animal nutrition, particularly in chicks, prompted us to examine the plant quinone.

Extraction of commercial alfalfa meal with petroleum ether followed by chromatography on Florisil and on Decalso yielded a crystalline yellow quinone, m.p. 48–49°.[9] Ultraviolet: $E^{1\%}_{1cm.}$ = 247 at 254 mμ and 226 at 262 mμ in isoöctane. Reduction with sodium borohydride gave the hydroquinone: $E^{1\%}_{1cm.}$ = 48 at 290 mμ in ethanol. The infrared spectrum in carbon disulfide differs from that of coenzyme Q_{10} mainly in the absence of the intense 7.8 μ band associated with the methoxyl function; all other functional bands are similar.

The n.m.r. spectra[10] of I and its side-chain reduction product and of 2,3-dimethyl-5-farnesylbenzoquinone (II) and its side-chain reduction product when interpreted in comparison with the spectrum of Q_{10}[11] led to structure I for alfalfa quinone. It shows a ring proton as a triplet at 4.5, 6, and 7 c.p.s. and no methoxy protons. The latter are replaced by ring CH_3-functions which show at 178 c.p.s. in the side-chain reduction product which does not have the interference caused by the $=C-CH_2-CH_2-C=$ functions. The fact that the ring proton is a triplet and not a quartet signifies that its ortho group is the side-chain $-CH_2-$ and not CH_3-. Since the ring methyl protons are not spin-coupled, no ring proton is ortho to them. The ratio of the area of the doublet at 134, 141 c.p.s. to the ring proton triplet is 2 to 1. Thus, only one long side-chain is present ortho to the ring proton, and the two ring CH_3- are ortho to each other. This is confirmed by the 6 to 1 area ratio of the ring CH_3- resonance (178 c.p.s.) to the ring proton resonance in the quinone reduction product. All these deductions are quantitatively supported by the n.m.r. spectra of 2,3-dimethyl-5-farnesyl-1,4-benzoquinone and its side-chain reduction product.

2,3-Dimethyl-5-farnesylbenzoquinone (II) was synthesized from 2,3-dimethylhydroquinone and farnesol as a yellow oil; *anal.* Found: C, 81.39; H, 9.22; ultraviolet in isoöctane, E_M = 18,000 at 253 mμ, and 15,800 at 261 mμ. Combining this with the ultraviolet data of the alfalfa quinone leads to a value of 9 for *n* in I.

(9) Crane's Q-254 and our quinone were not separated on Vaseline impregnated paper using dimethylformamide as the mobile phase.

(10) Proton resonances are in cycles per second relative to and on the high field side of benzene protons as external standard. All spectra run in carbon tetrachloride solutions at 40 mc.

(11) D. E. Wolf, C. H. Hoffman, N. R. Trenner, B. H. Arison, C. H. Shunk, B. O. Linn, J. F. McPherson and K. Folkers, THIS JOURNAL, **80**, 4752 (1958).

CONTRIBUTION FROM THE
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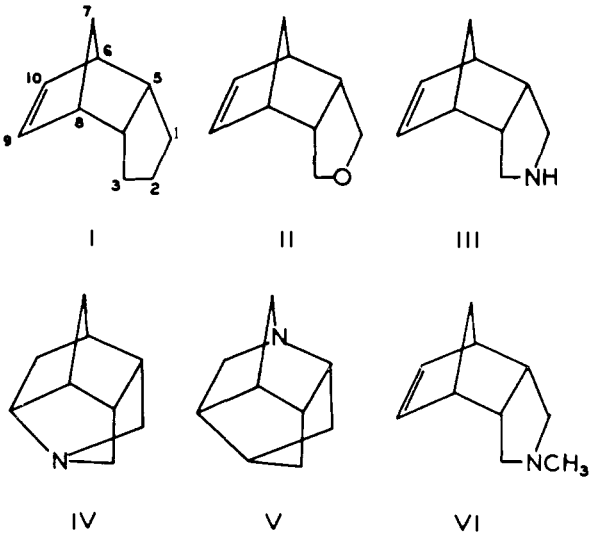
A CYCLIZATION OF 2-AZA-1,2-DIHYDRO-*endo*-DICYCLOPENTADIENE

