fragments of the polypeptide chain of staphylococcal nuclease.[6] This communication reports an alternative procedure, the hydrazine cleavage of a blocked peptide from the Merrifield polymer.[7] This method of cleavage yields the protected peptide hydrazide, which may be directly coupled to another peptide after conversion to the azide. Kessler and Iselin have shown that hydrazine cleavage of a peptide from the Merrifield polymer is accompanied by side reactions causing low yields.[8] However, this procedure seems to be applicable for the preparation of water-insoluble, blocked peptide hydrazides which do not contain ω-protected aspartic or glutamic acid residues or other groups labile to hydrazine. In preliminary experiments, both *t*-butyloxycarbonylglycyl polymer and *t*-butyloxycarbonyl-L-leucyl-L-tyrosyl-L-alanyl polymer were treated with 30 equiv of hydrazine in dimethylformamide. Complete cleavage of the blocked amino acid or peptide from the polymer support was observed. Amino acid analyses of the cleaved products in the case of the protected tripeptide indicated equimolar amounts of each amino acid. The solid-phase polymers, after cleavage, were hydrolyzed with hydrochloric acid–dioxane. No traces of amino acid residues were found upon analysis.

We report here the use of hydrazine cleavage of the synthesis of *t*-butyloxycarbonyl-L-leucyl-L-alanyl-L-tyrosyl-L-isoleucyl-L-tyrosyl-L-alanine hydrazide, which comprises residues 100–105 in the sequence of staphylococcal nuclease. The blocked hexapeptide polymer was synthesized from 5.0 g of *t*-butyloxycarbonyl-L-alanyl polymer (0.32 mmole/g) in the usual manner using N,N′-dicyclohexylcarbodiimide as the condensing agent and a threefold excess of each *t*-butyloxycarbonyl amino acid. Tyrosine was added as *t*-Boc-tyrosine, with an unprotected phenolic hydroxyl group. The blocked hexapeptide polymer was suspended in 25 ml of dimethylformamide, and 1.54 ml (48 mmoles) of anhydrous hydrazine was added. The mixture was allowed to stir for 2 days at room temperature. The supporting resin was removed by filtration and was washed with dimethylformamide. The filtrate and washings were combined and evaporated nearly to dryness *in vacuo*. The residue was then treated with water, whereupon 1.88 g of insoluble product was obtained. The product was recrystallized from methanol–ether (1.25 g, 95%, mp 224–225° dec). An aliquot (0.43 g) of the product was further purified by countercurrent distribution (upper phase 10 ml, lower phase 10 ml, 250 transfers), using the system chloroform–methanol–cyclohexane–dimethylformamide–water–acetic acid (5:5:2:2:2:0.2 by volume). The distribution pattern is shown in Figure 1. Fractions 117–160 were combined, neutralized with ammonia, and evaporated to dryness. Treatment of the residue with water yielded 0.37 g of the product. It was recrystallized from dimethylformamide–ether, 0.34 g, 79%, mp 225–226° dec, $[\alpha]^{20}D$ −24° (*c* 1.10, dimethylformamide). Single spots were obtained upon thin layer chromatography: R_f[9] 0.90, R_f[10] 0.62. *Anal.* Calcd for $C_{41}H_{62}O_{10}N_8 \cdot H_2O$: C, 58.27; H, 7.51; N, 13.26. Found: C, 58.06; H, 7.21; N, 13.85. Amino acid analysis of an acid hydrolysate (6 *N* HCl, sealed evacuated tube, 110°) gave the molar ratios: leucine 1.1, tyrosine 2.0, isoleucine 1.0, and alanine 2.0. The hexapeptide hydrazide ditrifluoroacetate (R_f[9] 0.79, R_f[11] 0.66, single spots) obtained from treatment of the *t*-butyloxycarbonyl hexapeptide hydrazide with anhydrous trifluoroacetic acid was digested with leucine aminopeptidase.[12] Amino acid analysis gave the ratios: leucine 1.1, tyrosine 2.0, isoleucine 1.0, and alanine 2.0.

