

Figure 2. Relative acidities of the HF and the HSO_3F solvent on SbF_5 addition: ■ and ●, ref 3; insert on the right from ref 4; ○, this work; □, our previous work, ref 8.

Table I. ^{13}C Chemical Shifts at -30°C ^a of Mono- and Diprotonated *p*-Methoxybenzaldehyde^b

Solvent	C=O	C ₄	C ₁	CH ₃ O
HSO_3F	193.4	176.9	121.4	57.4
HF	193.8	177.2	121.9	57.4
$\text{HSO}_3\text{F}:\text{SbF}_5$ (1:1)	205.5	162.3	128.1	71.8
$\text{HF}:\text{SbF}_5$ (1:1)	207.2	162.2	127.9	72.0

^a Owing to the relative instability of *p*-methoxybenzaldehyde in some of these media all ^{13}C NMR measurements have been carried out at -30°C . ^b In parts per million from Me_4Si ; external capillary with Me_4Si and $\text{C}_3\text{D}_8\text{O}$ lock solvent.

protonated *p*-methoxybenzaldehyde has not been proven to behave like a Hammett base; nevertheless, as our results overlap and are complementary with Gillespie's results, this will not alter significantly the following conclusions. (1) $\text{HF}:\text{SbF}_5$ is weaker than $\text{HSO}_3\text{F}:\text{SbF}_5$ only when the SbF_5 content is below 0.6 mol %. The reason for this is that pure HF is a much weaker acid ($H_0 = -11$) than HSO_3F ($H_0 = -15$). (2) The acidity increase is much stronger in HF than in HSO_3F on SbF_5 addition as can be seen from the slopes on Figure 2. With 4 mol % SbF_5 the HF solvent is already 10^3 times more acidic than HSO_3F with the same SbF_5 concentration. To obtain the same acidity in HSO_3F , one has to add ~ 20 mol % SbF_5 .

This is, to our view, a direct confirmation of the above statement on relative acidities⁵ suggested by many indirect experimental data. Considering now the slope of the HF curve, the probable increase to much higher acidities on further SbF_5 addition is not a rash prediction.

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Insertion vs. Addition of Oligomeric Difluorosilylenes. Evidence for the Attack of Oligomeric Difluorosilylenes on the Carbon-Carbon Double Bond as an Initial Step in the Insertion Reactions with *trans*- and *cis*-Difluoroethylene

Sir:

When a comparison between the chemistry of silylenes and carbenes is attempted, as a number of review articles have done,¹⁻³ the failure to find any evidence for the existence of silacyclopropane in the reactions of SiF_2 with ethylene and fluoroethylenes has greatly confused our understanding of their mechanisms.

While insertion products are found to be the sole type of product in the case of fluoroethylenes,^{4,5} the products in the reaction of ethylene are best interpreted as a result of addition.⁴ It is generally accepted that in such cases reactions along two paths are likely to occur: SiF_2 attacking either a carbon-carbon double bond or a carbon-fluorine single bond. All identified addition products involve the dimeric unit $\cdot\text{SiF}_2\text{SiF}_2\cdot$ (and higher units in small yields);^{6,7} on the other hand, monomeric SiF_2 has only been found in insertion products.^{1,8} From a general mechanistic point of view for reactions with ethylene and fluoroethylenes, it would be hardly conceivable to accept the implication that monomeric SiF_2 , being a unique member of the reactive homologue $\cdot(\text{SiF}_2)_n\cdot$, reacts only with carbon-fluorine single bonds.

We now report new results of the reactions of silicon difluoride with *trans*- and *cis*-difluoroethylene which provide evidence for the attack on carbon-carbon double bonds by $(\text{SiF}_2)_n$ ($n = 1, 2, \dots$) as an initial step in the insertion reactions.

Silicon difluoride was generated and reacted with *trans*- and *cis*-difluoroethylene in the manner described previously.⁹ Products were characterized by their mass, IR, and NMR spectra. The mass spectra clearly indicate that in both reactions 1:3 (difluoroethylene to SiF_2 ratio), 1:2, and small quantities of 1:1 products were formed. The structures of these products are unequivocally determined on the basis of their ^1H and ^{19}F NMR spectra. Some of the NMR parameters are shown in Table I. For all known compounds of insertion products, detailed NMR parameters of the 1:1 and 1:3 types have not been obtained before.

