Journal of Organometallic Chemistry, 121 (1976) 293—306

THE BROMINATION, DEBROMINATION AND DEBROMOSILYLATION OF SILYLSTYRENES AND OTHER VINYLSILANES

A.G. BROOK *, J.M. DUFF * and W.F. REYNOLDS
Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario M5S 1A1 (Canada)
(Received May 18th, 1976)

Summary

The bromination of some vinylsilanes, and the debrominations and debromosilylations of their dibromides are stereospecific. Based on the crystal structure of the dibromide derived from *trans*-triphenylsilylstyrene, it is shown that bromination and debromination of silylstyrenes occur with *syn* stereochemistry, and that debromosilylation occurs with *anti* stereochemistry in polar solvents. Different stereochemistries may prevail with other vinylsilanes. Other elimination and substitution reactions are also described.

In the course of other research, we looked at the reactions of a number of vinylsilanes with bromine, and also at the debromination or debromosilylation of these dibromides. Examples of these reactions have been investigated before and while many of them are known to be stereospecific, it has not always been clear what the stereochemical course of an individual reaction was.

Jarvie [1] reported that bromination of *trans*-propenyltrimethylsilane gave a single dibromide which on treatment in polar medium underwent debromosilylation yielding mainly *cis*-1-bromopropene. On the assumption that bromination occurred with *anti* stereochemistry, it followed that debromosilylation occurred in a predominantly *anti* manner. Weber [2] investigated the same reactions with both *cis*- and *trans*-trimethylsilylstyrene. He found that the dibromide derived from the *trans* alkene cleanly decomposed in acetonitrile to *trans*-β-bromostyrene, whereas the isomeric dibromide derived from the *cis* alkene decomposed to a mixture of *cis*- and *trans*-bromostyrenes in which the *cis* compound predominated. These results were interpreted as arising from *syn*-bromination of the alkene and *anti*-debromosilylation. While there can be no doubt about the stereochemical identities of the starting materials and final products, there is no evidence which unambiguously defines the stereochemistry of the individual steps.

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* Dow Corning Postdoctoral Fellow, 1973—75.

TABLE 1

DATA FOR VINYLSILANES BROMINATION AND DEBROMINATIONS

Vinylsilane	Geometry	Proportions of debromination products [a]	
		% *trans*	% *cis*
$Ph_3SiCH{=}CHPh$	*trans*	100	0
	cis	44	56
$Ph_3SiCH{=}CHMe$	*trans*	83	17
	cis	43	57
$Ph_3SiCH{=}CH\text{-}i\text{-}Pr$	*trans*	100	0
	cis	100	0
$Me_3SiCH{=}CHPh$	*trans*	[b]	
	cis	[b]	
$Me_3SiCH{=}CH\text{-}i\text{-}Pr$	*trans*	77	23
	cis	68	32

[a] The proportions of the vinylsilanes derived from the debrominations were determined by NMR. [b] Attempted debromination led to complete decomposition to β-bromostyrene.

The opposite stereochemistry for each of bromination and debromosilylation would have given the same overall results.

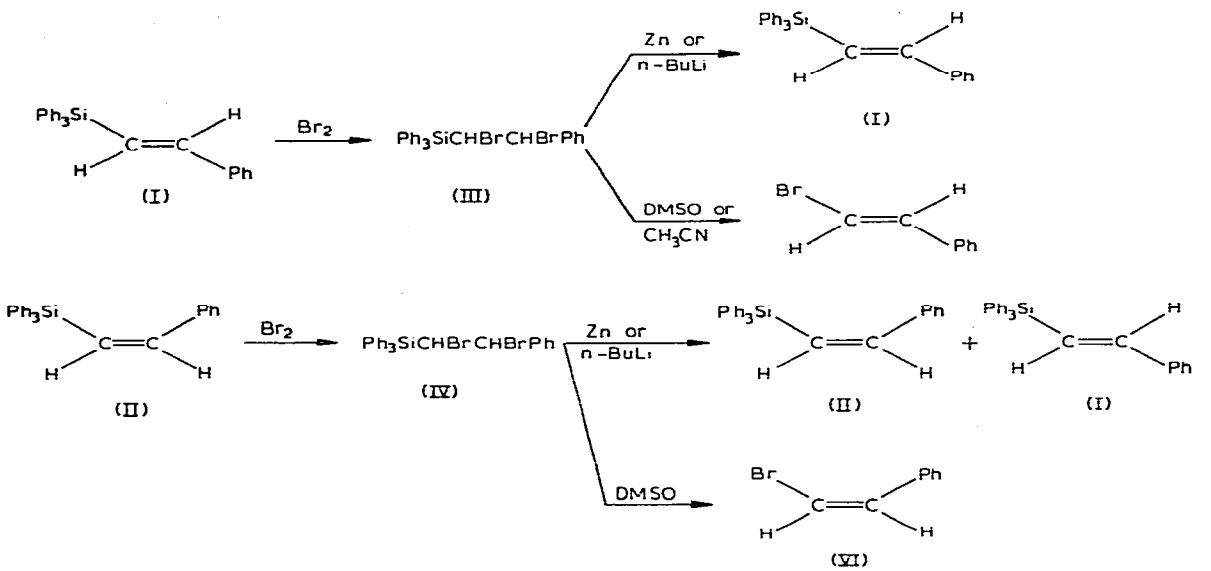
Our results of bromination and debromination are summarized in Table 1, and those from *trans*- and *cis*-triphenylsilylstyrene are definitive. Bromination of *trans*-triphenylsilylstyrene in dichloromethane at −78° C gave a single stable dibromide III, characterized by the NMR spectrum of the cold reaction mixture prior to work-up and isolation: the pure isolated dibromide had an identical spectrum. A different single isomer IV was similarly characterized and isolated from bromination of the *cis*-silylstyrene under the same conditions. Thus the bromination reaction is highly stereospecific. III, when treated with zinc, at room temperature, or with an equivalent of n-butyllithium at −78° C, gave pure *trans*-triphenylsilylstyrene. III decomposed in dimethyl sulfoxide at 25° C over 20 h (or in acetonitrile over 12 days), to yield pure *trans*-β-bromostyrene. In contrast, dibromide IV from *cis*-silylstyrene, treated with zinc as above, gave a 56 : 44 mixture of *cis*- and *trans*-silylstyrenes, whereas treatment witn n-butyllithium gave a 40 : 60 mixture. IV decomposed in DMSO solution over 20 h to yield pure *cis*-β-bromostyrene. These results are summarized in Scheme 1.

