stirring bar and reflux condenser, if required, was charged with the hydroxide base (0.01 mol), which has been powdered, MeCN (10 mL), benzaldehyde (0.01 mol), 18-crown-6 (if used), and cumene (ca. 0.00375 mol), which was used as the internal standard. The suspension was stirred at the indicated temperature under an atmosphere of dry N_2. After the given period of time, an aliquot was removed and analyzed (GLC, comparison with a standard solution). For experiments conducted at reflux (83 ± 3 °C), the reaction vessel was immersed in an oil bath maintained at ca. 100 °C, and the aliquot was immediately frozen in liquid nitrogen until GLC analysis could be performed.

General Procedure for the Hydrogenation of α,β- and β,γ-Unsaturated Nitriles. A thick-walled hydrogenation bottle (473 mL) was charged with 95% ethanol (10 mL), Pd catalyst (5–10% on carbon, 1 g %) and the unsaturated nitrile (0.01 mol). The mixture was then shaken under 2–3 atm of H_2 in a Parr apparatus at ambient temperature until H_2 consumption ceased. The crude reaction mixture was filtered through alumina (ca. 20 g) and then evaporated in vacuo to give the corresponding saturated nitrile. This procedure was followed for all substrates unless otherwise specified.

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Registry No. 1, 100-52-7; **2**, 529-20-4; **3**, 104-87-0; **4**, 123-11-5; **5**, 86-51-1; **6**, 120-57-0; **7**, 121-33-5; **8**, 148-53-8; **9**, 99-61-6; **10**, 459-57-4; **11**, 89-98-5; **12**, 104-88-1; **13**, 500-22-1; **14**, 98-01-1; **15**, 790-16-9; **16**, 98-86-2; **17**, 532-27-4; **18**, 495-40-9; **19**, 119-61-9; **20**, 486-25-9; **21**, 96-22-0; **22**, 123-19-3; **23**, 502-56-7; **24**, 120-92-3; **25**, 108-94-1; **27**, 583-60-8; **28**, 464-49-3; **29**, 99-49-0; **30**, 106-51-4; **31**, 98-53-3; **32**, 1579-21-1; **33**, 502-42-1; **34**, 502-49-8; **35**, 830-13-7; **37**, 3531-24-6; **38**, 4435-18-1; **39**, 6975-71-9; **40**, 53153-81-4; 41, 49673-58-7; (*E*)-**42**, 1885-38-7; (*Z*)-**42**, 24840-05-9; (*E*)-**43**, 26155-19-1; (*Z*)-**43**, 57103-23-8; (*E*)-**44**, 35121-93-8; (*E*)-**45**, 14482-11-2; (*Z*)-**45**, 30115-95-8; (*E*)-**46**, 71750-07-7; (*Z*)-**46**, 71750-08-8; (*E*)-**47**, 49711-07-1; (*E*)-**48**, 71750-09-9; (*Z*)-**48**, 71750-10-2; (*E*)-**49**, 71750-11-3; **50**, 1504-76-3; (*E*)-**51**, 27530-50-3; (*Z*)-**51**, 71750-12-4; (*E*)-**52**, 51220-00-9; (*Z*)-**52**, 51219-99-9; (*E*)-**53**, 14378-04-2; (*E*)-**54**, 54356-27-3; (*Z*)-**54**, 54356-28-4; (*E*)-**55**, 6125-63-9; (*Z*)-**55**, 6137-73-1; **56**, 71750-13-5; (*E*)-**57**, 14799-78-1; (*Z*)-**57**, 14799-79-2; **58**, 71750-14-6; (*E*)-**59**, 64723-70-2; (*Z*)-**59**, 64723-71-3; **60**, 4425-74-5; **61**, 17190-25-9; **62**, 5631-82-3; **63**, 54353-88-7; **64**, 54353-88-7; **65**, 5732-88-7; **67**, 37107-50-9; **68**, 71750-15-7; **69**, 64723-67-7; **70**, 22734-05-0; **71**, 63909-22-8; **72**, 64723-66-6; MeCN, 75-05-8; *m*-nitrobenzyl alcohol, 619-25-0; (4-*tert*-butyl-1-cyclohexenyl)acetonitrile, 67674-39-9; 1-(cyanomethyl)-1-hydroxy-4-*tert*-butylcyclohexane, 71750-16-8; 3-(cyanomethyl)bicyclo[4.4.0]dec-2-ene, 64723-68-8; (1-cyclooctenyl)acetonitrile, 71750-17-9.

