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The Regiochemistry of Cyclopropylcarbinylstannane Ring Fission.

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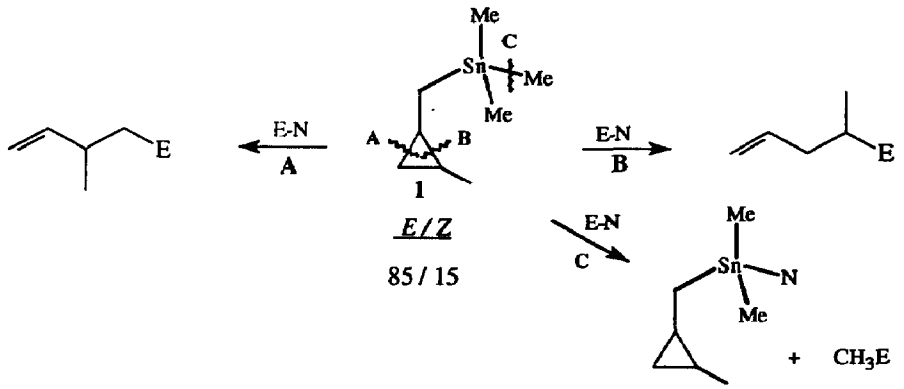
Abstract: The reaction of 2-methylcyclopropylcarbinyltrimethylstannane 1 in chloroform with the electrophiles sulphur dioxide, trifluoroacetic acid, and iodine proceeds preferentially with ring cleavage and addition at the unsubstituted cyclopropyl methylene. Iodination and acidolysis in methanol proceeds exclusively with tin-methyl bond cleavage.

The electrophilic cleavage of cyclopropylcarbinyl (CPC) metal compounds is a natural extension of the corresponding allyl metal chemistry which has received such wide attention in recent years[1]. There have been a relatively small number of reports describing CPC silicon ring fission[2], but little is known about the chemistry of the corresponding stannanes which are predicted undergo stereospecific cleavage reactions[3].

We previously reported[4] the electrophilic ring cleavage of CPCSnMe3 and CPCSnBu3 (Scheme 1) with sulphur dioxide and iodine in chloroform which yields the corresponding homoallylic tin sulfinates and iodides respectively.

Scheme 1

We now report the results (Table 1) of a study of regiochemistry involving electrophilic cleavage of predominantly *E* 2-methylCPCSnMe3 **1** which can occur with ring or methyl cleavage as indicated (Scheme 2).



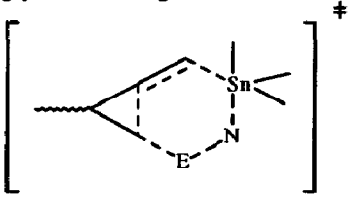
Scheme 2

Table 1. Product distribution on Electrophilic Cleavage of 2-MethylCPCtrimethylstannane[a].

E-N	Solvent	%A	%B	%C
TFA	$CDCl_3$	90	10	0
TFA[b]	CD_3OD	0	0	*ca* 100
I_2[c]	$CDCl_3$	90	10	0
I_2[c]	CD_3OD	0	0	*ca* 100
SO_2[d]	$CDCl_3$	80	20	0
SO_2[d]	CD_3OD	77	23	0

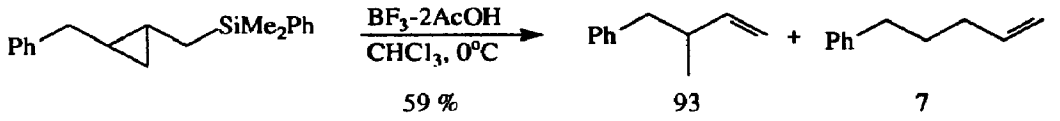
[a] All reactions were conducted using 1 mmol of electrophile and substrate (unless otherwise stated) at ambient temperature (ca 25°C) in 0.7ml of solvent. Product ratios were determined by ^1H and ^{13}C nmr spectroscopy. [b] Acidolysis in methanol required 3.0 eq of TFA in methanol and only proceeded to *ca* 70% completion due to competing [$^2H_3$]-methyl trifluoroacetate formation. [c]Iodinations were performed in the dark. [d]Sulfur dioxide was bubbled through the solution for *ca* 15 min to ensure complete reaction. Insertion yields the trimethyltin homoallylsulfinates[4].

Both acidolysis and iodination of **1** proceeds with ring fission in chloroform (pathways **A** and **B**) and with methyl cleavage (pathway **C**) in methanol while sulfur dioxide insertion proceeds with ring fission in both solvents. The reason for this electrophile-dependent solvent effect on the mode of reaction is not immediately apparent. It may be that a cyclic, "S_E'-like" mechanism is operative for all three electrophiles in chloroform (Scheme 3) while in methanol, solvent-tin coordination disrupts the internal coordination of iodine and acid but not that of the more strongly coordinating sulfur dioxide[5].



Scheme 3

The trifluoroacidolysis of 1 in chloroform was complete within 5 minutes at ambient temperature which is considerably faster than the corresponding reaction of substituted CPC silanes. Cleavage with TFA proceeded with preferential electrophilic attack at the less substituted ring carbon as has been observed for the acidolysis of an *E* substituted cyclopropylcarbinylsilane (Scheme 4[2e]).



59 % 93 7

Scheme 4

The reaction of 1 with one equivalent of iodine in chloroform (ca 25°C) proceeded to yield (>95%) the ring opened products 4-iodo-3-methyl-1-butene and 4-iodo-1-pentene in a ratio of 90 / 10. This reaction was carried out in the dark to reduce the possibility of a free radical participation[4, 6]. The corresponding reaction of sulphur dioxide in chloroform or methanol provided the homoallylic tin sulfinates quantitatively, again with preferential electrophilic attack at the less substituted carbon. It may be that even greater discrimination between the substituted and unsubstituted carbon would be observed with the Z-2-methylCPC stannane. In this case, "Sgi' like" addition at the substituted carbon would be even more hindered and we are currently investigating this possibility.

Haloboronation[2b] and stannic chloride[2f] cleavage of substituted CPC silicon derivatives have also been reported to proceed regioselectively with attack predominantly at the unsubstituted methylene. The authors of the latter report propose a two step elimination process involving attack at the less sterically hindered site to yield a β-silyl stabilised cation intermediate. The relatively large σ–σ conjugative interaction observed for CPC stannanes[3] suggests to us that a concerted mechanism is equally probable with these substrates and that the regiochemistry observed is a result of steric congestion at the substituted carbon.

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