

age of agaritine to 4-hydroxymethylphenylhydrazine and L-glutamic acid. In the presence of an excess of glyoxylic or certain other α -keto acids, the hydrolysis may be followed spectrophotometrically by observing the rate of formation of the corresponding phenylhydrazone derivatives, which exhibit absorption maxima in the region of 325 μ . A variety of β -N-acylphenylhydrazine analogs have been prepared⁹ in order to investigate the substrate specificity of the enzyme. Preliminary results suggest that the enzyme is non-specific with respect to the position or nature of alkyl substituents on the phenyl ring. It will, however, hydrolyze only those analogs in which an unsubstituted γ -glutamyl residue is present as the acyl moiety.

A high degree of generic localization of this system is indicated from the results of tissue distribution studies. Thus far, the phenylhydrazone derivative and its hydrolase have been detected only in a group of basidiomycetes belonging to the genus *Agaricus*.¹⁰

During the later phases of this work, Drs. J. W. Hinman and E. G. Daniels of the Upjohn Company succeeded in isolating agaritine by modification of procedures furnished by the author. He is indebted to these workers for providing him with samples of high purity, and for valuable suggestions concerning certain aspects of the problem. Acknowledgment is also expressed to Dr. A. H. Smith, Curator of Fungi at the University of Michigan, for aid in the collection and classification of basidiomycetes. This investigation was supported in part by Grant E-2966 from the National Institute of Allergy and Infectious Diseases, United States Public Health Service.

(9) By modification of a procedure described by H. L. Yale, K. Losee, J. Martins, M. Holsing, F. M. Perry and J. Bernstein, *J. Am. Chem. Soc.*, **75**, 1933 (1953), for the synthesis of acid hydrazides.

(10) Agaritine (or substances of closely-related structure) has been detected in fruiting bodies from the following species: *campestris*, *comptulidis*, *crocodilinus*, *diminutivus*, *edulis*, *micromegathus* and *perrarus*.

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RADICAL REARRANGEMENTS IN BROMOALKYL RADICALS

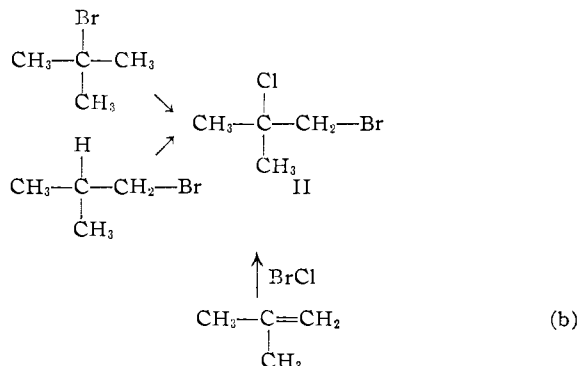
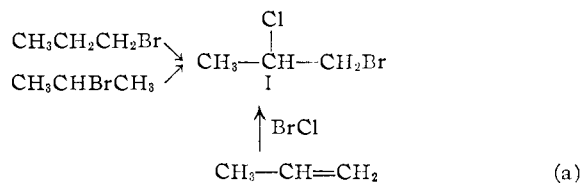
Sir:

Rearrangements of carbonium ion systems are much faster than rearrangements in the same radical systems. For example, neopentyl, neophyl and isobutyl systems undergo complete rearrangement of the carbon skeletons in any sequence which involves a carbonium ion intermediate, but often survive conversions through the radical with little or no rearrangement. Radical-chain chlorination of neopentane yields neopentyl chloride¹ unaccompanied by rearrangements.

We wish here to report a very rapid rearrangement in radical systems. Radical chain chlorinations of (a) *i*-propyl and *n*-propyl bromides yield a common product, 1-bromo-2-chloropropane (I),

(1) F. C. Whitmore and G. H. Fleming, *J. Am. Chem. Soc.*, **55**, 4161 (1933).

and (b) *i*-butyl bromide and *t*-butyl bromide are converted to 1-bromo-2-chloro-2-methylpropane (II).



