

While our results confirm the theory within the experimental error, the results of Powles and Mosley⁴ on solutions of potassium biphenylide are only in rough agreement with the theoretical predictions. The exchange frequency they estimate at -62° in tetrahydrofuran gives a second-order rate constant for spin exchange about ten times larger than our value at -60° in the same solvent. Although the two systems differ in the anion, this cannot account for such a large discrepancy. It seems probable that their solutions of potassium biphenylide contained substantial amounts of unreduced hydrocarbon. Such solutions would give apparently high values for exchange rates because of the contribution of electron exchange between free radical and parent hydrocarbon.

Acknowledgment.—We gratefully acknowledge the support of this work by the National Science Foundation.

(4) J. G. Powles and M. H. Mosley, *Proc. Phys. Soc. (London)*, **78**, 370 (1961).

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Derivatives of 3H-Azepine¹

Sir:

Despite the fact that the introduction of hetero atoms into the tropylium ion π -lattice is predicted to lower the energy of the resulting species and render it highly susceptible to oxidation,² effort in many laboratories continues to be directed to eventual syntheses of azepine (I, X = NH), oxepine (I, X = O), and thiepine (I, X = S).

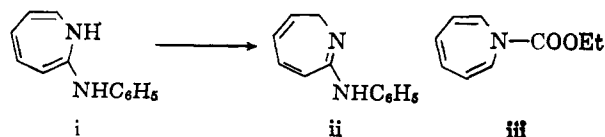
Recent reports in the area of azepine chemistry^{3,4} prompt us to report a ready synthesis of derivatives of 3H-azepine.

A remarkable ring expansion of 2,6-dialkyl- and 2,4,6-trialkylphenols to 1,3-dihydro-2H-azepin-2-ones was recently reported from this Laboratory.⁵ We have now found that the dihydroazepinones react readily with triethyloxonium fluoroborate⁶ to afford 2-ethoxy-3H-azepines. For example, reaction of 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-one (II) with triethyloxonium fluoroborate in methylene chloride solution at room temperature gave a very good yield of 2-ethoxy-3,5,7-trimethyl-3H-azepine (IIIa). The structure of IIIa follows from its analysis,⁷ its infrared spectrum which shows the absence of the amide absorption patterns associated with II, and its ultraviolet [$\lambda_{\max}^{\text{EtOH}}$ 257 μ (6300)] and n.m.r. spectra.⁸ The n.m.r. spec-

(1) Dihydroazepinone Chemistry. VII. For paper VI of this series, see L. A. Paquette, *J. Am. Chem. Soc.*, in press.

(2) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 280-281.

(3) R. Huisgen and M. Appl [*Ber.*, **91**, 12 (1958)] have postulated the aminoazepine (i) as an intermediate in the decomposition of phenyl azide in aniline; if formed, it tautomerizes rapidly to the more stable 7H-azepine (ii).

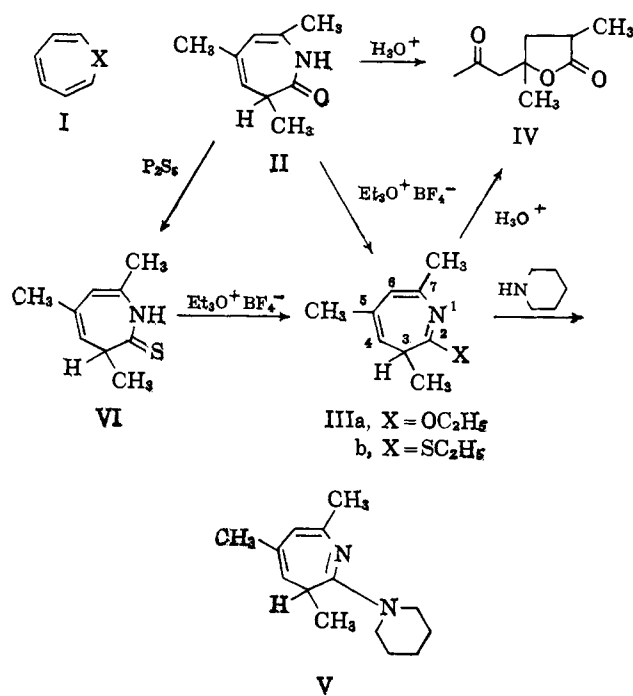


(4) K. Hafner and C. Koenig [*Angew. Chem.*, **75**, 89 (1963)] and W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr. [*J. Am. Chem. Soc.*, **85**, 1200 (1963)] have shown that generation of carbethoxynitrene in the presence of benzene affords *N*-carbethoxyazepine (iii), which readily isomerizes to phenylurethane.