Sir:

During an investigation of the effect of a hetero atom in the 2-position of 1,2-dihydro-*endo*-dicyclopentadiene (I) on the course of reactions with acidic reagents, we have found that 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene[1-3] (II) resists the rearrangement to the *exo*-configuration characteristic of its hydrocarbon analog.[4] Stabilization of the initial carbonium ion by the 2-oxa atom is proposed to explain the anomalous behavior. The steric possibility of such participation is proved by cyclization of 2-aza-1,2-dihydro-*endo*-dicyclopentadiene (III) with hydrobromic acid (48%) followed by 25% sodium hydroxide yielding the tertiary amine IV, the first member of a new heterocyclic ring system. Amine IV is identical with structure V.



I II III

IV V VI

The secondary amine III (m.p. 117–119° with sublimation at about 55°. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.84; H, 9.81), prepared by lithium aluminum hydride reduction of *endo*-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid imide[5-7] by the method of Rice, *et al.*,[8] forms an alkali insoluble benzenesulfonamide (m.p. 107–108°. Calcd. for $C_{15}H_{17}NSO_2$: C, 65.42; H, 6.22. Found: C, 65.26; H, 6.24), and is reduced readily by catalytic hydrogenation to the saturated amine, isolated as the benzenesulfonamide (m.p. 168–168.5°. Calcd. for $C_{15}H_{19}NSO_2$: C, 64.95; H, 6.90. Found: C, 64.80; H, 6.76). The tertiary amine IV (m.p. 126–128° with sublimation at about 70°. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; mol. wt., 135. Found: C, 79.67; H, 9.51; 149) precipitates when a solution of the *endo* amine III in hydrobromic acid, heated under reflux for five hours, is made basic with 25% sodium hydroxide. The infrared spectrum of the new amine IV is in agreement with the saturated tertiary amine structure proposed. With benzenesulfonyl chloride the amine IV forms an alkali insoluble benzenesulfonamide of 9-chloro-2-azatetrahydro-

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(3) N. O. Brace, *ibid.*, **77**, 4157 (1955).

(4) Unpublished work in this Laboratory.

(5) M. S. Morgan, R. S. Tipson, A. Lowy and W. E. Baldwin, THIS JOURNAL, **66**, 404 (1944).

(6) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

(7) S. C. Harvey, THIS JOURNAL, **71**, 1121 (1949).

(8) L. M. Rice, E. E. Reid and C. H. Grogan, *J. Org. Chem.*, **19**, 884 (1954).

dicyclopentadiene (m.p. 176–177.5°. Calcd. for $C_{15}H_{18}ClNO_2S$: C, 57.77; H, 5.82. Found: C, 57.56; H, 5.83) identical with the product obtained by addition of hydrochloric acid to the norbornylene double bond of the benzenesulfonamide of amine III. Hofmann degradation of amine IV yields N-methylamine VI (b.p. 80–81° (15 mm.). Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13. Found: C, 80.61; H, 10.04), the structure of which is confirmed by synthesis from the N-methyl imide[9] by lithium aluminum hydride reduction as well as from the *endo* amine III by methylation.

exo-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid imide (m.p. 163.5–164°. Calcd. for $C_9H_9NO_2$: C, 66.24; H, 5.56. Found: C, 66.06; H, 5.46), prepared from the corresponding anhydride,[10] yields 2-aza-1,2-dihydro-*exo*-dicyclopentadiene (b.p. 73–74° (7.5 mm.). Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 79.58; H, 9.89) upon reduction with lithium aluminum hydride. The *exo* amine forms a benzenesulfonamide (m.p. 112–113°. Calcd. for $C_{15}H_{17}NO_2S$: C, 65.42; H, 6.22. Found: C, 65.26; H, 6.26) and treatment with 48% hydrobromic acid gives 9-bromo-2-azatetrahydro-*exo*-dicyclopentadiene (b.p. 94–95° (0.2 mm.). Calcd. for $C_9H_{14}BrN$: C, 50.01; H, 6.53. Found: C, 50.01; H, 6.74) which is dehydrohalogenated readily by alcoholic potassium hydroxide to regenerate the *exo* amine.