Rationalization of the preceeding results requires either that bromination and debromination each occur with complete or at least preferred *anti* stereochemistry (with low specificity for the bromination of IV and that debromosilylation occurs with *syn* stereochemistry, or, that bromination and debromination each occur with *syn* stereochemistry and that debromosilylation occurs with *anti* stereochemistry.

Similar reaction sequences, i.e. bromination and debromination, (see Table 1) were carried out on a number of other pairs of isomeric vinylsilanes, whose geometry about the double bond could be adduced from the method of synthesis and confirmed on the basis of the magnitudes of the NMR coupling constants between the vinylic protons, those for the *trans* isomers being about 4 Hz greater than for the *cis* isomers (see Table 2). The behavior of the 1-triphenylsilylpropenes closely resembled that of the related triphenylsilylstyrenes. Under our

SCHEME 1

REACTIONS OF VINYLSILANES AND THEIR DIBROMIDES



conditions we could not observe the debromination of Weber's trimethylsilylstyrene dibromides, since they underwent complete debromosilylation in ether at room temperature. Both dibromides from the isomeric 1-triphenylsilyl-3-methylbutenes gave the same *trans* alkene on debromination, thus providing no unequivocal information about the stereochemistry of bromination and debromination, while the related trimethylsilyl analogs both showed considerable preference for forming the *trans* alkene during debromination.

In order to try to resolve this ambiguity, the crystal structure of the dibromide formed by bromination of *trans*-triphenylsilylstyrene was determined using X-ray diffraction techniques [3]. The crystal structure showed unambiguously that the dibromide possessed the *threo* configuration, arising from *syn* addition of bromine to the double bond. This finding, therefore, indicates that debromination of the dibromide occurred by *syn* elimination, and that the debromosilylation occurred by *anti* elimination in complete agreement with the proposals of Koenig and Weber [2].

It is known that the polar addition of bromine to stilbenes [4] and styrenes [5,6] often occurs with preferred *anti* stereochemistry, although in some cases the selectivity, particularly with the *cis* isomers, is not great. Similarly, zinc-catalyzed debrominations are often found to follow *anti*-coplanar stereochemistry, particularly with *erythro* forms, although in some cases where bulky groups would lead to severe *gauche* interactions (*threo* forms) large departures from pure *anti* stereochemistry may be observed [7]. However, we are not aware of any previous case where *syn* addition has been proven to be the preferred stereochemistry of bromination for both of the alkene isomers and/or where *syn* elimination is the preferred stereochemistry in zinc-catalyzed debrominations for both of the stereoisomeric dibromides. In fact the reverse, *anti* addition and *anti* elimination, is generally true. It is evident, therefore, that there are important in-

TABLE 2

PROPERTIES OF VINYLSILANES

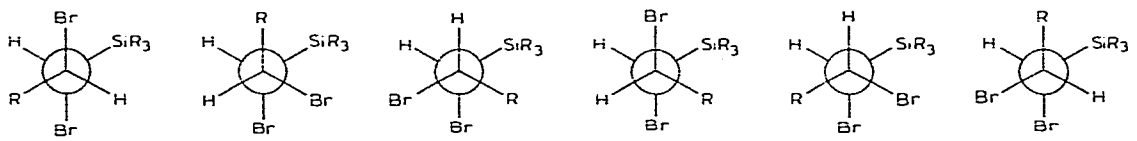
Compound	Stereo-chemistry	Method of [a] prep.	Yield (%)	m.p. or b.p./mmHg	IR(μ) [b]		NMR [c]
					C=C	*trans* HC=CH	*J*(HC=CH) (Hz)
$Ph_3SiCH=CHPh$	*trans*	A	76	154—155		10.09	19
	cis	B	30	93.5—94			15
$Ph_3SiCH=CHMe$	*trans*	C	22 [d]	94.5—97	6.18	10.16	19
	cis	D	59	39—39.5	6.21		14
$Ph_3SiCH=CH$-i-Pr	*trans*	A	66	82—83	6.18	10.08	19
	cis	D	55	56.5—57.5			14
$Me_3SiCH=CHPh$	*trans*	A	79	55/30	6.22	10.11	19
	cis	D	70	71—72/5.0			15
$Me_3SiCH=CH$-i-Pr	*trans*		38 [e]		6.18	10.10	18
	cis		81 [e]		6.22		14
$Me_3SiCH=CHSiMe_3$	*trans*	*g*	38	144—145/760		9.91	23
	cis	*g*		[e]			20
$Me_3SiCH=CH$-t-Bu	*trans*	*h*	71				19
	cis	*h*	58	*h*			16
$Ph_3SiCH=CH$-t-Bu	*trans*	A	73	84—85	6.18	10.05	18
$Ph_3SiCH=CHSiMe_3$	*trans*	*f*	22	92—93		9.88	23

