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ELECTROPHILIC SUBSTITUTION WITH ALLYLIC REARRANGEMENT (S_E'). *SYN* OR *ANTI* STEREOSELECTIVITY IN TRIFLUOROACETOLYSIS OF 4-ALKYLCYCLOHEX-2-ENYLSILANES, -GERMANES AND -STANNANES

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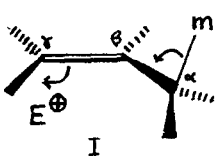
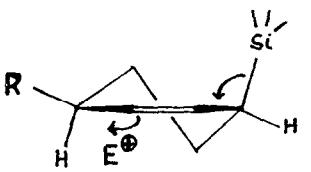
ABSTRACT: *Cis*-4-alkylcyclohex-2-enyl derivatives of silicon, germanium and tin, with quasi-axial metallo groups, experience stereospecific γ-*anti* trifluoroacetolysis (to yield 4-alkylcyclohexene), whereas the corresponding *trans*-isomers show less specificity.

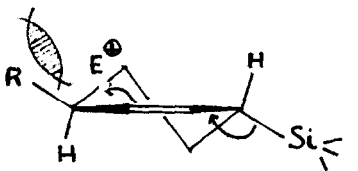
The preferred stereochemistry of the regiospecific γ-electrophilic substitution (S_E') of allylic derivatives of silicon, germanium and tin is a subject of considerable interest. With respect to (protonic) acid cleavage, results for an optically active acyclic silane,[1] and the diastereomeric 5-methylcyclohex-2-enylsilanes, germanes and stannanes,[2] indicated a clear preference for *anti* alignment of electrophile and leaving metallo group (I).[3]



I



IIa

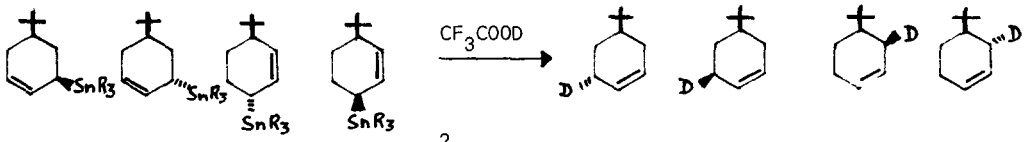


IIb

However, trifluoroacetolysis data for *cis* and *trans*-4-trimethylsilyl- and 4-t-butylcyclohex-2-enyltrimethylsilanes required an analysis based on stereospecific γ-*anti* substitution of the *cis* isomers (IIa) but non-specific γ-cleavage of the *trans* isomers, in which steric hindrance to electrophile approach was suggested to operate (IIb).[4] We have conducted more extensive studies of the stereochemistry of acid cleavage ($CF_3COOD/CDCl_3$) of various 4- and 5-alkylcyclohex-2-enyl metal derivatives which confirm that the steric demands of δ-substituents are significant determinants of stereochemistry.

Confirmation of the preferred *anti*-S_E' course when steric factors and conformational mobility are both minimised, was achieved by studies of the CF_3COOD cleavage of various 5-t-butylcyclohex-2-enylstannanes.[5] Some of these 5-stannanes were contaminated with low levels of the 4-t-butyl isomers which did not interfere, but which in fact, provided a strong indication of the variable stereo outcomes in the latter systems. Determination of ^2H-location in the product cyclohexenes was possible by direct ^2H nmr analysis,[6] or by examination of the ^2H nmr spectra of the derived dibromides, the ^1H spectra of which have been fully assigned.[2]

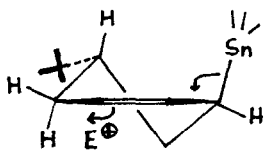
The results are shown below.



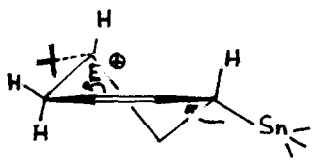
					^{2}H nmr:	δ2.00	δ2.08	δ1.78	δ2.06
R = CH_3	53	35	8	4		53	36	1	10
	21	67	4	8		34[a]	66	>1	a
	25	66	~3	6		~35[a]	66		
R = Ph[b]	44	56	-	-		47	53	-	-
	85	15	-	-		70	30	-	-

[a]Possible overlapping of ^{2}H signals of 4-t-butylcyclohexene. [b]Significant phenyl cleavage (yielding C_6H_5D) occurs, and could influence the observed ratio of ^{2}H signals.[7]

These results demonstrate a highly preferred *anti*-mode of cleavage in both the *cis* and *trans*-5-t-butylcyclohex-2-enylstannanes, for which, in the latter, *anti*-approach is opposite to "normal" axial electrophilic attack in cyclohexenes,[8] but in which "σ-π activation" is greater than in the *cis*-isomer, on the basis of a cosine dependence.

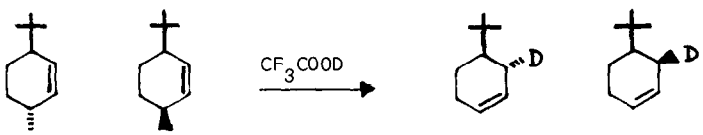


trans



cis

With respect to cleavage of the (minor) *cis* and *trans*-4-t-butylcyclohexenyl stannanes (above), the results very strongly indicate predominantly γ-*syn* cleavage of the *trans* but γ-*anti* cleavage of the *cis* isomer. This conclusion can be discussed in more detail on the basis of the data below for trifluoroacetolysis of mixtures of the 4-t-butylcyclohex-2-enyl derivatives alone.[5]

