Tetrahedron Letters,Vol.24,No.51,pp 5793-5796,1983 0040-4039/83 $3.00 + .00
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ELECTROPHILIC SUBSTITUTION WITH ALLYLIC REARRANGEMENT (S_E'). SYN-STEREOSPECIFICITY ACCOMPANYING SULFUR DIOXIDE INSERTION INTO 4- AND 6-ALKYLCYCLOHEX-2-ENYLTRIMETHYLSTANNANES

David Young and William Kitching*
Department of Chemistry, University of Queensland, Brisbane 4067, Australia.

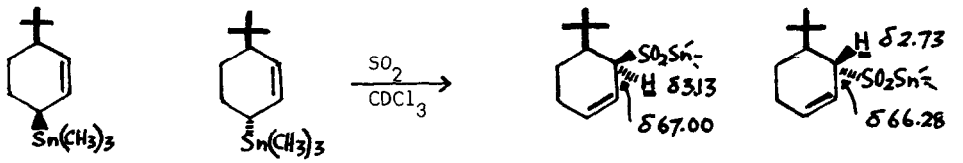
ABSTRACT: Sulfur dioxide insertion (chloroform solvent) into *cis* and *trans*-4 and -6-methyl- and 4-t-butylcyclohex-2-enyltrimethylstannanes is γ-regio and *syn*-stereospecific and hence less sensitive to steric effects by δ-substituents than trifluoroacetolysis (CF_3COOD in $CHCl_3$).

In the previous paper,[1] we demonstrated that acid cleavage ($CF_3COOD/CHCl_3$) of cyclohex-2-enyl derivatives of silicon, germanium and tin, although γ-regiospecific (i.e. with allylic rearrangement), was sensitive in a stereochemical sense, to δ-alkyl groups, to the extent that *trans*-4-t-butylcyclohex-2-enyl derivatives exhibited predominantly γ-*syn* deuterolysis. In view of the demonstrated γ-*syn* mode of sulfur dioxide insertion into 5-methyl- and 5-t-butylcyclohex-2-enyltrimethylstannanes (e.g. (I) below)[2] the possibility existed that the stereo course of SO_2-insertion also could be influenced by steric congestion in the γ-region (i.e. by δ-substituents). Below is the demonstration that SO_2-insertion follows unwaveringly the γ-*syn* stereocourse.

.... (I)

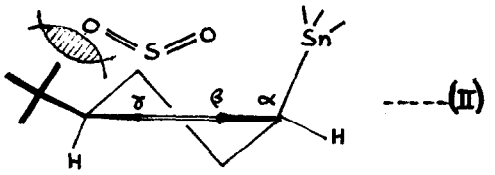
Exposure of a predominantly *cis* mixture of *cis* and *trans*-4-t-butylcyclohex-2-enyltrimethylstannanes ($CDCl_3$) to SO_2 resulted in clean consumption of stannane on the basis of (300 MHz) ^1H nmr monitoring of the disappearance of the resolved $(CH_3)_3Sn$ signals (δ0.061 (*cis*); δ0.053 (*trans*)) of the stannanes, and the production of a new $(CH_3)_3Sn$ signal (δ0.52; $J_{^{119}Sn-^1H}$ ~70 Hz) characteristic of the $(CH_3)_3Sn-O-S-$ moiety.[3] Signals appropriate for $>C(H)-SO_2-$ at δ2.73 (br,d) and δ3.13 (br,t) also developed,[2] and it was clear that the former signal arose from the *trans*-stannane. In addition, it was noted that the *trans*-stannane reacted *ca* 5-8 times as fast as the *cis*-isomer. At completion, the 72:28 *cis:trans* stannane mixture had provided the sulfinates in a 73:27 ratio on the basis of the $(CH_3)_3C$ signals (δ0.97 (major) and δ0.86) and $>C(H)-SO_2-$ region of the spectrum. The ^{13}C spectrum provided confirmation of these conclusions, with the $>C(H)-SO_2-$ signals at 67.00 (major) and 66.23 ppm. All aspects of the ^{13}C spectra were

in accord with the *cis* and *trans*-6-t-butylcyclohex-2-enylsulfinate structures. A predominantly *trans*-stannane mixture (67:33) afforded a 65:35 sulfinate mixture. The results are shown below.