[a] A. $Ph_3SiH + R'C{\equiv}CH$ (H_2PtCl_6 catalyst). B. $Ph_3SiC{\equiv}CPh + H_2$ (Ra/Ni catalyst). C. $R'CH=CHMgBr + R_3SiX$. D. $R_3SiC{\equiv}CR' + (i\text{-}Bu)_2AlH$ + *N*-methylpyrrolidine. E. $R_3SiC{\equiv}CR' + (i\text{-}Bu)_2AlH$. [b] Infrared spectrum of solids run in CCl_4; liquids neat as films. [c] NMR spectra in CCl_4. [d] Commercial 1-bromopropene (mixed isomers) was used. Many recrystallizations were required to give pure product. [e] Product not distilled, but purified by preparative gas chromatography. Yields estimated from NMR spectra of crude product. See ref. 23. [f] See ref. 25. [g] See ref. 26. [h] See ref. 23 for method of synthesis. [i] Determined from ^{13}C satellites.

fluences on the reactions of the triphenylsilylstyrenes, which favour *syn* addition and elimination; σ—π conjugation (hyperconjugation), of the sort proposed by Eaborn et al. [8], as applied by Weber [2], appears to account adequately for the observed stereochemical results.

It does not follow, however, that *syn* bromination applies to alkenylsilanes, as distinct from the silylstyrenes. We had hoped that the question of the stereochemistries of the dibromides and thus of the bromination of vinylsilanes might be resolved from the magnitudes of the NMR vicinal coupling constants of the dibromides in solvents of different polarity. This approach has allowed the determination of the relative stability of conformational isomers in dibromophenylalkanes [10a] and dibromoalkanes [10b]. Increasing solvent polarity leads to an increase in population of the more polar conformational isomers [11] (where the vicinal bromines are *gauche*).

From the data in Table 3, it can be seen that with four pairs of isomers, the product of bromination of the *trans* isomer has a significantly larger vicinal coupling constant than does the dibromide from the *cis* vinylsilane (isomer pairs 3, 5, 6, 7). In these cases, the R group attached to the double bond is not aromatic and in each case R is relatively bulky. The possible conformational isomers for *erythro* (I*e*—III*e*) and *threo* (I*t*—III*t*) dibromides are illustrated below. When R is very bulky, R—SiR_3 interactions should be the largest steric interactions, leaving I*e* and II*t* as the favoured conformational isomers (I*e* also minimizes



Br—Br steric and dipolar interactions). Assuming that *anti* H—H couplings are larger than *gauche* coupling constants, this implies that the *erythro* isomer has the larger coupling constant and that bromination of these four alkene pairs involves *anti* stereochemistry, i.e. the *trans* alkene yields the *erythro* dibromide, as proposed by Jarvie [1]. The assignment of *erythro* and *threo* dibromides is supported by the observation that the larger coupling constant for isomer pairs 3, 5, 6, 7 generally decreases with increasing solvent polarity while the smaller coupling constant is nearly solvent independent. Polar isomers II*e* and III*e* should increase in population with increasing solvent polarity (leading to a decreased coupling constant) while the *threo* isomer should be less sensitive to solvent since the most stable isomer II*t* is polar.

On the other hand, three pairs of isomers yielded results where there is little difference between the coupling constants of the dibromides derived from the *cis* and *trans* alkenes. In two of these cases, (1, 4) the R group is aromatic, where specific solvent effects may apply [12] and where *syn* bromination now appears to be established. In the third pair, 2, the R group is a non-bulky group, Me (whose trimethylsilyl analog appears to undergo *anti* bromination if *anti* debromosilylation also applies in this case, as has been proposed [1]). The combination of steric and dipolar interactions in this case is particularly complex and the difference in coupling constants is small. However, by analogy with 1,2-dibromo-

