Asymmetric Reductions of Carbocations by Chiral Organosilicon Hydrides. The Stereochemical Nature of the Carbocation Captured

James L. Fry* and Merwyn G. Adlington

Contribution from Bowman-Oddy Laboratories, Department of Chemistry, The University of Toledo, Toledo, Ohio 43606. Received May 30, 1978

Abstract: The 2-phenyl-2-butyl cation, formed from optically active or racemic 2-phenyl-2-butanol (**2**) or 2-phenyl-1-butene, was reduced by optically active α-naphthylphenylmethylsilane (**3**) or triethylsilane to 2-phenylbutane (**1**) in trifluoroacetic acid–dichloromethane. When (*R*)-(+)-**3** was used as the reducing agent, **1** was obtained with the same small predominance of *R* enantiomer (~2% ee) regardless of whether the cation precursor was (*S*)-**2**, (*R*)-**2**, (±)-**2**, or 2-phenyl-1-butene. Similarly, (*S*)-(−)-**3** yielded the same small predominance of (*S*)-**1** regardless of starting material. Triethylsilane gave completely racemic **1** from (*R*)-**2**. The results are interpreted in terms of enantioface-differentiating capture of a prochiral carbenium ion which is common to all the precursors.

In a previous communication we reported the formation of 2-phenylbutane (**1**) which was enriched with a small predominance (2–3%) of one enantiomer from the reduction of racemic 2-phenyl-2-butanol (**2**) by optically active α-naphthylphenylmethylsilane (**3**) in a trifluoroacetic acid–dichloromethane medium.[1] Organosilane of (*R*)-(+) configuration gave an enantiomeric excess of hydrocarbon with (*R*)-(−) configuration, whereas (*S*)-(−) organosilane yielded an excess of (*S*)-(+)-2-phenylbutane. These results may be explained as enantioface-differentiating reactions[2] in which the (*R*)-(+) or (*S*)-(−) silane delivers hydride preferentially to the *si* or *re* face, respectively, of a prochiral 2-phenyl-2-butyl cation (**4**) formed by loss of water from either enantiomer of the protonated alcohol (Scheme I). Additional studies have since been performed using other alcohols and chiral organosilicon hydrides with similar results. In every case optically active hydrocarbon products have been obtained.[3]

If the interpretation is correct, then these results are of special interest. They indicate that relatively unstable, highly reactive carbocation intermediates may be subject to observable discriminate partitioning among two or more accessible reaction pathways, even when these pathways differ only slightly in free energy and lead to energetically indistinguishable products (enantiomers). That carbocations of such

Scheme I

high reactivity may exhibit this subtle kind of stereoselectivity is unexpected.[4]

Such an interpretation is justified, however, only if the carbocation intermediate is symmetrically solvated or, perhaps equivalently, if a set of water-separated, enantiomerically related ion pairs (**5** and **5′**) interconvert at a rate much faster than the rate of capture by organosilane. If the rate of interconversion of such asymmetric ion pairs were comparable to the rate of hydride transfer, then the reactions would be more properly regarded as enantiomer differentiating rather than as enantioface differentiating.[2] Although the two cases are in principle distinguishable, our original experiments did not allow an unambiguous distinction to be made. Evidence favoring interpretation in the former terms exists. For example, both *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexanol are reported to undergo reduction with organosilanes when treated with trifluoroacetic acid in dichloromethane to yield mixtures of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexane in which the trans/cis ratio depends upon the organosilane used, but not upon the isomer of alcohol.[5] Additional evidence favoring an interpretation based on the capture of a symmetrically solvated carbocation or its functional equivalent is found in the report that the 2-phenylbutane formed through the reduction of optically active 2-phenyl-2-butanol by achiral triethylsilane in a trifluoroacetic acid–chloroform medium was devoid of optical activity.[6]

Nevertheless, the recent suggestion that unsymmetrically solvated ion pairs may be involved in the reduction of alkyl alcohols upon treatment with organosilanes and trifluoroacetic acid[7] and the report of net inversion of configuration in the nucleophilic-capture products from certain optically active 2-phenyl-2-butyl substrates under ionizing conditions[8] militate against ion **4** being the only kind of ion which might lead to final products. This uncertainty led us to the studies reported here which address the problem of the stereochemical nature of the cations involved in the reduction of chiral benzylic alcohols by organosilicon hydrides in a medium of trifluoroacetic acid and dichloromethane.

