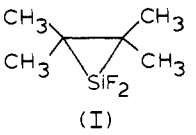
New Evidence for the Involvement of Monomeric Silicon Difluoride in Reactions with Olefins

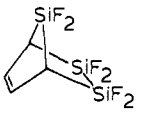
Sir:

The recent communications of Margrave[1] and of Seyferth and Duncan[2] concerning the mechanism of the reaction of SiF_2 with olefins have prompted us to report some of our results which support Seyferth's postulate of the involvement of monomeric SiF_2 in these reactions.

Seyferth has reported the synthesis of 1,1-difluoro-2,2,3,3-tetramethyl-1-silirane (I). The stability of I, its thermolysis reactions, its ability to add to unsaturated bonds, and the ability of dimethylsilylene to insert into siliranes to give

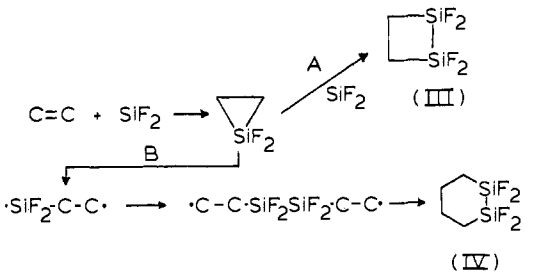


(I)



(II)

1,2-disilacyclobutanes led Seyferth to suggest that the reaction of SiF_2 with olefins initially involves formation of a silirane which then undergoes further reactions.[2]



(IV)

Margrave, on the other hand, has proposed a biradical $\dot{S}iF_2$–$\dot{S}iF_2$ mechanism to explain the preponderance of Si_2F_4 units in the volatile products from the reactions of SiF_2 with olefins when SiF_2 is generated by the quartz tube method.[3] If Seyferth's mechanism is correct, one might expect to find significant amounts of products involving monomeric SiF_2 units. In fact the only well-characterized addition product with a monomeric SiF_2 unit is 2,2,3,3,7,7-hexafluoro-2,3,7-trisilanoborn-5-ene (II) produced in the reaction with acetylene.[4,5] Thus, although Seyferth's evidence is compelling, one cannot, on the evidence in the literature, rule out the possibility that Margrave's mechanism is the correct one under his experimental conditions.

We have carried out an extensive investigation of the reactions of olefins with SiF_2 generated by the quartz tube method, characterizing the products by ^1H, ^{13}C, ^{19}F, and ^{29}Si NMR. Full details will be reported elsewhere.[6] However, certain of these results are presented below since they bear directly on the mechanistic controversy discussed above. The key observations concern the composition of the polymers which form the major products (typically 60–70%) of the reactions of SiF_2 with olefins. These polymers have not previously been characterized since both ^1H and ^{19}F spectra are uninformative. However, ^{29}Si spectra provide a clear indication of the structure. A typical spectrum is that of the polymer from the reaction of propene with SiF_2 (Figure 1). The ^1H-decoupled spectrum shows a triplet at 3.8 ppm to high field of $^{29}Si(CH_3)_4$ with splitting (J_{SiF} = 314 Hz) characteristic of a one-bond SiF coupling. Polymers from *cis*- and *trans*-butene show similar spectra (δ − 4.9 (J_{SiF} = 325 Hz)) plus a minor component which is a triplet of triplets (δ − 7.6 (J_{SiF} = 355, 48.5 Hz)). The polymer generated by thermolysis of the 1,2-disilacyclobutane product (III) from the reaction of *trans*-butene with SiF_2 gives an identical spectrum with that of this minor component. Therefore, the main triplet spectrum can be assigned to units of the type

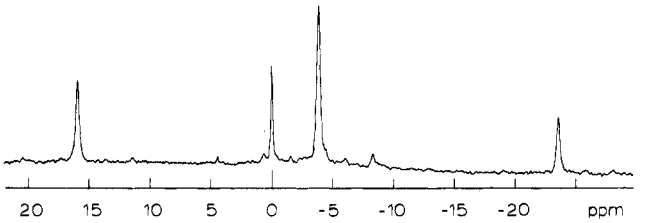
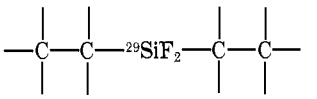
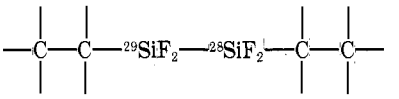


Figure 1. ^1H decoupled 15.9-MHz ^{29}Si spectrum of the polymer from the reaction of SiF_2 with propene. Me_4Si is at 0 ppm.

