bath at the appropriate temperature. At various times, individual tubes were cooled and then analyzed for unreacted **2** by gas chromatography.

The solvolysis rate of **3** in TFE was determined by NMR spectroscopy. A sealed NMR tube containing **3** in TFE (also containing 0.025 M Et_3N) was heated in a constant temperature bath for given times and then quenched in cold water. The disappearance of the methyl singlet at δ 1.79 was monitored directly by 300-MHz NMR.

The rates of solvolyses of **4**, **5**, and α-phenethyl chloride (**12**) in TFE (0.025 M in Et_3N) were determined titrimetrically with the previously described TFE rate procedure.[23] Aliquots were quenched in cold HOAc, and unreacted base was back-titrated with 0.01 M $HClO_4$ in HOAc.

Solvolysis rates of sulfinate esters **6** and **7** in TFE (10^{-3} M in Et_3N) were spectrophotometrically determined by monitoring the absorbance change at 244 nm. Rates of **6** in methanol containing methanesulfonic acid or trifluoromethanesulfonic acid were determined spectrophotometrically at 226 nm.

The methanolysis rate of cumyl chloride was determined spectrophotometrically at 25 °C at 225 nm. Our directly determined rate at this temperature is 4.6% smaller than the previously reported rate[16] at 25 °C determined by extrapolation of titrimetric data from lower temperatures.

The solvolysis rate of *p*-methoxybenzyl chloride (**13**) in TFE was determined spectrophotometrically by monitoring the absorbance decrease at 240 nm.

The solvolysis rate of *p*-methoxybenzyl *p*-nitrobenzoate (**14**) in TFE (0.025 M Et_3N) was determined by titration of the unreacted Et_3N with 0.01 M *p*-nitrobenzoic acid in methanol. End points were not sharp and the rate constant reported is ±10%.

Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 1, 98821-05-7; 2, 25195-63-5; 3, 53439-66-0; 4, 98821-06-8; 5, 98821-07-9; 6, 98821-08-0; 7, 98821-09-1; 8 (R = CH_3), 935-67-1; 8 (R = CH_2CF_3), 98821-11-5; 12, 672-65-1; 13, 824-94-2; 14, 53218-10-3; $Ph(CH_3)_2CCl$, 934-53-2; $Ph(CH_3)_2COPNB$, 7429-06-3; CH_3SH, 74-93-1; benzyl trifluoromethyl sulfone, 4855-02-1; triflic anhydride, 358-23-6; cumyl bromide, 3575-19-7; cumyl methyl sulfide, 98821-10-4; thiophenol, 108-98-5; cumyl phenyl sulfide, 4148-93-0; potassium trifluoromethanesulfinate, 41804-89-1; *p*-methoxybenzyl chloride, 824-94-2; cumyl alcohol, 617-94-7; methanesulfinyl chloride, 676-85-7; *p*-toluenesulfinyl chloride, 10439-23-3.

Solvolytic Hydroperoxide Rearrangements. 2. Oxa Bicyclic Hemiketal Peroxides from Homoallylic and Cyclopropylcarbinyl Precursors

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Studies in this laboratory have resulted in the discovery of a novel hydrogen peroxide mediated ring expansion that is suitable for the synthesis of medium to large ring oxa bicyclic compounds. This rearrangement involves the solvolysis of homoallylic brosylates or spiro cyclopropyl carbinols in THF–H_2O_2 and results in a two-carbon ring expansion producing hydroxy ketone derivatives in excellent yields. The reaction involves initial solvolytic entry into the cyclopropylcarbinyl–cyclobutyl carbocation manifold followed by an electron-deficient oxygen rearrangement of the cyclobutyl isomer.

Ring expansions have played an important part in synthetic organic methodology. Many methods are available for expanding rings by one, two, or more carbons. Recently, we communicated the development of a new and efficient two-carbon ring expansion reaction of carbocycles that yields medium-sized rings by hydrogen peroxide mediated solvolysis of homoallylic brosylates.[1] In this paper we describe the details of that study and its further development as a stereoselective ring expansion reaction.

