When the reaction was terminated, the solution was cooled and then passed over short alumina columm (80–100 mesh) to remove most of the catalyst. The unreacted alkenes and the solvent were distilled off under vacuum into a cold trap and analyzed by GLC: *n*-octane, 14.2%; 1-octene, 64.0%; *trans*-2-octene, 15.7%; *cis*-2-octene, 6.1%. The yield of *n*-octane, based on silane, corresponded to 38%. The product (1.95 g, 95%) was analyzed by GLC, IR, and NMR (Table II). Hydrogenation of the product ($RhCl(PPh_3)_3$, $PhCH_3$, 70 °C, 2–3 atm of H_2, 3.5 h) gave tetraalkylsilane: ^{29}Si NMR δ 2.70; mass spectrum, *m/e* (% relative intensity) 438 (0, P^+), 423 (0.1, P - $CH_3)^+$, 325 (26, $CH_3Si^+(C_{10}H_{21})_2$), 297 (64, $CH_3Si^+(C_8H_{17})(C_{10}H_{21})$), 185 (100, $CH_3Si^+(H)(C_{10}H_{21})$), 157 (60, $CH_3Si^+(H)(C_8H_{17})$), 113 (41, $CH_3Si^+(H)C_5H_9$)), 99 (33, $CH_3Si^+(H)C_4H_7$)), 85 (28, $CH_3Si^+(H)C_3H_5$)), 73 (29, $CH_3Si^+(H)C_2H_5$)), 59 (18, $CH_3Si^+(H)CH_3$)), 45 (5, $CH_3Si^+H_2$). Anal. Calcd for $C_{29}H_{62}Si$: C, 79.36; H, 14.24. Found: C, 79.41; H, 14.26.

Preparation of Methyldi-*n*-decylsilane. Into a 2-L, four-necked flask, equipped with a mechanical stirrer, reflux condensor, addition funnel, and a thermometer, was added magnesium chips (28.4 g, 1.17 mol) and several crystals of iodine. The flask, while vigorously stirred, was heated to about 50° C under nitrogen for 30 min and cooled. After addition of 100 mL of diethyl ether and 20 mL of 1-bromodecane solution (198.5 g of 1-bromodecane in 720 mL of THF), the reaction began almost immediately as noted by a temperature rise of 5 °C. The addition of halide was continued over 4 h, while a temperature of 25–30 °C was maintained, and the mixture was stirred overnight. Titration of an aliquot with hydrochloric acid showed that 0.88 mol of Grignard reagent was formed. After filtration (N_2 blanket) and washing of magnesium turnings with THF, methyldichlorosilane (51.0 g, 0.44 mol) dissolved in THF (170 mL) was added to the filtrate over 2 h, maintaining a temperature of 35–40 °C. The reaction mixture was then heated at 62 °C for 12 h, cooled, poured over cracked ice, and hydrolyzed with 1 N HCl. After extraction with ether, washing with water, drying ($MgSO_4$), and evaporation of ether gave 133.2 g of product. Analysis by GLC indicated the presence of *n*-eicosane (6.3%), 1-decanol (17.9%), and methyldi-*n*-decylsilane (75.0%) as major products. Distillation gave one major fraction, bp 200 °C (0.3 mmHg), which corresponded to a 23% yield of methyldi-*n*-decylsilane: IR 2100 cm^{-1}s, SiH; NMR δ 3.7 (m, 1 H, SiH), 1.3 (s, 32 H, CH_2), 0.9 (distorted t, 6 H, CH_3CH_2), 0.57 (m, 4 H, $SiCH_2$), 0.05 (s, 3 H, $SiCH_3$); GLC 99% purity; ^{29}Si NMR δ -9.85.

Mass Spectra of Products from the Reaction of Triethylsilane with 1-Hexene (Table IV, first entry): $Et_3SiC_6H_{13}$, *m/e* (relative intensity) 200 (0, M^+), 171 (77, (M - Et)$^+$), 143 (27), 115 (27), 101 (15), 87 (100), 59 (27); *trans*-$Et_3SiCH{=}CHC_4H_9$, *m/e* (relative intensity) 198 (5, M^+), 169 (100, (M - Et)$^+$), 141 (95), 113 (28), 85 (15), 59 (15); the corresponding cis isomer had the same major ions; *trans*-$Et_3SiCH_2CH{=}CHC_3H_7$, 198 (11, M^+), 169 (3, (M - Et)$^+$), 115 (100, Et_3Si^+), 87 (97), 59 (25); the corresponding cis isomer had the same major ions.

