propyllithium is far more reactive toward the unsubstituted carbon-carbon double bond than any known primary organometallic reagent, and that this high reactivity disappears as soon as, by addition of one ethylene molecule, the secondary organolithium reagent has been converted into a primary one. Since the addition reaction is almost certainly of polar type, this difference in reactivity must be associated with the higher anionic instability and nucleophilic tendency of an isopropyl group as compared with an ethyl or other primary group.

We are at present exploring the implications of these observations. The behavior of *t*-butyllithium is parallel to that of isopropylllithium: it can be handled in ether without attack upon this solvent at temperatures of -40 to $-50°$; it adds ethylene readily to give neohexyllithium, which can be carbonated to dineohexyl ketone, b.p. 230–235° (2,4-dinitrophenylhydrazone, m.p. 148–149°; calcd. for $C_{19}H_{30}N_4O_4$: C, 60.3; H, 7.99; N, 14.82; found: C, 60.12; H, 7.97; N, 14.92). Solutions of isopropyl and *t*-butyl lithiums when carbonated at intermediate temperatures (about 0° for isopropyl and $-25°$ for *t*-butyl) yield, in addition to the symmetrical isoamyl and neohexyl ketones, the unsymmetrical products, isopropyl isoamyl ketone (b.p. 171°, 2,4-dinitrophenylhydrazone, m.p. 81.5–82°; calcd. for $C_{15}H_{22}N_4O_4$: C, 55.9; H, 6.88; N, 17.39; found: C, 55.57; H, 6.84; N, 16.76) and *t*-butyl neohexyl ketone (2,4-dinitrophenylhydrazone, m.p. 130–131°; oxime, m.p. 113.5–114.5°; calcd. for $C_{11}H_{23}ON$: C, 71.35; H, 12.54; N, 7.57; found: C, 71.67; H, 12.54; N, 7.51), respectively.

If unsymmetrically substituted ethylenes were to react by addition with branched organolithium reagents, a polar mechanism might be expected to lead to a product having the lithium on the primary carbon atom. When isopropyllithium was stirred for twenty-four hours with propylene in ether below $-30°$ and the product then carbonated, a small amount of acidic material was isolated with a neutral equivalent of 308. The polymeric character of this acid suggests that the addition product is a secondary alkyl lithium with a reactivity toward olefins comparable to that of isopropyllithium itself, and that the orientation of the addition is dominated by steric factors rather than polar ones.

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AN INTERMEDIATE OF THE ENZYMATIC DEGRADATION OF HISTIDINE[1]

Sir:

We wish to report the isolation of a crystalline compound with the properties of α-formamidinoglutaric acid from digests of L-histidine or urocanic acid with cat liver extracts.

(1) This work was supported in part by grants from the Rockefeller Foundation, and from the National Institute of Neurological Disease and Blindness (Grant B-226) of the National Institute of Health, Public Health Service, and by a contract between the Office of Naval Research and the Psychiatric Institute. Taken from the doctoral dissertation of Blanche A. Borek.

In a representative experiment 5 g. of L-histidine·HCl·H_2O was incubated with 1 l. of a phosphate extract of cat liver (15 mg. protein/ml.) at *p*H 8.4 at 38°. After 24 hours all the histidine had disappeared (Pauly reaction) with the liberation of one equivalent of free ammonia. A second equivalent of ammonia was liberated upon digestion of the solution with 3 *N* NaOH. After removal of protein by trichloroacetic acid the intermediate was precipitated at *p*H 6 as mercuric salt. This was collected by centrifugation and decomposed with hydrogen sulfide. Free ammonia and traces of unreacted histidine were removed by adsorption on permutit and the intermediate reprecipitated as the mercuric salt. This was decomposed with hydrogen sulfide; the filtrate was lyophilized and the residue taken up in absolute ethanol. Upon concentration of the alcoholic solution colorless crystals of the intermediate separated (yield 1.8 g., 45%). The substance is very hygroscopic and melts at 80 to 87°. *Anal.* Calcd. for $C_6H_{10}N_2O_4·H_2O$: C, 37.5; H, 6.3; N, 14.6; alkali-labile ammonia, 7.3. Found, sample I: C, 37.5; H, 6.5; N, 14.0; sample II: C, 39.6; H, 6.7; N, 14.1; alkali-labile ammonia, 7.0. Mercury salt: Calcd. for $C_6H_{10}N_2O_6Hg_2$; C, 11.9; H, 1.7; N, 4.6; Hg, 66.0. Found: C, 11.6; H, 1.5; N, 4.7; Hg, 67.0; pK'_1 2.4, pK'_2 4.7, pK'_3 11.1. Upon alkaline or acid hydrolysis, respectively, 1 mole of ammonia and 1 mole of formic acid were liberated; 0.8 mole of L-glutamic acid was isolated from the hydrolysate of the intermediate by HCl.