Results

Reductions of 2-phenyl-2-butanol were conducted under a dry nitrogen atmosphere at 0 °C by adding trifluoroacetic acid over a short interval (~30 s) to mixtures of the alcohol and a slight molar excess of the appropriate organosilicon hydride in dichloromethane. GLC analysis of aliquots showed that the formation of 2-phenylbutane was essentially quantitative within 1 min after addition of the acid. Formation of naphthalene was observed in the reaction mixtures in which α-
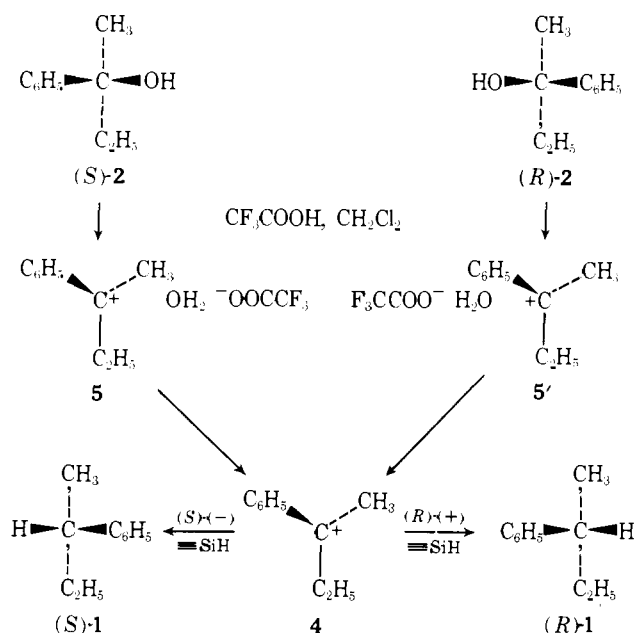
Table I. Enantiomeric Compositions of 2-Phenylbutane Products Obtained from the 2-Phenyl-2-butyl Cation

silane	cation precursor	2-phenylbutane product			
		isolated yield, %	α_{589}^{25} (*l* 1 dm, neat), deg[a]	enantiomeric excess,[b] %	configuration
(R)-(+)-3[c]	(±)-2	82	−0.493[d]	2.21	R
(R)-(+)-3[e]	(R)-(+)-2[f]	81	−0.490	2.03	R
(R)-(+)-3[e]	(S)-(−)-2[g]	75	−0.485	2.01	R
(S)-(−)-3[h]	(R)-(+)-2[f]	84	+0.461	2.19	S
(S)-(−)-3[h]	(S)-(−)-2[g]	75	+0.473	2.25	S
(C₂H₅)₃SiH	(R)-(+)-2[f]	85	0.000	racemic	
(R)-(+)-3[e]	2-phenyl-1-butene	19	−0.505	2.09	R

[a] ±0.002°. [b] Corrected for optical purity of starting silane. Based on $[\alpha]^{25}_D$ 29.3° (neat) for maximum rotation of 1.[31] Estimated error is ±0.05. [c] Optical purity 88.8%. [d] Rotation taken at 26 °C, with error of ±0.010°. [e] Optical purity 96.2%. [f] Optical purity 86.7%. [g] Optical purity 89.0%. [h] Optical purity 83.6%.

naphthylphenylmethylsilane was used as a reducing agent, but only after 2-phenylbutane production was complete.[9] The hydrocarbon product was isolated by distillation, then purified by preparative GLC, and examined for optical activity.

Both racemic and optically resolved samples of 2-phenyl-2-butanol were reduced with optically active α-naphthylphenylmethylsilane[10] in order to determine whether or not the initial configuration of the tetrahedral precursor of the cationic intermediates would influence the stereochemistry of the hydrocarbon product (Table I). Optically active 2-phenyl-2-butanol was also reduced under the same reaction conditions using achiral triethylsilane. The hydrocarbon product obtained from this reaction was racemic.

