When stirred in benzene under oxygen the compounds $(Ir(PPh_3)_2(CO)ClX(NO))$ are converted to the nitrato complexes $Ir(PPh_3)_2(CO)ClX(NO_3)$ (**4**), which can be isolated as crystals upon the addition of hexane. These nitrato compounds have ir frequencies[13] at 1520 m, 1250 vs, and 950 cm^{-1} (KBr). There was no ir spectral indication of the formation of nitro or nitrito complexes (vide infra). The nitrosyl complexes, **3**, are gradually air-oxidized even in the solid state to the corresponding nitrates, **4**.

The kinetics of oxygenation of **3** was studied by measuring the change in absorbance in the 380–410-nm region using pseudo-first-order conditions with oxygen at a partial pressure of 619 Torr (8.11×10^{-3} *M*)[14] and the iridium complexes at $5 \pm 2 \times 10^{-4}$ *M*. The kinetic data presented in Table I indicate that the rates of oxygenation decrease with X as I > Br > Cl > NCS > NCO > N_3, which is roughly the order attributable to decreasing electron release by X. If only electronic contributions are important the rate for the N_3 complexes is anomalously low, perhaps as a result of steric contributions from the bulky PPh_3 and the bent $Ir-N_3$ system. It is likely that oxygenation proceeds by electrophilic attack of dioxygen on the NO^- ligand such as has been proposed for reactions of cobalt nitrosyls,[5] followed by rearrangement of the N-coordinated O-N-O-O moiety.

When a dichloromethane solution of **1** was stirred under oxygen for 12 hr, no noticeable reaction was observed. In the presence of pyridine or picoline, reaction of **1** with oxygen was rapid, giving a mixture[15] of nitrato, nitro, and nitrito complexes.

The enhanced oxidation of the NO^- ligand in **1** in the presence of base or X^- has been observed, but reasons for the exclusive nitrato formation in the presence of X^- as contrasted to formation of nitrato, nitrito, and nitro complexes in the presence of pyridine remain to be elucidated. We are continuing studies on the accelerating influence of a sixth ligand on the reactions of five-coordinate nitrosyl complexes with other electrophiles.

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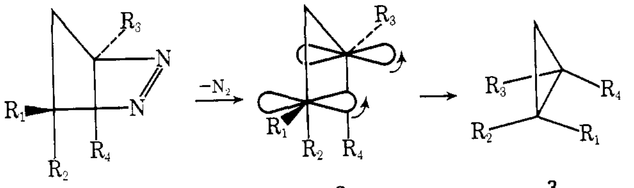
The Synthesis, Absolute Configuration, and Stereochemistry of Thermal Decomposition of (+)-(3*R*,5*R*)- and (+)-(3*R*,5*S*)-3-Ethyl-5-methyl-1-pyrazolines

Sir:

Thermal decomposition of *cis*- and *trans*-3,5-dimethyl-1-pyrazolines (**1C** and **1T**) proceeds with predominant single inversion of stereochemistry.[1] This observation provided the first experimental evidence for the existence of simply substituted π-cyclopropanes or "0,0" diradicals (e.g., **2**), and for their predicted preference for conrotatory closure.[2] However, the requirement that planar intermediate **2** give achiral products has never been adequately tested, because a complete elucidation of the stereochemistry of this reaction via the use of compounds **1C** and **1T** is precluded by the fact that **1C** and **3C** are meso diastereomers and are therefore incapable of exhibiting optical activity even if formed via chiral intermediates. Stimulated by the observation that optically active **1T** does in fact give rise to **3T** having significant optical activity,[3] we have now carried out a study of the thermal decomposition of optically active *cis*- and *trans*-3-ethyl-5-methyl-1-pyrazolines (**4C** and **4T**). This system is not subject to the loss of stereochemical information caused by the existence of meso diastereomers, and it provides results which indicate that the present understanding of the mechanism of 1-pyrazoline thermal decomposition (and perhaps of thermal decomposition in general) will require substantial revision.



