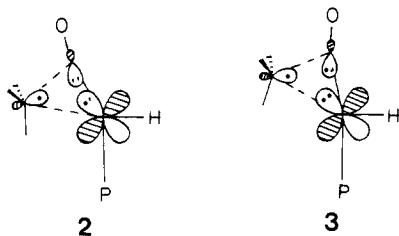


Figure 2. Interactive hybrid molecular orbitals of CH_3 and $\text{Pd}(\text{H})(\text{CO})(\text{PH}_3)$ for (left) the reactant, (middle) the transition state, and (right) the product.

that the reaction coordinate is methyl migration through a three-center transition state, consistent with the experimental results.^{4d} The CH^1 bond lengths of the product and the transition state are 1.089 and 1.090 Å, respectively, and thus the agostic interaction which would make the CH bond longer is absent.⁸

Here two questions emerge; the first one is why the carbonyl group does not migrate and the second one is what kind of factor stabilizes the three-center transition state.

In order to answer the first question, we assume the transition state for the carbonyl group migration in which the angles ($\text{C}-\text{O})\text{Pd}(\text{H})$ and $(\text{CH}_3)\text{Pd}(\text{PH}_3)$ of the true transition state are exchanged. The assumed transition state is less stable by about 7 kcal/mol than the true transition state. This instability is ascribed to the repulsion between two carbonyl lone pair electrons and d_{xy} electrons, as shown in 2. The repulsion in the true transition state, as shown in 3, is weaker, because the carbonyl lone pair is no longer directed toward the $\text{Pd } d_{xy}$ electrons and because the long distance and the small electron density (~ 1) keep the increase of the methyl sp^3 - $\text{Pd } d_{xy}$ repulsion to a minimum. Therefore, the alkyl group migration is expected to be common in late transition-metal complexes.



The answer to the second question is given by the paired interactive hybrid molecular orbitals (IHMO's), as shown in Figure 2, into which the dominant orbital interactions between the methyl group and the remaining part of the complex are condensed.⁹ Although the IHMO of the methyl group remains almost unchanged during the course of reaction, that of the $\text{Pd}(\text{H})(\text{C}-\text{O})(\text{PH}_3)$ fragment changes its shape smoothly. While the pair of IHMO's for the reactant describes the CH_3 - Pd bond and that for the product describes the CH_3 - CO bond, at the transition state the pair of IHMO's has a character between the two and shows that the three-center transition state is stabilized by the interaction

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between the methyl group sp^3 -like orbital and $\text{CO } \pi^*$ and the $\text{Pd } (d + p)$ orbitals.

The activation energy for the carbonyl insertion reaction of **1** is low, consistent with the experimental fact that the reaction of the Pd complex proceeds easily.¹⁰ On the other hand, the Pt complex is known to be less reactive.¹⁰ Actually, we obtained an activation energy for the reaction of $\text{Pt}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3)$ to be higher by 8 kcal/mol. The analysis of the difference between Pd and Pt complexes and other details of the present calculations will be published elsewhere.

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Exciton Delocalization of the Excited Singlet State of Chlorophyll *a* Monohydrate Dimer and Fluorescence Lifetimes of Translationally Equivalent Aggregates

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Recently, it was found that the triplet states of the in vivo P700 Chl *a* dimer¹ and the in vitro monohydrate Chl *a* dimer, $(\text{Chl } a \cdot \text{H}_2\text{O})_2$, are not delocalized by exciton interactions.^{1,2} On the other hand, exciton interactions are generally assumed to play a role in the excited singlet state properties of these dimers, although hitherto there has been little clear-cut evidence for such interactions. The redshifts observed for the P700 and $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ bands at 695 nm compared³ to the 662-nm absorption band of Chl *a*· H_2O are largely due to bathochromic shifts arising from intermolecular interactions participating in the dimer structures. Earlier interpretations^{4,5} of exciton splittings in the observed P700⁺ minus P700 absorption-change spectra have recently been disputed.^{6,7} In this paper we report evidence, based on fluorescence lifetime measurements, for exciton delocalization in the $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ S_1 state and provide two criteria for using fluorescence lifetime measurements as a diagnostic tool for determining the size of an *n* aggregate.

