mixture of **14**, $n$ = 4 and 5) showed ester $OCH_3$ signals at $\delta$ 3.68, 3.87, and 3.92 ppm; and tertiary H at $\delta$ 4.72 (s, 7.2% relative to the $OCH_3$ signals; calcd 8.3% for tetramer **14a** and 6.3% for pentamer **14a**).

**Oxidative Oligomerization of Cyanamide 5d.**—To a solution of 4.56 g (20 mmol) of cyanamide **5d** (mp 128.9–130.1°) in 120 ml of acetone there was added 3.6 g of $KMnO_4$ followed by 40 ml of concentrated ammonia. After stirring for 1 hr the mixture was acidified with 4 $N$ hydrochloric acid and the $MnO_2$ was dissolved by the addition of $Na_2S_2O_3$. Chloroform extraction gave 4.2 g of a noncrystallizable foam, the gpc and nmr analysis of which corresponds with **14d** ($n$ = 6–8).

Oxidation of **5d** in $CHCl_3$ at 20° with $O_2$ and $Cu_2Cl_2$–TMEDA as a catalyst and $MgSO_4$ as anhydrant gave an oxygen uptake of 0.5 mol/mol of **5d** in 45 min. The oxygen uptake time curve did not show a discontinuity at the oxygen amount required for oxidative C–C coupling (0.25 mol of $O_2$/mol of **5d**). A similar mixture of oligomers **14d** was obtained in 93% yield: gpc (oxidized with $KMnO_4$) found $\overline{M}_n$ = 1500 $\overline{M}_w$ = 2100 $\overline{M}_v$ = 2000; nmr ($CDCl_3$) ratio of aromatic protons/$CH_2$ protons, found 0.41 [calcd 0.50 for monomer and C–C dimer, 0.433 for the trimer, 0.413 for the hexamer, and 0.400 for the polymer (based on structure **14d**)].

**Registry No.**—**1a**, 30698-30-7; **1b**, 30698-31-8; **1c**, 30758-60-2; **1d**, 30698-32-9; **1e**, 30698-33-0; **2a′**, 30698-34-1; *meso*-**2a**, 30698-35-2; *dl*-**2a**, 30698-36-3; *meso*-**2b**, 30698-37-4; *dl*-**2b**, 30698-38-5; *meso*-**2c**, 30698-39-6; *dl*-**2c**, 30698-40-9; *meso*-**2d**, 30698-41-0; *dl*-**2d**, 30698-42-1; *meso*-**2e**, 30698-43-2; *dl*-**2e**, 30698-44-3; **3a**, 4468-48-8; **3b**, 27243-91-0; **3c**, 5415-07-6; *meso*-**4a**, 30698-48-7; *dl*-**4a**, 30698-49-8; *meso*-**4b**, 30698-50-1; *dl*-**4b**, 30698-51-2; **5a**, 30698-52-3; **5b**, 30698-53-4; **5c**, 30698-54-5; **5d**, 1440-29-5; **6a**, 30758-62-4; **6b**, 30698-55-6; **6c**, 30698-56-7; *meso*-**7**, 30698-57-8; *dl*-**7**, 30698-58-9; **8**, 30698-59-0; **9**, 30698-60-3; **14a** ($n$ = 4), 30698-61-4; **14a** ($n$ = 5), 30698-62-5; **15a** ($a$ = 1; $b$ = 0), 30698-63-6; $[Cu(OH)(TMEDA)]_2Cl_2$, 30698-64-7; DPPH monomer, 30698-65-8.

**Acknowledgment.**—The authors are greatly indebted to Drs. A. J. Leusink, W. Drenth, and G. J. M. van der Kerk of the Organisch Chemisch Instituut TNO, Utrecht, and W. G. B. Huysmans of AKZO Research, Arnhem, for many stimulating discussions. Special thanks are due to Dr. W. G. B. Huysmans for his valuable nmr contributions, to Dr. S. van der Werf for the mass spectrometry, and to Mr. D. J. Goedhart for his gpc work.

# Asymmetric Reductions. XIV. Reductions of Phenyl Trimethylsilyl Ketone and Phenyl Triphenylsilyl Ketone and Configurational Studies on the Corresponding Carbinols[1]

MICHAEL S. BIERNBAUM[2] AND HARRY S. MOSHER*

*Department of Chemistry, Stanford University, Stanford, California 94305*

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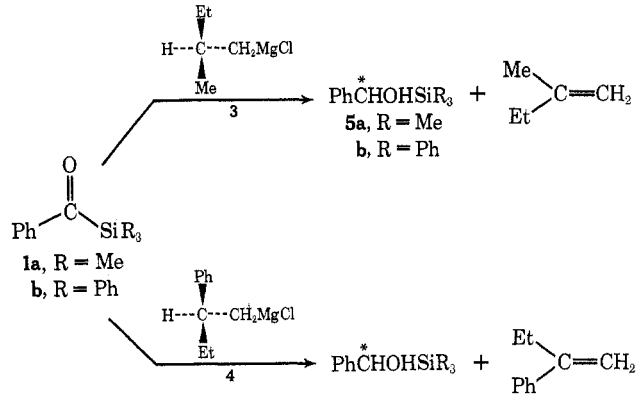
The asymmetric reduction of phenyl trimethylsilyl ketone (**1a**) and phenyl triphenylsilyl ketone (**1b**), by the Grignard reagent **3** from (*S*)-(+)-1-chloro-2-methylbutane, gave the corresponding (*R*)-phenylsilylcarbinols **5a** and **5b** in 3.1 and 10.6% enantiomeric excess (% ee), respectively. Reduction of the same two silyl ketones by the Grignard reagent **4** from (*S*)-(+)-1-chloro-2-phenylbutane gave the corresponding *S* carbinols in 33 and 13.7% ee, respectively. These results are rationalized in terms of steric and electronic interactions in competing six-membered transition states for the hydrogen transfer step and are compared with the results from the reduction by the same chiral reagents of the corresponding carbon ketones. The configurational assignments of these silyl carbinols are consistent with the results from the asymmetric reductions, with the ORD and CD spectra, with application of the Freudenberg rule of shifts to the benzoate and *p*-bromobenzoate derivatives but were not in accord with Horeau's kinetic resolution method.

We sought to extend our studies on asymmetric reductions[3] to include more groups which possessed $C_{3v}$ symmetry. This has led to an investigation of the asymmetric reduction of phenyl trimethylsilyl ketone[4a] (**1a**) and phenyl triphenylsilyl ketone[4b] (**1b**). The corresponding carbon compound phenyl *tert*-butyl ketone (**2a**) had been investigated previously but phenyl trityl ketone[3,5] (**2b**) had not and is included in the present study.

Since $\alpha$-silyl ketones are readily reduced by Grignard reagents with the requisite $\beta$ hydrogen, by virtue of their exceptionally polar carbonyl function,[4a,6] they are well suited to such a study. These two silyl ketones **1a** and **1b** were each reduced by the chiral Grignard reagents **3** and **4** from (*S*)-(+)-1-chloro-2-methylbutane and (*S*)-(+)-1-chloro-2-phenylbutane, respectively.




(1) We acknowledge with gratitude support of these studies by the National Science Foundation, NSF GP 9432.

(2) From the Ph.D. thesis of M. S. Biernbaum, Stanford University, Aug 1970.

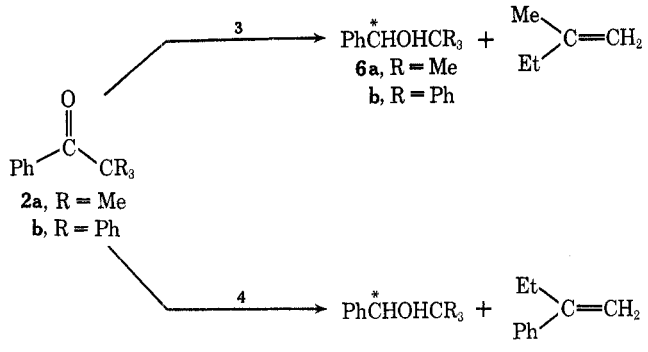
(3) (a) D. M. Feigl and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968); see references cited therein for prior publications. (b) A preliminary publication of some of the same material in this present paper has appeared: M. Biernbaum and H. S. Mosher, *Tetrahedron Lett.*, 5789 (1968).

(4) (a) A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz, and C. M. Warner, *J. Amer. Chem. Soc.*, **82**, 5102 (1960); (b) A. G. Brook, *ibid.*, **79**, 4373 (1957).

(5) R. C. Fuson and P. E. Wiegert, *ibid.*, **77**, 1138 (1955).

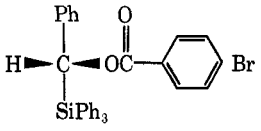
(6) H. Bock, H. Alt, and H. Seidl, *ibid.*, **91**, 355 (1969), and references cited therein.

Information concerning the different stereochemical and/or electronic requirements of $SiMe_3$ *vs.* $CMe_3$ and $SiPh_3$ *vs.* $CPh_3$ in the transition state should be revealed by a comparison with the stereoselectivities observed in the corresponding reductions of the carbon analogs phenyl *tert*-butyl ketone (**2a**) and phenyl trityl ketone (**2b**).