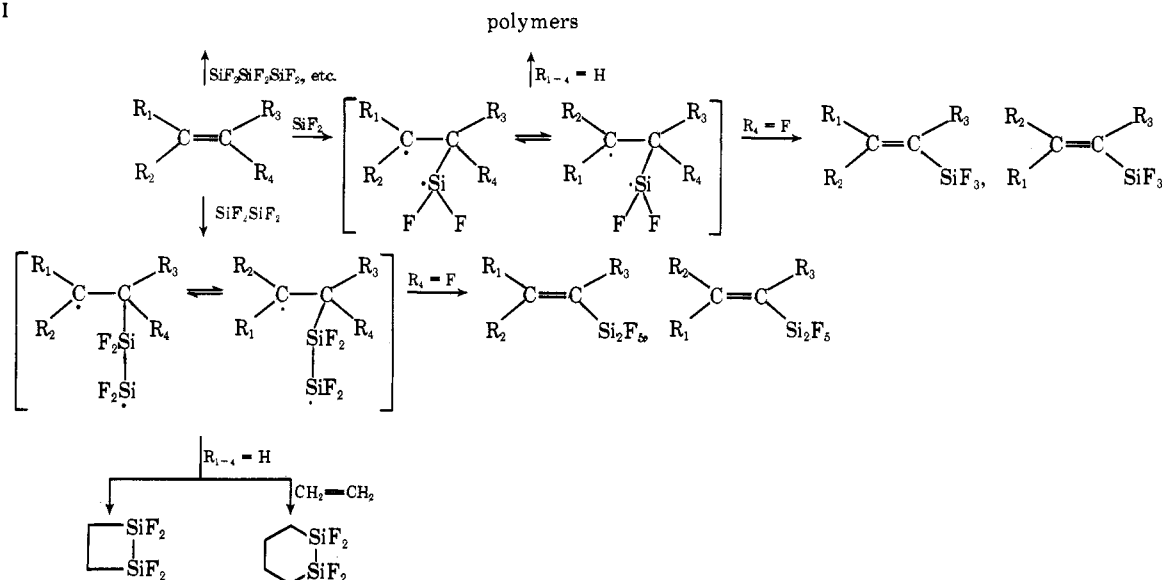
All products are "insertion" products; no silacyclopropanes or disilacyclobutanes are observed. The most interesting result is the fact that both reactions appear to be nonstereospecific. The relative abundances of the various isomers are shown in Table I. Since no *trans*-*cis* isomerization of the starting materials was observed, the only reasonable reaction path which leads to both *trans* and *cis* isomers in the products of each reaction is an initial attack of $(\text{SiF}_2)_n$ on the carbon-carbon double bond, followed by rearrangement. Margrave has proposed a silacyclopropane intermediate for the mechanism of monomeric SiF_2 insertion, which suggested that SiF_2 attacked the carbon-carbon double bond rather than a carbon-fluorine bond;¹⁰ the present work is the first time any relevant evidence has been revealed. However, this evidence does not guarantee

Table I. ^1H and ^{19}F NMR Parameters and Relative Yields of the Products from SiF_2 Reactions with *trans*- and *cis*-Difluoroethylenes

Compd	Chemical shifts, ^a ppm						Coupling constants, Hz	Relative yields (%)	
	A	B	C	D	E	F		Cis ^b	Trans ^b
<i>cis</i> -HFC=CHSiF ₃	H	H	F	SiF ₃			$J(\text{AB}) = 6.5, J(\text{BC}) = 88.8, J(\text{AC}) = 59.6$	5	1
<i>trans</i> -HFC=CHSiF ₃	H	F	H	SiF ₃			$J(\text{AB}) = 29.0, J(\text{BC}) = 84.0, J(\text{AC}) = 13.5$	2	2
<i>cis</i> -HFC=CHSiF ₂ SiF ₃	H	H	F	SiF ₂	SiF ₃		$J(\text{AB}) = 6.0, J(\text{BC}) = 89.0, J(\text{AC}) = 62.0$	57	27
<i>trans</i> -HFC=CHSiF ₂ SiF ₃	H	F	H	SiF ₂	SiF ₃		$J(\text{AB}) = 29.5, J(\text{BC}) = 85.0, J(\text{AC}) = 13.5$	11	50
<i>cis</i> -HFC=CHSiF ₂ SiF ₂ -SiF ₃	H	H	F	SiF ₂	SiF ₂	SiF ₃	$J(\text{AB}) = 6.0, J(\text{BC}) = 91.0, J(\text{AC}) = 62.0$	18	7
<i>trans</i> -HFC=CHSiF ₂ SiF ₂ SiF ₃	H	F	H	SiF ₂	SiF ₂	SiF ₃	$J(\text{AB}) = 30.5, J(\text{BC}) = 85.5, J(\text{AC}) = 13.5$	7	13

