

bottom "U-bend" was kept in a -80° bath during the irradiations in order to freeze down the product. A water-cooling coil kept the nickel walls of the light absorbing chamber at about room temperature. A metal pressure gage of the Bourdon type was used to observe the reaction rate during irradiation.

The photochemical data are summarized in Table I. The product ratio, F_2/Xe (last column), was calculated from results of chemical analyses made by heating the product with an excess of H_2 for one hour at 400° , and subsequent separate weighings of xenon and hydrogen fluoride trapped and transferred to weighing cans.² The relative proportions of F_2 and Xe reacting also were confirmed by pressure measurements made with and without the use of liquid O_2 to freeze down the xenon. A F_2/Xe ratio of 0.89 found for run 1 may be in error due to impurities introduced by the use of a silica vessel. With this exception, the ratios correspond to the formation of relatively pure XeF_2 . A Bendix time-of-flight mass spectrometer showed principally XeF_2 and traces of XeF_4 in our samples. No oxyfluorides were observed. Studies on the infrared spectra of the products of some of the irradiations showed an intense band with peaks at 549 and 565 cm^{-1} due to XeF_2 and showed no absorption at 590 cm^{-1} where the XeF_4 has a strong absorption.² It is estimated that 1% of XeF_4 would have been detected by this method.

TABLE I
PHOTOLYSIS OF Xe AND F_2

Run	Initial pressure		Final press.,		Product coll., g.	Anal. prod. ratio, F_2/Xe
	$F_2 + Xe$ Mm.	Ratio F_2/Xe	$F_2 + Xe$ mm.			
1 ^a	990	2.00	447		0.31	0.89
2	890	2.35	546		0.73	1.04
3	979	5.20	640		0.61	0.98
4	1030	0.91	73		2.11	1.01
5	971	5.03	654		0.60	1.01

^a Run in silica vessel; all other runs in nickel system with sapphire windows.

XeF_2 , much like XeF_4 , is a solid at room temperature and easily forms crystals which can be made to sublime readily or to grow on a slightly cooled wall of a containing vessel. X-Ray diffraction patterns of samples produced in either quartz or nickel cells are identical. Room temperature powder patterns of samples which have been condensed at liquid nitrogen temperatures from the vapor indicate that the cell is body-centered tetragonal with $a = 4.316$ kx. and $c = 6.993$ kx. Single crystals grown from the vapor phase at room temperature also give the same symmetry and cell dimensions. No vapor pressure measurements have been attempted, but XeF_2 appears to have a room temperature vapor pressure of about 2 mm.

A quantum yield for Xe reacted has been determined. For this work, an Osram HBO 500 mercury arc was used with a fused silica lens to give a fairly uniform, parallel beam. A chemical filter solution⁵ was used in a 4 cm. length fused silica cell placed just behind the lens. This solution transmitted about 70% of the 2500–3200 Å. light from the lamp and less than 1% of wave lengths outside the

(5) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

2200–3400 region. Uranyl oxalate actinometry was used with the sapphire-windowed cell. The initial F_2/Xe ratio in the cell was 0.95. During the irradiation the total pressure decreased from 966 to 791 mm. Using a quantum yield for the actinometer of 0.60 as effective in this spectral range, the preliminary value of the quantum yield for Xe reacted was found to be 0.3,⁶ showing a rather efficient photochemical reaction. Typically, the rate of pressure decrease falls as reactants are used up. It is not yet known how the quantum yield may vary with pressure or intensity.

Negative results were obtained when several other reactions were tried under conditions similar to the xenon plus fluorine photolyses. These were: Kr and F_2 (this mixture also was irradiated at -60° with negative results), Xe and Cl_2 , Rn and Cl_2 , and Xe and O_2 . This last mixture was irradiated with 1849 Å. light from a low pressure mercury resonance lamp.

Further experiments designed to give information on the mechanism of the photolysis of xenon and fluorine are planned.

We wish to thank several Argonne staff members for their cooperation: M. Studier and E. Sloth for the mass spectrometry, H. Claassen for the infrared, and S. Siegel for the crystallographic studies.

(6) Correction for dark reaction due to heating tape. Quantum yield of 0.3 also found without heating tape, when no dark correction is needed.

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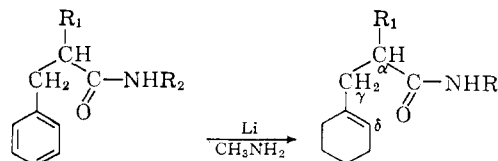
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NON-ENZYMATIC CLEAVAGE OF PHENYLALANYL PEPTIDE BONDS

Sir:

We wish to report a chemical cleavage of phenylalanyl peptide bonds utilizing "Birch reduction"¹ of the aromatic ring and an oxidative cleavage with N-bromosuccinimide.^{2–5}

Partial reduction of ethylbenzene (1) by the Birch reduction leads to 1-ethylcyclohexene. It might be expected that such a reduction of phenylalanyl peptides would lead to a double bond γ - δ with respect to the carbonyl of the peptide. Since tryptophyl (2), tyrosyl (4) and histidyl (5) peptides which all contain γ - δ double bonds are



cleaved by brominating agents, similar cleavage

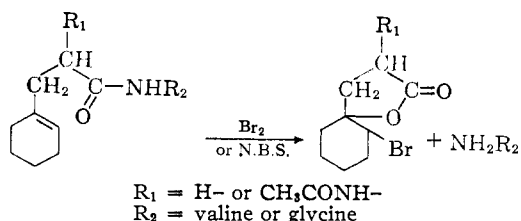
(1) R. A. Benkeser, R. E. Robinson, D. M. Saure and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

(2) A. Patchornik, W. B. Lawson, E. Gross and B. Witkop, *ibid.*, **82**, 5923 (1960).

