

num catalyst, barium hydroxide and then formic acid-formaldehyde into the crystalline α -methyl glycoside of amosamine VI, identical with the natural product by mixture melting point determination and examination of the infrared spectra, which were superimposable. Hydrolysis of the α -methyl glycoside gave the free sugar, 4,6-dideoxy-4-dimethylamino-D-glucose (VII), which traveled with the same R_f values as amosamine upon paper chromatography in a pyridine-ethyl acetate-water (5:12:4) system and in a pyridine-ethyl acetate-acetic acid-water (5:5:3:1) system. The free sugar VII was converted to theitol VIII using sodium borohydride. The crystalline itol hydrochloride was identical with the natural derivative as shown by mixture melting point determination and paper chromatographic comparisons.

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BASE-CATALYZED ISOMERIZATION OF MEDIUM RING DIENES AND TRIENES¹

Sir:

The observation that dimethyl sulfoxide enhances the base strength of potassium *t*-butoxide has led to rather extensive use of this system for carbanion reactions.² Noteworthy applications are the recently described isomerization of 2-methyl-1-pentene³ and the study of *endo* \rightleftharpoons *exo* kinetics with alkylidenecycloalkanes.⁴ While these studies dealt primarily with isomerization rates, equilibrium compositions appeared to be in qualitative agreement⁴ with data available from other investigations. The present investigation was in fact initiated on the premise that product ratios would reflect relative thermodynamic stabilities of the isomers.

The thermal isomerization of allenes to mixtures of acetylenes and 1,3-dienes is well known.⁵ More recently, 1,2-cyclodecadiene was reported to undergo isomerization to 1,3- and 1,4-cyclodecadiene when heated at 190° in diethyl carbitol containing potassium hydroxide.⁶

(1) The authors are indebted to the Robert A. Welch Foundation for the financial support of this study. Generous quantities of cyclooctene, 1,3-cyclooctadiene and 1,5-cyclooctadiene were kindly provided by the Petrochemical Research Laboratory, Cities Service Research and Development Co., Lake Charles, La.

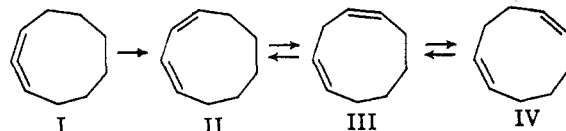
(2) D. J. Cram, B. Rickborn and G. R. Knox, *J. Am. Chem. Soc.*, **82**, 6412 (1960).

(3) A. Schriesheim and C. A. Rowe, Jr., *ibid.*, **84**, 3160 (1962).

(4) A. Schriesheim, R. J. Muller and C. A. Rowe, Jr., *ibid.*, **84**, 3164 (1962).

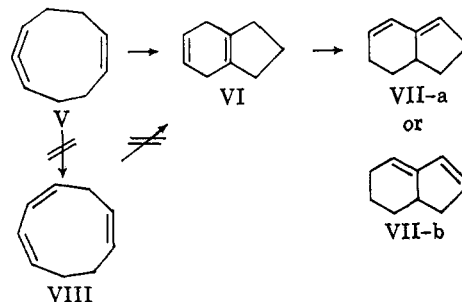
(5) Ya. M. Slobodin, *J. Gen. Chem. USSR*, **22**, 1958 (1952); *Chem. Abstr.*, **47**, 8630 (1953), and preceding papers.