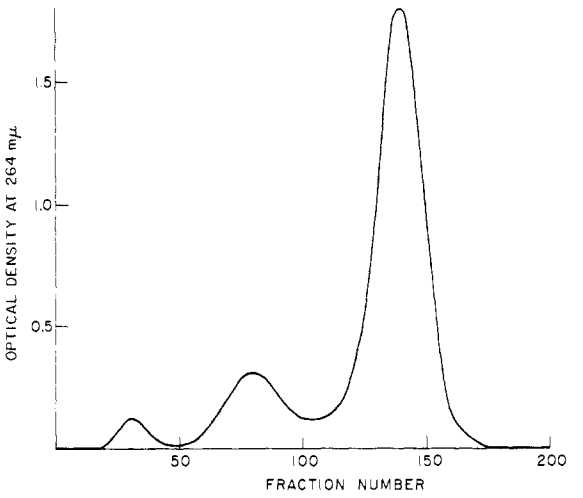

Figure 1. Countercurrent distribution pattern of the hydrazine cleavage product. The curve is based on measurements of 264-mμ absorption.

(6) H. Taniuchi, C. B. Anfinsen, and A. Sodja, *J. Biol. Chem.*, in press.
(7) See ref 15 in M. Bodanszky and J. T. Sheehan, *Chem. Ind.* (London), 1423 (1964).
(8) W. Kessler and B. Iselin, *Helv. Chim. Acta*, **49**, 1330 (1966).
(9) 1-Butanol–acetic acid–pyridine–water (4:1:1:2).
(10) Ethyl acetate–methanol (2:1).
(11) 1-Butanol–acetic acid–water (4:1:5).
(12) R. L. Hill and W. R. Schmidt, *J. Biol. Chem.*, **237**, 389 (1962).

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Additions and Corrections

Proximity Effects. XLIV. Stereospecific Synthesis and Solvolysis of *cis*- and *trans*-5-Phenylcyclooctyl and *cis*- and *trans*-5-Phenylcyclooctyl-1,2,2,8,8-d_5 Tosylates [*J. Am. Chem. Soc.*, **88**, 752 (1966)]. By ARTHUR C. COPE and ROBIN B. KINNEL. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

On page 760, the following material should be added immediately following column 1.

Elution with ether yielded 183 mg of crystalline alcohol. Fractional crystallization of the combined alcohol fractions gave 483 mg (32%) of **10**, mp 82.0–84.0°.

Anal. Calcd for $C_{14}H_{15}D_5O$: C, 80.32; H, 9.63. Found: C, 80.18; H, 9.83. Average number of D/molecule, 4.79 (falling drop).

1-Phenylcyclooctene-4,4,5,6,6-d_5 (11). A sample of 622 mg of crystalline *cis*-5-phenylcyclooctyl-1,2,2,8,8-d_5 tosylate was prepared and solvolyzed as described for the undeuterated material. Work-up afforded 269 mg of oil. Cleavage of the formates with lithium aluminum hydride, followed by chromatography, gave 228 mg of olefins (82.5%) of which 94% was **11**; collection from column E (180°) gave analytically pure **11**; λ_{max}^{EtOH} 249 mμ (ε 11,800); $n^{20}D$ 1.5588; nmr: δ 5.86 (triplet, 1 H, J = 8 cps), 2.42–2.70 (multiplet, 2 H), 2.23 (doublet, 2 H, J = 8 cps), and 1.38–1.75 (multiplet, 3 H).

Anal. Calcd for $C_{14}H_{13}D_5$: C, 87.89; H, 9.48. Found: C, 87.73; H, 9.50. Average number of D/molecule, 4.67 (falling drop).