In order to compare the stereochemical fate of a carbocation generated from a known trigonal planar precursor with that of cations formed from tetrahedral progenitors, 2-phenyl-1-butene was subjected to the same reaction conditions using (R)-(+)-α-naphthylphenylmethylsilane as the reducing agent (Table I). In contrast to the high synthetic yields of hydrocarbon obtained from the alcohols, the olefin gave 2-phenylbutane in only 19% yield together with a considerable quantity of viscous material of low volatility.

Discussion

It is apparent from the results presented in Table I that both the direction and magnitude of the chirality predominant in the hydrocarbon products are determined solely by the nature of the organosilicon hydride reducing agent used and are essentially independent of the configuration of the starting alcohol in the ionic reductions of 2-phenyl-2-butanol. Thus, use of silane 3 which has the *R* configuration is seen to lead to essentially the same small predominance of (R)-(−)-2-phenylbutane regardless of whether the alcohol substrate is racemic or of *R* or *S* configuration. Similarly, (S)-(−)-3 yields 2-phenylbutane with the same excess of the *S* enantiomer from either enantiomer of alcohol. The achiral reducing agent triethylsilane produces only purely racemic hydrocarbon from optically active alcohol.

The latter result is consistent with that observed by Carey for a similar experiment carried out in chloroform solvent.[6] We were compelled to perform the experiment using our standard dichloromethane solvent because of considerable uncertainty over whether the results obtained in chloroform solution would of necessity be the same as those obtained in dichloromethane. This uncertainty was fostered by previous studies which indicated the existence of large solvent effects upon the predominant stereochemistry at silicon in the hydride–halide exchange reaction of trityl halides and optically active 3:[11,12]

$$3 + Ph_3CX \rightarrow \alpha\text{-NpPhMeSiX} + Ph_3CH \qquad (1)$$

Thus, whereas the reaction of 3 with trityl chloride in refluxing benzene solution was reported to give chlorosilane with com-

plete retention of configuration at silicon,[11] reaction in chloroform solvent produced chlorosilane with net inversion at silicon and reaction in dichloromethane solvent produced totally racemic chlorosilane.[12] These profound changes in the stereochemistry were explained on the basis of the differing ability of the different solvents to affect the relative tightness of an "ion-pair framework of the activated complex".[12] Although such effects may be important in determining the stereochemical fate of the silicon product in such hydride-gegenion exchanges, it would seem that the change from chloroform to dichloromethane solvent does not greatly affect the stereochemical outcome at carbon of the reactions studied here.[13,14]

It is of particular importance to note that there is neither a qualitative nor any important quantitative difference in the stereochemistry of the 2-phenylbutane product derived from the reductions of the alcohols or from 2-phenyl-1-butene. In all cases, the stereochemical results are determined entirely by the nature of the organosilicon hydride and not by the alcohol or olefin substrate. From this, one infers that there can be no important difference in the stereochemical nature of the product-forming carbocations which are derived from each kind of precursor, be it tetrahedral alcohol or trigonal olefin.

It was recently suggested that there may be a fundamental difference in the stereochemical nature of the mechanism of organosilicon hydride reductions in trifluoroacetic acid–dichloromethane solvent of alcohols compared with olefins.[7] According to the view which was developed, carbocations formed from olefins (presumed to occur via the corresponding trifluoroacetate esters[15,16]) are symmetrically solvated (6). Because of this symmetrical solvation, stereoselectivities observed in the ionic reductions of olefins were thought to be entirely due to steric interactions between the organosilane and carbocation 6. By way of contrast, it was contended that the cationic intermediates formed by loss of water from certain protonated alcohols were unsymmetrically solvated (7), with

HOOCCF₃   HOOCCF₃
  \   \
   C⁺—   C⁺—
  ╱ |
HOOCCF₃   OH₂

   6   **7**
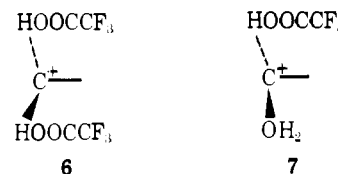
a water molecule disposed near one face. This water molecule was thought to attract the organosilicon hydride preferentially to that face where reduction then occurred with net retention of configuration in the hydrocarbon product.[17]