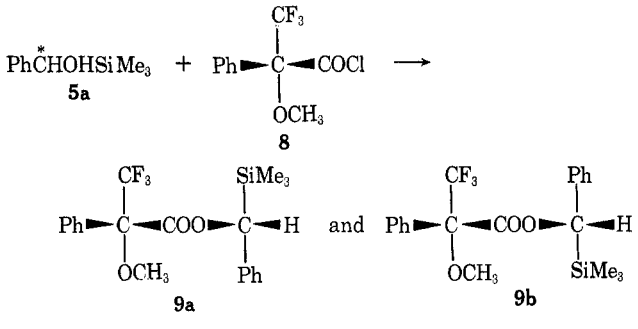

**Configurations.**—Prior to these studies the configurations, either absolute or relative, of the α-silylcarbinol products **5a** and **5b** were unknown, whereas the configuration of phenyl-*tert*-butylcarbinol is known with absolute certainty[7,8] and that of phenyltritylcarbinol with a high degree of certainty.[9] If empirical correlations could be established for **5a** *vs.* **6a** and **5b** *vs.* **6b**, using standard methods for assigning relative configurations, it might then be possible to determine the configurations of the silylcarbinols. The results reported in our preliminary communication[3b] indicated that (+)-**5b** and (+)-**6b** were of opposite configuration based upon Fredga's quasiracemate method[10] or on the atrolactic acid asymmetric synthesis method (Prelog[9]) while the D-line rotations of selected derivatives (Freudenberg's displacement rule[11]) indicated that (+)-**5b** and (+)-**6b** were of the same configuration. ORD studies and reductions by chiral Grignard reagents were inconclusive. Extension of these studies to include a kinetic resolution based on the method of Horeau[12] did not resolve the situation. Direct chemical correlation by synthesis of either **5a** or **5b** from compounds of known configuration appears at this time to be impossible since the silicon is bound to the asymmetric carbon center.[13]

Although CD studies have now clarified the situation, it became necessary to have an absolute configurational determination by X-ray diffraction analysis of a suitable derivative for the crucial stereochemical correlations in this series. Professor H. Hope has now completed an X-ray diffraction study on crystals of the (−)-*p*-bromobenzoate ester from (+)-phenyltriphenylsilylcarbinol and has established the *R* configuration[14] for this substance as shown in **7**. The following discussion of the asymmetric Grignard reductions and configurational correlations are therefore firmly anchored to the X-ray-determined absolute configuration of *R*-(−)-**7** prepared from *R*-(+)-**5b**.




*R*-(−)-**7** [from *R*-(+)-**5b**]

**Enantiomeric Purities of 5a and 5b.**—The maximum rotation of **5a** was determined from partially active carbinol by application of the nmr method[15] utilizing the ester prepared from enantiomerically pure α-methoxy-α-trifluoromethylphenylacetyl chloride [**8**, MTPA-Cl].[16] The 60-MHz nmr spectrum of the mixture of diastereomers **9a** and **9b**, prepared by treating carbinol **5a** ($[\alpha]^{25}D$ −30.99 ± 0.16°, neat) with enantiomerically pure (−)-**8**, gave signals for the respective benzylic protons at 358 and 350 Hz downfield from the trimethylsilyl signal, whose areas were in the ratio of 56:28. This represents a 33.3% excess of the (−) enantiomer and corresponds to a calculated maximum rotation of $[\alpha]^{25}D$ −93 ± 1.5° (neat).




The resolution of **5b** *via* the brucine salt of its acid phthalate yielded (+)-**5b** with $[\alpha]^{22}D$ +49.5 ± 1.1° (*c* 1.775, $CHCl_3$) and (−)-**5b** with $[\alpha]^{21}D$ −48.6 ± 1.1° (*c* 1.915, $CHCl_3$).

**Stereochemical Interpretations.**—Models for the preferred transition states for the asymmetric reductions of the trimethylsilyl and *tert*-butyl ketones **1a** and **2a** by the Grignard reagents **3** and **4** are shown in Scheme I. Those for the reductions of the triphenylsilyl and trityl ketones (**1b** and **2b**) are shown in Scheme II. The carbinols which would be formed from these preferred transition state models are also shown along with the experimentally determined sign and appropriate configurational designation.

The key to the stereochemical interpretation of the results summarized in Scheme I is the reaction of **1a** + **4**, which showed the highest stereoselectivity in this series, namely, 33%. Those Grignard reductions involving two phenyl groups show a decided preference for the phenyl groups to assume positions remote from each other in the preferred transition state as illustrated in [**1a** + **4**]. This is an effect which may be due to

(7) O. Červinka and L. Hub, *Z. Chem.*, **9**, 267 (1969).

(8) D. R. Clark and H. S. Mosher, *J. Org. Chem.*, **35**, 1114 (1970).

(9) V. Prelog, E. Philbin, E. Watanabe, and M. Wilhelm, *Helv. Chim. Acta*, **39**, 1086 (1956).

(10) A. Fredga, "The Svedberg Memorial Volume," A. Tiselius and K. O. Pederson, Ed., Almquist and Wiksells, Uppsala, Sweden, 1944, pp 261–273.

(11) K. Freudenberg, "Stereochemie," Franz Deuticke, Lepizig and Vienna, 1933, p 677.

(12) A. Horeau and H. B. Kagan, *Tetrahedron*, **20**, 2432 (1964).

(13) (a) An attempt to apply Cram's rule to the reaction of a silyl ketone which was chiral at silicon, thereby inducing asymmetry at the carbon, has been described [A. B. Brook, C. M. Warner, and W. W. Limburg, *Can. J. Chem.*, **45**, 1231 (1967)]. (b) This is discussed in the companion paper (M. S. Biernbaum and H. S. Mosher, *J. Amer. Chem. Soc.*, in press).

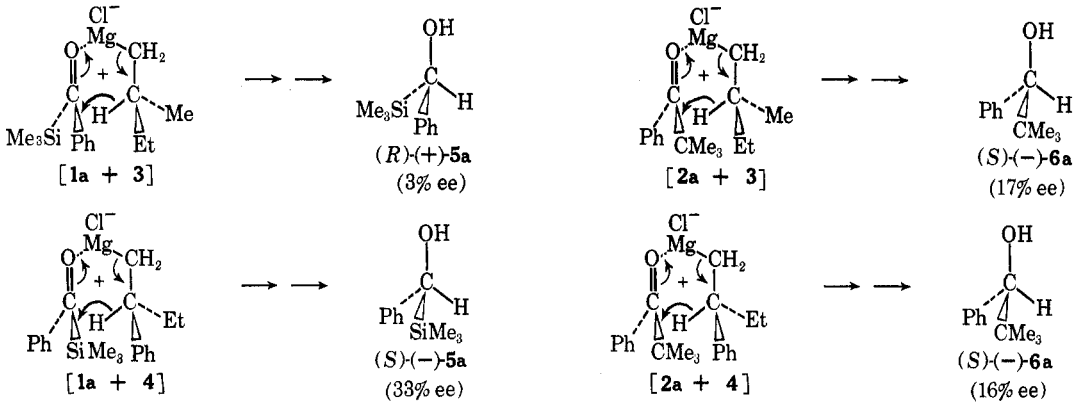
(14) We are greatly indebted to Professor H. Hope at the University of California, Davis, for this valuable cooperation. The details and interpretation of this X-ray study on (−)-phenyltriphenylsilylcarbinyl *p*-bromobenzoate crystals (orthorhombic, space group $P2_12_12_1$, one molecule per asymmetric unit cell) have been published. K. T. Black and H. Hope, *ibid.*, **93**, 3054 (1971).

(15) M. Raban and K. Mislow, *Top. Stereochem.*, **2**, 199 (1967).

(16) Both the reagent and method involved have been described in detail by J. A. Dale, D. L. Dull, and H. S. Mosher, *J. Org. Chem.*, **34**, 2543 (1969).

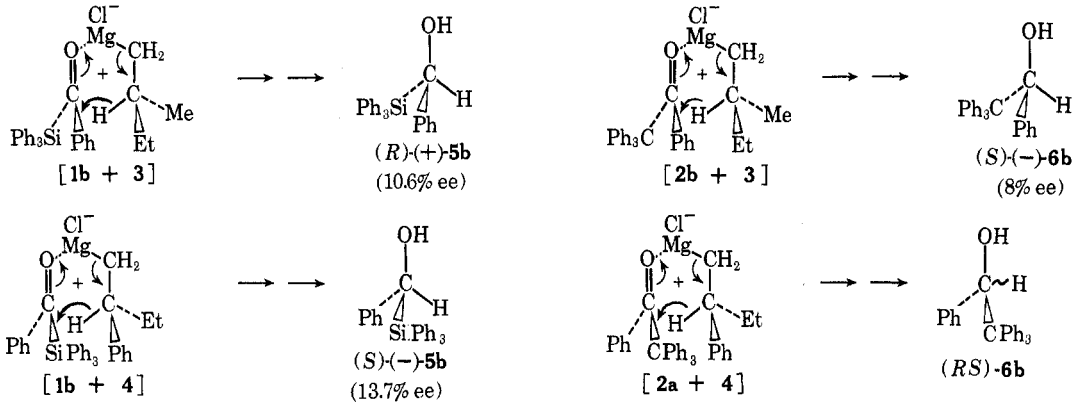
SCHEME I

MODELS FOR PREFERRED TRANSITION STATES AND CONFIGURATIONS OF THE PREDOMINANT PRODUCTS FROM THE REDUCTIONS OF PHENYL TRIMETHYLSILYL KETONE (**1a**) AND PHENYL *tert*-BUTYL KETONE (**2a**) BY THE GRIGNARD REAGENTS **3** AND **4**. THE MODELS FOR THE NONPREFERRED TRANSITION STATES, IN WHICH THE KETONE SUBSTITUENTS ARE INTERCHANGED, ARE NOT SHOWN