Effect of Solvents. In present work, *n*-decane, toluene, and excess olefin were used as solvents. These experiments were carried out by employing the basic procedure previously described for the hydrosilylation of methyldi-*n*-decylsilane with 1-octene. The reaction conditions, reactant ratios, and other information are given in Table III as footnotes.

Relative Reactivity. Relative reactivity of olefins with methyldi-*n*-decylsilane was carried out in a competitive experiment using equimolar ratio of 1-decene and styrene in benzene solvent, which also served as internal standard. The reactivities were based on the disappearance of the starting olefins.

Acknowledgment. We thank Drs. L. G. Galya and D. C. Young for obtaining ^{29}Si and ^{13}C NMR spectra and Mr. D. A. Danner for the GC/MS work.

Registry No. 1, 83584-71-8; **2a**, 90584-14-8; **2b**, 90584-15-9; **3a**, 90584-16-0; **3b**, 90584-17-1; **4**, 90584-18-2; **5**, 18408-00-9; **6a**, 90584-19-3; **7a**, 90605-21-3; **7b**, 90605-22-4; $RhCl(PPh_3)_3$, 14694-95-2; $Ru_3(CO)_{12}$, 15243-33-1; H_2PtCl_6, 16941-12-1; $Et_3SiC_6H_{13}$, 13810-04-3; *trans*-$Et_3SiCH{=}CHC_4H_9$, 42067-72-1; *cis*-$Et_3SiCH{=}CHC_4H_9$, 62621-38-9; *trans*-$Et_3SiCH_2CH{=}CHC_3H_7$, 79643-98-4; *cis*-$Et_3SiCH_2CH{=}CHC_3H_7$, 90584-20-6; methyldi(*n*-decyl)silane, 51502-65-9; triethylheptylsilane, 18414-81-8; *trans*-triethyl-1-heptenylsilane, 53335-87-8; *trans*-triethyl-2-heptenylsilane, 90584-21-7; *cis*-triethyl-2-heptenylsilane, 90584-22-8; triethylsilane, 617-86-7; methyldichlorosilane, 75-54-7; 1-octene, 111-66-0; 1-octyne, 629-05-0; 1-decene, 872-05-9; *n*-octane, 111-65-9; *trans*-2-octene, 13389-42-9; *cis*-2-octene, 7642-04-8; 1-bromodecane, 112-29-8; *n*-eicosane, 112-95-8; 1-decanol, 112-30-1; 1-hexene, 592-41-6; 1-heptene, 592-76-7.

Synthesis of 1-Acyl-1,4-dihydropyridines via Copper Hydride Reduction of 1-Acylpyridinium Salts

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For many years there has been considerable interest in the synthesis, synthetic utility, and biological activity of various dihydropyridines.[1] The discovery that a 1-acyl substituent stabilizes[2,3] the dihydropyridine system has encouraged the study and use of 1-acyldihydropyridines as synthetic intermediates. Although 1-(alkoxycarbonyl)-1,2-dihydropyridines can be prepared by a regioselective sodium borohydride reduction of 1-(alkoxycarbonyl)pyridinium salts,[3] a regioselective reduction to give 1-acyl-1,4-dihydropyridines has not been reported.

Alkyl Grignard reagents add to 1-acylpyridinium salts to give a mixture of 1,2- and 1,4-dihydropyridines;[4a,5] however, when a catalytic amount of cuprous iodide is present, the addition is regiospecific and nearly exclusive 1,4-addition results.[4] Stoichiometric organocopper reagents (e.g., R_2CuLi, RCu, $RCu{\cdot}BF_3$) also give 1,4-addition.[6] On the basis of these results, it appeared that an analogous 1,4-addition of hydride to 1-acylpyridinium salts might occur with copper hydride reagents and effect a regiospecific one-pot synthesis of 1-acyl-1,4-dihydropyridines.

We report herein our study on the reduction of 1-(phenoxycarbonyl)pyridinium chloride with copper(I) borohydride and copper hydride reagents, which led to the development of a convenient method for the regiospecific synthesis of 1-acyl-1,4-dihydropyridines. The regioselectivity of the reduction of 1-(phenoxycarbonyl)pyridinium chloride[7] with various hydride reagents is shown in Table

(1) For reviews on dihydropyridines, see: (a) Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223. (b) Kutney, J. P. *Heterocycles* **1977**, *7*, 593. (c) Lyle, R. E. "Pyridine and its Derivatives"; Abramovitch, R. A., Ed.; Wiley-Interscience: New York, 1974; Vol. 14, Part 1, p 137. (d) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1.

