

teractions deduced for the $(\text{Chl } a \cdot 2\text{H}_2\text{O})_n$ aggregate. The observed¹⁹ downfield ^{13}C NMR effect observed for C-9 is thought to provide unequivocal evidence for the unsymmetrical interaction (a). However, reexamination¹⁸ of the ^{13}C NMR data of Boxer et al.²⁰ reveals that the C-10 resonance has apparently undergone an even larger shift upon Chl a aggregation.²²

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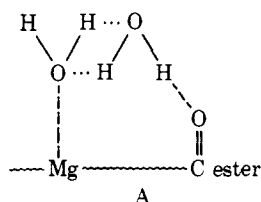
Francis K. Fong,*²¹ Vaughn J. Koester
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received November 23, 1974

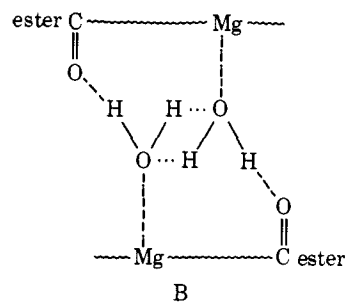
Ester and Keto Carbonyl Linkages in Chlorophyll a, Pyrochlorophyll a, and Protochlorophyll a

Sir:

In recent work, we concluded¹ that the existing experimental observations^{2,3} relevant to the primary light reaction can be interpreted on the basis of the C_2 1:1 $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ adduct structure in which two chlorophyll molecules are held by two complementary ester $\text{C}=\text{O} \cdots \text{HO}(\text{Mg})\text{H}$ linkages. This conclusion presents an alternative to that of the earlier Katz-Norris postulate that the reaction center "special pair"^{2c} consists of two chlorophyll a molecules interlinked by a single water molecule through the unsymmetrical interaction ester $\text{C}=\text{O} \cdots \text{HO}(\text{Mg})\text{H} \cdots \text{O}=\text{C}$ keto. Independently and simultaneously, Strouse⁴ found from single-crystal x ray work that the unit interactions in ethyl chlorophyllide $a \cdot 2\text{H}_2\text{O}$ polymeric aggregate are given by

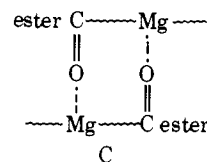


(See Figure 1 of ref 4). We observe that a symmetrical addition of a second Chl a molecule to A results directly in the self-aggregating interactions proposed¹ for the symmetrical $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ adduct.



In both A and B, the coordination interaction occurs on the same side of the chlorin plane as the C-10 ester group, thus taking advantage of the 0.4 Å displacement of the Mg atom in the same direction as the ester group.⁴ The Katz structure invokes water coordination from the direction *opposite* to that of the Mg atom displacement.

In a reexamination of the current literature on the infrared⁵ and NMR⁶ spectra of Chl a, it has been pointed out⁷ that self-aggregating ester $\text{C}=\text{O} \cdots \text{Mg}$ linkages may play an important role in Chl a dimerization. A probable structure for the Chl a dimer can be given by the bonding interactions:⁷



We note that in C the self-aggregating interactions again take advantage of the out-of-plane displacements of the Mg atoms. Structure C is a modification of the earlier conclusion that the Chl a dimer occurs through the asymmetrical keto $\text{C}=\text{O} \cdots \text{Mg}$ linkage. Both the present model C and the Ballschmider-Katz model are distinctly different from yet another model by Houssier and Sauer⁸ who proposed that Chl a dimerization involves both the C-9 keto oxygen and the propionic ester at C-7. In this communication, we attempt to evaluate the validity of the various dimer models.

In pyrochlorophyll a, no ester $\text{C}=\text{O} \cdots \text{Mg}$ interactions are allowed due to the absence of the ring V carbomethoxy group. The upfield ^1H NMR shift difference⁹ (produced by intermolecular aggregation) of the proton at C-10 is 50 ppm. This value is remarkably lower than the corresponding shift difference 185 ppm observed in chlorophyll a,^{2c,6a} and reflects the probable role of the carbomethoxy carbonyl group in the dimerization of Chl a molecules.