The properties of the intermediate correspond best to the structure of α-formamidinoglutaric acid, a compound which has been postulated as the intermediate of enzymatic histidine breakdown on the basis of the appearance of a second ionizing group in an enzymatic digest of histidine[2] in conjunction with other evidence accumulated by Edlbacher and associates.[3]

Since Sera, *et al.*,[4] and Oyamada[5] have claimed the isolation from enzymatic digests of histidine of N-formylisoglutamine this compound was synthesized by formylation[6] of L-glutamic acid-γ-benzyl ester[7] and conversion of the formylated benzyl ester into the amide by the procedure of Boissonas.[8] The benzyl group was removed by catalytic hydrogenation. N-Formyl-L-isoglutamine differed from the intermediate isolated by us not only in its solubility and the number of ionizing groups but also in its greater stability toward hydrolysis. Furthermore, the intermediate was degraded by extracts of *Pseudomonas fluorescens* at a rapid rate whereas N-formyl-L-isoglutamine was not attacked. However, it is conceivable that the intermediate was converted to N-formylisoglutamine under the conditions of isolation employed by the Japanese investigators or that guinea

(2) A. C. Walker and C. L. A. Schmidt, *Arch. Biochem.*, **5**, 461 (1944).

(3) S. Edlbacher, *Erg. Enzymforsch.*, **9**, 131 (1943).

(4) K. Sera and S. Yada, *Osaka Igk. Z. (Japan)*, **38**, 1107 (1939).

(5) V. Oyamada, *J. Biochem. (Japan)*, **36**, 227 (1944).

(6) V. du Vigneaud and W. J. Patterson, *J. Biol. Chem.*, **109**, 99 (1935).

(7) W. E. Hanby, S. G. Waley, J. Watson and E. J. Ambrose, *J. Chem. Soc.*, 3239 (1950).

(8) R. A. Boissonas, *Helv. Chim. Acta*, **34**, 879 (1951).

pig liver differs from cat liver in its histidine metabolism.

Although degraded by extracts of *Pseudomonas fluorescens* the intermediate was not attacked by slices of rat liver or kidney. This finding is in accord with the fact that L-histidine was quantitatively converted into the intermediate by cat liver extract. It may well be that the mammalian tissue preparations lacked the components necessary for further breakdown of the intermediate. These compounds may either be unstable enzymes or the acceptors for the one-carbon unit or the amidine group.

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(9) Atomic Energy Commission Predoctoral Fellow 1949/50, 1950/51; U. S. Public Health Predoctoral Fellow 1951/52.

BOOK REVIEWS

Ultraviolet Radiation. By LEWIS R. KOLLER, Ph.D., Research Associate, General Electric Research Laboratory, Schenectady, New York. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1952. ix + 270 pp. 16 × 23.5 cm. Price, $6.50.

This book has been written to meet in part the practical needs of the non-specialists in radiation for information concerning ultraviolet light. Minimum facts are given regarding the nature of radiation and the units commonly employed in its measurement. Much space is given to sources of radiation. The characteristics of arcs of various types are treated in considerable detail. This is especially true of mercury arcs and carbon arcs which were chosen, respectively, as examples of enclosed and open types. A short chapter is devoted to incandescent sources of radiation including their limitations as ultraviolet emitters. A useful discussion of solar radiation is given, including variations of intensity with seasons, latitudes, altitudes and times of day. The importance of sky radiation as an ultraviolet source is emphasized.