Evidence for such differences in the stereochemical nature and behavior of 2-phenyl-2-butyl cations formed from alcohols or olefins is not found in the present work. The only substantial differences found in the reductions of the alcohol compared

with the alkene were the much lower synthetic yield of 2-phenylbutane and extensive formation of polymer from the latter. Decreased synthetic yields of hydrocarbons and increased formation of polymers from olefin substrates compared with alcohol substrates have been noted previously in similar organosilicon hydride reductions.[16] The results of the present study make it unlikely that this behavior is a manifestation of any fundamental differences in the cations formed from the two sources. Rather they indicate the introduction of a parallel reaction path when alkene is present (eq 2). Thus electrophilic

$$(2)$$
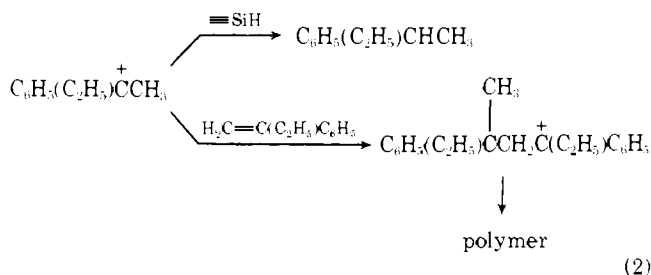
attack by the carbocation on organosilicon hydride, a path which leads to hydrocarbon product, and attack on neighboring alkene, a path which leads to polymer, can both occur.

Indeed, it seems highly unlikely for the benzylic system studied here that the water molecules formed concomitantly with the carbocation reaction intermediates from the alcohols are perturbing the cybotactic region of the solvent to any great extent. Any such perturbation could not be as great as that suggested by representation **7**. Neither is it likely that chiral water-separated ion pairs such as **5** and **5'** are the species actually leading directly to the final hydrocarbon products. If they were, they would, fortuitously, have to behave in a manner identical with that of the ions derived from olefin which must be bereft of water in their solvation sphere.

Consequently, the carbocation intermediate which is the species *actually intercepted* by the organosilicon hydride and reduced to hydrocarbon is best regarded as the prochiral carbenium ion **4**. This ion's symmetrical solvation sphere and the time-averaged position of its gegenion are independent of its genesis.[21] As suggested earlier,[1] it is therefore appropriate to regard these and related asymmetric reactions of carbocations with chiral organosilicon hydrides as examples of enantio-face-differentiating reactions.[2] The dependence of the extent of asymmetric synthesis on the carbocation and organosilicon hydride structures constitutes a forthcoming report.[3]

Experimental Section

General. Nuclear magnetic resonance spectra were obtained on either a JEOLCO JNM-4H-100 or Varian T-60A instrument using tetramethylsilane as an internal standard. Optical rotations were measured on samples in either 1.6 mm × 1 dm or 4.0 mm × 1 dm polarimeter tubes using a Rudolph Research Model 26202 automatic digital polarimeter. Infrared spectra were run using either a Perkin-Elmer 137 or 621 spectrophotometer. Gas–liquid partition chromatographic analyses were conducted on either a Varian Aerograph 90-P instrument or on a Hewlett-Packard 5722A instrument equipped with an electronic integrating recorder. Preparative GLC work was carried out either on the Varian Aerograph chromatograph using a 9.5 mm × 1 m column packed with 20% Apiezon L on Chromosorb W AW or on a Hewlett-Packard Model 776 preparative chromatograph equipped with either a 19 mm × 2 m column packed with 20% Apiezon L on Chromosorb W AW or (in initial work) a 19 mm × 2 m column packed with 20% diisodecyl phthalate on Chromosorb P.

Melting points (Thomas-Hoover apparatus) and boiling points are uncorrected. All glassware was normally oven dried and assembled while hot. Reagent grade dichloromethane was dried over Linde 4A molecular sieves prior to use. Trifluoroacetic acid (Mallinckrodt "Organic Reagent") was used as received.

General Syntheses. 2-Phenyl-2-butanol[23] was obtained in 88% yield (Kugelrohr distillation, 45–50 °C, 1 Torr) from the reaction of ethylmagnesium bromide with acetophenone in diethyl ether. The NMR

spectrum (CCl$_4$) displayed resonances at δ 0.73 (3 H, t), 1.43 (3 H, s), 1.72 (2 H, q) 2.55 (1 H, br s), and 7.0–7.42 (5 H, m).

