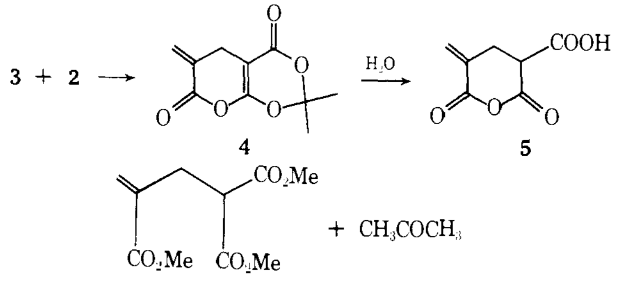
infrared spectrum (Nujol mull) showed complex carbonyl absorption including peaks at 1785, 1740, and 1685 cm^{-1}. On the basis of the methanolysis described below we consider the glassy solid to be a mixture containing principally the bicyclic compound **4**, formed by the addition of methylene ketene **3** to the 5-methylene compound **2**, and the anhydrido-acid **5** formed by partial hydrolysis of **4**.



4

5

6

The ^1H NMR spectrum of the glassy solid in $CDCl_3$ showed the presence of free acetone, and signals assigned to the bicyclic compound **4** (δ 1.80, s, CMe_2; 3.47, t, $J_{allylic}$ ca. 2.2 Hz, ring CH_2; 6.0, m, and 6.7, m, $=CH_2$) and to the anhydrido-acid **5** (δ 3.06, br m, CH_2CH; 3.88, t, J ca. 6.5 Hz, CH_2CH; signals due to $=CH_2$ assumed to be coincident with those of **4**).

Methanolysis of the glassy solid and treatment with a limited amount of diazomethane gave an oily product which we have shown to contain at least 90% of the unsaturated triester **6** (approximately 20% yield from adduct). In some runs this triester (mol wt 230) could be shown by mass spectrometry to contain a minor congener of *m/e* 316, which we suspect to be a tetraester formed by further addition of methylene ketene to the bicyclic compound **4**, with subsequent methanolysis and esterification. The identity of the triester **6** was confirmed by synthesis from trimethyl hydrogen propane-1,1,3,3-tetracarboxylate with formaldehyde and diethylamine.[10]

The range of reactions which has been demonstrated for substituted methylene ketenes is extremely limited;[1-4] despite repeated attempts we have so far failed to achieve an intermolecular cycloaddition to an alkene or diene, and our current work on systems which would permit intramolecular trapping has as yet yielded no result. An apparent exception to this experience, the addition of a ketene formed from dimethylacryloyl chloride and triethylamine to cyclopentadiene, is considered[11] to involve initial attack by a vinyl ketene rather than a methylene ketene. Thus, the ready cycloaddition of methylene ketene to its precursor **2**, shown by the present results, is the first unambiguous example of a cycloaddition other than dimerization.

Methylene ketene does react with nucleophiles in these experiments, but we have so far failed to isolate or detect any product of recombination with cyclopentadiene or any dimer, although the substituted methylene ketenes[1] which we have studied dimerize so readily as to frustrate all attempts to obtain them in solution.

Acknowledgment. This project was supported by the Australian Research Grants Committee.

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(7) Adduct **1** showed IR 1770 m and 1735 s cm^{-1}. ^1H NMR, δ ($CDCl_3$) 1.48 (1 H, d, J = 8.8 Hz) and 2.09 (1 H, d, J = 8.8 Hz) (7-CH_2), 1.74 (3 H, s) and 1.89 (3 H, s) (CMe_2), 1.6–2.0 (1 H, m) and 2.57 (1 H, d of d, J = 11.7 and 3.6 Hz) (3-CH_2), 3.15 (1 H, br s) (4-CH), 3.46 (1 H, br s) (1-CH), 5.98 (1 H, d of d, J = 5.4 and 2.9 Hz) and 6.49 (1 H, d of d, J = 5.4 and 3.3 Hz) (–CH=CH–).
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Photochemical Reactions in Organized Monolayer Assemblies. 5. Photochemical and Thermal Reactions of Reactive Intermediates Formed by Ligand Photoejection in Ruthenium Porphyrins

Sir:

During recent years, much effort has been directed toward the synthesis of metalloporphyrin complexes to serve as models for the biologically important oxygen transport and redox systems.[1-9] In recent studies of other surfactant molecules containing reactive chromophores, we have found that reactivity in the semirigid environment of organized monolayer assemblies is often quite different from behavior of the same compounds in solution.[10-17] Spectroscopic study of such assemblies has allowed the investigation of a variety of photochemical and photophysical processes. Results of such studies demonstrate that the monolayer environment may exert a striking influence on reactivity which can be explained in terms of the structure of the organized monolayer assembly.[18] In the present paper we report an extension of our investigations to the study of surfactant ruthenium(II) carbonyl porphyrins. This study was initiated on the premise that the monolayer assembly technique could be utilized to isolate and study reactive intermediates which are not isolable in solution.

