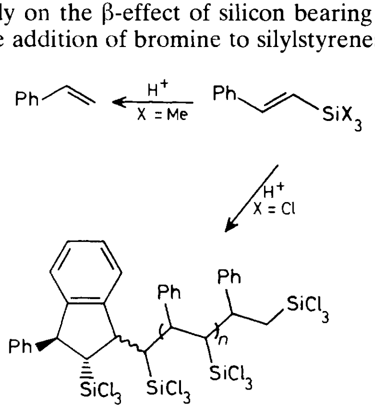
An Examination of the β-Effect in an Addition Reaction with Different Ligands on Silicon

Michael A. Brook,* Mahmud A. Hadi, and Axel Neuy

Department of Chemistry, McMaster University, 1280 Main St. W., Hamilton, Ontario, Canada L8S 4M1

The degree of *cis*-addition of bromine to a series of β-silylstyrenes may be used to compare the ability of silicon atoms bearing a variety of different ligands to stabilize a β-carbocation.

We recently observed[1] that under the appropriate conditions certain acids add to β-trichlorosilylstyrene (Scheme 1, X = Cl) to give a series of indane-terminated oligomers, whereas the trimethylsilyl derivative undergoes the normal substitution reaction[2] to give styrene[3] (Scheme 1, X = Me). We reasoned that the change from a protiodesilylation–substitution process to the oligomerization–addition process must result from the balancing of the β-effect (ability of organosilicon groups to stabilize a carbonium ion in the β-position) and the leaving group abilities of the silyl groups. The relationship of the ligands on silicon to the degree of β-carbocation stabilization in addition reactions has not been reported.† In this paper, we report a study on the β-effect of silicon bearing a variety of ligands in the addition of bromine to silylstyrenes.[4]



Scheme 1

The starting materials were prepared by traditional routes. Styrylsilanes were obtained by the hydrosilation of phenylacetylene by the appropriate chloro(methyl)silane in the presence of H_2PtCl_6; fluoro-derivatives were prepared from the chloro-derivatives using $ZnF_2 \cdot 2H_2O$; the trimethoxy-derivative was prepared by the addition of methanol to trichlorosilylstyrene in the presence of 3.3 equiv. of $HC(OMe)_3$. A solution of bromine in CS_2 (1 M) was added at −75 °C to each styrylsilane in CS_2 (0.5 mmol/1 ml).

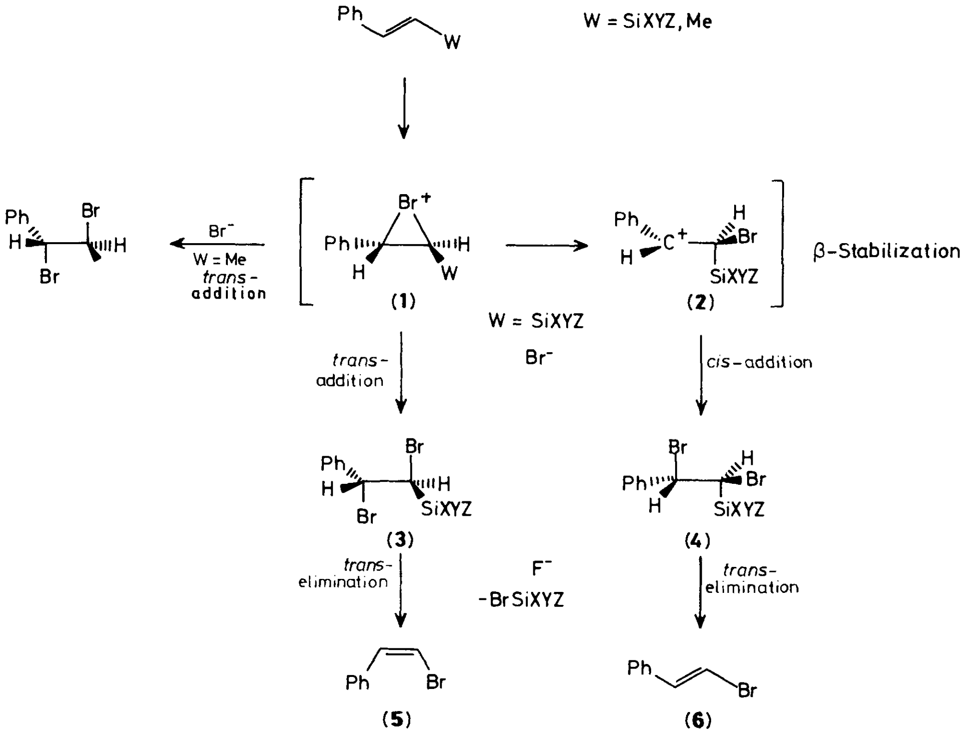
The relative geometries of (**3**) and (**4**) were established by their conversion to the known (*Z*)- and (*E*)-β-bromostyrenes, (**5**) and (**6**), respectively. The elimination of BrSiXYZ is known to take place in an *anti*-fashion for Me_3Si.[4] In all cases, the ratio of the two dibromo adducts (**3**)/(**4**) correlated directly with the ratio of (**5**)/(**6**). The reasonable assumption that only one elimination mechanism is operating for the series of compounds then leads to stereochemical assignment of (**3**) to the *l*-isomer and that of (**4**) to the *u*-isomer (*l* = like, *u* = unlike) as shown in Scheme 2. The fluoride-induced eliminations were performed in $CDCl_3$ using Bu_4NF(TBAF) as the fluoride source.‡

The ratio of the two dibromo-products (**3**) and (**4**) resulting from *trans*- and *cis*-addition, respectively, was determined in the crude mixture by integration of the α-Si-C*H* proton signals in the ^1H n.m.r. spectrum and correlated with the peak intensity of the α-Si-*C*H carbon signals in the ^{13}C n.m.r. spectrum and of the Si peaks in the ^{29}Si n.m.r. spectrum. The ratio of (**5**) and (**6**) was similarly obtained from ^1H n.m.r. data.

