(Figure 1) gave five distinct areas (a–e) of relative intensities 2:1:1:1:1. By analogy with tricyclo-[4.1.0.0^{3,7}]heptene,[6] the signal at δ 0.73 can be assigned to the *endo* methylene proton H_2. Although primary coupling of H_2 with H_3 and H_4 should produce a quartet, secondary coupling of an unknown nature has complicated the pattern. Irradiation of the signal at e caused an effect on the patterns at a and b but not c and d. Since H_1 should give a quartet through primary coupling with H_3 and H_6 ($J_{H_1H_2}$ = 0),[6] we can tentatively assign c to H_5, d to H_6, and place H_1 in a. Although the placement of H_3 and H_4 cannot be made at this time,[7] the gross features of the spectrum are consistent with the proposed structure.

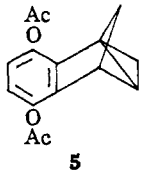
Irradiation of a 1% solution of *p,p'*-diacetoxybenzonorbornadiene[8] (**2**) in ether containing 0.01% acetophenone for 24 hr gave an 80% yield of white leaflets melting at 160–160.5° (recrystallized from acetone–ether). *Anal.* Calcd for $C_{15}H_{14}O_4$: C, 69.83; H, 5.86; mol wt, 258. Found: C, 70.19; H, 5.50; mol wt, 258 (mass spectroscopy).

The ultraviolet spectrum of the diacetoxy photoproduct, **4**, $\lambda_{max}^{CH_3CN}$ 266 mμ (log ε 2.53), and its carbonyl absorption at 1750 cm^{-1} (Nujol), were similar to those of the starting material **2**, λ_{max}^{EtOH} 260 mμ (log ε 2.50),[8] ν 1748 cm^{-1} (Nujol). The nmr spectrum consisted of an AB pattern centered at δ 6.81 (J_{AB} = 9 cps), a complex absorption centered at δ 3.25, a triplet similar to b in Figure 1, a triplet at δ 2.50, a sharp peak at δ 2.30 and 2.20, a multiplet at δ 2.04, and a poorly resolved quartet at δ 0.88. The relative areas were 2:2:1:1:3:3:1:1, corresponding to two *ortho* aromatic protons, two acetoxy methyl groups (δ 2.30 and 2.20), and six aliphatic protons. Except for the two methyl peaks, the absorptions in the aliphatic region were the same as those in compound **3**.

Reduction of the photoproduct, **4**, with hydrogen over Pd–C gave *p,p'*-diacetoxybenzonorbornene,[8] identical with an authentic sample prepared from **2**. Reduction of **4** with deuterium over Pd–C gave a benzonorbornene containing 0.9 mole of deuterium, none of it at the aromatic, acetoxyl methyl, or benzylic positions. The analytical and spectral data and chemical behavior[9] are consistent only with structure **4** and establish it as the photoproduct.

Irradiation for 24 hr of degassed 1% solutions of **2** in ether in sealed quartz tubes with a bank of 16 G8T5 bulbs[3] in the absence of a sensitizer gave no detectable concentration of **4**. Irradiation of **1** under the same conditions gave less than 1% conversion to **3**. These results suggest that the rearrangement proceeds *via* an excited triplet state of the benzonorbornadienes and that the efficiency of intersystem crossing in these compounds must be very poor. Work on the mechanism of the rearrangement is currently underway.

(6) P. R. Story, *J. Am. Chem. Soc.*, **83**, 3348 (1961).
(7) The choice between areas a and b cannot be made on the basis of the decoupling experiment.
(8) J. Meinwald and G. A. Wiley, *J. Am. Chem. Soc.*, **80**, 3667 (1958).
(9) The analytical and spectral data could conceivably fit structure **5**.



5

Reduction of the photoproduct with hydrogen over Pd–C to a benzonorbornene is characteristic of the tricyclo[4.1.0.0^{3,7}]heptane ring: W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961). Barring rearrangements, reduction of **4** with deuterium should not introduce any deuterium in the benzylic positions of the resulting benzonorbornene. This is not true of structure **5**.

