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# REACTIONS OF SILICON DIFLUORIDE WITH UNSATURATED COMPOUNDS

## III. ALLENE

C. S. LIU* and J. C. THOMPSON**
*Lash Miller Chemical Laboratories, University of Toronto, Toronto 181, Ontario (Canada)*

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## SUMMARY

The reaction between allene and silicon difluoride has been studied. Two compounds, $H_2C{=}C{=}CH{-}SiF_2{-}SiF_2{-}CH_2{-}CH{=}CH_2$ and $H{-}C{\equiv}C{-}CH_2{-}SiF_2{-}SiF_2{-}CH_2{-}CH{=}CH_2$, are identified in the mixture of reaction products.

## INTRODUCTION

As a part of our continuing studies of the chemistry of silicon difluoride, we have carried out the reaction between it and allene. In much of its chemistry[1], allene behaves as a simple substituted mono-olefin, and the products formed in this reaction thus offer an interesting contrast with those formed in other olefin reactions[2] and from conjugated dienes such as butadiene[3]. There is also a strong connection between the chemistry of allenes and that of substituted acetylenes[1,4], so that, in view of our results from acetylene reactions[5], there might be expected to be some similarity of products in this case.

## EXPERIMENTAL

Silicon difluoride was prepared as previously described[6] and co-condensed with allene (Matheson) at −196°. In a typical reaction $SiF_2$ (0.121 mole) and allene (0.274 mole) were co-condensed over a period of 1 h. The resulting brown deposit yielded upon fractional distillation of volatile species $SiF_4$ (0.078 mole), allene (0.183 mole), other volatile material (1.59 g, 0.0075 mole based on a molecular weight of 212) and a yellow involatile spontaneously inflammable residue (7.4 g). Based on allene used in the reaction, the yield of volatile products was 16.5%. In other reactions with slightly different reaction ratios the yields were 15–20%, considerably higher than in many other $SiF_2$ reactions[5].

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* Present address: Department of Chemistry, National Tsing-Hua University, Sinchu, Taiwan, Republic of China.

** To whom correspondence should be addressed.

Vacuum line distillation of the volatile products yielded a colourless liquid trapped between 0 and −20°. No other volatile species were obtained in any appreciable quantity. Subsequent investigation showed that the liquid contained two isomeric compounds, which could not be separated by gas chromatography (on a column containing diisodecyl phthalate on Chromosorb W) or by low temperature fractional distillation. Their structures are deduced from the properties of the mixture.

## RESULTS

The mass spectrum showed its highest mass peak at $m/e = 212$, corresponding to $C_6H_8Si_2F_4$, a molecular formula which was confirmed by gas phase molecular weight determinations. The mass spectrum was very similar to that observed for an isomeric compound[5] obtained from $SiF_2$ and propyne: $H_2C{=}C{=}CH{-}SiF_2{-}SiF_2{-}CH{=}CHCH_3$.

The infrared data are listed in Table 1. Of particular interest are the bands at

TABLE 1

GAS PHASE INFRARED SPECTRUM OF THE ALLENE REACTION PRODUCTS

| *Frequency* ($cm^{-1}$) | *Assignment* | *Frequency* ($cm^{-1}$) | *Assignment* |
|---|---|---|---|
| 3330 w | $\nu$(H–C≡C) | 1400 w | $\delta$(C–H) |
| 3090 w | | 1200 m | $\nu$(C–C) |
| 2980 w | $\nu$(H–C) | 1170 m | |
| 2890 w | | 980 s | |
| 2120 m | $\nu$(C≡C) | 928 s | $\nu$(Si–F) |
| 1940 m | $\nu$(C=C=C) | 888 s | |
| 1635 w | $\nu$(C=C) | 867 s | |
| 1570 w | | | |