Ring Opening of 1,2-Bis(trimethylsiloxy)-1,2-dimethylcyclopropane with Hydrogen Bromide and Bromine

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The reaction of HBr and Br_2 with 1:1 mixtures of *cis*- and *trans*-1,2-bis(trimethylsiloxy)-1,2-dimethylcyclopropane (**1** and **2**) in CCl_4 under anhydrous conditions at 0 °C was examined. In both cases cyclopropane cleavage occurred exclusively at the 1,3-bond. With HBr, 3-methyl-3-hydroxy-2-butanone (**6**), 3-bromo-3-methyl-2-butanone (**7**), and 1,3,3,4,6,6-hexamethyl-2,5,7-trioxabicyclo[2.2.1]heptane (**8**) were formed in yields of 38, 26, and 36%, respectively. With Br_2 (dark), a 63% yield of 4-bromo-3-hydroxy-3-methyl-2-butanone (**12**) was obtained along with di-, tri-, and tetrabromo-substituted 1,3,3,4,6,6-hexamethyl-2,5,7-trioxabicyclo[2.2.1]heptanes. Both reactions produced bromotrimethylsilane (**4**) and hexamethyldisiloxane (**5**).

With the recent interest in the mechanism of attack of electrophiles on cyclopropane rings,[1a,b] and especially cyclopropanols and their derivatives,[2] we wish to report the results of the anhydrous HBr and Br_2 ring opening of a bis(trimethylsiloxy)cyclopropane.

Results and Discussion

A mixture of *cis*- and *trans*-1,2-bis(trimethylsiloxy)-1,2-dimethylcyclopropanes (**1** and **2**) was synthesized by carbene insertion on 2,3-bis(trimethylsiloxy)-2-butene.[3]

The 2,3-bis(trimethylsiloxy)-2-butene *E*, *Z* mixture was prepared in 58% yield by using the procedure of Ruhlmann and Poredda.[4] Methylene insertion in the 3*Z*, 3*E* mixture was carried out by using the modified Simmons–Smith reagent of Rawson and Harrison,[5] and an approximate 1:1 mixture of **1** and **2** was obtained in 42% yield. Neither the butene nor the cyclopropane mixtures could be separated by spinning-band distillation. The IR and NMR spectra of the **1** and **2** mixture agrees with that reported by Audibrand and co-workers,[3] but there is a discrepancy in the NMR spectrum proton assignments. The partial NMR spectrum of the mixture of **1** and **2** in Figure 1 shows our proton assignments. Spin–spin decoupling experiments indicate that the broadening of H_a and H_c is due to long-range coupling to the methyl groups. We suggest that this indicates a W arrangement[6] of H_a and H_c with the methyl groups. The only proton which does not show such broadening or W relationship then must be H_b.

Ring openings were carried out on 20% solutions of an approximate 1:1 mixture of **1** and **2** in anhydrous CCl_4 at 0 °C by using 1 equiv of HBr in one experiment and 1 equiv of Br_2 in another.

For the reaction with HBr, distillation of the reaction mixture gave three distinct fractions: a CCl_4 fraction containing trimethylsilyl bromide (**4**) and hexamethyldisiloxane (**5**), a fraction containing 3-hydroxy-3-methyl-2-butanone (**6**) and 3-bromo-3-methyl-2-butanone (**7**), and a third fraction containing 1,3,3,4,6,6-hexamethyl-2,5,7-

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[1] (a) C. J. Collins, *Chem. Rev.*, **69**, 543 (1969); (b) S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Am. Chem. Soc.*, **94**, 4615 (1972), and references contained within.

