presence of air, Table I, support the above mechanism. Oxygen has a pronounced quenching effect on the dimerization, far surpassing its effect on anthracene fluorescence. It follows that in addition to ^{1}A other dimer precursors are intercepted by oxygen. Inclusion of eq 12–14 in the mechanism leads to eq 15

$$\left.\begin{array}{r} {}^1\mathrm{A} + \mathrm{O}_2 \xrightarrow{k_{12}} \\ {}^1(\mathrm{AA}) + \mathrm{O}_2 \xrightarrow{k_{13}} \\ {}^1(\mathrm{AD}) + \mathrm{O}_2 \xrightarrow{k_{14}} \end{array}\right\} \text{loss of singlet excitation} \qquad \begin{array}{r} (12) \\ (13) \\ (14) \end{array}$$

$$\phi_{\mathrm{A}_2} = \left(\frac{k_4\tau_0[\mathrm{A}]k_7/(k_6 + k_7)}{1 + k_{13}[\mathrm{O}_2]/(k_6 + k_7)} + \frac{k_5\tau_0[\mathrm{D}](k_{10}/k_8)[\mathrm{A}]}{1 + (k_{10}/k_8)[\mathrm{A}] + (k_{14}/k_8)[\mathrm{O}_2]}\right) \times \frac{1}{1 + k_4\tau_0[\mathrm{A}] + k_5\tau_0[\mathrm{D}] + k_{12}\tau_0[\mathrm{O}_2]} \tag{15}$$

for ϕ_{A_2} in the presence of oxygen. The quenching of anthracene fluorescence in benzene by air gives $k_{12} \cdot [\mathrm{O}_2] = 4.2 \times 10^7$ sec^{-1}.[16,17] Assuming that steps 12–14 are equally efficient, use of eq 15 gives $(k_6 + k_7)^{-1} = 8.0 \times 10^{-9}$ sec and $k_8^{-1} = 30 \times 10^{-9}$ sec as excimer and exciplex lifetimes, respectively.[20] As shown in Table I, calculated and observed ϕ_{A_2} values in the presence of air are in excellent agreement.

While no exciplex emission could be detected from degassed anthracene–*trans,trans*-2,4-hexadiene solutions in benzene, a broad, weak emission is observed from benzene solutions of 9,10-dichloroanthracene (DCA) and 2,5-dimethyl-2,4-hexadiene. As the diene concentration is increased the blue 9,10-dichloroanthracene emission shifts to a green exciplex emission, $\lambda_{\max}$ ~470 nm.[17] Apparently, the better donor–acceptor characteristics of the components of this exciplex give rise to emission in this case. No change in the absorption spectrum of DCA could be detected upon addition of diene, nor was there any loss of DCA detected following prolonged irradiation of benzene solutions of DCA and the diene.

Formally, the diene-catalyzed photodimerization of anthracene is a quencher-sensitized reaction. Electronic excitation is stored in a relatively long-lived intermediate giving rise to enhanced chemical reactivity for one of its components. It seems likely that the 1,3-pentadiene-catalyzed 9-phenylanthracene photodimerization can be similarly explained.[23,24]

It should be noted here that, while the mechanism in eq 1–10 adequately accounts for the observations, it may be incomplete. For example, excimer and exciplex[3] formation may be reversible, step 10 may not give dimer with unit efficiency, and there may be an additional dimer forming step[26] involving interaction of the excimer with the diene. Work is in progress on these aspects of the mechanism.[26a]

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[20] Rate constants for the quenching of the ^{1}S states of several aromatic hydrocarbons by oxygen in cyclohexane are diffusion controlled, being in the range of 2.5–3.1 × 10^{10} M^{-1} sec^{-1}.[21,22] However, since it is not certain that the quenching of singlet excimers and exciplexes will be as efficient, the values of these lifetimes may have been underestimated.

[21] L. K. Patterson, G. Porter, and M. R. Topp, *Chem. Phys. Lett.*, 7, 612 (1970), and references cited therein.

[22] C. S. Parmenter and J. D. Rau, *J. Chem. Phys.*, **51**, 2242 (1969).

[23] R. O. Campbell and R. S. H. Liu, *Chem. Commun.*, 1191 (1970).