From a qualitative comparison of the optical properties of dimeric Chl a, and pyroChl a and protochlorophyll a (PChl a), Sauer and co-workers⁸ arrived at the conclusions (i) that the ring V carbomethoxy group has no significant influence on the dimer structure and (ii) that the C-7 propionic ester and the C-9 keto function are both involved in dimerization. These conclusions were based on the fact that while the circular dichroism (CD) and absorption spectra of dimeric Chl a and pyroChl a are "similar", the corresponding spectrum of PChl a is dramatically different.¹⁰

A reexamination of Houssier and Sauer's data reveals that the spectroscopic differences and similarities between the dimers of Chl a, pyroChl a, and PChl a appear to be a matter of degree. The CD spectrum of PChl a is different from those of Chl a and pyroChl a, but the CD spectra of Chl a and pyroChl a dimers are less so. (Compare, for ex-

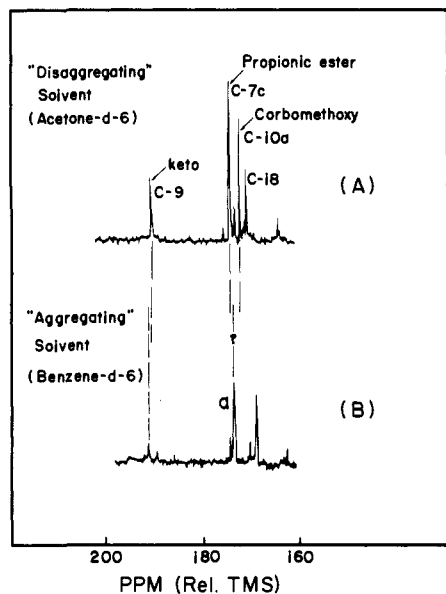


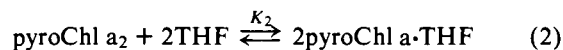
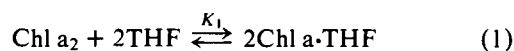
Figure 1. The C-10 carbonyl question: The 22.63-MHz ^{13}C NMR spectra (taken from ref 11) of 18% ^{13}C Chl a, 0.1 M in (A) acetone- d_6 and (B) benzene- d_6 . The relatively small downfield shift of the C-9 line in (B) has been considered (ref 12) to be unequivocal proof of direct involvement of only the C-9 keto carbonyl in Chl a dimerization. If line a in (B) originates both from C-7c and C-10a, then the carbomethoxy group must play a dominant role in aggregation in the "downfield hypothesis". If line a originates only from C-7, then one must account for the absence of the C-10a line. Thus, the evidence does not unequivocally rule out the C-10a carbonyl involvement in dimeric aggregation even if the C-10a line turns out to be upfield shifted. Theoretical calculations based on simplified model interactions may be misleading in predicting the sign of the observed chemical shifts.

ample, the *ratios* of the two long-wavelength positive and negative CD components in Figures 5 and 6 in ref 8a.) The Sauer model appears to conflict with the ^{13}C NMR data¹¹ displayed in Figure 1, in which the aggregation effects on the chemical shift differences of the C-9 keto, C-7 propionic ester and C-10 carbomethoxy ester carbonyl carbons are compared. If one speculates that the downfield effect of aggregation observed for C-9 implies direct involvement in aggregation, then the corresponding chemical shift observed for C-7c would suggest that the propionic ester plays a negligible role.¹² The possibility that the carbomethoxy group is involved in aggregation cannot be discounted (especially in view of the apparent disappearance of the C-10a line in Figure 1B). The origins of the observed incremental shifts in Chl a remain obscure. Model calculations based on simplified interactions are of questionable value in dealing with large molecules such as Chl a.¹²

The anomalous spectroscopic behavior^{8a} of PChl a can be rationalized also. An examination of CPK molecular models reveals that the loss of the asymmetrical center at C-7 in PChl a makes possible closely fitting self-aggregating C-7 ester C=O...Mg linkages in PChl a similar to those given in C. Such linkages are sterically impossible in Chl a and pyroChl a due to the fact that the propionic ester group is trans to the C-10 carbomethoxy group. It is clear that while aggregation with either the C-9 keto group or the C-10 ester group can lead to approximately "similar" overlap of the region about ring V, the self-aggregating C-7 ester linkages would lead to drastically different regions of overlap for the two PChl a molecules.