[2] D. H. Gibson and C. H. DePuy, *Chem. Rev.*, **74**, 605 (1974).

[3] M. Audibrand, R. LeGoaller, and P. Arnaud, *C. R. Hebd. Seances Acad. Sci.*, **268**, 2322 (1969).

[4] V. D. Ruhlmann and S. Poredda, *J. Prakt. Chem.*, 12, 18 (1961).

[5] R. J. Rawson and I. T. Harrison, *J. Org. Chem.*, **35**, 2057 (1970).

[6] F. W. Breitbeil, D. T. Dennerlein, A. E. Fiebig, and R. E. Kuznicki, *J. Org. Chem.*, **33**, 3389 (1968), and examples cited therein.

0022-3263/79/1944-4649$01.00/0

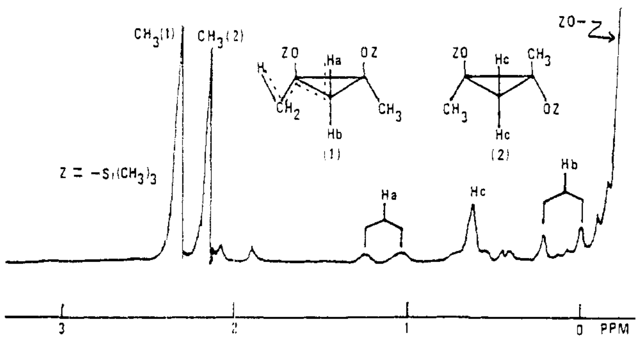
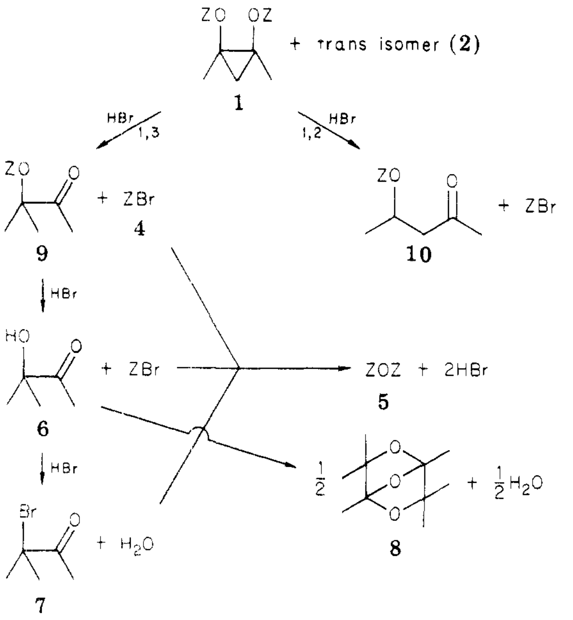


Figure 1. Partial 60-MHz ^1H NMR spectrum of *cis-* and *trans*-1,2-bis(trimethylsiloxy)-1,2-dimethylcyclopropane (1 and 2) in CCl_4 (sweep width 250 Hz).