2-Phenyl-1-butene[24] was prepared in 42% yield by the Wittig reaction from propiophenone and triphenylmethylphosphonium bromide in diethyl ether.[25] GLC (Apiezon L, 160 °C) and IR analysis of this material showed it to contain ~2% propiophenone, but to be isomerically pure. Products obtained using either the Corey modification of the Wittig procedure[26] or the KOH-induced dehydration of 2-phenyl-1-butanol,[27] in our hands, were found to be mixtures containing all three 2-phenylbutene isomers.

Optically Active α-Naphthylphenylmethylsilane (3). Sommer and co-workers have reported the synthesis and resolution of this compound.[10] In their method, the diastereomeric (+)-α-naphthylphenylmethyl-(−)-menthoxysilanes are formed by KOH-catalyzed alcohol exchange from racemic α-naphthylphenylmethoxysilane and (−)-menthol, the diastereomers are separated by fractional recrystallization first from pentane and then from ethanol, and each of the pure diastereomers is then reduced to the corresponding organosilicon hydride with lithium aluminum hydride.[10] However, we experienced serious difficulties in effecting the base-catalyzed preparation of the mixture of diastereomeric (±)-α-naphthylphenylmethyl-(−)-menthoxysilanes. On numerous occasions the reaction would proceed only slightly or not at all. We also experienced extensive solvolysis of the menthoxysilane diastereomers during the extended periods often needed for crystallization to occur from ethanol solution. Large amounts of ethoxysilane products were obtained along with the desired diastereomer. For these reasons, we altered Sommer's preparation of **3** by incorporating several of the modifications suggested by the work of Holt et al.[28]

α-Naphthylphenylmethylmethoxysilane[10] was prepared in 58% overall yield by addition first of α-naphthyl Grignard and then methyl Grignard reagent to phenyltrimethoxysilane (ROC/RIC).[29] Reduction of the methoxysilane with lithium aluminum hydride in diethyl ether gave a 96% yield of racemic **3**.[10] The mixture of diastereomeric α-naphthylphenylmethyl-(−)-menthoxysilanes was prepared from racemic **3** in the following way.

Into a 2-L, three-necked flask equipped with a nitrogen inlet and bubbler were placed 400 g (1.61 mol) of α-naphthylphenylmethylsilane (3), 500 g (3.19 mol) of *l*-menthol (Aldrich), and 400 mL of dry dichloromethane. The flask was purged with dry nitrogen and 1.0 g of 10% palladium on carbon (Sargent-Welch) was added. After 4 h no visible signs of reaction were evident. Additional 2.0-g portions of 10% Pd/C were therefore added at intervals over the next 24 h. Visual signs (hydrogen gas evolution) of reaction were observed after a total of 9.0 g of 10% Pd/C had been added. The mixture was stirred for 1 week, at which point the reaction was complete as determined by GLC analysis (9.5 mm × 0.5 m Carbowax 20M at 212 °C). The flask was flushed with nitrogen and the contents was filtered through Celite to remove the solid catalyst. Removal of solvent and subsequent distillation gave a 95% yield (616.7 g) of the diastereomeric α-naphthylphenylmethyl-(−)-menthoxysilanes as a pale lime-yellow, viscous syrup having bp 203–215 °C (0.75 Torr) (lit.[10] bp 173–177 °C (0.07 Torr)), and a specific rotation of [α]^{27}D −50.22° (*c* 9.68, cyclohexane). The infrared spectrum (CCl$_4$) showed the absence of bands at 2130, 878, and 836 cm^{-1} present in the starting silane and displayed an intense band at 1061 cm^{-1}. The NMR spectrum (CCl$_4$) displayed resonances at δ 0.38–2.60, most prominent at 0.44 (d), 0.50 (d), 0.75, 0.82, 0.84, and 0.93 (21 H, m), 3.47 (1 H, br m), and 7.02–8.06 (12 H, m).