[24] The *trans,trans*-2,4-hexadiene-catalyzed photodimerization of anthracene has been observed independently by Professor N. C. Yang's group,[25] and similar observations have been made by Professor D. O. Cowan's group[25] for the methyl ester of 9-anthroic acid in the presence of 1,3-pentadiene.

[25] Private communication of unpublished observations.

[26] R. S. H. Liu, private communication.

[26a] NOTE ADDED IN PROOF. A comparison of the efficiency of *trans,trans*-2,4-hexadiene quenching of anthracene fluorescence in the presence and in the absence of air suggests strongly that exciplex formation is not freely reversible in this system.

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Cyclic Peptides. VI. Europium-Assisted Nuclear Magnetic Resonance Study of the Solution Conformations of *cyclo*(L-Pro-L-Pro) and *cyclo*(L-Pro-D-Pro)[1]

Sir:

Europium[2] has been found to bind the carbonyl oxygen of amides.[3] We have utilized this finding in conjunction with minimum energy calculations for detailed conformational analysis of cyclic dipeptides. The nmr analysis was possible even though europium bound at either oxygen affects all protons. The present study differs from previous nmr investigations of amino acids[4a,b] and linear peptides[4c] which have employed binding of lanthanides to the carboxylate group.

Nmr spectra of *cyclo*(L-Pro-L-Pro) (Figure 1) and *cyclo*(L-Pro-D-Pro) (Figure 2) were obtained by additions of a 0.2 *M* Eu(fod)$_3$-d_{27}–chloroform-*d* solution[5] in 25-μl aliquots to 0.5 ml of a 0.2 *M* chloroform-*d* solution of peptide. The shift of each proton was plotted (as ordinate) against the europium:peptide molar ratio up to an arbitrarily chosen limit of 1:4. All shifts were linear in this range,[6] and the least-squares slopes of these lines were employed as $\Delta\nu_i/\nu_0$ in the pseudocontact shift relation,[2,7] $\Delta\nu_i/\nu_0 = K(3\cos^2\theta_i - 1)r_i^{-3}$, where K is a proportionality constant, θ_i is the O–Eu–H$_i$ angle, and r_i is the Eu–H$_i$ distance. The y intercepts of these plots represent the initial chemical shifts.

The various resonances in the spectra of the europium-treated material were identified with α, β, γ, and δ protons by the use of chemical-shift and coupling data, and these identifications were confirmed by Fourier

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[1] For the preceding paper, see L. G. Pease, C. M. Deber, and E. R. Blout, *J. Amer. Chem. Soc.*, **95**, 259 (1973).

[2] For general reviews, see: (a) R. von Ammon and R. Dieter Fischer, *Angew. Chem., Int. Ed. Engl.*, 11, 675 (1972), and references therein; (b) J. K. M. Sanders and D. H. Williams, *J. Amer. Chem. Soc.*, **93**, 641 (1971), and references therein.

[3] (a) A. H. Levin, *Tetrahedron Lett.*, 3583 (1971); (b) L. R. Isbrandt and M. T. Rogers, *Chem. Commun.*, 1378 (1971); (c) G. Montaudo and F. Finocchiaro, *J. Org. Chem.*, **37**, 3434 (1972).

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[5] R. E. Rondeau and R. E. Sievers, *J. Amer. Chem. Soc.*, **93**, 1522 (1971).

[6] Although the plots remain linear up to europium:peptide ratios higher than 0.25, further europium additions were not necessary to separate proton resonances and led to considerable line broadening.