Scheme I



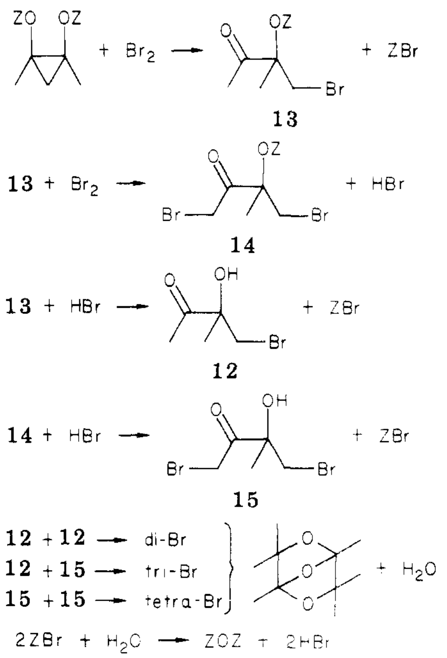
Z = Si$(CH_3)_3$

trioxabicyclo[2.2.1]heptane (8). It is suggested that cleavage by HBr at the 1,3-bond in 1 and 2 initially gives 3-methyl-3-(trimethylsiloxy)-2-butanone (9) which yields 4, 6, and 7 by further reaction. Treatment of 6 with 1 equiv of anhydrous HBr gave reaction products with an NMR spectrum in the δ 1.0–2.5 region qualitatively identical with that of the reaction of HBr with 1 and 2 (only the trimethylsiloxy groups were absent). α-Ketols tend to dimerize with loss of water under acid conditions to give trioxabicyclo[2.2.1]heptanes. Hennion and Watson[7] obtained 8 by condensing 2 equiv of 6 with HCl. The Hennion and Watson experiment was repeated. The product obtained was identical with that in the third fraction cited above. The occurrence of the ketol dimerization subsequent to the ring-opening step could explain the presence of 5, since in the presence of water, 4 forms 5.

The products expected from the HBr 1,2-cleavage of 1 and 2, 4-(trimethylsiloxy)-2-pentanone (10) and its HBr cleavage product, 4-hydroxy-2-pentanone (11), were synthesized. Neither of these compounds were present in the crude reaction as determined from the NMR spectrum.

A summary of these results is depicted in Scheme I.

Scheme II



Z = Si$(CH_3)_3$

An NMR spectrum of the product mixture for the reaction of 1 and 2 with Br_2 showed the presence of 4 at δ 0.60, an intense trimethylsiloxy absorption at δ 0.10, singlets at δ 2.10 and 1.25, a possible AB pattern centered at δ 3.40, and a cluster of singlets at δ 0.85–1.20. Distillation of the product and spectral analysis of the fractions showed that the NMR absorption at δ 0.10 is due to 5, and the absorptions at δ 2.10, 1.25, and 3.4 are due to 4-bromo-3-hydroxy-3-methyl-2-butanone[8] (12). The latter, a new bromohydrin, was independently synthesized by reacting *N*-bromosuccinimide with 3-methyl-3-buten-2-one in water according to the general procedure of Guss and Rosenthal.[9] Bromohydrin 12 was probably formed by HBr cleavage of initially formed 4-bromo-3-methyl-3-(trimethylsiloxy)-2-butanone (13). Since HBr is not a reactant, it must have come from a secondary reaction of Br_2 with 13 and 12 to produce 3-(trimethylsiloxy)-1,4-dibromo-2-butanone (14) and 1,4-dibromo-3-hydroxy-2-butanone (15), respectively. When 9 is reacted with Br_2 under the same conditions as 1 and 2, a product is obtained with an NMR showing a peak due to 5 and a cluster of eight peaks in the δ 0.85–1.20 region (CCH_3) along with the expected AB pattern (δ 3.4) for 1,4-bis(bromomethyl)-3,3,6,6-tetramethyl-2,5,7-trioxabicyclo[2.2.1]heptane (16).

The absence of 10, 11, and 2,4-pentanedione in the reaction product, as determined by NMR, indicates that cleavage of 1 and 2 occurred exclusively at the 1,3-bond. The cluster of singlets in the δ 0.85–1.20 region of the NMR spectrum of the product is probably due to ketol dimerizations of bromohydrins 12 and 15 with loss of water which could then convert 4 to 5. An explanation for the multiplicity of CCH_3 peaks in the NMR spectrum along with a summary of the results of the reaction of Br_2 with 1 and 2 is depicted in Scheme II.

Although we cannot rule out the possibility of a free radical mechanism,[11] the conditions of the reactions and the nature of the products suggest that ring opening oc-

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(7) G. F. Hennion and E. J. Watson, *J. Org. Chem.*, **23**, 658 (1958).

(8) The hydroxyl proton showed up at δ 4.8 in the fraction boiling at 112 °C (7 mm).

(9) C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).

(10) J. E. Dubois, *Bull. Soc. Chim. Fr.*, **66** (1949).

(11) Pasto and co-workers [D. J. Pasto, G. R. Meyer, and B. Lepeska, *J. Am. Chem. Soc.*, **96**, 1858 (1974)] resorted to extraordinary measures to suppress bromine radical production (triple-freeze degassing) while studying the ionic addition of HBr to the 2-butenes.

curred by electrophilic attack.

