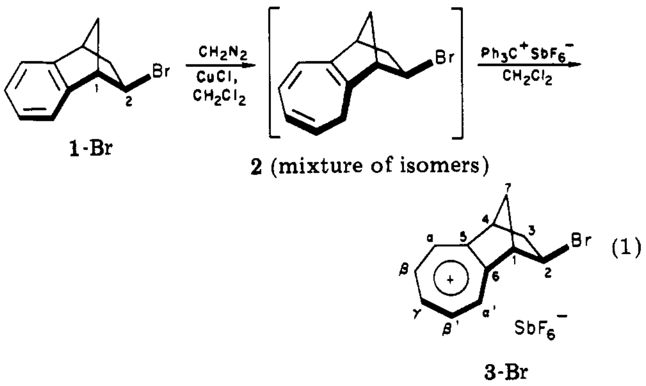
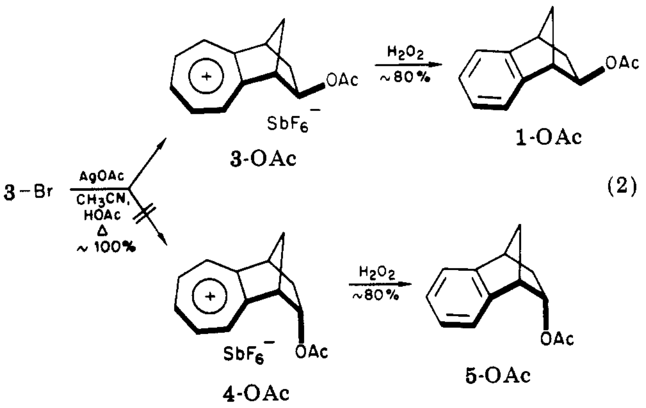
hexafluoroantimonate salt 3-Br (eq 1). Thus, in a typical preparation, a mixture of *exo*-2-bromobenzonorbornene (1-Br,[6] 0.60 g, 2.7 mmol) and copper(I) chloride (freshly prepared, 30 mg) in dry methylene chloride (10 mL) was treated at room temperature with gaseous diazomethane (**CAUTION: carcinogen and explosion danger**) generated from *N*-nitrosomethylurea (3 g).[7] The heterogeneous material was filtered to remove solids and the mixture of tropilidenes 2[8] treated with trityl hexafluoroantimonate[7] in further methylene chloride (20 mL). After having stood at room temperature overnight, the material was diluted with ether–hexane (1:1), v/v, 75 mL) to precipitate 3-Br. Dissolution in dry methylene chloride and reprecipitation with ether–hexane was repeated until no further physical change in 3-Br was observed, 125 mg (40% yield based upon 25% conversion of 1-Br to 2). The salt is a white, microcrystalline solid; mp 173 °C; UV λ_{max} (CH_3CN) 223 (log ϵ 4.41), 281 (br, log ϵ 3.68), 300 (sh, log ϵ 3.64) nm; ^1H NMR (CD_3CN) δ (Me_4Si) 9.03 (near s, 5, tropenium Hs), 4.27 (sharp m, 1, CHBr), 4.07 (m, 2, H-1, 4), 2.67–2.30 (series of sharp m, 4, H-6, 7); ^{13}C NMR (CD_3CN), δ(Me_4Si) 179.3 (C-6), 173.9 (C-5), 154.5 (α'), 154.2 (α), 150.2 (γ), 148.5 (β'), 147.4 (β), 59.6 (C-1), 51.3 (C-4), 48.3 (C-7), 44.7 (C-2), 37.4 (C-3); IR (3% in KBr, ±3 cm^{-1}), 3140 w, 3090 w, 3020 m, 2950 w, 1560 w, 1450 s, 1340 w, 1300 m, 1280 m, 1270 m, 1250 sh, 1240 m, 1140 m, 1120 w, 980 m, 960 m, 910 m, 870 w, 800 w, 750 m, 720 m.



(1)

In contrast to 1-Br which reacted immediately,[6] 3-Br gave a precipitate with alcoholic silver nitrate very slowly at 25 °C. Reaction of 3-Br with silver acetate (each 0.0125 M) in dry acetic acid–acetonitrile (3:1, v/v) was followed kinetically[9] at 30.5 °C, 56 °C, and 76 °C, affording titrimetric rate constants 10^5k ($M^{-1}\ s^{-1}$) = 3.71 ± 0.08, 73.7 ± 1.3, and 377 ± 17, respectively. The calculated activation parameters were $\Delta H^{\ddagger} = 20.9 \pm 0.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.9 \pm 2.8$ eu. Treatment of the acetolyzed reaction material with excess hydrogen peroxide (30%)[11] produced *only* exo-2-acetoxybenzonorbornene (1-OAc).[12] The reactions are shown in eq 2. Synthesis of *exo*- and *endo*-2-acetoxytropenonorbornene hexafluoroantimonates (3-OAc and 4-OAc, respectively) was accomplished from the corresponding benzo analogues[14] in the same way as was 3-Br. Their oxidation with hydrogen peroxide re-formed the benzo esters in good yield. Control studies showed that small amounts of 4-OAc (~1–2%) were readily detected in mixtures with 3-OAc by this oxidation technique followed by GLPC analysis.



