolute Configuration

Nobuo Machinaga and Chihiro Kibayashi*

Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo 192-03, Japan

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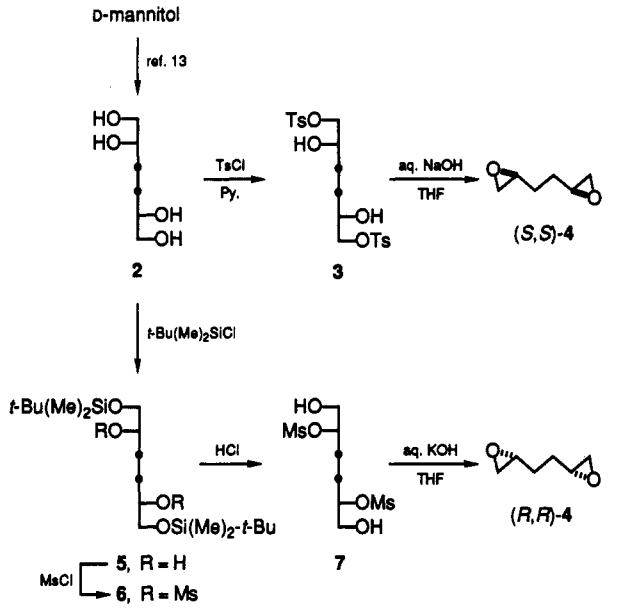
Enantioselective total synthesis of both enantiomers of pyrrolidine 197B (1), a new class of dendrobatid alkaloid, is described. The synthesis begins with the C_2 symmetric *S,S* or *R,R* diepoxides **4**, derived from (*S,S*)-1,2,5,6-hexanetetraol (**2**) as a single common chiral synthon, and involves pyrrolidine formation via the cyclic sulfonates to afford (+)- or (−)-**1**, respectively. The (+) and (−) enantiomers of **1** were converted to the corresponding *N*-benzoyl derivatives (+)-**27** and (−)-**27**, which were directly compared with **27** derived from natural **1** by HPLC using a Chiralcel column. This comparison established the absolute stereochemistry of the natural enantiomer of pyrrolidine 197B as 2*S*,5*S* [(+)-**1**].

Neotropical poison-dart frogs of the dendrobatid species have been shown to contain more than 200 alkaloids.[1] Many of these alkaloids occur in only trace amounts and have been characterized by gas chromatography–mass spectrometry techniques. Recently, such techniques led to the identification of a new class of dendrobatid alkaloid, *trans*-2-butyl-5-pentylpyrrolidine (**1**), named pyrrolidine 197B, in skin extracts of the Colombian populations of *Dendrobates histrionicus*.[2] Interestingly, **1** has also been detected in the alkaloidal venoms of fire ants of the genus *Solenopsis*[3] and the old world ants of *Monomorium*.[4,5] Owing to the minute quantities of **1** available, however, the absolute configuration has remained unknown, and no physical and detailed spectral characteristics have been reported.[6]

In continuation of our work on the synthesis of dendrobatid alkaloids,[7] we have now developed a general synthesis of optically active *trans*-2,5-dialkylated pyrrolidines and investigated its application to this alkaloid.[8-10]

Scheme I



In this paper we describe the enantioselective preparation of both enantiomers of **1**[11,12] based on a stereodefined

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