In summary, HBr and Br_2 cleave the cyclopropane rings of **1** and **2** exclusively at the 1,3-bond, which is the most accessible site. With HBr, **6** and its ketol dimerization product, **8**, are the major products; some **7** is formed from **6** as well. With Br_2, the major product is **12**; a lesser yield of brominated trioxabicyclo[2.2.1]heptane isomers is also produced. The products from both reactions are readily rationalized by electrophilic attack as the mode of ring opening, but a free radical mechanism has not been ruled out.

Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were taken on a Varian A-60 spectrometer in CCl_4 with Me_4Si as external standard. Infrared spectra were recorded with a Perkin-Elmer Model 337 grating spectrometer on thin films.

***cis*- and *trans*-1,2-bis(trimethylsiloxy)-1,2-dimethylcyclopropane (1, 2)** were prepared according to the method of Audibrand and co-workers[3] by using the modified Simmons–Smith reagent described by Rawson and Harrison.[5] A 42% yield of an approximate 1:1 mixture of **1** and **2** was obtained by distillation at 69–71 °C (5 mm): NMR (neat) of **2** δ 1.23 (s, 3 H), 0.05 (s, 18 H), 0.45 (s, 2 H); of **1** δ 1.32 (s, 3 H), 0.07 (s, 18 H), 0.72 (d, 1 H), 0.25 (d, 1 H); IR (neat) 3070, 1250 cm^{-1}.

1,3,3,4,6,6-Hexamethyl-2,5,7-trioxabicyclo[2.2.1]heptane (8) was prepared according to the method of Hennion and Watson[7] in a 74% yield: bp 60–65 °C (20 mm); NMR (CCl_4) δ 1.07 (s, 6 H), 1.25 (s, 6 H), 1.33 (s, 6 H); IR (neat) 1370, 1160, 960 cm^{-1}.

4-(Trimethylsiloxy)-2-pentanone (10). To a mixture of 10.0 g (98 mmol) of **11** and 8.14 g (103 mmol) of pyridine in 100 mL of dry benzene, cooled to 0 °C, was added dropwise with stirring 11.2 g (103 mmol) of chlorotrimethylsilane in 10 mL of benzene. The mixture was stirred 2 h at 25 °C and cooled and the pyridine hydrochloride filtered. Benzene was removed by distillation, and 7.95 g (71%) of **10** was obtained: bp 170–173 °C (760 mm); NMR (CCl_4) δ 0.10 (s, 9 H), 1.20 (d, 3 H), 2.15 (s, 3 H), 2.57 (AB, 2 H, J = 5 Hz), 4.37 (m, 1 H); IR (neat) 1700, 1360, 830 cm^{-1}.

3-(Trimethylsiloxy)-3-methyl-2-butanone (9) was prepared in the same manner as were **10** and **6** (Aldrich Chemical Co., Milwaukee, WI). The product was isolated in 85% yield by distillation: bp 156–158 °C (760 mm); NMR (CCl_4) δ 0.15 (s, 9 H), 1.30 (s, 6 H), 2.12 (s, 3 H); IR (neat) 1725, 1250, 840 cm^{-1}.

4-Hydroxy-2-pentanone (11) was prepared according to the procedure of Dubois[10] in a 47% yield: bp 99 °C (32 mm); n^{22}_{D} 1.4273; NMR (CCl_4) δ 1.20 (d, 3 H), 2.15 (s, 3 H), 2.60 (d, 2 H), 4.15 (s, 1 H), 4.20 (m, 1 H); IR (neat) 3450, 1710 cm^{-1}.