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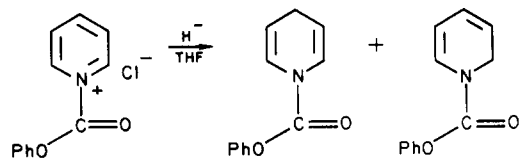
(7) Sodium borohydride reduction of 1-(phenoxycarbonyl)pyridinium chloride in ethanol at -78 °C gives 1-(phenoxycarbonyl)-1,2-dihydropyridine in 51% yield. Sundberg, R. J.; Bloom, J. D. *J. Org. Chem.* **1981**, *46*, 4836.

0022-3263/84/1949-3392$01.50/0

Table I



1 2

entry	hydride reagent[a]	product ratio[b] 1	2
a	$NaBH_4$[3]	60	40
b	$NaCNBH_3$	60	40
c	$(Ph_3P)_2CuBH_4$[10]	70	30
d	$(Ph_2MeP)_3CuBH_4$[11]	70	30
e	Semmelhack's "$NaCuH_2$"[8]	70	30
f	Semmelhack's "$LiCuH_2$"[8]	79	21
g	Comins' copper hydride[c]	100	0

[a] Reactions were performed on a 2-mmol scale by using hydride reagents (1 molar equiv for entries a–d and 2 molar equiv for entries e–f) which were purchased or prepared according to literature procedures. [b] The ratio was determined by GC analysis of the crude products. The crude yields were 50–75%. [c] Excess reagent was used; see Experimental Section.

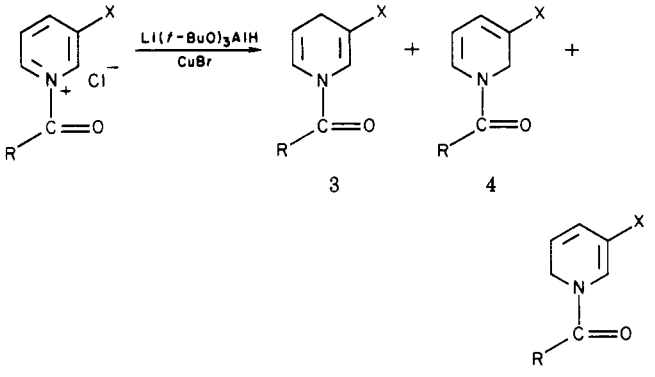
I. The borohydride reductions (entries a–d) were not very regioselective. We next investigated the reduction using Semmelhack's hydrido copper reagents, which have been reported to reduce the olefin unit in conjugated ketones and esters.[8] Both the "Na complex" and "Li complex", entries e and f, failed to give the desired regiospecific 1,4-reduction, and a mixture of 1,4- and 1,2-dihydropyridines 1 and 2 resulted. The desired regiospecificity was finally obtained by using a hydrido copper reagent prepared from lithium tri-*tert*-butoxyaluminum hydride (3 equiv) and cuprous bromide (4.4 equiv.)[9] Although the yields are only moderate, the reduction is completely regiospecific in most cases and is amenable to the synthesis of 1-acyl-1,4-dihydropyridines with either an alkoxycarbonyl or alkylcarbonyl N-substituent (see Table II).

This convenient, one-pot preparation of 1-(alkoxycarbonyl)-1,4-dihydropyridines complements the two-step procedure developed by Fowler.[3,12] The synthesis of 1-(alkylcarbonyl)-1,4-dihydropyridines via our method is significant since Fowler's reaction ($NaBH_4$, pyridine, THF, ROC(O)Cl)[3] fails with acid chlorides.

Experimental Section

Reactions were performed in oven-dried glassware under an N_2 atmosphere. Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl prior to use. Cuprous bromide (98%) was obtained from Aldrich Chemical Co. and used without further purification. Lithium tri-*tert*-butoxyaluminum hydride (90% min) was purchased from Alfa Products as a white powder. Other solvents and reagents from commercial sources were generally used without further purification.

