

expects a variation of isotope effect with structure in the SN2 reaction class,¹¹ it is important to note that such variations are here shown to be much smaller than those associated with the structural and solvent changes in the "intermediate region" of solvolysis.

Isotope effects in SN2 reactions will depend also on the nature of the leaving and incoming groups.¹² For different leaving groups the variations will be in the same direction as those characterized for the limiting reactions³ but smaller. This trend is discernible in the data of Robertson and coworkers.^{9,10} For different nucleophiles the variations should be in the opposite direction.

The solvolyses of substituted benzyl tosylates show plots of σ or σ^+ vs. $\log k/k_0$ which are strongly curved near the point for the unsubstituted compound but which tend to linearity in regions of high positive and high negative σ .^{13,14} It was suggested that this behavior might be a manifestation of a mixture of two extreme reaction types.¹³ However, the simple two-reaction scheme was shown to be inconsistent with the solvent dependence of the rates¹⁴ and the effects of added salts on some of the solvolyses.¹⁵ The "hybrid mechanism" postulate of a transition-state structure which varied with substituent and solvent was therefore preferred.

The observed isotope effects are consistent with a two-mechanism scheme of reaction with characteristic α - d effects for each type (k_H/k_D of 1.23 for the limiting and 1.00 for the nucleophilic reactions) *only* if the ρ value for the limiting reaction is around -3.5 ; earlier results¹⁵ indicate that this reaction should have a ρ close to -5.0 under our reaction conditions. The ρ value of -1.6 for the nucleophilic reaction, from the solvolysis rates for the p -CF₃ and p -NO₂ derivatives, is close to that ob-

tained in the earlier work for a solvent of similar polarity.¹⁶ The lack of agreement of the α -isotope effects with the simple assumptions based on the two-mechanism scheme may be due to: (1) the variable transition state structure for borderline solvolyses (the decrease in the isotope effect with increasing reagent nucleophilicity is in accord with the early prediction of Swain for this mechanism¹⁷ and with the original suggestion of the Swain-Thornton Rule¹⁸ but contrary to a more recent formulation);¹⁹ (2) a dependence of α -isotope effects for the *nucleophilic* reaction upon substituent; or as appears more reasonable (3) the occurrence in the intermediate region of a third type of mechanism, nucleophilic attack on the tight ion pair.²⁰ However, we do not believe that the SN2 extreme we have here characterized can be formulated as a nucleophilic attack on the tight ion pair. The low isotope effect corresponds to a much more tightly bound transition state and the variations of isotope effect with leaving group found for reactions of the methyl derivatives⁹ are too small to correspond to a large degree of leaving group ionization in the transition state.³

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Book Reviews

Mechanisms of Molecular Migrations. Volume 2. Edited by B. S. THYAGARAJAN, University of Madras, Madras, India. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1969. ix + 464 pp. 16 × 23.5 cm. \$22.50.

This second volume in a new series on molecular rearrangements contains nine articles:

V. J. Traynelis, in "Rearrangement of *O*-Acylated Heterocyclic *N*-Oxides," summarizes current understandings of reactions converting pyridine *N*-oxide and various analogs to ring-substituted and deoxygenated products, and some alkyl- and alkenylpyridines to products involving changes in the side chain, upon treatment with acid anhydrides, acid chlorides, or sulfonyl chlorides. Variable blends of free-radical, cationic, and concerted electrocyclic processes may account for the numerous types of products observed. "1,3-Alkyl Migrations" from nitrogen, oxygen, or sulfur to carbon, nitrogen, or oxygen, as in the intermolecular radical mediated conversion of vinyl ethers to ketones, is handled in a unified manner by P. S. Landis. R. J. Steltenkamp and W. E. Truce give a terse ac-

count of "Oxidative Rearrangements of Vinylic Derivatives." The chapter on "Base-Catalyzed Rearrangements of Acetylenic Derivatives" by I. Iwai illustrates mechanistic studies and synthetic exploitations of reactions leading to allenes and conjugated dienes, generating new carbocyclic and heterocyclic systems, passing through carbenoid intermediates, and involving 1,2 and 1,4 migrations in carbanionic species. The examples are judiciously drawn, illustrating a few types of reactions with many classes of compounds.