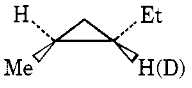
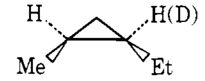
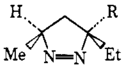
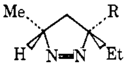
1 **2** **3**

1C and **3T**, $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$
1T and **3C**, $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

Optically active **4C** and **4T** were prepared by methods analogous to those used by Crawford and coworkers[4] and their optical purities and absolute configurations established and then confirmed by the double correlation outlined in Chart I. Absolute configurations and maximum rotations of the cyclopropane products **5C** and **5T** have been previously established.[5] Product distributions from the gas-phase thermal decomposition of **4C** and **4T** (Table I) correlate very closely with those observed[1a] from **1C** and **1T**, suggesting that changing one substituent from CH_3 to CH_2CH_3 has a negligible effect on the decomposition mechanism.

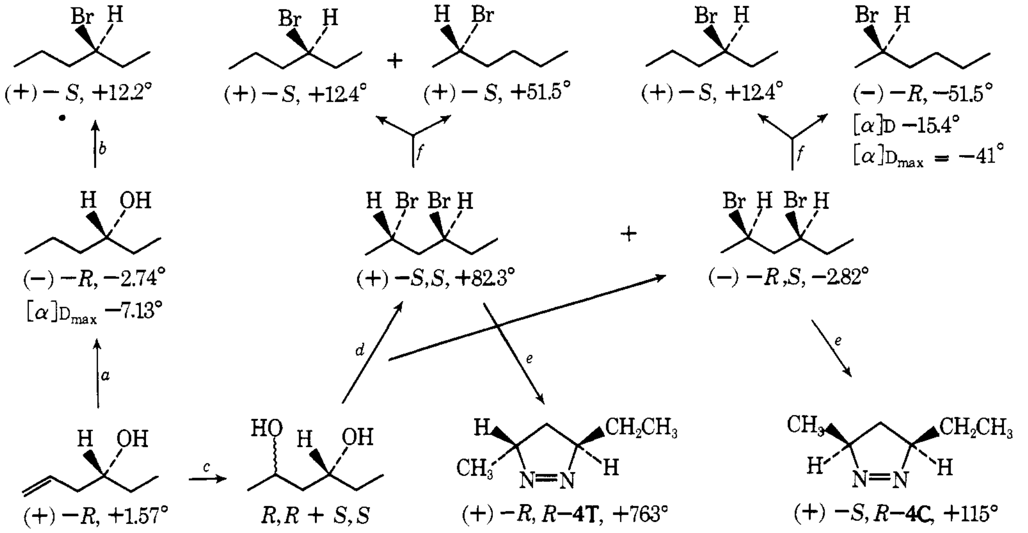
The complete stereochemical results of the decomposition of optically active **4C** and **4T**, corrected to 100% optical pu-

Table I. Per Cent Yields and Absolute Stereochemistry of Cyclopropane Products Formed in the Thermal Decomposition of (+)-(3*R*,5*R*)- and (+)-(3*R*,5*S*)-3-Ethyl-5-methyl-1-pyrazolines at 292° (gas phase, He flow system (atmospheric pressure))

	Products[a]						
	 (+)-**5T**			 (+)-**5C**			
Starting material	% yield	Predom stereochem	% preservn of opt purity	% yield	Predom stereochem	% preservn of opt purity	Olefin, % yield
 (+)-**4C** R = H	65.7	Ethyl rotation	14.2 ± 0.4	32.1	Double retention	36.5 ± 2.9	1.8
R = D	67.6		16.9 ± 0.6	31.1		29.9 ± 1.5	1.3
 (+)-**4T** R = H	27.1	Double inversion	22.5 ± 0.5	70.6	Methyl rotation	0.85 ± 0.02	1.9
R = D	28.6		23.8 ± 1.2	68.6		0.87 ± 0.03	2.6

[a] Product percentages determined by vapor phase chromatography (Hewlett Packard 5750) using digital integration (Autolabs System I). Optical rotations were taken in solution at five wavelengths between 589 and 365 nm using a Perkin-Elmer 141 digital polarimeter.