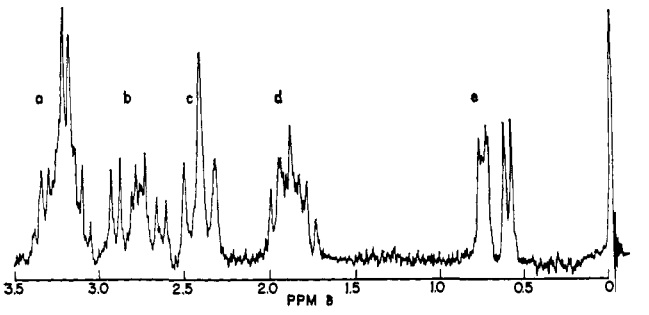


Figure 1.

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Synthetic Peptide Models of Enzyme Active Sites. III. Stereoselective Esterase Models[1]

Sir:

The pentapeptide L-threonyl-L-alanyl-L-seryl-L-histidyl-L-aspartic acid (I) previously has been shown[1] to exhibit catalytic activity more than six times greater than that reported for any other synthetic peptide in the hydrolysis of *p*-nitrophenyl acetate. In addition, we have now found that treatment with diisopropyl fluorophosphate (DFP), a known inhibitor of α-chymotrypsin,[2] leads to a 48% decrease in the catalytic coefficient of I. We now wish to report the preparation of an even more potent esterase model (Table I), as

Table I. Hydrolysis of *p*-Nitrophenyl Acetate[a]

Catalyst	Catalytic coefficient,[b] l./mole/min
Histidine·HCl[3]	6
Gly-His-Ser[3]	15
Copoly His, Ser[b]	9.7
Imidazole[c]	20
Ser-His-Asp	45
His + Ser + Asp	19
I[1]	92
I + DFP	48
II	147
III[3]	7
α-Chymotrypsin[b]	10[4]

[a] The experimental conditions of Sheehan and McGregor (ref 3) were employed in all kinetic runs. [b] E. Katchalski, G. D. Fasman, E. Simons, E. R. Blout, F. R. N. Gurd, and W. L. Koltun, *Arch. Biochem. Biophys.*, **88**, 361 (1960). [c] Unfortunately the catalytic coefficient of imidazole was reported in ref 1 as 2 rather than 20 by typographical error.

(1) Paper II in this series: P. A. Cruickshank and J. C. Sheehan, *J. Am. Chem. Soc.*, **86**, 2070 (1964).
(2) A. K. Balls and E. F. Jansen, *Advan. Enzymol.*, **13**, 321 (1952).
(3) J. C. Sheehan and D. N. McGregor, *J. Am. Chem. Soc.*, **84**, 3000 (1962).

well as the observation that both of these synthetic peptides show catalytic stereoselectivity (Table II) in the hydrolysis of the enantiomers of an optically active amino acid ester derivative. Stereoselectivity is a striking characteristic of true enzyme action and has not previously been reported for a synthetic peptide enzyme model.[4]

Table II. Hydrolysis of N-Methoxycarbonylphenylalanine *p*-Nitrophenyl Esters[a]

Substrate	Catalyst	Catalytic coefficient,[b] l./mole/min
L-Ester	I	62
D-Ester	I	32
L-Ester	II	155
D-Ester	II	112
L- or D-Ester	Imidazole	60

[a] See Table I, footnote *a*. [b] See Table I, footnote *b*.

L-Seryl-γ-aminobutyryl-L-histidyl-γ-aminobutyryl-L-aspartic acid (II), mp 165–168°, $[\alpha]^{25}D$ +25.6° (*c* 1.0, H_2O), was prepared in a linear fashion employing the water-soluble carbodiimide 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride.[5] This pentapeptide contains L-serine and L-histidine, which are considered to be constituents of the α-chymotrypsin active site.[6] It was hoped that introduction of γ-aminobutyric acid residues into the peptide chain would lead to increased flexibility and allow for the interaction of the amino acid side chains in solution. Relatively rigid models, *e.g.*, cyclo-glycyl-L-histidyl-L-serylglycyl-L-histidyl-L-seryl (III),[3] did not exhibit catalytic activity greater than would be expected on the basis of imidazole content.