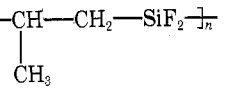


while the minor component in the *cis*- and *trans*-butene polymers can be assigned to



units (with the smaller coupling due to ^{29}Si–Si–^{19}F coupling). Thus, it is seen that the major polymeric product from the reaction of olefins with SiF_2 contains isolated SiF_2 units with only a small proportion of Si_2F_4 units. This demonstrates that monomeric SiF_2 is the major reactive $(SiF_2)_n$ species in these reactions, eliminating one possible major objection to Seyferth's mechanism.

The ^1H-decoupled ^{13}C spectrum of the propene polymer shows only three major peaks (one singlet at δ 15.3 and two triplets at 11.3 and 10.4, each with J_{C-F} = 15 Hz). This simple spectrum plus the fact that the ^{29}Si spectrum shows only one type of silicon both indicate that the polymer has a regular



structure. This structure is entirely consistent with the intermediacy of either a silirane or its open biradical isomer[2] in the reaction pathway yielding polymer. Polymerization involves Si–C bond formation. The minor amounts of disilacyclohexanes (IV)[6,7] and their open-chain isomers[6,8] which are formed in reactions of olefins with SiF_2 can be attributed to a pathway involving formation of the thermodynamically less favorable Si–Si bonds (pathway B in Seyferth's mechanism[2]). The minor component with Si_2F_4 units in the butene polymers probably arises from disilacyclobutane intermediates.[9]

We have not succeeded in detecting siliranes in the products of the reactions of either ethylene or dimethylbutene with SiF_2.[10] However, it is improbable that these products would survive the course of the reaction, particularly in view of the likely high reactivity of difluorosiliranes.[2] In addition to the polymers, some of the volatile products observed in the olefin reactions are also suggestive of silirane intermediates. This will be discussed in the full paper.[6]

Acknowledgments. Financial support from the Natural Science and Engineering Research Council of Canada and the Department of Chemistry of the University of Toronto is gratefully acknowledged.

References and Notes

(1) Margrave, J. L.; Perry, D. L. *Inorg. Chem.* **1977**, *16*, 1820–1822.
(2) Seyferth, D.; Duncan, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 7734–7736.
(3) Timms, P. L.; Kent, R. A.; Ehlert, T. C.; Margrave, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 2824–2828.
(4) Liu, C. S.; Margrave, J. L.; Thompson, J. C.; Timms, P. L. *Can. J. Chem.*

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1972, *50,* 459–464.
(5) Insertion products involving monomeric SiF_2 are more common (Liu, C. S.; Hwang, T. L. *J. Am. Chem. Soc.* **1978,** *100,* 2577–2579 and references therein).
(6) Thompson, J. C.; Wright, A. P. G.; Reynolds, W. F., unpublished work.
(7) Thompson, J. C.; Margrave, J. L.; Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1966,** 566–567.
(8) Liu, C. S. Ph.D. Thesis, University of Toronto, Toronto, 1971.
(9) The observation that the polymer from the *trans*-butene reaction contains the highest proportion of Si_2F_4 units is consistent with the observation that this reaction also gives a higher yield of disilacyclobutane product (III) than any of the other olefin reactions.[6]
(10) A minor product of empirical formula $C_2H_4SiF_2$ has been detected in the mass spectrum of the products of the reaction of SiF_2 with ethylene.[7]

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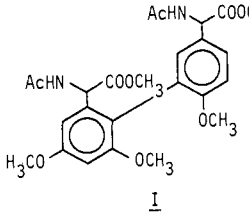
Avoparcin[1]

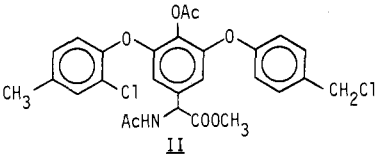
Sir:

Avoparcin, vancomycin, actinoidin, ristomycin, ristocetin, and compound A35512B are a class of complex water-soluble glycopeptide antibiotics with Gram-positive activity which have been isolated over the past 20 years.[2] Vancomycin is the only member of this antibiotic class the structure of which is known with certainty. Recently Williams at Cambridge prepared modified vancomycin (CDP-I) which was suitable for single-crystal X-ray work and thus obtained the unequivocal structure of this material.[3] Avoparcin has commercial importance as a feed additive for agricultural uses. In this communication, we present chemical and spectral evidence that leads us to propose the structure of the aglycone rhamnoside of avoparcin α and β. That avoparcin consists mainly of two components α and β present in about the ratio of 1:3 or 1:4 is readily observed by LC.[4]