(2)

To our knowledge these results are the first reported on the solvolysis of tropenium-related benzonorbornene substrates. To make any mechanistic comparison of the two systems is premature at this point and we resist the strong temptation to do so. Nonetheless it is clear that solvolytic data *can*[15] be obtained on such charged aromatic analogues and that product formation *can* be stereospecific. Intensive further work is in progress.

Acknowledgment. We thank the Loyola Research Committee for financial support of this work.

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Received April 5, 1984

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[5] This name was chosen in order to relate the tropenium ion and benzo cases. Its more orthodox name would be *exo*-5-bromo-1,2-bicyclo[2.2.1]heptenotropenium hexafluoroantimonate. The numbering system used was likewise selected to make the analogy more apparent.

[6] Wilt, J. W.; Chenier, P. J. *J. Org. Chem.* **1970**, *35*, 1562.

[7] The procedure used was that developed for the parent system by Thummel, R. P.; Chayangkoon, P. *J. Org. Chem.* **1983**, *48*, 596.

[8] As did Thummel and Chayangkoon,[7] we expanded 1-Br to 2 to the extent of only 20–25% (GLPC and ^1H NMR monitoring). Several isomers of 2 were evident but no detailed characterization was performed.

[9] No pretense is made that the kinetic data determined is uncomplicated. Silver ion mediated solvolyses are complex, with reactivity orders resembling those commonly associated with limiting solvolysis (S_N1).[10] However, silver ion (as the soluble salt) and silver bromide (as precipitated) undoubtedly enter the mechanism. The data given are therefore those from a second-order plot of the titrimetric data. Reaction in trifluoroacetic acid–acetonitrile (3:1, v/v) was dramatically *slower*.

[10] Gould, E. S. "Mechanism and Structure in Organic Chemistry"; H. Holt and Co.; new York, 1959; pp 273–274.

[11] Volpin, M. E.; Kursanov, D. N.; Dulova, V. G. *Tetrahedron* **1960**, *8*, 33. This reaction led to 1-Br from 3-Br in high yield (~80%).

[12] Prepared from the exo alcohol[13] and confirmed by comparison with reported material (Wilt and Chenier, ref 2).

[13] Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240.

[14] Ester 5-OAc was prepared from the endo alcohol.[13] Acetates 4-OAc and 5-OAc are readily distinguishable by GLPC (Carbowax 20 M, 180 °C) and by the δ values of their CHOAc resonances (1-OAc, 4.60 br t; 5-OAc, 5.15 dt). The tropeno salts 3-OAc and 4-OAc are similarly distinguishable by NMR. Their full characterization will be given later in the full paper.

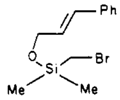
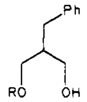
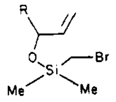
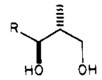
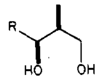
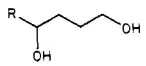
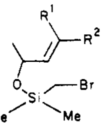
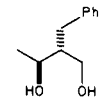
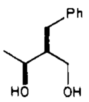
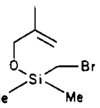
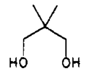
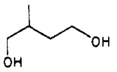
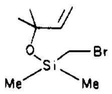
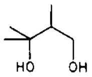
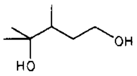
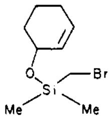
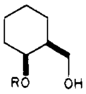
[15] This report is dedicated to those anonymous referees of a research proposal who doubted this fact.

Silylmethyl Radical Cyclization: New Stereoselective Method for 1,3-Diol Synthesis from Allylic Alcohols

Summary: Cyclizations of (bromomethyl)dimethylsilyl allylic ethers by treatment with tri-*n*-butyltin hydride in a free-radical process followed by oxidation in a one-pot manner with hydrogen peroxide gave the corresponding 1,3-diols predominantly with high stereoselectivity.