The observed stereoselectivity of these catalysts strongly indicates that imidazole-type catalysis cannot be the sole explanation for the rate increase phenomena, but that some of the polyfunctional effects associated with enzyme active sites might indeed be operative in these peptide models.

(4) Bacitracin, a polypeptide antibiotic, has been reported to exhibit stereoselective catalysis in the hydrolysis of the L and D isomers of N-methoxycarbonylphenylalanine *p*-nitrophenyl ester: D. T. Elmore and J. J. Smith, *Biochem. J.*, **94**, 563 (1965).
(5) J. C. Sheehan, J. Preston, and P. A. Cruickshank, *J. Am. Chem. Soc.*, **87**, 2492 (1965).
(6) M. L. Bender and F. Kézdy, *ibid.*, **86**, 3704 (1964).
(7) National Science Foundation Graduate Fellow, 1964–1966.
(8) National Institutes of Health Predoctoral Fellow, 1963–1966.

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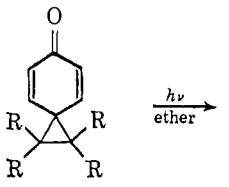
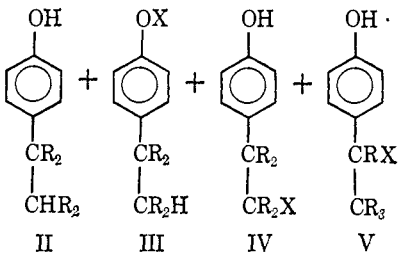
Evidence for a 1,2-Hydrogen-Atom Migration in a Photochemically Generated Diradical[1,2]

Sir:

Photolysis of spirodienone Ia in ethyl ether was recently shown to lead to products IIa–Va.[3] It was postulated that the reaction proceeded *via* a diradical VIa on the basis of the nature of the products. Other mechanisms were demonstrated to be inconsistent with the results. It was noted[3] that Va was formally a rearrangement product, and the mechanism suggested for its formation was a 1,2-hydrogen-atom migration in diradical VIa to give the quinoid structure VIIa (multiplicity not specified), followed by a photochemical or thermal reaction with ether to give Va.

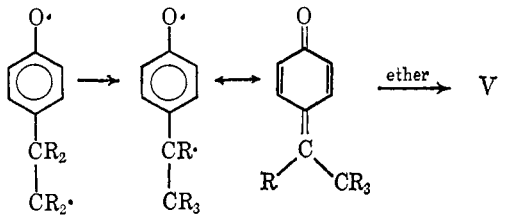


I
Ia, R = H
b, R = D



II III IV V

X = $CH_3CHOCH_2CH_3$



VI VII

The 1,2 shift postulated in the above reaction is analogous to some other 1,2 shifts postulated by Griffin and co-workers[4] in the photochemical interconversions of various phenyl and benzoyl-substituted cyclopropanes and propenes in solution. These involved apparent methyl and phenyl as well as hydrogen migrations. However, in all the above cases the intramolecularity of the rearrangement was not actually proven, as a series of intermolecular abstraction steps (particularly for H rearrangement) could lead to the same products. Such intramolecular rearrangements, if demonstrated, would be especially significant in light of the virtual absence of such hydrogen and alkyl rearrangements in ground-state radical chemistry in solution.[5–7] The occurrence of an intramolecular 1,2-hydrogen shift has now been demonstrated by a study of spiro[2.5]octa-4,7-dien-6-one-1,1,2,2-d_4 (Ib).

(1) Part VIII of a series on the photochemistry of unsaturated ketones in solution. Part VII: D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **88**, 1825 (1966).
(2) Supported in part by a grant from the U. S. Army Research Office (Durham), No. DA-ARO(D)-31-124-G425.
(3) D. I. Schuster and C. J. Polowczyk, *J. Am. Chem. Soc.*, **88**, 1722 (1966); **86**, 4502 (1964).
(4) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *ibid.*, **87**, 1410 (1965); H. Kristinsson and G. W. Griffin, *ibid.*, **88**, 378 (1966); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, **No. 34**, 2951 (1965).
(5) C. Walling in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 416 ff.
(6) L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).
(7) D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960).