The synthesis of porphyrins capable of forming monolayer assemblies was accomplished by converting mesoporphyrin IX to the corresponding dioctadecyl ester, from which the ruthenium(II) carbonyl derivative [Ru^{II}(CO)(py)Meso IX, DOE] (**1**) was readily obtained.[19] The compound was found to form stable films both from the pure compound (via spreading of chloroform solutions) or from mixtures with arachidic acid. Pressure–area studies indicate that films containing (**1**) and arachidic acid in various proportions were stable over a pressure range of 5–30 dyn/cm. Monolayers containing **1** were readily transferred to glass support slides, and several layers of **1** could be deposited in the usual manner.

Spectra of condensed assemblies of **1** were similar to those of dilute solutions of **1** and/or other ruthenium(II) carbonyl porphyrins and indicate that the porphyrin in the assemblies absorbs as a monomeric species. This behavior is in contrast to the ground-state dimer formed with accompanying spectral alteration when monolayer assemblies of the corresponding free base porphyrin were constructed.[15] For **1** a surface pressure–area isotherm similar to that for the free base[15] is obtained even though significant spectral interaction does not occur; thus stacking of two rings occurs but probably with a larger interporphyrin distance. Studies of the spectra of assemblies of **1** with polarized light reveal that the porphyrin

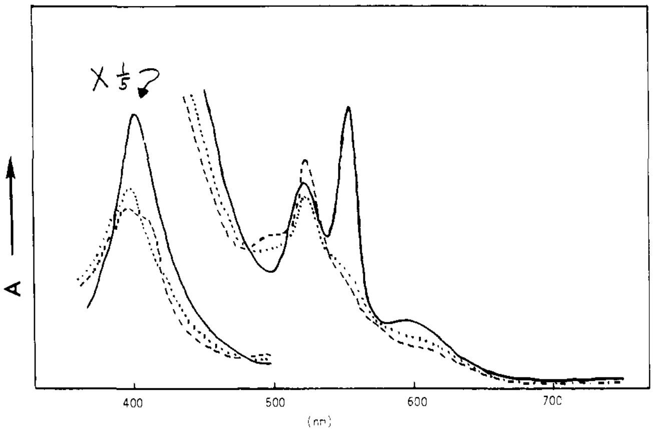


Figure 1. (—) $Ru^{II}(CO)(py)$ Meso IX, DOE; (- - - -) decarbonylated species, [$Ru^{II}(py)$Meso IX, DOE]; (····) $Ru^{II}(N_2)(py)$Meso IX, DOE.

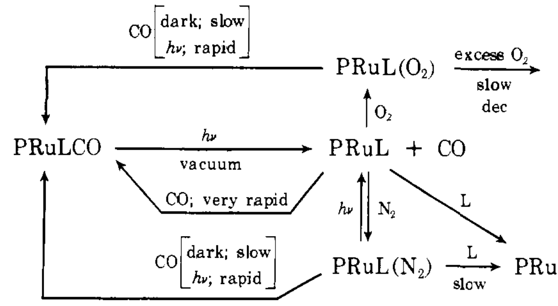
rings are oriented with the porphyrin rings parallel to the plane of the support for assemblies obtained at a pressure of 15 dyn/cm.

Irradiation (Pyrex-filtered, 100 W, G.E. 100PSP44-4 bulb) of slides containing deposited assemblies of **1** with arachidic acid in various mixing ratios and various numbers of layers (5–8) was conducted in an evacuable quartz cell. For assemblies of **1**, irradiation with wavelengths from 300 to 600 nm in air or in oxygen led only to slow decomposition of the metalloporphyrin as indicated by the slow bleaching of the visible spectrum. However, irradiation of assemblies containing **1** under high vacuum conditions resulted in formation of a product (**2**) with a visible spectrum similar to the unstable and previously unisolable decarbonylated species formed by irradiation of $Ru^{II}(CO)(py)P$ in solution (Figure 1).[20] From the similarity of the spectra and from the observation that **2** rapidly and quantitatively reverts to **1** upon admission of CO,[21] it is reasonable to conclude that **2** is the monomeric ruthenium porphyrin monopyridinate that has lost CO. This result is in remarkable contrast to the behavior of $Ru^{II}(CO)(py)P$ in solution and in the crystalline state.[19] Hence in organized assemblies the $Ru^{II}(L)P$ species is isolable in the absence of suitable ligating molecules. As further evidence that **2** is the monomeric decarbonylated species, introduction (gas phase) of coordinating ligands such as pyridine or piperidine causes rapid quantitative conversion of **2** to the well-characterized diligated species $Ru^{II}(L)_2P$. Likewise decarbonylation of **1** on a vacuum line in the presence of a very low concentration of pyridine resulted only in formation of the diligate.