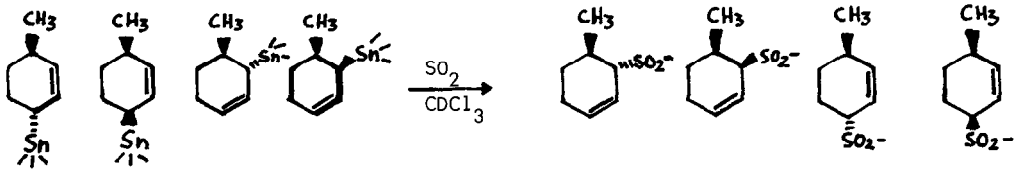
72	28	73	27
33	67	35	65

The γ-*syn* stereo course is thus followed and the modest rate difference in favour of the *trans*-stannane is explicable on the basis that γ-*syn* approach of SO_2 is slightly impeded in the *cis*(η), although such impedance is insufficient to promote detectable γ-*anti* substitution, as occurred in trifluoroacetolysis.[1]



(II)

As detailed elsewhere,[4] *cis* and *trans*-4-methylcyclohex-2-enyltrimethylstannanes were obtained as mixtures with the *cis* and *trans*-6-methyl isomers, and determining the stereochemistry of SO_2-insertion into this four component system appeared daunting. Fortunately, key regions of the ^1H and ^{13}C nmr spectra were well resolved and permitted unequivocal conclusions. Reaction of stannane mixture A, below, with $SO_2/CDCl_3$ produced a four component sulfinate mixture, and detailed scrutiny of the ^1H and ^{13}C nmr spectra led to the scheme summarised below, demonstrating stereo and regio-specific γ-*syn* insertion into each of the four stannane isomers.

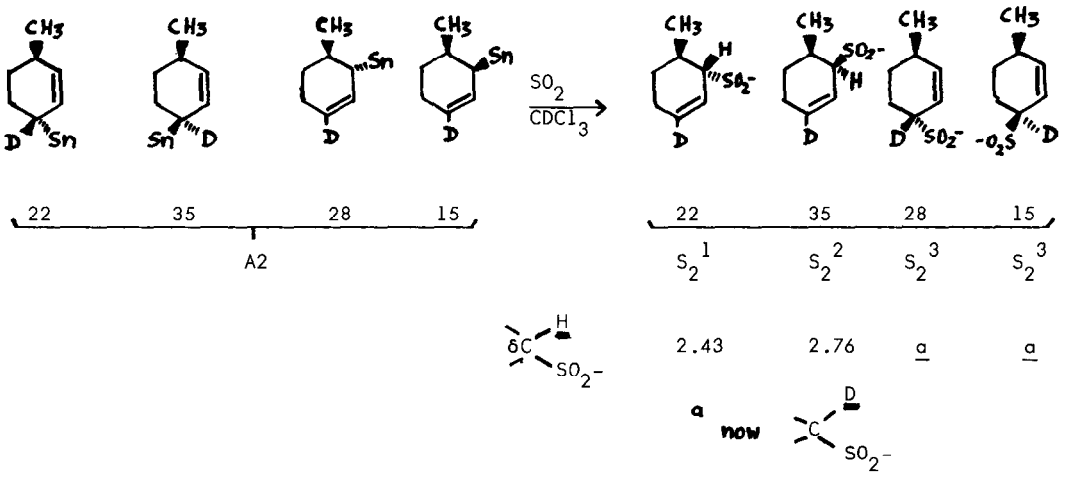


42	17	31	10
A1			

	S_1^1	S_1^2	S_1^3	S_1^4	Basis
	40	16	34	10	$\geq CH\text{-}SO_2$-
	38	15	34	13	$^{13}\geq CHSO_2$-
	40	13	36	11	$CH_3\text{-}CH\leq$
^1H nmr δ$\geq$CH-SO_2-	2.45 ($W_{\frac{1}{2}}$ ~10 Hz)	2.76(11)	2.70(16)	2.63(10)	
δCH_3-CH$\leq$	1.00	1.02	0.94	0.96	
^{13}C nmr δ$\geq$CHSO$_2$	71.33	70.48	65.50	65.24	
δCH_3-CH	19.36	16.22	21.09	21.09	