We have found that 1,5-cyclooctadiene is converted rapidly and essentially quantitatively to 1,3-cyclooctadiene by potassium *t*-butoxide in dimethyl sulfoxide (1 hr., 70°). Similarly, 1,2-cyclononadiene (I)⁷ under identical conditions gave rise to 1,3-cyclononadiene (II) which is 98% pure by vapor-liquid chromatography. The properties of II are in good agreement with those reported.⁸ Extending the reaction time to 3 hr. afforded a mixture comprised of 70% of II and 23% and 7% of two new substances. The first of these was separated by vapor-liquid chromatography as 97–98% pure material. Quantitative microhydrogenation required two mole-equivalents of hydrogen and gave cyclononane, identified by comparisons of its chromatographic retention time and infrared spectrum with those of authentic material. Ozonolysis afforded malonic acid and adipic acid which, as a mixture, were converted to their methyl esters and identified chromatographically. It is thus clear that this substance is 1,4-cyclononadiene (III).⁹ Very strong infrared absorption at 13.5 μ suggests that both double bonds are *cis*. The second of the two new compounds was shown to be *cis,cis*-1,5-cyclononadiene (IV) by the usual comparisons with a sample prepared by an independent synthesis.^{9,10} Equilibration experiments (144 hr., 70°) using either I or IV gave the same equilibrium composition: 94% IV, 6% II and only a trace of III. It thus would appear that *cis,cis*-1,5-cyclononadiene (IV) is, by a substantial margin, the most stable of the isomeric cyclononadienes. The typical 1,3-diene stability is lacking in II as a result of the large interplanar angle imposed by ring strain.



The isomerization of 1,2,6-cyclononatriene (V)⁷ for 2 hr. (70°) gave a mixture of two products which was easily separated by vapor-liquid chromatography. The minor component (40%) proved to be 4,7-dihydroindane (VI) when comparison was made with authentic material.¹¹ The major product (60%) gave a mixture of hexahydroindane and tetrahydroindane upon catalytic hydrogenation. It can be formulated as either bicyclo[4.3.0]nona-1,8- or 4,6-diene (VIIa or b) on the basis of its ultraviolet spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 236 μm , ϵ 15,000) and n.m.r. spectrum (3 vinyl protons).

Two short-lived intermediates in the V \rightarrow VI isomerization have been detected. It appeared likely that one of these might be 1,3,5-cyclononatriene an



(6) W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).

(7) L. Skattebøl, *Tetrahedron Letters*, **5**, 167 (1961).

(8) R. W. Fawcett and J. O. Harris, *J. Chem. Soc.*, 2673 (1954).

(9) All new substances gave satisfactory analytical data. A later publication will present a fully detailed description of each.

(10) D. Devaprabhakara and P. D. Gardner, *J. Am. Chem. Soc.*, **85**, 648 (1963).

(11) E. Giovannini and H. Wegmüller, *Helv. Chim. Acta*, **41**, 933 (1958).

this hypothesis was explored by submitting 1,3,6-cyclonatriene (VIII)^{9,12} to the isomerizing conditions used in the earlier experiments (144 hr., 70°). Quite surprisingly, this substance is not isomerized under these conditions and can be recovered essentially quantitatively. It therefore must be concluded that VIII is probably the most stable of the isomeric cyclonatrienes and that it is certainly not an intermediate in the isomerization of V to VI.

(12) This substance was unexpectedly obtained from an attempt to prepare 1,2,4-cyclononatriene from 9,9-dibromo[6.1.0]non-2-ene.⁹ It has b.p. 62° (20 mm.), $\lambda_{\text{max}}^{\text{EtOH}}$ 205 m μ , ϵ 3920, and yields oxalic acid, malonic acid and succinic acid on ozonolysis. Catalytic hydrogenation (3 mole-equivalents) afforded cyclononane.

It has been established that VI precedes VII in the isomerization sequence.

While identification of the two intermediates in the V \rightarrow VI conversion has not yet been successful, examination of the n.m.r. spectrum of an isomerization mixture which was quenched before the appearance of VI (2 hr., 27°) suggests that they are also bicyclo[4.3.0]-nonadiene isomers. The assignment of their structures is necessary before it will be possible to determine the nature of the bridging reaction leading to VI.

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BOOK REVIEWS

Shock Waves in Chemistry and Physics. By JOHN BRADLEY, Lecturer in Inorganic and Physical Chemistry at the University of Liverpool. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. xiv + 370 pp. 16 X 24.5 cm. Price, \$11.00.

