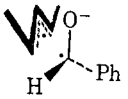
ceeds *via* a doubly suprafacial transition state **4**, and it is likely that the other examples of this process[1] involve a similar geometry.



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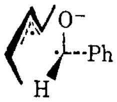

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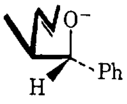

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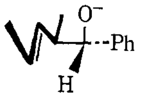

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Stereoselective Attack at One Enantiotopic Face of a Carbonium Ion by Chiral Nucleophile

Sir:

Reactions in which the unsymmetrically substituted trigonal central atom of an achiral substrate (point group C_s) is transformed into a tetrahedral configuration are known to result in asymmetric syntheses when chiral reagents are employed.[1] The formation of optically active alcohols from the reaction of unsymmetrically substituted carbonyl compounds with chiral reducing agents has received particular attention.[2] Although symmetry considerations lead to the prediction that optically active products should also arise from the capture of suitably substituted carbonium ions by chiral nucleophiles, the high reactivity of such ions suggests that the necessary discrimination between enantiotopic faces of the cations by nucleophile might be too small to detect experimentally. We now report the formation of optically active 2-phenylbutane through capture of the 2-phenyl-2-butyl cation by a chiral organosilicon hydride.

Carbonium ions generated from a variety of sources are reduced by organosilicon hydrides.[3-11] Moreover, the transition states for these reactions are known to be sensitive to stereochemical features of the reactants.[6,11] We have found that either (*R*)-(+)- or (*S*)-(−)-1-naphthylphenylmethylsilane[12] smoothly captures the 2-phenyl-2-butyl cation generated from racemic 2-phenyl-2-butanol to give an enantiomeric excess (2–3%) of either (*R*)-(−)- or (*S*)-(+)-2-phenylbutane,[13] respectively.

In a typical experiment, 7.5 ml of trifluoroacetic acid was added dropwise with stirring over a 2.5-min interval to a methylene chloride (40 ml) solution of 30.7 mmol of (*R*)-(+)-1-naphthylphenylmethylsilane (88.8% optical purity) and 30.0 mmol of racemic 2-phenyl-2-butanol which was maintained at 0° under a dry nitrogen atmosphere. After 15 min, the reaction mixture was quenched with 20 g of anhydrous potassium carbonate, filtered, and carefully distilled through a 4-in. glass spiral-packed column. The 2-phenylbutane so obtained [82%, bp 77.0–77.5° (31 Torr)] was purified by preparative vpc (0.75 × 80 in. 20% diisodecyl phthalate on Chromosorb P, 120°) and its optical activity was measured. The data for three runs are summarized in Table I.[14]

Table I. Enantiomeric Compositions of 2-Phenylbutanes Obtained from the 2-Phenyl-2-butyl Cation

			2-Phenylbutane product	
Run	Silane	Temp, °C	α^{26}D (*l* 1 dm, neat), deg	Enantiomeric excess,[a] %
1	(*R*)-(+)[b]	0	−0.493 ± 0.010	2.3 ± 0.1, *R*
2	(*R*)-(+)[b]	−30[d]	−0.636 ± 0.011	3.0 ± 0.1, *R*
3	(*S*)-(−)[c]	−15[d]	+0.539 ± 0.016	2.3 ± 0.1, *S*

[a] Corrected for optical purity of starting silane. Based on α^{23}D −24.2° (*l* 1 dm, neat) for maximum rotation of 2-phenylbutane.[13] [b] $[\alpha]^{26.5}$D +30.45 ± 0.11° (*c* 10.9, cyclohexane); optical purity 88.8%.[12a] [c] $[\alpha]^{26}$D −33.61 ± 0.08° (*c* 10.9, cyclohexane); optical purity 98.0%.[12a] [d] ±5°.