[7] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

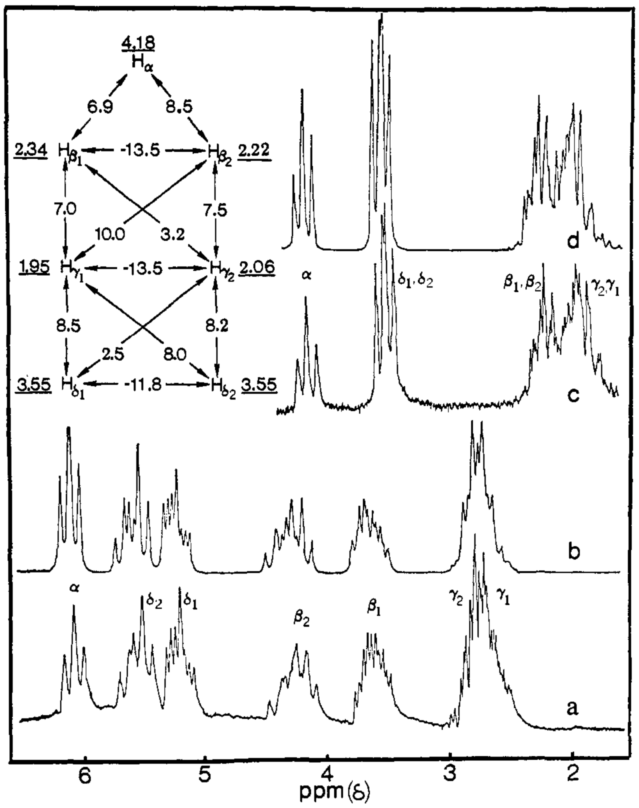

Figure 1. Comparison of 100-MHz spectra of ~0.2 *M* *cyclo*(L-Pro-L-Pro) in chloroform-*d*. Chemical shifts in parts per million are relative to TMS: (a) with $Eu(fod)_3$-d_{27}, ~0.042 *M*; (b) computer simulation of spectrum 1a using the displayed coupling constants (hertz); line width = 2.5 Hz; (c) without europium; (d) computer simulation of spectrum 1c using the displayed coupling constants (hertz) and chemical shifts (underlined); line width = 1.5 Hz.

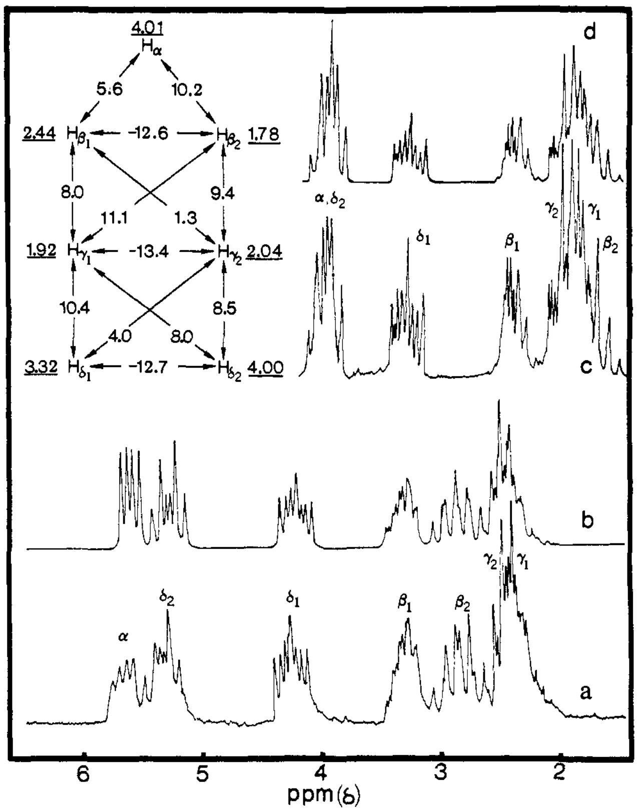

Figure 2. Comparison of 100-MHz spectra of ~0.2 *M* *cyclo*-(L-Pro-D-Pro) in chloroform-*d*. Chemical shifts in parts per million are relative to TMS: (a) with $Eu(fod)_3$-d_{27}, ~0.034 *M*; (b) computer simulation of spectrum 1a using the displayed coupling constants (hertz); line width = 2.0 Hz; (c) without europium; (d) computer simulation of spectrum 2c using the displayed coupling constants (hertz) and chemical shifts (underlined); line width = 1.25 Hz.

transform spin decoupling. In order to distinguish between the two β and between the two δ protons (the two γ protons behave similarly so that their differentiation was not critical), a computer program (SHIFT) was devised[8] to locate europium. The minimum energy peptide coordinates used by SHIFT were obtained from the consistent force field method[9] and parameters developed by Lifson and coworkers.[10]

It was found that the two europium binding sites are related by C_2 symmetry for *cyclo*(L-Pro-L-Pro)[11a] and S_2 symmetry for *cyclo*(L-Pro-D-Pro).[11b] The best match in both cases was found for the assignment of protons such that H_{β_2} and H_{δ_2} (protons anti to H_α) experience larger shifts than H_{β_1} and H_{δ_1} (protons syn to H_α).[12] It is apparent (Figures 1 and 2) that for each compound a single set of coupling constants provides simulations in good agreement with the experimental spectra.