The equilibrium constants for the disaggregation of the Chl a dimer and the pyroChl a dimer have been measured

by Ballschmitter and Katz.⁵ For the reactions



these authors obtained $K_1/K_2 \sim 10$. This result can be understood in terms of simple statistical considerations if Chl a_2 assumes the molecular configuration C. The equilibrium constant in (1) or (2) can be written¹³ $K = \omega^2 \Omega^{-1} \exp(\epsilon/kT)$, where ω and Ω are the configuration degeneracies of the monomer and dimer, respectively, and ϵ is the aggregation energy. In C, the two Chl a molecules are rigidly interlocked so that $\omega_1 \sim \Omega_1$. On the other hand, the two molecules in pyroChl a_2 , being held only by a single keto C=O...Mg bond, retain partial orientational freedom with respect to each other. We thus obtain $\omega_2^2 \gg \Omega_2 \gg \omega_1 \sim \omega_2 \sim \Omega_1$. Since there are two aggregating interactions in C compared to only one in pyroChl a_2 , we estimate $|\epsilon_2| \sim 0.5|\epsilon_1| = E$ and arrive at the inequality $\Omega_2/\Omega_1 > \exp(+E/kT)$ for $K_1/K_2 > 1$. The Ballschmitter-Katz ratio $K_1/K_2 \sim 10$ is thus attributed to entropy effects favoring the dimerization of pyroChl a over that of Chl a in spite of the *larger* attractive aggregation energy of the latter process.

In the Katz model, the two dimers have similar configurations, i.e., $\Omega_1 \sim \Omega_2$, and the requirement $K_1/K_2 > 1$ is tantamount to the condition $|\epsilon_1| < |\epsilon_2|$. It is tempting to account for the weakened interaction ϵ_1 by the rationalization that steric hindrance in Chl a forces the keto C=O...Mg linkage to occur on the opposite side of the Mg atom displacement, but this reasoning leads to an inconsistency in that it is corollary to the premise of Mg-atom-displacement-strengthened ester linkages in B and C.

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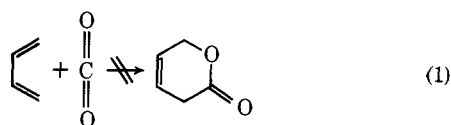
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- Sauer and his co-workers did not rigorously dry their solvents⁸ and, according to Ballschmitter and Katz,⁵ the presence of water contamination in Sauer and co-workers' samples apparently led to large errors in their estimated monomer-dimer equilibrium constants.⁵ Also, Sauer and co-workers' calculated absorption spectra for dimeric Chl a appear to differ qualitatively and quantitatively from the corresponding spectra given by Katz and Norris.^{2c} (Compare, for example, the dashed curve of Figure 1 in ref 8b and Figure 8 of ref 2c.)
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Francis K. Fong¹⁴
 Department of Chemistry, Purdue University
 West Lafayette, Indiana 47907
 Received December 4, 1974

A Carbon Dioxide Equivalent for the Diels-Alder Reaction

Sir:

Carbon dioxide does not undergo 4 + 2 cycloaddition with dienes¹ (eq 1) nor is there a well-defined procedure which effects this transformation.² This communication reports a method which allows for a general synthesis of lactones by use of a carbon dioxide equivalent and describes some useful transformations of these adducts.

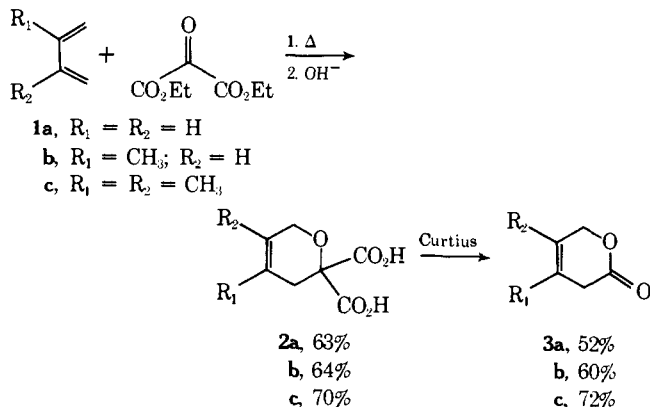


The simplest members in the triad of carbon and oxygen cumulated systems, allene, ketene, and carbon dioxide ($\text{CH}_2=\text{C}=\text{CH}_2$, $\text{O}=\text{C}=\text{CH}_2$, $\text{O}=\text{C}=\text{O}$) are considered poor partners for the Diels-Alder reaction. Indeed, only allene shows any propensity towards 4 + 2 cycloaddition. Recently, however, new methods have been developed which allow for the facile introduction of the $-\text{CH}_2\text{C}(\equiv\text{CH}_2)-$ ³ and $-\text{CH}_2\text{C}(\equiv\text{O})-$ ⁴ grouping in a Diels-Alder sense. Clearly, the addition of a $-\text{OC}(\equiv\text{O})-$ group to a diene requires a substance with a strongly polarized carbon-oxygen double bond. Also attached to this carbonyl, must be a grouping which could readily be transformed into the lactone carbonyl moiety. Furthermore the last step, the release of the lactone carbonyl, would have to be accomplished under mild conditions so as not to effect conjugation of the β,γ -double bond. We considered that diethylketomalonate^{2,5} might well serve as a carbon dioxide equivalent, the unmasking step being a bis-Curtius degradation⁶ followed by hydrolysis (Scheme I).

