

Preliminary communication

GENERATION OF A VINYLIDENE CARBENE FROM AN
 α -CHLOROVINYLSILANE

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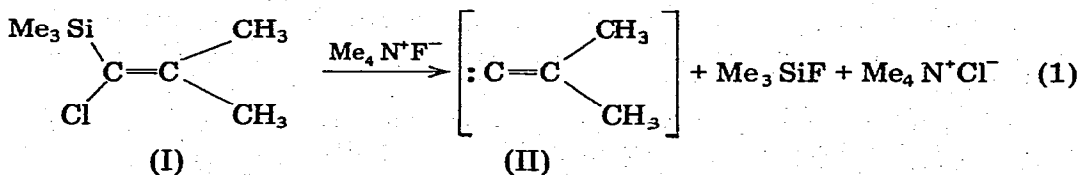
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Summary

The reaction of 1-chloro-1-trimethylsilyl-2-methylpropene with anhydrous tetramethylammonium fluoride in the presence of carbenophiles affords dimethylvinylidene insertion products.

The observation that fluoride ion serves as an effective reagent for the vicinal dehalosilylation of β -chlorovinylsilanes to acetylene [1] has been followed by applications to benzyne [2] and allene [3] syntheses. We now report a novel reactivity* of 1-chloro-1-trimethylsilyl-2-methylpropene with anhydrous tetramethylammonium fluoride in which *geminal* dehalosilylation occurs to afford a vinylidene carbene (or carbenoid) species (II) (eq. 1)**. The transformation is viewed as being initiated by nucleophilic attack of fluoride ion at silicon followed by loss of chloride ion from the incipient carbanionic center***. Although potassium fluoride in aprotic solvents has proven a potent dechlorosilylating reagent for vicinal eliminations [1-3,8], it was ineffective for the present purpose. Evidence for the generation of II was provided by in situ trapping with the carbenophiles listed in Table 1.



The carbene precursor I was prepared as follows. To a mixture of 120 ml (180 mmol) of 1.5 N n-butyllithium in hexane, 265 ml of THF and 32 ml of


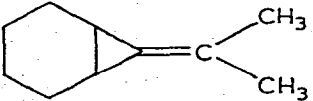
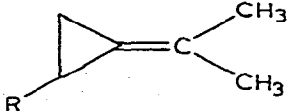
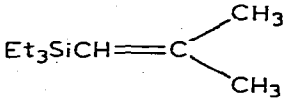
*The thermolysis of α -haloalkyltrihalosilanes is known to afford dihalocarbene ($X_2C:$) species [5, 6]. Dichlorocarbene is also produced from the reaction of $\text{Cl}_2\text{C}(\text{O})(\text{OEt})_2$ with fluoride ion [7].

**For other routes affording these species, see ref. 4.

***No evidence is yet at hand concerning the concertedness or non-concertedness of this process, or of the state of complexation of the resulting "carbene".

TABLE 1

PRODUCTS OBTAINED FROM THE REACTION OF 1-CHLORO-2-METHYLPROPENE (I) WITH TETRAMETHYLAMMONIUM FLUORIDE AND CARBENOPHILES

Carbenophile	Product ^a	R	Yield (%) ^b	Reference
			55	12
RCH=CH ₂		OEt	66	12
		Ph	55	13
		Me ₃ Si	35	This work ^c
Et ₃ SiH			65	14

^a Also accompanied by 4-15% of 1-chloro-2-methylpropene. ^b Yields determined by GLC. ^c NMR (CDCl₃, PhH int. std.) δ 1.63 (3H, s), 1.62 (3H, s), 0.96 (1H, m), 0.63 (1H, m), 0.40 (1H, m), -0.19 (9H, s). Found: C, 70.08; H, 11.70. C₉H₁₈Si calcd.: C, 70.05; H, 11.76%.

ether prepared at -100°C was added 21 g (180 mmol) of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) followed by precooled (-78°C) 1-chloro-2-methylpropene (16 g, 180 mmol). After 4 h at -100°C , precooled (-78°C) trimethylchlorosilane (19 g, 180 mmol) and 10 ml of hexamethylphosphortri- amide (HMPA)* in 30 ml of THF were added in turn. The reaction mixture was held 1 h at -100°C , 4 h at -78°C and worked up by dilute acid and exhaustive water extraction. Fractionation afforded a forerun containing *n*-butyltrimethylsilane (26% by GLC)**, followed by 11.3 g (39%) of I*** (91% pure by GLC), b.p. $160-162^{\circ}\text{C}/760$ mmHg. Refractionation gave material of 99% purity. Generation of the dimethylvinylidene insertion products can be illustrated by the reaction employing ethyl vinyl ether. Thus, a mixture of 0.95 g (5.8 mmol) of I, 0.57 g (6.2 mmol) of anhydrous Me₄NF****, 7.5 g (0.10 mmol) of ethyl vinyl ether and 10 ml of diglyme was prepared in a dry box. After two days at 25°C in a closed system, workup afforded a 66% yield of 2-ethoxy-1,1-isopropylidenecyclopropane and a 15% yield of 1-chloro-2-methylpropene, as determined by GLC. Trimethylfluorosilane was also identified as a reaction product. Total consumption of I occurred under these conditions.

The appearance of 1-chloro-2-methylpropene among the reaction products is presumably due to inherent**** and adventitious moisture present within the system which prevents carbene formation by protonation

* A much lower yield of I is realized (ca. 10%) under similar conditions if HMPA is omitted.

** Optimization of metalation was not investigated. The literature contains references to unsuccessful attempts at the metalation of 1-chloro-2-methylpropene [9].

*** IR: 3.35m, 6.21w, 6.95w, 7.31w, 8.0s, 11.2m, 11.96s, 13.24m μm ; NMR (CCl₄): δ (ppm) 1.28 (9H, s), 1.87 (3H, s), 1.90 (3H, s). Found: C, 51.68, H, 9.47. C₇H₁₅ClSi calcd.: C, 51.67; H, 9.29%.

**** Prepared as reported [10] employing hydrogen fluoride dried over phosphorus pentafluoride [11]. Elemental analysis indicated a maximum water content of 11% for this material.

of I during or after silicon-carbon cleavage. In a separate experiment utilizing cyclohexene as the carbenophile, but employing a sample of anhydrous tetramethylammonium fluoride to which one equivalent of water had been added, a slow consumption of I occurred (72% over 75 h) which resulted in a 62% yield of 1-chloro-2-methylpropene and a 15% yield of insertion product.

It is worthy of note that the present system affords a mild method for the transfer of the dimethylvinylidene function which is unique in that the strongly basic conditions (alkoxide, organolithium reagents) usually employed in its generation are avoided.

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