Shock waves, the discontinuities in pressure, temperature and density which form when waves of finite amplitude propagate through gases, were of little interest and largely unknown to chemists prior to the last war. As a matter of fact very little had been done with them by aerodynamicists either. The wartime interest in shock waves produced by explosives, as well as the development of high speed aircraft and missiles, changed that and both the theory and the experiments advanced rapidly. By 1950, the shock wave, usually produced in a remarkably simple apparatus, the shock tube, had become a powerful tool for the study of energy transfer processes of all sorts as well as for the study of elementary chemical kinetics over a wide range of temperatures. This volume is an excellent introduction to the subject.

Almost a third of the book is devoted to the theory of shock waves. Included are not only the theory of ideal one-dimensional flows in shock tubes, including the effects of relaxation, chemical reaction and ionization, but a welcome discussion of some of the effects which complicate the behavior of real experimental apparatus. These include the growth and properties of the boundary layer, the attenuation of shock waves, the behavior of the contact surface and the difficulties which arise in the use of reflected shock waves.

Another sixty pages describe the experimental techniques which have been used in shock wave investigations. The discussion is a good one, beginning with a description of the construction of shock tubes and going on to the various methods which have been used to measure density, pressure, temperature and gas flow velocity in the very short times, usually measured in microseconds, available for measurement. It goes on to discuss methods of following the chemical composition, a critical problem in kinetic experiments.

In the last half of the book some of the new results which have been obtained with the aid of shock waves are outlined. These include the measurement of thermodynamic properties, vibrational and rotational relaxation, ionization and a variety of chemical reactions, such as dissociation, pyrolysis, oxidation of hydrocarbons and so forth. The discussion gives an excellent picture of what has been done and what is possible.

This book is a welcome successor to the earlier work in German by Toennies and Greene. The field has been moving very rapidly and there have been many developments which make an expanded volume desirable. The bibliography is reasonably complete through 1959 and includes some work published in 1961. No major new developments seem to be omitted. This

work should be on the reference shelf of any one contemplating or beginning work with shock waves and will, indeed, be useful to most chemists already utilizing them.

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Advances in Chemistry Series. Number 36. Free Radicals in Inorganic Chemistry. Papers presented at the Symposium on Inorganic Free Radicals and Free Radicals in Inorganic Chemistry, Division of Inorganic Chemistry, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 10-12, 1962. Robert F. Gould, Ed. American Chemical Society, 1155 Sixteenth Street, N.W., Washington 6, D. C. 1962. vi + 175 pp. 15.5 X 23.5 cm. Price, \$7.00.

This volume is a collection of the 17 papers presented for general discussion by chemists interested in the preparation, detection, properties and reactions of inorganic free radicals. The papers run over a broad range from such topics as "Mass Spectroscopy of Inorganic Free Radicals" by S. N. Foner and R. L. Hudson and "Experimental Determination of the Electron Affinities of Inorganic Radicals" by F. M. Page to "Inorganic Free Radicals in Solution and Some Aspects of Autoxidation" by N. Uri and "A New Deep Violet Compound (O₂ClF₃)_n, Dioxygen Chlorine Trifluoride" by A. G. Streng and A. V. Grosse. About half the papers are concerned with studies using classical chemical methods and approaches and the other half of the papers discuss results in which use has been made of more physical methods and tools. Somewhat brief and sketchy reviews are given of several physical methods of studying radicals and their properties. However, even these papers are not meant by the authors to be reviews; they are primarily papers meant to inform the audience of some interesting results and methods. The main appeal of this volume is to those who are new to the field and who want a partial summary of work in an expanding and changing field.

I believe that this book is a glaring example of the absurdity of publishing in book form a collection of talks loosely connected by a general topic. The error is further compounded by including the book in a series, "Advances in Chemistry," which implies a cohesiveness and generality not possible from 17 diverse topics. The papers would separately be good articles in several journals or even collected together in a single issue of one journal. Such publication would make for a more rapid and a more widespread use of the information contained in these papers. However, I see little excuse for publication as an expensive book with a paper cover.

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