Table I. Low-Field Nuclear Magnetic Resonance Assignments for Chlorophyll *c* (approximately 0.1 *M* in TFA or TFA-*d*)

Chemical shift[a]	|J|, cps	Relative area	Assignment
A_1 = 6.64[b]	A_1B_1, < 1.8[b]	3	Porphyrin vinyl methylenes (–CH=C*H*$_2$)
A_2 = 6.64[b]	A_2B_2, < 1.8[b]		
B_1 = 6.51[b]	A_1X_1, = 12.0[b]		
B_2 = 6.42[b]	A_2X_2, = 11.7[b]		
7.28	16.8, doublet	1	Porphyrin *trans*-acrylate (–CH=C*H*COOH)
7.62	Singlet	1	Porphyrin carbomethoxycyclopentanone (C-10)
X_1 = 8.27	Multiplet[b]	1.5	Porphyrin vinyl methine (–C*H*=CH$_2$)
X_2 = 8.24			
9.30	16.8, doublet	1	Porphyrin *trans*-acrylate (–C*H*=CHCOOH)
11.01	Singlets	3	Porphyrin methine protons
11.03			
11.16			

[a] Nmr spectra were determined with a Varian HA-100 nmr spectrometer. Chemical shifts are in parts per million from internal TMS (δ). [b] The observed resonances were superimposed ABX patterns. It was not possible to solve the ABX problem (J. A. Pople, W. S. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 132) explicitly; however, the assignments of chemical shift and coupling parameters are self-consistent with the observed spectrum. These parameters were obtained by assuming that only two different vinyl groups were present in the sample. [c] This resonance was absent in spectra taken in TFA-*d*, due to ready exchange of the ring V proton.

entirely analogous to the parent substance. The mass spectrum[9] of this chlorophyll *c* derivative did not give a strong parent ion because of the free carboxylic acid group. Thus, esterified derivatives were prepared.

Treatment of chlorophyll *c* with dry methanolic hydrochloric acid under reflux for 18 hr produced a methylated pheoporphyrin c. The nmr spectra of the methylated pheoporphyrin c were consistent with electrophilic addition of methanol to the acrylic ester (a broad one-proton multiplet, 5.0 ppm in TFA, porphyrin $-CH(OCH_3)CH_2COOCH_3$). Mass measurement of the parent (base) peaks at *m/e* 632 and 634 required empirical formulas of $C_{37}H_{36}N_4O_6$ and $C_{37}H_{38}N_4O_6$. The relative intensity of these two ions was roughly equal, suggesting that chlorophyll *c* may be an approximately 1:1 mixture of two pigments that differ only in the degree of hydrogenation.

Hydrogenation at 1 atm of pheoporphyrin c_5 in TFA with palladium followed by methylation with methanolic hydrochloric acid produced one compound (by thin layer chromatography) in high yield. Under these reduction conditions, chlorins were not formed and acrylic acid residues were not reduced to propionic acid side chains. The mass spectrum of this pheoporphyrin c_6 derivative showed only one parent ion (*m/e* 636, formula $C_{37}H_{40}N_4O_6$). The observed intense fragment ions, 605, 604, 578, and 577, correspond to loss of CH_3O, CH_3OH, $C_2H_2O_2$, and $C_2H_3O_2$, as would be anticipated for a structure similar to pheoporphyrin a_5.[10] The absence of a peak (intensity >0.1% base) at *m/e* 297 in the doubly ionized portion of the spectrum suggested that no propionic ester side chain is present in this compound. The most intense peak in the doubly ionized portion of the spectrum corresponded exactly to loss of $C_4H_6O_4$ from M^{2+}. This observation is consistent with the proposed structure for this compound, 7′-methoxypheoporphyrin a_5 dimethyl ester. The nmr spectrum in TFA was also highly consistent with this structure.

