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Preliminary communication

An estimate of the steric bulk of the trimethyltin group

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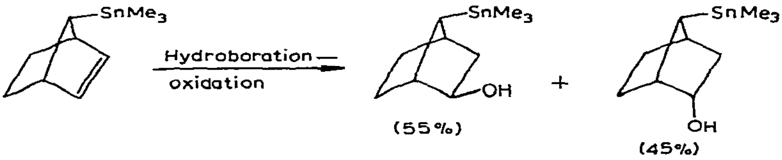
SUMMARY

Epoxidation and hydroboration reactions of *syn*-7 substituted norbornenes have been used as probes for effective steric bulk of several substituents including the Me_3Sn group. Steric hindrance in these reactions decreases in the following order: t-Bu > Me > Br > Me_3Sn > Cl > H.

During the synthesis of some trimethyltinnorbornanols[1] for use in the study of 1-3 elimination reactions[2], we observed an unusual isomer distribution in the hydroboration of *syn*-7-trimethyltinnorbornene.



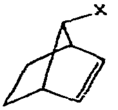
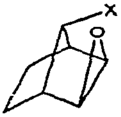
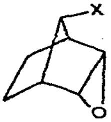
Based on Brown's result of 78% *endo* alcohol[3] for the analogous 7,7-dimethylnorbornene we expected the *endo* isomer to predominate greatly. The stereoselectivity observed here suggests a relatively small effective steric bulk, certainly an unexpected situation. Quantitative comparisons of the relative effective steric bulks of Group IV Me_3M substituents are not available, although it has been suggested that the trimethylsilyl group is similar to a t-butyl group[4]. An estimation of the size of a Me_3Sn group based on models or bond lengths shows that the Me_3Sn group is, indeed, large. However, effective steric bulk might be better discussed in terms of other factors, such as size and distance. The Me_3Sn group offers a unique possibility to study the steric influence of a large group situated at a considerable distance from the reactive-center, both factors due to the long tin–carbon bond length.

Brown and coworkers have developed both the hydroboration[3] and epoxidation[5] reactions as useful measures of the steric effects of *syn*-7 substituents in the norbornyl system. We have used both of these reactions to measure relative steric effects, with major emphasis on the epoxidation reaction.

syn-7-Bromo-[6], *syn*-7-chloro[7] and *syn*-7-trimethyltinnorbornenes[1] were prepared by published procedures. The epoxidation reactions with *m*-chloroperbenzoic acid were carried out for 24 hours at room temperature in dichloromethane. Work-up was accomplished according to the procedure of Brown *et al.*[5]. The stereoselectivity ratios were determined by direct NMR analyses of three sets of peaks, due to the 2,3 protons; the 1,4 (bridgehead) protons, and the *anti*-7 proton (bridge), of the epoxides. Mass spectral parent ions and cracking patterns as well as the NMR and IR spectra are consistent with the proposed structures. *syn*-7-Trimethyltin-*exo*-2,3-epoxynorbornane decomposes slowly at room temperature and therefore the error limits on the *exo*/*endo* ratio are somewhat larger than for the other compounds. Table 1 lists the NMR data for the expoxides and starting norbornenes.

TABLE 1

CHEMICAL SHIFTS OF *syn*-7-SUBSTITUTED NORBORNENES AND 2,3-EPOXYNORBORNANES
(ppm downfield from TMS, CH_2Cl_2 solvent)

	H	*Substituent*		
		Br	*Cl*	*SnMe*$_3$
	1,4 7	2.95 3.80	2.95 3.81	2.97
	1,4 2,3 7	2.65 3.24 3.43	2.63 3.26 3.50	2.50 2.97
	1,4 2,3 7	2.43 3.67 4.05	2.38 3.70 4.11	2.37 3.45

The hydroboration reactions were carried out using the *in situ* method and analysis was by NMR and gas chromatography.

The *exo*/*endo* ratios from the epoxidation and hydroboration reactions are listed in Table 2 along with values for the parent, *syn*-7-methyl[3,5] (7,7-dimethylnorbornene) and *syn*-7-t-butyl[8] analogs.

TABLE 2

EPOXIDATION AND HYDROBORATION OF *syn*-7-SUBSTITUTED NORBORNENES

Substituent	*Epoxidation exo/endo ratio (% exo)*	*Hydroboration exo/endo ratio (% exo)*
H	100–200[a](99–99.5)	200[b](99.5)
Cl	1.60±0.06(62)	
$Sn(CH_3)_3$	1.2±0.1(55)	1.2±0.2(55)
Br	0.82±0.05(45)	1.0±0.1(50)
CH_3	0.10±0.04[a](6–14)	0.28[b](22)
t-Bu		(0)[c]

[a] Ref. 5. [b] Ref. 3. [c] Ref. 8.

These data indicate an effective steric order of t-Bu > CH_3 > Br > $Sn(CH_3)_3$ > Cl > H. Most importantly, the steric bulk of the Me_3Sn group is very similar to Cl and Br substituents. Polar and other directive effects seem to be ruled out as important because of the correspondence of results for two widely different reactions, hydroboration and epoxidation, and the varied nature of the substituents.

A consideration of either bond length or Van der Waals radii alone will not satisfactorily account for these results (Table 3). If the differences in bond length alone are considered a discrepancy develops between the comparisons of the Br with CH_3 and Cl with CH_3. Br has a longer bond length than CH_3 by 0.40 Å and has an *exo/endo* ratio 11.8 times larger than CH_3. Cl on the other hand has a bond length only 0.23 Å longer than CH_3 or 0.17 Å shorter than Br and produces a ratio 23.3 times larger. A Br substituent has a radius 0.05 Å smaller than CH_3, hardly enough difference to account for the large difference in their *exo/endo* ratios.

TABLE 3

COMPARISONS OF EFFECTIVE STERIC BULK

Substituent	*exo/endo Ratio epoxidation reaction*	*A-value (kcal/mole)*	*C–X bond length*[c] *(Å)*	*Van der Waals radii*[d] *(Å)*
H	100	0.00	1.10	1.20
Cl	1.6	0.53[a]	1.77	1.80
$SnMe_3$	1.2		(2.18)	
Br	0.8	0.48[a]	1.94	1.95
Me	0.1	1.70[b]	1.54	2.0
t-Bu	(0)	>4	(1.54)	
$SiCl_3$		0.61[a]	(1.88)	

[a] Ref. 8. [b] Ref. 9. [c] Ref. 12. [d] Ref. 13.

A combination of these factors is shown in another measure of effective steric bulk, the conformational free-energy difference between an axial and equitorial position on a cyclohexyl ring[9,10]. The results here are in general correspondence with *A* values as shown in Table 3, however, a minor discrepancy develops with respect to the halogen order. Using Wilcox's method[11] to calculate the distance between the *syn*-7 substituent and the center of the 2,3-carbon bond in conjunction with Van der Waals radii (or covalent radii) of the groups, an estimate of the "open space" between the double bond and substituent gives the following order: $H > Cl > Br > CH_3$. "Open spaces" correspond to the observed *exo/endo* ratios and rationalize the halogen order showing that decreased bond lengths do not overcome the shrinking radii. We are not proposing the geometrical model as a measure of steric effects since other factors such as polarizability and bending force constants have not been considered, it does however provide a reasonably satisfying pictorial argument.

The variations in the relative steric effects of the Group IV trialkyl substituents could aid in developing an understanding of the importance of some of the factors mentioned here and we are continuing our investigations in this area.

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