for 0.5 h at 10 °C and filtered under N_2. The product, which is hygroscopic, was washed with ether (2 × 250 mL) and dried in a vacuum oven for 5 h at 40 °C. The yield of **2** was 101 g (97%); mp 149–150 °C. Anal. Calcd for $C_5H_{10}BrN_7O_6$: C, 17.44; H, 2.91; Br, 23.24; N, 28.49. Found: C, 17.31; H, 3.08; Br, 23.13; N, 28.43.

1-(Azidomethyl)-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane (3). A solution of sodium azide (354 g, 5.45 mol) in water (1200 mL) was cooled to 5 °C, and with good stirring a solution of acetyl chloride (286 g, 3.64 mol) in methylene chloride (640 mL) was added in 2.5 h, maintaining the temperature at 5 °C with external cooling. The upper aqueous layer was siphoned off, and **2** (101 g, 0.294 mol) was added. The mixture was stirred for 3 h at 10–15 °C and filtered. The white solid was washed with methylene chloride (2 × 200 mL), water (200 mL), and ether (2 × 200 mL) and dried in a vacuum oven overnight at 40 °C. The yield of **3** was 71 g (79%): mp 130–131 °C; IR (KBr) 2080 (N_3), 1540 cm^{-1} ($N-NO_2$). HPLC analysis showed a single peak. Anal. Calcd for $C_5H_{10}N_{10}O_6$: C, 19.61; H, 3.27; N, 45.75. Found: C, 19.99; H, 3.28, N, 44.99.

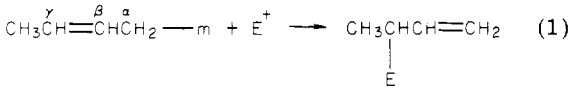
Registry No. **1**, 5754-75-6; **2**, 84454-93-3; **3**, 84454-92-2; CH_3CON_3, 24156-53-4; CH_3COBr, 506-96-7.

Communications

Electrophilic Substitution with Allylic Rearrangement (S_E'). Anti Stereoselectivity in Trifluoroacetolysis of Some Cyclohex-2-enylsilanes, -germanes, and -stannanes

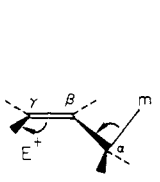
Summary: Trifluoroacetolysis of various cyclohex-2-enylsilanes, -germanes, and -stannanes is demonstrated to be γ regiospecific and highly anti stereoselective, as predicted for a dominating LUMO–HOMO interaction in a concerted S_E2' process.

Sir: Regiospecific γ cleavage by electrophiles is the most characteristic reaction of main-group σ-allyl metallics and renders allylsilanes, -stannanes, etc. very useful allylation reagents (eq 1).[1,2] These demetalations display the

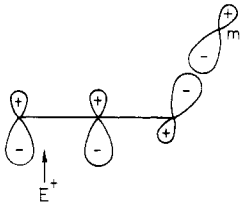


(1)

characteristics of S_E2' (or S_Ei') processes,[3] the stereoelectronic aspects of which have been considered theoretically.[4] Anti alignment of the approaching electrophile and the leaving group is the (qualitative) theoretical prediction for a fully concerted S_E2' process,[4] a result understandable in FMO terms (below) for the LUMO(E^+)–HOMO interaction.[5,6]



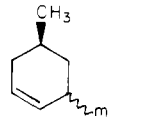
"anti"



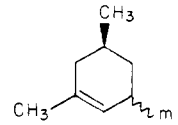
"distorted" HOMO[5,6] of σ-allyl metallic

Although the degree of concertedness in these substitutions may be unresolved,[7] the question of any intrinsic stereochemical preference is a valid matter for enquiry and is of synthetic importance, particularly for carbon electrophiles.[8] Regrettably the information available has been derived from structurally diverse, atypical systems, involving some unusual electrophiles.[9] Despite the criticism that it has an inbuilt conformational bias,[10] the cyclohex-2-enyl system is widely abundant and has provided considerable mechanistic information.[11] In this paper we report that trifluoroacetolysis of various cyclohex-2-enyl metallics displays a pronounced anti stereoselectivity.