TABLE 3

NMR DATA FOR DIBROMIDES OF VINYLSILANES

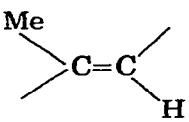
Pair No.	Compound	J(Hz) H—C=C—H	Isomer	Vicinal coupling constant [a] for dibromide in				
				CCl_4	$CDCl_3$	$(CD_3)_2CO$	$CD_3C{\equiv}N$	$(CD_3)_2SO$
1a	$Ph_3SiCH{=}CHPh$	19	*trans*	5.29	6.03	7.28	7.88	8.51 [b]
b		15	*cis*	6.42	6.50	7.51	8.40	8.98 [b]
2a	$Ph_3SiCH{=}CHMe$	19	*trans*	2.75	2.65	2.59		
b		14	*cis*	3.14	3.42	3.31		3.18
3a	$Ph_3SiCH{=}CH\text{-}i\text{-}Pr$	19	*trans*	10.10 [c]	9.63	9.62	10.13	
b		14	*cis*	2.69 [d]	2.89	3.27	3.41	
4a	$Me_3SiCH{=}CHPh$	19	*trans*	10.13	10.41	10.62	10.68 [b]	10.85 [b]
b		15	*cis*	9.77	9.42	8.80	9.07 [b]	8.48 [b]
5a	$Me_3SiCH{=}CH\text{-}i\text{-}Pr$	19	*trans*	11.95 [e]	11.51	11.01	10.82	10.62
b		14	*cis*	2.86 [f]	3.08	2.99	3.13	3.19
6a	$Me_3SiCH{=}CH\text{-}t\text{-}Bu$	19	*trans*	4.45	4.16	3.88	3.79	3.75
b		16	*cis*	1.59	1.51	1.57	1.54	1.55
7a	$Me_3SiCH{=}CHSiMe_3$ [g]	23	*trans*	10.80	10.54 [h]	9.16	8.62	
b			*cis*	2.39		2.25	2.18	
8a	$Ph_3SiCH{=}CHSiMe_3$	23	*trans*	8.44	8.38	8.30	9.02	8.49

[a] Average of 4–8 determinations. The measurements were made directly on the reaction mixture of vinylsilane plus bromine. [b] Sample decomposing during NMR measurements. [c] $J(-BrHC-CHMe_2)$ = 2.0–2.2 Hz (first order approximation). [d] $J(-BrHC-CHMe_2)$ = 8.0–8.7 Hz (first order approximation). [e] $J(-BrHC-CHMe_2)$ = 2.4–2.7 Hz (first order approximation). [f] $J(-BrHC-CHMe_2)$ = 8.2–8.6 Hz (first order approximation). [g] ca. 20% solution; values measured from ^{13}C satellites. [h] Neat liquid.

3,3-dimethylbutane where the $C(CH_3)_3$—Br interaction determined the stable conformation [10b], the dominant steric interaction should be SiR_3—Br, i.e. III*e* and III*t* should be the most stable conformational isomers for R = Me. On this basis, the *threo* isomer should have the larger coupling constant, again consistent with *anti* bromination.

The above interpretation, which has assumed for bulky R groups that steric effects largely outweigh dipolar and other electronic effects, is undoubtedly oversimplified. Thus, in view of the complex interactions involved, the assignment of configurations to these diastereomeric pairs of dibromides is far from definitive, and the inference from the NMR data that alkenylsilanes undergo *anti* bromination is speculative, although consistent with previous work [1]. If the assignment for alkenylsilanes is correct then interactions associated with the phenyl group must play a significant role in determining the stereochemistry of bromination to explain the *syn* bromination observed for the triphenylsilylstyrenes.

Several other reactions of the dibromides of *trans*- and *cis*-triphenylsilylstyrene were investigated. Thus, each of the dibromides was found to react stereospecifically with methanol to yield different isomers of 1-triphenylsilyl-1-bromo-2-methoxy-2-phenylethane, whose stereochemistry was not ascertained. The dibromides III and IV obtained from the silylstyrenes were dehydrobrominated in boiling pyridine. Compound III, the *threo* isomer on the basis of the preceding evidence, gave rise to two isomeric β-bromo-β-triphenylsilylstyrenes, VII and VIII, isolated in 44% and 20% yields respectively, whereas similar treatment of IV gave only VII, isolated in 54% yield. Both VII and VIII on treatment with n-butyllithium at low temperature [13] followed by hydrolysis gave the same product, *trans*-triphenylsilylstyrene, I, and both on treatment with n-butyllithium followed by methyl iodide afforded the same methylated product, X, assigned the structure 2-triphenylsilyl-1-phenylpropene having a *trans*-silylstyrene(*E*) configuration. This assignment was based on the independent synthesis of X by platinum-catalyzed addition of triphenylsilane to 1-phenylpropyne, known to occur by *syn* addition [14]. The NMR spectrum of X had the expected quartet and doublet (J 1.5 Hz) consistent with allylic coupling in a *trans*



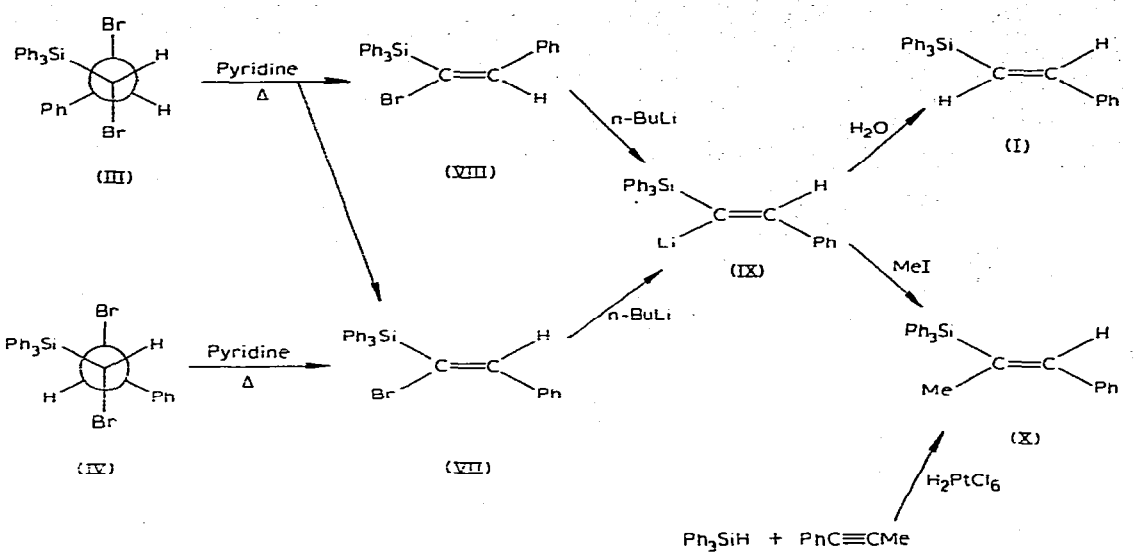
structure. This chemistry is outlined in Scheme 2.