Reduction of chlorophyll *c* with hydriodic acid yielded a single product indistinguishable from authentic pheoporphyrin a_5 monomethyl ester.[8]

The data presented above, in addition to previously reported information,[3,11,12] suggest that chlorophyll *c* obtained by our procedure is a mixture of compounds Ia and Ib. These structures are in close agreement with Granick's original surmise[11] about the nature of chlorophyll *c*. The groups around the ring were located only by analogy with those of other known porphyrin natural products.[13]

---

(9) Measured on an AEI MS-9 mass spectrometer at Battelle Memorial Institute, Columbus, Ohio, by Dr. R. Foltz.

(10) A. H. Jackson, G. W. Kenner, K. M. Smith, R. T. Aplin, H. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **21**, 2913 (1965).

(11) S. Granick, *J. Biol. Chem.*, **179**, 505 (1949).

(12) A. S. Holt in ref 3, p 116.

(13) J. Lascelles, "Tetrapyrrole Biosynthesis," W. A. Benjamin, Inc., New York, N. Y., 1964.

R. C. Dougherty
Evans Laboratory of Chemistry, Ohio State University
Columbus, Ohio 43210

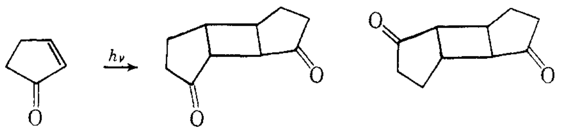
H. H. Strain, Walter A. Svec
R. A. Uphaus, J. J. Katz
Argonne National Laboratory
Argonne, Illinois 60439

Received August 8, 1966

Photodimerization of Cyclopentenone. Singlet or Triplet?[1]

Sir:

We wish to establish here that the photodimerization[2] of 2-cyclopentenone is an excited triplet state reaction. It is our hope that this communication will erase the uncertainties that now exist on this point.[3]



A B

The quantum yield for the photodimerization of cyclopentenone is reduced toward zero if the reaction is carried out in the presence of such triplet quenching agents as piperylene. A plot (Figure 1) of the inverse of the relative quantum yield against the concentration of added piperylene is linear over the concentration range studied. If the singlet excited state of cyclopentenone accounted for even 5% of the reaction, the line would curve distinctly in the higher concentration region.

---

(1) This work was supported by generous grants from the National Institutes of Health (GM 10572 and GM 13451).

(2) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(3) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 537; N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 203; G. S. Hammond and N. J. Turro, *Science*, **142**, 1541 (1963); J. Saltiel in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, p 302; P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2454 (1962); J. L. Ruhlen and P. A. Leermakers, private communication.

Table I[a]

Solvent	Cyclopentenone, *M*	Ratio A:B
Cyclopentenone neat	12.4	43:57
Benzene	10.0	41:59
	9.0	40:60
	8.1	40:60
	6.9	38:62
	6.1	37:63
	5.0	35:65
	4.0	34:66
	3.0	31:69
	2.0	27:73
	1.1	23:77
	0.093	15:85
1.0 *M* cyclopentanone in benzene	1.0	27:73
Ethyl acetate	1.0	30:70
t-Butyl alcohol	1.0	24:76
1,4-Dicarbomethoxy-cyclohexane	2.0	35:65
	1.0	33:67
Methanol	10.5	41:59
	1.0	41:59
	0.1	39:61

[a] The reactions were run to approximately 10% completion using the light from a Hanovia, 450-w, mercury arc lamp filtered through Pyrex glass. The ratios were determined as noted in footnote *d*, Table II.

Table II[a]

Solvent	Cyclopentenone, *M*	Sensitizer,[b] quencher,[c] or trap (*M*)	Ratio[d] A:B
Benzene	1.0	None	23.3:76.7
		Xanthone (0.1)	23.4:76.6
		Cyclopentene (1.0)[e]	23.2:76.8
Benzene	3.0	None[f]	31.4:68.6
		Xanthone (0.1)	31.5:68.5
		Xanthone (0.2)	31.7:68.3
		Piperylene (0.3)	31.6:68.4
		Piperylene (2.1)	31.4:68.6
Ethyl acetate	1.0	None	29.4:70.6
		Xanthone (0.1)	29.6:70.4
Ethyl acetate	3.0	None	35.0:65.0
		Xanthone (0.1)	35.1:64.9