(5) L. A. Paquette, *J. Am. Chem. Soc.*, **84**, 4987 (1962); **85**, 3288 (1963).

(6) H. Meerwein, *et al.*, *J. prakt. chem.*, **147**, 257 (1937); **154**, 83 (1939).

(7) All new compounds reported herein have satisfactory carbon, hydrogen, and nitrogen elemental analyses.



trum is in full agreement with the proposed structure (IIIa); a broad singlet at 345 c.p.s. was assigned to the proton at position 6, a doublet centered at 282 c.p.s. ($J = 5$ c.p.s.) to the proton at position 4, and a 5-line pattern centered at approximately 120 c.p.s.⁹ to the ring proton at 3. In addition, the absorption peaks of the various methyl groups were located at 123 (singlet, 7-methyl), at 109 (triplet, $J = 1.5$ c.p.s., 5-methyl), at 82.5 (doublet, $J = 7$ c.p.s., 3-methyl), and at 73 c.p.s. (triplet, $J = 7.5$ c.p.s., CH_3 of the ethoxy moiety). The interesting aspect of this spectrum was the appearance of the methylene portion of the ethoxy group as an AB system, indicating restricted rotation of this grouping. This complex system of four mutually overlapping quartets was centered at 245 c.p.s.

Acid hydrolysis of IIIa proceeded rapidly to give the keto-lactone (IV), identical in all respects with the product arising from acid hydrolysis of II.⁵ Therefore, a rearrangement of the carbon skeleton of II can be precluded in the triethyloxonium fluoroborate reaction.

The 3H-azepine (IIIa) is a remarkably stable substance under normal conditions and has been stored for prolonged periods at room temperature without apparent change. In addition, IIIa surprisingly can be recovered in excellent yield after heating with excess methyl iodide at 100° for 7 hr. in a sealed tube. Prolonged heating (5 days) of IIIa in refluxing excess piperidine afforded 58% recovery of IIIa and a 72% yield (based on recovered 3H-azepine) of 2-piperidino-3,5,7-trimethyl-3H-azepine (V), characterized as its perchlorate salt, m.p. $156-157^\circ$.⁷ Thus, IIIa is capable of nucleophilic substitution.

We have also found that II could be converted to its thio analog, 1,3-dihydro-3,5,7-trimethyl-2H-azepin-2-thione (VI), m.p. $136.5-137^\circ$,⁷ in good yield with phosphorus pentasulfide in refluxing pyridine. Similar reaction of VI with triethyloxonium fluoroborate gave a good yield of 2-ethylthio-3,5,7-trimethyl-3H-azepine (IIIb), b.p. 76° (0.25 mm.).⁷ The n.m.r. spectrum of this material was very similar to that of IIIa, with the

(8) All n.m.r. spectra herein discussed were obtained on a Varian A-60 spectrometer in dilute deuteriochloroform solutions, using tetramethylsilane as internal reference (TMS = 0).

(9) This absorption pattern is complicated because of the overlapping absorptions of the methyl groups at positions 5 and 7.

exception of the methylene portion of the ethylthio grouping which now appeared as a simple quartet centered at 173 c.p.s. ($J = 8$ c.p.s.). The increased van der Waals radius of the sulfur atom now permits free rotation of this grouping which was restricted in the oxygen analog.

Preliminary attempts to desulfurize IIIb with various

Raney nickel reagents have not yet afforded an unsubstituted 3H-azepine.

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BOOK REVIEWS

Comparative Biochemistry, A Comprehensive Treatise. Volume V. Constituents of Life, Part C. By MARCEL FLORKIN and HOWARD S. MASON. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1963. 637 pp. 16 × 24 cm. Price, \$20.00; subscription price, \$18.50.

Volume V of this ambitious work contains six chapters which treat, respectively, of the amino acids, inorganic nitrogen compounds, organic acids, collagen, photosynthesis, and the halides as components of biological systems. Of the authors of these chapters, five are French, three Japanese, two German, one Dutch, and one American. As a result, the treatment of the several topics is decidedly international in flavor and there is no overemphasis upon American accomplishments. The bibliographies attached to each chapter are extensive, and references to little-known journals are by no means uncommon.

Except for the chapter on photosynthesis which deals exclusively with plants, and that on collagen which deals only with animals, the authors have considered the biochemical relationships of the substances they discuss over the entire field of biology. Since a great deal has been done with unicellular organisms in recent years, considerable space is devoted to them.

In the chapter on amino acids, the discussion of the twenty-two which are the common products of the hydrolysis of proteins is somewhat perfunctory and contains far too many erroneous or misleading statements. Students should not be directed to this chapter for information regarding these substances. The subject is more thoroughly and authoritatively treated in many current textbooks. However, the remainder of the chapter is valuable. It gives references to and brief discussions of no less than ninety-six amino acids that have been found in recent years either free or combined in various plants and animals, and is of great interest to anyone concerned with this somewhat esoteric field. The key references are here, and one can easily, with this information as a start, acquire all that is known today regarding such curiosities as albizziine and alline should he feel so inclined.