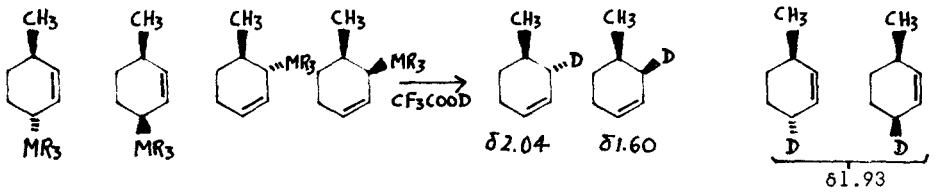


					$\frac{k\,syn}{k\,anti}$ (in *trans*)
$-MR_3=Sn(CH_3)_3$	67	33	83	17	3
	28	72	93	7	3
$SnPh_3$	89	11	86	14	5
	19	81	92	8	~2[a]
$Ge(CH_3)_3$	93	7	56	44	1.1
	17	83	90	10	1.0[a]
$Si(CH_3)_3$	46	54	78	22	1.1

[a]Approximate as based on low starting concentration of *trans*.

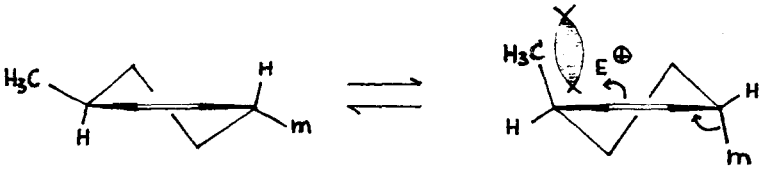
These results require analysis on the basis of stereospecific γ-*anti* cleavage of the *cis* isomer (irrespective of leaving group) but with varying proportions of *syn*/*anti* cleavage of the *trans* isomers as a function of leaving group. The former aspect, on the basis of (II), is understandable in terms of an essentially unimpeded γ-approach of electrophile to a π-bond face strongly activated by the quasi-axial metallo groups. In view of the results of the 5-t-butyl-cyclohex-2-enyl systems, the predominating *syn*-mode of cleavage of the *trans*-4-t-butyl systems must be primarily a reflection of steric impedance to γ-approach by the electrophile.

If this reasoning is correct, the *trans*-4-methylcyclohex-2-enyl derivatives should exhibit much smaller k_{syn}/k_{anti} ratios, and the results below conform to this view.



								$\frac{k_{syn}}{k_{anti}}$	
MR_3=$Sn(CH_3)_3$	22	40	24	14	⟶	42	20	.1	38
	42	17	31	9.6	⟶	32	28	.5	40
$SnPh_3$	89	4	5	2	⟶	44	48	.8	8
	22	39	18	21	⟶	42	22	∿.1	36
$Ge(CH_3)_3$	87	13	-	-	⟶	23	77	∿.13	-

The 4-methylstannanes were formed as mixtures with the 6-methyl isomers[5] and CF_3COOD cleavage of these mixtures is γ-regio specific. However significant "stereo-leakage" occurs in trifluoroacetolysis of the *trans*-4-methylcyclohex-2-derivatives, but in all cases, a predominant *anti*-cleavage is nevertheless observed, in contrast to the results above for the corresponding *trans*-4-t-butyl compounds. These results indicate that any σ-π effect operating in the quasi-equatorial conformation synergic with a (presumed) preference for axial approach in cyclohexenes,[8] largely overcomes the steric inhibition to approach exercised by the 4-methyl group. Although the σ-π effect in the *trans*-4-methyl series will be more pronounced in a conformation with both the methyl and metal groups quasi-axial, and presumably promote *anti* cleavage on stereoelectronic grounds, electrophile approach is more severely hindered in this conformation.



It follows from this work that cycloalk-2-enylation of carbonyl compound-Lewis acid complexes (e.g. $RCHO.BF_3$) would also be particularly sensitive to steric factors. Of considerable interest then, is the observation that sulfur dioxide insertion into 4- and 6-alkylcyclohex-2-enyl stannanes (in $CHCl_3$) is γ-*syn*-specific. This is discussed in the following paper.

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

REFERENCES AND NOTES:

1. T. Hayashi, H. Ito and M. Kumada, Tetrahedron Lett., 4605 (1982).
2. G. Wickham and W. Kitching, J. Org. Chem., 48, 614 (1983).
3. Other investigations have also been reported. See footnote 9 in ref. 2 above.
4. G. Wickham and W. Kitching, Organometallics, 2, 541 (1983).
5. All new compounds employed in these studies have been fully characterised by spectra and analyses etc. Details of their formation and characterisation will be reported separately. D. Young and W. Kitching, Manuscript in preparation.
6. ^2H nmr spectra was obtained as described previously,[4] normally at both 15.24 and 46.05 MHz.
7. For example, initial phenyl cleavage, would provide the cyclohex-2-enyl(diphenyl)tin acetate, which may exhibit a different stereochemistry of cleavage, although such cleavage under our conditions would be much slower than that of starting stannane.
8. See, for example, O. Eisenstein, J. Klein and L.M. Lefour, Tetrahedron, 35, 225 (1979).
9. Primarily because of the known stabilising influence of a β-silyl group, the involvement of "cationic" intermediates in protodesilylations is frequently inferred. In cases where the cation is especially stabilised e.g. by two β-silyl groups, rate-determining intermediate formation followed by silyl groups loss has been postulated. See I. Fleming and J.A. Langley, J. Chem. Soc., Perkin I, 1421 (1981); G. Wickham and W. Kitching, Organometallics, 2, 541 (1983). Irrespective of whether these substitutions are "concerted" or involve the rate limiting (irreversible) γ-addition of the electrophile to form an intermediate, the stereochemistry of the entering group relative to other functionality is established at this stage.

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