dicyclohexylurea; some of the urea remained in the product, as shown by tlc in $CHCl_3$–MeOH 2:1 (R_f 0.9), and the melting point was low (about 167–169°; pure Bz-Leu-OSu has mp 172–174° [8]). This product was found to be easily racemized in the work-up, and Bz-Leu-Gly-OEt made from it was racemic (2% or more).

The effects of other additives commonly used to make active esters were also studied. Thus, in the Z-Gly-Phe-Gly-OEt synthesis, the addition of 1 or 1.1 equiv of additive yielded the following: N-hydroxyphthalimide, 0% DL, 81% L; N-hydroxypiperidine, 0% DL, 26% L; *p*-nitrophenol, 13% DL, 70% L; 2,4,5-trichlorophenol, 15% DL, 58% L; pentachlorophenol, 15% DL, 60% L; and 8-hydroxyquinoline, 9% DL, 70% L. The superiority of derivatives of hydroxylamine is clear. Results are in accord with those found in similar experiments using the mixed anhydride method.[8]

(8) G. W. Anderson, F. M. Callahan, and J. E. Zimmerman, *J. Am. Chem. Soc.*, **89**, 178 (1967).

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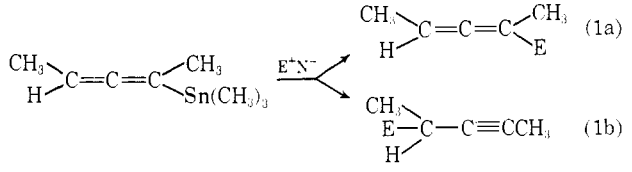
Electrophilic Displacement Reactions. SE and SE′ Reactions of Allenyltins

Sir:

We wish to report some observations on electrophilic displacement reactions of allenyltins which indicate that the reaction may proceed by a direct displacement of the organotin function (SE reaction) to produce an allene as a product (eq 1a) or by attack at the γ-carbon of the allenyl triad (SE′ reaction) to produce an acetylene as product (eq 1b).

Penta-2,3-dien-2-yltrimethyltin and 2,4-dinitrobenzenesulfonyl chloride reacted readily in methylene chloride at room temperature to produce 69% (isolated) 2-(2,4-dinitrophenylthio)-3-pentyne (**1**) (E = 2,4-$(NO_2)_2$-C_6H_3). The product was characterized by elemental analysis, infrared spectrum (band at 2245 cm^{-1}, none



(1a)

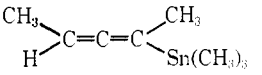
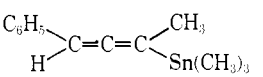
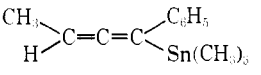
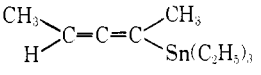
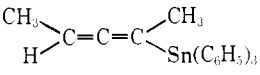
(1b)

around 1950 cm^{-1}), and nmr spectrum (three-proton doublets at τ 8.29, J = 7.1 cps, and τ 8.16, J = 2.3 cps, and a one-proton multiplet centered at τ 5.92).

Similarly, chlorine and bromine reacted with **1** in methylene chloride to yield the corresponding 2-halo-3-pentynes in yields of 77 and 92% as determined by the method of Barcza.[1]

In contrast, protonolysis with hydrogen chloride at 25° in methanol containing 4% water[2] produced a mixture of **1a** and **1b** (E = H). Similarly, four other allenyltins also produced mixtures containing allene and acetylene as products.[3] Examination of the kinetics of the reaction, taking advantage of intense absorptions in the region 205–210 mμ, showed it to be first order in substrate and in lyonium ion. The rate coefficients could be partitioned into those for SE and SE′ reaction upon determination of the proportions of allene and acetylene in the product by gas–liquid partition chromatography. Given in Table I are the over-all second-order rate coefficients for proximate (SE2) attack, presumably at the carbon–tin σ bond, and remote (SE2′) attack, presumably on the π electrons of the β,γ double bond by the acid.

Table I. Protonolysis Rates of Allenyltins at 25°

Compound[a]	k_2, $(M\ sec)^{-1}$	k_2(SE2), $(M\ sec)^{-1}$	k_2(SE2′), $(M\ sec)^{-1}$
 **1**	0.519	0.296	0.223
 **2**	0.111	0.0441	0.0670
 **3**	0.125	0.1061	0.0188
 **4**	0.299	0.100	0.199
 **5**	0.00739	0.00082	0.00657

[a] Each compound gave satisfactory elemental analyses and had infrared and nmr spectra consistent with the assigned structure.

Detailed analysis of the data must await determination of activation parameters. However, certain points of interest may be noted. First, the rate coefficients observed here for **1** are greater than those for the SE2′ protonolysis of *cis*- and *trans*-crotyltrimethyltins (0.0508 and 0.0274 M^{-1} sec^{-1}, respectively) under the same conditions.[2] In other words, attack at the vinyl carbon of the allene is faster than the SE′ attack in either the allenyl or allylic system, in contrast to the general observation that allyllic organometallics are more reactive in electrophilic reactions than vinyl organometallics.