It follows from the above chemistry that the dehydrobrominations of III and IV, both involved the loss of the benzylic bromine, as expected from the proposed mechanism of bromination. Unfortunately the halogen—metal exchange reaction failed to establish the geometries of VII and VIII, since even when the reaction was carried out at —78° C in non-polar solvents, only the *trans* products I and X were obtained. While it is known that the halogen—metal exchange reactions of vinyl halides occur with retention of configuration, it is also well known that *cis*-stilbenyllithium and related reagents are relatively unstable and readily isomerize to the stabler less sterically hindered *trans* compounds [15,16]. A similar isomerization evidently occurred in this case, both the vinyllithium reagents derived from VII and VIII yielding the more stable species IX, which subsequently reacted to give I and X.

Fortunately, it is possible to assign the configurations of VII and VIII with

SCHEME 2

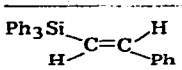
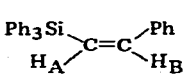
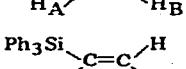
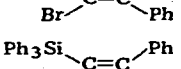
DEHYDROBROMINATION AND OTHER REACTIONS OF SILYLSTYRENE DERIVATIVES



some certainty through comparison of their NMR spectra with those of I and II (Table 4). The spectrum of *cis*-triphenylsilylstyrene, II, is unusual in that the benzal proton appears at abnormally low field (δ 7.58 ppm) and the aromatic multiplet is spread out to much higher field (δ 6.7—7.6 ppm) than is usual (7.1—7.8 ppm). Since the *trans* compound I does not show these phenomena it appears that both abnormalities are associated with the *cis*-triphenylsilylstyryl system, a conclusion supported by studying models of the compounds which show an unfavourable steric interaction between the *cis*-triphenylsilyl and phenyl substituents. The bromostyrene VIII shows the same sort of spectral abnormalities as II (vinyl proton at δ 8.40, aromatic multiplet at 6.7—7.7 ppm) while VII does not, suggesting that VIII has the *cis*-silylstyrene structure. These assignments are

TABLE 4

NMR DATA FOR VINYLSILANES [a]

Compound		Vinyl protons	Phenyl multiplet
	(I)	6.95 [b]	7.1—7.8
	(II)	H_A 6.22 H_B 7.58 [c], J 15 Hz	6.7—7.6
	(VII)	[d]	7.2—7.8
	(VIII)	8.40	6.7—7.7

[a] Spectra run in $CDCl_3$ using internal TMS. [b] Broad, 2H. In DMSO/CS_2 (2 : 1) an *AB* pattern was obtained, δ 6.87, 7.15 ppm and J 19.5 Hz. [c] The benzal proton H_B was identified by its broader peaks due to coupling with the phenyl *ortho* protons. [d] The vinyl proton was buried in the phenyl multiplet.

supported by the observations that compounds II and VIII, assigned *cis*-silylstyrene configurations, have lower melting points (95° C and 147° C respectively) and higher solubility than compounds I and VII, (m.p. 154° C and 162° C respectively) which have been assigned the *trans* configurations.

Finally, based on the assigned configurations of III, IV, VII and VIII, it appears that IV underwent clean *syn* elimination and that III underwent both *syn* and *anti* elimination of HBr. The lack of stereospecificity in the latter case, and the *syn* stereochemistry in the former case presumably reflect the unfavourable steric interactions involved in achieving the products of "normal" *anti* elimination.

Experimental

Reactions involving organometallic reagents were carried out under purified nitrogen in dried solvents. Microanalyses were performed by A.B. Gygli, Toronto.

Triphenylsilylphenylacetylene, m.p. 101—102° C [17], 1-triphenylsilylpropyne, m.p. 112—113° C [18], trimethylsilylphenylacetylene, b.p. 83.5° C/5 mmHg [19], *trans*-triphenylsilylstyrene [20], *trans*-1-triphenylsilylpropene [21], *cis*- and *trans*-1-trimethylsilylstyrene [22], and *cis*- and *trans*-1-trimethylsilyl-3-methylbutene [23] were prepared as described in the literature. The properties of all the vinylsilanes used are listed in Table 2.

1-Triphenylsilyl-3-methylbutyne-1

A solution of 3-methylbutyne-1 (1.36 g, 0.02 mol) in 20 ml ether at 0° C was treated with phenyllithium (8.8 ml of 1.7 *M* solution, 0.015 mol) in ether/benzene solution. After 30 min a solution of triphenylchlorosilane (2.94 g, 0.01 mol) in 1 : 1 ether/benzene (20 ml) was added. After two days work-up with saturated aqueous ammonium chloride gave a sticky solid, recrystallized from methanol to give 2.51 g (77%) of white solid, m.p. 79—80.5° C. Found: C, 84.72; H, 7.01. $C_{23}H_{22}Si$ calcd.: C, 84.60; H, 6.79%.

