

the other solvents. While the polar structure II should become more important with increasing dielectric constant of the solvent, the solvent effects observed in this study cannot be explained satisfactorily on this basis if one notes the marked deviations from any such trend in Table I. It seems more likely that the predominant effect is that of hydrogen bonding which can be represented by an increased importance of structure III in the valence-bond description. This interpretation is supported by the fact that intramolecular hydrogen bonding in methyl salicylate and related compounds has been shown to cause a downfield shift of about 3 to 8 p.p.m.<sup>5,17</sup> However, dielectric favoring of structure II and Lewis base interaction represented by structure IV most likely contribute to these solvent shifts and are probably primarily responsible for the 3.1-p.p.m. range in solvent shift between cyclohexane and N,N-dimethylformamide. The question of the relative importance of the various solvent-solute interactions in determining the solvent effects will be discussed more completely in future publications dealing with other carbonyl compounds as well as different classes of solute substances.

(17) G. E. Maciel and G. B. Savitsky, unpublished results.

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### Photoisomerization of Pyrazolenines and Formation of 7,7-Dimethylbicyclo[4.1.0]heptene- $\Delta$ -1,6<sup>1</sup>

Sir.

Recently, we reported the preparation of some alkylpyrazolenines and their photolysis to cyclopropenes.<sup>2</sup> We now wish to communicate a photoisomerization of pyrazolenines and a remarkable solvent dependence of this reaction. In addition, we have prepared the unusually strained 7,7-dimethylbicyclo[4.1.0]heptene- $\Delta$ -1,6 (IIb) and have found it a highly labile compound.

Photolysis<sup>3</sup> of pyrazolenine Ia in pentane at 13° gave the stable cyclopropene derivative IIa in high yield.<sup>2</sup> However, on irradiating a solution of Ia in methylene chloride at -60° no nitrogen was evolved. Under these conditions, Ia was isomerized quantitatively to a labile compound, which we believe to have the tricyclic structure IVa. The n.m.r. spectrum of the photoisomer IVa (singlets at  $\delta$ , from tetramethylsilane, 1.10 and 1.38 p.p.m. and multiplets centered around 1.6 and 2.3 p.p.m., in methylene chloride at -60°, relative intensities 3:3:8:2) indicates nonequivalent methyl groups attached to saturated carbon. This, together with the occurrence of a band in the infrared at 1604

cm.<sup>-1</sup> (—C=N—), and, most significant, the spontaneous reversal of the photoisomerization upon warming to 0°, strongly support the structure assignment.

Photolysis of pyrazolenine Ib in methylene chloride at -60° yielded the photoisomer IVb (n.m.r. CH<sub>2</sub>Cl<sub>2</sub>, -60°, singlets at  $\delta$  1.08 and 1.35 p.p.m., unresolved multiplet between 1.6 and 2.3 p.p.m., relative intensities ~3:3:8; infrared 1608 cm.<sup>-1</sup>) which on warming to 0° converted back to Ib. Irradiation in pentane at -60° led to loss of nitrogen (70% of calcd.). The isolation of 7,7-dimethylnorcarane (V) from the hydrogenated (-40°) reaction mixture<sup>4</sup> is taken as evidence for the

(1) This work was supported by NSF Grants NSF-G19927 and NSF-GP-1027.

(2) G. L. Closs and W. Böll, *Angew. Chem.*, **75**, 640 (1963); *Intern. Ed.*, **2**, 399 (1963).

(3) All irradiations reported here were carried out with a Hanovia type A lamp, using Pyrex reaction vessels.

(4) For comparison V was synthesized independently by pyrolysis of the corresponding pyrazoline.

TABLE I  
SOLVENT DEPENDENCE OF PRODUCT DISTRIBUTION  
ON PHOTOLYSIS OF Ib

Solvent	Temp., °C.	Product distrib. <sup>a,b</sup>	
		% IIb	% IVb
n-Pentane	-60	70 <sup>c</sup>	30 <sup>c</sup>
Cyclopropane	-60	70	30
Butadiene	-57	40	60
Monoglyme	-59	25	75
Tetramethylsilane	-55	5	95
Methylene chloride	-60	0	100
Methanol	-58	0	100