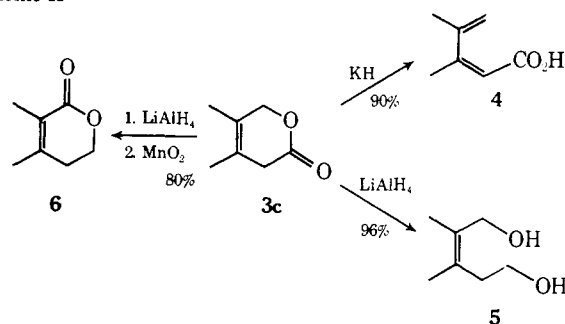
Warming acetonitrile solutions of dienes **1a-c** and diethylketomalonate with a trace of hydroquinone to 130° for 4 hr, afforded the known adducts in good yield.^{1,7,8} Hydrolysis of these adducts proceeded smoothly with KOH in aqueous THF at room temperature to afford the diacids **2a-c** in overall yields of 63–70%.⁸

The conversion of these stable diacids to their corre-

Scheme I



Scheme II



sponding lactones could be accomplished in less than 5 hr, without isolation of intermediates. Treatment of the diacids with oxalyl chloride in benzene with a trace of pyridine at reflux for 2–2.5 hours afforded almost pure diacid chloride. Removal of the solvent at reduced pressure and redissolution in acetonitrile followed by the addition of excess activated sodium azide⁹ afforded, after 1 hr at room temperature, the bisacylazide. Filtration of the acetonitrile solution to remove excess sodium azide and replacement of the acetonitrile with cyclohexane followed by heating the solution for 1 hr at reflux effected the rearrangement. It should be noted that benzene and other moderately polar solvents were inefficacious and led to little or none of the desired bisisocyanate. The final step, hydrolysis of the bisisocyanate, was accomplished with 5% aqueous oxalic acid in THF at room temperature for 30 min. The overall yield of lactone, after distillation, from diacid was quite acceptable (see Scheme I).^{10,11}

These adducts show promise as being versatile intermediates in synthesis. A few examples of their utility are described below (Scheme II). Treatment of lactone **3c** with 1 equiv of potassium hydride in THF at 0° afforded the dienoic acid **4**¹⁰ (mp 54.5–56°). The tetrasubstituted olefin **5** (λ_{max} 3.0 μm), could be readily prepared by reduction of **3c** with lithium aluminum hydride in THF at 0°. This diol could then be transformed to a new lactone **6** (λ_{max} 5.83 μm), simply by stirring a CH_2Cl_2 solution of **5** with activated MnO_2 .¹²

We are continuing to explore the chemistry of these adducts.¹³

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- Diene **1b** gave an 11:1 mixture of **2b** and its isomer **2d**, $\text{R}_1 = \text{H}$, $\text{R}_2 = \text{CH}_3$ by NMR analysis.
- Yield is based on diethylketomalonate. **2c** was crystalline (mp 138–140°). **2a** and **2b** were both oils.
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- Infrared, NMR, and mass spectral data were all in agreement with the assigned structures.
- The sodium azide Curtius degradation was found to be superior to the following alternate procedures: (a) Oxidative decarboxylation using lead tetraacetate directly afforded 60% of **3c**, 40% of **3b**, and no lactone **3a**. (See J. J. Tufariello and W. Kessel, *Tetrahedron Lett.*, 6145 (1966), and references within.) (b) One-pot bisisocyanate formation using trimethylsilylazide on the bisacid chloride in refluxing cyclohexane followed by hydrolysis yielded 55% of **3c**, 30% of **3b**. (See S. S. Washburne and W. R. Peterson, Jr., *Synth. Commun.*, **2**, 227 (1972).) (c) Standard Curtius degradation as well as modified Curtius degradation (see J. Wienstock, *J. Org. Chem.*, **26**, 3511 (1961)) afforded less than 20% of the desired lactones.