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THE REACTION OF BROMINE WITH CIS AND TRANS-β-TRIMETHYLSILYL STYRENE

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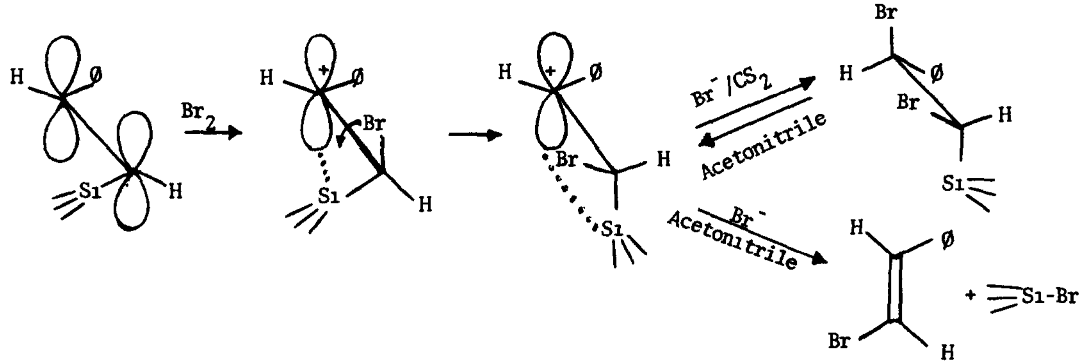
While the reactions of aryl trimethylsilanes with electrophiles have been extensively studied,[1] the reactions of vinyl silanes with electrophiles have been examined in much less detail.[2] We have been interested in the reaction of β-trimethylsilylstyrene with bromine since it exhibits an unusually high degree of stereospecificity for an ionic reaction. The reaction of bromine with trans-β-trimethylsilylstyrene at -20°C in CCl_4 has been reported to yield largely trans-β-bromostyrene.[3] We find that trans-β-trimethylsilylstyrene[4] reacts with bromine in CS_2 at -100°C to yield a dibromo adduct. Once formed this adduct can be warmed to room temperature where it is stable for several hours. Addition of acetonitrile to the dibromo adduct of trans-β-trimethylsilylstyrene causes an elimination reaction to occur the products of which are trimethylbromosilane and pure trans-β-bromostyrene.[4] Likewise, cis-β-trimethylsilylstyrene[4] reacts with bromine at -100°C in CS_2 to form a dibromo adduct which can be warmed to room temperature. Addition of acetonitrile to the dibromo adduct of cis-β-trimethylsilylstyrene results in an elimination reaction to yield trimethylbromosilane and a mixture consisting largely of cis-β-bromostyrene contaminated with a small amount of trans-β-bromostyrene. The stereochemical purity of the β-bromostyrene products was determined by nmr on a Varian HA-100 and by gplc on a Ucon 550 column at 195°

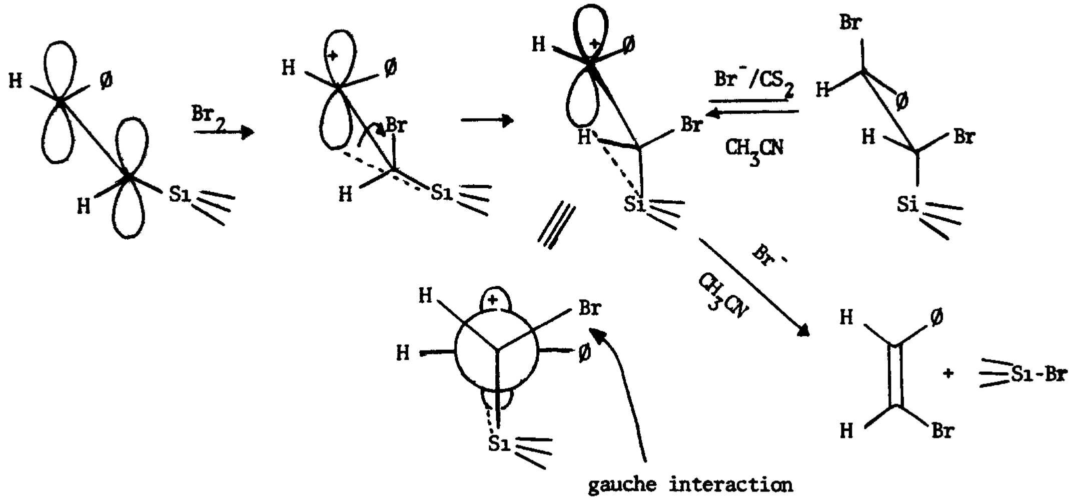
The following mechanism can explain these results. Simultaneously with attack of bromine on the double bond rotation occurs about the developing carbon-carbon single bond in such a direction to permit the trimethylsilyl group to continuously stabilize the benzylic carbonium ion center by bridging[5,6] or by hyperconjugation[7] of the Si-C sigma bond. Rotation in the opposite direction would bring the trimethylsilyl group into the nodal plane of the developing carbonium ion center, and so would not permit continuous stabilization of the carbonium ion center by the trimethylsilyl group. It is well established that a trimethylsilyl group is better able to stabilize a carbonium ion center beta to it than a bromine atom.[8,9] Attack by the nucleophilic bromide anion now occurs on the carbon of the benzylic carbonium ion from the topside, since the bridging trimethylsilyl group is blocking attack on the bottom side. This will result in a cis addition of bromine. Ionization of the benzylic bromide in acetonitrile is assisted by backside participation of the trimethylsilyl group. Attack by the nucleophilic bromide anion can now occur either on the benzylic carbon to reform the cis-dibromo adduct or on silicon leading to trimethylbromosilane and trans-β-bromostyrene. Trans elimination of trimethylbromosilane from erythro-1,2-dibromopropyltrimethylsilane under solvolytic conditions has been observed by Jarvie.[10,11]