The Criegee perester–hydroxy ketone rearrangement of decalin hydroperoxide has long been known to produce an oxa-bridged bicyclic product; however, this reaction has received little attention other than investigation of its rather unusual mechanism.[2] Our interest in the Criegee-type rearrangement and ring expansions in general grew out of consideration of possible synthetic approaches to a relatively new class of sesquiterpenes that have an

(1) Ronald, R. C.; Lillie, T. S. *J. Am. Chem. Soc.* **1983**, *105*, 5709–5710.
(2) Criegee, R. *Ber. Dtsch. Chem. Ges.* **1944**, *77*, 722–726.

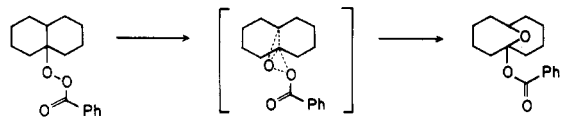
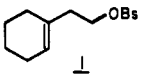
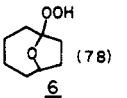
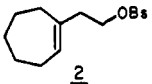
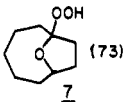
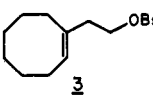
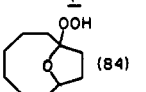
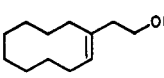
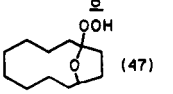
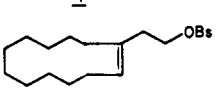
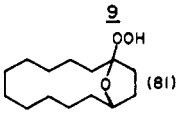


Table I. Solvolyses of Brosylates in H_2O_2–THF

substrate	time, h (temp, °C)	product (yield, %)
 1	0.5 (25)	 6 (78)
 2	1 (25)	 7 (73)
 3	3 (25)	 8 (84)
 4	26 (40)	 9 (47)
 5	72 (37)	 10 (81)

11-oxabicyclo[6.2.1]undecane ring structure.[3] This ring structure along with other oxygen-bridged systems can be

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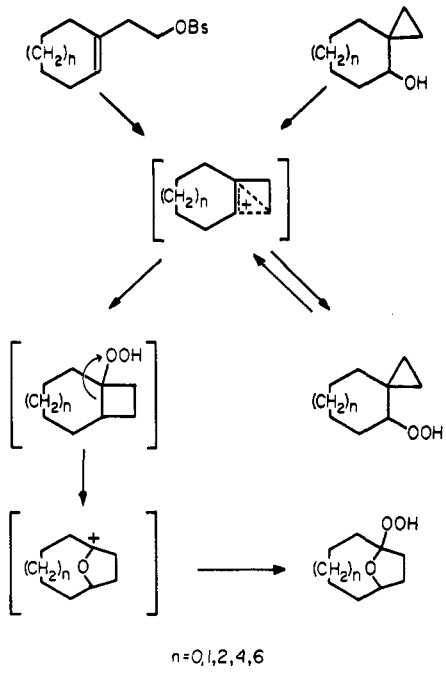


Figure 1.

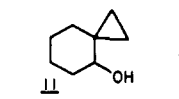
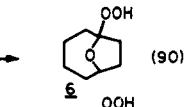
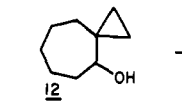
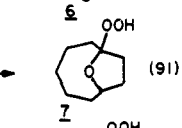
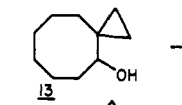
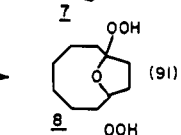
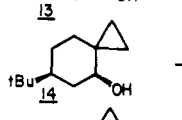
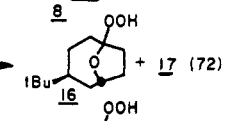
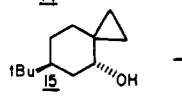
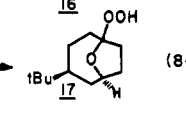
prepared by the reaction of cycloalkenylethyl brosylates or spiro[*n*.2]alkan-4-ols in 1:1 90% hydrogen peroxide–tetahydrofuran (Figure 1). The reaction proceeds through solvolytically generated cyclobutyl hydroperoxides that undergo facile Criegee-type rearrangements, affording oxa-bridged, hydroperoxy hemiketals of the corresponding 4-hydroxy ketones. The rearrangement represents a two-carbon ring-expansion reaction that generates 4-hydroxycycloalkanones.