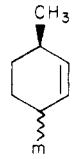
The cyclohex-2-enyl metallics I–III resulted from stan-



I, m = $Si(CH_3)_3$, $Ge(CH_3)_3$, $Sn(CH_3)_3$



II, m = $Ge(CH_3)_3$, $Sn(CH_3)_3$



III, m = $Ge(CH_3)_3$

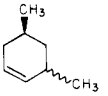
nylation, germylation, and silylation of the appropriate cyclohex-2-enyl chlorides and have been fully characterized.[12] Isomeric mixtures were obtained, but by manipulation of the precursor, "lopsided" cis/trans mixtures could be obtained.

Trifluoroacetolysis (CF_3COOD in $CHCl_3$, CH_2Cl_2, or dioxane) proceeded with complete allylic rearrangement in each system.[13] In (symmetrical) I, stereochemical conclusions were based on ^2H and ^{13}C NMR examination

(1) See, for example: Fleming, I. *Chem. Soc. Rev.* **1981**, *10*, 83.
(2) Negishi, E. I. "Organometallics in Organic Synthesis"; Wiley: New York, 1980; Vol. 1. Pereyre, M.; Pommier, J. C. *J. Organomet. Chem. Libr.* **1976**, *1*, 161.
(3) For a review see: Mangravite, J. A. *Organomet. Chem. Rev.* **1979**, *7*, 45.
(4) Anh. N. T. *Chem. Commun.* **1968**, 1089. Fukui, K.; Fujimoto, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2018; **1966**, *39*, 2116. Miller, S. I. *Adv. Phys. Org. Chem.* **1968**, *6*, 185. Gilchrist, T. L.; Storr, R. C. "Organic Reactions and Orbital Symmetry"; Cambridge University Press: London, 1972.
(5) Liotta, C. *Tetrahedron Lett.* **1975**, 523.
(6) Burgess, E. M.; Liotta, C. L. *J. Am. Chem. Soc.* **1981**, *46*, 1703.
(7) For kinetic information on protodemetalations of allylic systems see: Verdone, J. A.; Mangravite, J. A.; Scarpa, N. M.; Kuivila, H. G. *J. Am. Chem. Soc.* **1975**, *97*, 843. Mangravite, J. A.; Verdone, J. A.; Kuivila, H. G. *J. Organomet. Chem.* **1976**, *104*, 303. Although a fully concerted mechanism would exhibit stereospecificity, second-order kinetics does not distinguish between such a mechanism and others involving the slow or reversible formation of an intermediate. See also: Fleming, I.; Langley, J. A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 1421. Fleming, I.; Marchi, D.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2518.
(8) The stereochemical aspects of these substitutions will be reported later.
(9) For example see: Au-Yeung, B. W.; Fleming, I. *J. Chem. Soc., Chem. Commun.* **1977**, 79. Carter, M. J.; Fleming, I. *Ibid.* **1978**, 679. Overton, K. H. *Chem. Soc. Rev.* **1979**, *8* (4), 447. de la Mare, P. B. D.; Wilson, R. D. *J. Chem. Soc., Perkin Trans 2* **1977**, 157. Wetter, H.; Scherer, P.; Schneizer, W. *Helv. Chim. Acta* **1979**, *62*, 1985. Kashin, A. N.; Bakunin, V. N.; Khutoryanskii, V. A.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1979**, *171*, 309.
(10) For a review see: Magid, R. M. *Tetrahedron* **1980**, *36*, 1910.
(11) For example see: Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1981**, *46*, 2149 and previous papers by the former author.
(12) Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884.
(13) Protonolysis of deuterated analogues of 1 [m = $Ge(CH_3)_3$, $Sn(CH_3)_3$] established complete allylic rearrangements.

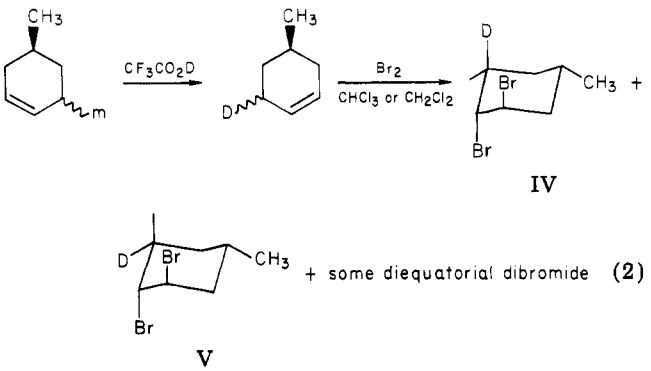
0022-3263/83/1948-0612$01.50/0

Table I. Stereoselectivity Accompanying Trifluoroacetolysis of Cyclohex-2-enyl Metallics