SCHEME II

MODELS FOR PREFERRED TRANSITION STATES AND CONFIGURATIONS OF THE PREDOMINANT PRODUCTS FROM THE REDUCTIONS OF PHENYL TRIPHENYLSILYL KETONE (**1b**) AND PHENYL TRITYL KETONE (**2b**) BY GRIGNARD REAGENTS **3** AND **4**. THE DIASTEREOMERIC NONPREFERRED TRANSITION STATE MODELS, IN WHICH THE KETONE SUBSTITUENTS ARE INTERCHANGED, ARE NOT SHOWN




mutual repulsion of the electron-rich $\pi$ clouds of the phenyl rings.[17] If [**1a** + **4**] is a model for the preferred transition state for this reaction, using the Grignard reagent from (*S*)-(+)-chloride, then the levorotatory product **5a** must have the *S* configuration as shown. The dextrorotatory product from the reaction **1a** + **3** must therefore have the *R* configuration. In this case the extent of asymmetric reduction is very low and the presumption is that, in the competing transition states involving $SiMe_3$ *vs.* Me or Et as compared to those involving interactions of Ph *vs.* Me or Et, the steric requirement of $SiMe_3$ slightly outweighs that of phenyl as shown in the preferred transition state [**1a** + **3**]. This interpretation is in accord with the *S* configuration now assigned to (−)-phenyltrimethylsilylcarbinol based both on the CD study (*vide infra*, Figure 3) and on the stereoselective base-catalyzed rearrangement of (−)-phenyltrimethylsilylcarbinol-O-*d* to (*R*)-benzyl-$\alpha$-*d* trimethylsilyl ether.[13b]

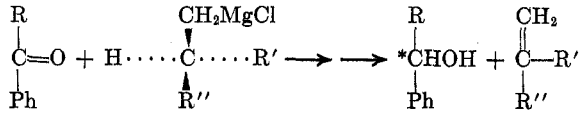
The key to the stereochemistry of the asymmetric reductions of the triphenylsilyl and trityl ketones summarized in Scheme II is the reaction of **1b** + **3**. The configuration of the dextrorotatory product is known[14] to be *R* and the model for the preferred transition state must therefore be [**1b** + **3**] when the Grignard reagent from (*S*)-(+)-1-chloro-2-methylbutane is used. In this transition state model the larger ketone substituent, the $Ph_3Si$ group, is in juxtaposition to the smaller methyl group of the Grignard reagent, and the smaller ketone substituent, phenyl, is in juxtaposition to the larger ethyl group of the Grignard reagent. This is in accord with the stereochemistry one would have predicted if the configuration of the product had not been known.[18] Again the known configuration of product (*S*)-(−)-**5b** requires that the model for the preferred transition state for the reaction of **1b** + **4** be written as shown in [**1b** + **4**] with the phenyl group of the ketone situated remote from the phenyl group of the Grignard reagent. The rationalization for such a preferred transition state is that the repulsions of phenyl for phenyl, in the nonpreferred transition state in which the Ph and $Ph_3Si$ groups of ketone in [**1b** + **4**] are inter-

(17) J. S. Birtwistle, K. Lee, J. D. Morrison, W. A. Sanderson, and H. S. Mosher, *J. Org. Chem.*, **29**, 37 (1964).

(18) We must in all candor state that *if the results had emerged to the contrary* we were prepared to rationalize them by arguing that, although $Ph_3Si$ is obviously a larger group than Ph alone, the C–Si bond (1.86 Å) is longer than the corresponding C–C bond (1.47 Å), thereby in effect reducing the steric hindrance of the $Ph_3Si$ group with respect to reactions in which the transition state is relatively close to the carbonyl carbon along the reaction coordinate. With respect to the system under study, this hypothesis can now be disregarded.

TABLE I

ASYMMETRIC GRIGNARD REDUCTIONS OF SILYL AND ANALOGOUS CARBON KETONES



1 or 2 3 or 4 5 or 6

| Ketone No. | Ketone R | Grignard (3, R′ = Me,[a] R″ = Et; 4, R′ = Et,[b] R″ = Ph) | Carbinol product: Yield, % | Optical rotation[c]: Observed $\alpha_D$, deg (l., c, °C) | Specific $[\alpha]_D$, deg | Maximum $[\alpha]_D$, deg (c, °C) | Enantiomer excess: % ee | Confign |
|---|---|---|---|---|---|---|---|---|
| 1a | $Me_3Si$ | 3 | 85[d] | +1.42 (0.5, neat, 25) | +2.94 ± 0.04 (neat)[e] | 93[d] (neat, 25)[e] | 3 | R |
| | | 4 | 83[d] | −14.43 (0.5, neat, 24) | −30.71 ± 0.04 (neat)[e] | | 33 | S |
| 2a | $Me_3C$ | 3 | 90[f] | −0.75[f] (2, 9.04, 20) | −4.63[f] (benzene) | 27.3[f,g] (9, 20) | 17[f] | S |
| | | 4 | 77[h] | −1.05[h] (2, ether, 27) | −5.72[h] (ether) | 36.2[h] (9, 20) | 16[h] | S |
| 1b | $Ph_3Si$ | 3 | 96 | +1.06 (1, 20, 26) | +5.25 ± 0.10 | 49.5 ± 1.1[d] (1.8, 25) | 10.6 | R |
| | | 4 | 24[d] | −1.48 (1, 22.4, 23) | −6.79 ± 0.09 | | 13.7 | S |
| 2b | $Ph_3C$ | 3 | 95 | −0.20 (1, 5.8, 24) | −3.45 ± 0.45 | 42.8 ± 0.4[i] (5.1, 25) | 8 | S |
| | | 4 | 7.5[d] | +0.02 (0.5, 5.16, 23) | +0.08 ± 0.08 | | (0.2) | (S) |

[a] Grignard reagent prepared from (S)-(+)-1-chloro-2-methylbutane, enantiomerically pure. [b] Grignard reagent prepared from (S)-(+)-1-chloro-2-phenylbutane, 97.3% enantiomerically pure. [c] Rotations taken in $CHCl_3$ unless designated "neat." Readings taken to ±0.02° or better. Specific rotations given for the same conditions as observed rotations, and in reductions of 4 the specific rotation has been corrected for the enantiomeric purity (97.3% ee) of the chloride. [d] See Experimental Section. [e] $d^{20}_4$ 0.966. [f] Taken from ref 19. [g] Corresponds to $[\alpha]^{20}_D$ 36.2° (c 9, ether). [h] Taken from ref 17; the chloride was 97.7% enantiomerically pure. [i] Corresponds to $[\alpha]^{25}_D$ 62.4° (c 5.19, EtOH).

changed, override the adverse effect of having the larger group of the Grignard reagent, namely phenyl, opposing the larger group from the ketone, namely triphenylsilyl, as represented in the preferred transition state [**1b** + **4**]. The stereoselectivity has decreased from the 33% observed in **1a** + **4** to 13.7% in **1b** + **4**, presumably because of this added adverse steric effect.[17]

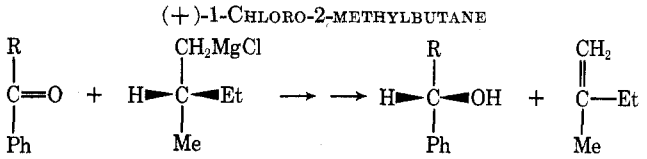
**Comparison of Stereoselectivities Observed for Corresponding Silicon and Carbon Ketones.**—The first and third rows in Table I summarize the data on the relative stereoselectivities for reduction of phenyl trimethylsily ketone (**1a**) and phenyl *tert*-butyl ketone (**2a**) by the Grignard reagent **3** from (+)-1-chloro-2-methylbutane to give (*R*)-phenyltrimethylsilylcarbinol (**5a**, 3% ee) and (*S*)-*tert*-butylphenylcarbinol (**6a**, 17% ee). The stereochemical results are compared in the top four formulas of Scheme I. It is apparent that substitution of silicon for carbon in this pair of reactions has resulted in reduced stereoselectivity and reversal of configuration in the predominant product. It is instructive to consider the asymmetric reduction of the complete series of substituted phenyl ketones[19] by this aliphatic Grignard reagent **3** as shown in Table II.

These substituents have been arranged in a series which is intended to represent their increasing steric bulk as measured by their steric requirements in this reaction. Within this series the stereoselectivities rise to a maximum of 24% at isopropyl, decrease to a minimum of 3% with trimethylsilyl, and then start to increase again. The configurations of the carbinols of the last three examples (bracketed numbers) are opposite to that shown in the equation; the interpretation is that, although *tert*-butyl is effectively smaller than phenyl, trimethylsilyl exerts a slightly greater effective bulk than phenyl, thereby bringing about a reversal in the stereochemistry of the predominant product. In the degenerate case where R = Ph (reduction of benzophenone) both groups attached to the

(19) R. MacLeod, F. J. Welch, and H. S. Mosher, *J. Amer. Chem. Soc.*, **82**, 876 (1960).

TABLE II

PER CENT ASYMMETRIC REDUCTION[a] OF PHENYL KETONES BY THE GRIGNARD REAGENT FROM (+)-1-CHLORO-2-METHYLBUTANE



| R = | Me | Et | *i*-Pr | *tert*-Bu | $Me_3Si$ | $Ph_3C$ | $Ph_3Si$ |
|---|---|---|---|---|---|---|---|
| % ee[b] | 4 | 6 | 24 | 17 | [3] | [8] | [11] |

[a] The data from the first four examples are from ref 19. Numbers in brackets from the present study represent products with absolute configuration opposite to that shown in the equation. [b] % ee is per cent enantiomer excess over racemate.

carbonyl carbon are identical and have exactly the same steric requirement. This would result in the formation of benzhydrol and can be considered "zero per cent" asymmetric synthesis. Thus in this series phenyl can be located between *tert*-butyl and trimethylsilyl in its steric requirements.

