

Preliminary communication

REGIOCHEMISTRY OF SOME ELECTROPHILIC CLEAVAGES OF PENTA-2,4-DIENYL-SILANES, -GERMANES AND -STANNANES

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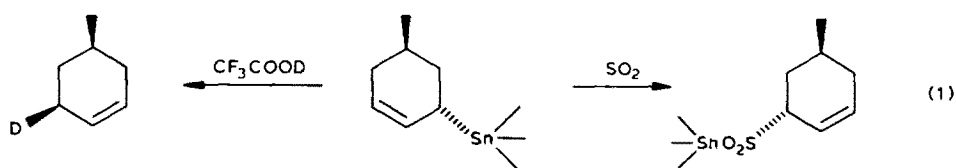
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Summary

(2,4-Pentadienyl)- and (2,4-hexadienyl)-trimethyl-silanes, -germanes and -stannanes experience trifluoroacetolysis regioselectively at the ϵ -position, whereas sulfur dioxide reacts regiospecifically at the γ -position of the stannanes. The kinetic γ -sulfinato efficiently rearranges to the (conjugated) dienylmethylsulfinates.

Recently we reported that trifluoroacetolysis of 5-alkylcyclohex-2-enyl-silanes, -germanes and -stannanes was regiospecific (γ -attack) and stereoselectively *anti* [1]. In contrast sulfur dioxide insertion into these stannanes, although regiospecifically γ , was stereospecifically *syn* [2] e.g. eq. 1. This difference was attributed in part, to a stabilising $O \cdots Sn$ interaction in the transition state for this insertion.



As a prelude to examining the stereochemistry of electrophilic cleavage of 2,4-pentadienylmetallics, it was necessary to establish the regiochemistry of substitution (i.e. α , γ or ϵ , $C^\epsilon=C-C^\gamma=C-C^\alpha-M$) by simple electrophiles. We have examined the reactions of selected systems with CF_3COOD and SO_2 and the results are herein.

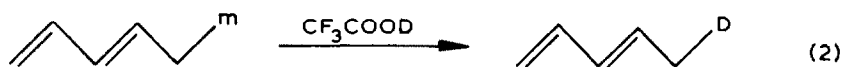
Pentadienyllithium [3] (in THF) was trimethylsilylated ($-70^\circ C$) to provide a mixture of the *trans*- and *cis*-trimethylsilyl-2,4-pentadienes [4], on the basis

of GC-MS behaviour and ^{13}C and ^1H NMR spectra. Germylation and stannylation provided very similar mixtures. Silylation and stannylation of lithium hexadienide proceeds only at the primary carbon, again to give an isomeric mixture. The product distributions are shown in Table 1.

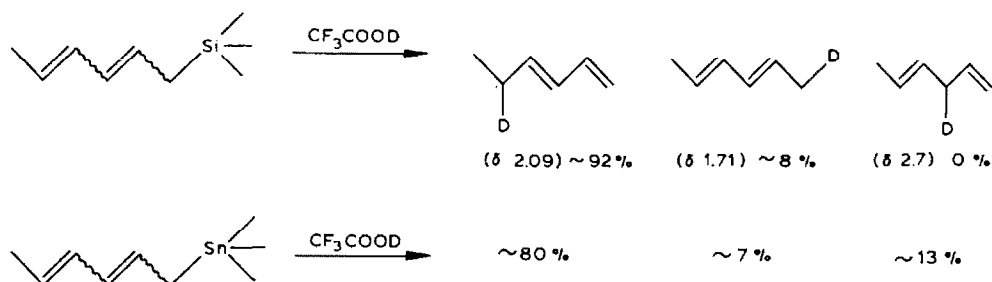
TABLE 1

	Lithium pentadienide		Lithium hexadienide		
$(\text{CH}_3)_3\text{SiCl}$	88.1	11.9	68.9	28.7	24
$(\text{CH}_3)_3\text{GeBr}$	88.2	11.8			
$(\text{CH}_3)_3\text{SnCl}$	83.4	16.6	65.5	16.1	18.4

Trifluoroacetyloxylation. The ^2H NMR spectrum of the total product consisted of one signal at δ 1.74 ppm, while the ^{13}C spectrum exhibited signals appropriate for *trans*-1,3-pentadiene. The product is thus 5-deutero-1,3-pentadiene with no evidence for formation of 1,4-pentadiene, which would result from



γ -attack (eq. 2). Distinction between α and ϵ attack was achieved by examining the 2,4-hexadienyl systems, and the results based on ^{13}C and ^2H spectra are summarised below. Of additional interest to this predominant ϵ -attack by CF_3COOD , was the strong likelihood of significant γ -attack on the stannane ($\sim 13\%$) [5].