system	% cis	% trans	solvent	product[b]	% cis[a]	% trans[a]
I, M = $Si(CH_3)_3$	88	12	CH_2Cl_2	 A	16	84
I, M = $Ge(CH_3)_3$	36	64	$CHCl_3$	A	62	38
	36	64	dioxane	A	58	42
	40	60	$CHCl_3$	A	57	43
	49	51	$CHCl_3$	A	51	49
	65	35	$CHCl_3$	A	37	63
	90	10	$CHCl_3$	A	16	84
	90	10	dioxane	A	19	81
I, M = $Sn(CH_3)_3$	31	69	$CHCl_3$	A	65	35
	59	41	$CHCl_3$	A	46	54
	67	33	$CHCl_3$	A	40	60
II, M = $Ge(CH_3)_3$	75	25	$CHCl_3$	 B	76	24
	72	28	$CHCl_3$	B	73	27
II, M = $Sn(CH_3)_3$	72	28	$CHCl_3$	B	69	31
III, M = $Ge(CH_3)_3$	13	87	$CHCl_3$		77	23

[a] Corrected for 86% diaxial dibromide and 14% diequatorial dibromide. This correction was based on the demonstration that the signal for H_{5e} in *cis*-3,*trans*-4-dibromo-1-methylcyclohexane (diequatorial dibromide) is coincident with the signal for H_{5a} in *trans*-3,*cis*-4-dibromo-1-methylcyclohexane (diaxial dibromide). Similarly, H_{5a} in the former is coincident with H_{5e} in the latter. [b] The favored stereochemistry for all examples is anti.

of the dibromide of the product 4-methylcyclohexene, such bromine addition being reported[14] and confirmed by us to be ca. 86% *trans*-diaxial. The sequence is outlined in eq 2.



IV

+ some diequatorial dibromide (2)

V

The ^2H shifts assigned to IV and V (2.45 and 1.91 ppm, respectively, relative to internal $CDCl_3$ at 7.24 ppm) were confirmed by a sequence involving deuterolysis (CH_3COOD/D_2O) of the silyl enol ether of 4-methylcyclohexanone, resulting in preferential axial ^2H incorporation (73%). Reduction, tosylation, elimination, and bromination of the resulting 6-^2H-labeled 4-methylcyclohexene provided predominantly IV. This agrees with our complete assignment of the 300-MHz ^1H spectrum of the (diaxial) dibromide of 4-methylcyclohexene. Full details will be reported elsewhere.[15] For series II, dehydration of 3,5-dimethylcyclohexanol afforded principally *cis*-3,5-dimethylcyclohexene (^{13}C NMR and hydrogenation to *cis*-3,5-dimethylcyclohexane) which had ^{13}C shifts distinguishable from those of the trans isomer. In series III, the ^2H signals for *cis*- and *trans*-4-methyl-3-deuterio-cyclohex-1-ene were well resolved (1.60 and 2.04 ppm, respectively), and their identities were established from the 300-MHz ^1H NMR of the corresponding dibromides. The stereoselectivities[16] accompanying trifluoroacetolysis of I–III are shown in Table I.

The data in Table I demonstrate a pronounced anti stereoselectivity for trifluoroacetolysis, and several results strongly suggest stereospecificity. In the solvents employed, it may have been anticipated that molecular acid could coordinate to the departing MMe_3 group, thus favoring the syn mode, but the apparent stereoelectronic advantage for anti cleavage must dominate. It is not clear how easily the present results may be extrapolated to other systems and for different electrophiles, but in view of the experiences with S_N2' reactions,[10] syn and anti transition states for S_E2' are likely to be comparable in energy in some circumstances.[17] This is demonstrated in the following paper in which the stereospecific syn insertion of SO_2 into cyclohex-2-enyl stannanes is described.

Registry No. *cis*-I (M = $Si(CH_3)_3$), 84454-68-2; *trans*-I (M = $Si(CH_3)_3$), 84454-69-3; *cis*-I (M = $Ge(CH_3)_3$), 83269-41-4; *trans*-I

(14) Barili, P. L.; Bellucci, G.; Berti, G.; Marioni, F.; Marsili, A.; Morelli, I. *J. Chem. Soc., Chem. Commun.* **1970**, 1437.
(15) Wickham, G. Ph.D. Thesis, University of Queensland, 1983.