Table II



3 4 5

X[a]	RC(O)Cl	yield,[b] %	product ratio[c] 3	4	5
H	phenyl chloroformate	65	100	0	
H	benzyl chloroformate	35	100	0	
H	ethyl chloroformate	20	100	0	
H	acetyl chloride	36	100	0	
H	*n*-butyryl chloride	32	100	0	
Me	phenyl chloroformate	52	98.2	0.9	0.9
Et	phenyl chloroformate	40	98.5	<1.5[d]	<1.5[d]
Cl	phenylchloroformate	40	100	0	0
COOMe	phenyl chloroformate	45	>90[e]		

[a] The reactions were performed on a 2-mmol scale in THF. [b] Yield of purified product obtained from radial preparative layer chromatography (silica gel, EtOAc/hexanes). The products, mainly oils, were >90% pure by GC analysis. All products gave the expected IR and ^1H NMR spectra.[3] Due to their instability at room temperature, the products were not submitted for elemental analysis. [c] Ratio determined by GC. [d] The exact ratio of 4/5 could not be determined. [e] Ratio estimated by ^1H NMR.

^1H NMR spectra were recorded on a Varian EM-360 spectrometer. Gas–liquid chromatography (GC) was performed with a Hewlett-Packard Model 5830 A gas chromatograph equipped with a 30 m × 0.25 mm FSOT column coated with OV-17.

General Procedure for the 1,4-Reduction of 1-Acylpyridinium Salts. Synthesis of 1-(Phenoxycarbonyl)-1,4-dihydropyridine. A solution of lithium tri-*tert*-butoxyaluminum hydride (1.52 g, 6.0 mmol) in 15 mL of THF was cooled in an ice bath (0–5 °C). Cuprous bromide (1.26 g, 8.8 mmol) was added in one portion and the mixture was stirred with cooling (0–5 °C) for 30 min. The resulting brown-black suspension was cooled to −23 °C. Pyridine (0.24 mL, 3.0 mmol) was added via syringe followed by the dropwise addition of phenyl chloroformate (0.25 mL, 2.0 mmol). The mixture was stirred rapidly at −23 °C for 1.5 h; then 20 mL of aqueous 20% NH_4Cl was added. The mixture was filtered through Celite and the filtrate was extracted with ether. The combined organic layer was washed with 20-mL portions of water and brine. After being dried (K_2CO_3), the solution was concentrated to give the crude product as an oil. Purification by radial preparative layer chromatography (silica gel, EtOAc–hexanes) gave 260 mg (65%) of 1-(phenoxycarbonyl)-1,4-dihydropyridine as an oil which crystallized on standing (white crystals): mp 71–72 °C (hexane); ^1H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 6.9 (d, 2 H), 5.0 (m, 2 H), 2.9 (m, 2 H); IR (KBr) 1720, 1640, 1485 cm^{-1}.

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Registry No. 1, 90838-83-8; 2, 79328-86-2; 3 (X = H; R = $PhCH_2O$), 54732-54-6; 3 (X = H; R = EtO), 40339-63-7; 3 (X = H; R = Me), 67402-83-9; 3 (X = H; R = Pr), 90838-84-9; 3 (X = Me; R = PhO), 90838-85-0; 3 (X = Et; R = PhO), 90838-86-1; 3 (X = Cl; R = PhO), 90838-87-2; 3 (X = CO_2Me; R = PhO), 90838-88-3; PhOC(O)Cl, 1885-14-9; $PhCH_2OC(O)Cl$, 501-53-1; EtOC(O)Cl, 541-41-3; $CH_3C(O)Cl$, 75-36-5; $CH_3(CH_2)_2C(O)Cl$,

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(12) A three-step synthesis of 1-carbomethoxy-1,4-dihydropyridine from piperidine has been reported. Shono, T.; Matsumura, Y.; Tsubata, K.; Sugihara, Y.; Yamane, S.; Kanazawa, T.; Aoki, T. *J. Am. Chem. Soc.* **1982**, *104*, 6697.

141-75-3; Li(t-BuO)$_3$AlH, 17476-04-9; CuBr, 7787-70-4; NaCNBH$_3$, 25895-60-7; $(Ph_3P)_2CuBH_4$, 34010-85-0; $(Ph_2MeP)_3CuBH_4$, 63371-86-8; $NaCuH_2$, 90838-89-4; $LiCuH_2$, 53201-99-3; $NaBH_4$, 16940-66-2; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 3-ethylpyridine, 536-78-7; 3-chloropyridine, 626-60-8; methyl 3-pyridinecarboxylate, 93-60-7.

