tions (eq 7) is disproportionation to IPA and acetone via the enol.[10]

The dip in the plot for CHD quenching of **3** and **5** in IPA (not seen in MeOH or CF_3CH_2OH) is tentatively attributed to scavenging by CHD (<0.05 M) of radicals which would otherwise react to some extent with **3** and **5**. At higher [CHD], triplet quenching becomes significant, and normal Stern–Volmer kinetic behavior is observed.

Several points of general significance emerge from this study. (1) Light intensity effects should be important in solution for photochemical reactions involving radical intermediates, especially when chain processes or induced decomposition of reactant is involved.[9] This may be quite general in IPA and related H-donor solvents. (2) Dienes acting as radical traps can efficiently quench photochemical reactions involving radical intermediates by processes other than triplet energy transfer.[8] Radical quenching may indeed be involved in systems where differential quenching of two or more products is observed, heretofore used as evidence for two reactive quenchable triplets.[2k,11] (3) There are increasingly frequent reports of dramatic changes in the course of a photochemical reaction as the wavelength of light is varied.[12] Since I^0 changes drastically as λ varied (often comparison is made between experiments at 254 and 366 nm using different lamps) it is frequently not possible without further study to unequivocally attribute such differences to one or the other factor.

Acknowledgment. Early portions of this research were supported by Grant GP-10828 from the National Science Foundation. We are grateful for this support.

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David I. Schuster,* George Conrad Barile, Kou-chang Liu
Department of Chemistry, New York University
Washington Square, New York, New York 10003

Received March 24, 1975

Direct Evidence for Reversal of Helicity in the Stereoisomerization Mechanism of Bis(β-diketonato)titanium(IV) Complexes

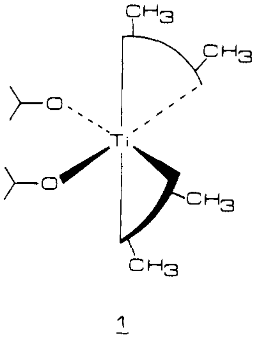
Sir:

In connection with our recent studies of isomerism and isomerization in propeller-like molecules[1] we became aware of a report[2] dealing with studies on static and dynamic stereochemistry of some *cis*-dialkoxybis(acetylacetonate)titanium compounds, in which prochiral groups were introduced as ligands. In particular, Bradley and Holloway[2] observed that "the kinetic parameters for methyl isopropyl group exchange (in **1**) were the same as for methyl (acac group) exchange" and that "at low temperature the α-protons of the neopentyl glycollate group in Ti(acac)$_2$(O-CH$_2$CMe$_2$CH$_2$O) broadened and split into an AB group".

The purpose of this communication is to note that such experiments provide *compelling evidence for reversal of helicity in the stereoisomerization mechanism of such molecules*. The relevance of such a conclusion is borne out in the following.

The cumulative weight of circumstantial evidence so far accumulated has pointed out that dialkoxybis(chelate)titanium compounds[2,3] as well as a large number of structurally related dihalogenobis(β-diketonato) derivatives of group 4 elements[4] adopt a cis octahedral structure. Such structure has C_2 skeletal symmetry point group and thus is chiral. It follows that **1** can be regarded[1d,e] as a two-bladed propeller-shaped molecule, and thus two enantiomeric forms are possible, which differ only in the sense of twist (helicity) of the chelate acetylacetonate rings.[5]

Therefore, when interconversion of the two enantiomeric forms is slow on the NMR time scale the methyl isopropoxy groups in **1**, as well the α-protons of the neopentyl glycol-



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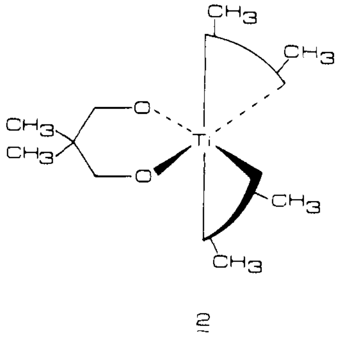

2

late in **2**, reside in diastereomeric environments[6] and thus are expected to give rise to separate signals even under conditions of rapid (on the NMR time scale) rotation or molecular flexibility of these groups.

An immediate consequence of this analysis is that the data indicate that the stereoisomerization mechanism of lowest energy in such propeller-like molecules involves a reversal of helicity of the structure.