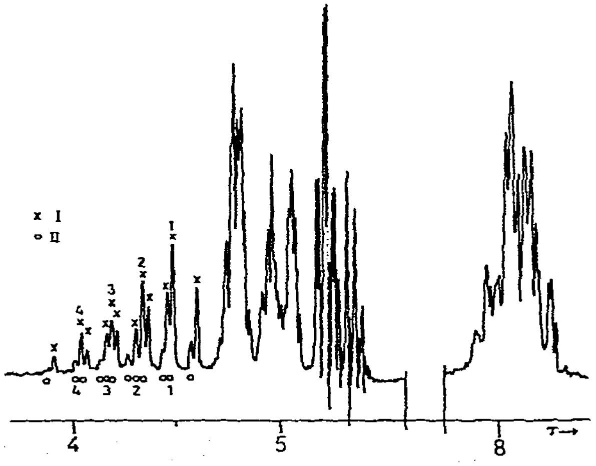


Fig. 1. Proton NMR spectrum (60 MHz) of allene reaction products. The two sets of four triplets (from $CH_2$ coupling) in the A part of the ABC vinylic multiplets are indicated by × (I) and ○ (II).

2120 cm$^{-1}$ [$\nu$(C≡C)] and 1940 cm$^{-1}$ [$\nu$(C=C=C)] in addition to the $\nu$(C=C) and $\nu$(Si–F) modes.

The proton NMR spectrum at 60 MHz is shown in Fig. 1. The main features are complex patterns which may be assigned to olefinic and allenic type protons at lower field and to saturated or perhaps acetylenic protons at higher field. The characteristic pattern above $\tau$ 5 is very similar to that found for the allenic protons in the compound $H_2C{=}C{=}CH{-}SiF_2{-}SiF_2{-}CH{=}CHCH_3$ obtained in the propyne reaction[5]. The lower field group of multiplets resembles an ABC-type pattern of a vinyl group. These interpretations lead to the identification of the compound as $H_2C{=}C{=}CH{-}SiF_2{-}SiF_2{-}CH_2{-}CH{=}CH_2$ (I). However, the integrated intensities of peaks due to the unsaturated protons relative to those of the saturated protons do not agree with the 6/2 ratio expected for such a structure, since the high field peaks are too intense. Careful examination of the proton spectra at 60, 100 and 220 MHz reveals that there are two sets of patterns in the A part of the low-field ABC multiplets, with slightly different chemical shifts. In addition there are also two or more types of proton in the high-field ($\tau \approx 8$) multiplet pattern. Taken with the infrared evidence the presence of a second isomeric compound with structure $HC{\equiv}C{-}CH_2{-}SiF_2{-}SiF_2{-}CH_2{-}CH{=}CH_2$ (II) is indicated. This would have a ratio of low field to high field peaks of 3/5, which when taken with the ratio for compound (I), indicates a mixture of 70±5% (I) and 30±5% (II) over several preparations. The $^{19}$F spectra reinforce this view (Fig. 2),

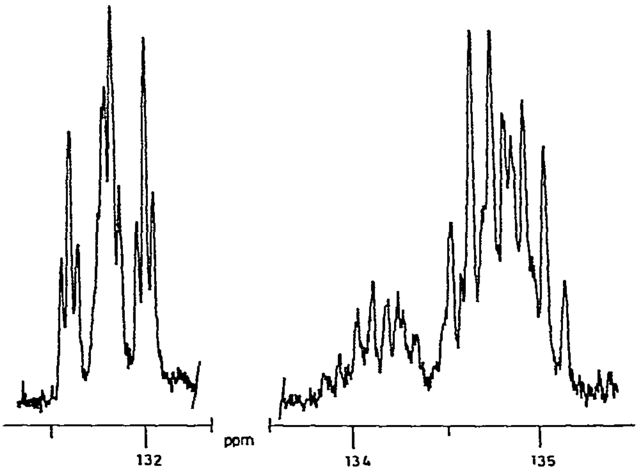


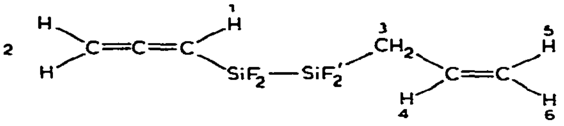
Fig. 2. $^{19}$F NMR spectrum (56.4 MHz) of allene reaction products.

