to conjugated enones,[6] but hetisine, which has been oxidized to mono- and dicarbonyl compounds, gives no such enone. Further, the infrared spectrum of Jacobs' desmethylhetisine,[2] III, shows no $>C{=}O$ absorption but does have peaks at 8.75 and 8.99 μ consistent with a hemiketal formulation.[7] Similar peaks 8.72 and 8.98 μ, no $C{=}C$ absorption, are found in the spectrum of an aqueous sulfuric acid-catalyzed isomerization product of hetisine, m.p. 278–279.5°. (*Anal.* Found: C, 72.94; H, 8.04.)

CrO_3–pyridine oxidation of hetisine produces the keto-"lactam," IV, $C_{20}H_{23}NO_3$, m.p. 236–238° (*Anal.* Found: C, 74.01; H, 7.02). The low pK_a' of IV (6.72) compared to that of hetisine (9.85) (both in 1:1 methanol–water) is explicable in IV on the basis of inductive effect,[8] but is too great to be so explained by a carbonyl further removed from nitrogen than the α-position.[9,10] A comparison of the infrared spectrum of VI (5.82 μ with shoulder at 5.81 μ) with that of 2,2-dimethylquinuclidone-6 (5.77 μ)[11] is the basis of the assignment of an N-C_9 bond (bicyclo-2,2,2 system) rather than a N-C_3 or N-C_{10} bond (bicyclo-2,2,1 system) to hetisine.[12] Base hydrolysis of IV produces a keto-carboxylate, 5.85 μ ($C{=}O$), 6.33 and 7.27 μ (CO_2^-).

Jacobs' oxidation product of dihydrodesmethylhetisine must be a carbinol–amine ether[3] because borohydride reduction reconverts it to dihydrodesmethylhetisine (infrared evidence) and because its spectrum shows reduced hydroxyl absorption, no carbonyl absorption, but has peaks at 8.67, 8.75, 8.90 and 9.07 μ (O—C—O and O—C—N). If the nitrogen is bonded to C_9 or C_{10}, the third hydroxyl must be *cis* to nitrogen and on C_3 or C_4. The stability of the hydrolysis product of IV leads us to tentatively assign the hydroxyl to C_3.[13]

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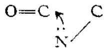
[6] S. W. Pelletier and W. A. Jacobs, THIS JOURNAL, **76**, 4496 (1954).

[7] Models indicate that the ketone derived from the secondary alcohol in I would not be suitably disposed for internal hemiketal formation.

[8] 2,2-Dimethylquinuclidone-6 has a pK_a' 5.33 (water)[11]; quinuclidine has a pK_a' 10.65 (water).

[9] The low pK_a's reported for some alkaloids having carbonyl groups γ or δ to the nitrogen atom undoubtedly are caused by transannular effects the type [10] The stereochemistry of hetisine prohibits such an interaction.

[10] N. J. Leonard, R. C. Fox and M. Oki, *ibid.*, **76**, 5708 (1954).

[11] H. Pracejus, *Chem. Ber.*, 988 (1959).

[12] As no evidence has appeared to the contrary, hypognavine also may have a N–C_9 rather than an N–C_{10} bond.

[13] If the hydroxyl is at C_4, then IV would give a β-ketocarboxylate on hydrolysis.

[14] This investigation was supported in part by grant RG5807 from the National Institutes of Health, United States Public Health Service.

BOOK REVIEWS

Gmelins Handbuch der Anorganischen Chemie. Achte Völlig Neu Bearbeitete Auflage Zirkonium. System-Nummer 42. E. H. ERICH PIETSCH, Editor. Verlag Chemie-G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. xxxvii + 448 pp. 17 × 25 cm. Price, Kart. DM 261.--; Geb. DM 266.--.

Gmelins Handbuch der Anorganischen Chemie. Achte Völlig Neu Bearbeitete Auflage. Hafnium. Ergänzungsband. System-Nummer 43. E. H. ERICH PIETSCH, Editor. Verlag Chemie, G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1958. ii + 23 pp. 17 × 25 cm. Price, Kart. DM 17.--; Geb. DM 22.--.

The high standards of the earlier volumes of the eighth edition of Gmelin have been continued in the digest of zirconium publications. Both the breadth of the coverage and the absence of errors in the details were noted with approval; the extensive use of diagrams and graphs is commendable. The discovery, geochemistry, and mineralogy of zirconium are covered in the first 50 pages. The treatment of ores and the applications of the metal and its compounds require 34 pages. Then a very complete discussion of the preparation of the element in various forms and of the physical properties is contained in the next 70 pages. The rest of the book describes the preparations and the properties of alloys and compounds of zirconium.

The short supplementary volume on hafnium devotes a proportionate amount of space to each of the above topics to review articles published mostly between 1940 and 1949. The Table of Contents shows in parallel columns the page numbers of the items in the supplement and in the main volume on hafnium, system number 43, published in 1941.

Although there are a few references to articles published after 1949 and some books published as late as 1957 are listed, the complete coverage as stated in the publication pages extends only through 1949 for both books. As examples of what can be done, the volume on selenium published in 1953 reviews the literature through 1952 and the volume on platinum published in 1957 reviews through 1953, and it seems unfortunate that the coverage for zirconium and hafnium, particularly the latter as a supplementary volume, was not extended beyond 1949.

Despite this limitation these books will be valuable additions to the shelves of every major chemistry library. One only wishes that a lower price could be established for individual purchasers, as is done by *Chemical Abstracts*, so that the specialist could afford pertinent volumes for his private library.

DEPARTMENT OF CHEMISTRY
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Vapor-Liquid Equilibrium. By EDUARD HÁLA, JIŘÍ PICK, VOJTĚCH FRIED and OTAKAR VILIM. Translated by G. STANDART. Pergamon Press, Inc., 122 East 55th Street, New York 22, N. Y. 1958. xviii + 402 pp. 16 × 23.5 cm. Price, $14.00.

This book is intended primarily for the chemical engineer or technologist who is concerned with vapor–liquid composition data in the design and operation of fractional distillation equipment.

For convenience the book is divided into three parts. The first deals with the basic thermodynamic equations expressing the relation between the vapor–liquid composition and the temperature and pressure. An excellent review is given of the various methods that have been proposed for calculating these data. The practical value to the technologist is greatly enhanced by the inclusion of illustrative examples showing how to apply the theoretical equations.

In the second part the direct determination of vapor–liquid equilibrium data including the measurement of temperature and pressure and the correlation of the results, is described in considerable detail. Much helpful information is given about the design and operation, and the weak points