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**Preliminary communication**

# *syn*-BROMINATION OF *trans*-TRIPHENYLSILYLSTYRENE AND ITS *anti*-DEBROMOSILYLATION

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## Summary

Bromination of the triphenylsilylstyrenes occurs with *syn(cis)*-stereochemistry, as does debromination of the dibromide with zinc, but debromosilylation occurs with *anti(trans)*-stereochemistry.

It has been suggested previously [1], perhaps somewhat unexpectedly, that the bromination of *trans*-trimethylsilylstyrene occurs with *syn*-stereochemistry, and that debromosilylation of the dibromide occurs with *anti*-stereochemistry. We wish to confirm these proposals in the light of work done with *trans*-triphenylsilylstyrene. *trans*-Triphenylsilylstyrene [2] gives on bromination in chloroform at 0°C or in $CH_2Cl_2$ at −78°C a single crystalline dibromide, m.p. 129—130°C, after recrystallization from $CH_2Cl_2$, NMR ($CDCl_3$) $\delta$ 7.2—7.8 (m, 20 H, aryl) 4.50, 5.52, (m AB, 2 H ($J$ 6 Hz) CH—CH) ppm. A carefully grown crystal of this material was submitted to X-ray structure analysis**, which showed unambiguously that the compound had the *threo*-configuration I resulting from *syn(cis)*-bromination*** (Fig. 1). Treatment of the dibromide with zinc in acetic acid/ether gave pure recovered *trans*-triphenylsilylstyrene, m.p. 154—155°C in near quantitative yield resulting from *syn*-elimination with no evidence of the *cis*-isomer. Dissolution of the dibromide in dry DMSO in an NMR tube showed that during 20 h at 25°C complete debromosilylation involving *anti*-elimination occurred to yield pure

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**The crystals are triclinic, space group $A\bar{1}$, with $a$ 15.83, $b$ 28.24, $c$ 10.51 Å, $\alpha$ 89.9°, $\beta$ 84.1°, $\gamma$ 81.2°, $Z = 8$. $R = 0.063$ based on 2210 reflexions (Cu-$K_\alpha$, absorption correction) with $I_{obs} > 3\sigma(I_{obs})$. The asymmetric unit contains two crystallographically non-equivalent but enantiomeric molecules.

***Full details of the crystal structure will be published later by PH and RM.

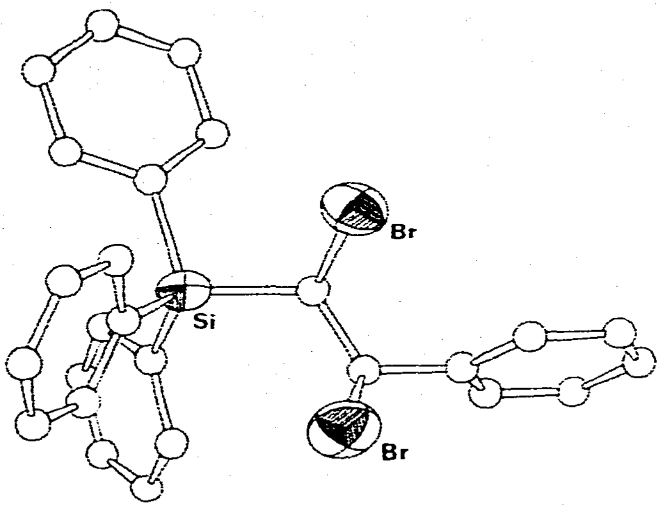
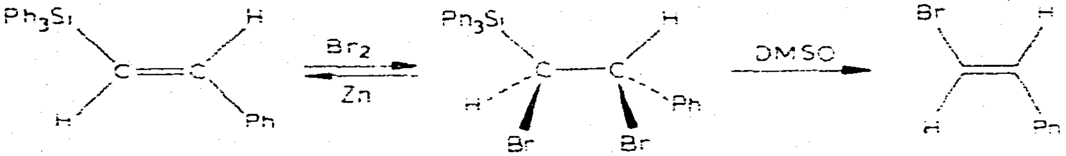


Fig. 1. Structure of the bromination product of *trans*-triphenylsilylstyrene.

*trans*-β-bromostyrene (no *cis* material could be detected) and hexaphenyldisiloxane, isolated in 80% yield, m.p. 223–224°C.

The results establish the following stereochemistry as occurring, and completely confirm the proposals of Koenig and Weber regarding related reactions of the trimethylsilylstyrenes.



(I)

*cis*-Triphenylsilylstyrene synthesized by partial hydrogenation of triphenylsilylphenylacetylene [3] gave an isomeric dibromide, m.p. 122–124°C, NMR ($CDCl_3$) δ 7.1–7.7 (m, 20 H, aryl), 4.81, 5.46 (m, AB, *J* 6.5 Hz) CH—CH) ppm, which on debromination gave a 56:44 mixture of *cis*- and *trans*-triphenylsilylstyrene respectively, and which gave on treatment with DMSO pure *cis*-β-bromostyrene.

Further results obtained with these and other vinylsilanes will be given in the full paper.

## References

1 K.E. Koenig and W.P. Weber, Tetrahedron Lett., (1973) 2533.
2 R.A. Benkeser and R.A. Hickner, J. Amer. Chem. Soc., 80 (1958) 5298.
3 H. Gilman, A.G. Brook and L.S. Miller, J. Amer. Chem. Soc., 75 (1973) 3757.