Sir: Free-radical cyclization has been currently visualized as a new potent methodology for ring construction via C–C bond-forming processes.[1] However, further development

Table I. Synthesis of 1,3-Diols from (Bromomethyl)dimethylsilyl Allyl Ethers[a]

run	substrate 1	yield,[b] %	products [ratio,[c] %]		
					
1	1a	85	3a, R = H [100]		
2	1a	80	3b, R = Ac [100][d]		
					
3	1b, R = Me	95	3c [69]	3d [15]	4a [16]
4	1c, R = *i*-Pr	90	3e [82]	[~0]	4b [18]
5	1d, R = *t*-Bu	91	3f [71]	[0]	4c [29]
6	1e, R = CH$_2$=CH	85	3g [61]	3h [11]	4d [28]
7	1f, R = Ph	88	3i [54]	3j [5]	4e [41]
					
8	1g, R^1 = H; R^2 = Ph	85	3k [84]	3l [16]	
9	1h, R^1 = Ph; R^2 = H	94	3k [100]	3l [0]	
					
10	1i	52	3m [35]		4f [65]
					
11	1j	83	3n [91]		4g [9]
					
12	1k	75	3o, R = H [100]		
13	1k	76	3o, R = Ac[100][d]		

[a] To a solution of 1 (2 mmol) in 36 mL of benzene was added dropwise a mixture of *n*-Bu$_3$SnH (1.2–1.5 mmol) and AIBN (0.03 mmol) in 4 mL of benzene at reflux over a 2-h period followed by heating for an additional 1–2 h. The reaction can be carried out in 0.025–0.05 M solution. After evaporation of benzene under reduced pressure (under atmospheric pressure for 3, 4, 6, 10, and 11), the residual oil was treated with 1.2 mL of 30% H$_2$O$_2$ (method A) in 5 mL of DMF and KF (10 mmol) at 60 °C for 7–8 h (run 1, 2, 7, 8, and 9) or (method B) in 3 mL of MeOH and 3 mL of THF and Na$_2$CO$_3$ (2 mmol) at reflux for 5 h (run 3–6 and 10–13). After the usual workup, purification was achieved by column chromatography (silanized SiO$_2$, Merck 7719; ether–hexane). Structures were determined by ^{1}H NMR (90 MHz) after purification of HPLC. Stereochemical assignment of the 1,3-diols for runs 3–9 was determined by ^{1}H NMR data of the diols and their ketals; see supplementary material for their spectral data. For run 12, the cis configuration was assumed since the diol was not identical with the trans product from the Prins reaction with cyclohexene; see ref 8. [b] Isolated yields. [c] After separation of 1,4-diols, the ratio was determined by HPLC of their ketals with acetone and cyclohexanone (run 3, 8, and 9), ^{1}H NMR of a mixture of 1,3-diols (run 7, see ref 7), or ^{1}H NMR of the benzoates of a mixture (run 4 and 6). [d] Acetylation was performed with acetic anhydride in pyridine and KF at 40 °C for 2 days.

and variations could add considerably to its usefulness to synthetic problems. Our attention was given to the possibility of intramolecular cyclization of silylmethyl radical species (α-silyl radical) to unsaturated function, since it has been elaborated by Wilt that the halogen abstraction of α-halosilanes is considerably enhanced in radical chain sequence.[2] A new oxidation method of the Si–C bond[3] also prompted subsequent oxidative cleavage of cyclization products, silacycles, to diols.

We report here a new approach to the synthesis of 1,3-diols, one basic substructure in several natural polyols, by formal "hydro-hydroxymethylation" of allylic alcohols via silylmethyl radical cyclization followed by oxidative cleavage of a Si–C bond.

Starting silyl ethers 1 were obtained in good yields upon treatment of allylic alcohols and (bromomethyl)di-

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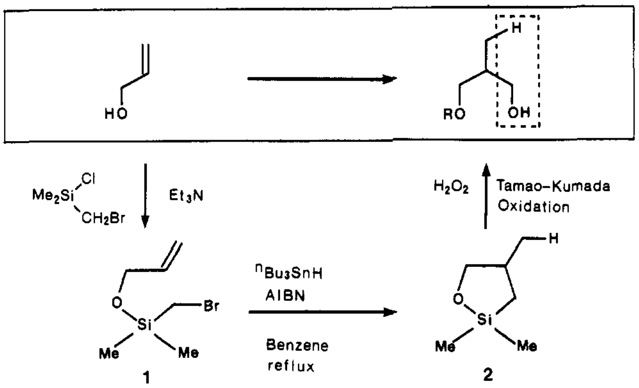
(1) (a) Beckwith, A. L. J. *Tetrahedron*, **1981**, *37*, 3073. (b) Stork, G.; Sher, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6765 and references cited therein. (c) Ueno, Y.; Chino, K.; Watanabe, M.; Moriya, O.; Okawara, M. *Ibid.* **1982**, *104*, 5564. (d) Hart, D. J.; Tsai, Y.-M. *Ibid.* **1982**, *104*, 1430. (e) Choi, J.-K.; Hart, D. J.; Tsai, Y.-M. *Tetrahedron Lett.* **1982**, *23*, 4765. (f) marinovic, N. N.; Ramanathan, H. *Ibid.* **1983**, *24*, 1871. (g) Okabe, M.; Abe, M.; Tada, M. *J. Org. Chem.* **1982**, *47*, 1775. (h) Danishefsky, S.; Chackalamannil, S.; Uang, B.-J. *Ibid.* **1982**, *47*, 2231. (i) Nagashima, H.; Wakamatsu, H.; Itoh, K.; Tomo, Y.; Tsuji, J. *Tetrahedron Lett.* **1983**, *24*, 2395.

