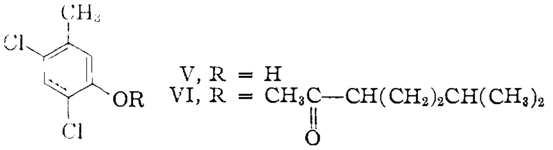

$$\text{V, R} = \text{H}$$

$$\text{VI, R} = \text{CH}_3\underset{\underset{\text{O}}{\|}}{\text{C}}\text{—CH(CH}_2\text{)}_2\text{CH(CH}_3\text{)}_2$$

correspondence of infrared, and n.m.r. spectra, and by identical retention times in vapor phase chromatography. Synthetic and "natural" III showed a single peak when a mixture was examined by v.p.c. An isomer of III, 2-isoamyl-3,7-dimethylbenzofuran, prepared from *o*-cresol and the above bromo ketone, showed marked differences from III in its infrared, ultraviolet and n.m.r. spectra and in its retention time.

The structure of IV is assigned on the basis of analysis and the similarity of its ultraviolet and infrared spectra to those of 1-methyl-2-isopropylbenzene.[8]

Although alcohol-I contains fifteen carbon atoms, plus methoxyl, its structure, as deduced here,[2] does not follow the isoprene rule completely. Stereochemical and synthetic studies are now under way.[9]

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(8) Infrared spectrum of methylisopropylbenzene: A.P.I. Project 44, Catalog of Infrared Spectra, 1585 and 1640; the spectrum of 1-methyl-2-*n*-propylbenzene (*ibid.*, no. 1964) is markedly different from that of IV.

(9) We are indebted to Abbott Laboratories for supplies of fumagillin, for fellowship support, and for many microanalyses by Mr. E. F. Shelberg and his staff. Other analyses are by Micro-Tech, W. Manser, and Thomas Montzska of this laboratory. Dr. D. J. Wilson and Mr. Y. Kawazoe supplied n.m.r. spectra and helped in their interpretation. Ultraviolet spectra were determined by Mr. Carl Whiteman. We are particularly grateful to many colleagues, from this and other laboratories, for stimulating discussions during the progress of this work.

(10) Abbott Laboratories Fellow, 1959–1960.

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RECEIVED JANUARY 4, 1960

RACEMIZATION, ACETOLYSIS AND RADIO-CHLORIDE EXCHANGE OF TWO ALKYL CHLORIDES[1]

Sir:

In rearrangement, exchange and solvolysis reactions of neutral organic substrates proceeding by way of carbonium ions, it is important to distinguish between ionization and dissociation and to consider explicitly the role of different ionic intermediates representing various stages of ionization-dissociation.[2,3] This situation is best understood with certain rearranging systems.[2,3] More recently, ion pairs also have been considered or invoked in the interpretation of solvolysis and exchange reactions of halides of the benzhydryl[4] or trityl[5] type. With these systems, no clear measure of ionization rate and the importance of ion pair return has been available. However, extra information about ionization rate would be provided by rates of racemization of optically active substrates.

TABLE I

RATE CONSTANTS IN ACETIC ACID AT 25.0°

M	[MOAc] 10^2M	[MCl] 10^2M	—k Values (sec.$^{-1}$)— 10^5k_α	10^5k_t	10^5k_e	Rate ratios (k_α/k_t)	(k_α/k_e)
			$ClC_6H_4CHClC_6H_5$				
Bu_4N	1.25	..	21	0.30	..	70	..
Bu_4N	1.25	1.27	60	.87	0.52	69	115
Li	1.20	..	6.8	.21	..	32	..
Li	1.25	2.12	7.2	.25	0.32	29	23
			$(CH_3)_3C_6H_2CHClCH_3$				
Bu_4N	2.50	..	57	5.5	..	10	..
Li	2.54	..	57	4.4	..	13	..
Li	2.51	2.40	63	5.5	7.8	11	8

We have now compared first order rate constants for racemization[2,3] (k_α), solvolysis[2,3] (k_t) and radio-chloride exchange[6] (k_e) for both *p*-chlorobenzhydryl[7] and α-mesitylethyl[8] chlorides in anhydrous acetic acid solvent and for chlorobenzhydryl chloride in 80% aqueous acetone. The various rate constants in acetic acid containing lithium or tetrabutylammonium acetate and chloride (MY) are summarized in Table I, along with the corresponding (k_α/k_t) and (k_α/k_t) ratios. With *p*-chlorobenzhydryl chloride it is clear that racemization is faster than acetolysis by factors of *ca.* 30–70. Also, racemization is more rapid than radio-chloride exchange by similarly large factors, rate of exchange being comparable to that of acetolysis. With α-mesitylethyl chloride in acetic acid solvent, acetolysis and exchange also occur at comparable rates. The (k_α/k_t) ratios of polarimetric and acetolysis rates are 10–13, somewhat smaller than those for chlorobenzhydryl chloride.