Freed considered⁸ the radiative decay and internal conversion

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of the delocalized dimer S_1 state to the one-molecule product state of the ground electronic level, S_0 . He suggested that the fluorescence lifetime of a covalently linked Chl *a* dimer would be about one-half that of the corresponding disaggregated pair. However, Freed did not consider intersystem crossing of S_1 involving the triplet as the terminal state, an important decay path of the excited chlorophyll. Furthermore, there are many known cases of excitonically coupled excited states of molecular aggregates that do not follow Freed's generalized scheme. For example, the room-temperature fluorescence lifetime of excimeric naphthalene in cyclohexane is 117 ns, indistinguishable from that, 120 ns, for the corresponding monomer.⁹ Likewise, in a study of the monomer-dimer system of 1,4-dibromonaphthalene (DBN), only two of the three phosphorescence components have been observed to possess dimer lifetimes half those of the monomer.¹⁰

Chlorophyll *a* was extracted from fresh spinach and purified according to published methods.¹¹ A 1.2×10^{-5} M hydrated Chl *a* monomer solution in water-saturated 1:1 *n*-P/MCH (*n*-pentane/methylcyclohexane) was prepared by the procedure of Fong and Koester.³ A 2.3×10^{-5} M $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ solution in rigorously dried 3-methylpentane was prepared by the method described by Hoshino et al.² Fluorescence spectra were obtained with the experimental apparatus described by Alfano and Fong.¹² Fluorescence lifetimes were measured and determined according to the method of Alfano and co-workers.¹³

On the basis of Freed's theory⁸ the symmetric $\Psi(+)$ and antisymmetric $\Psi(-)$ wavefunctions for the pair of Chl *a* molecules in $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ are written

$$\Psi(\pm) = C_1|\Psi_A^*\Psi_B\rangle \pm C_2|\Psi_A\Psi_B^*\rangle \quad (1)$$

where the asterisk denotes the one-molecule localization of the S_1 excitation. The dimer transition probability rate, W , from S_1 via radiative and nonradiative couplings to the lowest, localized triplet state, T_1 , and the ground state, S_0 , is given by

$$W = \sum_i \sum_{\pm} W_{\pm}^i = [|C_1|^2 + |C_2|^2 + (C_1 C_2 + C_2 C_1)] \sum_i W_A^i \quad (2)$$

where W_{\pm} and W_A respectively denote dimer and monomer transition probability rates, and the i summation is carried over the radiative ($S_1 \rightarrow S_0$), internal conversion ($S_1 \rightsquigarrow S_0$), and intersystem crossing ($S_1 \rightsquigarrow T_1$) processes. For exciton resonance the mixing coefficients C_1 and C_2 are equal, i.e., $|C_1|^2 = |C_2|^2 = 1/2$, so eq 2 reduces to

$$W = 2W_A \quad (3)$$

where $W_A = \sum_i W_A^i$ is the total monomer S_1 transition probability rate.

Equation 3 thus predicts that the fluorescence lifetime of a symmetrical dimer is half that of the monomer provided that the triplet state is localized on a single molecule.^{1,2} This condition is not met in the following situation, which was not considered previously.⁸ Had a delocalized dimer triplet been involved as the final state in intersystem crossing, the decay rate for the dimer-monomer system would have been related by the expression

$$W^{ns} = [|C_1|^4 + |C_2|^4 + 2|C_1|^2|C_2|^2] W_A^{is} = W_A^{is} \quad (4)$$

In the event that triplet trapping of the singlet excitation is a dominant pathway, as is the case for Chl *a*,¹⁴ eq 4 would have resulted in a dimer fluorescence lifetime approximately equal to

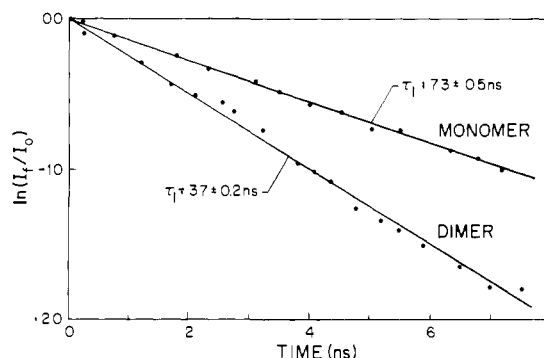
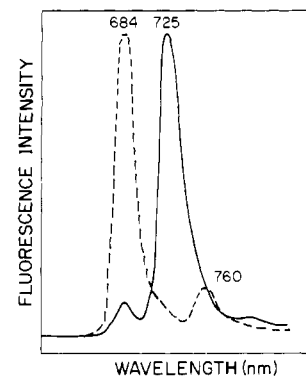


Figure 1. Upper figure: Fluorescence spectra of (---) hydrated Chl *a* monomer at 90 K and (—) monohydrate dimer, $(\text{Chl } a \cdot \text{H}_2\text{O})_2$, at 77 K. Lower figure: Fluorescence lifetime measurements corresponding to the monomer and dimer spectra shown above.

but less than the monomer lifetime.