---

† Some studies of silanes bearing electron-withdrawing groups have been reported for substitution reactions, including allylfluorosilanes[6] and one study of vinylsilanes which focused on the effect of the degree of co-ordination on silicon.[7]

‡ A 1 M solution of TBAF in $CDCl_3$ was prepared by removing and replacing with $CDCl_3$ the tetrahydrofuran from a commercially available (Aldrich) solution of Bu_4NF.



Scheme 2

Table 1. Degree of *cis*-addition.

SiXYZ	% *cis*-Addition	Group electronegativity[8]
$SiMe_3$	100	2.05
$SiMe_2Cl$	100	2.12
$SiMe_2F$	87	2.23
$Si(OMe)_3$	81	2.47
$SiMeCl_2$	68	2.19
$SiCl_3$	57	2.26
$SiMeF_2$	40	2.41
SiF_3	17[a]	2.59

[a] Based on the ratio of bromostyrenes after elimination.

The results are presented in Table 1. Assuming, as is generally accepted,[2,5] that hyperconjugation is the mechanism of β-stabilization as shown in Scheme 2, the greater the negative charge on the α-carbon, the greater the β-stabilization leading to a greater percentage of *cis*-addition product [the absence of such an extra stabilizing group, *e.g.* methylstyrene (Scheme 2, W = Me), leads to *trans*-addition, presumably because the bromonium ion (**1**) does not open up to (**2**), Scheme 2].§ As the groups on silicon become increasingly electron donating, an increase in the formation of the *cis*-addition product is observed as expected. There is a reasonable correlation between the group electronegativities of the SiXYZ groups[8] and the degree of *cis*-addition (Table 1) which follows from the mechanism in Scheme 2. The only exception is trimethoxysilylstyrene.

This procedure for evaluating the β-effect is extremely simple both in the preparation of the starting materials and in the evaluation of the degree of stabilization. Extensions to silyl groups with more or less stabilizing ability should be readily accomplished by modifications to the phenyl group. Further work in this context, and in the evaluation of the leaving group ability and the rôle of steric effects of the silyl groups is currently underway.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work. The awarding of a McMaster University-Universität Duisburg Exchange Fellowship by the Deutscher Akademischer Austauschdienst and a scholarship by the Studienstiftung des Deutschen Volkes to A. N. is greatly appreciated.

Received, 23rd December 1988; Com. 8/05013I

References

1 M. A. Brook, E. Jefferson, and T. Sebastian, 'Polytrihalosilylstyrenes: Exploiting the β-Effect for Polymer Synthesis,' 3rd North American Chemical Congress, June 1988, Toronto, Canada, Abstract ORGN-50; to be published elsewhere.
2 E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981; W. P. Weber, 'Silicon Reagents for Organic Synthesis,' Springer, Berlin, 1983; I. Fleming, in 'Comprehensive Organic Chemistry,' vol. 3, ed. D. N. Jones, Pergamon, Oxford, 1979, Ch. 13.
3 K. E. Koenig and W. P. Weber, *J. Am. Chem. Soc.*, 1973, **95**, 3416.
4 K. E. Koenig and W. P. Weber, *Tetrahedron Lett.*, 1973, 2533; R. B. Miller and G. McGarvey, *J. Org. Chem.*, 1978, **43**, 4424.
5 T. H. Chan, *Acc. Chem. Res.*, 1977, **10**, 442; J. B. Lambert, G. Wang, R. B. Finzel, and D. H. Teramura, *J. Am. Chem. Soc.*, 1987, **109**, 7838; S. G. Weirschke, J. Chandrasekhar, and W. L. Jorgensen, *ibid.*, 1985, **107**, 1496.
6 T. Hayashi, T. Matsumoto, and Y. Ito, *Organometallics*, 1987, **6**, 884.
7 K. Tamao, M. Akita, K. Maeda, and M. Kumada, *J. Org. Chem.*, 1987, **52**, 1100.
8 Calculated using the equations and values in J. Mullay, *J. Am. Chem. Soc.*, 1985, **107**, 7271; 1984, **106**, 5842.

---

§ The referees expressed concern that no conclusive evidence of the mechanism shown in Scheme 2 is offered. In particular, no proof is offered to indicate that the least motion 60° rotation in the reaction (**1**) → (**2**) is necessarily being followed nor that a change from 60° to 120° can be precluded. We acknowledge this, although we believe that the mechanism is consistent with our observations. Irrespective of the degree and direction of bond rotation which may take place, the net effect of adding electron-withdrawing groups on silicon is an increase in the degree of *trans*-addition of bromine to the styrene.