1-Triphenylsilyl-3-methylbutyne-1

This compound was prepared as above, but using an equivalent of trimethylchlorosilane. After 2—3 h stirring the ether was removed through a Vigreux column and distillation of the residue gave the desired product, b.p. 115—120° C/760 mmHg in 66% yield. Purification was performed by preparative GLC using 20% S.E. 30 on Chromosorb G. Found: C, 68.24; H, 11.30. $C_8H_{16}Si$ calcd.: C, 68.48; H, 11.50%.

cis-Triphenylsilylstyrene

A solution of 7.2 g (0.020 mol) of triphenylsilylphenylacetylene in 50 ml of 1 : 1 benzene/ethanol was rapidly stirred with 5 g of Raney nickel (activity grade W1) under hydrogen (1 atm) at 22° C until 0.0208 mol had been consumed (27 h). Benzene was added to dissolve some white precipitate, and after filtration and concentration an NMR spectrum indicated the mixture contained 29% of 2-phenylethyltriphenylsilane, 42% of the *cis*-styrene and 29% of the starting acetylene. Crystallization from ethanol removed most of the 2-phenylethyltriphenylsilane.

The residual material (after removal of the ethanol) was stirred in 20% aqueous dioxane containing 2 g of potassium hydroxide for 20 h to convert the silylacetylene to phenylacetylene and triphenylsilanol. Work-up with ether and water and crystallization of the resultant mixture from ethanol gave 2.13 g (30%) of pure *cis*-triphenylsilylstyrene, m.p. 93—94° C. Found: C, 85.99; H, 6.19. $C_{26}H_{22}Si$ calcd.: C, 86.13; H, 6.12%.

cis-1-Triphenylsilylpropene-1

1-Triphenylsilylpropyne-1 (2.80 g, 9.4 mmol) was added to a solution of diisobutylaluminium hydride in heptane (8.6 ml, 11 mmol) containing 0.94 g (11 mmol) of *N*-methylpyrrolidine. After 6 h at reflux and 16 h at room temperature, work-up with dil. hydrochloric acid gave a mixture, shown by NMR to contain about 90% of the desired alkene and 10% of starting material. The mixture was stirred overnight with 75 ml of 3% aqueous dioxane containing 0.2 g of potassium hydroxide. Work up and crystallization from methanol at —20° C gave 1.67 g (59%) of *cis*-triphenylsilylpropene-1, m.p. 39—39.5° C. Found: C, 84.09; H, 6.75. $C_{21}H_{20}Si$ calcd.: C, 83.94; H, 6.71%.

trans-1-Triphenylsilyl-3-methylbutene-1

To a stirred mixture of triphenylsilane (2.59 g, 0.01 mol) and 1 drop of a saturated solution of chloroplatinic acid in 2-propanol, in a small flask, fitted with a condenser, immersed in an oil bath at 90° C was added over 1—2 min 1.36 g (0.02 mol) of 3-methyl-1-butyne. A vigorous initial reaction occurred (caution!) and then subsided, and the mixture was refluxed for 1 h. Removal of the solvent and recrystallization from methylene chloride/methanol gave 2.17 g (66%) of the required compound, m.p. 82—83° C. Found: C, 83.94; H, 7.11. $C_{23}H_{24}Si$ calcd.: C, 84.09; H, 7.36%.

cis-1-Triphenylsilyl-3-methylbutene-1

To a suspension of 1.63 g (5 mmol) of 1-triphenylsilyl-3-methylbutyne-1 in 3 ml heptane and 0.43 g (5 mmol) of *N*-methylpyrrolidine was added 5.1 ml (6 mmol) of a solution of diisobutylaluminium hydride in heptane. After 4 h reflux, work-up using dil. hydrochloric acid gave, after recrystallization from methanol at —20° C, 0.90 g (55%) of the *cis*-alkene, m.p. 56.5—57.5° C. Found: C, 84.08; H, 7.18. $C_{23}H_{24}Si$ calcd.: C, 84.09; H, 7.36%.

threo-1-Triphenylsilyl-1,2-dibromo-2-phenylethane (III)

A 7.5% solution of bromine in CCl_4 was added to a solution of 0.50 g of *trans*-triphenylsilylstyrene in 10 ml of $CHCl_3$ at 0° C until the bromine colour persisted. The solvent was removed under reduced pressure without heating to give an oil, shown by NMR to be a single isomer. Crystallization from petroleum ether (b.p. 60—70° C) at —20° C gave 0.63 g (87%) of dibromide m.p. 123—127° C: recrystallization from CH_2Cl_2/pentane or pentane raised the m.p. to 129—130° C. NMR ($CDCl_3$) δ 7.2—7.8, m, 20H (aryl); 4.50, 5.52 m, *AB*, 2H(*J* 6 Hz) (CH—CH) ppm. This spectrum was the same as that observed from the cold reaction mixture prior to work-up. Found: C, 59.79; H, 4.22. $C_{26}H_{22}SiBr_2$ calcd.: C, 59.78; H, 4.25%.