Equations 3 and 4 can be readily generalized to an aggregate containing n equivalent monomeric units. Fluorescence lifetime measurements provide a diagnostic tool for determining the size of an n aggregate given the following two criteria: (1) The delocalized exciton state is radiatively and/or radiationlessly coupled to one or more localized, one-molecular states. (2) The Franck-Condon factor for transitions in the aggregate is approximately the same as that for the monomeric units, so the vibrational modes obtained on aggregate formation do not contribute to electronic transitions either as promoting or accepting modes.

Given the localization² of the triplet state of $(\text{Chl } a \cdot \text{H}_2\text{O})_2$, the results in Figure 1 showing halving of the monomer fluorescence lifetime in the dimer provide evidence for the delocalization of the S_1 exciton state in a dimer structure composed of two identical monomeric units. Condition 1 for observing eq 3 is corroborated by the fact that the triplet-sublevel phosphorescent transition in DBN, whose lifetime does not follow eq 3, is attributed to dimer symmetry selection involving transition to a vibrationally excited ground state delocalized by vibronic exciton interactions.¹⁰ In this case a rate expression for the dimer-monomer system analogous to eq 4 is applicable. The breakdown of eq 3 upon violation of condition 2 is exemplified by the naphthalene excimer in cyclohexane.⁹ For this system there exists a strong contribution of the intermolecular modes to internal conversion, as evidenced by the disaggregation of a bound excimer in the excited state to separated molecules in the ground state. An important feature of the Chl *a* dimer relaxation theory is the argument that the water bridges involve relatively strong bonding and high-frequency vibrations that are virtually unaffected in transitions between the ground and excited states.⁸

The requirement of translational equivalence for the two Chl *a* molecules in a dimeric configuration is tantamount to requiring a C_2 symmetry for the dimer. The diagnostic tool developed above for determining the size of an n aggregate thus also provides crucial information for assigning the structural details of $(\text{Chl } a \cdot \text{H}_2\text{O})_2$.¹⁵

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The analysis reported above for (Chl *a*-H₂O)₂ evidently applies also to that of closely analogous fluorescence lifetime measurements described for the monomer-dimer system involving covalently linked Chl *a* pairs.¹⁶

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Application of Allenylsilanes in [3 + 2] Annulation Approaches to Oxygen and Nitrogen Heterocycles

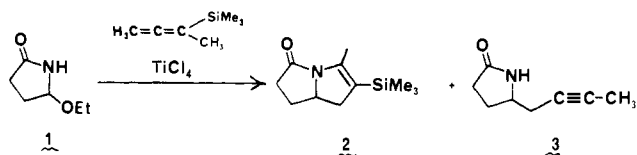
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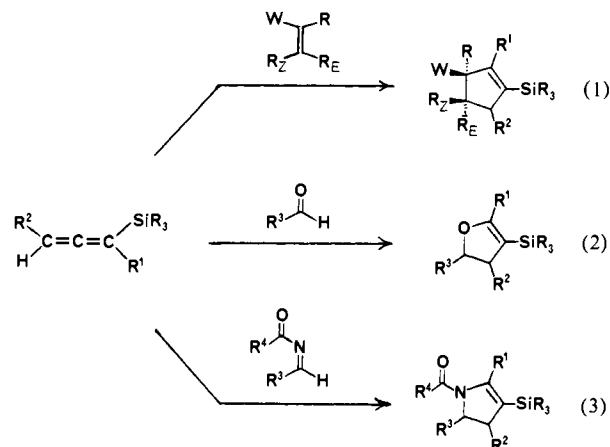
The reaction of allenylsilanes with electron-deficient olefins and acetylenes constitutes a powerful method for the regio- and stereocontrolled synthesis of highly substituted cyclopentenes (eq 1).² In this paper we report that carbonyl and *N*-acyl imine derivatives can participate as "heteroallenophiles" in a related [3 + 2] annulation approach to five-membered heterocyclic compounds (Scheme I).