It is clear from these data that the (*R*)-(+)-silane preferentially attacks the *si* face of the 2-phenyl-2-butyl cation to give (*R*)-(−)-2-phenylbutane, whereas (*S*)-(−)-silane selectively attacks the *re* face to give (*S*)-(+)-2-phenylbutane.[15] The observed stereoselectivity requires a difference in activation (transition state) free energies of about 25 cal/mol for attack at

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(1) For recent discussions of terms, theory, and examples see: (a) K. R. Hanson, *J. Amer. Chem. Soc.*, **88**, 2731 (1966); (b) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965; (c) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967); (d) R. Bentley, "Molecular Asymmetry in Biology," Vol. 1, Academic Press, New York, N. Y., 1969; (e) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," Prentice-Hall, Englewood Cliffs, N. J., 1971; (f) E. L. Eliel, *J. Chem. Educ.*, **48**, 163 (1971).

(2) See ref 1e, Chapter 5.

(3) D. N. Kursanov, Z. N. Parnes, G. I. Bossova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, 23, 2235 (1967).

(4) Z. N. Parnes, G. A. Khotimskaya, M. Y. Lukina, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **178**, 620 (1968).

(5) D. N. Kursanov and Z. N. Parnes, *Russ. Chem. Rev.*, **38**, 812 (1969).

(6) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, **90**, 2578 (1968).

(7) F. A. Carey and H. S. Tremper, *ibid.*, **91**, 2967 (1969).

(8) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, **34**, 4 (1969).

(9) F. A. Carey and H. S. Tremper, *ibid.*, **36**, 758 (1971).

(10) F. A. Carey and C. L. W. Hsu, *J. Organometal. Chem.*, **19**, 29 (1969).

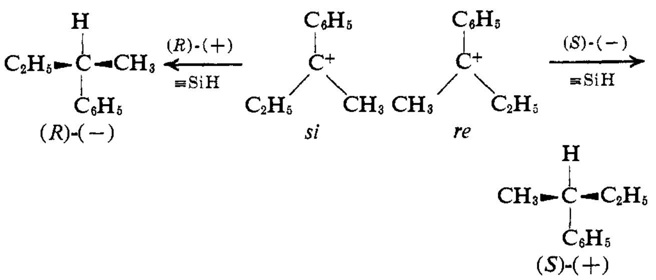
(11) H. S. Tremper, Ph.D. Thesis, University of Virginia, 1969.

(12) (a) L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964); (b) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

(13) D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, **76**, 4516 (1954).

(14) The reaction is essentially complete and quantitative within 1 min after the acid is added. 2-Phenyl-1-butene and the two 2-phenyl-2-butene isomers also are reduced under these conditions to 2-phenylbutane. At higher reaction temperatures the acid-catalyzed cleavage of naphthalene from the silane becomes important; *cf.* R. A. Benkeser and H. R. Krysiak, *ibid.*, **76**, 6353 (1954).

(15) It has recently been reported that optically active 2-phenylbutane (7–8% enantiomeric excess) is produced by homogeneous hydrogenation of 2-phenyl-1-butene in the presence of various chiral rhodium catalysts: L. Horner, H. Siegel, and H. Büthe, *Angew. Chem.*, **80**, 1034 (1968); *Angew. Chem., Int. Ed. Engl.*, **7**, 942 (1968); J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, **93**, 1301 (1971).



the two faces of the cation.[16] Judged on the basis of what is known concerning the nature of the transition states for such hydride transfers,[6,10,11,17] it is difficult to rationalize why the stereoselectivity is in the direction observed if only differences in steric bulk are important. We are continuing our investigations in this area in an effort to determine the factors responsible for the magnitude and direction of this stereoselectivity.

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(16) It should be emphasized that the stereoselectivities reported here are probably *minimum* values. It seems quite likely that under the experimental conditions, especially in the latter stages of reaction, newly formed hydrocarbon might compete with silane for hydride donation—with attendant racemization. See C. D. Nenitzescu in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, pp 463–520.

(17) J. D. Austin and C. Eaborn, *J. Chem. Soc.*, 2279 (1964).