We do not in general, however, have a wholly satisfactory interpretation of the quantitative aspects of these asymmetric reductions. Note that, in the case of reductions by Grignard reagent **3**, the stereoselectivity for the reaction of silyl ketone **1a** (3%) is much less than that for the carbon analog **2a** (17%) while the stereoselectivity in the corresponding reduction of silyl ketone **1b** (10.6%) is roughly the same as that for the carbon analog **2b** (8%). The situation is very different when Grignard reagent **4** is used: the stereoselectivity observed in the reduction of silyl ketone **1a** (33%) is considerably higher than that for the analogous carbon ketone **2a** (16%), and for silyl ketone **1b** the stereoselectivity changes from 13.7% for the trimethylsilyl ketone to essentially zero for the carbon analog.

Several factors which complicate the evaluation of these stereoselectivities should be considered. One such factor is the greater distance between the carbonyl group and the adjacent silicon atom [$C_{sp^2}$–$Si_{sp^3}$ bond

length 1.87 Å[14,20]] compared to that between the carbonyl group and the adjacent carbon atom [$C_{sp^2}$–$C_{sp^3}$ bond length 1.47 Å[21]]. The effective diameter[22] of the trimethylsilyl group (6.9 Å) is also greater than that for the *tert*-butyl group (6.3 Å) due to the critical difference between the $C_{sp^3}$–$Si_{sp^3}$ bond distance (1.87 Å) and the $C_{sp^3}$–$C_{sp^3}$ bond distance (1.54 Å). At the same time, however, the distance between the center of the carbonyl carbon and the adjacent hindering substituent is increased in the silyl ketones over that in the carbon ketones. The net effect of this increased bond distance and the concurrent increase in steric size (of the silicon substituent) on the stereoselectivity of the reactions is difficult to evaluate quantitatively, but these two factors should, to some extent, act to counteract each other.

The greater C–Si bond lengths must also be reflected in the conformation of the triphenylsilyl *vs.* triphenylmethyl groups. In the more open tetraphenylsilane[20] the measured dihedral angle of the phenyl rings with respect to the "normal" nondistorted position is 30° as compared to a 55° angle in the more tightly packed tetraphenylmethane.[21] The result is that the phenyl rings in triphenylmethyl describe a propeller with a steeper pitch than do the phenyl rings in the triphenylsilyl group; this is a structural feature which must be carried over to the triphenylmethyl *vs.* triphenylsilyl groups. The effective diameter of the triphenylsilyl "propeller" in the crystalline *p*-bromobenzoate of phenyltriphenylsilyl carbinol (**1b**) is 13.2 Å.[14]

One additional complicating factor should be considered. Ultraviolet spectral evidence[23–27] indicates that the phenyl ring of phenyl *tert*-butyl ketone is seriously out of coplanarity with the carbonyl group. The extinction coefficient for the benzoyl $\pi$–$\pi^*$ transition at 424 nm in phenyl *tert*-butyl ketone is $8.1 \times 10^{-3}$ compared to 13.0, 11.4, and $11.5 \times 10^{-3}$, respectively, for the methyl, ethyl, and isopropyl homologs. The corresponding extinction coefficients for the trimethylsilyl phenyl ketone (**1a**) and phenyl triphenylsilyl ketone (**1b**) are 11.7 and $16.2 \times 10^{-3}$ while that for phenyl trityl ketone (**2b**) is $10.2 \times 10^{-3}$. The extent to which the coplanarity of the phenyl ring and the carbonyl group is important in the transition states of these asymmetric reduction reactions, during which the carbonyl carbon changes from $sp^2$ to $sp^3$ hybridization, is difficult to assess but has been considered.[17,28] However, it is clear that the steric and electronic effects will be quite different depending upon whether it is the electron-rich face of the benzene ring or the hydrogen-bearing edge which interacts with neighboring groups in the transition state.[17]

(20) M. Yokoi, *Bull. Chem. Soc. Jap.*, **30**, 100 (1957).

(21) H. T. Sumsion and D. McLachlan, *Acta Crystallogr.*, **3**, 217 (1950).

(22) The effective diameter was taken as the maximum diameter perpendicular to the axis of rotation of the group considered as a spinning top and using tetrahedral bond angles and standard van der Waals radii: R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).

(23) G. D. Hedden and W. G. Brown, *J. Amer. Chem. Soc.*, **75**, 3744 (1959).

(24) F. Agolini, S. Klemenko, I. G. Csizmadia, and K. Yates, *Spectrochim. Acta, Part A*, **24**, 169 (1968).

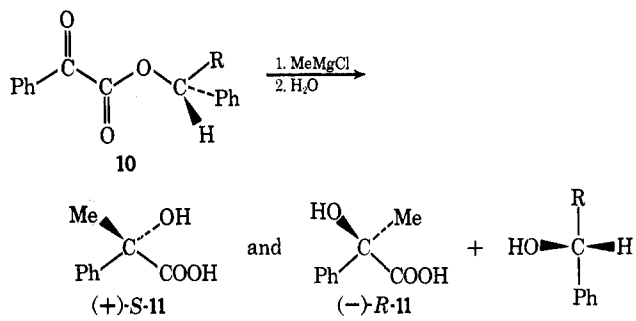
(25) A. G. Brook, R. Kivisikk, and G. E. LeGrow, *Can. J. Chem.*, **43**, 1175 (1965).

(26) A. G. Brook, D. G. Anderson, J. M. Duff, P. F. Jones, and D. M. MacRae, *J. Amer. Chem. Soc.*, **90**, 1076 (1968).

(27) H. Bock, H. Alt, and H. Seidl, *ibid.*, **91**, 355 (1968).

(28) D. Nasipuri, G. Sarkar, and C. K. Ghosh, *Tetrahedron Lett.*, 5189 (1967).

**Benzoylformate to Atrolactate Asymmetric Synthesis.**—The asymmetric addition of methylmagnesium iodide to chiral benzoylformate esters **10** followed by hydrolysis to give optically active atrolactic acid **11** according to the McKenzie–Prelog method has been a reliable procedure for the correlation of configurations of secondary carbinols.[9] The benzoylformate ester **10**, R = $SiPh_3$, from (+)-phenyltriphenylsilylcarbinol gave (+)-atrolactic acid (**11**) corresponding to a 25% excess of the *S*




enantiomer, while the benzoylformate from (+)-phenyltritylcarbinol **10**, R = $CPh_3$, gave (−)-atrolactic acid corresponding to a 27% excess of *R* enantiomer. This indicates that these two carbinols with the same sign of rotation (at the D line of sodium) have opposite configurations. Furthermore the application of Prelog's generalization predicts that (+)-phenyltriphenylsilylcarbinol has the *R* configuration as has now been proven unequivocally by X-ray studies.[14]

**ORD–CD Study.**—It seems reasonable that the ORD spectra (Figures 1 and 2) of the configurationally related silicon and carbon carbinols **5a** *vs.* **6a** and **5b**, *vs.* **6b** should resemble each other. As reported earlier,[2b] the ORD spectra were such that it was not possible to draw any certain conclusion by such a comparison. We have now measured the circular dichroism (CD) spectra of these four compounds[29] which are shown in Figures 3 and 4. It is to be noted first that the ultraviolet spectra of the four compounds are typical for monosubstituted benzene derivatives showing a low intensity $^1L_b$ band[30] with characteristic fine structure in the region 250–285 nm (Figures 1 and 2, lower curves). The $^1L_a$ band in the two nonsilicon carbinols **6a** and **6b** is not apparent in the steeply increasing absorption below 240 nm, whereas it appears as a distinct peak in **5a** at 223 nm and as a shoulder at 222 nm in **5b**, indicating a bathochromic shift of 5–10 nm induced by silicon in the latter two compounds. Below 220 nm no clear maximum for the $^1B_a$ band could be reached for **5a**, **5b**, and **6b**.

Whereas the uv spectra for the phenyltriphenylsilyl- and phenyltritylcarbinols **5b** and **6b** are made up of the sum of the four phenyl groups in these compounds, the CD spectra should be influenced mainly by the phenyl group directly attached to the asymmetric center. It is known that the intensity of the Cotton effect corresponding to an aromatic transition decreases rapidly when the phenyl group is separated from the asymmet-

(29) The previous ORD data[2b] were reported as specific rotations in *chloroform* while the present spectra were taken in ethanol and are plotted as molecular rotations. We are indebted to Dr. Günter Barth, Mrs. Ruth Records, and Dr. Edward Bunnenberg of the Stanford Chemistry Spectropolarimetry Laboratory for their generous and able assistance in this study.

(30) According to nomenclature of J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).

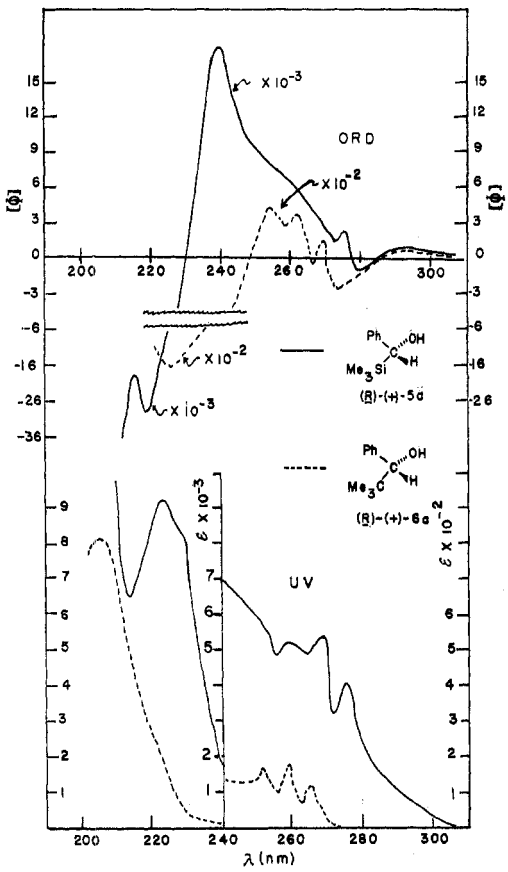



Figure 1.—ORD (upper) and uv (lower) curves of (+)-phenyltrimethylsilylcarbinol [*R*-(+)-**5a**, ——] and of (+)-phenyl-*tert*-butylcarbinol [*R*-(+)-**6a**, - - - - - - -]; ethanol solvent. The determination was made on (−)-**5a** of 33% enantiomeric purity; the curve reported here is the mirror image corrected to 100% enantiomeric purity.