The monolayer bound species **2** exhibits a remarkable reactivity with small molecules such as nitrogen and oxygen. Placing a slide containing **2** under 1 atm of N_2 causes moderately rapid uptake of N_2 to form a new species (**3**) which is formulated as the dinitrogen complex, $Ru^{II}(N_2)(py)P$. The spectrum of **3** is clearly different from either **1** or **2**. The complex **3** is fairly stable in the monolayer assembly and does not revert to **2** even upon long term evacuation on a high vacuum line. Likewise **3** is stable in air but a low concentration of pyridine vapor slowly replaces the N_2 to form the dipyridinate. However, when slides of **3** are placed under 1 atm of CO a very slow reversion to **1** occurs. This reaction can be accelerated by irradiation with visible light. Apparently photoejection of N_2 occurs, followed by rapid reaction of **2** with CO to regenerate **1**; this was confirmed by irradiation of **3** in vacuo followed by treatment of the re-formed **2** with CO.

One atmosphere of oxygen placed over slides containing **2** results in a rapid thermal reaction in which a new species (**4**) is generated. The visible spectrum of **4** is similar to **3**. This product is believed to be the dioxygen complex. Assemblies of this complex are stable to high vacuum. Long term standing under oxygen apparently leads to further oxidation and destruction of the metalloporphyrin although **4** is stable in oxygen-free atmosphere. Analogous to the dinitrogen complex, CO very slowly replaces the O_2 in **4** to regenerate **1**. This reaction is also photoaccelerated, presumably again via ligand (O_2) photoejection.

Scheme I. Reactions of PRuLCO in Organized Monolayer Assemblies



Scheme I summarizes the photochemical and thermal reactions observed to date for ruthenium porphyrins in condensed monolayer assemblies.[22] Once again the results observed are in rather sharp contrast to those obtained for the same compounds in solution. Here the lack of diffusion in the assemblies permits the isolation of the coordinatively unsaturated species **2** which occurs only as a short-lived intermediate in solution. The subsequent reaction of isolated **2** with selected reagents enables the preparation of novel adducts not obtainable in solution. These results suggest that the assemblies may be useful in preparing a wide variety of complexes, both with other metalloporphyrins and other small molecules; we are continuing to explore the scope of these reactions.

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(20) The solution spectrum was obtained on the transient product from a difference spectrum following intense irradiation in very dry degassed benzene.

(21) Even in monolayer assemblies **2** is extremely reactive towards CO or pyridine; exposure of slides containing **2** to even low pressures of CO results in an almost instantaneous visual change in the porphyrin.

(22) Similar results were observed in preliminary experiments with the corresponding surfactant derivatives of *meso*-tetra(4-carboxyphenyl)porphine.

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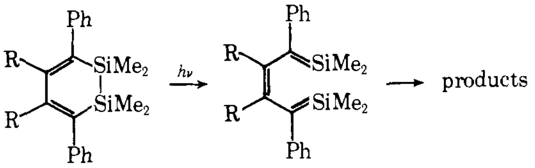
New Photochemical Reactions of Vinyldisilanes through Silaethene or Silacyclopropane Intermediates[1]

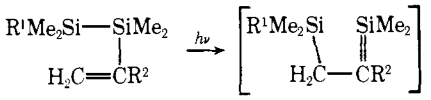
Sir:

Although photochemical reactions of aryldisilanes, which involve silaethene intermediates, have been reported recently,[2,3] no work on the photolysis of vinyldisilanes has been reported. Since vinyldisilanes have characteristic absorption due to the conjugation between the carbon-carbon double bond and the silicon-silicon bond,[4] it is expected that photochemical transformation of vinyldisilanes would be an intriguing problem. We have recently reported that the photochemical isomerization of 1,2-disilacyclohexadienes occurs in an analogous way to that of cyclohexadiene involving 1,6-disilahexatrienes as intermediates.[5] In this paper we report two types of new photochemical reactions of vinyldisilanes.