(16) Conversion of the deuterated methylcyclohexenes to methylcyclohexanes by hydrogenation (noble metals or diimide) was found to be unsuitable.[15]
(17) It should be noted that the results for the *trans*-5-alkylcyclohex-2-enyl systems, in which carbon–metal σ–π interaction is maximized (for a quasi-axial metal group), are more relevant to considerations based on the form of the HOMO (of the allyl–metal fragment) which was derived for full σ–π interaction. Additionally, note that for *cis*-5-alkylcyclohex-2-enyl systems in which σ–π interaction (from a quasi-equatorial metal group) will be reduced, anti approach nevertheless corresponds to normal axial electrophilic addition for an "unperturbed" cyclohexene. These aspects will be considered in detail later. Studies of trifluoroacetolysis of 4-alkylcyclohex-2-enyl systems indicate that steric congestion in the γ region is another influence regulating the stereo- but not the regiochemistry (exclusive γ attack). For example, *cis*-4-alkylcyclohex-2-enylstannanes, with a quasi-axial tin group, exhibit stereospecific anti trifluoroacetolysis, whereas cleavage of the *trans*-4-alkyl compounds is nonspecific, the selectivity depending on the alkyl group (Young, D., unpublished results). These considerations apply to the significant "stereoleakage" apparent in the last entry in Table I.

(M = $Ge(CH_3)_3$), 83269-42-5; *cis*-I (M = $Sn(CH_3)_3$), 74089-88-6; *trans*-I (M = $Sn(CH_3)_3$), 74089-89-7; *cis*-II (M = $Ge(CH_3)_3$), 83269-44-7; *trans*-II (M = $Ge(CH_3)_3$), 83269-45-8; *cis*-II (M = $Sn(CH_3)_3$), 83269-39-0; *trans*-II (M = $Sn(CH_3)_3$), 83269-40-3; *cis*-III (M = $Ge(CH_3)_3$), 84454-70-6; *trans*-III (M = $Ge(CH_3)_3$), 84454-71-7.

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Electrophilic Substitution with Allylic Rearrangement (S_E'). Syn Stereoselectivity in Sulfur Dioxide Insertion into Some Cyclohex-2-enylstannanes

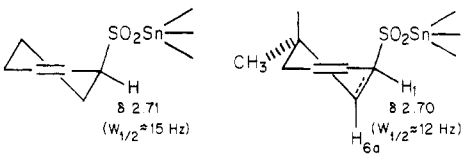
Summary: Sulfur dioxide insertion into *cis*- and *trans*-(5-alkylcyclohex-2-enyl)trimethylstannanes is demonstrated to be γ regio- and syn stereospecific, in contrast to the γ regiospecific but anti stereoselective trifluoroacetolyses of these stannanes.

Sir: In the previous paper[1] we demonstrated a pronounced anti stereoselectivity in trifluoroacetolysis of cyclohex-2-enyl metallics and speculated that syn selectivity may be observed when participation by a nucleophilic appendage of the (electrophilic) reagent was possible. Sulfur dioxide insertion into carbon–tin bonds has been well studied and leads to *O*-sulfinato derivatives[2,3] with complete rearrangement of the allylic moiety[4] (eq 1). Second-order

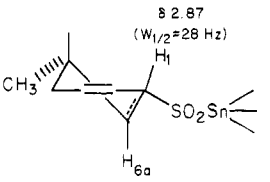
$$(CH_3)_3SnCH_2CH{=}CHCH_3 + SO_2 \rightarrow CH_2{=}CHCH(CH_3)SOSn(CH_3)_3 \quad (1)$$

kinetics[5] (for methanol solvent) have been demonstrated for some systems, and substituent effects[5] and other features[2] support an electrophilic mechanism possibly involving significant O···Sn interaction in the transition state. We report that SO_2 insertion into some (cyclohex-2-enyl)trimethylstannanes proceeds with syn stereoselectivity (if not stereospecificity).

