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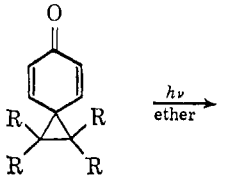
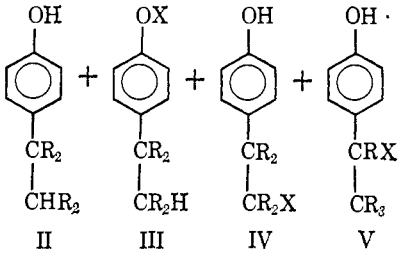
Evidence for a 1,2-Hydrogen-Atom Migration in a Photochemically Generated Diradical[1,2]

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.

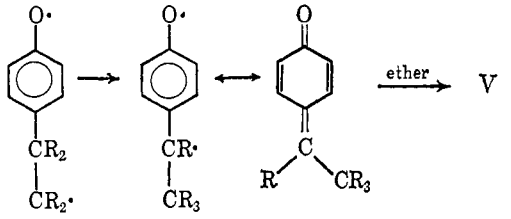


I
Ia, R = H
b, R = D



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).

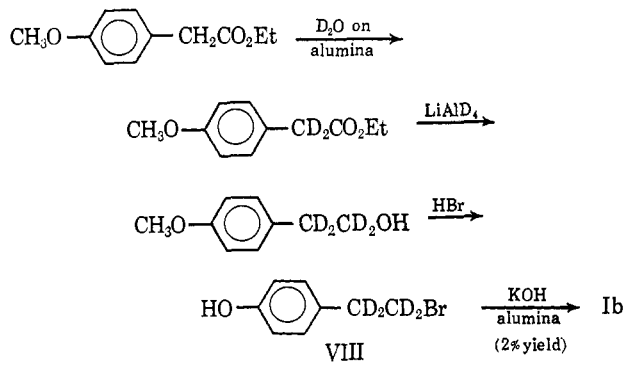
(1) Part VIII of a series on the photochemistry of unsaturated ketones in solution. Part VII: D. I. Schuster and D. J. Patel, *J. Am. Chem. Soc.*, **88**, 1825 (1966).
(2) Supported in part by a grant from the U. S. Army Research Office (Durham), No. DA-ARO(D)-31-124-G425.
(3) D. I. Schuster and C. J. 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 I, 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).

Table I. Mass Spectroscopic Results[9]

Compound	Peaks analyzed[a]	Isotopic distribution, mole % D_0	D_1	D_2	D_3	D_4	Total excess D content, %[b]
VIII	200–206	1.31	0.51	10.6	37.2	50.5	84.6 ± 0.4
	121–125	1.54	1.4	12.2	37.4	47.3	81.8
	107–109	6.1	19.9	73.8	...	...	84.0
IIb	122–126	1.4	1.2	10.3	36.0	51.2	83.7 ± 1.7
	107–109	5.14	18.9	75.9	...	...	85.5
IVb	194–198	3.4	1.9	11.7	35.4	47.7	80.8 ± 0.8
	107–109	12.1	25.2	62.7	...	...	75.5
Vb	194–198	3.31	0.70	12.3	39.8	44.0	80.5 ± 0.5
	122–126	4.55	6.77	12.0	36.8	39.9	75.0

[a] Calculated after comparison with the protium compound spectrum as per procedure described in K. Biemann, "Mass Spectrometry: Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. [b] On the basis of replacement of four protons.

Ib was prepared by the following route, adapted from the synthesis of Ia.[3,8]



The photolysis of Ib in ethyl ether was carried out as reported previously,[3] and the products were collected by preparative gas–liquid partition chromatography. The very small quantities of separated products IIb, IVb, and Vb were identified by comparison with IIa, IVa, and Va[3] and were analyzed for deuterium distribution by mass spectrometry[9] and nuclear magnetic resonance. The nmr spectra obtained using a time averaging computer[10] were compatible with the mass spectrometric results, but were not definitive in themselves. The pertinent mass spectroscopic data are given in Table I. The total per cent of excess deuterium in the dienone precursor 2-(*p*-hydroxyphenyl)ethyl bromide (VIII) as found by mass spectrometry agreed well with an independent analytical determination of 85.0%.

It is clear from the data in Table I that products IIb, IVb, and Vb are formed by routes that lead to retention of at least 95% of the original isotopic content. Moreover, the distribution of deuterium is almost exactly as predicted by the diradical mechanism and provides direct evidence for the formation of V by a 1,2-H(D) migration mechanism and not by a series of hydrogen (deuterium) abstraction steps. Also, II is seen to arise solely *via* VI, and not VII.

(8) R. Baird and S. Winstein, *J. Am. Chem. Soc.*, **85**, 567 (1963).

(9) Analyses at Columbia University on a Hitachi–Perkin-Elmer Model RMU-6D mass spectrometer operating at 13 and 75 v. with a heated inlet system at 100°. The protium compounds were analyzed as controls at the same time as the deuterium compounds. A discussion of the interesting fragmentation patterns will be reported in a later paper.

(10) These spectra were obtained at the Union Carbide Research Laboratories, Tarrytown, N. Y., through the generosity of Dr. Donald Arnold, Dr. Earl Whipple, and Mr. Mike Ruta. We are deeply grateful to these gentlemen for these measurements.

Further evidence for the lack of involvement of intermolecular hydrogen abstraction in the formation of V was the observation that the ratio V/IV was not increased on photolysis of Ia in the presence of excess *p*-ethylphenol (IIa). If anything, the ratio V/IV decreased in this experiment.

The intramolecular 1,2-hydrogen-atom shift demonstrated in this case is in contrast with the well-known lack of such processes in ground-state radical chemistry in solution.[5–7] This suggests that an important driving force which provides much-needed stabilization for the transition state for such a rearrangement[11] is the formation of a structure in which all electrons are paired (in this case VII) from a diradical (in this case VI).[12] This is an added argument in favor of diradical VI as a reactive intermediate in the photochemistry of I. This type of rearrangement is probably general[4] and should be observed in other favorable systems.

(11) H. E. Zimmerman and A. Zweig, *J. Am. Chem. Soc.*, **83**, 1196 (1961).

(12) It could be argued that the hydrogen migration is facilitated by dipolar contributions to the diradical VI (however, see ref 3), although this argument would clearly not be applicable to the rearrangements reported by Griffin, *et al.*[4] It has been suggested by a referee that such dipolar contributions would be significantly more important for VI generated from singlet- rather than triplet-excited states, although this is a subject of much debate at this time. This matter will be discussed fully in a later paper in this series, along with results of excited-state studies in this system now in progress.

(13) National Institutes of Health Predoctoral Fellow, 1965 to present

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Fluorine-19 Nuclear Magnetic Resonance Studies of π Interactions in Pentafluorophenylphosphines and Their Complexes. A Correlation of Coupling Constants with Chemical Shifts

Sir:

The nature of the metal–ligand interaction is a principal concern of coordination chemistry. Recently, in an important extension of the approach developed by Taft[1] for organic compounds, Parshall[2] has shown that the F^{19} chemical shifts of monofluorophenylplatinum(II) complexes can provide a valuable insight into the electronic character of the bond between platinum and its anionic ligands.

(1) R. W. Taft and J. W. Rakshys, Jr., *J. Am. Chem. Soc.*, **87**, 4387 (1965), and references cited therein.

(2) G. W. Parshall, *ibid.*, **86**, 5367 (1964); **88**, 704 (1966).