the two larger multiplets not being of equal intensity, but becoming so when the intensity of the small group of peaks is added in. Evaluation of the intensities yields the same composition for the mixture. The two SiF resonances for (II) have only a small chemical shift difference (0.73 ppm) which is reasonable since both $SiF_2$ groups are bound to $CH_2$ whereas in (I) with a shift of 3.08 ppm, one $SiF_2$ is bound to an allene group and the other to $CH_2$. The fluorine shifts of both compounds fall well within the range found for similar compounds[2,5].

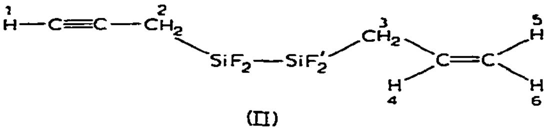
Hydrolysis of the mixture with dilute HF gives an inseparable mixture of allene, propyne and propene, identified from the proton NMR spectrum. Integration

TABLE 2

NMR DATA AND ASSIGNMENTS FOR COMPOUNDS (I) AND (II)



(I)



(II)

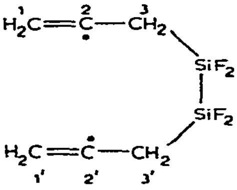
| *Atom* | *Chemical shift*[a] | *Coupling constant (Hz)* |
|---|---|---|
| *Compound (I)* | | |
| H 1 | ≈4.92 | $J$(1,F) 0.9 |
| 2 | 5.30 | $J$(2,F) 2.2 |
| | | $J$(1,2) 7.2 |
| 3 | ≈8.08 | $J$(3,F') 6.0 |
| 4 | 4.24 | $J$(3,4) 6.9 |
| 5 | ≈4.92 | $J$(4,5) 18.0 |
| 6 | ≈4.75 | $J$(4,6) 8.8 |
| F | 131.81 | $J$(F,F') ≈11.0 |
| F' | 134.89 | |
| *Compound (II)* | | |
| H 1 | ≈8.08 | |
| 2 | ≈8.08 | |
| 3 | ≈8.08 | $J$(3,4) 6.4 |
| 4 | 4.22 | $J$(4,5) 18.0 |
| 5 | ≈4.92 | $J$(4,6) 9.0 |
| 6 | ≈4.75 | |
| F or F' | 134.16 | $J$(F,F') ≈11.0 |
| F' or F | 134.89 | |

[a] Proton peaks in ppm (τ scale), fluorine peaks in ppm upfield from $CD_3F$.

of the peaks gives the respective proportions of the three species as 2/1/7, which is roughly in accord with the composition of the mixture.

## DISCUSSION

The formation of these two compounds is quite reasonable if one accepts the type of mechanism proposed for other $SiF_2$ reactions with unsaturated hydrocarbons[2,5], and invokes a reaction intermediate formed between two moles of allene and one $Si_2F_4$ unit:



Hydrogen migration from 1 to 2′ would form the acetylenic derivative (II) and from 3 to 2′ would form (I). The formation of (II) requires an 8-membered cyclic transition state while (I) requires a 6-membered ring intermediate. In the propyne reaction the 8-membered state was thought to be most favourable on steric grounds[5]. However, in this case, the hydrogen atom would be removed from a formally $sp^2$-hybridised carbon atom which may make the specific geometry required less favourable. The observation of (I) being formed in over twice the yield of (II) reinforces this latter view. The formation of these two products is consistent with the predominantly terminal addition of free radicals to one of the double bonds in allene[1].

We can find no evidence for any of the possible ring compounds which might be formed in this reaction, either 4-membered or 6-membered. It thus appears that the hydrogen migration processes are in this case, as in some of the alkyne reactions[5], the most important in determining the nature of the eventual products.

## ACKNOWLEDGEMENT

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