4-Bromo-3-hydroxy-3-methyl-2-butanone (12). A mixture of 8.4 g (100 mmol) of 3-methyl-3-buten-2-one (K & K Laboratories, Inc., Plainview, NY) and 17.8 g (100 mmol) of recrystallized *N*-bromosuccinimide in 70 mL of H_2O was stirred 18 h at 25 °C. The filtered solution was extracted with CCl_4 (3 × 15 mL). Drying (Na_2SO_4), concentration at 25 °C, and distillation at 112 °C (7 mm) gave an 81% yield of **12**: NMR (CCl_4) δ 1.30 (s, 3 H), 2.10 (s, 3 H), 3.50 (AB, 2 H, J = 11 Hz), 4.10 (s, 1 H); IR (neat) 3500, 1700 cm^{-1}.

Anal. Calcd for $C_5H_9BrO_2$: C, 33.17; H, 5.01. Found: C, 32.84; H, 4.95.

Reaction of Br_2 with 3-(Trimethylsiloxy)-3-methyl-2-butanone (9). Synthesis of 1,4-Bis(bromomethyl)-3,3,6,6-tetramethyl-2,5,7-trioxabicyclo[2.2.1]heptane (16). A solution of 1.6 g (10 mmol) of Br_2 in 10 g of dry CCl_4 was added dropwise with stirring to 1.74 g (10 mmol) of **9** in 5.0 g of dry CCl_4 at 0 °C in a N_2 atmosphere. The red Br_2 color disappeared in 20 min, and the solution became cloudy. Attempted vacuum distillation led to decomposition. The NMR (CCl_4) spectrum of the crude reaction mixture showed the following absorptions: δ 0.00 (s, 5 H), 0.50 (s, 4, H), 1.20 (s, 6 H), 1.40 (s, 6 H), 3.45 (AB, 4 H, J = 12 Hz).

Cyclopropane Ring Cleavage of 1:1 (*Z*)- and (*E*)-1,2-Bis(trimethylsiloxy)-1,2-dimethylcyclopropane (1 and 2) with HBr. By means of a gas syringe, 200 mL (8.0 mmol) of HBr (taken directly from lecture bottle) was added at 0 °C in a N_2 atmosphere to 2.0 g (8.0 mmol) of a 1:1 mixture of **1** and **2** dissolved in 8.0 g of dry CCl_4. The rate of addition was controlled by the atmospheric pressure exerted on the plunger coupled with the rate of uptake of HBr—addition took about 15 min. Distillation after completed addition gave three fractions: (1) 25–77 °C (760 mm) containing CCl_4, **4**, and **5**, (2) 88 °C (133 mm) containing **6** and **7**, (3) 109 °C (130 mm) containing **8**. The yields of **6**, **7**, and **8** in the undistilled reaction product were respectively 38, 26, and 36%, as determined by NMR analysis.

Cyclopropane Ring Cleavage of 1:1 (*Z*)- and (*E*)-1,2-Bis(trimethylsiloxy)-1,2-dimethylcyclopropane (1 and 2) with Br_2. A solution of 1.3 g (8 mmol) of Br_2 in 6.5 g of dry CCl_4 was added dropwise with stirring to 2.0 g (8 mmol) of **1** and **2** in 8.0 g of dry CCl_4 at 0 °C under a N_2 atmosphere in the dark. After complete addition, distillation of the reaction mixture to 76 °C (760 mm) gave CCl_4, **4**, and **5**. Further distillation at 112 °C (7 mm) gave 0.9 g of **12** (5 mmol, 63% yield). The residue decomposed on attempted low-pressure distillation. The crude reaction product, with CCl_4, **4**, and **5** removed, had the following spectral characteristics: NMR δ 1.30 (s), 2.10 (s), 3.50 (AB, J = 11 Hz), 4.80 (s), 0.9–1.5 (m); IR (neat) 3500, 1700 cm^{-1}.

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Registry No. **1**, 23510-58-9; **2**, 23510-59-0; **4**, 2857-97-8; **5**, 107-46-0; **6**, 115-22-0; **7**, 2648-71-7; **8**, 7045-89-8; **9**, 55816-60-9; **10**, 71700-27-1; **11**, 4161-60-8; **12**, 71700-28-2; **16**, 23386-69-8; 3-methyl-3-buten-2-one, 814-78-8; HBr, 10035-10-6; Br_2, 7726-95-6.