In "Orbital Symmetry and Electrocyclic Rearrangements," K. Fukui and H. Fujimoto present basic principles governing molecular wave functions and molecular orbital interactions, show how these principles may govern the stereochemistry of concerted electrocyclic reactions, and discuss many specific cases where pertinent experimental facts are available. Their perspective provides a valuable alternative to the approach developed into such a powerful analytical and predictive theory by R. B. Woodward and R. Hoffmann; it merits thoughtful study. H. J. Shine summarizes evidence on and dissects mechanistic suggestions for "The Benzidine Rearrangements" with clarity and candor. The subject is noteworthy for the

variety of mechanistic tools applied, the kinetically distinct pathways recognized, and the manner in which perceptual models for these reactions have evolved. R. A. W. Johnstone, writing on "The Meisenheimer Rearrangement of Tertiary Amine Oxides" to hydroxylamines, stresses mechanistic studies and parallels with other 1,2-electrophilic isomerizations such as Stevens, Wittig, and Grovenstein-Zimmerman rearrangements. "Rearrangements Involving Nitrene Intermediates" by J. H. Boyer presents a good selection of reactions leading from nitrene precursors to isolable products, often by way of nitrenes and occasionally through mazy combinations of valence isomerizations, hydrogen and group migrations, insertions, cycloadditions, and fragmentations. "The Uncatalyzed Rearrangement of Tervalent Phosphorus Esters" by V. Mark treats the thermal conversions of 2-alkenyl, 2,3-alkadienyl, and 2-alkynyl esters to the corresponding phosphoryl compounds through a five-atom six-electron cyclic process. The historical, synthetic, and mechanistic aspects of the topic are covered thoughtfully and thoroughly; thirty-nine well organized tables supplement the text.

The book as a whole is informative, engagingly written, and well indexed. It should be a valuable reference and an invigorating spur to further research.

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Organic Chemistry of Stable Free Radicals. By A. R. FORRESTER, J. M. HAY, and R. H. THOMSON, Department of Chemistry, University of Aberdeen. Academic Press Inc. (London), Ltd., Berkeley Square House, Berkeley Square, London, England. 1968. xi + 405 pp. 16 × 23.5 cm. \$18.00.

The publication of this book is timely proof of the renaissance in the chemistry of stable free radicals induced by the development of electron spin resonance spectroscopy. As implied in the title, the authors restrict coverage to those radicals that may be examined in static systems by conventional spectroscopic methods including esr. The book is divided into eight chapters, the first of which is largely concerned with an intentionally brief review of esr. Triarylmethyl and other carbon radicals are examined in the second chapter. Although the text itself was not revised in light of the new-old structure for the dimer of the triphenylmethyl radical, these developments are outlined in a footnote on page 61. Chapters 3 and 4 deal with diarylamino radicals and hydrazyls, respectively. Nitroxides are considered in Chapter 5, the longest in the book. Although this chapter does contain a brief section on nitroxides as radical traps, it is unfortunate that the major development in this area, trapping with N-oxides of aldimines, appeared too late for inclusion. Other nitrogen radicals including Wursters salts are discussed in Chapter 6. The last two chapters are devoted to aroxyl and miscellaneous radicals, respectively. Most of the chapters are divided into sections on preparation, spectra, and chemical properties. The writing is lucid and, more importantly, the authors make a serious attempt to evaluate a considerable part of the work reported and in so doing suggest a number of research problems. The book is well documented with almost 1400 references, and the coverage is through 1966 with many citations in 1967 and at least one from 1968. The printing and binding are of good quality and the text is lavishly illustrated with structural formulas. Errors are

surprisingly few in number, and those noted by this reviewer were self-evident.

Although few specialists in the field will be completely satisfied with this volume, it will serve them as a primary source and as a means of introducing new members of a research group to the discipline. For the general reader this book provides a fascinating account of a part of organic chemistry that first waxed strong when many of them were unborn.

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