Similar results were obtained when the bromination was done in CH_2Cl_2 at —78° C. Large scale (>1 g) preparations gave poorer yields of product.

erythro-1-Triphenylsilyl-1,2-dibromo-2-phenylethane (IV)

Bromination was effected exactly as above. Crystallization of the oily dibromide from methylene chloride/pentane at —20° C gave 0.57 g (80%) of the *erythro* dibromide IV, m.p. 112—120° C, which on subsequent recrystallization was raised to 122—124° C. Due to the facile decomposition of this material, no satisfactory analysis was obtained: NMR ($CDCl_3$) δ 7.1—7.7, m, 20H(aryl); 4.81, 5.46, m, *AB*, 2H(*J* 6.5 Hz) (CH—CH) ppm. This spectrum was identical to that obtained from the cold reaction mixture, prior to work-up.

Brominations and debrominations of other vinylsilanes

The vinylsilanes listed in Table 1 were conveniently brominated in dichloromethane at —78° C by the careful addition of bromine in dichloromethane. After removal of the solvent in the cold under reduced pressure the NMR spectra of the residue indicated in each case that single isomeric dibromides were present, generally in quantitative yield, although in a few cases, especially the styrenes, traces of decomposition products were present. The vicinal coupling constants were measured in several solvents, as listed in Table 3, to assist in making configurational assignments [5,6,24]. The dibromides were debrominated in good yield over several hours at room temperature with zinc using the procedures described below. The proportions of alkenes which resulted were determined by NMR spectroscopy and are listed in Table 1.

Debromination of the threo dibromide III

(a) With zinc. A small sample of III dissolved in 4 : 1 ether/acetic acid was stirred with excess zinc dust for 30 min at room temperature. Filtration and removal of the solvent gave a white solid, m.p. 154—155° C, shown to be pure *trans*-triphenylsilylstyrene.

(b) With n-BuLi. A solution of 0.3 g (5.7 mmol) of III in 10 ml ether at —78° C was treated with n-butyllithium in hexane (0.47 ml, 7 mmol). The resulting suspension was allowed to warm to room temperature. Aqueous acidic work up gave a white solid, shown by NMR to be pure *trans*-triphenylsilylstyrene, obtained in 87% yield after recrystallization from chloroform/hexane, m.p. 153—155° C.

Debrominations of the erythro-dibromide IV

(a) With zinc. A solution of *erythro* dibromide IV, (0.26 g, 0.5 mmol) in 10 ml dry ether containing 2 drops glacial acetic acid was stirred with 0.3 g zinc dust for 2 h. Filtration, and removal of the solvents, gave a white solid, shown by its NMR spectrum to be a 56 : 44 mixture of the *cis*- and *trans*-β-triphenylsilylstyrenes, respectively.

(b) With n-BuLi. A solution of IV (0.11 g, 0.21 mmol) in 10 ml of dry ether at —78° C was treated with a 10% excess of n-butyllithium in hexane solution. The suspension was allowed to warm to room temperature. Aqueous work up gave an oil, shown from its 100 mHz NMR spectrum to consist of a 40 : 60 mixture of *cis*- and *trans*-β-triphenylsilylstyrenes.

Debromosilylations of the threo dibromide III and erythro dibromide IV

(a) in DMSO. A 10% solution of III in dry DMSO in an NMR tube completely

decomposed in less than 20 h at 25° C. The products were shown by their NMR spectrum to be pure *trans*-β-bromostyrene and hexaphenyldisiloxane, isolated in 80% yield, m.p. 223—224° C. When acetonitrile-d_3 was used as solvent, 12 days were required for complete decomposition.

Similar results were found with the *erythro* dibromide IV under similar conditions, except that *cis*-β-bromostyrene, uncontaminated with the *trans* isomer was observed, together with hexaphenyldisiloxane.

(b) With heat. threo Dibromide III (1.45 g, 2.8 mmol) was heated in a Kugelrohr apparatus at 0.4 mmHg pressure at 100—110° C. Over 30 min 0.42 g (83%) of distillate was collected, shown by its NMR spectrum to be 88 : 12 mixture of *trans*- and *cis*-bromostyrene respectively. The residue, a brown oil, was crystallized and recrystallized from dry hexane to give 0.71 g (75%) of triphenylbromosilane, m.p. 118—121° C. Similar treatment of *erythro* dibromide IV gave the same 88 : 12 mixture of *trans*- and *cis*-bromostyrenes; 83% of slightly impure triphenylbromosilane, m.p. 118—124° C was also isolated.

Dehydrobrominations of threo and erythro dibromides III and IV

The unrecrystallized bromination product from 5.20 g (0.014 mmol) of *trans*-β-triphenylsilylstyrene in 25 ml of dry pyridine was added dropwise to 150 ml of refluxing pyridine over 20 min. The pyridine was removed under reduced pressure, and the residue was shaken with ether and dilute hydrochloric acid, after which 0.69 g (18%) of hexaphenyldisiloxane m.p. 223—225° C was removed by filtration. The ether layer gave, after recrystallization from 160 ml of 1 : 3 methylene chloride/methanol, 2.87 g (45%) of the silylbromostyrene VII, m.p. 150—158°C, raised by recrystallization to 161—162°C.

Concentration of the mother liquor to 100 ml gave 1.20 g (19%) of silylbromostyrene VIII, m.p. 120—140° C, raised by recrystallization to 146—147° C. Found: C, 70.81; H, 4.67. $C_{26}H_{21}SiBr$ calcd.: C, 70.74; H, 4.80%.

