Photolysis of Acyl Group IV Metalloids: the Formation of Silyl Radicals

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The photolyses of several acylsilanes and one acylgermane in carbon tetrachloride have been shown to involve Norrish Type I cleavage of the metalloid–acyl bond to give metalloidal radicals. These radicals readily abstract chlorine from the solvent.

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Recently, the photolyses of acetyltriphenylsilane and (-)-acetyl-1-naphthylphenylmethylsilane in carbon tetrachloride were shown to involve the formation of silyl radicals which subsequently abstracted halogen from the solvent, in the latter case with significant retention of optical configuration (1). In other studies it was demonstrated that photolysis of acylsilanes in alcohols proceeded via a siloxycarbene intermediate (2).

$$\begin{array}{ccc} R_{3}SiCOPh & \xrightarrow{h\nu} & [R_{3}SiO\ddot{C}Ph] & \longrightarrow & R_{3}SiO & H \\ \hline R'OH & [R_{3}SiO\ddot{C}Ph] & \longrightarrow & R'O & Ph \end{array}$$

In order to further investigate the apparent duality of the reaction pathway (radical or siloxycarbene formation) a more detailed investigation was begun; the photolysis of a variety of acylsilanes in carbon tetrachloride is reported here.

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The photolysis of acetyltrimethylsilane in carbon tetrachloride produced trimethylchlorosilane (99%), acetyl chloride (67%), 1,1,1-trichloropropanone (30%), and hexachloroethane (61%). These results are in accord with those found previously for acetyltriphenylsilane (1). The nature of the products suggests that acetyl and trimethylsilyl radicals are formed by Norrish Type I cleavage of the acyl-silicon bond followed by reactions of the radicals with the solvent, as shown in Scheme 1.

shown in Scheme 1. [1] hv $Me_3SiCOMe \rightarrow Me_3Si. + \cdot COMe$ [2] $Me_3Si. + CCl_4 \rightarrow Me_3SiCl + \cdot CCl_3$ [3] $\cdot COMe + CCl_4 \rightarrow CICOMe + \cdot CCl_3$

[4] $\cdot COMe + \cdot CCl_3 \rightarrow Cl_3CCOMe$

$$\begin{array}{c} [5] \\ 2 \cdot CCl_3 \rightarrow Cl_3C - CCl_3 \\ \\ SCHEME 1 \end{array}$$

If Scheme 1 adequately describes the overall process, then the sum of the yields of acetyl chloride and 1,1,1-trichloropropanone, representing products derived from the acetyl radical, and the sum of the yields of 1,1,1-trichloropropanone and hexachloroethane, representing products derived from the trichloromethyl radical, will each be 100%. These were found to be 97 and 91% respectively.

The possible occurrence of other minor reactions was briefly investigated. Hexamethyldisilane, which would result from a combination of trimethylsilyl radicals, trimethylsilane from hydrogen abstraction, and trichloromethyltrimethylsilane from cross-combination of radicals, could not be detected in the reaction mixture. It can be concluded therefore, that the reaction pathways depicted in Scheme 1 adequately describe the photolysis of acetyltrimethylsilane in carbon tetrachloride.

The yields of 1,1,1-trichloropropanone, acetyl chloride and hexachloroethane were found to be temperature dependent, the yield of trichloropropanone being observed to decrease with increasing temperature while the yields of acetyl chloride and hexachloroethane increased with increasing temperature, as shown in Table 1. These observations are explained if the activation energy for the abstraction of chlorine by the acetyl radical, step 3, Scheme 1, is greater than that for the radical combination reactions, steps 4 and 5, as would be expected.

