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THE ELECTROPHILIC CLEAVAGE OF CYCLOPROPYLCARBINYLSTANNANES. CONFIRMATION OF TRAYLOR'S PREDICTION.

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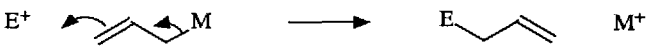
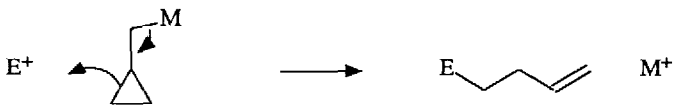
ABSTRACT The reaction of cyclopropylcarbinyltrialkylstannanes (CPCSnR$_3$) **1a** (R=Me) and **1b** (R=Bu) with sulfur dioxide in chloroform or methanol yields the homoallylic tin sulphinates **2a** and **2b** respectively The reaction of **1a** with iodine in chloroform yields predominantly 4-iodo-1-butene (**3**) and trimethyltin iodide while in methanol the corresponding reaction yields CPCSnMe$_2$I (**4**) and methyl iodide

The electrophilic cleavage of allylic metal compounds is a reaction of considerable mechanistic and synthetic interest[1-4] High levels of regio- and stereoselectivity have been achieved by careful choice of metal[1a] and reaction conditions[2] Particularly important is the enantiospecific cleavage of chiral substrates with carbon electrophiles[3,4] which has been applied in natural product synthesis[3]



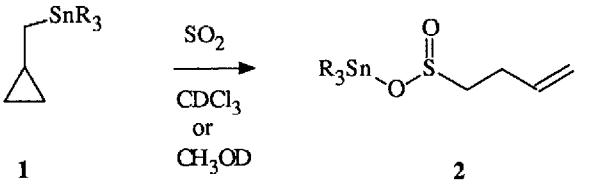
A logical extension to this reaction is the analogous cleavage of cyclopropylcarbinyl (CPC) metal derivatives which, by comparison, has received little attention[5]



The cleavage of CPC silicon derivatives with iodine[5a], bromine[5a], acetyl chloride[5b], stannic chloride[5c], haloboranes[5d] and acid[5e,f] have been reported (the latter being utilized in the synthesis of *cis*-jasmone[5e] and a constituent of the melon fly pheremone[5f]) We are unaware of any reports concerning the corresponding reaction of the potentially more reactive CPC stannanes A UV photoelectron study by Traylor *et al* has indicated that the σ-σ interaction between the cyclopropane orbitals and carbon-tin bond of CPCSnMe$_3$ (**1a**) is only marginally less (0 6eV) than the corresponding σ-π interaction in allylSnMe$_3$[6] This orbital overlap should significantly increase the reactivity of the cyclopropane ring towards electrophilic cleavage and may infer a stereoelectronic bias as observed for allylic systems[6,7]

The reaction of allylic stannanes with sulfur dioxide in chloroform or methanol proceeds with allylic rearrangement to yield the corresponding allylic tin sulfinates[8] In a weakly coordinating solvent such as

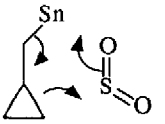
chloroform this reaction proceeds with *syn* approach of the electrophile, consistent with an S_Ei' mechanism This stereospecificity is lost in methanol[8] We now report the reaction of CPCSnMe3 (**1a**) and CPCSnBu3 (**1b**) with sulfur dioxide in chloroform and methanol These reactions both proceeded with ring fission to yield the corresponding homoallylic tin sulfinates **2a** and **2b** respectively[9]



1 **2**

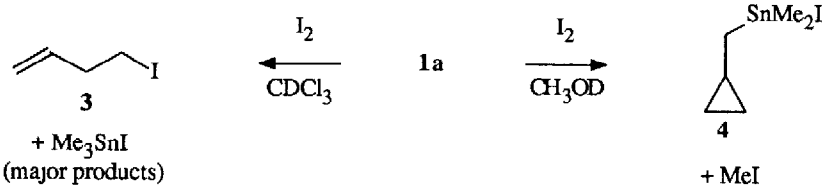
a R = Me
b R = Bu

By analogy with the corresponding allylic system, it is probable that the reaction in chloroform proceeds via a concerted "S_Ei' like" mechanism



In methanol a cyclic transition state is less likely[8] A competitive experiment involving **1b** and allylSnBu3 in chloroform indicated that the latter was completely consumed before any **2b** was detected We are currently examining the stereochemistry of this reaction in both solvents

Cleavage of **1a** with one equivalent of iodine in chloroform (*ca* 20°) also proceeded predominantly with ring fission (> 90%) to yield 4-iodo-1-butene (**3**) and trimethyltin iodide Small quantities of CPCSnMe2I (**4**) and methyl iodide were also observed Analysis of the corresponding reaction of **1b** was complicated by the presence of tetrabutyltin (formed by the redistribution of Bu3SnLi during the synthesis of **1b**[11]), although it was clear that in this case also **3** was the major product Reaction of **1a** with one equivalent of iodine in methanol (*ca* 20°C), however, yielded **4** and methyl iodide in equal amounts[12]



3
+ Me_3SnI
(major products)