Initial attempts to extend our [3 + 2] annulation strategy to the synthesis of heterocyclic systems met with limited success. As we have previously noted,³ the TiCl₄-promoted addition of allenyltrimethylsilanes to ketones and aldehydes leads predominantly to the formation of homopropargylic alcohols. More promising results were obtained, however, when we examined the reaction of allenylsilanes with *N*-acyl iminium ions.⁴ For example, addition of 1-methyl-1-(trimethylsilyl)allene to 5-ethoxy-2-pyrrolidinone (1) in the presence of titanium tetrachloride (0 → 25 °C, CH₂Cl₂) produced the desired pyrrolizinone 2 in 28% yield, in addition to the acetylenic lactam 3 (59% yield).



In this reaction we considered it likely that the lactam products 2 and 3 were being generated via a pathway analogous to that involved in our earlier [3 + 2] cyclopentene annulation.^{2b} Thus, regioselective electrophilic substitution of the *N*-acyl iminium ion derived from 1 at C-3 of the allenylsilane produces a vinyl cation stabilized by hyperconjugative interaction with the adjacent

Scheme I



carbon-silicon σ bond. A 1,2-cationic trimethylsilyl shift then occurs affording an isomeric vinyl cation, which is intercepted by the nucleophilic nitrogen atom to generate the new heterocyclic ring. Alternatively, either intermediate carbocation may undergo chloride-initiated desilylation and thus produce the acetylenic product 3.

Upon considering this mechanism, it appeared evident to us that by simply increasing the steric shielding about silicon we might effectively suppress the unwelcome desilylation pathway and thereby direct the course of these reactions to afford exclusively the desired heterocyclic products. This simple stratagem proved eminently successful: in contrast to the reactions of allenyltrimethylsilanes, (*tert*-butyldimethylsilyl)allenes⁵ smoothly combine with aldehydes and *N*-acyl imine derivatives to afford five-membered heterocycles (Table I and II). In a typical reaction, 1.1 equiv of TiCl₄ is added to a 0.2 M solution of the aldehyde in CH₂Cl₂ at -78 °C. After 10 min, 1.2 equiv of allenylsilane is added, and the resulting solution is stirred at -78 °C for 15-45 min. The reaction mixture is quenched by rapid addition of 7 equiv of Et₃N,⁷ and then transferred into a mixture of ether and water. Ether extraction followed by chromatographic purification (or distillation) furnishes the desired 2,3-dihydrofurans.⁸ For the synthesis of nitrogen heterocycles, a similar procedure is employed except that the reaction is carried out at 0-25 °C rather than at -78 °C.

A variety of aldehydes⁹ function as heteroallenophiles in this [3 + 2] annulation (Table I). Reactions of the C-3 substituted allenylsilane 7 with achiral aldehydes (entries 3-5) afforded predominantly *cis*-substituted dihydrofurans,¹⁰ as predicted based on the well-documented stereochemical course of Lewis acid promoted additions of 3-substituted allenylsilanes to aldehydes.^{11,12} Addition of the achiral allene 4 to the chiral α -alkoxy aldehyde 13 also proceeds as expected to produce exclusively 14 via che-

(5) 1-Methyl-1-(*tert*-butyldimethylsilyl)allene (4) was prepared in 63% overall yield (35-g scale) from propargyl alcohol by a procedure analogous to that previously used to prepare 1-methyl-1-(trimethylsilyl)allene.^{2b,6} 1,3-Dimethyl-1-(*tert*-butyldimethylsilyl)allene (7) [bp 78-80 °C (20 mmHg)] was prepared from 4 by sequential treatment with 1.2 equiv of *n*-BuLi (-78 °C, 0.5 h) and then 4 equiv of CH₃I (-78 → 0 °C) in THF.

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(9) Thus far annulations employing ketones as heteroallenophiles have been less successful. For example, reaction of the allenylsilane 4 with cyclohexanone produces the expected 2,3-dihydrofuran in only 20-25% yield.

(10) The major isomers produced in these annulations were identified as the *cis*-substituted dihydrofurans by ¹H NMR spectroscopic analysis. These assignments are consistent with the stereochemical course of the reactions of the corresponding (trimethylsilyl)allenes.¹²

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