(Na-PLG). In order to induce the helix–coil transition, the pH was decreased on adding HCl. The H^+ ions thus introduced into the solution form a covalent bond with the ionized carboxylic groups while the polyion-bound Na^+ ions are released. This brings about a disappearance of the absorption associated with the site binding of Na^+ by the poly-L-glutamate polyion (see below). However, when most of the carboxylic groups are protonated reaction 1 must begin to contribute to the absorption of the PLGA solution. This contribution which has been shown to exist for carboxylic acid[11] and for polycarboxylic acid[12] solutions

$$-CO_2H \rightleftharpoons -CO_2^- + H^+ \quad (1)$$

is known[4] to go through a maximum when the pH is changed. From the above, one should therefore expect proton transfer as well as site binding to contribute to the absorption of PLGA solutions.

Distinction between the absorption due to the counterion site binding process and that resulting from the helix–coil transition can be made by studying solutions of the tetramethylammonium (TMA) salt of PLGA. TMA^+ is such a large ion that it does not give rise to any excess absorption in becoming site bound by a polyion.[5,6] A tetramethylammonium poly-L-glutamate (TMA-PLG) was prepared by passing a Na-PLG solution through an ion-exchange resin which had been preallably neutralized by TMA-hydroxide. The ultrasonic absorption of the TMA-PLG solution was found to be lower than that of an equimolecular solution of Na-PLG. Since both Na-PLG and TMA-PLG have coiled conformations at neutral pH, as shown by optical rotation measurements, this decrease (of about 25×10^{-17} cm^{-1} sec^2 at 2.82 MHz) is concluded to be associated with the vanishing of the absorption due to the binding of Na^+. The effect of pH on the ultrasonic absorption of the TMA-PLG solution was then studied and ultrasonic absorption maxima were obtained at the same pH value (5.1) and with the same amplitude as with Na-PLG: 11 and 17 cm^{-1} sec^2 at 5.04 and 2.82 MHz, respectively. These results thus discard counterion site binding as a process responsible of the absorption maximum reported in ref 1.

In order to distinguish between the ultrasonic absorption due to the helix–coil transition and to proton transfer, comparative measurements were made on PLGA and poly-DL-glutamic acid (PDLGA). These two polypeptides are chemically identical but structurally different. (The sample of PDLGA studied in this work had a molecular weight of 15,000 and was of the type "A," *i.e.*, composed of long sequences of dextrorotatory and levorotatory monomeric units.[13]) Potentiometric and viscosimetric measurements performed on the PDLGA sample did not show any evidence of a helix–coil transition although these techniques are usually quite sensitive to conformational changes.[14] If the absorption maximum reported in ref 1 were due to reaction 1, an identical absorption *vs.* pH curve should be found for both PLGA and PDLGA. On the contrary, the absorption maximum should be strongly affected if it were due to the helix–coil transition. Our experiments support this last prediction since the absorption maximum observed with PLGA disappeared completely with PDLGA. However, the excess absorption measured at neutral pH, *i.e.*, outside the pH range in which the helix–coil equilibrium occurs, was about the same for PLGA and PDLGA. These results definitely show that the absorption maximum observed at pH 5.1[1] is indeed due to the helix–coil equilibrium.

In ref 1 an evaluation of the relaxation time τ characterizing the helix–coil transition, on the basis of our results at 5.04 and 26.2 MHz, led to a value about 10^{-8} sec. These calculations, however, were strongly dependent on the very small and thus inaccurate value of the amplitude A of the absorption maximum at 26.2 MHz. Moreover a much too large value of the nucleation parameter σ was used in these calculations. Using the value of A at 2.82 MHz and values of 5.1×10^{-3} and 1 cm^3/mol, respectively, for σ[15] and for the volume change[16] associated with the transition of PLGA, a value of $\tau \sim 10^{-6}$ sec is found by recalculation by means of eq 1–3 (ref 1). This result is in good agreement with that recently reported by Barksdale and Stuehr.[10]