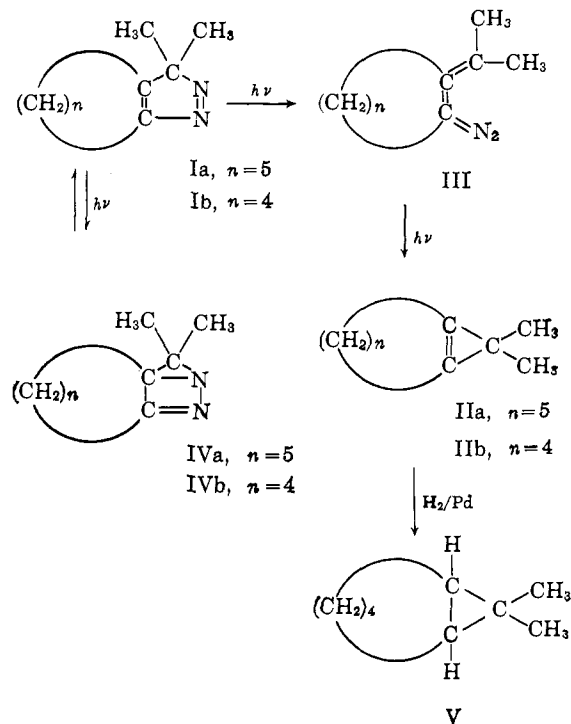
<sup>a</sup> Determined from integrated intensities of methyl resonances in n.m.r. spectra. <sup>b</sup> Probable accuracy not better than  $\pm 5\%$ . <sup>c</sup> Determined from volume of nitrogen evolution.

formation of cyclopropene derivative IIb under these conditions. The n.m.r. spectrum of IIb, obtained on an irradiated solution of Ib in cyclopropane, at -60° (singlet at  $\delta$  1.21 p.p.m., multiplets centered at 1.7 and 2.3 p.p.m., relative intensities ~6:4:4), confirms the structure assignment.<sup>5</sup> At temperatures above -20° IIb dimerizes rapidly to give a mixture of hydrocarbons with as yet undetermined structures.

The low stability of IIb can be attributed to the additional bond angle deformation imposed on the cyclopropene system by the tetramethylene chain. The exocyclic bond angle



ca. 150° in monocyclic cyclopropenes, will be considerably decreased in the fused ring system. The resulting diminished overlap of the orbitals forming the "bent" cyclopropene single bonds (C<sub>1</sub>-C<sub>7</sub> and C<sub>6</sub>-C<sub>7</sub>) will be responsible for the enhanced reactivity of IIb.<sup>6</sup>



(5) The spectrum obtained this way was a superposition of the spectra of 30% of IVb and 70% of IIb. The spectrum given here is that obtained after subtracting the resonances of IVb.

(6) R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963), reported the failure to obtain cyclohexenocyclopropene by a modified Favorskii reaction, which has been shown to give less strained cyclopropenes in high yields. Their conclusion, that this failure might be

The strong solvent dependence of the photoreactions of pyrazolenines is indicated in Table I. It is apparent that solvents of low dielectric constant direct the partition of the photoexcited state in favor of cyclopropene formation. Experiments are in progress to determine whether the different pathways involve excited states of different multiplicities.

Finally it should be pointed out that the conversion of pyrazolenines to cyclopropenes might well be a two-quantum process, in which the first step is the formation of diazoalkene III. Supporting this hypothesis is due to the instability of the desired compound, receives strong support from our observations on IIb.

the observation of an induction period in nitrogen evolution and the buildup of a steady-state concentration of III as evidenced by the development of a strong red color of the photolysis solutions. The light-induced conversion of III to II finds its analogy in previously reported examples of cyclopropene formation from diazoalkenes.<sup>7</sup>

- (7) G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).  
 (8) A. P. Sloan Foundation Fellow.

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## BOOK REVIEWS

**Inorganic Thermogravimetric Analysis, Second and Revised Edition.** By CLÉMENT DUVAL, Directeur de Recherche au C.N.R.S., Directeur du Laboratoire de Recherches Micro-analytiques (E.N.S.C., Paris), President du Groupe de Chimie analytique. Translated from the French manuscript by RALPHE E. OESPER, Ph.D., Professor Emeritus of Analytical Chemistry, University of Cincinnati. American Elsevier Publishing Company, Inc., 52 Vanderbilt Avenue, New York 17, N. Y. 1963. 16 × 23 cm. xv + 722 pp. Price, \$22.00.

The second and revised edition of this book covers a wider range of topics than its title implies, but as the author states in the preface the word *analytical* has been retained because up to now analytical chemistry has profited most from the recent progress in thermogravimetry. In addition to applications in analytical chemistry, the book deals with "kinetic studies, investigations of catalysis, reactions in the solid state, and studies of the behavior of standard materials for titrant solutions, and also of various substances which are not employed in analysis."