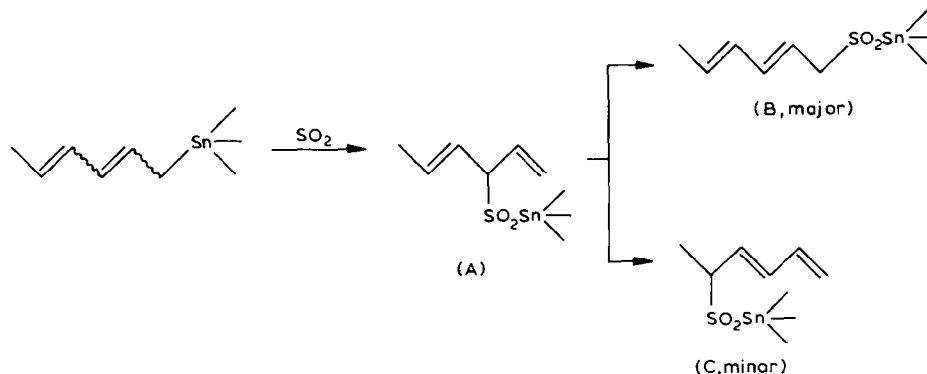


Sulfur dioxide insertions. Reaction of penta-2,4-dienyltrimethylstannane with gaseous SO_2 provided a sulfinate, characterised by a doublet (2H) at δ 3.1 ppm consistent with eq. 3.



The ^{13}C NMR confirmed this overall structure, with the dual $\geq\text{C}-\text{SO}_2-$ signals (64.74 and 60.18 ppm) indicating a *cis,trans* mixture. This result, while not distinguishing between α or ϵ attack of SO_2 , suggested that γ -attack was unimportant, in spite of our suggestion that γ -attack might be favoured by possible $\text{O}\cdots\text{Sn}$ coordinative stabilisation of the leaving group (formally $(\text{CH}_3)_3\text{Sn}^+$), this interaction being less likely for the more remote ϵ -attack.

However, careful examination of the hexa-2,4-dienyltrimethylstannane- SO_2 system (CDCl_3) confirmed (kinetic) γ -attack, with the doubly allylic secondary γ -sulfinato rearranging efficiently to a mixture of the (conjugated) dienylmethylsulfinates, readily characterised by ^{13}C and ^1H NMR spectra [6].



Early NMR observations (after 3 minutes at 0°C) showed A to be characterised by a ^{13}C signal for the doubly allylic $\geq\text{C}-\text{SO}_2-$ at 76.44 ppm and by ^1H signals at δ 3.28 (1H, "t", $>\text{CHSO}_2-$) and 5.15 (1H) and 5.27 ppm (1H) for $=\text{CH}_2$. This kinetic product rearranged completely within 30 minutes at 25°C to B (doublet (2H) at δ 3.03 and $^{13}\text{C}(\geq\text{C}-\text{SO}_2-)$ at 64.95 and 65.71 ppm) and C (δ 2.29) (1H, "quintet", $\text{CH}_3-\text{CH}-\text{CH}=\text{CH}_2$); δ 1.17 ppm (CH_3 , d).

The mechanism of the $\text{A} \rightarrow \text{B} + \text{C}$ change remains to be established.

The stereochemistry of these ϵ -selective trifluoroacetolyses and γ -specific SO_2 -insertions is currently under study.

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References

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- Sakurai has reported that aldehydes, ketones and acetals reacted selectively at the ϵ -position of penta-dienylsilanes, whereas acid chlorides exhibited significant γ -attack. (A. Hosomi, M. Saito, H. Sakurai, *Tetrahedron Lett.*, (1980) 3783.
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