Normally, *exo* substituents are preferred over *endo* substituents for steric reasons.[15] However, solvent will stabilize the carbonium ion intermediates in these reactions preferentially from the *exo* side. Obviously there are no substituents (other than hydrogen) to inhibit this in ions D and XII, while the *exo*-3-OH and *exo*-3-phenyl in ions A and XI can both inhibit carbonium ion solvation.

We are currently directing our efforts toward the synthesis of appropriately substituted diols which might afford pinacol rearrangement products *via endo*-3-hydrogen migration. We also plan to determine the rates of hydrolysis of the 3-*exo*- and 3-*endo*-hydroxy-2-phenyl-2-norbornyl chlorides, which should give a quantitative measure of the relative stabilities of ions A and D.

Acknowledgment. We are grateful to Mr. Louis Joris for performing the hydrogen bonding measurements.

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[15] For references, see P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

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Photochemistry of Adsorbed Organic Molecules. III. The Photosensitized *cis–trans* Isomerization of Piperylene in Silica Gel–Benzene Matrices

Sir:

Recently we have been investigating aspects of the physical adsorption of organic molecules and the proposed resulting electronic perturbations.[1,2] Specifically, we have been examining the electronic configurations of relatively polar molecules "bound" to the adsorbing surface of finely powdered activated silica gel in solvent matrices. Obviously these electronic configurations on silica gel vary to a substantial degree from the "normal" or "free" species in solution. Corresponding disturbances therefore should be expected in the photochemical behavior of a molecule in these differing surroundings, purely from environmental considerations.

The data thus far reported from these laboratories have concerned spectral shifts in ultraviolet and visible absorption of "bound" molecules,[1] as well as photodecomposition product and reaction rate variations due to the effect of the matrix.[2] We now wish to report the effect of a benzene–silica gel matrix on the vertical triplet excitation donating ability of three carefully chosen donors to the acceptor piperylene (1,3-pentadiene). The polarity of the sensitizers used in this study is far greater than that of the piperylene (as, for that matter, is the benzene solvent to a smaller degree), and thus we have reason to believe that a silica gel–solvent matrix will produce adsorption effects primarily upon the electronic configuration of the sensitizers, leaving the piperylene relatively unaffected. This fact is born out by the very small (~50 A) red shift of the spectrum of piperylene in a cyclohexane–silica gel matrix alone.

Table I[a]

Sensitizer	Triplet energy,[b] kcal	% *trans* from *cis*	% *trans* from *trans*
Benzophenone	68 (n,π^*)		
Matrix		59	58
Solution		59	58
Solution (lit.)[c]		57	56
2-Acetonaphthone	59 (π,π^*)		
Matrix		71	71
Solution		75	76
Solution (lit.)[c]		72	72
Biacetyl	55 (n,π^*)		
Matrix		73	73
Solution		80	80
Solution (lit.)[c]		77	77

[a] Solutions were 0.1 *M* in sensitizer and 0.2 *M* in piperylene. Irradiation was at 3660 A using a Hanovia 450-w lamp. Analyses were carried out on a 12-ft β,β'-oxydipropionitrile column at 60°. [b] Values from W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [c] Values from G. S. Hammond, J. Saltiel, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964). The discrepency between our solution values and those of Hammond is due to the fact that we measured vpc peak *areas*, whereas in Hammond's data most measurements were based on peak heights.

The donors selected were benzophenone, 2-acetonaphthone, and biacetyl. Table I lists the sensitizers, their triplet energies, and the values for the *cis–trans* photostationary states of piperylene in benzene solution and in a benzene–silica gel matrix. Results in solution are compared with literature values.

The trend in the data, in view of our previous experience with the matrices and in view of the dependence of photostationary states on triplet energy of sensitizer,[3] is both interesting and reasonable. The triplet n,π^* state of benzophenone in the matrix should be at higher energy[1] than in solution, but "*high-energy*" *sensitizers all give the same photostationary state*;[3] thus we see no effect of the matrix. "Low-energy" sensitizers, on the other hand, show a high preponderance of *trans* over *cis* at the photostationary state, and small (3–4 kcal) energy differences affect the ratio markedly, lower energy favoring *trans*. Biacetyl has as its lowest triplet the n,π^* configuration; the effect of the matrix would be to substantially raise the energy and lower the *trans*/*cis* ratio. This is clearly what is observed, with the per cent *trans* changing from 80 to 73. To round out the study, another low-energy sensitizer, acetonaphthone, with a lowest π,π^* triplet, was investigated. According to our predictions[1] the excited-state energy should be very slightly lowered in this case, thus, if anything, *increasing* slightly the ratio of *trans*. This, however, was *not* observed, the per cent *trans* lowering from 75 to 71. Thus it appears that the lowest π,π^* triplet of this particular molecule is less polar, rather than more polar, than the ground-state molecule. This is perhaps not too surprising since we have recently observed in absorption spectroscopy (singlet–singlet) in the matrix some π–π^* transitions in certain molecules are blue shifted rather than red shifted (azulene being a notable example).[4] Obviously, theoretical and experimental calculations of dipole moments of excited states of a great many molecules

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[1] P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

[2] P. A. Leermakers, L. D. Weis, and H. T. Thomas, *ibid.*, **87**, 4403 (1965).

[3] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

[4] P. A. Leermakers and L. D. Weis, unpublished results.

(particularly π,π^* states since their solvent shifts are unpredictable both in terms of direction and magnitude) are in order. With our technique we hope to help empirically obtain some of this information.