With chlorobenzhydryl chloride at 25° in 80% acetone instead of acetic acid solvent, the (k_α/k_t) ratio has decreased to 4.9, and rate of exchange in the presence of 0.0155 *M* Bu_4NCl has dropped to *ca.* one-tenth of the solvolysis rate.

In contrast with rearranging systems such as norbornyl[2b] or *threo*-3-anisyl-2-butyl[3], the polarimetric rate in the present cases is not equal, but instead represents a lower limit, to the rate of ionization. This is because considerable ion pair return may occur with retention of configuration. However, the present results shed considerable light on the behavior of the ionic intermediates involved. The observed polarimetric:titrimetric and titrimetric:exchange ratios show that there are carbonium ion pairs from ionization of both organic chlorides in acetic acid, or chlorobenzhydryl chloride even in 80% acetone, which lose configuration and return to the covalent condition

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(1) Research supported by the National Science Foundation.

(2) (a) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951); (b) S. Winstein, *et al.*, *ibid.*, **7**,. 1154, 2165, 2171 (1952); (c) C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

(3) S. Winstein, *et al.*, THIS JOURNAL, **76**, 2597 (1954); **78**, 328, 2763, 2767, 2784 (1956); **80**, 169, 459 (1958); *Chemistry and Industry*, 664 (1954); *Helv. Chim. Acta*, **41**, 807 (1958).

(4) (a) S. Winstein, A. H. Fainberg and E. Grunwald, THIS JOURNAL, **79**, 4146 (1957); (b) G. Kohnstam and B. Schillaker, *J. Chem. Soc.*, 1915 (1959).

(5) (a) R. F. Hudson and B. Saville, *Chemistry and Industry*, 1423 (1954); *J. Chem. Soc.*, 4130 (1955); (b) C. G. Swain and M. M. Kreevoy, THIS JOURNAL, **77**, 1122 (1955); (c) E. D. Hughes, C. K. Ingold, S. F. Mok, S. Patai and Y. Pocker, *J. Chem. Soc.*, 1265 (1957); (d) C. G. Swain and E. E. Pegues, THIS JOURNAL, **80**, 812 (1958).

(6) *E.g.*, L. J. leRoux and E. R. Swart, *J. Chem. Soc.*, 1475 (1955).

(7) S. Winstein and J. S. Gall, *Tetrahedron Letters*, in press.

(8) J. C. Charlton and E. D. Hughes, *J. Chem. Soc.*, 2939 (1954).

considerably more rapidly than they dissociate, exchange their chloride ion component with added common ion salt, or solvolyze to yield solvolysis product.

As regards the magnitude of the discrepancy between polarimetric and titrimetric rates, the present systems have proven to be rather similar to the norbornyl[2b] one, since norbornyl bromide at 75° displays (k_α/k_t) ratios[9] of 24 and 4.9 in acetic acid and 75% acetone, respectively.

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(9) E. Clippinger, unpublished work.

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RECEIVED JANUARY 15, 1960

BOOK REVIEWS

Gmelins Handbuch der Anorganischen Chemie. Achte Völlig Neu Bearbeitete Auflage. **Fluor.** Erganzungsband. System-Nummer 5. Verlag Chemie, G.m.b.H., (17a) Weinheim/Bergstr., Pappelallee 3, Germany. 1959, xviii + 258 pp. 17.5 × 25 cm. Price: Kart. DM 145.--; Geb. DM 150.--.

This supplementary volume continues the tradition of excellence for which Gmelin's Handbuch is well known. The book is organized in the same manner as the volume published in 1926 and constitutes a thorough summary of the literature from 1926 through 1950. Many references later than 1950 are included. The increasing difficulty of preparing a book of this sort is illustrated by the fact that the part published in 1926 contained only 86 pages and summarized the literature to June of 1926 while the supplementary part contains 258 pages and is eight years behind the date of publication in its complete coverage of the literature.