The three Japanese authors of the chapter on the distribution and metabolism of inorganic nitrogen compounds have prepared a thorough and authoritative review of the subject. The emphasis is naturally upon plants, especially microorganisms, since only a few single-celled organisms have the capacity to fix molecular nitrogen, and much that has been learned about the reduction of nitrate in nature has been acquired from the study of these lower forms.

The chapter on organic acid metabolism is concerned mainly with the many enzyme-catalyzed reactions which these substances undergo, and the way these reactions are linked in the metabolism of both animals and plants. The several discussions are brief, but this chapter would afford quick information concerning these reactions and is a good place to obtain the fundamental references.

The chapter on collagen is short but thorough, and is illustrated with reproductions of many beautiful electron micrographs of fibers showing details of their structure.

The longest chapter is that on photosynthesis. With its bibliography, it runs to 145 pages. Its author points out that he has of necessity restricted himself to only parts of the story, and has selected those parts that he regards as "rather closed" in the sense that this much at least seems to be securely known. He adds that a comprehensive treatment of the subject has needed upward of two thousand pages in each of two recent treatises. The outcome of his approach is an excellent discussion of the present position in this vitally important but extremely complex field. The few pages devoted to the controversial subject of the quantum yield of photosynthesis are outstanding for their measured and critical judgment.

The final chapter on halides deals briefly with the distribution in nature of chlorine, bromine, and iodine in both ionized form

and in organic compounds. A great deal of unusual information is included.

We come now to an appraisal of the book as a whole. Although well printed, the proof-reading and, occasionally, the editing leave something to be desired. The book is heavy to hold, and the binding broke during the reviewer's reading. One wonders also about the audience that this volume, as the fifth in a projected series of seven, is designed to reach. The price of the five volumes that have appeared is over one hundred dollars even by advance subscription, so that few individuals are likely to buy, the incomes of graduate students and professors being what they are in most cases. The matter then reduces to the question whether the set is essential in the department library as a reference and for assigned reading. The answer to this question must be sought by the heads of interested departments.

THE CONNECTICUT AGRICULTURAL
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Nouveau Traité de Chimie Minérale. Professeur M. HAISSINSKY avec la collaboration de M. P. FAUGERAS, Mlle. C. FERRADINI, M. H. FRANCOIS, Mlle. M. HEUBERGER, Mme. M. PAGES, M. R. PLASCARD, and Mme. C. PEREBASKINE-COURTEVILLE. Published under the direction of Paul Pascal, Masson et Cie., 120 Boulevard Saint-Germain, Paris VI, France. 1962. L + 1090 pp. 17 × 26 cm. Broché, 180 NF., cartonne toilé, 192 NF.

Section III of Volume XV of the monumental "Nouveau Traité de Chimie Minérale" is entitled "Transuraniens," but about one-hundred seventy pages are devoted to nuclear and radiochemistry and sixty to a discussion of various aspects of the problem of contamination of the atmosphere by artificial and natural radioactivity.

Because of the large number of individual subjects which are covered in these portions of the book, the treatment of each necessarily is largely qualitative and superficial.

To illustrate, about two-hundred words are devoted to the effects of radiation in accelerating phase changes in solids, about two-hundred fifty to the Bohr-Mottelson collective model of the nucleus, a page to photonuclear reactions, and so on.

Students approaching the field of nuclear chemistry for the first time no doubt will be fascinated by the many facets of the subject which are revealed by Professor Haissinsky's survey.

The bulk of the book is devoted to the physical and chemical properties of the transuranium elements. Here the coverage is comprehensive, the organization logical, and the treatment highly lucid. The literature has been thoroughly examined up through 1960, and two addenda dealing with the discovery of lawrencium and with the properties of the transuranium metals, respectively, include work published in 1961.

No other single volume now available compares with this in comprehensiveness of coverage of published data on the chemical, metallurgical, and physical properties of the transuranium elements.

One notes that more than five hundred pages are devoted to plutonium alone, as compared with less than one hundred in Katz and Seaborg's "The Actinide Elements."

One can only feel grateful to Professor Haissinsky and his collaborators for their heroic effort in compiling and correlating so much information.

It is not to be expected that such a vast amount of data could be transcribed without error, but in fact such errors are surprisingly few. Of course, any reader seriously interested in using a datum from this or similar compilations should check the original source.

For a number of years Professor Haissinsky has been a vigorous and consistent opponent of the actinide concept of the heavy