4-Phenyl-4-hydroxycyclooctanone Hemiketal (12). A solution of phenyllithium was prepared from 208 mg of lithium wire and 2.35 g of redistilled bromobenzene in 25 ml of ether. This was added dropwise to a solution of 2.0 g of 1,4-cyclooctanedione [A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, and G. W. Wood, *J. Am. Chem. Soc.* **79**, 3900 (1957)] in 20 ml of ether at 0° over a period of 15 min. After the mixture had been stirred for 1 hr, 3 ml of saturated ammonium chloride solution was added, followed by 10 ml of water. The layers were separated, and the the ether layer was washed with water. Drying and removal of the solvent, followed by evaporation overnight at 0.1 mm, left 1.597 g of an oil. An 800-mg sample of the oil was dissolved in 5 ml of ether, diluted with 50 ml of pentane, and washed with three portions of water.

Aromatic Azapentalenes. I. Dibenzo-1,3a,4,6a-tetraazapentalene and Dibenzo-1,3a,6,6a-tetraazapentalene. New Heteroaromatic Systems [*J. Am. Chem. Soc.*, **89**, 2618 (1967)]. By R. A. CARBONI, J. C. KAUER, J. E. CASTLE, and H. E. SIMMONS. Central Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

On page 2625, column 1, second paragraph, a line was omitted. The first sentence should read: A mixture of 250 g of *o*-phenylenediamine, 500 g of *o*-chloronitrobenzene, 500 g of anhydrous sodium acetate, 50 g of copper powder, and 2 l. of absolute alcohol was mechanically stirred and heated to reflux on a steam bath for 3 days.

Book Reviews

Free Radicals. By WILLIAM A. PRYOR, Associate Professor of Chemistry, Louisiana State University. McGraw-Hill Book Co., Inc., 330 West 42nd St., New York, N. Y. 1966. xii + 354 pp. 15.5 × 23 cm. $12.00.

Since comparison with C. Walling's classic monograph on free radicals is inevitable, it seems best to begin with this problem. In fact, the books are so different in conception and scope as to make comparison meaningless.

Pryor's "Free Radicals" aims to introduce the advanced undergraduate or beginning graduate student to the chemistry of free radicals. The approach is that of a modern organic chemist with an emphasis on mechanistic (as opposed to synthetic) insight. Most of the important methods of investigation and results are covered. Data are drawn freely from the extremes of gas-phase kinetics and solution-phase product studies. After a general introduction, the book follows the organization of most radical reactions, "Production," "Reactions," and "Termination." References to the literature are common, and each chapter ends with a list of suggestions for further reading. Problems are also included; their utility is enhanced by further references and a "Solutions Manual" published in 1967.

In general, the book is clearly written and the coverage is both thorough and up-to-date. The current thinking on a given problem is usually well presented, although the author occasionally creates an atmosphere of certainty which is not apparent from reading the literature. I routinely recommend the book to research students as the best place to begin.

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BOOKS RECEIVED, *September 1967*

ARTHUR W. ADAMSON. "Physical Chemistry of Surfaces." Second Edition. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. 747 pp. $15.00.

SAM ARONOFF. "Techniques of Radiobiochemistry." Hafner Publishing Co., 31 East 10th St., New York, N. Y. 1967. 228 pp. $8.50.

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THOR A. BAK and JONAS LICHTENBERG. "Series, Differential Equations, and Complex Functions. Mathematics for Scientists." Volume 3. W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1967. 169 pp. $2.95.

B. R. BAKER. "Design of Active-Site-Directed Irreversible Enzyme Inhibitors. The Organic Chemistry of the Enzymic Active-Site." John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1967. 325 pp. $13.50.

J. O'M. BOCKRIS, Editor. "Modern Aspects of Electrochemistry." Number 4. Plenum Publishing Corp., 227 West 17th St., New York, N. Y. 1966. 316 pp. $12.00.

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HARRIS BUSCH, Editor. "Methods in Cancer Research." Volume 1. Academic Press Inc., 111 Fifth Ave., New York, N. Y. 1967. 612 pp. $28.00.

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