Soc., **97**, 277 (1975).
(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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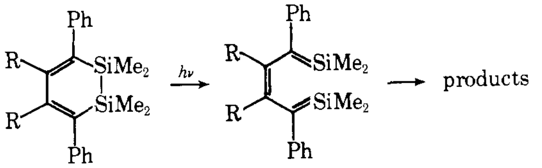
New Photochemical Reactions of Vinyldisilanes through Silaethene or Silacyclopropane Intermediates[1]

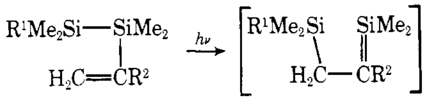
Sir:

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.



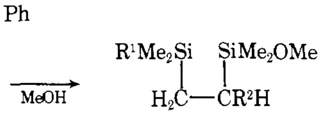
(1)

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, $R^1 = CH_2{=}CPh{-}$; $R^2 = Ph$



$$\xrightarrow[\text{MeOH}]{} \begin{matrix} R^1Me_2Si & SiMe_2OMe \\ | & | \\ H_2C & \!\!-\!\!\; CR^2H \end{matrix} \quad (2)$$

3

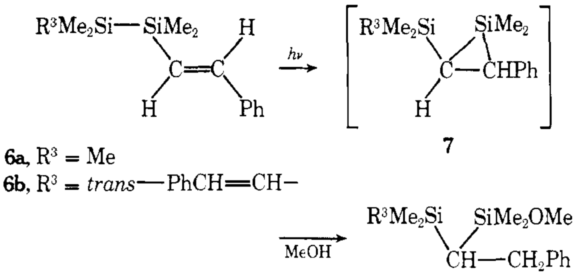
Yield (%) **3a**, 40.5
3b, 18.0
3c, 34.4
3d, 27.1
3e, 35.8
3f, 38.0

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.

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

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

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



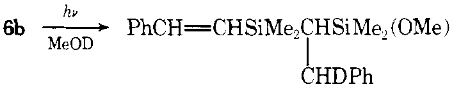
7

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

(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).



$$\mathbf{6b} \xrightarrow[\text{MeOD}]{h\nu} PhCH{=}CHSiMe_2\underset{\substack{|\\ CHDPh}}{C}HSiMe_2(OMe) \quad (5)$$

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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(6) All yields described in this paper are based on the amounts of isolated products which were purified by TLC or GLC. New compounds were characterized by their IR, NMR, and mass spectra. Satisfactory elemental analyses were obtained for all new compounds.

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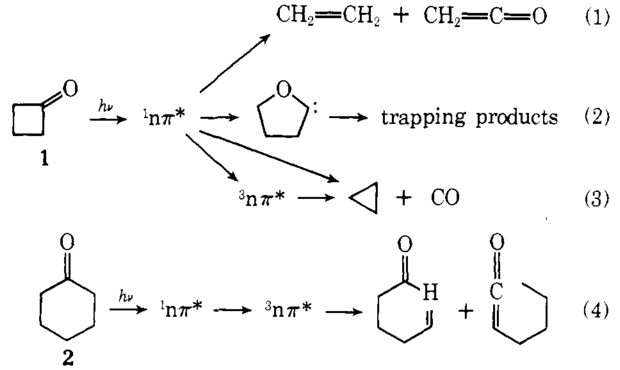
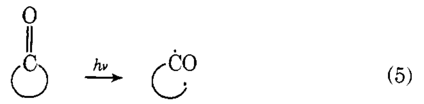
Salem Diagrams as a Device for the Elucidation of Photochemical Reaction Mechanisms. Application to the Cleavage of Cyclic Alkanones

Sir:

The photochemical behavior of cyclobutanones contrasts sharply with that of higher cyclanones[1] (e.g., cyclohexanone). The main differences between the photoreactivities of cyclobutanone, **1**, and cyclohexanone, **2**, in condensed phases are as follows: (1) **1** undergoes α-cleavage from both the singlet and triplet n,π* excited states[2] whereas **2** cleaves exclusively from the triplet state.[3] (2) The singlet n,π* of **1** yields fragmentation (ketene and olefin, eq 1) cyclization (oxacarbene, eq 2) or decarbonylation (cyclopropane and CO, eq 3) products.[4] The parent triplet exclusively loses CO to form cyclopropane, presumably via trimethylene (eq 3), whereas the triplet of **2** undergoes disproportionation reactions (eq 4).[5] (3) The photochemical activity of **1** persists even at very low temperatures where **2** is photostable.[6]