The diastereomeric mixture was diluted with twice its own volume of 30–60 °C petroleum ether and chilled in a dry ice-acetone bath. After 2 days, 225 g of crude crystals was obtained with mp 75–80 °C. The mother liquor was concentrated to one-half its original volume and again chilled in a dry ice-acetone bath. After 2 days, an additional 61 g of crude crystals was obtained with mp 73–78 °C. The combined crude material was diluted with 210 mL of 30–60 °C petroleum ether and placed in a freezer (−20 °C) for 3 days to give 155 g (25% yield) of (−)-α-naphthylphenylmethyl-(−)-menthoxysilane, mp 81.8–83.1 °C (lit.[10] mp 82–84 °C, specific rotation [α]$_D$ −53.9° (*c* 11.32, cyclohexane)). The NMR spectrum (CCl$_4$) displayed resonances at δ 0.4–2.58, most prominent at 0.45 (d), 0.75 and 0.86 (21 H, m), 3.50 (1 H, br m), and 7.05–8.10 (12 H, m).

The original mother liquor remaining after removal of the less soluble diastereomer was evacuated free of pentane and was then taken up in twice its volume of absolute ethanol. Refrigeration for several weeks failed to produce crystals. Addition of a small amount of water and further refrigeration still yielded no crystals. The ethanol was

removed at reduced pressure on a rotary evaporator. The NMR spectrum of the material thus obtained showed that much of the *l*-menthol moiety had been replaced by the solvent ethanol.

A second synthesis of the diastereomers afforded, after removal of the less soluble diastereomer, a syrup enriched in (+)-α-naphthyl-phenylmethyl-(−)-menthoxysilane. To this syrup was added an equal volume of 30–60 °C petroleum ether and the solution was placed in a dry ice–acetone bath. After 1 week 30 g of crystals was obtained. A second recrystallization afforded 5.3 g of essentially pure (via NMR)[28] (+)-α-naphthylphenylmethyl-(−)-menthoxysilane, mp 53.8–55.0 °C (lit.[10] 56.5–59 °C). Having thus obtained reasonably pure crystals of both diastereomers it was then possible to selectively seed the various mother liquor fractions.

Using 30–60 °C petroleum ether as solvent, selective seeding afforded numerous fractions of reasonably high diastereomeric purity as determined by NMR.[28] Thus, from 240 g of original mother liquor enriched in the more soluble diastereomer were obtained (after combining all fractions) 172.0 g of (+)-α-naphthylphenylmethyl-(−)-menthoxysilane of specific rotation $[\alpha]^{23}_D$ −48.72° (c 1.79, cyclohexane) (lit.[10] $[\alpha]_D$ −47° (c 1.4, cyclohexane)) and 61 g of (−)-α-naphthylphenylmethyl-(−)-menthoxysilane of specific rotation $[\alpha]^{23}_D$ −54.69° (c 2.315, cyclohexane) (lit.[10] $[\alpha]_D$ −53.9° (c 11.32, cyclohexane)). A typical NMR spectrum (CCl$_4$) of the more soluble diastereomer displayed resonances at δ 0.44–2.60, most prominent at 0.51 (d), 0.75, 0.82, and 0.93 (21 H, m), 3.50 (1 H, m), and 7.00–8.15 (12 H, m).

Reduction of (−)-α-naphthylmethyl-(−)-menthoxysilane with lithium aluminum hydride in di-*n*-butyl ether following the method of Sommer[10] gave a 71% first-crop yield of (R)-(+)-3, mp 62.3–63.6 °C, $[\alpha]^{26}_D$ +33.71° (c 10.91, cyclohexane) (lit.[10] mp 63.5–64.5 °C, $[\alpha]_D$ +34.3° (c 10.9, cyclohexane)). An additional 16% of second-crop product was obtained with mp 58.6–60 °C, $[\alpha]^{27}_D$ +27.17° (c 10.95, cyclohexane). The NMR spectrum of this material (CCl$_4$) showed signals at δ 0.73 (3 H, d), 5.33 (1 H, q), and 7.10–8.11 (12 H, m). The infrared spectrum (CCl$_4$) showed major bands at 3035, 2950, 2130, 1500, 1422, 1312, 1248, 1140, 1108, 1020, 981, 878, 836, and 697 cm^{-1}. These spectra were identical with those of racemic **3**.

Similarly, (S)-(−)-3, mp 56–61.5 °C, $[\alpha]^{27}_D$ −27.92° (c 10.92, cyclohexane) was obtained in 75% yield from (+)-α-naphthylphen-ylmethyl-(−)-menthoxysilane.