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The Role of Bacteriochlorophyll in Photosynthetic Hydrogen Transfer[1]

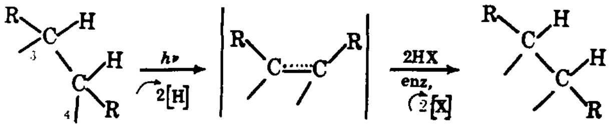
Sir:

The participation of chlorophyll as a hydrogen transfer agent in the water-splitting reaction of photosynthesis has been the subject of considerable speculation. Some of the chemical mechanisms that have been proposed for green plant photosynthesis involve a reversible photochemical oxidation–reduction cycle of the following type for either one- or two-electron transfers.[2]

$$\text{chlorophyll a} \longrightarrow \text{dehydrochlorophyll a} + [\text{H}]$$
$$\text{dehydrochlorophyll a} + \text{HOH} \longrightarrow \text{chlorophyll a} + 0.5\text{O}_2$$

Proposals of this type have been centered on the hydrogens in the 7,8 positions, the δ hydrogen, and the C_{10} hydrogen of chlorophyll a. Investigations designed to evaluate such mechanisms, using tritium as a hydrogen tracer, have been inconclusive; the results show small amounts of incorporation, but these cannot be considered as evidence for or against a hydrogen donor mechanism.[3–5] Deuterium experiments have eliminated δ-hydrogen participation, but not the C_{10}, C_7, or C_2 positions.[6]

We wish to introduce the notion that the 3,4 positions of ring II are photosynthetically important. If this is true, then in the oxygen-producing green plants and algae, which contain the chlorin type of pigments, it is possible that chlorophyll is reduced and then oxidized in the 3,4 positions. In the anaerobic photosynthetic organisms, such as the purple bacteria, which contain reduced chlorin pigments, the bacteriochlorophyll could be oxidized and then reduced in the 3,4 positions as shown in the following scheme for 2H transfer.



It would be equally feasible to formulate the transfer in terms of a single hydrogen atom and a partially oxidized bacteriochlorophyll. The immediate impetus for such a proposal came from the work of Holt, *et al.*,[7] and Olson and Romano,[8] who demonstrated the presence of both chlorin and dihydrochlorin pigments in the green photosynthetic bacteria, *Chlorobium*. This proposal cannot be tested on the green algae, since the pigment is isolated as chlorophyll and would not contain the photosynthetically important hydrogens. However, with anaerobic purple bacteria, the bacteriochlorophyll is isolated in the reduced state and changes in the 3,4 positions can be evaluated. The recent discovery of the specific oxidation of bacteriochlorophyll[9] in the 3,4 positions using 2,3-dichloro-5,6-dicyanobenzoquinone, converting the dihydrochlorin to the chlorin 2-desvinyl-2-acetylchlorophyll a, makes it possible for us to determine how much of the incorporated tritium is in the 3,4 positions.

In order to obtain a sufficient amount of bacteriochlorophyll for measurement, the experiment was performed using an extremely dense suspension (0.5-ml packed cells suspended in 3 ml of medium) of 4-day-old *Rhodospirillum rubrum*. Tritiated water (0.92 curie) was added to give a molar specific activity of 1.09×10^{13} dpm/mole; the suspension was placed in a flat cell with a path length of 5 mm. It was then illuminated from both sides with 23,000 foot-candles of white light for 15 min. The bacteriochlorophyll was isolated by acetone extraction, purified on powdered polyethylene tlc, and counted. The bacteriochlorophyll was then oxidized to give the 3,4-dehydro compound and purified on mannitol tlc, and its radioactivity was again determined.[10]

From the specific activity of the initial bacteriochlorophyll it was determined that approximately 2% of the bacteriochlorophyll molecules had incorporated tritium, and that from 62 to 96% (five separate photoexperiments, three of them in duplicate) of the incorporated radioactivity was in the 3,4 positions. Since we have no independent way of determining the rate of photosynthesis, we cannot yet relate this 2% labeling to an electron turnover rate, or a bacteriochlorophyll synthesis rate. However, because of the relatively great age of the cell culture and the extremely high density of the suspension in which the experiment was performed, and the fact that the dark control showed less than 0.03% tritium incorporation, we believe that, for the most part, this incorporation does not represent new bacteriochlorophyll synthesis. Under optimal growth conditions for dilute suspensions (one-twentieth of those of the experiment) the rate of bacteriochlorophyll increase is 1.7% for a 15-min period. A succeeding exposure of the tritium-labeled bacteria to light in a nontritiated medium for 15 min removes approximately 20% of the initially incorporated tritium. The fact that so much activity is removed requires a photoinduced hydrogen turnover. The fact that it is not all removed seems to necessitate a migratory active site.

In addition, a tritium isotope effect has not been included in the calculation of the reported 2% incorporation. It seems probable that this incorporation does indeed represent photoinduced electron turnover in the bacteriochlorophyll. However, the experiments

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[1] The work described in this paper was sponsored, in part, by the U. S. Atomic Energy Commission.

[2] E. I. Rabinowitch, "Photosynthesis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p 548; M. Calvin, "Horizons in Biochemistry," M. Kasha and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1962, p 34.

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[4] T. H. Norris, S. Ruben, and M. B. Allen, *J. Am. Chem. Soc.*, **64**, 3037 (1942).

[5] W. Vishniac and I. A. Rose, *Nature*, **182**, 1089 (1958).

[6] J. J. Katz, *et al.*, *J. Am. Chem. Soc.*, **86**, 4220 (1964).

[7] A. S. Holt, D. W. Hughes, H. J. Mende, and J. W. Purdie, *Plant Cell Physiol.*, **4**, 49 (1963).

[8] J. M. Olson and C. A. Romano. *Biochim. Biophys. Acta*, **59**, 726 (1962).

[9] J. R. Lindsay Smith and M. Calvin, submitted for publication.

[10] M. Byrn, Ph.D. Thesis, University of California, Berkeley.