Results and Discussion

Substrates for the solvolysis were readily obtained with either previously published methods[4] or the methods outlined below. The brosylate substrates were synthesized from cyclic ketones via Wittig–Horner olefination using methyl(diethoxyphosphinyl)acetate and lithium diisopropylamide followed by deconjugation, hydride reduction, and brosylation with *p*-bromobenzenesulfonyl chloride in pyridine. The spiro carbinol substrates were produced by the reaction of dimethyl(2-chloroethyl)sulfonium iodide with cyclic ketones followed by reduction of the carbonyl.[5]

The ring expansions of cycloalkenyl ethyl brosylates **1–5** were accomplished in a two-stage process (see Table I). In the first stage, the brosylate was solvolyzed in 1:1 THF–90% H_2O_2 buffered with K_2HPO_4 to produce a mixture of spirocyclopropylcarbinyl and oxa bicyclo hydroperoxides. To avoid the small, but significant, exotherm that accompanied the mixing of high strength H_2O_2 with organic solvents,[6] the solutions were cooled in an ice bath while the requisite amount of 90% H_2O_2 was added.[7] The reaction flask was then transferred to a water or oil bath at the desired reaction temperature. The second stage was completed after all of the brosylate had reacted, by the addition of 2.1–2.5 equiv of toluenesulfonic acid (1.1–1.4 equiv over the amount of buffer) which served to convert all of the spiro hydroperoxides to the ring expanded products **6–10**. Single-stage solvolyses in the absence of buffer led directly to ring expansion; however, the yields were drastically reduced.

Table II. Solvolyses of Cyclopropyl Carbinols in H_2O_2–THF

substrate	product (yield, %)
	 (90)
	 (91)
	 (91)
	 + 17 (72)
	 (84)

The hydroperoxy hemiketal products **6–10** of the ring expansion were isolated by a normal aqueous workup. In many cases, because of the instability of the hydroperoxy products to loss of H_2O_2 and subsequent decomposition, the crude expansion products were immediately reduced to the corresponding hemiketals. These hemiketals were derivatized as their *p*-nitrobenzoates or phenylurethanes for analyses. These reactions have successfully been performed on milligram to gram quantities of substrate without major affects on reaction times or yields. Increased temperatures and longer reaction times became necessary as the size of the substrates increased due to their limited solubility in the polar reaction medium. The additional THF required to dissolve these larger substrates also reduced the solvolysis rates.

Spiro[*n*.2]alkan-4-ols **11–15** were also shown to rearrange in a similar fashion, yielding the same ring-expanded products. There, however, are several advantages in using these spirocarbinols in place of cycloalkenyl ethyl brosylates as substrates in that the carbinols usually have increased solubility in the polar reaction mixture and also require a much smaller excess of acid to produce expansion the products in somewhat higher yields.

The solvolyses of the spiro[*n*.2]alkan-4-ols **11–15** were typically performed in 1:1 THF–90% H_2O_2 acidified with $TsOH{\cdot}H_2O$. Prior to the addition of the 90% H_2O_2 the THF solution of the substrate was cooled in ice; after addition of the H_2O_2 the reaction flask was warmed to the desired reaction temperature. Rearrangement occurred rapidly upon addition of the acid. Usually only 10 mol % of acid was required, and in most cases the rearrangement was complete in less than 1 h. The data for the rearrangement of cyclopropyl carbinols are listed in Table II.

The course of these solvolysis is dependent upon the reaction conditions; however, generally the carbinols were

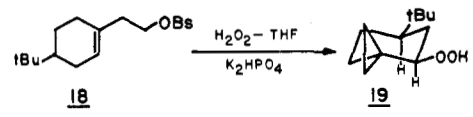
(3) Cowall, P.; Cassidy, J.; Chang, C.; Kozlowski, J. F. *J. Org. Chem.* **1981**, *46*, 1108–1111. Baush, N.; Sharma, R.; Madhusudahan, K.; Thyagarajan, G.; Hertz, W.; Murari, R. *J. Org. Chem.* **1979**, *44*, 1831–1835. Herz, W.; Wahlberg, I. *J. Org. Chem.* **1973**, *38*, 1485–2489. Romo de Vivar, A.; Guerrero, C.; Diaz, E.; Oretega, A. *Tetrahedron* **1970**, *26*, 1657–1659.

