

synthesis and that we have synthesized B₁₂ coenzyme chirally labeled at C-5'.⁷

The coupling constant between the C-4' proton and the *pro-R* C-5' proton is ~9 Hz, while the coupling constant between the C-4' proton and the *pro-S* C-5' proton is ~0 Hz. This suggests the dihedral angle between the C-4' proton and the *pro-S* C-5' proton to be ~90° and the dihedral angle between the C-4' proton and the *pro-R* C-5' proton to be ~170°. ^{8,9}

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- (4) [5',5'-²H₂]Adenosylcobalamin was synthesized by exchanging the C-5' protons of adenosylcobalamin in D₂O in the presence of ribonucleotide reductase.¹⁰
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- (6) The chirally labeled coenzyme was synthesized using a modified procedure of Hogenkamp.¹¹ In this procedure, 5.5 mg of (5'-*R*)-[5'-²H]adenosine (20.5 μmol)⁹ was converted into (5'-*S*)-[5'-²H]-5'-chloro-5'-deoxyadenosine as described. The nucleoside synthesized was reacted with cob(II)alamin generated by the reduction of 50 mg of aquocobalamin (36 μmol) with Zn/NH₄Cl (300 mg of Zn and 625 mg of NH₄Cl) in 5 mL of H₂O for 40 min in the dark. After the excess Zn was filtered off, the coenzyme was purified by phenol extraction, CM cellulose column chromatography (H⁺ form, developed with H₂O and eluted with 5 mM acetic acid), and paper electrophoresis on Whatman 3MM paper (using 0.5 N NH₄OH as electrolyte, ~10 V/cm). The final yield was ~15 mg (~50% from adenosine).
- (7) The stereochemistry at the C-5' position of the chiral B₁₂ coenzyme is assumed to be of the *R* configuration. This assignment is based on the assumption that the chlorination of adenosine undergoes inversion as suggested by Hogenkamp¹¹ and that the displacement of the chlorine of 5'-chloroadenosine by cob(II)alamin is by an S_N2 mechanism. With this assumption, one can assign the *pro-R* proton to be at 0.6 ppm and the *pro-S* proton to be at 1.56 ppm.
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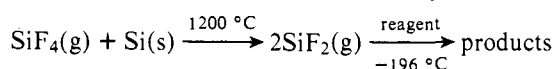
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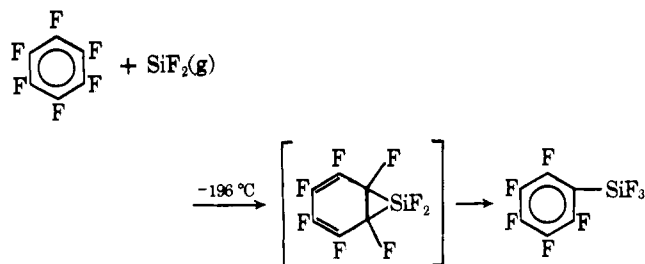
Rediscovery of the Gas-Phase Chemistry of Difluorosilylene Generated by Thermal Reduction

Sir:

Difluorosilylene (silicon difluoride), though often referred to as a carbene analogue, has not shown a behavior quite parallel to that of carbenes.¹⁻³ Ever since Margrave et al. opened the study of the chemistry some 14 years ago, it has been believed that SiF₂ in the gas phase is not very reactive.⁴ As a result, practically all SiF₂ chemistry has been done by cocondensation with other reagents at -196 °C, and reactive diradicals •(SiF₂)_n• (in most cases *n* = 2) are believed to be responsible for much of the observed chemistry:



There are several reactions¹ (SiF₂ + H₂O, SiF₂ + H₂S, SiF₂ + C₆F₆, etc) which yielded products containing only one SiF₂. In the reaction of SiF₂ with C₆F₆, one gets insertion into the



C-F bond, perhaps through the mechanism involving a short-lived siliarane intermediate. Similar mono-SiF₂ reaction products were obtained from SiF₂ reaction with HFC=CH₂, F₂C=CH₂, etc. In most of this cocondensation work, the gas-phase reactants were mixed in the vacuum system before trapping them at -196 °C.