The low reactivity of **5** is consistent with the notion that substitution of phenyl for methyl on tin makes the organotin function a poorer leaving group, suggesting that the phenyl groups play no role in stabilizing organotin cations, as observed in the allyl system.[2]

Comparison of the rate coefficients of compounds **1**, **2**, and **3** reveals an interesting effect when the phenyl group is substituted for methyl. The effect is to decrease the rate in both the α (or proximate) position and in the γ (or remote) positions. However, the effect is more pronounced in each case when the phenyl group is remote from the point of electrophilic attack. When

(1) S. Barcza, *J. Org. Chem.*, **28**, 1914 (1963).
(2) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, 119 (1964).
(3) The hydrocarbon products did not undergo interconversion in the presence of either hydrogen chloride or trimethyltin chloride under the reaction conditions.

the phenyl group is in the position proximate for either σ or π attack, the rate is decreased to about one-third of that for the methyl analog. When it is in the position remote to the point of electrophilic attack, the decrease is to about one-seventh for σ and one-twelfth for π attack.

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Book Reviews

The Proteins. Composition, Structure, and Function. Second Edition. Volume IV. Edited by HANS NEURATH, Department of Biochemistry, University of Washington, Seattle, Wash. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1966. xv × 508 pp. 16 × 23 cm. $20.00.

This fourth volume of "The Proteins" deals with only three topics: genetic control of protein structure, the basic structure of glycoproteins, and the structure proteins. The editor states that although this volume was intended to conclude the second edition, it was impossible to include all the remaining material, so a fifth volume is in preparation. This may have been in part due to the extensive treatment given the above three topics.

The first chapter, Chapter 18, on "Genetic Control of Protein Structure" was written by P. R. Helsinki and C. Yanofsky. The authors emphasize the important contributions that genetical studies have made to studies on protein structure and synthesis. Under the determination of primary structure are discussed the effects of mutations on enzyme activity and structure, gene, protein, and coding relationships. Then the determination of the folding of polypeptide chains and the role of primary structure, mutational alterations, organization, and assembly of protein components are treated. Finally, the mutational effects on cell components in protein synthesis and the expression of genetic potential are discussed.

Chapter 19, "The Basic Structure of Glycoproteins," by A. Gottshalk and E. R. B. Graham begins with a discussion of the distribution and function of glycoproteins and chemistry of amino sugars. Then the three most studied glycoproteins are reviewed in detail. The section on the α-acid glycoprotein from serum deals with its occurrence, isolation, carbohydrate and amino acid composition, and the nature of the carbohydrate–protein linkage. A similar discussion of egg albumin which contains about 3% carbohydrate follows. The last section deals with the submaxillary gland glycoproteins which have a high carbohydrate content made up of only two sugars. This chapter includes an interesting discussion of the linkage of the carbohydrate to the protein and the types of carbohydrates found in glycoproteins and their biosynthesis.

More than half of Volume 4 or 327 pages are devoted to an excellent Chapter 20 by S. Seifter and P. M. Gallop on "The Structure Proteins." The physiological function of these proteins may be described in physical terms such as forming boundaries, insulation, and connections, or to impart elasticity, tensile strength, and the capacity for extension or contraction. Seven types of structure proteins are discussed in detail. The authors are commended for including considerable interesting information about the occurrence and function of each as well as data on isolation, chemical composition, and properties. The section on the rubber-like protein, resilin, also deals with the nature of the arthopod cuticle, cross-linkages, and deposition. Elastin, the constituent protein of elastic fiber, is described in terms of its occurrence, isolation, amino acid composition, unusual cross linkages, and biosynthesis. The section on silk proteins deals with sericin and fibroins. It considers conformations, amino acid composition, and biosynthesis with an interesting description of how moths escape from their cocoons. The section on collagen is outstanding. It begins with a discussion of the tropocollagen molecule, then treats the subunits of collagen, the hexoses and aldehydes, structure, reticulin, elastoidin, biosynthesis, turnover, and collagenases. The section on keratin deals with mechanism of keratinization, keratoses, the sulfur amino acids in keratin, sequence studies, and structure. The organization, structure, amino acid composition, and soluble derivatives of feather are reviewed. A short sections deals with proteins of cilia. The last 70 pages consider the structure proteins of the myofibril. After describing the muscle cell and myofibril, the protein components actin, myosin, and tropomyosin are considered. Several models of muscle contraction and the use of antibodies in localization of components are described.

The high standard of prior volumes has been maintained. The chapter on structure proteins is outstanding. It cites over 1000 original papers and critically summarizes their findings. This volume will be of particular value to research workers and to advanced students of biology and biochemistry.

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