The unrecrystallized bromination product from 0.20 g (0.55 mmol) of *cis*-β-triphenylsilylstyrene was refluxed in 5 ml of pyridine for 3 h. Work up as above gave a yellowish solid whose NMR spectrum indicated the presence of silylbromostyrene VII, with no VIII present. Recrystallization from methylene chloride/pentane gave 0.13 g (54%) of silylbromostyrene VII m.p. 161—162° C. Found: C, 70.86; H, 4.83. $C_{26}H_{21}SiBr$ calcd.: C, 70.74; H, 4.80%.

Methanolysis of threo and erythro dibromides III and IV

The bromination product III from 1.0 g of *trans*-β-triphenylsilylstyrene (I), was dissolved with gentle warming in 30 ml of dry methanol. After 20 h at room temperature, the solution was cooled to —20° C to give 1.10 g (85%) of 1-triphenylsilyl-1-bromo-2-methoxy-2-phenylethane, m.p. 118—122° C, raised to 125.5—127° C on recrystallization from benzene-methanol: NMR ($CDCl_3$) δ 7.2—7.8, m, 20H(aryl); 4.46, 4.01, *AB*, 2H, *J* 5 Hz (CH—CH); 2.97 ppm, s, 3H(OMe). Found: C, 68.56; H, 5.45. $C_{27}H_{25}BrOSi$ calcd.: C, 68.49; H, 5.32%.

A similar treatment of the bromination product from 0.1 g (0.27 mmol) of *cis*-β-triphenylsilylstyrene, in 10 ml of methanol gave 0.11 g (85%) of methoxy derivative m.p. 135—139° C, raised to 140—142° C by recrystallization from methylene chloride/pentane: NMR ($CDCl_3$) δ 7.2—7.8, m, 20H, (aryl), 4,15, s, 2H (CH—CH), 2.70 ppm, s, 3H(OMe): NMR (DMSO) δ 7.2—7.8 (aryl), 4.56,

4.10 ppm, *AB*, 2H, *J* 9 Hz. Found: C, 68.44; H, 5.47. $C_{27}H_{25}BrOSi$ calcd.: C, 68.49; H, 5.33%.

(E)-1-Triphenylsilyl-1-methyl-2-phenylethene (X)

(a) By methylation. A solution of 0.32 g (0.73 mmol) of bromostyrene VII in 20 ml of ether at −23°C was treated with 0.50 ml (0.80 mmol) of n-butyllithium solution. The solution turned yellow immediately, and after 30 min an excess of methyl iodide was added. After 4 h at −23°C, when the yellow colour had faded, aqueous acidic work up and recrystallization from hexane gave 0.22 g (81%) of pure material, m.p. 180—181°C: NMR ($CDCl_3$) δ 7.1—7.8, m, 20H-(aryl); 6.96, q, 1H, *J* 1.5 Hz (CH); 2.10 ppm, d, 3H, *J* 1.5 Hz (CH_3). Found: C, 86.03; H, 6.26. $C_{27}H_{24}Si$ calcd.: C, 86.12; H, 6.42%.

The same product was obtained when the isomeric bromostyrene VIII was used.

(b) By hydrosilylation. A solution of 2.60 g (0.01 mol) of triphenylsilane in 1.28 g (0.011 mol) of 1-phenylpropyne was heated in an oil bath to 130°C. Addition of 1 drop of a saturated solution of chloroplatinic acid in propanol led to darkening, and after 10 min the solution solidified. An NMR spectrum indicated a 2 : 1 ratio of (*E*)-1-triphenylsilyl-1-methyl-2-phenylethene (X) and (*E*)-1-triphenylsilyl-2-methyl-1-phenylethene, respectively. Recrystallization from benzene/methanol and then from methylene chloride-pentane gave 1.26 g (35%) of pure (*E*)-1-triphenylsilyl-1-methyl-2-phenylethene, m.p. 180—181°C, identical to the product described above.

Several recrystallizations from heptane of the material in the methylene chloride/pentane mother liquors led to 0.20 g (6%) of pure (*E*)-1-triphenylsilyl-2-methyl-1-phenylethene, m.p. 176—178°C: NMR ($CDCl_3$) 6.8—7.6, m, 20H, (aryl), 6.76, q, 1H, *J* 6.5 Hz; 1.69 ppm, d, 3H, *J* 6.5 Hz(Me). Found: C, 86.01; H, 6.37. $C_{27}H_{24}Si$ calcd.: C, 86.12; H, 6.42%.

Preparation of trans-1-triphenylsilyl-2-t-butylethylene

A solution of triphenylsilane (2.60 g, 0.010 mol) and 3,3-dimethyl-1-butyne (2.16 g, 0.026 mol) and 1 drop of a saturated solution of chloroplatinic acid in 2-propanol was heated at reflux for 2 h. The mixture was cooled and the resultant brown solid was recrystallized from methylene chloride/methanol to give 2.51 g (73%) of the desired product, m.p. 82—84°C. Recrystallization for the same solvent gave m.p. 84—85°C. Found: C, 84.32; H, 7.44. $C_{24}H_{26}Si$ calcd.: C, 84.15; H, 7.65%.

Acknowledgement

This research was supported by the National Research Council of Canada and by the Dow Corning Corporation through a Fellowship to J.M.D. A.G.B. wishes to acknowledge the hospitality of Professor Colin Eaborn and the School of Molecular Sciences, University of Sussex, during a Sabbatical leave where part of this research was performed.

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