(4) Rathke, M. W. *J. Am. Chem.* **1970**, *92*, 3222–3223. Shiner, R. L. *Org. React.* (*N.Y.*) **1942**, *1*, 1. Hauser, C. R.; Breslow, D. S. "Organic Syntheses"; Wiley: New York, **1955**, Collect. Vol. 3, p 408.

(5) Ronald, R. C.; Ruder, S. M. *Tetrahedron Lett.* **1984**, *25*, 5501–5504.

(6) Concentrated H_2O_2 (90%) is available from FMC Corp. Investigators should read FMC *Technical Bulletin 46* for information on the safe handling and disposal of high strength H_2O_2. In addition, investigators should read: Shanley, E. S.; Perin, J. R. *Jet. Propul.* **1958**, *28*, 382–385.

(7) Concentrated hydrogen peroxide (90%) contains ~36 mmol of H_2O_2 per mL.



18 19

Figure 2.

less sensitive to changes than the brosylates. Solvolysis of the brosylates in less than a 50-fold molar excess of hydrogen peroxide or in the absence of buffer resulted in formation of a larger amount of unidentified highly polar peroxy compounds along with dialkyl peroxides resulting from the trapping of carbocations with various hydroperoxy products. When the percentage of THF in the solvolysis medium was increased, this markedly decreased the reaction rate but produced little effect on the overall yield. Using 30% H_2O_2 instead of 90% H_2O_2 in THF produced reaction mixtures that were much more complicated with products arising from reaction with water as well as hydrogen peroxide even under prolonged reaction times. Acyclic brosylates proved to be satisfactory precursors for the rearrangement since the principal reaction mode was direct displacement by hydrogen peroxide.

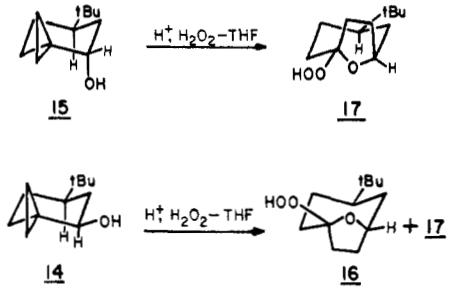
While introduction of the *tert*-butyl group in the cyclohexane ring did not result in gross changes in the ring expansion process, **14** and **15** were the first compounds which enabled us to observe stereochemical effects on the rearrangement. The results are interesting and merit a more detailed discussion. The observations that stereochemical control of these rearrangements is possible is an important development in these reactions.

Solvolysis of 2-(4-*tert*-butylcyclohexenyl)ethyl brosylate (**18**) under buffered conditions afforded principally *cis*-6-*tert*-butyl-4-hydroxyperoxyspiro[5.2]octane (**19**) along with a small amount (5–7%) of a mixture of diastereomeric ring expansion products (Figure 2). Since in this case the rearrangement of the homoallylic substrate did not appear promising, we decided to investigate the isomeric *cis*-**14** and *trans*-**15** carbinols that were readily prepared from **19**. We were very pleased to discover that these isomeric carbinols showed remarkably different reactivities and that in the case of the axial isomer **15** the H_2O_2 rearrangement proceeded with a high level of stereoselectivity.

The cis-carbinol **14** was available directly from **19** by simple reduction. The trans-carbinol **15** was prepared from **14** by Jones oxidation followed by reduction with L-Selectride (Aldrich) in THF. The selectivity for the axial carbinol was about 90%, and the small amount of cis isomer contaminant was readily removed by chromatography on silica gel.

Acid-catalyzed solvolysis of cis-carbinol **14** afforded a 1:1 mixture of diastereomeric ring expansion products **16**–**17** in 33% yield. Solvolysis of *trans*-**15** also resulted in the same pair of hydroperoxy hemiketals in 84% yield but also with 19:1 selectivity for isomer **17** (see Figure 3). By comparison of the NMR spectra of the products from **14** and **15** the expansion products were assigned the structures **16** and **17**, respectively.[8]

In addition to the remarkable difference in stereoselectivity obtained in the reactions of **14** and **15**, there was also a corresponding difference in the facility of their reactions. The stereoselective reaction of **15** (the axial isomer) was complete in less than 15 min at room temperature and required only 0.01M acid for catalysis. Under these conditions almost no substitution to form hydroperoxide **19** was observed and the oxa-bridged product appeared to be formed directly.