Optically Active 2-Phenyl-2-butanol (2). Racemic alcohol **2** was resolved by means of the brucine salts of the hydrogen phthalate. Hydrogen 2-phenyl-2-butyl phthalate was prepared in 67% yield by the method of Davies et al.[30] The brucine salts were then separated by repeated selective extraction of one diastereomer by hot acetone.[6] The brucine salts were then decomposed with cold 2 N hydrochloric acid and the alcohols were obtained by treatment of the resolved hydrogen phthalates with lithium aluminum hydride. In this way (R)-(+)-2 with $[\alpha]^{26}_D$ +15.95° (neat) and (S)-(−)-2 with $[\alpha]^{24}_D$ −16.38° (neat) were obtained. Assuming a maximum value of $[\alpha]^{22}_D$ 18.4° (neat),[30] these samples were 86.7 and 89.0% optically pure, respectively.

Organosilicon Hydride Reductions. All of the reduction reactions were conducted in essentially the same way. The following reduction of 2-phenyl-1-butene by (R)-(+)-3 is illustrative of the method used. Into a 100-mL, three-necked flask equipped with a magnetic stirring bar, an addition funnel, and a reflux condenser topped with a dry nitrogen bubbler was placed a solution of 7.60 g (30.7 mmol) of (R)-(+)-3 (96.2% optically pure) and 3.96 g (30.0 mmol) of 2-phenyl-1-butene in 40 mL of dry dichloromethane. The solution was stirred rapidly and the reaction flask was chilled in an ice–water bath. Over a period of less than 30 s, 7.5 mL of neat trifluoroacetic acid was added via the addition funnel to the contents of the reaction flask. Stirring was continued for 20 min and then the reaction mixture was quenched by the (careful) addition of 20 g of solid anhydrous potassium carbonate. After foaming had subsided, the pale yellow reaction solution was filtered through a glass frit to remove the insoluble salts. The salts were washed with 6 × 10 mL of dichloromethane. The original filtrate was combined with the dichloromethane washings and distilled through a 7-cm Vigreux column. There was obtained 0.90 g of material boiling ~50–60 °C (10 Torr). GLC analysis (6.4 mm × 2 m 10% DC-11 on Anakrom ABS 80/90 column, 140 °C) indicated the presence of 5.8 mmol (19% yield) of 2-phenylbutane in this product. The 2-phenylbutane product was purified by preparative GLC on a 9.5 mm × 1 m 20% Apiezon column. At 145 °C, 30 mL/min carrier gas flow, the retention time of 2-phenylbutane was 12.5 min.

The optical activity measured for the purified 2-phenylbutane product was α^{25}_D −0.505° (l 1 dm, neat). From the maximum specific rotation ($[\alpha]^{25}_D$ 29.3° (neat)[31]) and the density (d$_4^{25}$ 0.858[32]) reported for 2-phenylbutane, one calculates that optically pure 2-phenylbutane should have α^{25}_D 25.1° (l 1 dm, neat). The product of this reduction, corrected to the optical purity of the silane used, thus corresponds to a 2.09% enantiomeric excess of (R)-(−)-2-phenylbutane.