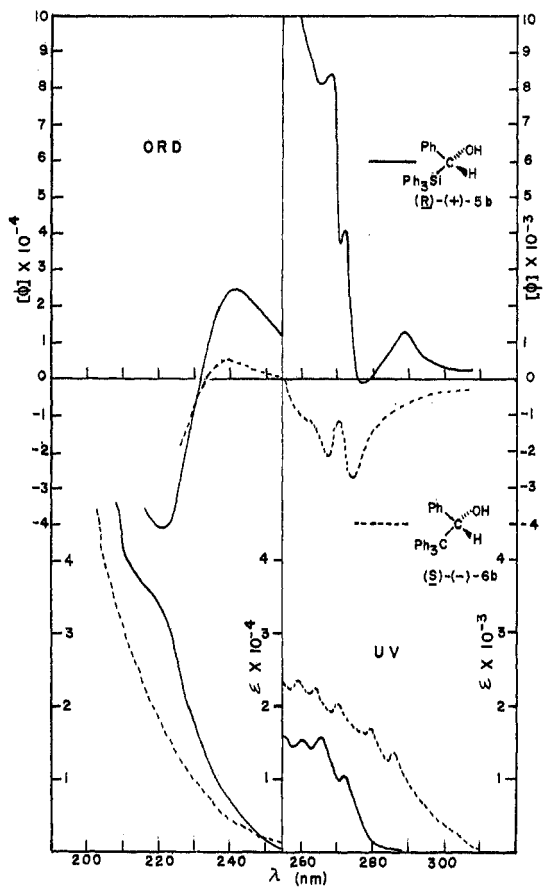



Figure 2.—ORD (upper) and uv (lower) curves of (+)-phenyltriphenylsilylcarbinol [*R*-(+)-**5b**, ——] and of (−)-phenyltritylcarbinol [*S*-(−)-**6b**, - - - - - -]; ethanol solvent. The determination was actually made on (+)-**6b** and the mirror image curve reported here for clarity of comparison.

ric center of saturated compounds.[31] The Cotton effects for the $^1L_b$ band are clearly visible with characteristic fine structure in the ORD and CD spectra of **5a**, **5b**, **6a**, and **6b**. Although the sign of the ORD Cotton effect of this band cannot be clearly recognized, that for the CD spectra can be ascertained unambiguously. This inherent difficulty in interpreting ORD spectra is also evident in the spectral region below 250 nm and again emphasizes the superiority of CD over ORD in resolving overlapping Cotton effects.[32]

Below 250 nm the CD spectra of the triphenylsilyl- and tritylcarbinols, (+)-**5b** and (−)-**6b** (Figure 4), clearly show CD Cotton effects of the same sign.[33] That the 230-nm band of **6b** is split into two maxima at 227 and 235 nm may be due to vibrational components. This splitting was observed in chloroform and cyclohexane as well as ethanol. Since the Cotton effects at 215 nm in **5b** and 206 nm in **6b** seem to be at too high a wavelength for the $^1B_{a,b}$ transition, the appearance of these bands may correspond to $^1L_a$ transitions of different conformers. This interpretation is in accord with the fact that at −192° in EPA glass (−)-**6b** exhibited a single maximum in this region at 225 nm, $[\theta] \cong +28{,}000$ as shown in Figure 5.

The overall sign of the Cotton effect from the $^1L_b$ band in the 250–280-nm region is, in an important sense, a summation of the overlapping, individually signed, conformation-related progressions[34] and to this extent configurational correlations based on it must be viewed with caution. This is illustrated by the observation that at −192° in EPA glass the longest wavelength Cotton effect at 276 nm in the complex $^1L_b$ band of **6b** was seen to reverse its sign as shown in Figure 5. Nevertheless, the three remaining peaks in this broad band retained their negative signs and it appears that correlations based on this general region, without too great attention to fine structure, should be useful. Therefore, based upon the premise that the 250–280-nm region is meaningful for configurational correlations for these secondary carbinols, we must conclude that (+)-**5a**, (+)-**6a**, (+)-**5b**, and (−)-**6b**, all of which have an overall negative CD band at room temperature in this region, are configurationally related and that each has the absolute configuration represented by **12** based upon the known configuration of **5b**[14] and **6a**.[8] This corroborates the configurational assignments made for **6b** based upon the atrolactic asymmetric synthesis,[9] and that for **5a** made on the basis of Grignard reductions. That *R*-(+)-**5b** and *S*-(−)-**6b** have "related configura-

(31) L. Verbit, *J. Amer. Chem. Soc.*, **87**, 1617 (1965); **88**, 5340 (1966). See also L. Verbit and P. J. Heffron, *Tetrahedron*, **24**, 123 (1968).

(32) P. Crabbé, *Top. Stereochem.*, **1**, 93 (1967); P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, San Francisco, Calif., 1965.

(33) In fact the ORD and CD measurements were made on (+)-**6b** but for clarity in presentation the mirror image of the spectra actually measured are represented in Figures 2, 4, and 5.

(34) J. Horowitz, E. H. Strickland, and C. Billups, *J. Amer. Chem. Soc.*, **91**, 184 (1969).

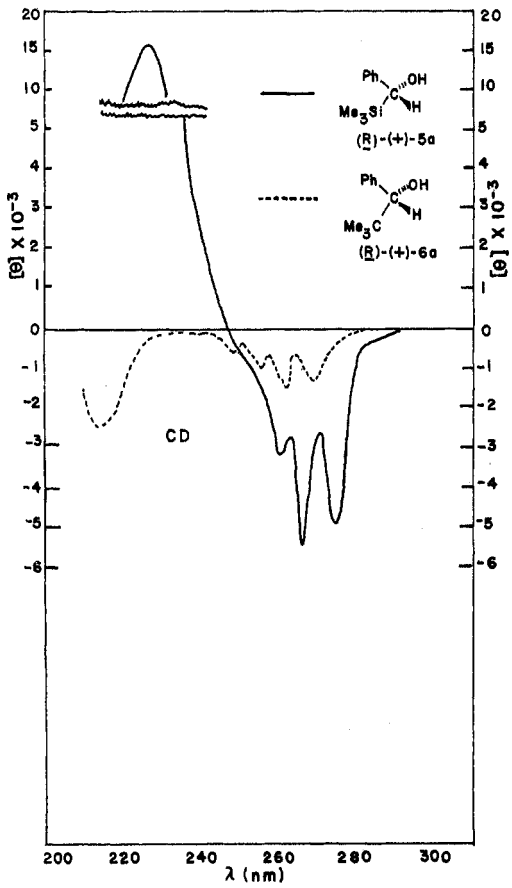
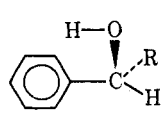



Figure 3.—CD curves of (+)-phenyltrimethylsilylcarbinol [*R*-(+)-**5a**, ——] and of (+)-phenyl-*tert*-butylcarbinol [*R*-(+)-**6a** - - - - - - -]; ethanol solvent. Determination made on (−)-**5a** of 33% enantiomeric purity; curve here presented is the mirror image corrected to 100% enantiomeric purity.

tions" but opposite configurational designations according to the Cahn–Ingold–Prelog rules is a consequence of the fact that oxygen takes precedence over carbon, silicon takes precedence over oxygen, and phenyl takes precedence over *tert*-butyl, but trityl takes precedence over phenyl.



**12**

| R | Configuration | $^1L_b$ Cotton effect |
|---|---|---|
| a, $Me_3Si$ | *R*-(+)-**5a** | (−) |
| b, $Me_3C$ | *R*-(+)-**6a** | (−) |
| c, $Ph_3Si$ | *R*-(+)-**5b** | (−) |
| d, $Ph_3C$ | *S*-(−)-**6b** | (−) |

These conclusions also follow the empirically derived sector rule for conformationally mobile aromatic compounds which have a chiral center adjacent to the aromatic nucleus as developed by Brewster and Buta.[35] This octant rule is portrayed in **13a** where plus and minus indicate the sign of the $^1L_b$ Cotton effect due to a strongly interacting group in the indicated quadrant above the plane of the benzene ring; **13b** is the equivalent "end-on" view. The benzene ring is a symmetric chromophore ($C_{2v}$), dissymmetrically perturbed by the groups on the chiral center (C*). In the compounds belonging to the methylphenylcarbinol series the perturbing group is presumed to be hydroxyl on the basis of hydrogen bonding evidence. The observed CD curve

(35) J. H. Brewster and J. George Buta, *J. Amer. Chem. Soc.*, **88**, 2233 (1966).