FABLE	1.	Yields of photolysis products	
	at	various temperatures	

	Temp	erature (°C)
Product	-23	0	76
$Me_{3}SiCl \\Cl_{3}CCOMe \\MeCOCl \\Cl_{6}C_{2}$	100 38 63 48	99 30 67 61	99 14 74 63

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TABLE 2. Products of photolyses in carbon tetrachi	or.	rı	Ŀ	l	l	J	đ	U	I	ļ		Ľ	ſ	I	I	l	ų	J	l	l	I	I	I	I	I	L	L	L	I	í	L	L	I	I	I	J	l	
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Acylmetalloid*	Products
Me₃SiCOEt	Me ₃ SiCl (~ 100%), EtCOCl (53%), Cl ₆ C ₂ (54%), Cl ₃ CCOEt (yield undetermined)
Et ₃ SiCOMe	Et ₃ SiCl (94%), MeCOCl (65%), MeCOCCl ₃ (35%), Cl ₆ C ₂ (64%)
<i>n</i> -Pr ₃ SiCOMe	<i>n</i> -Pr ₃ SiCl, MeCOCl, MeCOCCl ₃ , Cl ₆ C ₂ (yields undermined)
n-Bu₃SiCOMe	<i>n</i> -Bu ₃ SiCl, MeCOCl, MeCOCCl ₃ , Cl ₆ C ₂ (yields undetermined)
Me₃SiCOPh	Me ₃ SiCl (87%), PhCHO, PhCOCl, Cl ₆ C ₂
Ph₃SiCOPh	No reaction
Ph ₃ GeCOPh	Ph ₃ GeCl (94%), PhCOCl (91%), Cl ₆ C ₂ (98%)
Me Me Si O	$\begin{array}{l} Me_2ClSi(CH_2)_4COCl~(48\%),~Me_2ClSi(CH_2)_4COCCl_3\\ (14\%), \uparrow~Cl_6C_2~(yield~undetermined) \end{array}$

*In all photolyses 0.2 g of acylmetalloid was irradiated in 5 ml of dry carbon tetrachloride at 0° under nitrogen for about 1-2 h using a low pressure 100 W mercury lamp. †Yields are those of product isolated by fractional distillation.

The photolysis of a number of other acylsilanes and one acylgermane in carbon tetrachloride were also investigated and analogous results were obtained for all other acylmetalloids studied (except benzoyltriphenylsilane), as shown in Table 2.

When benzoyltrimethylsilane was photolyzed, benzaldehyde was found, presumably because the benzoyl radical abstracts hydrogen from the trimethylsilyl group. This is supported by the observation that no benzaldehyde was formed in the photolysis of benzoyltriphenylgermane, where only aromatic protons are available. Acetaldehyde was not observed in the reactions involving the acetyl radical.

Benzoyltriphenylsilane was inert to photolysis even over prolonged periods of time. This is in marked contrast to its rapid photochemical decomposition in the presence of alcohols (2) and its unique behavior is not understood. Benzoylsilanes and benzoylgermanes exhibit an $n \to \pi^*$ absorption maximum at about 420 mµ, whereas acetylsilanes and acetylgermanes have a maximum at about 380 mµ. The energy absorbed appears sufficient to cause rupture of the siliconacetyl bond on one hand, but is insufficient to break the silicon-benzoyl bond. Since the carbon-germanium bond is considerably weaker than the silicon-carbon bond, the photolytic decomposition of benzoyltriphenylgermane is not unexpected. This explanation of the above

observations does not, however, satisfactorily explain the photolysis of benzoyltrimethylsilane, whose absorption maximum is virtually identical to that of benzoyltriphenylsilane.

The reaction of the cyclic acylsilane, 1,1dimethyl-1-silacyclohexan-2-one, is noteworthy. Preliminary investigations of the photolytic decompositions of cyclic acylsilanes in a variety of media have indicated that cyclic siloxycarbenes are involved (3–5). The products obtained on photolysis of the silacyclohexanone in carbon tetrachloride are 5-(chlorodimethylsilyl)pentanoyl chloride and 1,1,1-trichloro-6-(chlorodimethylsilyl)hexan-2-one as expected from a simple Norrish Type I cleavage of the siliconcarbonyl bond followed by reactions as in Scheme 1; thus siloxycarbenes do not appear to be involved under these conditions.

From the preceding results it appears that aliphatic acylsilanes when photolyzed in carbon tetrachloride undergo Norrish Type I cleavage exclusively: further work is underway to establish more clearly the factors which determine whether siloxycarbene formation or Norrish Type I cleavage will occur in other solvents.