An elegant rationalization of the nature of the major products found in the photochemistry of alkanones is based on the postulate of homolytic type I α-cleavage (eq 5).[7] This postulate,



in combination with the concept of "ring strain" is usually invoked to explain the antithetic behaviors of **1** and **2**—in particular, points 1 and 3 above—but the question arises as to how the "memory" of strain release can persist after the cyclobutanone ring is cleaved and the 1,4 diradical formed. To probe this question Salem theoretical diagrams[8] for the coplanar α-cleavage of **2** (Figure 1) and **1** (Figure 2) were combined with available thermochemical and spectroscopic data on these systems. These diagrams use distinct reaction coordinates to depict two major types of coplanar α-cleavages. On the right hand side the CO···C bond is stretched while maintaining a bent acyl moiety. The left hand side represents the elongation of the CO···C linkage with concomitant linearization of the acyl fragment. Let us note that both processes are formally [σ,(σ,π)] tritopic.[8] Still the energy gap between the σ and π radical sites of the bent acyl is large enough (σ below π) for the $D_{\sigma\pi}$ singlet and triplet pair of diradical states to be much higher in energy than the parent $D_{\sigma\sigma}$ pair.[9] The manifold of states associated with the cleavage to a bent acyl fragment is somewhat reminiscent of the simpler bitopic pattern.[8]

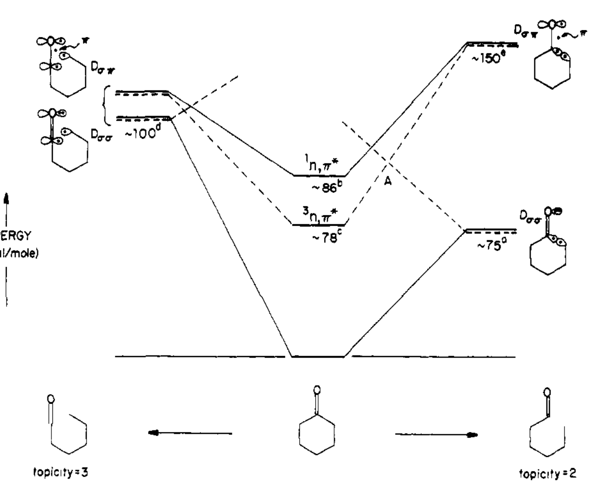


Figure 1. Comparison of α-cleavage of cyclohexanone to produce bent (reaction to the right) and linear (reaction to the left) acyl fragments. Dots indicate electron in various orbitals. All electrons indicated have σ-symmetry with respect to the molecular plane except for the π electrons which are explicitly indicated in the figure: (a) group additivity, ref 13a; (b) ref 4 (for cyclopentanone); (c) ref 3a, ref 4 (for cyclopentanone); (d) ΔH_f bent diradical + calculated linearization energy ref 8b (acetyl), ref 15 (formyl); (e) ref 8b (for acetone). The cleavage to form a bent acyl radical, although formally tritopic, is more realistically treated as ditopic because of the large energy gap between the $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ states at the diradical geometry.

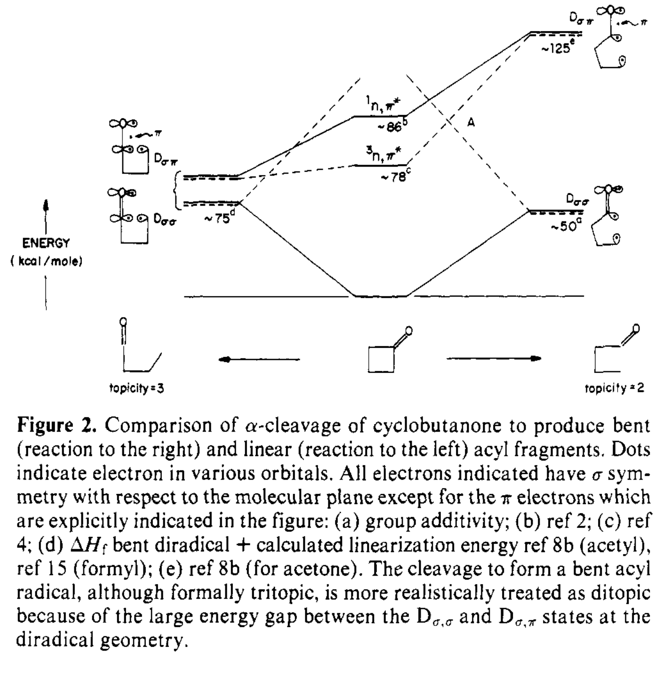


Figure 2. Comparison of α-cleavage of cyclobutanone to produce bent (reaction to the right) and linear (reaction to the left) acyl fragments. Dots indicate electron in various orbitals. All electrons indicated have σ symmetry with respect to the molecular plane except for the π electrons which are explicitly indicated in the figure: (a) group additivity; (b) ref 2; (c) ref 4; (d) ΔH_f bent diradical + calculated linearization energy ref 8b (acetyl), ref 15 (formyl); (e) ref 8b (for acetone). The cleavage to form a bent acyl radical, although formally tritopic, is more realistically treated as ditopic because of the large energy gap between the $D_{\sigma,\sigma}$ and $D_{\sigma,\pi}$ states at the diradical geometry.

Figure 1 reveals that both cyclohexanone cleavages—with retention of the bent geometry or with linearization—are