^a Proton chemical shifts in δ ; fluorine chemical shifts in parts per million upfield from internal reference CCl_3F . ^b Cis, reaction with *cis*-difluoroethylene. Trans, reaction with *trans*-difluoroethylene.

Scheme I



the existence of silacyclobutanes, nor does it rule out the alternative insertion path, direct attack of $(\text{SiF}_2)_n$ on the carbon-fluorine bonds. The best that one can say at this moment is that, while there is possibly more than one path for $(\text{SiF}_2)_n$ reactions, one proven mechanism involves an initial $(\text{SiF}_2)_n$ attack on the carbon-carbon double bond. The higher ratio of configuration retention for the reaction of *cis*-difluoroethylene seems to agree with the known fact that *cis*-difluoroethylene is more stable than its *trans* isomer.¹¹

In fact, when one considers the "addition" reaction with ethylene in which the only identified products are disilacyclobutanes and disilacyclohexanes,⁴ one would favor the implication that the present observation infers, because it brings about a more or less integrated view of the reaction mechanism of silicon difluoride with both ethylene and fluoroethylenes (Scheme I).

This type of reaction pattern can be extended to $\cdot\text{SiF}_2$ - SiF_2SiF_2 - or even higher units. In fact, both addition and insertion products involving trimeric units are known.^{10,13} In this reaction scheme both insertion and addition reactions can be rationalized with the same initial attack of $(\text{SiF}_2)_n$ on the double bond, monomeric SiF_2 being no exception. It is the fluorine atoms that cause the different preferences in reaction paths after the initial attack. The true reason for such preference may be complicated; however, it is worth noting that the bond energies decrease in the order, Si-F (135 kcal/mol) > C-F (116 kcal/mol) > C-H (98 kcal/mol) > Si-H (76 kcal/mol).¹² The formation of an exceedingly strong Si-F bond must have contributed to the driving force of insertion whenever a fluorine is attached to an olefinic carbon.

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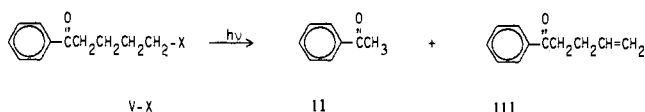
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Rates of Radical β Cleavage in Photogenerated Diradicals¹

Sir:

The Norrish type II photoreaction² provides a unique probe for studying substituent effects on radical reactions, since intramolecular hydrogen atom abstraction is so regioselective. Because of the intense interest in β -haloalkyl radicals,³ we have studied the photochemistry of three δ -halovalerophenones. They each undergo loss of HX competitive with type II photoelimination. The halogens are eliminated from the 1,4-diradical intermediate involved in type II photoelimination.² Moreover, δ -benzoyl sulfides, sulfoxides, and sulfones behave similarly. Our combined results provide the first extensive set of relative β -cleavage rates of radicals.



We had noted previously that V-Cl undergoes a minor reaction in competition with type II elimination.⁴ We have now identified 4-benzoyl-1-butene (III) as a minor product from V-Cl, the major product for V-Br, and the only volatile product for V-I.⁵ Table I lists quantum yields for product formation and for ketone disappearance in benzene containing 0.1 M pyridine. The pyridine captures the HBr and HI which otherwise react with products⁶ and maximizes type II yields.⁷ Under these conditions, the material balance for the chloro and bromo ketones is close to 100%.