The identities of sulfinates S_1^1 and S_1^2 above were established by their significantly lower field ^{13}C(H)(SO_2^-) shifts (a result of the downfield β-effect[5] of the methyl at C_6) compared with S_1^3 and S_1^4. Distinction between S_1^1 and S_1^2 was based on the $^{13}\underline{C}H_3$-$\underline{C}$H shifts with the *cis* (S_1^2) isomer experiencing a substantial γ-shielding effect of the $SO_2Sn(CH_3)_3$ moiety.[2] Distinction between S_1^3 and S_1^4 was made easily on the shapes and $W_{\frac{1}{2}}$ of the C(H)(SO_2^-) signals, with the quasi-axial proton in S_1^3 being substantially broader ($W_{\frac{1}{2}}$ ~16 Hz).[6] (The ^{13}C nmr spectra of all four sulfinates were completely assigned by INEPT sequences, effects of ^2H-labels, spectra of different mixtures etc.).

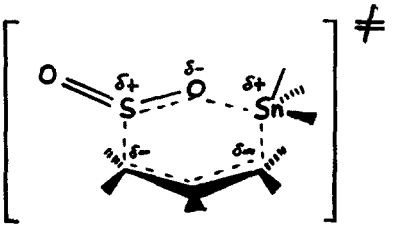
The above approaches to sulfinate identification were supplemented in the following way. 4-Methylcyclohex-2-enol-1-d was chlorinated and trimethylstannylated to yield stannane mixture A_2 below.[4] In the resulting sulfinate mixture S_2, <u>two</u> signals in the C(H)(SO_2^-) region (δ2.76 and δ2.43) in a ratio of 1.55:1) were observed, and on the basis of γ-insertion must correspond to the *cis* and *trans*-6-methylcyclohex-2-enylsulfinates, as shown below.



The distribution of sulfinates in mixture S_2 was based on ^1H and ^{13}C intensities as described above, and taken together, the sets of results establish the γ-regio and *syn*-stereospecific nature of SO_2-insertion. A stannane mixture A_3, very similar in distribution to A_2, but lacking ^2H-labelling, was examined after partial and complete reaction, and indicated very minor rate differences between the four stannanes, with the two *trans* isomers reacting slightly faster (1.8 rel. rate) than the *cis*-4-methyl stannane (1.4), with the *cis*-6-methylstannane the slowest (1.0).

The strict adherence to the γ-*syn* stereocourse, the insensitivity of steric source to a δ-t-butyl group, and the very narrow rate spread, provides contrasts with the γ-acidolysis reactions.[1] Taken together, the data suggest that C-S bond formation lags behind C-H bond formation (in acidolysis), reflecting the difference in bond strengths and ability of sulfur to form bonds at longer distances. In addition, for chloroform solvent, oxygen co-ordination

may serve to stabilise developing positive charge on the leaving $(CH_3)_3Sn$ group, and this can operate efficiently for a *syn*-state.



SO_2-insertion for methanol solvent is γ-regio but not stereo-specific, and the data suggests competing *syn* and *anti*-SO_2 approach, with methanol stabilisation of the leaving group ($SnMe_3$) reducing the necessity for "internal" co-ordination postulated for $CHCl_3$ solvent.[7] Details of this work will be reported at a later date.

ACKNOWLEDGEMENT: The authors are grateful to the Australian Research Grants Scheme for partial funding of this research.

REFERENCES AND FOOTNOTES:

1. D. Young, W. Kitching and G. Wickham, Tetrahedron Lett., 5789, (1983).
2. D. Young and W. Kitching, J. Org. Chem., 48, 614 (1983).
3. For a review, see W. Kitching and C.W. Fong, Organometal. Chem. Rev. Sec. A., 5, 281 (1970).
4. D. Young and W. Kitching, Manuscript in preparation.
5. This β-effect of the methyl group also moves C_3 in $S_1{}^3$ and $S_1{}^4$ to much lower field than C_3 in $S_1{}^1$ and $S_1{}^2$.
6. See G. Wickham, D. Young and W. Kitching, J. Org. Chem., 47, 4884 (1982).
7. An analogous situation applies in electrophilic brominolysis of certain alkylstannanes for which inversion of configuration at carbon is observed when the remote positive and negative charges are stabilised by solvent methanol. With non-polar carbon tetrachloride as solvent, the energy of the inversion transition state for electrophilic substitution would be greatly increased, and now retention is observed with the anionic leaving group (Br^-) interacting with the leaving R_3Sn group. See J.M. Fukoto and F.R. Jensen, Acc. Chem. Res., 16, 177 (1983).

(Received in UK 20 September 1983)