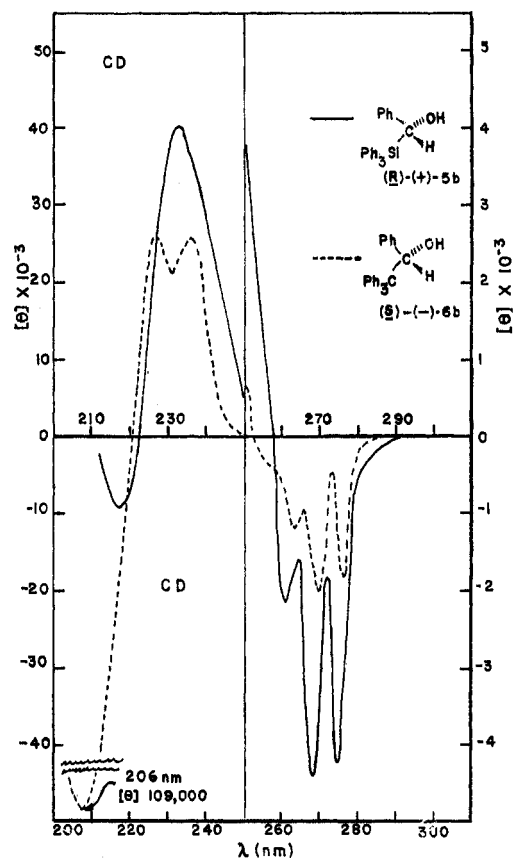
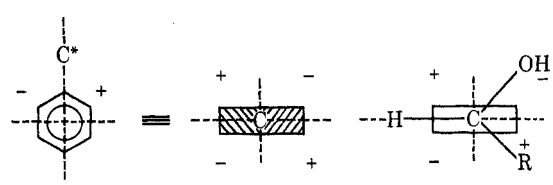



Figure 4.—CD curves of (+)-phenyltriphenylsilylcarbinol [*R*-(+)-**5b**, ——] and of (+)-phenyltritylcarbinol [*S*-(−)-**6b**, - - - - - - -]; ethanol solvent. Determination made on *R*-(+)-**6b**, mirror image curve reported here.



**13a** **13b** **14**

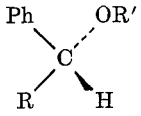
is composed of the population-weighted contributions of the Cotton effects of all conformers present.[36] Some conformers, not necessarily the most abundant, will contribute to the optical rotation much more strongly than others. One can rationalize that conformation **14** in which the benzylic hydrogen eclipses the edge of the benzene ring will make the most important contribution to the optical rotation in such conformationally mobile molecules.[35] This conformation becomes even more important as the size of the R group increases. The compounds in the present study, **12a–12d**, all have a structured negative $^1L_b$, CD, Cotton effect in the 260–280-nm region in accord with the known configuration and negative $^1L_b$ Cotton effect of (*R*)-(+)-phenylmethylcarbinol[31] and in accord with the Brewster sector rule.[35]

**Freudenberg's Rule of Rotational Shifts.**[11]—The Na D-line rotations of derivatives of the configurationally related phenyltriphenylsilylcarbinol, (+)-**5b**, and phenyltritylcarbinol, (−)-**6b**, are given in Table III. It is seen that the rotational shifts in going from the carbinol to the glyoxylate to the acid phthalate are

(36) W. S. Briggs and C. Djerassi, *Tetrahedron*, **21**, 3455 (1965).

TABLE III

MOLECULAR ROTATIONS, $[M]_D$ ($CHCl_3$), FOR (+)-PHENYLTRIPHENYLSILYLCARBINOL, (+)-**5b**, AND (−)-PHENYLTRITYLCARBINOL, (−)-**6b**, AND THEIR DERIVATIVES




| | R′ | | | | |
|---|---|---|---|---|---|
| | Carbinol | Glyoxylate | Phthalate | Benzoate | *p*-Bromobenzoate |
| R | H | O O ‖ ‖ -C-CPh | O ‖ $-CC_6H_4COOH$ | O ‖ -CPh | O ‖ $-CC_6H_4$-*p*-Br |
| $SiPh_3$ (**5b**) | +181 | +209 | +266 | −262 | −413 |
| $CPh_3$ (**6b**)[a] | −150 | −265 | −349[b] | −1080 | −1149 |

[a] See footnote 33; the derivatives were actually prepared from the enantiomeric carbinol. [b] The value of +256 for the enantiomer in the previous communication[2b] was in error. This value is based upon a repetition of the resolution of phenyltritylcarbinol according to L. Ellison and J. Kenyon, *J. Chem. Soc.*, 779 (1954).

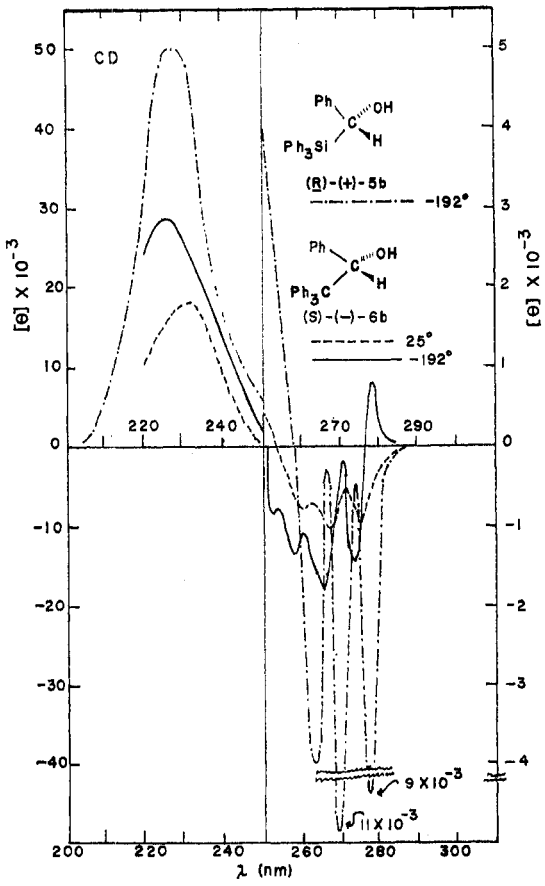
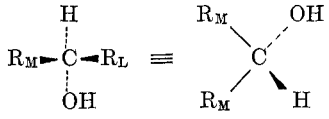



Figure 5.—Comparison of CD curves of (+)-phenyltriphenylsilylcarbinol [*R*-(+)-**5b**, —·—·—·—] and (−)-phenyltritylcarbinol [*S*-(−)-**6b**, ——] in EPA glass (ether–isopentane–ethanol, 5:5:2) at −192°. Note that the EPA solution of **6b** at 25° has a maximum in the 250–280-nm region about 0.5 as intense as in ethanol (Figure 4), and that the double peak at 230 nm in ethanol becomes a single peak in EPA both at 25 (------) and −192 (——).

the opposite as written for the two series. The shifts are relatively small, however, in comparison to those observed in going from the carbinols to benzoates or *p*-bromobenzoates which are substantial negative numbers in both cases. This latter large shift is in consonance with the known configurations. The contrary but lesser shifts shown in the first three derivatives could easily be misinterpreted if the configurations of these carbinols were not independently established. These results emphasize again the necessity of basing configurational correlations of this type on the CD curves and sign of the Cotton effects, not on the rotational shift as measured at a single wavelength.[32]

**Horeau's Method of Partial Kinetic Resolution.**[37]—The preferential esterification of one of two enantiomers of α-phenylbutyric acid (used in excess in the form of racemic anhydride) by an optically active secondary alcohol gives residual acid whose sign of rotation has been empirically correlated with the absolute configuration of a large number of starting alcohols by Horeau and coworkers.[37] If the recovered residual α-phenylbutyric acid is *levorotatory* the secondary carbinol has the configuration represented by formula **13**, where $R_L$ and $R_M$ represent the large- and medium-sized groups with respect to hydrogen. When this method was applied to (*R*)-(+)-phenyltriphenylsilylcarbinol, (+)-α-phenylbutyric acid, $[\alpha]^{23}D$ +3.53 ± 0.11° (*c* 10, $CHCl_3$), corresponding to 3.7% enantiomeric purity and 11% "optical yield" was recovered. Assigning $R_L$ to triphenylsilyl and $R_M$ to phenyl, this predicts the incorrect configuration. This result indicates a limitation of the Horeau method which should be investigated further before it is applied to such silicon carbinols. Curiously, when (+)-phenyltriphenylcarbinol was tested by the Horeau method, the recovered α-phenylbutyric acid was racemic within experimental error.




**13**

## Experimental Section[38]

**Phenyl Silyl Ketones 1a and 1b.**—Phenyl trimethylsilyl ketone (**1a**) and phenyl triphenylsilyl ketone (**1b**) were prepared by the method of Brook, *et al.*,[3,4] from trimethylsilyl chloride and

(37) R. Weidman and A. Horeau, *Bull. Soc. Chim. Fr.*, 117 (1967), and references therein.

(38) Unless otherwise noted, physical data were collected as follows. Routine nmr determinations were done at 60 MHz (Varian T-60 instrument) in $CHCl_3$ or $CDCl_3$ solvent with chemical shifts reported in parts per million, δ, downfield from internal tetramethylsilane standard. Melting points were determined on a hot stage unless designated "capillary" and are uncorrected. Solution optical rotations were determined in center-filled polarimeter tubes on a Zeiss instrument; ORD measurements were made on a Durrum-JASCO Model ORD/UV/CD-5 instrument.[29] Infrared spectra were taken on a Perkin-Elmer Model 137 spectrophotometer in KBr wafers when solids and neat if liquids. Analytical and preparative gas chromatography were done on a Varian P-90 instrument using helium carrier gas. Elemental analyses were performed by Messrs. E. Meir and J. Consolo of the Stanford Chemistry Department analytical laboratories.

triphenylsilyl chloride in overall yields of 59 and 48%, respectively.

**Resolution of Phenyltriphenylsilylcarbinol.**—A solution of *dl*-phenyltriphenylsilylcarbinol, made by standard lithium aluminum hydride ($LiAlH_4$) reduction of the ketone[3] (15.7 g, 42.9 mmol, mp 120–121°), and phthalic anhydride (7.00 g, 47.2 mmol) in pyridine (8 ml) was stirred at 110° (2 hr) and refluxed at 135° (12 hr). The cooled reaction mixture was poured into cold dilute hydrochloric acid (350 ml of 15%) and extracted with chloroform. These extracts were washed ($H_2O$, dilute HCl, $H_2O$), dried ($Na_2SO_4$), and concentrated to give 17.2 g (80% yield) of the crude acid phthalate which was recrystallized from benzene: mp 188–190°; ir (KBr) 1725 (COOH), 1700 (COOR), 1420 and 1105 (SiPh), 1275, 1250, 1055, and 690 $cm^{-1}$.