The methods outlined above unequivocally show that the absorption maximum found in the megahertz range for aqueous solutions of PLGA is due to the helix–coil equilibrium. These methods are applicable to any polypeptide and should aid workers in avoiding misinterpretation of results as was done in the studies on PLO[2] and PLL.[3]

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Dependence of Sigmatropic Mechanisms on Excited State Multiplicity. Mechanistic and Exploratory Organic Photochemistry. LXVII[1]

Sir:

In studying the photochemistry of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexene (**1a** and **1b**) and of the 4,5-diphenylbicyclo[3.1.0]-2-hexenes (**2a** and **2b**) we have encountered some fascinating sigmatropic rearrangements. We report: (1) selectivity in the interconversion of these compounds, (2) a unique 1,1-antara–antarafacial rearrangement and a novel 1,3-antarafacial sigmatropic migration with migrating carbon inversion, (3) evidence for a concerted singlet electrocyclic interconversion, (4) an interesting multiplicity-dependent partitioning of sigmatropic pathways, (5) support for nonintersecting potential energy

(1) For paper LXVI, see H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 3245 (1972).

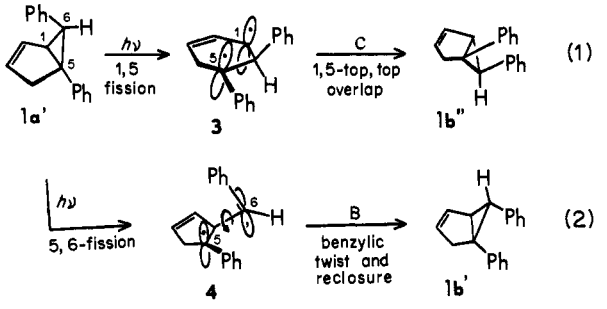
surfaces and lack of ordinary microscopic reversibility in the sigmatropic processes of the singlet, and (6) a generalization relating multiplicity and preferred excited state geometry.

Thus the cis–trans interconversion of the stereoisomeric 5,6-diphenylbicyclo[3.1.0]-2-hexenes (**1a** and **1b**) as well as the interconversion of these isomers with the 4,5-diphenylbicyclo[3.1.0]-2-hexenes (**2a** and **2b**) were observed both on direct and sensitized photolysis.[2] Results summarized in Table I show that product distribution is a function of reactant, reactant stereochemistry, and multiplicity—despite a potentially common biradical intermediate.

Table I. Results of Direct and Sensitized Photolyses

Reactant	Conditions	Products and efficiencies (ϕ)
trans-5,6-Olefin **1a**	Direct	*trans*-4,5-Olefin **2a** (0.030)
		cis-5,6-Olefin **1b** (0.0072)
	Sensitized	*trans*-4,5-Olefin **2a** (0.017)
		cis-5,6-Olefin **1b** (0.039)
cis-5,6-Olefin **1b**	Direct	*trans*-5,6-Olefin **1a** (0.0066)
		trans-4,5-Olefin **2a** (0.0018)
	Sensitized	*trans*-5,6-Olefin **1a** (0.12)
trans-4,5-Olefin **2a**	Direct	*trans*-5,6-Olefin **1a** (0.054)
	Sensitized	*trans*-5,6-Olefin **1a** (0.058)
cis-4,5-Olefin **2b**	Direct	*cis*-5,6-Olefin **1b** (0.024)
	Sensitized	*trans*-5,6-Olefin **1a** (0.026)

It is seen that the cis–trans interconversions have the *a priori* possibility of using internal or external bond fissions followed by conformational change and rebonding. But for optically active *trans*- or *cis*-5,6-olefin (*i.e.*, **1a**′ or **1b**′) a different enantiomer of product results from external bond scission (mechanisms A and B) than from internal bond scission (mechanism C). Although not pictured, path A (involving 1,6



fission) differs little from path B, and affords the same enantiomer. The reverse reaction converting cis to trans similarly gives retention of the C-5 configuration in mechanisms A and B, whereas mechanism C inverts C-5.