Another exception is the study of the reactions of conjugated dienes with ³¹SiF₂ formed in nuclear recoil systems by Tang and his co-workers.^{5,6} The ³¹SiF₂ molecules generated in such systems possess very high thermal energies and the reaction conditions are very different from those of cocondensation; nonetheless, Tang's work does show that monomeric ³¹SiF₂ in gas phase is reactive toward conjugated diene systems. Also, Margrave et al.¹ have reported the gas-phase reactions of SiF₂ with O₂ to form SiOF₂ and higher silicon oxyfluorides.

Recently Seyferth's group reported their study on the chemistry of difluorosilane and reinterpreted our previous results of the reactions with olefins and alkynes through the formation of unstable silirane and silirene intermediates.⁷ In supporting Seyferth's view, Thompson's group reported in a recent communication the ²⁹Si NMR spectroscopic evidence for the participation of monomeric SiF₂ in the formation of the copolymer which accounts for 70% of the total products in the cocondensation reaction of SiF₂ and propene.⁸

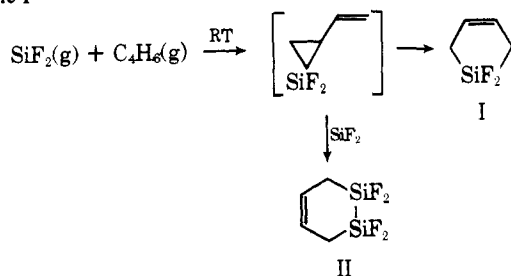
These results seem to suggest that the observed chemistry of SiF₂ in cocondensation systems could actually be the results of direct reactions between monomeric SiF₂ and unsaturated organic molecules in gas phase. This implication prompted us to reinvestigate the chemistry of SiF₂ in the gas phase, which has not been examined carefully. A natural first choice for such a study is the reaction with 1,3-butadiene, to see how the results compare with those of the nuclear recoil ³¹SiF₂ reactions studied by Tang. This is our first report of these studies.

Difluorosilylene was generated by Margrave's method¹ and reacted with butadiene which was introduced into the system from another inlet. The mixture stayed in a closed 12-L bulb for 25 min—ten times the half-life of SiF₂ under a pressure of 0.1 Torr,⁴ before it was pumped out and condensed at -196 °C. The evacuated bulb was filled with the gas mixture again and the procedure repeated. Such a procedure ensured that little SiF₂ would be left over when the gas mixture was finally condensed and formation of •(SiF₂)_n• diradicals should be negligible. The wall of the bulb became cloudy during the reaction, presumably owing to the formation of a thin layer of SiF₂-containing material which hydrolyzed immediately on exposure to moisture. However, no polymeric materials were observed on condensation at -196 °C.

The reaction was studied under three different conditions: (i) total pressure of 0.2 ~ 0.4 Torr with approximately equal molar of SiF₂ and C₄H₆, (ii) total pressure of 400 Torr with a SiF₂-C₄H₆ ratio of ~1:2000, and (iii) total pressure of 2 Torr with a SiF₂-C₄H₆ ratio of ~1:1.

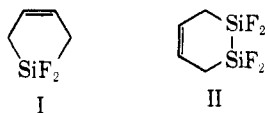
Condition i was a simulation of the conditions used in cocondensation experiments; ii and iii were chosen arbitrarily to get a rough idea of pressure effect. However, the results from

Scheme I



various reaction conditions are so far rather similar.

In all cases the results showed that thermally generated SiF_2 is indeed reactive toward butadiene in gas phase. The total yield of reaction products based on recovered butadiene was estimated to be at least 30%. The products were isolated from SiF_4 and excess starting material by prolonged pumping through a trap at -96°C , and were identified unequivocally by means of mass spectrometry and IR and NMR spectroscopy. The major product was found to be 1,1-difluorosilacyclohex-3-ene (I). The existence of a small amount of 1,1,2,2-tetrafluoro-1,2-disilacyclohex-4-ene (II) was also in-



dicated by mass spectral data. In the case of experimental condition iii, II was isolated by passing the product mixture through a trap at -45°C and characterized by spectroscopic methods. The relative yields of I and II in all cases were estimated to be $\geq 20:1$.