4
+ MeI

There are a number of possible explanations for the effect of solvent on the regiochemistry of these reactions The cleavages of **1a** and **1b** with iodine in chloroform were performed in the dark but, although unlikely[13], a

free radical mechanism cannot be ruled out An electrophilic process in this solvent could proceed via a cyclic ("S_Ei' like") transition state involving iodine-tin coordination In methanol, however, solvent-tin coordination appears to promote S_E methyl cleavage although, again, a free radical process is possible No cyclopropylcarbinyl iodide was observed in the ^1H or ^{13}C nmr spectra of the iodine/methanol reaction suggesting both a statistical and steric bias against this mode of cleavage These solvent effects are being investigated further

We have presented results which confirm Traylor's prediction of an activating influence by the carbon-tin bond on the cyclopropane ring in CPC stannanes[6] but in addition, suggest a solvent dependency The possibility of a stereoelectronic bias with these and other electrophiles (including the synthetically more useful carbon electrophiles) is under investigation

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Notes and References

1 For reviews see (a) Hoffman, R W *Angew Chem Int Ed Engl* 1982, **21**, 555 (b) Fleming, I , Dunogues, J , Smithers, K *Org Reactions* 1989, **37**, 57

2 For example Keck, G E , Andrus, M B ; Castello, S *J Am Chem Soc* 1989, **111**, 8136 and references therein

3 Marshall, J A , Gung, W Y *Tetrahedron Lett* 1989, **30**, 2183 and references therein

4 (a) Imwiekelried, R , Seebach, D *Angew Chem Int Ed Engl* 1985, **24**, 765 (b) Corey, E J , Yu, C M , Kim, S S *J Am Chem Soc* 1989, **55**, 5495 (c) Riedeker, M , Duthaler, R O *Angew Chem Int Ed Engl* 1989, **28**, 494

5 (a) Grignon-Dubois, M , Dunogues, J , Calas, R *J Chem Research (S)* 1979, 6 (b) Grignon-Dubois, M , Dunogues, J , Calas, R *Can J Chem* 1981, **59**, 802 (c) Ryu, I , Suzuki, H , Murai, *Org Chem* 1990, **55**, 1409 (e) Ochiai, M , Sumi, K , Fujita, E *Chem Pharm Bull* 1983, **31**, 3931 (f) Wilson, S R , Zucker, P A *J Org Chem* 1988, **53**, 4682

6 Brown, R S , Eaton, D F , Hosomi, A , Traylor, T G , Wright, J M *J Organometal Chem* 1974, **66**, 249

7 Wickham, G , Young, D , Kitching, W *Organometallics* 1988, **7**, 1187

8 Young, D , Kitching, W *Organometallics* 1988, **7**, 1196

9 Reactions with sulfur dioxide in chloroform or methanol were conducted at room temperature in an nmr tube and examined directly by ^{1}H and ^{13}C nmr spectroscopy Whereas the reactions of allylic stannanes were over within seconds, CPC stannanes required approximately thirty minutes exposure to ensure complete reaction Removal of the solvent gave a white solid which could be purified further by trituration with pentane IR spectroscopy confirmed that the products were O-sulphinates[10] ^{1}H and ^{13}C nmr spectra for **2a** are representative ^{1}H nmr (CH_3OD) δ 5 87 (1H, m), 5 12 (2H, m), 2 65 (2H, t, J = 7 7Hz), 2 41 (2H, q, J = 7 7Hz), 0 62 (9H, s, $^{2}J_{Sn-H}$ = 68 9, 65 8Hz) ^{13}C nmr (CH_3OH) δ 137 04 (CH), 117 22 (CH_2), 59 38 (CH_2), 26 93 (CH_2), -0 19 (CH_3, $^{1}J_{Sn-C}$ = 504 9, 482 7Hz)

10 Fong, C W , Kitching, W *J Organomet Chem* 1970, **22**, 107

11 Olszowy, H A PhD Thesis, University of Queensland, 1984

12 **4**, ^{1}H nmr (CH_3OD) δ 1 41 (2H, d, J = 7 5Hz, $^{2}J_{Sn-H}$ = 52 9Hz), 1 05 (1H, m), 0 84 (6H, s, $^{2}J_{Sn-H}$ = 62 2, 59 6Hz), 0 55 (2H, m), 0 18 (2H, m) ^{13}C nmr (CH_3OD) δ 26 94 (CH_2, $^{1}J_{Sn-C}$ = 466 4, 445 3Hz), 9 04 (CH, $^{2}J_{Sn-C}$ = 29 9Hz), 7 98 (CH_2, $^{3}J_{Sn-C}$ = 56 7Hz), 1 05 (CH_3, $^{1}J_{Sn-C}$ = 410 4, 392 4Hz)

13 The reaction of iodine with 3-butenyltributylstannane in chloroform or dichloromethane[13] proceeds with electrophilic addition and cyclopropane formation to give cyclopropylcarbinyl iodide in approximately 80% yield together with small amounts of **3** and 1-iodobutane Given the similarities between this and our own system we believe a predominating free radical mechanism to be unlikely

13 Peterson, D J , Robbins, M D *Tetrahedron Lett* 1972, 2135

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