The optically active enantiomers **1a**′ and **1b**′ were synthesized[2] from the available resolved *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]-2-hexanones[4] whose relative configurations were known. In view of evidence for inefficient intersystem crossing, the results of direct and sensitized runs (given in Table II) may be taken as reflecting singlet and triplet reactivities.

(2) Compounds were irradiated using the Black Box apparatus[3] and ferrioxalate actinometry. All compounds analyzed properly. Full experimental details will be given in our full paper.

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Table II. Photolysis of Enantiomeric Reactants

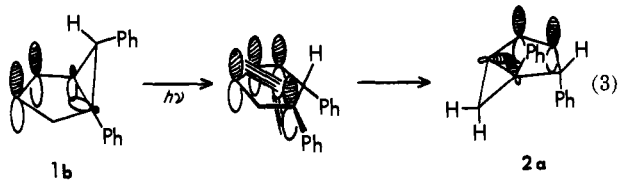
Reactant	Multiplicity	5,6-prod racem, %	Fission mechanism, % Ext bond[a]	Int bond[b]
trans-5,6-Olefin **1a**′	Singlet	5.0	97.5	2.5
trans-5,6-Olefin **1a**′	Triplet	6.3	96.9	3.1
cis-5,6-Olefin **1b**′	Singlet	39.4	80.3	19.7
cis-5,6-Olefin **1b**′	Triplet	5.0	97.5	2.5

[a] *I.e.*, retention of configuration at C-5. [b] *I.e.*, inversion at C-5.

It is seen that external bond fission mechanisms A and B are the nearly exclusive processes except for the singlet of *cis*-5,6-olefin **1b** where one-fifth of the process is internal fission.

We also note that stereoisomerization of *cis*-5,6-olefin **1b** by internal bond fission proceeds by a 1,1-antara–antarafacial sigmatropic rearrangement (note path C, eq 1) in which first two bottom lobes form the internal σ bond and then a rocking action leads to overlap of the two top lobes.

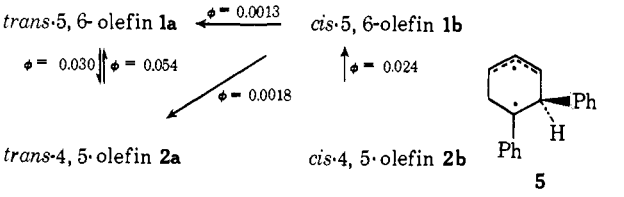
The formation of *trans*-4,5-olefin **2a** from *cis*-5,6-olefin **1b** (note Table I) is another unique process and



can be seen to involve an antarafacial 1,3-sigmatropic rearrangement with inversion of the migrating group; note eq 3. This is a concerted, singlet process and novel in organic photochemistry.

The evidence presented in Chart I, which dissects the singlet processes involving internal bond fission, shows that a common biradical such as **5** cannot be common to all of these processes, and some, if not all, must be concerted. Thus, if it is assumed that the direct photolysis of *cis*-4,5-olefin **2b** to give exclusively *cis*-5,6-olefin **1b** proceeds *via* biradical **5**, then this reactivity defines the relative rates of biradical closure to give *cis*-5,6-olefin **1b**. But then neither the reaction of *trans*-4,5-olefin **2a** nor that of *trans*-5,6-olefin **1a** could proceed *via* **5** since in each case only *trans*-olefins **1a** and **2a**, respectively, result from internal bond fission.[5]

Chart I. Singlet Reactions Involving Internal Bond Cleavage



Another intriguing aspect is the different partitioning between internal and external bond fission mechanisms in the singlet interconversion of *cis*- and *trans*-5,6-olefins **1b** and **1a** depending on the direction of the reaction (note Table II). This is further demonstra-

(5) Photochemical vinylcyclopropane rearrangements are well known. Thus, see R. S. Cooke, *Chem. Commun.*, 454 (1970), for references. However, in contrast to the case in this reference, it presently was possible to establish concertedness.