(3) N. Izumiya, J. E. Francis, A. V. Robertson and B. Witkop, *ibid.*, **84**, 1702 (1962).

(4) G. L. Schmir, L. A. Cohen and B. W. Witkop, *ibid.*, **81**, 2228 (1959).

(5) Sh. Shaltiel and A. Patchornik, *Bull. Res. Coun. Israel*, **10A**, 79 (1961).



would be expected to occur in partially reduced phenylalanyl peptides.

A number of model compounds containing phenylalanine were synthesized in order to study the proposed method of cleavage (table). In all cases the amino group of the phenylalanine was blocked by an acetyl residue. Benzoyl or carbobenzyloxy substituents were not used because these aromatic groups also would be subject to reduction.

TABLE I

REDUCTION AND CLEAVAGE OF PHENYLALANYL PEPTIDES

Peptide ^a	M.p., °C.	Yield of reduced peptide, %	Extent of cleavage of the reduced peptide, %
Phenylpropionyl-L-valine	173	75	70
Acetyl-DL-phenylalanyl-glycine	180	52	65
Acetyl-DL-phenylalanyl-DL-valine	178	54	65

^a The peptides were synthesized by dicyclohexylcarbodiimide method.

For the reduction 1 g. of each model peptide was dissolved in 25 ml. of methylamine and 5-6 equiv. of metallic lithium was added. The reaction mixture was kept at -70 to 80° (acetone/ CO_2 bath) for 2-3 hours, and a small amount of ethanol or

ammonium chloride then was added to discharge the blue color of the mixture. After 10 min., the solvent was drawn off *in vacuo* at room temperature. The reduced derivative was dissolved in water, acidified with HCl and purified by recrystallization from ethyl acetate/petroleum ether. The yields averaged 50%. Elemental analysis of the reduced peptides, and quantitative catalytic hydrogenation over Pt indicated the presence of a mixture of cyclohexene and cyclohexadiene derivatives.

The reduced products were dissolved in 50% aqueous acetic acid and treated with bromine or N-bromosuccinimide. Paper chromatography of the reaction mixtures showed the presence of free valine or glycine, respectively, in yields averaging 65-70%.

In a second series of experiments, designed to show that the method is applicable to milligram quantities, 2-mg. portions of the model peptides were reduced and cleaved successively without isolation of intermediates. Again paper chromatography of the reaction mixture showed the liberated amino acids in yields averaging 70%.

Thus, phenylalanyl peptides, after reduction with lithium in methylamine, can be cleaved with either N-bromosuccinimide or bromine. The application of this procedure to sequence analysis of proteins is now being studied.

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BOOK REVIEWS

Advances in Comparative Physiology and Biochemistry Volume 1. Edited by O. LOWENSTEIN, Department of Zoology and Comparative Physiology, University of Birmingham, England. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1962 15.5 × 23.5 cm. Price, \$12.00.

This volume initiates a new series of "Advances" added to the many parallel series currently issued by this publisher. Volume 1 consists of six extensive monographs by seven authors, all of whom reside in Great Britain. Each attempts to show how a "theme and variations" of animal function serves to accomplish different tasks for different species.

"Digestive enzymes" (E. J. W. Barrington) especially emphasizes cellulases. A review of the occurrence of cellulases in various phyla of animals describes the properties and regulations that effect the utilization of normal and experimental diets. In turn, the properties of the enzymes secreted differ appreciably in accordance with the food available. Unsuspected specificities of enzyme action have been revealed by use of purified substrates and of newer methods of chromatography, viscosimetry, turbidimetry and others.

"Amine oxidases of mammalian blood plasma" (H. Blaschko) illustrates the variation of substrate specificities in a single kind of enzyme. The variations reside in the

enzyme protein, and probably in its amino acid composition. Differences in immune reactions aid in their comparison among species. Further, these differences bear upon the taxonomic relationships among mammals. Since study of these extracellular enzymes is a relatively new development in biochemistry, the review includes tables of species examined, enzyme differences and substrates tested. Physiological significances are discussed; for instance, spermine oxidase is especially abundant in plasmas of herbivorous animals with large absorbing surfaces in the stomach and caecum. However, absence of this enzyme in other herbivora has not been accounted for.

"Temperature receptors" (R. W. Murray) presents the difficulties of identification of organs specifically sensitive to heat and to temperature change. Very likely, many animals avoid harmfully hot environments without use of particular receptors. Four stages of investigation are indicated: (a) behavioral responses, particularly in a gradient of temperatures; (b) effects of blocking or amputation of parts; (c) impulse codes revealed by electrophysiological recordings; and (d) the analysis of receptors-transducers. The latter analysis includes a new hypothesis of transducer action, based on the exploration of membrane potentials in sensitive cells. The main problem is: how specific are temperature receptors? The present answer is that all degrees of specificity can be found, and often within a single species.