Absolute Configuration of Optically Active Propargyl Alcohols: A Circular Dichroism Approach

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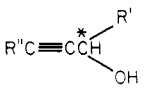
Optically active α-acetylenic alcohols are useful intermediates in the synthesis of natural products as alkaloids, pherormones, prostaglandines, steroids, and vitamins.[1] However, in spite of their importance in organic synthesis, only the empirical method of Mori and Akao[2] for determining their absolute configuration has been proposed so far. Recently, the comparison of the experimental values of the circular dichroism (CD), allied to electrically allowed transitions, with those of the CD calculations by means of the De Voe model[3] has permitted nonempirical configurational determinations of simple organic molecules where a chromophore is perturbed by alkyl groups only.[4] Unfortunately, in the case of simple α-acetylenic alcohols, the absence of an electrically allowed transition in the spectral range accessible to the commercial CD instruments ($\lambda > 185$ nm) prevents an immediate application of the above method, on the basis of the De Voe calculations. This difficulty can be overcome by means of the use of the benzoates of propargyl alcohols, which, having an intense transition band at 230 nm ($\epsilon \simeq 14000$)[5] well separated from other absorptions, can provide the systems suitable for the De Voe calculations.

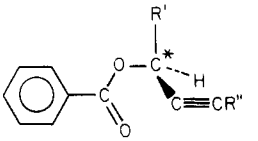
A quantitative evaluation of the benzoate CD absorptions will be carried out, taking into account the chiral perturbation on the above transition due to the acetylenic and the alkyl groups.

A series of α-acetylenic carbinols, having general formula I, has been obtained by enantioselective reduction of the corresponding ketones with optically active organoaluminum compounds.[6] Their enantiomeric purity has been determined by analysis of the ^{19}F NMR spectra of



Ia, R′ = Me; R″ = *n*-Bu
Ib, R′ = Et; R″ = *n*-Bu
Ic, R′ = *i*-Pr; R″ = *n*-Bu
Id, R′ = *t*-Bu; R″ = *n*-Bu
Ie, R′ = *t*-Bu; R″ = H
If, R′ = *t*-Bu; R″ = Br

the corresponding MPTA esters. The alcohols have been then converted into the corresponding benzoates: they all show around 230 nm a positive Cotton effect having $\Delta\epsilon$ from +1 to +3 (Table I). The conformational analysis, taking into account only the steric hindrance of the groups surrounding the chiral carbon atom shows that the same preferred conformer should be dominant in solution for all the compounds examined. In fact, three limit conformers can exist for the alcohols Ia–f, as reported in Chart I, assuming a *S* absolute configuration. Inspection of molecular models suggests that the conformer II, in which the largest groups (i.e., the benzoate and R′) are in an "antiperiplanar" position, should be the most populated one, since the steric interactions between the benzoate and R′, particularly when R′ is the bulky *t*-Bu group, make conformers III and IV less stable.[7] Therefore the conformation II, depicted below to show the overall molecular structure, was chosen to carry out the CD calculations.



De Voe calculations of the CD of electrically allowed transitions in simple organic molecules have been described in detail elsewhere:[4] in this model each allowed electronic transition is represented in terms of experimental data such as polarization direction of absorption bands and ultraviolet spectra of suitable model compounds. In the present case (i) the triple-bond chromophore is described by only the allowed $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$ transition, polarized along the C≡C axis. Only a few data are known on the far uv spectra of internal and terminal acetylenes (models of compounds Ia–d and Ie, respectively); however, it is generally accepted[8] that the above transition is allied to the band having the maximum around 170 nm, with $\epsilon \simeq 10000$. As far as the 1-bromo-1-alkynylcarbinol, If, is concerned, this allowed transition has been placed at about 185 nm.[9] (ii) The benzoate chromophore is represented by only its allowed 230-nm transition ($\epsilon \simeq 14000$), polarized along the long axis and then approximately parallel to the alcoholic C*–O bond.[5] (iii) The methyl and *tert* butyl groups are described by a set of three mutually perpendicular oscillators: each of them is attributed with a fixed fraction of the UV spectrum of methane and 2-methylpropane, respectively, as previously reported in detail.[4] Unfortunately, since only for these groups a satisfactory description has been provided so far, De Voe calculations have been actually carried out only for the compounds having these substituents. The results of the calculations executed for II with the above-mentioned parametrization are reported in Table I. The present calculations can reproduce the sign and a large part of the intensity of the experimental CD values, indicating that

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