[a] The reactions were run using 3130-A light to 10% completion. [b] In the order of entry, the xanthone absorbs 91, 76, 87, 92, and 80% of the incident light. [c] The piperylene used contained 26% of the *cis* isomer. Under the conditions of the reaction, little piperylene was consumed. [d] The dimers were separated by vpc on a 5 ft × $^3/_8$ in. column of 10% Carbowax 20M on 45–60 Chromosorb G DMCS at 240°. The ratios were calculated from calibrated integration of the vapor phase chromatograms and are good to ±0.2. [e] The adduct of cyclopentenone to cyclopentene was the major (75%) product. [f] The quantum yield for dimer formation was approximately 0.27.

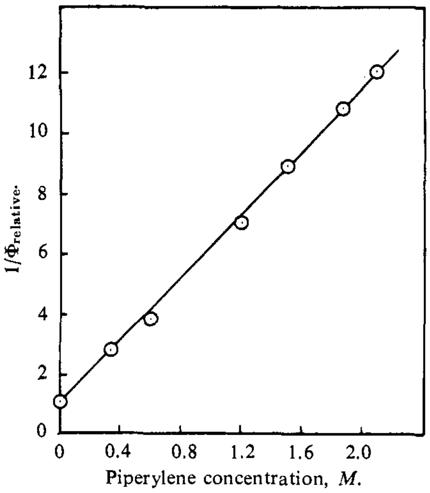


Figure 1. The reactions were run using benzene solutions 3.0 *M* in cyclopentenone and were taken to 11% completion with 3130-A light. The piperylene used contained 26% *cis* isomer. Very little of the piperylene was consumed during the reaction.

The photodimerization of 2-cyclopentenone in the presence of xanthone (E_{T_1} = 74.2 kcal/mole[4]), under conditions where xanthone absorbs most of the incident light, proceeds at nearly the same rate as the dimerization performed in the absence of the sensitizer.[5] This result is in accord with the now classic operational test for the intermediacy of an excited triplet state.[6]

The ratio of the photodimers produced on irradiation of cyclopentenone is a function of the reaction solvent and the concentration of cyclopentenone (Table I). Although on first thought it might appear reasonable to interpret the concentration dependence as an indication that a short-lived, excited singlet state plays a significant role at the higher concentrations, such an interpretation cannot be reconciled with the fact that the dimer ratio (Table II) is independent of the concentration of added sensitizer (xanthone), quencher (piperylene), or trap (cyclopentene). At this time it appears that the concentration effect is no more than a manifestation of a solvent effect; that is, the character of the reaction solvent is strongly dependent on the concentration of cyclopentenone. As is apparent in Table I, the concentration effect can be imitated by alterations in the nature of the solvent. For example, the ratio of the dimers formed on irradiation of 10 *M* cyclopentenone in benzene is very nearly the same as that for irradiation of 1 *M* cyclopentenone in methanol.

It is important to note that the variation in the ratio A:B is really rather small. The extreme values are about 43:57 and 15:85. In our opinion it would be unwarranted to assign special significance to such changes.

---

(4) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). We wish to thank Professor Hammond for suggesting in informal conversation the use of xanthone as a sensitizer.

(5) Xanthone, 0.1 *M*, depresses the rate of dimerization of 1 *M* cyclopentenone in benzene by only a factor of 1.16 even though the xanthone absorbs 91% of the incident light. The reduction in rate may be due to either a small amount of quencher present in the xanthone or to a basic inefficiency in the energy-transfer process; *cf.* ref 4.

(6) See, for example, G. S. Hammond, P. A. Leermakers, and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

(7) Fellow of the Alfred P. Sloan Foundation.

(8) National Institutes of Health Predoctoral Fellow.

Philip E. Eaton,[7] William S. Hurt[8]
Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

Received July 20, 1966

Energy Barrier of the *cis–trans* Isomerization of Difluorodiazine

Sir:

We wish to report a first attempt at studying the *cis–trans* isomerization of difluorodiazine and deter-