(9) H. W. Arnold and N. E. Searle, U. S. Patent 2,462,835 (1949).
(10) D. Craig, THIS JOURNAL, **73**, 4889 (1951).

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BOOK REVIEWS

Surface Chemistry. Theory and Applications. Second Edition. Revised and Enlarged. By J. J. BIKERMAN, Massachusetts Institute of Technology, Cambridge, Massachusetts. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1958. x + 501 pp. 16 × 23.5 cm. Price. $15.00.

The change of title from "Surface Chemistry for Industrial Research" does not appear to be justified and one reviewer does not believe that it is a suitable book for students and teachers. A much less sketchy treatment of many of the topics is necessary for the future student, who should, by preference, receive a more thorough and rigorous treatment of a smaller range of topics. The book may be considered as a source-book in surface chemistry and allied subjects. As such, it can fill a useful purpose for the industrial research worker with a large number of examples of and references to the importance of surfaces in technology. The enthusiasm of the author for his subject is evident throughout, but discrimination is not so obvious.

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Biochemical Preparations. Volume 6. CARL S. VESTLING, Editor-in-Chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1958. ix + 105 pp. 15.5 × 23.5 cm. Price, $5.25.

The sixth volume of "Biochemical Preparations" has been published. In the fine tradition of the "Organic Syntheses" series, the "Biochemical Preparation" series has reached the point where it no longer seems necessary to review each book. The usefulness of "Biochemical Preparations" for biochemical research workers and for students is obvious.

The biochemist still faces problems in obtaining sufficient amounts of good materials. It is the purpose of this series to present procedures which have been checked and which will be useful in demonstrating research techniques. "Biochemical Preparations" emphasizes isolation procedures and new methods which are simpler and therefore more satisfactory and are constantly being developed. The editors of this series do not hesitate to replace older methods which have been published in earlier volumes with improved methods for the same material.

Excellent examples of this policy are presented in volume 6. The isolation for cytochrome c was presented in volume 2, an addendum was added in volume 5 and a new procedure is presented in the present volume 6. The procedure for the preparation of crystalline muscle phosphorylase has also been modified from the procedure published in an earlier volume.

This volume also presents methods for obtaining deoxyribonucleic acid, 2,3-diphosphoglyceric acid, L-α-glycerophosphorylcholine, 3-hydroxyanthranilic acid, β-hydroxy-β-methylglutaric acid, insulin, lanosterol, leucine aminopeptidase, α-methylserine and bis-(hydroxymethyl)-glycine, crystalline horse oxyhemoglobin, old yellow enzyme, crystalline papain and benzoyl-L-argininamide, phosphoserine, ribonucleic acid, ribulose diphosphate and DL-tryptophan-7a-C^{14}.

The properties and purity of the products of each procedure are described and alternate methods for obtaining each product are referenced. There is a cumulative index and a list of compounds of biochemical interest which have appeared in "Organic Syntheses" through volume 38.

DEPARTMENT OF BIOCHEMISTRY
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Conference on Extremely High Temperatures. Boston, Massachusetts, March 18–19, 1958. Sponsored by Electronics Research Directorate, Air Force Cambridge Research Center. Editors: HEINZ FISCHER and LAWRENCE C. MANSUR. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. xi + 258 pp. 22.5 × 28.5 cm. Price, $9.75.

For purposes of this conference, extremely high temperatures were taken to mean the range from just below a million degrees to above a hundred million degrees Kelvin.

The first portion of the conference was devoted to methods of production of these high temperatures using magnetic acceleration, various types of electric arcs, and other electrical methods. Electrical currents of millions of amperes were required for most methods. The next section of the conference was devoted to the measuring of temperature by various optical methods as well as a microwave thermometer. The third section of the conference was entitled "Plasma Analysis" and dealt with some of the processes taking place within plasmas. The final section dealt with application of high temperature plasma. These applications ranged from the consideration of some of these plasma sources as reactor motors for interplanetary travel to labora-