Based on the work of Williams et al., we carried out reductive alkaline hydrolysis (refluxing 11 N NaOH, 20% $NaBH_4$) on avoparcin.[5] Following suitable derivatization and intensive chromatographic efforts, a number of important fragments were obtained, such as I (M^+ 502, $C_{25}H_{30}N_2O_9$), II (M^+ 545, $C_{27}H_{25}NO_7Cl_2$), and III (M^+ 671, $C_{33}H_{34}NO_{12}Cl$).[6]



I



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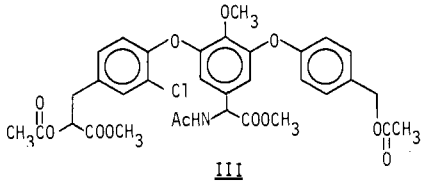
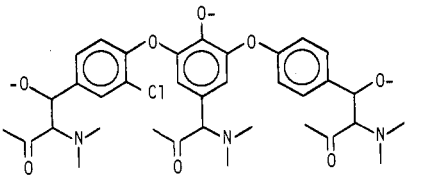


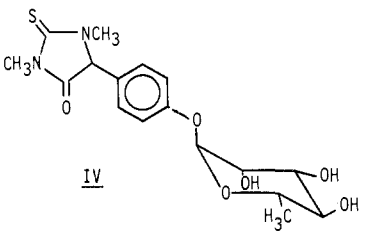
III

The formation of the aromatic methyl groups as well as the benzyl and lactate moieties in II and III suggests a common origin for these groups. They are reasonably explained in terms of the chemistry of the seryl side chains in the partial structure shown below. Such treatment of avoparcin leads to β elimination of one of the benzylic oxygens which gives rise to an enamide which may be hydrolyzed to a keto acid. Reductive conditions would provide the lactate whereas deoxalation would lead to the methylbenzene. The benzyl chloride unit

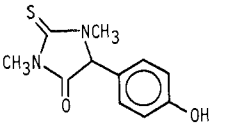


could arise by dealdolization, reduction of the intermediate aldehyde, and introduction of the chlorine during acidification with HCl.

Avoparcin was subjected to the Edman degradation sequence using the reagent methyl isothiocyanate.[7a,b] At the end of the first stage of the normal Edman two-stage cycle, it was possible to isolate the rhamnoside IV (M^+ 382, $C_{17}H_{22}N_2O_6S$).

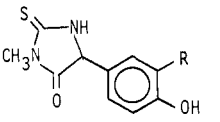


IV



V

If the two-stage cycle is completed normally, V (M^+ 236, $C_{11}H_{12}O_2N_2S$) is isolated. Subjecting the residue to a second complete Edman cycle yields VI (M^+ 256, $C_{10}H_9N_2O_2ClS$) and VII (M^+ 222, $C_{10}H_{10}N_2O_2S$) in about the ratio of 3:1 or 4:1. Because of the abnormality at the end of the first stage of



VI R = Cl
VII R = H

the first Edman cycle,[7c] these products released at the end of two actual Edman cycles arise because, in effect, three full cycles have been completed. Further the isolation of VI and VII in the ratio mentioned most likely means that the major β component contains the chlorinated *p*-hydroxyphenylglycine compared with *p*-hydroxyphenylglycine in the minor α component.

Although there are obvious differences between the ^{13}C NMR spectra of avoparcin (see below) and vancomycin, the general pattern of resonances is similar, especially with respect to the anomeric, aromatic oxycarbon and carbonyl areas, indicating that these antibiotics are structurally related, in agreement with isolation of the identical biphenyl and triphenyl diether (except for chlorine) units from both avoparcin and vancomycin. Further evidence for this relationship comes from the ^1H NMR comparison studies at 270 MHz in Me_2SO-d_6 (courtesy of Walter Krol, Yale University). An essentially pure sample of the β component and a small sample of mostly the α component were prepared by extensive, repetitive chromatography. Even though the spectra are complex, the two meta-substituted protons on the tetrasubstituted ring of the biphenyl have unique chemical shifts at δ 6.30 and 6.44 in vancomycin and 6.31 and 6.44 in avoparcin α and β.[8] The α and β curves are almost identical, except in the aromatic region, with the only difference being the extra chlorine in β. Prominent upfield patterns in the α and β spectra are three sharp three-proton doublets at δ 1.11, 1.17, and 1.23. One of these obviously belongs to rhamnose while the other two are assigned to two ristosamine units (see below). The four-proton complex at δ 2.07 is attributed to the C-2 methylene protons of these ristosamines. The *N*-methyl signal of the phenylsarcosine resonates at δ 2.12.

Thus, on the basis of the work described so far, the subunits of the rhamnoside of avoparcin α and β aglycones are depicted,

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