The chapter on transmission is devoted largely to the filter qualities of glasses, quartz, plastics and various solutions. Likewise the chapter on reflections deals principally with the fractions of radiation of different wave lengths which are reflected from surfaces; included are surfaces of metals, glass, pigments, snow, sand and skin. A chapter on applications and effects of ultraviolet light covers briefly such topics as erythema, prevention and cure of rickets, production of vitamin D, germicidal effects, fluorescence effects, etc. The final chapter has an instructive discussion of photoelectric tubes and a brief survey of other devices for measuring the intensity of ultraviolet radiation.

The book is a collection of assorted facts which have been selected to answer the questions which are raised most often by persons unfamiliar with the characteristics and limitations of radiant energy. It fulfills this purpose quite well.

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Tables for the Analysis of Beta Spectra. Applied Mathematics Series 13. By NATIONAL BUREAU OF STANDARDS. United States Government Printing Office, Washington 25, D. C. 1952. iii + 61 pp. 20 × 26 cm. Price, 35 cents.

The major portion of this booklet is devoted to a table of values of the factor representing the effect of nuclear charge upon the shapes of beta spectra. The numbers given are actually values of the expression $\eta^2 F(Z, \eta)/\varphi(Z)$, where η is the momentum of the electron, Z is the nuclear charge, $F(Z, \eta)$ is the spectrum correcting function, and $\varphi(Z)$ is a constant for the particular nucleus. Separate values, mostly precise to better than 0.05%, are given for both electrons and positrons, all values of Z from 1 through 100 being covered for eighty different values of η ranging up to 7.0 mc.

Also included are: a table of values of three parameters from which the range $\eta > 7.0$ mc. can be covered by substitution in an approximately valid equation; a table for use in making rough corrections for the small screening effect of atomic electrons; and an introductory theoretical discussion by U. Fano describing the significance of the various factors appearing in the formula for the shape of the allowed beta spectrum and also giving examples of the use of the tables in analyzing experimental data.

For many years there has been a serious need for such tables as these, largely because of the mathematical difficulties involved in the exact evaluation of the Fermi function. It seems safe to predict that this booklet, with its collection of excellent information conveniently arranged for use, will prove very popular with β-ray specialists.

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Paper Chromatography—A Laboratory Manual. By RICHARD J. BLOCK, Department of Biochemistry, New York Medical College, Flower and Fifth Avenue Hospitals, New York, N. Y., and Director, Biochemical Laboratories, The Borden Company, Yonkers, N. Y., RAYMOND LESTRANGE and GUNTER ZWEIG, Biochemical Laboratories, The Borden Company, Yonkers, N. Y. Academic Press, Inc., 125 East 23rd Street, New York 10, N. Y. 1952. x + 195 pp. 16 × 23.5 cm. Price, $4.50.

The present small volume is the first serious attempt to organize and correlate the vast amount of literature that has appeared in the short span of eight years past on the application of paper chromatography to the separation, identification, and estimation of organic and inorganic compounds.

The material of the book is arranged in twelve chapters illustrated with twenty-six diagrams and photographs of apparatus and chromatograms. The first two chapters deal with a brief introduction and discussion of the theory of paper chromatography. In chapters III and IV are described the general qualitative and quantitative procedures which are employed in chromatographic techniques. Chapters V to XI deal with the application of these techniques to the identification and estimation of amino acids, amines and proteins, aliphatic acids and steroids, carbohydrates, purines and pyrimidines, phenols, aromatic acids and porphyrins, miscellaneous organic compounds, antibiotics and vitamins. A very brief treatment of inorganic separations is given in chapter XII.

The section devoted to bibliography in which a good selection of references carries the reader up to the middle of 1951 is well done. It is inherent in a rapidly expanding field that literature should accumulate at such a rate as to