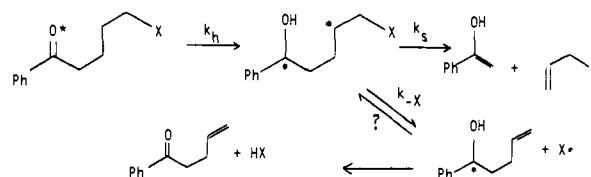
Neither 1 M ethyl iodide nor 1 M butyl bromide measurably quenches the photoelimination of butyrophenone. Likewise, irradiation of β -chloropropiophenone and γ -chloro- and γ -bromobutyrophenone does not form benzoylalkenes. These experiments indicate that the carbon-halogen bonds are not broken by direct interaction with the excited ketone. The only remaining mechanism for product formation involves competitive reactions of the diradicals formed by triplet state γ -hydrogen abstraction. The hydroxy radical formed by β elimination of a halogen atom⁸ from the diradical should either

Table I. Product Quantum Yields for δ -Substituted Valerophenones $\text{PhCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{X}^a$

X	Φ_{II}^b	Φ_{III}^b	Rel k_{-X}^c
Cl ^d	0.58	0.10	1
Br ^d	0.048	0.55	65
I ^d	<0.002	0.43	>1260
SCN	0.003 ^f	0.25 ^f	490
SBU ^e	0.21 ^f	0.006 ^f	0.16
SOBu ^e	0.03 ^f	0.39 ^f	76
SO ₂ Bu ^e	0.39 ^f	0.03 ^f	0.46
SPh	0.02 ^f	0.28 ^f	110
SOPh	0.003 ^f	0.32 ^f	630
SO ₂ Ph	0.19 ^f	0.22 ^f	6.8
SCOCH ₃	0.78 ^f	0.02 ^f	0.15
Cl ^{d,g}	0.54	0.08	
Cl ^{d,h}	0.36	0.06	
Cl ^{d,i}	0.045	0.008	
Cl ^{d,j}	0.63	0.07	

^a Degassed benzene solutions containing 0.1 M ketone irradiated at 313 or 366 nm, 25 °C. ^b An extra 12% cyclobutanol is also formed for V-Cl and presumably for the other ketones. ^c Some data from ref 4. ^d In the presence of 0.1 M pyridine. ^e Bu = *n*-C₄H₉. ^f In the presence of 1 M dioxane. ^g In CH₃CN. ^h In CH₃OH. ⁱ p-MeO. ^j p-CF₃.

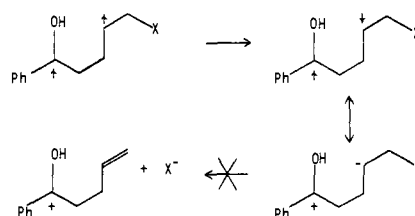
Scheme I



disproportionate or couple with the halogen atom in high yield, perhaps involving a rapid oxidation of the organic radical by X.⁹ Both Br₂ and I₂ are formed from V-Br and V-I; so there is some diffusion apart of the radical pairs.

Since thiyl radicals also add reversibly to olefins,^{8,10} we extended our studies to some δ -benzoyl sulfides, sulfones, and sulfoxides and found that they all undergo both forms of elimination, as noted in Table I. The corresponding γ -benzoyl homologues give only type II products. Unlike alkyl halides, sulfur compounds do quench excited ketones efficiently,¹¹ but do not undergo sensitized elimination themselves in the process. We conclude that all products come from the usual 1,4 diradical. With V-SR observation of disulfide as a minor product indicates the formation of thiyl radicals. With V-SOR, the expected coupling product of sulfanyl radicals, RS-SO₂R,¹² is observed.

Since it is now well established that photogenerated diradicals undergo typical monoradical rearrangements¹³ and bimolecular trapping,¹⁴ we expected them to also undergo β -elimination of labile halogen and sulfur-centered radicals. Therefore Scheme I represents the expected and most likely explanation for this novel and highly specific form of photoelimination. II/III product ratios vary only slightly with solvent polarity and with para substituents; so a strong zwitterionic contribution to the elimination is unlikely.



A cyclic concerted elimination has already been suggested for β -alkoxy ketones¹⁵ and remains a possibility here. Because an eight-membered ring is necessary, we doubt that this con-