Table III. Internal *vs.* External Bond Fission

Reactant	Multiplicity	Sigmatropic rearr, %	Internal bond stereoisom, %[a]	Ratio ext/int fission[b]
1a	Singlet	81	0.05	0.20
1a	Triplet	30	2	2.1
1b	Singlet	21	16	1.7
1b	Triplet	0	2	49.0

[a] Product of the per cent stereoisomerization in total reaction and the fraction occurring by internal bond fission. [b] In product formation.

tion[4] of the lack of applicability of ordinary microscopic reversibility to photochemical reactions and shows the absence of a common potential energy surface utilized in the singlet interconversion. This derives from the product excited state not being reached in such reactions.

Table III gives the relative amount of internal *vs.* external bond fission as a function of multiplicity and reveals a greater tendency for triplets to react with fission of external bonds than the corresponding singlets. This can be understood as a triplet tendency to lead to maximum odd electron separation, with an approach to a double doublet (*i.e.*, biradical) where spin change and intersystem crossing to product is facile.[6] External bond fission gives such maximum separation. Conversely, the cyclic delocalized half-reacted species involved in the internal bond sigmatropic rearrangements has the HOMO and LUMO degenerate, or nearly so, at half-reaction, and ground and excited singlet states can approach one another in energy. The delocalized array allows maximum vibronic mixing of S_0 and S_1 and facile collapse to product. It does appear that these two types of orbital situations—separated and cyclic delocalized—are involved in singlet *vs.* triplet differences more generally.

Acknowledgment. Support by the National Science Foundation and by NIH Grant No. GM-07487 is gratefully acknowledged.

(6) The preference of singlets for concerted reactions has been noted by us[7] in the case of the barrelene derivative reactions where singlets tend to cycloadd and the triplets react *via* biradicals. This general tendency has also been noted by Fukui.[8] However, there are really three factors controlling excited state reaction rates in such cases: (a) a potential rate inhibition if excited state reactant needs to change multiplicity to get to product, (b) energy gain by having maximum electron delocalization as in cyclic concerted mechanisms, and (c) energy changes due to separation of two electrons in the reacting excited state. The last factor is complex and will be considered in our full paper. Which of these three factors is controlling depends on the molecular system involved.

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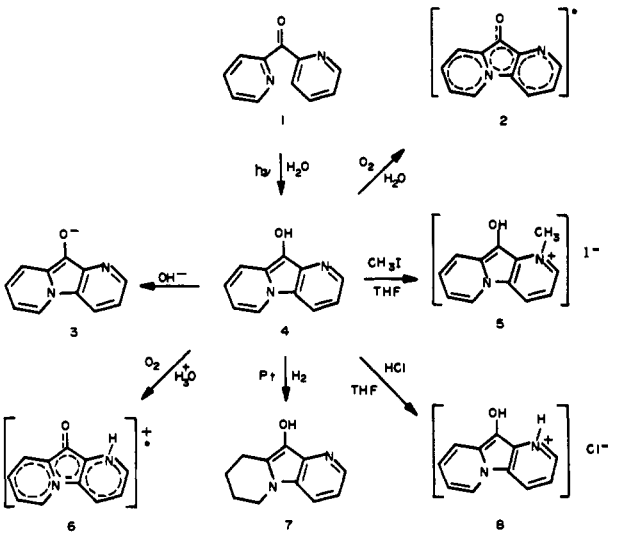
Photocyclization of Di(2-pyridyl) Ketone and 2-Benzoylpyridine in Aqueous Solution

Sir:

The mechanism of photoreduction of aromatic ketones is quite complex and still controversial.[1-20] Unlike benzophenone, which undergoes photopinacolization in a variety of solvents,[1,8,21-26] di(2-pyridyl) and di(4-pyridyl) ketones irradiated in isopropyl alcohol yield the corresponding hydrols.[20] There is general agreement by most investigators that an excited state (n-π^* triplet) of the ketone abstracts a hydrogen atom from the donor or solvent.

Here we report the unusual behavior of di(2-pyridyl) ketone (**1**) (Scheme I) and 2-benzoylpyridine (**9**) (Scheme II) when photolyzed in aqueous solution. Although

Scheme I



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