The book is divided into two parts: Part I (The Thermobalances), 162 pp., and Part II (The Thermolysis Curves), 521 pp. There are five chapters in Part I; they deal with the topics: a brief historical review, deflection type thermobalances, null type thermobalances, applications of the thermobalances, and precautions to be taken in the use of the thermobalance. Since the first edition was issued (1953), three world-renowned scientists have died: Honda (in 1954), and Guichard and Chevenard (in 1960). Appropriately, a photograph and short biographical sketch of each of these pioneers in thermogravimetry are included in the first chapter. As an appendix to Part I, the author gives an extensive table (15 pages) bringing together the methods which he suggests for automatic inorganic analysis (plutonium and americium excepted).

Chapters 6 to 84 are covered in Part II, a chapter being devoted to compounds or ions of each of the following 78 elements listed in the order of their atomic number: lithium, beryllium, boron, carbon, nitrogen, fluorine, sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, iodine, cesium, barium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, thallium, lead, bismuth, thorium, uranium, plutonium, and americium. The closing chapter is devoted to studies in organic chemistry and briefly discusses the results obtained with a number of purely organic compounds closely linked with inorganic analysis.

An idea of the rapid growth of thermogravimetry is gained by the fact that by January 1, 1961, there were 52 models of thermobalances, 10 of these being available from dealers throughout the world. The extensive and thorough coverage of the literature is indicated by the author's statement that he had read 2200 papers in periodicals from all quarters of the globe or, in more precise terms, had regularly consulted the leading analytical journals and abstracts through 1960, which he has listed in the preface.

The book concludes with author and subject indexes. Printing, paper, and cloth binding are of good quality.

It has been a special pleasure to review this book because of my close association with Professor Duval for some twelve years as a member of the IUPAC Commission on New Analytical Reagents. He is to be congratulated and thanked for this useful and up-to-

date treatise on thermogravimetry. A word of appreciation is also due the translator for making the French manuscript available in English.

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**Research in Surface Forces.** Edited by B. V. DERYAGIN. Authorized translation from the Russian. Consultants Bureau Enterprises, Inc., 227 W. 17th St., New York 11, N. Y. 1963. 190 pp. 21.5 × 27.5 cm. Price, \$27.50.

This monograph is a jubilee number commemorating "the twenty-fifth anniversary of the organization of the Laboratory of Surface Phenomena of the Institute of Physical Chemistry of the Academy of Sciences of the USSR, March, 1960. The organizer and permanent director of this laboratory is B. V. Deryagin, Corresponding Member of the Academy of Sciences of the USSR. The original staff of three—B. V. Deryagin, M. M. Kusakov, and V. P. Lazarev—was augmented somewhat later by the addition of L. S. Lebedeva (1936), N. N. Zakhavaeva (1937), and A. S. Titievskaya (1938)."

Fortunately, all of the contributions have been translated. The first one comprises a comprehensive review of the first 25 years in the Laboratory of Surface Phenomena. It is particularly useful to American readers in that the testing of the principal discoveries since 1935, their importance to science, and the names of the workers involved are set forth in clear, readable style by N. N. Zakhavaeva. It is helpful for an understanding of the papers that follow to have the evolution of the researches of this Institute so clearly depicted with the particular contributions of each of the authors set forth.

These six pages of historical review ends with the statement: "An extensive effort has been made to popularize the work of the Laboratory. More than 600 journal articles have been written since the Laboratory was founded; the staff has actively participated in various conferences and discussions (more than 100, many abroad) and carried out innumerable consultations. A colloquium functions regularly in the Laboratory and attracts numerous scientific workers from other institutions and representatives of industry. Representatives of other institutions have defended their dissertations under the direction of, or in consultation with, the Laboratory staff. The fact that the work of the Laboratory has embraced so extensive a field of surface phenomena is reflected in the title, Laboratory of Surface Phenomena, which it has carried since 1953.

"Thus, twenty-five years have seen a great change, from a laboratory engaged in the study of the properties of thin polymolecular liquid films to an extensive laboratory working with a wide range of surface effects."

The breadth and depth of the contributions of this volume can be seen from the following titles:

- Twenty-five Years in the Laboratory of Surface Phenomena of the Institute of Physical Chemistry of the Academy of Sciences of the USSR by N. N. Zakhavaeva
- Surface Forces and Their Effect on the Properties of Heterogeneous Systems by B. V. Deryagin
- A Study of the State of Connate Water in Oil Reservoirs by M. M. Kusakov and L. I. Mekenitskaya
- The General Theory of Type II Capillary Effects by L. M. Shcherbakov
- Diffusional Surface Forces in the Neighborhood of a Liquid Interface by S. S. Dukhin