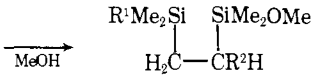
(1)

On irradiation externally with a 160-W low-pressure mercury arc lamp for 24 h at room temperature under nitrogen atmosphere, 100 mg (0.58 mmol) of isopropenylpentamethyldisilane (**1a**, $R^1 = R^2 = Me$) in methanol (4 ml) in a quartz tube yielded 1-trimethylsilyl-2-dimethyl(methoxy)silylpropane (**3a**) in 40.5% yield.[6] Similarly other vinyldisilanes of the type **1** gave **3** on irradiation in methanol under the same conditions.



1 **2**

1a, $R^1 = R^2 = Me$
1b, $R^1 = Me$; $R^2 = H$
1c, $R^1 = Me$; $R^2 = Ph$
1d, $R^1 = CH_2{=}CH-$; $R^2 = H$
1e, $R^1 = CH_2{=}CMe-$; $R^2 = Me$
1f, $R^1 = CH_2{=}CPh-$; $R^2 = Ph$



(2)

3

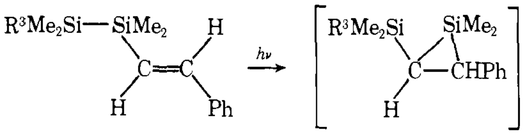
Yield (%)	
3a	40.5
3b	18.0
3c	34.4
3d	27.1
3e	35.8
3f	38.0

These photochemical reactions are best explained by an intermediacy of **2** since the products obtained are in accord with known reactions of silicon-carbon double-bonded species and alcohols,[7] and actually photolysis of **1f** in the presence of MeOD gave $CH_2{=}CPhSiMe_2CH_2CDPhSiMe_2OMe$. Interestingly, the photolysis of 1,2-dimethyl-1,2-divinyl-1,2-diphenyldisilane (**4**), which contains both Si-Ph and Si-vinyl bonds, afforded only **5**, as a reaction product of the vinyldisilane part, no product arising from the reaction of the phenyldisilane unit[2,3] being detected. This fact demonstrates the dominant reactivity of vinyldisilanes, at least in this example.

$$\underset{\mathbf{4}}{CH_2{=}CHSiMePhSiMePhCH{=}CH_2}$$

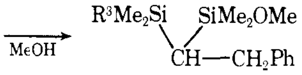
$$\xrightarrow[\text{MeOH}]{h\nu} \underset{\mathbf{5}}{CH_2{=}CHSiMePhCH_2CH_2SiMePh(OMe)} \qquad (3)$$

The second type of the photolysis of vinyldisilanes was observed for β-styryldisilanes. Irradiation of **6** in methanol under the same conditions gave **8.**



6a, $R^3 = Me$
6b, $R^3 =$ *trans*—PhCH=CH—

7

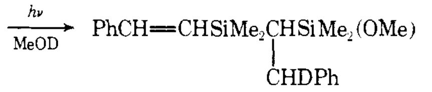


(4)

Yield (%) **8a**, 5.9
8b, 40.9

The styryl group in the product **8b** was found to be a cis/trans mixture in a ratio of approximately 2/1. This is probably due to a photochemical isomerization during the reaction, since the styryl group of the recovered **6a** (34.3%) was also isomerized to a cis/trans (2/1) mixture. The products of these reactions are now accounted for by the intermediate silacyclopropanes (**7**). As predicted by the reported reactions of silacyclopropane and alcohols,[8] photolysis of **6b** in MeOD gave **9** (cis/trans = 2/1).

6b



$$\xrightarrow[\text{MeOD}]{h\nu} \underset{\displaystyle CHDPh}{PhCH{=}CHSiMe_2\underset{|}{C}HSiMe_2(OMe)} \qquad (5)$$

9

We have recently reported the palladium complex-catalyzed intermolecular [σ + π] reactions of hexaorganodisilanes with acetylenes[9] and dienes.[10] These reactions and other evidence[11] demonstrated an interesting analogy in the reactivity between silicon-silicon σ and carbon-carbon π bonds. In this sense, the present reactions may be formally analyzed as photochemically allowed intramolecular [σ + π] process in an analogous way to the known photochemistry of 1,3-dienes.[12] Related works are in progress.

Acknowledgment. We thank Toshiba Silicone Co., Ltd., for gifts of chlorosilanes.

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