Our conformational energy calculations show that each of the dipeptides is restricted to a single, narrow region, and that there is a flattening of the diketopiperazine ring from a boat in *cyclo*(L-Pro-L-Pro) to a nearly planar form in *cyclo*(L-Pro-D-Pro).[14] Nevertheless, the calculated pyrrolidine ring conformers are similar (Table I). The calculated conformers agree with those inferred from experimentally determined coupling constants and observed pseudocontact shifts.

A previous study[15] has identified two major pyrrolidine ring conformers which can be distinguished by the sign of χ_1. The present results in conjunction with previous data suggest a correlation between peptide backbone and pyrrolidine ring conformations. For the three cyclic dipeptides whose proline ϕ values are within the range -42 to $-6°$, negative χ_1 is observed (Table I). In contrast, *cyclo*(L-Pro)$_3$, for which ϕ is about $-100°$, exhibits positive χ_1.[16] For L-Leu-L-Pro-Gly[17] and polyproline II[18] (compounds with ϕ_{Pro}

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[8] SHIFT locates the europium atoms and determines *K* to minimize the sum of the squared differences between calculated and observed shifts.

[9] (a) A. Warshel, M. Levitt, and S. Lifson, *J. Mol. Spectrosc.*, 33, 84 (1970); (b) A. Warshel and S. Lifson, *J. Chem. Phys.*, 53, 582 (1970).

[10] (a) J. A. Schellman and S. Lifson, *Biopolymers*, 12, 315 (1973); (b) S. Karplus and S. Lifson, *ibid.*, 10, 1973 (1971).

[11] (a) Eu-O distance, 3.0 Å; Eu-O-C' angle, 146°; *K* = 730; (b) Eu-O distance, 2.3 Å; Eu-O-C' angle, 175°; *K* = 550.

[12] *R* factors[13] (three degrees of freedom): (a) *cyclo*(L-Pro-L-Pro) = 0.046; second best assignment = 0.128; (b) *cyclo*(L-Pro-D-Pro) = 0.044; second best assignment = 0.096; (c) for *cyclo*(L-Pro-D-Pro), a second match was found for the best assignment (H_{β_2}, H_{δ_2} most shifted); Eu-O distance, 3.3 Å; Eu-O-C' angle, 149°; *K* = 770; *R* factor, 0.059.

[13] (a) M. R. Wilcott, III, R. E. Lenkinski, and R. E. Davis, *J. Amer. Chem. Soc.*, 94, 1742 (1972); (b) R. E. Davis and M. R. Wilcott, III, *ibid.*, 94, 1744 (1972).

[14] The deviations from planarity (Table I) give the diketopiperazine ring in *cyclo*(L-Pro-D-Pro) the appearance of a flattened chair.

[15] R. Balasubramanian, A. V. Lakshminarayanan, M. N. Sabesan, G. Tegoni, K. Venkatesan, and G. N. Ramachandran, *Int. J. Protein Res.*, 2, 303 (1970).

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[17] Y. C. Leung and R. E. Marsh, *Acta Crystallogr.*, 11, 17 (1958).

[18] D. A. Torchia, *Macromolecules*, 4, 440 (1971).