It is interesting to note that, although Thompson and Margrave⁹ have reported that the products in cocondensation of $\text{SiF}_2\text{-C}_4\text{H}_6$ were II and $\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{SiF}_2\text{SiF}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (III), we do find a small amount of I in a repeated cocondensation experiment. The relative quantity of I is only 1 ~ 2%; however, it is mechanistically significant.

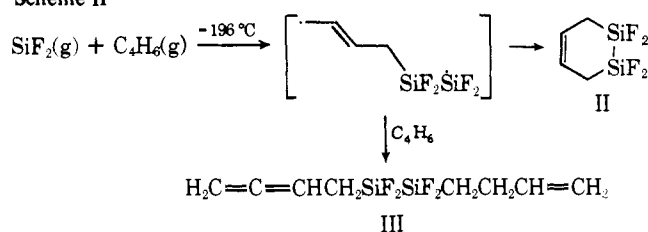
Since on condensation only a negligible amount of SiF_2 was left over in the present work, it seems very likely that monomeric SiF_2 reacts directly with 1,3-butadiene, perhaps via an initial formation of silirane as suggested by Seyferth,⁷ followed by either intramolecular rearrangement to form I or reaction with another molecule of SiF_2 to form II (Scheme I).

Comparing the results from gas-phase and cocondensation experiments, it is obvious that the major reaction occurring in gas phase is the monomeric SiF_2 reaction just like the case of recoiled $^{31}\text{SiF}_2$ reactions, whereas, in the case of cocondensation, the diradical mechanism seems to be important for the formation of volatile products (Scheme II).

The small quantity of I found in cocondensation reaction is very likely a result from the gas-phase reaction prior to condensation. On the other hand, since no polymeric material was observed when the gas-phase reaction mixture was condensed, it is evident that the formation of II had occurred in gas phase. (In cocondensation experiments the formation of II is accompanied by the formation of a large amount of polymers.) While the formation of II in Scheme I seems reasonable, a possible alternative is that II was formed from a small amount of Si_2F_4 which existed in the gas mixture. Margrave and Perry in a recent correspondence discussed the possible existence of $\text{F}_2\text{Si}=\text{SiF}_2$ under such conditions.¹⁰

Thus the results from this study suggest that SiF_2 reacts similarly to carbene species in gas phase, but in low-temperature cocondensations it may proceed via different pathways. It is perhaps premature to draw any further conclusion at this stage; nonetheless, the significance of the SiF_2 chemistry in gas

Scheme II



phase, i.e., the potential to provide genuine insights into the reaction mechanisms comparable with those in the development of carbene chemistry, is evident. Gaspar predicted in a review article¹¹ "in view of the poor Si-Si π interaction and the relative weakness of Si-Si single bond, it is very likely that characteristic reaction of SiF_2 other than polymerization will be found in the near future". This study demonstrates a true difluorosilylene chemistry.

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Mechanisms of Photooxygenation. 1. Substituent Effects on the [2 + 2] Cycloaddition of Singlet Oxygen to Vinyl Ethers

Sir:

The mechanism of [2 + 2] cycloaddition of singlet molecular oxygen to olefins and its relationship to the ene and [2 + 4] cycloaddition modes has been of interest for some time.¹ A wide variety of mechanisms has been proposed but conclusive evidence is, in general, lacking. Moreover, there is disagreement among theoreticians regarding the formulation of this process²—a controversy which has recently been enlivened.³ We now present the results of a study of the addition of singlet molecular oxygen ($^1\text{O}_2$) to a series of substituted vinylene diethers, which strongly restrict the mechanistic possibilities.

The 2,3-diaryl-1,4-dioxenes **1** undergo photooxidation to yield initially the dioxetanes **2** which thermolyze smoothly to the diesters **3** in 90-95% isolated yield (eq 1). Competitive experiments show formation of **2** to be an authentic $^1\text{O}_2$ reaction.⁴ Relative reactivities are unaffected by choice of sensitizer, presence of radical inhibitor, addition of the $^1\text{O}_2$