The fact that the dibromo adduct of cis-β-trimethylsilylstyrene yields a mixture consisting predominantly of cis-β-bromostyrene contaminated with small amounts of trans-β-bromostyrene may be explained in two ways. Certainly cis-β-bromostyrene is easily isomerized to the thermodynamically more stable trans isomer. In reactions run to low conversion (30%) with triethylamine added to capture any extraneous acid, pure cis-β-bromostyrene and starting dibromoadduct were the only species observed by nmr. Less than 2% trans-β-bromostyrene would have been detected. Reactions run to 100% conversion with no triethylamine added result in 85% cis-β-bromostyrene and 15% trans β-bromostyrene. On the other hand, ionization of the benzylic bromide assisted by backside participation of the trimethylsilyl group leads to an ion having significant gauche interactions between the bromine and the phenyl as well as between the trimethylsilyl group and the phenyl in the case of the cis dibromo adduct. Possibly this additional gauche interaction in the cis compound is sufficient to destabilize the silyl bridged benzylic carbonium ion compared to an open benzylic carbonium ion leading to the small amount of trans-β-bromostyrene observed.

Bridging trimethylsilyl groups which stabilize a beta carbonium ion center have been observed.

One of the most elegant examples was reported by Eaborn and Jarvie.[5,6] Reisolation of unreacted starting material from the partial solvolysis of 2-bromo-2,2-dideuterio-1-trimethylsilylethane yields material in which the deuterium has been extensively scrambled between C_1 and C_2.



References

1. C. Eaborn and R.W. Bott, "Organometallic Compounds of the Group IV Elements", Vol.I, A. MacDiarmid, Ed. Marcel Dekker, New York, N.Y., 1968, Chapter 2, pp. 407-435
2. Ibid. Chapter 2, pp. 392-395
3. J.H. Eisch and M.W. Foxton, J. Org. Chem., 36, 3520 (1971).
4. D. Seyferth, L.G. Vaughan, and R. Suzuki, J. Organomet. Chem., 1, 437 (1964).
5. M.A. Cook, C. Eaborn, and D.R.M. Walton, J. Organomet.,Chem., 24, 301 (1970).
6. A.J. Bourne and A.W.P. Jarvie, J. Organomet. Chem., 24, 335 (1970).
7. T.G. Traylor, W. Hanstein, MJ. Berwin, N.A. Clinton, and R.S. Braun, J.Am.Chem.Soc., 93, 5715 (1971).
8. L.H. Sommer and G.A. Braughman, J. Am. Chem. Soc., 83, 3346 (1961).
9. A. Streitwiesrer Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962 pp. 120-126
10. A.W.P. Jarvie, A. Holt, and J. Thompson, J.Chem.Soc. (B) 852 (1969).
11. An alternative mechanism *trans* addition of Br_2 followed by *cis* elimination of trimethylbromosilane, while not favored can not be absolutely eliminated.

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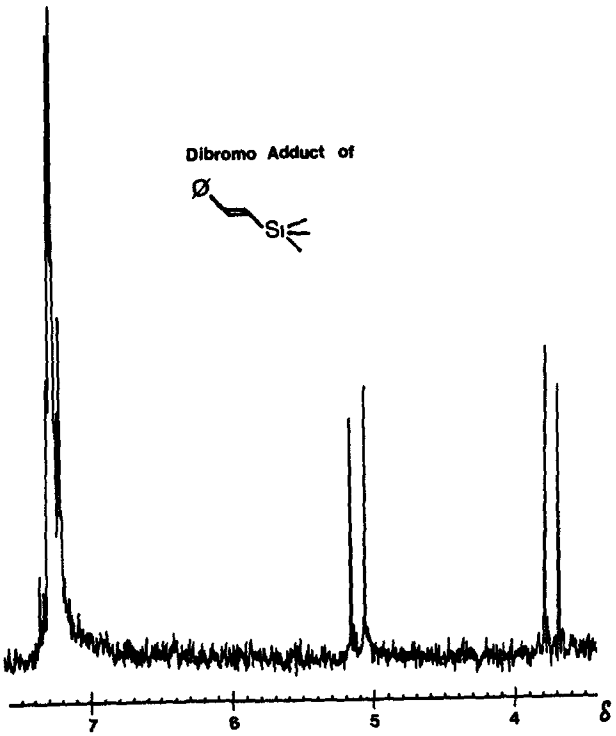
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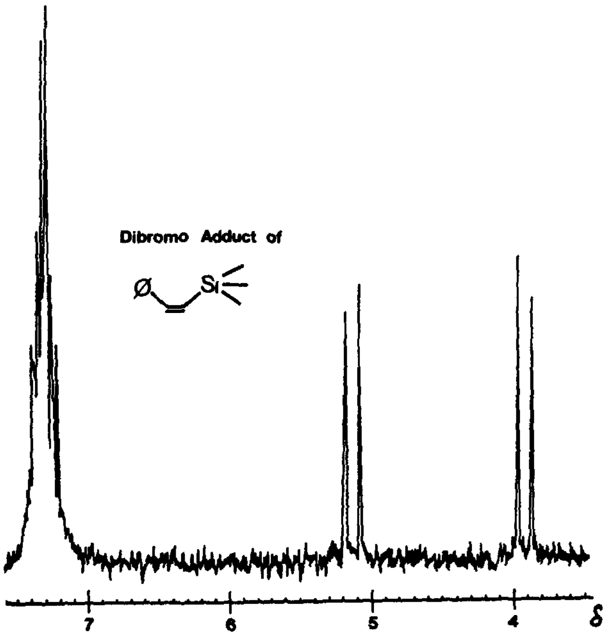
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