Two innovations started with this volume are: (1) English headings and subheadings on the margin of the text, (2) a German–English table of contents. All future parts of the series will contain these desirable features.

Topics regarding fluorine which are covered in system No. 5 include: (1) occurrence, (2) preparation and properties of F_2, (3) detection and determination, (4) hydrogen fluoride, (5) compounds with oxygen, (6) compounds with nitrogen. Other topics in fluorine chemistry may be found in other volumes of Gmelin's Handbuch. The chemist in search of information about fluorocarbons and their derivatives will not find a complete coverage even up to 1950 in this volume.

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Chemical Processing of Nuclear Fuels. By F. S. MARTIN, M.Sc., Ph.D. (Lond.), A.R.C.S., F.R.I.C., Principal Scientific Officer, Process Chemistry Group, A.E.R.E., and G. L. MILES, M.Sc., B.A. (W.A.), Ph.D. (Cantab.), F.R.I.C., F.R.A.C.I., Head of Chemistry Section, Australian Atomic Energy Commission. Academic Press, Inc., 111 Fifth Avenue, New York 3, N.Y. 1958. x + 242 pp. 14.5 × 22 cm. Price $7.50.

A nuclear power reactor differs from a coal-burning power plant in many respects; not least among these is the status of the fuel. In fission reactors the fuel cannot be "burned" anywhere near to completion. Since the unburned residue has considerable value, it has generally been taken for granted that recovery of the fissionable material would be necessary. The authors of this book address themselves principally to the technical principles of fuel recovery and to a lesser extent to the complex economic factors involved in the over-all problem.

For those who are unfamiliar with this general problem it might be well to point out that the fission products with which prodigious amounts of radioactivity are associated provide the principal difficulties in recovering the fuel. Fuel elements so far used in reactors are rather elaborate structures, hence thorough decontamination of the fuel material from fission products is required in order that the personnel fashioning the new elements not be over-exposed. Quite naturally attention has been given to the use of fuel systems which do not have these meticulous demands and this possibility for mode of operation is one of several discussed in this book.

Part 1 of the book outlines the basic considerations of fuel processing dictated by the reactor types and the nuclear and chemical properties of the substances which they produce. A concise discussion of neutron economy for different reactor systems is included. The next two parts (comprising about half of the book) discuss the many chemical processes which have been conceived for fuel recovery. Some of these are now embodied in working industrial plants, others are in the developmental stage.

One common feature of a group of these processes involves placing the fuel element into aqueous solution. From this starting point the methods diverge. In some, the actual chemical separations are accomplished by solvent extraction; in others, by precipitation; and still others, by ion exchange resins. Since solvent extraction methods have so far proved most practicable and widely used, most of the discussion is applied to this approach.

Chemical processes not involving aqueous dissolution of the fuel elements comprise a second major category. These include distillation of metals, liquid metal extraction and halide volatilization, among others. None of these are now used in practice but have received considerable attention because, in principle, they can eliminate or shorten some of the expensive operations in over-all fuel cycles.

The fourth part of the book is devoted to the problem of disposal of radioactive wastes following their removal from the fuel material. The recovery of selected or gross fission products of possible economic value is also treated in this section.

The book closes with a chapter summarizing present thoughts on the fuel processing problem and making projections into the future.

This book, which is refreshingly brief, nevertheless contains a great amount of information and thought-provoking speculation. Also it is well organized. It apparently has been written as a primer for the technically trained man and not for the layman. The authors have not presented the whole story whereby one can receive guidance in assessing the future of nuclear power but rather have concentrated on various aspects of fuel recovery which are now occupying the attention of those engaged in this aspect of the larger problem. Within this framework they have produced a laudable work. It should not detract from its value that this reviewer believes that some of the premises which they employ in discussing the usefulness of certain approaches may not prove to be sound.

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Crystal Structures. Supplement IV. By R. W. G. WYCKOFF. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. 1959. 664 pp. 19.5 × 24.5 cm. Price, $22.00.

Supplement IV brings the vast reference work, "Crystal Structures," undertaken by Dr. Wyckoff fifteen years ago, nearly to completion. Supplement V (still to be issued) will complete the project. This new supplement is prepared in the same style as the earlier sections of the work,