References and Notes

(1) J. L. Fry, *J. Am. Chem. Soc.*, **93**, 3558 (1971).
(2) Y. Izumi and A. Tai, "Stereo-Differentiating Reactions: the Nature of Asymmetric Reactions", Kodansha, Tokyo, Japan, and Academic Press, New York, N.Y., 1977.
(3) J. L. Fry, M. G. Adlington, and G. W. Erickson, to be submitted for publication.
(4) For a discussion of the reactivity–selectivity principle involved here see A. Pross, *Adv. Phys. Org. Chem.*, **14**, 69 (1977).
(5) F. A. Carey and H. S. Tremper, *J. Am. Chem. Soc.*, **90**, 2578 (1968).
(6) F. A. Carey, Ph.D. Thesis, The Pennsylvania State University, 1963; cited in ref 5.
(7) M. P. Doyle and C. C. McOsker, *J. Org. Chem.*, **43**, 693 (1978).
(8) L. H. Sommer and F. A. Carey, *J. Org. Chem.*, **32**, 800, 2473 (1967).
(9) Formation of naphthalene by protonolysis of 1-naphthylsilanes is a relatively facile process; R. A. Benkeser, W. Schroeder, and O. H. Thomas, *J. Am. Chem. Soc.*, **80**, 2283 (1958).
(10) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Am. Chem. Soc.*, **86**, 3271 (1964).
(11) J. D. Austin and C. Eaborn, *J. Chem. Soc.*, 2279 (1964).
(12) L. H. Sommer and D. L. Bauman, *J. Am. Chem. Soc.*, **91**, 7076 (1969).
(13) Because a complex mixture of silanols, disiloxanes, silyl trifluoroacetates, and ring-cleaved silicon products are obtained under our reaction conditions, we have been unable to observe the predominant stereochemistry at silicon in these reactions.
(14) It should not be thought that no solvent effects will be observed in asymmetric syntheses involving carbocation intermediates; quite the opposite is indicated. Thus (R)-(−)-3-methyl-2-phenylbutane is formed with 10.3% ee in the reduction of racemic 3-methyl-2-phenyl-2-butanol with (R)-(+)-3 in trifluoroacetic acid–dichloromethane solvent. Replacement of the dichloromethane with the poorly ionizing solvent toluene causes a drop to less than 6% ee in the hydrocarbon product.[3] This is likely a reflection of the decreased stability and, hence, decreased reaction pathway selectivity of a carbocation intermediate formed in a medium containing toluene instead of dichloromethane.[4]
(15) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, **23**, 2235 (1967).
(16) D. N. Kursanov, Z. N. Parnes, V. A. Tsyryapkin, Z. V. Knyazeva, and N. I. Yunosheva, *Dokl. Akad. Nauk SSSR*, **205**, 104 (1972).
(17) This idea seems to have been developed primarily from observations made on the 9-decalyl system where it is observed that the ratio of *cis*- to *trans*-decalin product depends on whether the starting material used is one of the Δ-octalins[18] or *cis*- or *trans*-9-decalol.[19] Alternative explanations based on the existence of substantial barriers to interconversion of diastereomerically discrete ions or ion pairs formed from the different progenitors cannot be overlooked in this case.[19,20]
(18) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **36**, 758 (1971).
(19) R. C. Fort, Jr., R. E. Hornish, and G. A. Liang, *J. Am. Chem. Soc.*, **92**, 7558 (1970).
(20) *Cf.* G. E. Gream, *Aust. J. Chem.*, **25**, 1051 (1972); K. B. Becker, A. F. Boschung, M. Geisel, and C. A. Grob, *Helv. Chim. Acta*, **56**, 2747 (1973).
(21) This conclusion holds strictly only for the system studied here and for similar reductions conducted on systems which could give rise to the intermediacy of carbenium ions at least as stable as tertiary benzylic ones. We do *not* conclude that enantiomerically or diastereomerically related ion pairs similar to **5** and **5′** may not be intercepted either by stronger nucleophiles than exist in our studies[8] or because of large barriers to interconversion imposed by structural constraints.[22]
(22) J. A. Bone, J. R. Pritt, and M. C. Whiting, *J. Chem. Soc., Perkin Trans. 2*, 1447 (1975); H. J. Storesund and M. C. Whiting, *ibid.*, 1452 (1975).
(23) H. H. Zeiss, *J. Am. Chem. Soc.*, **73**, 2391 (1951).
(24) D. J. Cram, *J. Am. Chem. Soc.*, **74**, 2137 (1952).
(25) G. Wittig and U. Schoellkopf, *Org. Synth.*, **40**, 66 (1960).
(26) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).
(27) S. Sabetay, *Bull. Soc. Chim. Fr.*, **47**, 614 (1930).
(28) A. Holt, A. W. P. Jarvie, and G. J. Jarvis, *J. Organomet. Chem.*, **21**, 75 (1970).
(29) R. J. P. Corriu, G. F. Lanneau, and G. L. Royo, *J. Organomet. Chem.*, **35**, 35 (1972).
(30) A. G. Davies, J. Kenyon, and L. W. F. Salame, *J. Chem. Soc.*, 3148 (1957).
(31) R. Menicagli and L. Lardicci, *Chem. Ind. (London)*, 576 (1974).
(32) D. Seyferth and Y. M. Cheng, *J. Am. Chem. Soc.*, **95**, 6763 (1973).