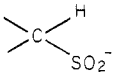
The various stannanes (in $CDCl_3$) reacted rapidly and quantitatively with gaseous SO_2 to provide viscous oils or solids which were fully characterized as *O*-sulfinato monoinsertion products by analyses, IR spectra, and ^1H, ^{13}C, and ^{119}Sn NMR spectra. Full details will be presented elsewhere. In the present context, the most notable feature of the 300-MHz ^1H NMR spectrum of the parent cyclohex-2-enylsulfinate (I) was the appearance of the proton shown in A at δ 2.71 ($W_{1/2} \approx 15$ Hz), indicative of a predominantly pseudoequatorial proton.[6]



I II

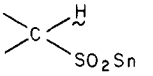


III



A

Reaction of 71:29 *trans*-/*cis*-(5-methylcyclohex-2-enyl)trimethylstannane[1,6] provided an insertion product, the ^{13}C spectrum of which consisted of two sets of signals in the ratio of ca. 75:25 (comparison of analogous signal intensities). The 300-MHz ^1H spectrum showed (in part) two doublets for CCH_3 (δ 0.94, $J \approx 6.4$ Hz; δ 1.01, $J \approx 5$ Hz), with the higher field signal being more intense (ca. 70:30). The major sulfinate showed a type-B proton signal



B

at δ 2.70 ($W_{1/2} \approx 12$ Hz; 70%), with the minor sulfinate signal at δ 2.87 ($W_{1/2} \approx 28$ Hz). The major sulfinate, with the narrower type-B proton signal, must be trans (see II) as this largely quasi-equatorial proton can experience no large *vic*-^1H coupling. However, in the cis isomer (**III**) H_1 will experience a large vicinal coupling to H_{6a}. This conclusion is supported by the C_5 chemical shift (25.28 ppm) in the major isomer (II) where γ-compressional shielding (by $SO_2Sn(CH_3)_3$) can operate in the trans case but not in the cis (C_5 shift of 27.98 ppm). Repetition with a 70:30 trans/cis stannane mixture provided a 66:34 trans/cis sulfinate mixture. Predominantly *cis*-(5-methylcyclohex-2-enyl)trimethylstannane (cis/trans ratio of 71:29) provided sulfinates which on the basis of arguments presented above had a cis/trans ratio of 67:33. Repetition with 59:41 cis/trans stannanes provided 60:40 cis/trans sulfinates. These results (Table I) require syn insertion in each stannane isomer.

Confirmation of allylic rearrangement in these cyclohex-2-enylstannane systems was demonstrated first by using appropriately ^2H-labeled stannanes and direct ^2H NMR analysis.[1,6] Thus a 70:30 cis/trans mixture of (5-methylcyclohex-2-enyl)trimethylstannane with the ^2H label ca. 58% at C_3 (vinylic) and 42% at C_1 (allylic) produced a 69:31 cis/trans sulfinate mixture with an ^2H distribution of ca. 66% allylic (δ 2.73)/33% vinylic (δ 5.76). Second, (3,5-dimethylcyclohex-2-enyl)trimethylstannane was synthesized and on reaction with SO_2 provided the tertiary allylic sulfinate regiospecifically, and ^{13}C NMR analysis is consistent with stereospecific syn insertion.[7] (Table I).

(1) Wickham, G.; Kitching, W. *J. Org. Chem.*, previous paper in this issue.
(2) For a review, see: Kitching, W.; Fong, C. W. *Organomet. Chem. Rev., Sect. A* **1970**, *5*, 281.
(3) Sulfur dioxide insertion into transition metal–carbon bonds has also been reviewed: Wojcicki, A. *Adv. Oganomet. Chem.* **1974**, *12*, 32.
(4) Fong, C. W.; Kitching, W. *J. Organomet. Chem.* **1970**, *22*, 107.
(5) Fong, C. W.; Kitching, W. *J. Am. Chem. Soc.* **1971**, *93*, 3791. Fong, C. W.; Kitching, W. *J. Organomet. Chem.* **1973**, *59*, 213.
(6) For analogous examples see our discussion of the ^1H NMR spectra of cyclohex-2-enyl metallics in; Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.* **1982**, *47*, 4884. Wickham, G. Ph.D. Thesis, University of Queensland, 1983.
(7) Determination of the cis or trans nature of tertiary allylic sulfinates is not straightforward by ^1H NMR (no type-A proton), but careful comparisons of the ^{13}C NMR spectra of our collection of cyclohex-2-enyl sulfinates very strongly support the indicated stereochemistry. However, there is *no* doubt that complete allylic rearrangement occurs to yield the thermodynamically less stable tertiary allylic sulfinate.

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