15 17

14 16

Figure 3.

In sharp contrast **14** (the equatorial isomer) was almost completely unreactive at this level of acid catalysis, the principal reaction being the slow substitution to form the hydroperoxide **19**. By increasing the acid to 0.3 M conversion via **19** to the mixture **16** and **17** required about 7 h.

The results obtained from rearrangement of the *tert*-butylspirocarbinols imply that different rearrangement pathways for generation of the crucial cyclobutyl cations must exist for the axial and the equatorial isomers. Clearly, the stereoselective reaction of **15** shows that in this isomer there is preferential migration of a single methylene group of the cyclopropyl ring which is, no doubt, due to the favorable orientation of the leaving group orbital with those of the cyclopropane. The stereochemical assignments of the rearrangement products by NMR suggests that a backside Wagner–Meerwein-type migration from the hydronium ion or a preferential migration of the pseudoaxial methylene of a bisected cyclopropylcarbinyl cation[9] is involved in directing the stereochemical outcome or rearrangement. Neither of these pathways would be available to the equatorial isomer. Since rearrangement of the equatorial alcohol is much slower and nucleophilic substitution occurs readily, the rearrangement of **14** probably involves initial formation of the more symmetrical cyclopropyl carbinyl–bicyclobutonium species which permits migration of either of the cyclopropyl methylenes with equal facility. We are pursuing labeling experiments to distinguish between these possibilities.

The hydrogen peroxide solvolysis of homoallylic and cyclopropylcarbinyl systems is shown to be a facile entry into medium and large ring systems. These reactions produce useful oxa-bridged 4-hydroxy ketone derivatives and their corresponding furanoid isomers in high yield and in certain cases with excellent stereochemical control.

Experimental Section

General Methods. Infrared spectra were determined with a Beckman Acculab 1 or a Nicolet MX-5 spectrophotometer. Nuclear magnetic resonance spectra were determined on the following spectrophotometers: Varian EM-360 (60 MHz), Joel FX90Q (90 MHz), and a Nicolet NT-200 (200 MHz). The proton nuclear magnetic resonance spectra were taken in carbon tetrachloride or deuterochloroform using tetramethylsilane (δ 0.00) or deuterochloroform (δ 7.25) as the internal standard. Carbon-13

(8) The two isomers **16** and **17** were identified by the location of the methine resonances. The major isomer from the solvolysis of **15** (peroxide **17**) showed the *tert*-butyl methine resonance at δ 2.59 and the bridged methine at δ 4.70. In the mixed peroxide from **14** the resonances of **17** were clearly visible while the bridged methine of **16** resonated at δ 4.17 and the *tert*-butyl methine of this isomer was moved upfield coincident with the other ring signals.

(9) Poulter, C. D.; Spillner, C. J. *J. Am. Chem. Soc.* **1974**, *96*, 7591–7593. For reviews on cyclopropylcarbinyl rearrangements, see: Bartlett, P. D. "Nonclassical Ions"; W. A. Benjamin, Menlo Park, CA, 1965. Hanack, M.; Schneider, H. J. *Angew. Chem., Int. Ed. Engl.* **1967**, 6, 666. Olah, G. A., Schleyer, P. v. R., Ed. "Carbonium Ions"; Wiley: New York, 1972; Vol. III. Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

spectra were taken in deuterochloroform using the central peak of deuterochloroform (δ 77.0) as the internal standard.

Gas chromatograms were obtained on a Packard-Becker Model 417 gas chromatograph equipped with a hydrogen flame ionization detector. Analyses were carried out on either a 3 mm × 2.7 m glass column packed with 3% OV-17 on 80/100 Chromosorb W-HP or a 25-m SE-30 glass capillary column. Peroxy compounds were visualized for TLC by spraying with a 1% w/v solution of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine dihydrochloride in 50% aqueous methanol containing 1 mL of acidic acid per 100 mL. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Melting points are uncorrected.

Materials. Concentrated hydrogen peroxide was obtained from FMC Corp. Investigators should read FMC *Technical Bulletin 46* for information on the safe handling and disposal of high-strength H_2O_2. Tetrahydrofuran was distilled from benzophenone ketyl under nitrogen.