*Anal.* Calcd for $C_{33}H_{26}O_4Si$: C, 77.01; H, 5.09. Found: C, 77.27; H, 5.13.

To a boiling solution of phenyltriphenylsilylcarbinyl acid phthalate (15.0 g, 29.1 mmol) and brucine tetrahydrate (13.3 g, 29.1 mmol) in acetone (200 ml) was slowly added water until the point of incipient crystallization was reached. An additional 10 ml of acetone was added and the mixture allowed to cool undisturbed overnight at 5°; 26.2 g of the brucine salt, mp 130–135°, was collected. This material was then subjected to a systematic four-stage crystallization using fresh 10% aqueous acetone, to recrystallize the most insoluble fractions, and using the mother liquors from the more insoluble fraction for recrystallization of the more soluble fraction. This gave 3.05 g of the less soluble brucine salt, mp 129–132°, $[\alpha]^{18}D$ −13.5° (*c* 5.6, $CHCl_3$), and 2.4 g of the more soluble form, $[\alpha]^{22}D$ −9.7° (*c* 13.2, $CHCl_3$), as well as several in-between fractions and more soluble fractions which did not crystallize.

The less soluble salt (3.05 g) dissolved in ethanol (100 ml) was heated (3 min, at boiling) with 300 ml of 7% HCl, followed by cooling, extraction with ether, drying ($Na_2SO_4$), and evaporation of the ether extracts. The residue was crystallized and recrystallized from benzene–petroleum ether to give 0.76 g of fibrous crystals, mp 108–109°, $[\alpha]^{21}D$ +47.9 ± 0.6° (*c* 4.3, $CHCl_3$).

An ether solution of this dextrorotatory acid phthalate (0.76 g) was reduced with $LiAlH_4$ (0.45 g) in ether for 5 min. The excess $LiAlH_4$ was destroyed (EtOAc); the mixture was acidified (dilute HOAc) and extracted with ether. The extracts were washed ($H_2O$) and dried ($Na_2SO_4$) and benzene was added. An oil, which separated upon concentration proved to be *o*-hydroxymethylbenzoic acid, was removed. Addition of petroleum ether (bp 30–60°) and cooling gave crystals of (+)-phenyltriphenylsilylcarbinol [0.34 g, mp 103–104°, $[\alpha]^{21}D$ +46.0 ± 1.3° (*c* 1.54, $CHCl_3$)] which were recrystallized from benzene–petroleum ether to give purified product: 0.25 g; mp 103–104°; ir (KBr) 3550, 3520, 1480, 1420, 1100 (SiPh), 1020, 980, 760, 730, and 685 $cm^{-1}$; $[\alpha]^{22}D$ +49.5 ± 1.1° (*c* 1.77, $CHCl_3$).

The acid phthalate from the more soluble brucine salt [2.4 g, $[\alpha]^{22}D$ −9.7° (*c* 13.2, $CHCl_3$)] was reduced with $LiAlH_4$ by the same procedure to give recrystallized (−)-phenyltriphenylsilylcarbinol [0.17 g, mp 102.5–104.5°, $[\alpha]^{21}D$ −48.6 ± 1.1° (*c* 1.91, $CHCl_3$)] whose ir spectrum was identical with that of the enantiomer. This procedure was successfully repeated on a larger scale.

**(+)-Phenyltriphenylsilylcarbinyl Phenylglyoxalate.**—A mixture of phenyltriphenylsilylcarbinol [0.334 g, 0.91 mmol, $[\alpha]^{25}D$ +48.4 ± 0.2° (*c* 11.0, $CHCl_3$)] and phenylglyoxalyl chloride (0.4 g, 2.4 mmol) in pyridine (10 ml) and benzene (15 ml) was stirred overnight at 20–25°, refluxed (4 hr), and hydrolyzed with dilute hydrochloric acid. The combined ether extracts were washed ($H_2O$), dried ($MgSO_4$), and concentrated, and the residue was crystallized from ethanol to give purified product: 0.41 g; 65% yield; mp 166–168°; $[\alpha]^{22}D$ +41.9 ± 0.9° (*c* 2.245, $CHCl_3$); ir (KBr), identical with spectrum of (analyzed) *dl* material, 1730 (ester C=O), 1420 and 1100 $cm^{-1}$ (SiPh).

*Anal.* Calcd for $C_{33}H_{26}O_3Si$: C, 79.47; H, 5.25. Found: C, 79.44; H, 5.26.

**Reaction of (+)-Phenyltriphenylsilylcarbinyl Phenylglyoxalate with Methylmagnesium Iodide.**—An ether solution of the above (+)-phenyltriphenylsilylcarbinyl phenylglyoxalate (0.200 g, 0.4 mmol) and the Grignard reagent prepared from magnesium (0.04 g, 1.8 mg-atoms), methyl iodide (0.247 g, 1.8 mmol), and ether was stirred for 2 hr at 20–25° and then refluxed for an additional 1 hr. After hydrolysis with saturated ammonium chloride solution, the combined ether extracts were dried ($MgSO_4$), concentrated, taken up in methanol, and saponified by refluxing overnight with a water–methanol (1:1) solution of potassium hydroxide. The aqueous layer was extracted with ether and the extracts were discarded; the aqueous layer was neutralized (HCl) and extracted with ether. The extracts were washed ($H_2O$), dried ($MgSO_4$), and concentrated to give atrolactic acid, 0.062 g (93% overall crude yield, addition and saponification), identified by melting point and ir, $[\alpha]D$ +9.6° (*c* 3.10, MeOH) corresponding to 25% asymmetric synthesis.[39]

In the control series, *dl*-carbinol gave the intermediate *dl*-phenyltriphenylsilylcarbinyl atrolactate (diasteriomeric mixture?): mp 158.5–160°; ir (KBr) 3525 (OH), 1730 (ester C=O), 1420, and 1105 $cm^{-1}$ (SiPh).

*Anal.* Calcd for $C_{34}H_{30}O_3Si$: C, 79.33; H, 5.88. Found: C, 79.31; H, 6.00

**Asymmetric Reduction of Phenyl Trimethylsilyl Ketone (1a) with the Grignard Reagent (4) from (+)-1-Chloro-2-phenylbutane.**—(+)-1-Chloro-2-phenylbutane[17] [2.83 g, 16.8 mmol, $\alpha^{24}D$ +5.76 ± 0.02° (neat, *l* 1) 97.3% enantiomerically pure] was treated with sublimed magnesium (0.41 g, 17 mg-atoms) in ether (200 ml) under a nitrogen atmosphere and the resulting Grignard solution added dropwise to a solution of phenyl trimethylsilyl ketone[3] (1.60 g, 8.9 mmol) in ether (25 ml) at 5°. The reaction mixture was allowed to warm to room temperature with stirring (3 hr); after stirring overnight the mixture was hydrolyzed with ammonium chloride solution. The residue from the dried ether layer was shown by glpc analysis (5 ft × 0.25 in. Carbowax 20M–TPA column, 165°) to contain ketone and carbinol in the ratio of 1:12; it was distilled to give 1.33 g (85% crude yield), bp 79–83° (0.2 mm). Preparative gas chromatography under the above conditions gave pure carbinol with the properties listed in Table I.

**Asymmetric Reduction of Phenyl Trimethylsilyl Ketone (1a) with Grignard Reagent (3) from (+)-1-Chloro-2-methylbutane.**—The Grignard reagent was made from enantiomerically pure chloride.[19] Addition of the ketone to the Grignard reagent caused a white precipitate to form which remained until hydrolysis. Glc purification was done on a 5 ft × 0.25 in. FFAP 60–80 HMDS column (Varian Aerograph) at 195° with the results given in Table I.

**Asymmetric Reduction of Phenyl Triphenylsilyl Ketone (1b) with Grignard Reagents 3 and 4.**—The same procedure as above was used. A white precipitate formed upon addition of the Grignard reagent in both cases. Unreacted ketone, 50%, was recovered from the reaction with Grignard reagent 4 when the product was purified by column chromatography on silica gel, eluting with petroleum ether (bp 65–68°) and ether; the results are reported in Table I.

**Asymmetric Reduction of Phenyl Trityl Ketone (2b) with Grignard Reagents 3 and 4.**—The Grignard reagents were made in ether, diluted with 40% benzene, and added to a benzene solution of **2b**. The reaction mixture was then refluxed (65°, 3 hr) and hydrolyzed as in the previous procedures. Purification was accomplished by preparative thin layer chromatography on silica gel using 5% hexane in acetone, with the results recorded in Table I.

**Enantiomeric Purity of (−)-Phenyltrimethylsilylcarbinol (5a) by MTPA Method.**[16,40]—A pyridine solution of phenyltrimethylsilylcarbinol [90 mg, $[\alpha]^{25}D$ −30.99 ± 0.16° (neat)] and distilled α-methoxy-α-trifluoromethylphenylacetyl chloride (MTPA-Cl, 250 mg) prepared from enantiomerically pure (−)-MTPA[16] was allowed to stand at room temperature for 1 week. The reaction mixture was diluted with ether and washed ($H_2O$, dilute HCl, dilute $Na_2CO_3$, $H_2O$), and the ether extracts were dried ($MgSO_4$) and evaporated. A carbon tetrachloride solution of the residue gave an nmr spectrum with separate benzylic proton signals for each of the diastereomers at 358 and 350 Hz downfield from the trimethylsilyl signal whose areas were in the ratio of 56:28 (the reproducibility of repetitive runs was about ±1%). This corresponds to 33.3% excess of one diastereomer and therefore a 33.3% excess of the levo enantiomer in the starting (−)-phenyltrimethylsilylcarbinol. The calculated maximum rotation for phenyltrimethylsilylcarbinol therefore is $[\alpha]^{25}D$ 93.0 ± 1.5° (neat).