In fact, although isomerizations of such complexes have mainly been discussed in terms of nonbond-rupture twist mechanism[4b,4i] which involves a reversal of helicity of the structure, alternative rearrangements in which isomerization is *not* accompanied by a reversal of helicity were not ruled out by the experimental results, since change of helicity was not directly monitored. In particular, use of the group theory has pointed out[4i,7-9] that for octahedral six-coordinate molecules all the possible permutations among the ligands form a group, termed the permutational group (S_6). Use of double cosets allows one to partition this group into five subsets termed modes,[7,9] where a mode is a set of permutations which are either rotationally equivalent or symmetry equivalent.[7] These modes have been designated $\mathbf{M}_0$, $\mathbf{M}_1$, $\mathbf{M}_2$, $\mathbf{M}_3$, $\mathbf{M}_4$ by Musher.[9]

Complete permutational analysis of such bischelate systems[10] indicates that rearrangements by modes $\mathbf{M}_1$, $\mathbf{M}_2$, and $\mathbf{M}_3$ include a reversal of helicity of the structure, whereas modes $\mathbf{M}_0$ and $\mathbf{M}_4$ do not.

Now the finding that the "kinetic parameters for methyl isopropyl group exchange were the same as for methyl (acac group) exchange"[2] provides strong evidence that the rate of enantiomerization of **1** (i.e., the rate of reversal of helicity, monitored by the isopropoxy groups) occurs at the same rate as the position exchange of the diastereotopic acetylacetonate methyl groups. Thus, the reinterpretation of these experimental results evidenciates that only rearrangements by modes $\mathbf{M}_1$, $\mathbf{M}_2$, and $\mathbf{M}_3$ need to be considered as the lowest energy stereoisomerization pathways in such molecules.[11] However, although mode $\mathbf{M}_2$ causes an inversion of helicity (enantiomerization) it is unable of exchanging the diastereotopic acetylacetonate methyl groups.

It should be remarked that similar experiments were already designated by several authors in order to detect change of helicity in propeller-like molecules.[12,13] The similarity between this analysis and the previous one[12] is not accidental but owes its existence to the fact that all these molecules can be regarded as propeller-shaped structures and thus may be analyzed in terms of the same abstract model.[1d,e,12]

NOTE ADDED IN PROOF. After this paper was accepted we became aware of a report in which conclusions along these lines were drawn by the authors.[14].

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Paolo Finocchiaro

Institute of Industrial Chemistry of the University, Viale A Doria, 8, 95125 Catania, Italy

Received January 28, 1975

Book Reviews

Guide to the Literature for the Industrial Microbiologist. Compiled by PETER HAHN. Plenum Publishing Corp., New York, N.Y. 10011. 1973. 206 pp. $25.00.

Microbiological literature is widely scattered through a large number of journals and books. Therefore, this guide will be welcomed enthusiastically by all microbiologists and especially newcomers to a rapidly expanding field. It is divided into four sections. The first is devoted to industrial microbiological textbooks and includes the table of contents of each volume. Section Two is a key to review literature in industrial microbiology containing 1700 citations under 57 subjects. Section Three contains a list of journals and abstract services with the type of information covered in each. Meetings and courses are included in Section Four.

M. C. W. Smith, *Ann Arbor, Michigan*

The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes. By RALPH G. WILKINS (New Mexico State University). Allyn and Bacon, Inc., Boston, Mass. 1974. xii + 403 pp. $17.95.

This book should fill a critical need for a suitable text in an inorganic kinetics course at the graduate level. The author discusses experimental methods in Part A with emphasis on rate law determination, deduction of mechanism, and description of experimental techniques, including relaxation and spectroscopic methods for determination of rates of reaction. The question of how a practicing chemist may benefit from a full arsenal of chemical kinetic methods seems to be foremost in the author's mind. Part B is concerned with results and deals with topics of current interest: substitution reactions, electron transfer reactions, modification of ligand reactivity by complex formation, stereochemical change and, finally, a brief survey of the transition elements. A comprehensive and current (end 1973) list of journal as well as textbook references is provided at the end of each chapter. The sets of problems at the end of each chapter are based on recent publications and have been well selected. A clear and readable account of the subject is presented. In this reviewer's opinion, some additional features, such as the use of ΔG instead of ΔF, determination of thermodynamic parameters from relaxation amplitudes, and mention of improved time resolution with the recent cable discharge temperature jump apparatus, would have been desirable.

In summary, this book can be highly recommended for use as a text in an advanced course in inorganic reaction kinetics.

Ramesh C. Patel, *Clarkson College of Technology*