The radical-chain chlorinations were carried out at -78° with *t*-butyl hypochlorite, employing photo-initiation. The products were isolated by distillation and vapor phase chromatography, capillary v.p.c. and infrared spectra being employed to demonstrate congruity of products.

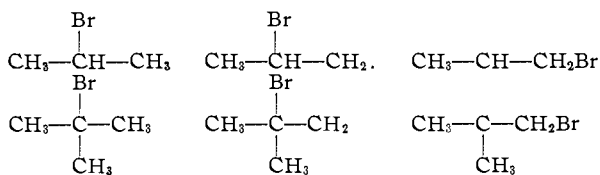
Chlorination of *t*-butyl bromide gave a single product (II) in 92% yield. The structure of (II) followed from the base dehydrohalogenation of crude (II) which converted it to $(\text{CH}_3)_2\text{C}=\text{CHBr}$, uncontaminated by $(\text{CH}_3)_2\text{C}=\text{CHCl}$.

Addition of BrCl to isobutylene also produced (II). Chlorination of *i*-butyl bromide produced (II) (57%), 1-bromo-1-chloro-2-methylpropane (20%), the remainder consisting of higher boiling products.

Chlorination of *i*-propyl bromide produced mainly 2-bromo-2-chloropropane (60%) and smaller quantities (15%) of (I). The latter had infrared absorption bands identical with those of the known 1-bromo-2-chloropropane,² and it was not contaminated by 1-chloro-2-bromopropane.²

The *n*-propyl bromide chlorination produced (I) in 40% yield along with the other expected normal chlorination products.

These experiments indicate 100% rearrangement results from removal of a hydrogen atom from the methyl groups of *i*-propyl and *t*-butyl bromides.



These rearrangements occur much more rapidly than the transfer of a chlorine atom to these radicals. Bromine atom migration is much faster than methyl migration.

(2) P. B. D. de La Mare and S. Galandauer, *J. Chem. Soc.*, **36** (1958).

Previous instances of halogen rearrangements in radical systems were reported by Demole,³ Swartz,⁴ Urry and Eiszner,⁵ and Nesmeyanov, *et al.*⁶

The details of this rearrangement are being investigated further. Since these same bromoalkyl

(3) E. Demole, *Ber.*, **11**, 315, 1302 (1878).

(4) F. Swartz, *Inst. intern. chim. Solvay*, 5eme Conseil de Chemie, 79 (1934).

(5) W. H. Urry and J. R. Eiszner, *J. Am. Chem. Soc.*, **74**, 5822 (1952).

(6) A. N. Nesmeyanov, R. Kh. Freidlina and V. N. Kost, *Tetrahedron*, 241 (1957).

radicals are also produced in the peroxide-induced additions of hydrogen bromide to olefins these halogenation studies also offer the promise of elucidating the details of hydrogen bromide additions.

(7) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF 49(638)-457.

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BOOK REVIEWS

Nouveau Traité de Chimie Minérale. Tome VII. Scandium, Yttrium. Éléments des Terres Rares. Actinium. (2 Fascicules). Edited by PAUL PASCAL. Masson et Cie., 120, Boulevard Saint-Germain, Paris 6, France. 1959. xxxix + 1473 pp. 17.5 × 26 cm. Price, brochés, 180 NF; cartonnés toile, 200 NF.

Some 27 years ago the original "Traité de Chimie Minérale," published under the direction of Professor Paul Pascal, treated the chemistry of those rare earth elements known at that time as completely as possible.

Obviously during the interim between that publication and the present an extensive amount of research on these elements has been done. The next development was to collect the data and ideas and compile them into one compact source. Such has been done in Volume VII of the *Nouveau Traité*. So great has been the amount of research that this volume has had to be published in two parts.

The form is similar to the old *Traité* but far more extensive: Part 1 (706 pages) begins with general statements regarding the rare earth elements scandium and yttrium and then deals with the history of these elements, which is most complete and well authenticated. This part is unusually well done. The remainder of this part of Volume VII is given over to the treatment of the various ores and the separation of the elements themselves plus the physical properties of the metals. Several such methods are given. Many specific separations are outlined. Limitations are pointed out in the various methods of separating the salts in a mixture. These separations range from the divalent state of the ions to complex ions. Even industrial separations are outlined. Schematic drawings of the processes are given.