**Phenyltriphenylsilylcarbinyl Benzoate.**—To a solution of phenyltriphenylsilylcarbinol [(0.237 g, 0.65 mmol, $[\alpha]^{24}D$ + 47.7 ± 0.4° (*c* 4.279, $CHCl_3$), 96.4% enantiomerically pure] in ether (5 ml) and pyridine (10 ml) was added benzoyl chloride

(39) Based on atrolactic acid $[\alpha]D$ max of 37.7° (MeOH). This rotation was determined in methanol on a JASCO photoelectric polarimeter.

(40) We are indebted to Dr. James Dale for his advice and assistance on this determination.

(0.14 g, 1.0 mmol). The solution was refluxed overnight, hydrolyzed (dilute HCl), and extracted (ether). The extracts were washed ($Na_2CO_3$ solution, $H_2O$), dried ($MgSO_4$), and concentrated, and the residue was crystallized from ethanol to give 0.176 g (58%) white crystals: mp 175–176°; ir (KBr) 1715 (ester C=O), 1425 and 1105 (SiPh), 1265 $cm^{-1}$; $[\alpha]^{25}D$ −55.6 ± 3.3° (*c* 2.2, $CHCl_3$).

*Anal.* Calcd for $C_{32}H_{26}O_2Si$: C, 81.66; H, 5.57. Found: C, 81.58; H, 5.68.

**Phenyltritylcarbinyl Benzoate.**—A solution of phenyltritylcarbinol [0.200 g, 0.57 mmol, $[\alpha]D$ +40.6 ± 1.6° (*c* 1.28, $CHCl_3$), 94% enantiomerically pure] and benzoyl chloride (0.14 g, 1 mmol) in pyridine (3 mmol) was treated as given for the phenyltriphenylsilylcarbinyl benzoate. The residue was crystallized from ethanol to give 0.220 g (85%) white crystals: ir (KBr) 1720 (ester carbonyl), 1275 $cm^{-1}$; $[\alpha]^{23}D$ +237.6 ± 2.1° (*c* 0.947, $CHCl_3$).

*Anal.* Calcd for $C_{33}H_{26}O_2$: C, 87.19; H, 5.77. Found: C, 87.24; H, 5.85.

**Phenyltritylcarbinyl *p*-Bromobenzoate.**—A solution of phenyltritylcarbinol (0.200 g, 0.57 mmol, 94% enantiomerically pure) and *p*-bromobenzoyl chloride (0.13, 0.59 mmol), in pyridine (4 ml) was treated as given for the preparation of phenyltriphenylsilylcarbinyl *p*-bromobenzoate. The residue, 0.275 g, was purified by preparative thin layer chromatography (silica gel with 5% benzene in hexane) eventually yielding 0.031 g of white crystalline material: ir ($CHCl_3$) 1715 (ester C=O), 1270 $cm^{-1}$ (aromatic ester); $[\alpha]^{26}D$ +215.5 ± 3° (*c* 3.1, $CHCl_3$).

*Anal.* Calcd for $C_{33}H_{25}O_2Br$: C, 74.29; H, 4.72; Br, 14.99. Found: C, 74.25; H, 4.89; Br, 15.05.

**Phenyltriphenylsilylcarbinyl *p*-Bromobenzoate.**—A solution of phenyltriphenylsilylcarbinol [0.366 g, 1.0 mmol, $[\alpha]^{24}D$ +47.7 ± 0.4° (*c* 4.28, $CHCl_3$), 96.4% enantiomerically pure] and *p*-bromobenzoyl chloride (0.22 g, 1 mmol) in pyridine (5 ml) was stirred overnight at 120° and then hydrolyzed (dilute HCl), the combined ether extracts were washed (saturated $NaHCO_3$ solution, $H_2O$), dried ($MgSO_4$), and concentrated, and the residue (0.54 g) was allowed to crystallize slowly from ethanol with slow evaporation to give 0.3 g (55%) of large translucent rectangular crystals: mp 146–148.5°; ir (KBr) 1725, 1715 (shoulder), 1585, 1485, 1480, 1450, 1425, 1395, 1305, 1280, 1265, 1206, 1170, 1110, 1095, 1070, 1030, 1015, 1000, 940, 910, 850, 775, 745, 730, 710, 700, 680 $cm^{-1}$; $[\alpha]^{26}D$ −70.0 ± 2.8° (*c* 0.70, $CHCl_3$).

*Anal.* Calcd for $C_{32}H_{25}BrO_2Si$: C, 69.94; H, 4.59; Br, 14.54. Found: C, 70.04; H, 4.68; Br, 14.51.

Upon continued evaporation the growth of tiny opaque nodules, mp 162.5–163.5° (capillary), was noted on the surface of the crystals. These nodules showed no ir absorption (KBr) at 1725 $cm^{-1}$ but otherwise were identical with those above, $[\alpha]^{27}D$ −21.9 ± 1.9° (*c* 1.05, $CHCl_3$). The nodules were similar to the irregular crystals, $[\alpha]^{27}D$ +4.0 ± 1.0° (*c* 1.98, $CHCl_3$), which formed in a control experiment using carbinol with $[\alpha]^{25}D$ −6.6 ± 0.1° (*c* 22.4, $CHCl_3$) and presumably are composed of (−) isomer contaminated with racemate from the 3.6% of (+) isomer present in the original carbinol. Selected crystals, from which the nodules had been removed manually, were used for the X-ray crystallographic study[14] and belong to the space group $P2_12_12_1$.

A second preparation, identical with the above except that the reaction mixture was stirred for 2 days at 115° and then refluxed 10 min, yielded upon crystallization from ethanol 0.28 g (51%), $[\alpha]^{24}D$ −75.2 ± 0.2° (*c* 2.30, $CHCl_3$). Recrystallization from ethanol with slow evaporation gave material in two forms (both assigned to the space group $P2_1$): thin translucent plates [mp 136.5–137.5°, $[\alpha]^{27}D$ −78.8 ± 3.2° (*c* 0.66, $CHCl_3$)] and thick irregular plates (mp 139.5–141.0°).

*Anal.* Calcd for $C_{32}H_{25}BrO_2Si$: C, 69.94; H, 4.59; Br, 14.54. Found (for translucent plates): C, 69.98; H, 4.67; Br, 14.53. Found (for the thick, irregular plates): C, 69.92; H, 4.65; Br, 14.84.

**Horeau's Method of Kinetic Resolution. A. With (+)-Phenyltriphenylsilylcarbinol.**—A solution of phenyltriphenylsilylcarbinol [0.366 g, 1.0 mmol, $[\alpha]^{22}D$ +48.2 ± 2.9° (*c* 0.685, $CHCl_3$)] and racemic α-phenylbutyric anhydride (0.620 g, 2.0 mmol) in pyridine (6 ml) was refluxed for 48 hr. The reflux was essential for esterification under these conditions. Water (10 ml) and benzene (5 ml) were added and after 2 hr the mixture was titrated to a phenolphthalein end point with 34.90 ml of 0.0982 *N* sodium hydroxide solution. This corresponds to 3.43 mequiv of acid present after hydrolysis or 57% esterification. The aqueous layer was acidified (dilute HCl) and extracted with ether, and the combined extracts were washed ($H_2O$), dried ($MgSO_4$), and concentrated. The residue [0.561 g, $[\alpha]^{24}D$ +3.75 ± 0.36° (*c* 5.6, benzene)] was distilled to give 0.425 g of α-phenylbutyric acid identified by ir (benzene), 3.7% enantiomerically pure based on lit.[40] value $[\alpha]^{23}D$ +96.5° (*c* 2, benzene).

**B. With (+)-Phenyltritylcarbinol.**—A solution of phenyltritylcarbinol [0.349 g, 1.0 mmol, $[\alpha]^{22}D$ +40.6 ± 1.6° (*c* 1.28, $CHCl_3$)] and racemic α-phenylbutyric anhydride (0.620 g, 2.0 mmol) in pyridine (10 ml) was treated exactly the same as the silicon analog above. Esterification was 100% complete. The crude α-phenylbutyric acid (0.431 g) was distilled to give 0.278 g, bp 117–120° (0.4–0.3 mm), $\alpha^{22}D$ 0.00 ± 0.002° (*c* 5, benzene, *l* 0.5, Perkin-Elmer 141 electronic polarimeter).

**Registry No.**—**1a**, 5908-41-8; **1b**, 1171-49-9; **2b**, 466-37-5; **3**, 29621-68-9; **4**, 23558-14-7; (+)-**5a**, 31280-61-2; (−)-**5a**, 31280-60-1; (+)-**5b**, 20989-51-9; (−)-**5b**, 20989-52-0; **5b** phenylglyoxylate, 21003-59-8; (−)-**5b** phthalate, 31280-65-6; **5b** benzoate, 31246-80-7; **5b** *p*-bromobenzoate, 31246-81-8; (±)-**5b** phthalate, 31280-66-7; **5b** phthalate brucine salt, 31280-67-8; (+)-**5b** phthalate 21003-61-2; (+)-**6a**, 23439-91-0; (−)-**6b**, 21003-64-5; **6b** phenylglyoxylate, 21003-60-1; (−)-**6b** phthalate, 21003-62-3; **6b** benzoate, 31280-73-6; **6b** *p*-bromobenzoate, 31280-74-7; (+)-**11**, 13113-71-8; (±)-phenyltriphenylsilylcarbinyl atrolactate, 31280-14-5.