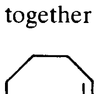
The Reaction between Bromine and (*E*)-1-Trimethylsilylcyclo-octene

Dashyant Dhanak, Colin B. Reese,* and David E. Williams

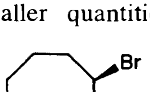
Department of Chemistry, King's College, Strand, London WC2R 2LS, U.K.

When (*E*)-1-trimethylsilylcyclo-octene (**4**) is treated with bromine in dichloromethane solution at −78 °C and the products are allowed to warm up to room temperature, (*Z*)-1-bromocyclo-oct-4-ene (**5**) is obtained and can be isolated in *ca.* 70% yield.

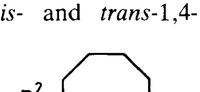
A number of years ago, we found[1] that (*Z*)-cyclo-octene (**1**) reacted with bromine in dichloromethane solution to give *trans*-1,2-dibromocyclo-octane (**2**) as the main product together with smaller quantities of *cis*- and *trans*-1,4-dibromocyclo-octanes [(**3a**) and (**3b**), respectively]. The isolated yields of (**2**), (**3a**), and (**3b**) were 73, 14, and 8%, respectively, when the reaction was carried out at −10 °C, and 51, 26, and 12%, respectively, when the reaction was carried out at −95 °C. We now report that when (*E*)-1-trimethylsilylcyclo-octene[2] (**4**) is treated with bromine† in dichloromethane solution at −78 °C and the products are



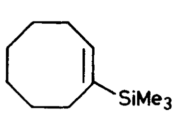
(**1**)



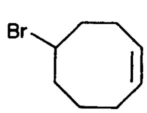
(**2**)



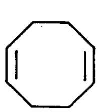
(**3**) a; $R^1 = Br, R^2 = H$
b; $R^1 = H, R^2 = Br$



(**4**)



(**5**)



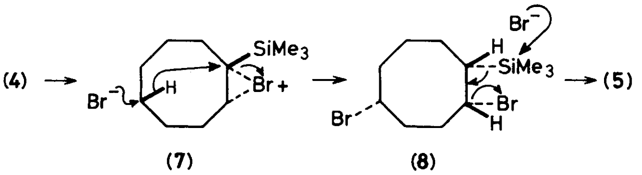
(**6**)

---

† The following experimental procedure was followed. A solution of bromine (8.7 g, 54.8 mmol) in dry dichloromethane (50 ml) was added dropwise over a period of 30 min to a stirred solution of (**4**) (10.0 g, 54.4 mmol) in dichloromethane (50 ml), maintained at −78 °C (acetone–dry ice bath). The products were allowed to warm up to room temperature and were then washed with saturated aqueous sodium hydrogen carbonate (100 ml). The organic layer was dried ($MgSO_4$), evaporated under reduced pressure, and then distilled to give (**5**) (7.5 g), b.p. 84—85 °C/14 mmHg; $\delta_C(CDCl_3)$ 25.37, 25.47, 27.22, 37.16, 39.91, 55.27, 129.31, 129.55; M^+: found, 188.0195 (calc. for $C_8H_{13}{}^{79}Br$, 188.0200).

allowed to warm up to room temperature, (*Z*)-1-bromocyclo-oct-4-ene (**5**) is obtained as virtually the only distillable medium ring product,‡ in *ca.* 70% isolated yield.

The (*Z*)-1-bromocyclo-oct-4-ene (**5**) obtained was identical (^{1}H and ^{13}C n.m.r. and i.r. spectra, g.c.) to authentic material prepared[3] by treating (*Z,Z*)-cyclo-octa-1,5-diene (**6**) with hydrogen bromide in acetic acid. A possible mechanism for the conversion of (**4**) into (**5**) is indicated in outline in Scheme 1. Although halogenodesilylation of vinylsilanes is a well documented reaction,[4] we are unaware of any previously reported example of transannular halogenodesilylation in the literature. The observed product (**5**) can result from an intermediate bromonium ion (**7**) following either a 1,4- or a 1,5-hydride shift on to the carbon atom bearing the trimethylsilyl group. As only 1,3- and 1,5-hydride shifts are believed to occur[5] in the solvolysis of *cis*-cyclo-octene oxide, a mechanism involving a 1,5-hydride shift (as illustrated in Scheme 1) would appear to be more likely.



Scheme 1

Other noteworthy features of the proposed mechanism for the conversion of (**4**) into (**5**) are the hydride shift being directed on to the carbon atom bearing the trimethylsilyl group, and the conversion of the putative intermediate (**8**) into (**5**) involving *syn*-elimination of trimethylsilyl bromide. *anti*-Elimination from an *erythro*-cyclo-octane system, leading to an (*E*)-cyclo-octene derivative, would be expected[6] to be much less favourable. Finally, our clear-cut observation that the transannular addition of bromine to (**4**) leads to a (*Z*)-cyclo-octene derivative must cast doubt on the recent conclusion[7] that the acid-catalysed hydrolysis and methanolysis of (*E*)-1-trimethylsilylcyclo-octene oxide leads to (*E*)- rather than to (*Z*)-cyclo-octene derivatives. The presence of bands at 985 cm^{-1} in the i.r. spectra[8] of the latter compounds cannot be regarded as firm evidence for their being (*E*)-cyclo-octene derivatives as (**5**) itself has a band at 989 cm^{-1} in its i.r. (film) spectrum.

One of us (D. D.) thanks the Science and Engineering Research Council for the award of a research studentship.

Received, 4th May 1984; Com. 619

---

‡ In contrast to the reaction between bromine and (*Z*)-cyclo-octene (**1**) proceeding mainly by direct addition[1] [to give (**2**)], there is no clear evidence that the reaction between bromine and (*E*)-1-trimethylsilylcyclo-octene (**4**) leads to the formation of any direct adduct [which would presumably be converted into (*E*)-1-bromocyclo-octene]. However, this matter is difficult to establish with certainty as we have been unable to obtain a sample of (**4**) which is not contaminated with at least *ca.* 3% of (*E*)-1-bromocyclo-octene, its synthetic precursor.[2] (*Z*)-1-Bromocyclo-oct-4-ene (**5**), obtained from (**4**), appears (g.c., ^{13}C n.m.r. spectrum) to be somewhat less contaminated with (*E*)-1-bromocyclo-octene than the starting material (**4**) itself.

References

1 M. S. Baird, C. B. Reese, and M. R. D. Stebles, *J. Chem. Soc., Chem. Commun.*, 1971, 1340.
2 G. Nagendrappa, *Synthesis*, 1980, 704.
3 K. Ziegler and H. Wilms, *Liebigs Ann. Chem.*, 1950, **567**, 1.
4 I. Fleming, in 'Comprehensive Organic Chemistry,' vol. 3, ed. D. N. Jones, Pergamon, Oxford, 1979, p. 619 *ff.*; E. W. Colvin, 'Silicon in Organic Synthesis,' Butterworths, London, 1981, p. 63 *ff.*
5 A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Am. Chem. Soc.*, 1960, **82**, 6366.
6 J. Sicher, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 200.
7 G. Nagendrappa, *Tetrahedron*, 1982, **38**, 2429.
8 L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1954, p. 40.