The last section of this part of Volume VII, dealing with the physical properties of the metals themselves, is particularly well done and most inclusive. Several pages are given over to these properties of each rare earth in its elemental state. On reading this volume one will be surprised to find many useful thermodynamic data available, from specific heats to the Gibbs function. Important electrical properties are also discussed.

Part 2 (740 pages) deals with the chemical properties of the metals and their salts, including methods of analysis for the cations. Much is also done with the alloys of the rare earths with other metals. This part of the book contains many two-component melting point diagrams. One ternary diagram, Fe-Al-Ce, is included.

Nuclear properties of the radioactive isotopes of the lanthanides along with their uses in the domains of physical chemistry, biology and medicine are fairly thoroughly treated.

The section devoted to detection of and analysis for the cations of the rare earths is outstandingly well done and highly specific. Pitfalls are pointed out in the various analytical procedures. Both chemical and physical analytical methods are treated. Fairly complete data on absorption spectra and flame spectra for these lanthanides are given.

This volume, all in all, is very well done, and is probably the most comprehensive work on scandium, yttrium and the lanthanides yet printed.

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Handbuch der Präparativen Anorganischen Chemie Zweite umgearbeitete Auflage. Erster Band. Edited by GEORG BRAUER, o. Professor für anorganische Chemie an der Univ. Freiburg i, Br. Ferdinand Enke Verlag, Hasenbergsteige 3, Stuttgart W. Germany. 1960. xiii + 884 pp. 16.5 × 24.5 cm. Price, Geheftet DM., 118.00; Ganzleinen DM. 124.00.

Chapter I contains one hundred and twelve useful pages on preparative methods, with ninety-one diagrams and sixteen tables. Authors Schenk and Brauer cover the topics glass, ceramic materials, metals, purification of mercury, electric furnaces, temperatures, high vacuum techniques, gases and purification of compounds.

Chapter II, in eighteen sections with seven hundred and sixty-six pages and one hundred and eighty-nine diagrams total, describes more than seven hundred and fifty detailed preparations of compounds and elements and indicates preparative methods for almost twelve hundred compounds and elements. The coverage includes hydrogen and all the elements of the seven regular groups in the Periodic Table except francium, radium, polonium and astatine. These authors include silver(I) fluoride as a derivative of fluorine. Much credit is due the thirteen authors of individual sections: Baudler, Becher, Dönges, Ehrlich, Fehér, Glemser, Hofmann, Klement, Kwasnik, Rüdorff, Schenk, Schmeisser and von Wartenberg. This reviewer selects the following as twenty typical preparations: AgF₂, AlCl₃·SO₂, BiF₃, CaCN₂, CF₃I, DBr, EuF₂, F₂O, GeH₄, HCl₄·4H₂O, InCl, KIBr₂, KSO₂F, LiAl(CN)₄, NH₄PF₆, (PNCl₂)_n, Pb(C₂H₅)₄, SO₂ClF, Si₂OC₂H₅ and TiOCOH.

In the foreword Editor Brauer considers the experimental descriptions reliable because of information from the laboratories of the authors or from other laboratories. An eight page formula index is at the end of Volume I. A future Volume II on the transitional elements will complete the book.

Some minor weaknesses are always inevitable. Careful fractional distillation receives little attention in either chapter. Preparation of tetrafluorosilane should employ either fluorosilicic and concentrated sulfuric acids, as in the book, or the heating of barium fluorosilicate. Page 291 could mention that a mixture of perchloric and concentrated sulfuric acids oxidizes moderate amounts of organic matter smoothly. Also, phosphorus and iodine (in the ratio one to five atoms, respectively) react with water to yield hydrogen iodide quite satisfactorily, with adequate drying by passage over a long tube of phosphorus pentoxide. Formulas are subject to slight improvement sometimes: Ga[GaCl₄] and