(2) Wilt, J. W.; Belmonte, F. G.; Zieske, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 5665.

(3) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2120.



methylchlorosilane in dichloromethane at room temperature for several hours with triethylamine. The silyl ether **1** was subjected to reaction with tri-*n*-butyltin hydride (1.2 equiv) and AIBN (0.03 equiv) in benzene under reflux, affording the corresponding cyclization products, which gave 1,3-diol **3** predominantly by Tamao–Kumada oxidation[3] (Table I).

Consequently, the cyclization of the silylmethyl radical has proved to be successful. The 5-exo mode cyclization predominates, but the 6-endo mode can also be observed for the allylic systems without terminal functionality to give 1,4-diols (runs 3–7, 10, and 11).[5] The stereochemical advantages of the cyclization led us to the selective formation of 2,3-threo-1,3-diols derived from the obtained trans-3,4-disubstituted 1-sila-2-oxacyclopentane **2** (runs 3–9).[6] Steric influence of the 1-substituent of the allylic skeleton is clear for increasing the threo formation. A terminal Z-phenyl function leads to exclusive formation of the threo diol (run 9). Bicyclic ring formation for run 12 is noteworthy in giving only the cis-fused product, which is converted to the cis-1,2-substituted cyclohexane **3o**. These regio- and stereochemical results parallel ones obtained in a related carbocyclic system reported by Stork.[1b]

Survival of one vinyl group for **1e**, without undesirable two-stage cyclization or other chain reaction, is important in that further homologation will be possible.

The practical usefulness of this cyclization lies not only in the one-pot procedure but also in differentiation of the diol functions by monoacetylation prior to the oxidation (runs 2 and 13).

Thus we have disclosed a new stereoselective approach to 1,3-diol synthesis. Further studies on its scope and limitations are currently underway.

Acknowledgment. We thank Dr. Kohei Tamao of Kyoto University for his advice about the oxidation method. H. N. is indebted to the Ministry of Education, Science and Culture for a Grant-in-Aid (No 58740227).

Registry No. **1a**, 90106-90-4; **1b**, 90106-91-5; **1c**, 90106-92-6; **1d**, 90106-93-7; **1e**, 90106-94-8; **1f**, 90106-95-9; **1g**, 90106-96-0; **1h**, 90106-97-1; **1i**, 90106-98-2; **1j**, 90106-99-3; **1k**, 90107-00-9; **3a**, 2612-30-8; **3b**, 90107-01-0; **3c**, 16897-85-1; **3d**, 16897-83-9; **3e**, 3876-47-9; **3f**, 90107-02-1; **3g**, 90107-03-2; **3h**, 90107-04-3; **3i**, 7087-77-6; **3j**, 14366-91-7; **3k**, 90107-05-4; **3l**, 90107-06-5; **3m**, 126-30-7; **3n**, 24893-35-4; **3o** (R = H), 4187-60-4; **3o** (R = Ac), 17373-51-2; **4a**, 626-95-9; **4b**, 38624-36-1; **4c**, 38624-38-3; **4d**, 41324-11-2; **4e**, 4850-50-4; **4f**, 2938-98-9; **4g**, 63521-36-8.

Supplementary Material Available: Typical procedures and NMR spectra for **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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Received February 24, 1984

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(4) The silyl ether **1** was purified by distillation after filtration and concentration. Column chromatography can be employed with SiO_2.

(5) Hart discribed the similar effect of olefin substitution in azacyclic systems; however, the problem remains to be solved whether the kinetic behavior or the relative thermodynamic stabilities of the included radical species is attributable.

(6) For nomenclature of threo and erythro, see: Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106.

(7) Canceill, J.; Jacques, J. *Bull. Soc. Chim. Fr.* **1970**, 2180.

(8) Kovacs, G.; Szekely, I.; Simonidesz, V.; Tomoskozi, I.; Grubber, L. *Tetrahedron Lett.* **1976**, 4639 and references cited therein.