Experimental

General

The n.m.r. spectra were recorded on either a Varian A-60 or A56/60 instrument using carbon tetrachloride. The i.r. spectra were obtained on a Perkin–Elmer Model 237-B IR Spectrometer. The u.v. spectra were obtained

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				Analyse	es (%)	
	D 111 • • /		Calc	ulated	For	und
Acylmetalloid	Boiling point (°C)	$n_{\rm D}^{20}$	С	H	С	н
Me ₃ SiCOCH ₂ CH ₃	140/760 mm	1.4191	55.32	10.83	55.05	10.98
Et ₃ SiCOMe	180/760 mm	1.4426	60.69	11.46	60.48	11.68
<i>n</i> -Pr ₃ SiCOMe	110/5 mm	1.4456	65.93	12.07	65.90	12.10
n-Bu ₃ SiCOMe	84/15 mm	1.4496	69.35	12.47	69.60	12.59

TABLE J. Analysis and Dhysical Diobernes of new actene actisinal	TABLE 3.	Analysis and	physical pro	perties of new	acyclic acylsilan
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TABLE 4. T	he i.r. a	and u.v.	spectra	of acylsilanes
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Acylmetalloid	v (C=0)	λ (ε)
Me ₃ SiCOMe	1647	388 (93), 372 (126), 358 (100) 346 (62), 333 (34), 323 (18)
Me ₃ SiCOC ₂ H ₅	1646	382 (115), 366 (126), 352 (100) 340 (60), 328 (32), 317 (14)
Et ₃ SiCOMe	1644	390 (101), 372 (131), 360 (102) 343 (63), 335 (35), 322 (15)
<i>n</i> -Pr ₃ SiCOMe	1644	389 (97), 374 (128), 360 (98), 347 (61), 334 (32), 322 (15)
n-Bu₃SiCOMe	1643	382 (115), 366 (126), 352 (100) 340 (60), 328 (32), 317 (14)

on a Unicam SP800 Spectrometer. A Varian Aerograph Series 200 Gas Chromatograph was used for product analysis with a $20' \times 1/4''$ aluminum column containing 20% SE30 on Chromasorb B. The photolysis employed a PAR-38 100 W mercury floodlamp.

Preparation of Acylmetalloids

All acylmetalloids were prepared by previously described methods (6-8). Physical data of new acylmetalloids are listed in Table 3 and spectroscopic data are given in Table 4.

Photolysis of Acylmetalloids in Carbon Tetrachloride

Products were identified by i.r. and n.m.r. spectroscopy, and by v.p.c., each product being identified by comparison of the retention time of an authentic sample with that of the appropriate peak in the v.p.c. Trichloromethyltrimethylsilane was prepared for comparison purposes by the method of Bamford and Pant (9). Its absence in the photolysate of acetyltrimethylsilane in carbon tetrachloride was demonstrated by v.p.c. Yields of all products were determined using an internal standard and the peak-weight method.

In the case of the cyclic acylsilane, the photolysate from the acylsilane (3.75 g) in CCl₄ (300 ml) was evaporated and the residual liquid was distilled on a semi-micro, spinning-band column to give 5-(chlorodimethylsilyl)pentanoyl chloride, 2.7 g (48%), b.p. 48-50°/0.12 mm, and somewhat impure 1,1,1-trichloro-6-(chlorodimethylsilyl)hexan-2-one, 1.1 g (14%), b.p. 73-74°/0.10 mm.

Anal. Calcd. for ClMe₂Si(CH₂)₄COCl: C, 39.44; H, 6.62; Cl, 33.26. Found: C, 39.23; H, 6.84; Cl, 33.40. The i.r. (film): 5.56 (C=O) μ.

- Anal. Calcd. for ClMe₂Si(CH₂)₄COCCl₃: C, 32.45; H,
- 4.77; Cl, 47.89. Found: C, 33.21; H, 4.78; Cl, 46.89. The i.r. (film): 5.70 (C=O) μ.

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