Chart I



[a] H_2–Pt–EtOAc. [b] 1. TsCl–pyridine; 2. LiBr–acetone (1 hr, 25°). [c] 1. $Hg(OAc)_2$–THF, H_2O; 2. $NaBH_4$, OH^-. [d] Ph_3PBr_2–CH_3CN; dibromides separated by preparative VPC. [e] 1. NH_2NH_2–EtOH; 2. HgO–pentane. [f] (*n*-Bu)$_3$SnH–2,6,10,14-tetramethylpentadecane. All rotations listed were taken at λ 365 nm in $CHCl_3$, except: pyrazoline rotations, λ 365 nm in *n*-heptane; 3-hexanol, λ 589 nm, neat.

rity, are summarized in Table I. We find that the stereochemistry of decomposition of **4T** parallels that of **1T** very closely;[3] **5C** is produced in nearly racemic form and **5T** is produced with 22.5% retention of optical purity and is predominantly doubly inverted. *Decomposition of* **4C**, *however, gives* **5T** *with 14.2% optical purity* (*predominant single inversion at the ethyl-bearing carbon*) *and* **5C** *with 36.5% retention of optical purity and predominant double retention of configuration.* Compounds **4C** and **4T**, optically active and labeled with deuterium only at the ethyl-bearing carbon, were also prepared and subjected to gas-phase thermal decomposition. As Table I shows, an isotope effect of approximately 10% *on the optical purities of the products* formed from **4C** is observed. Although a shortage of material (and smaller rotation in the case of **5C**) makes the inherent error in the **4T** decomposition somewhat higher, the data suggest that a real (but somewhat smaller) isotope effect on the optical purities of **5C** and **5T** formed from **4T** is observed also.

The surprisingly large fraction of optically active product formed from **4C** shows that the percentage of product which *must* have been formed from chiral intermediates (by pathways which avoid planar 0,0-diradical **2**) in 3,5-dialkylpyrazoline decompositions has previously been underestimated. The observation of an isotope effect on the optical purities of **5C** and **5T** supports this conclusion. It may be possible to construct mixed mechanisms in which 0,0-diradicals are the source of the achiral part of these product distributions and some other type of pathway accounts for the chiral part. This seems to us unlikely, however, in view of the fact that **5C** should decompose most easily from the "envelope" conformation assumed[1a] to be the source of 0,0-diradicals, yet it is this isomer that gives the larger proportion of optically active product. We conclude that none of the previously considered mechanisms[1a,c,7] for pyrazoline decomposition provides, in itself, a satisfactory means of accounting for the unusual product distributions calculated from the data in Table I. Consideration of Inagaki and Fukui's suggestion[8] that N_2 may be extruded from pyrazolines in "nonlinear"[9] fashion, and Salem and Goddard's prediction that pyramidal (i.e., "canted"[2f] or "crabbed"[2c]) biradicals may be important intermediates in these reactions, may provide some insight into the data. However, mechanisms generated using these hypotheses must at present be considered speculative and discussion of them is best deferred to a full paper. It is also possible (as Freeman, Pucci, and Binsch have suggested[10]) that a true understanding of these reactions will be obtained only after theoretical information on their energy surfaces *and* reaction dynamics becomes available.[11]

Acknowledgments. We are grateful to the National Science Foundation and Chevron Research Corporation for financial support of this work.

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*Book Reviews**

A Biographical Dictionary of Scientists. Second Edition. Edited by T. I. WILLIAMS. Wiley/Halsted, New York, N.Y. 1975. xv + 641 pp. $7.95.