Book Reviews

Jac. Berzelius: His Life and Work. By J. Erik Jorpes (Royal Carolinian Medico-Chirurgical Institute). Translated by Barbara Steele. University of California Press, Berkeley, Calif. 1971. 156 pp. $8.00.

This short, delightful book fills a long-standing gap in the chemical biographical literature. The first edition of this book, which is based on H. G. Söderbaum's 1929–1931 three-volume Berzelius biography, was printed in Sweden in 1966. The present book is the first American edition. American chemists should be grateful that the University of California Press and the translator have made this work available to them.

The book tells the story of that amazing man, Baron Jöns Jacob Berzelius (1779–1848), who discovered cerium, selenium, and thorium in an era when new elements could still be "scraped off the walls." Berzelius' magnificent contributions to chemistry are presented along with much interesting biographical and historical information. The book is impressively illustrated.

This book will provide enjoyable reading for many chemists and chemistry students.

David H. Kenny, *Michigan Technological University*

Quantum Chemistry. Volumes I and II. By I. N. Levine. Allyn and Bacon, Inc., Boston, Mass. 1970. Volume I: x + 591 pp. $14.50. Volume II: xvi + 477 pp. $11.50.

One might well have doubts about the need for yet another quantum chemistry text when the field already boasts half a dozen good ones in print: Eyring, Walter, and Kimball (1944), Kauzmann (1957), and Pilar (1968) to name just three. As implied by the dates of these last three books, the basic subject matter has not changed drastically in the last three decades. However, the unity and freshness of approach of Levine's book do combine to present a good case for it.

Volume I is subtitled "Quantum Mechanics and Molecular Structure." The chapter headings are typical of a quantum chemistry text. This volume covers the postulates and theorems of quantum mechanics, the exactly soluble eigenvalue problems, the essential theories and approximations, molecular symmetry, the virial and electrostatic theorems, and the electronic structure of diatomic and polyatomic molecules.

Volume II, subtitled "Molecular Spectroscopy," is concerned with the application of the material in the first volume. It treats vibration and rotation of diatomic/polyatomic molecules, and nuclear magnetic resonance, with short sections on electronic transitions of diatomics, on nqr, and on esr. The last chapter is a self-contained exposition on group theory and matrices.

This is a carefully written textbook, and is up-to-date in style, contents, and notation. The author integrates brief mathematical interludes into the body of the text as needed, and gives the student direction by considering the goals of the various interludes before embarking upon them. Physical intuition is fully exploited, and different theories and approximations are often applied to one and the same model (*e.g.*, the harmonic oscillator). The mathematical sophistication is approximately equal to that of the other three texts mentioned above. Closing each chapter are some two dozen problems which adequately reflect the material covered; many relate to current interest as well.

A number of figures, particularly in the second volume (*e.g.*, p 168), seem hastily drawn, and some three-dimensional figures are confusingly rendered into two dimensions. It is perhaps more unfortunate that the book had to be divided into two volumes. The last chapter in the first volume, which covers the electronic structure of polyatomic molecules, is also the first chapter in the second volume, ostensibly to strengthen the claim that the second volume is independent of the first. Volume I does indeed stand well alone, but the second volume relies rather more heavily on the first than the author is willing to admit. In this respect, Pilar's book, although somewhat large, was managed in but one volume and costs but $15.50 contrasted with the $26.00 of Levine's volumes.

As to the material he has chosen to cover, Levine is thorough enough, but one would have hoped for greater coverage of the more recent and more promising applications of quantum mechanics. For example, double resonance is restricted to a short paragraph in the chapter on magnetic resonance, and no mention at all is made of photoelectron spectroscopy, although most of the relevant theory is already present in the book.

Taken as a whole, this work complements the other books in its field, and the crucial introductory chapters are better than many.

Kent Lanini, *University of Michigan*

Advances in Macromolecular Chemistry. Volume II. Edited by W. M. Pasika. Academic Press Inc., London and New York. 1970. vii + 267 pp. £5.

In his preface to the first volume, the editor emphasized that reviews were essential for the specialist and nonspecialist because