Table I. Dihedral Angles (Degrees) of Selected Cyclic Dipeptides

Angles[a]	*cyclo*(L-Pro-L-Leu) Crystal structure[b]	*cyclo*(L-Pro-L-Pro) Calcd		*cyclo*(L-Pro-D-Pro) Calcd	
		Calcd	Exptl[c]	Calcd	Exptl[c]
χ_1	−32	−33	−30	−37	−40
χ_2	36	34	42	36	29
χ_3	−25	−23	−21	−22	−12
χ_4	4	2		−1	
ϕ	−42	−16		−6	
ψ	34	26		5	
ω	6	−10		−14	

[a] The reported dihedral angles are for the L-Pro residue and are the negative of the dihedral angles for the D-Pro residue. The conventions followed in this paper are given by: IUPAC-IUB Commission on Biochemical Nomenclature, *Biochemistry*, **9**, 3471 (1970). [b] I. L. Karle, *J. Amer. Chem. Soc.*, **94**, 81 (1972). [c] Calculated from Karplus' equations: M. Karplus (*J. Chem. Phys.*, **30**, 11 (1959)) using the parameters of ref 16b and averaging the values which depend on the same dihedral angle.

near −70°) equilibria between the two ring conformers have been observed. These observations are in accord with a theoretical study.[19]

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Arylcyclopropane Photochemistry. Stereospecific Carbene Elimination from 1,1-Diphenylcyclopropanes

Sir:

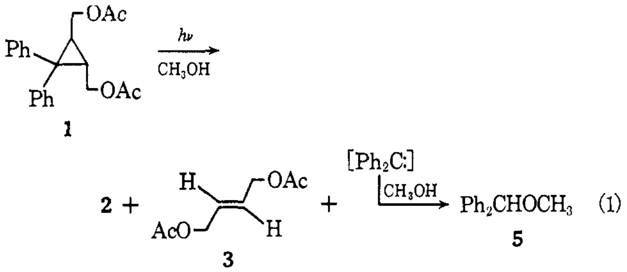
One of the most fascinating of the numerous photochemical reactions undergone by arylcyclopropanes is the fragmentation process leading to carbenes and olefins.[1] The reaction appears to be quite general, though it is often only a minor process since other more efficient reactions frequently predominate. Convincing chemical evidence for the formation of carbenes, *e.g.*, phenylcarbene from 1,2-diphenylcyclopropane[2] and diphenylcarbene from 1,1,2,3-tetraphenylcyclopropane,[3] is found in the isolation of the expected adducts when the cyclopropanes are irradiated in an alcoholic, olefinic, or hydrocarbon medium. Moreover, Griffin has shown that the selectivity of phenylcarbene for insertion into secondary *vs.* primary C–H bonds is the same when the phenylcarbene is produced from diphenylcyclopropane as from other, more usual sources of phenylcarbene.[2a]

The mechanism of this fragmentation is of special interest. Formally, it is a four-electron excited state process and may proceed in a concerted fashion with retention of cyclopropane stereochemistry in the product olefin. However, it has been noted by Griffin[1,4] and others[5] that several of the reactions of excited (singlet and triplet) arylcyclopropanes, diphenylcyclopropane in particular, seem well rationalized as proceeding *via* aryl-substituted trimethylene diradicals, and it has been speculated that excited states (singlet or triplet) having much trimethylene diradical character may be involved in the fragmentations of arylcyclopropanes to carbenes.[1,6] Some support for this idea has been provided by Becker and Griffin who observed long-wavelength phosphorescence from various polyarylcyclopropanes and ascribed this to such radical-like triplet states.[6] Arguments for the existence of corresponding singlet states were presented.

The exact nature of this diradical excited state is of course unknown, though one might expect on the basis of recent calculations[7] that it would be characterized by low barriers to rotation about the terminal carbons. Thus, to provide some concrete evidence about the excited states and possible intermediates involved in the fragmentation we have examined the reaction stereochemistry.

Cyclopropanes **1** and **2** were studied since (a) they are readily prepared[8,9] in stereochemically pure form, (b) they can eliminate the stable carbene diphenylcarbene, and (c) the expected product olefins **3** and **4** are stable and easy to analyze, do not absorb light significantly in the regions where **1** and **2** do, and should have high triplet energies so that they would not isomerize rapidly during the irradiation.

As predicted preparative irradiation of **1** (0.016 *M*) in methanol with Corex-filtered light followed by silica gel chromatography afforded olefins **3** (13%) and **4** (trace), benzhydryl methyl ether (**5**, 11%), and traces of **2** and other unidentified products along with 54% of recovered **1** (eq 1). Similarly, **2** (0.041 *M*) yielded



12% of **3** and **4** (**4**:**3** = 15:1), **5** (14%), **1** (36%), and other unidentified materials together with 17% of re-

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