Short biographies, averaging about half a page each, of over a thousand dead scientists and technologists make up the content of this interesting book. The biographies are discursive and eminently readable, such that the book is a pleasure to browse in. The period covered starts with Ancient Greece, and reaches as close to the present as Sir Robert Watson-Watt, pioneer developer of radar, who died in December 1973. Chemists are strongly represented. The editor could not reasonably be expected to avoid being somewhat subjective as to whom to include and to omit, and his choosing was obviously not easy, nor could his choice please everyone. Nevertheless it is unfortunate that Johan von Goethe, who was a great scientist as well as poet, and who originated the concept of morphology in biology, was overlooked. The inclusion of Ferdinand de Lesseps, the diplomat who successfully promoted the construction of the Suez Canal, also seems odd.

A 32-page chronological list of births and deaths is an interesting and useful appendix, and an innovation over the first edition.

Blastfurnace and Steel Slag. Production, Properties, and Uses. By A. R. LEE (The British Quarrying and Slag Federation Ltd.). Wiley/Halsted, New York, N.Y. 1975. ix + 119 pp. $11.75.

This little book is a lucid survey of a major industrial by-product whose annual production is about one hundred million tons. The presentation is technologically oriented but is suitable for the informed layman as well as the casual chemist, owing to the fact that the author carefully introduces each topic from a basic level and defines all terms. There are many illustrations, figures, references, and tables, including, oddly enough, one of conversion factors from British to metric units.

Chemical Process Economics. Second Edition. By JOHN HAPPEL and DONALD G. JORDAN. Marcel Dekker Inc., New York, N.Y. 1975. xii + 511 pp. $19.75.

The original 1958 edition of this book has been both revised and expanded to take into account the great changes that have occurred in the chemical industry since then. It is a textbook of economics to teach fourth-year students how to apply technical information to economic design and operation of chemical plants.

Colour 73. Edited by R. W. G. HUNT. Wiley/Halsted, New York, N.Y. 1974. xviii + 566 pp. $39.95.

This volume contains the survey lectures and the abstracts of the papers presented at the Second Congress of the International Colour Association, held at the University of York in 1973. The emphasis of the Congress was on color vision and on applications of color in printing, textiles, ceramics, etc. Chemistry was only a very peripheral concern and was most evident in the papers on colorimetry. The frontispiece is a portrait in black and white honoring the late Deane B. Judd of the Bureau of Standards.

Heat Exchangers: Design and Theory Sourcebook. Edited by N. H. AFGAN and E. U. SCHLUNDER. McGraw-Hill Book Co., New York, N.Y. 1974. xvi + 893 pp. $39.50.

The International Centre for Heat and Mass Transfer devoted its Fifth Seminar to heat exchangers and invited 58 contributors representing academic and government institutions and industries. The index of only 2¼ pages is inadequate for a book intended to be a "source book", and it is a pity that the eighteen blank pages headed "Design and Calculation Work Notes" were not devoted to a more substantial index.

Heat Transfer in Flames. Edited by N. H. AFGAN and J. M. BEER. Wiley/Halsted, New York, N.Y. 1974. viii + 502 pp. $28.50.

This book is a collection of selected papers from the 1973 seminar of the International Centre for Heat and Mass Transfer. The 34 papers are grouped under five headings: Method of Calculation; Radiative Properties; Experimental Methods; Heat Transfer in Unsteady Confined Flames; and Open-Flame Heat Transfer. The orientation is technological and applied, but there is much to interest the physical chemist concerned with combustion. Flames in internal combustion engines are the subject of several papers, an area of obvious importance to the chemist who must deal with engine emissions, pollution, and fuel efficiency.

The index, which amounts to less than one page, is absurd.

Hydrogen Energy. Edited by T. N. VEZIROĞLU (Clean Energy

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* Unsigned book reviews are by the Book Review Editor.