Elemental analyses were not performed on some of the expanded hydroperoxides due to their instability, but satisfactory results were obtained from their derivatives. All other new compounds gave satisfactory NMR, IR, and elemental analysis data.

General Procedure A: Reaction of Methyl (Dimethoxyphosphinyl)acetate with Cyclic Ketones. Methyl Cyclooctylideneacetate. A solution of lithium diisopropylamide (88.0 mmol) was prepared in THF (100 mL) at −78 °C and then warmed to ambient temperature. To this was added methyl (dimethylphosphinyl)acetate (15.9 g, 88.0 mL) in THF (10 mL). After 15 min cyclooctanone (10.00 g, 79.3 mmol) was added in THF (10 mL). The reaction was monitored by GC until the ketone was consumed; then it was quenched with water and extracted into petroleum ether, washed with water and brine, dried with anhydrous $MgSO_4$, and concentrated to yield the ester (12.1 g, 84%): bp 110–112 °C (20 mm); ^{1}H NMR δ 5.7 (1 H), 3.6 (3 H), 2.7 (2 H), 2.3 (2 H), 2.0–1.2 (10 H); IR 2930, 2860, 1720, 1630, 1440, 1380, 1200, 1030, 920, 840 cm^{-1}.

General Procedure B: Deconjugation. Methyl 1-Cyclooctenylacetate. A solution of methyl cyclooctylideneacetate (7.87 g, 43.2 mmol) in THF (5 mL) was added to lithium diisopropylamide (42.2 mmol) in THF (10 mL). After 15 min the reaction was quenched with 5 mL of 10% aqueous HCl. The mixture was extracted with petroleum ether. The organic phase was washed with $NaHCO_3$ (saturated) and then worked up as in procedure A. Chromatography on silica gel afforded 6.62 g (84%) of the acetate: ^{1}H NMR δ 5.4 (1 H, t, J = 8.6 Hz), 3.5 (3 H, s), 2.7 (2 H, s), 2.2–1.8 (4 H, m), 1.7–1.1 (8 H, m); ^{13}C NMR δ 170.02, 133.91, 128.30, 51.07, 39.45, 28.61, 27.18, 26.10, 25.63, 25.15, 24.73; IR 2932, 2860, 1738, 1437, 1275 914, 793 cm^{-1}.

General Procedure C: Ester Reduction. 2-(1-Cyclooctenyl)ethanol. $LiAlH_4$ (340 mg, 8.0 mmol) was added to an ice-cooled solution of methyl cyclooclenylacetate (1.52 g, 8.4 mmol) in ether (20 mL). After 30 min the excess hydride was quenched by dropwise addition of H_2O. Anhydrous $MgSO_4$ was added, and the mixture filtered and concentrated to yield the alcohol[10] (1.18 g, 92%): NMR δ 5.3 (1 H, t, J = 8.3 Hz), 3.6 (2 H, t, J = 6.7 Hz), 2.8 (1 H, m), 2.1 (6 H, m), 1.5 (8 H, s); ^{13}C NMR δ 136.94, 126.28, 60.37, 40.41, 29.56, 28.43, 26.28, 26.16, 235.98, 25.87; IR 3343, 2924, 1741, 1665, 1467 1440, 1044, 900 cm^{-1}.

General Procedure D: Brosylation. 2-(1-Cyclohexenyl)ethyl Brosylate (1). A solution of 2-(1-cyclohexenyl)ethanol (280 mg, 2.22 mmol) and *p*-bromobenzenesulfonyl chloride (623 g, 2.44 mmol) in pyridine (20 mL) was stirred 4 h at room temperature after which time the TLC (30% ether in petroleum) showed complete consumption of starting material. The milky orange reaction mixture was extracted into petroleum, washed with HCl (10%), and worked up as in procedure B to afford oily crystals. Recrystallization from CH_2Cl_2/hexane at −78 °C afforded 362 mg (47%): mp 49–51 °C; ^{1}H NMR δ 7.7 (4 H, m), 5.4 (1 H, br), 4.1 (2 H, t, J = 7.5 Hz), 2.2 (2 H, t, 7.5 Hz), 2.0–1.7 (4 H, m), 1.5 (4 H, m). ^{13}C NMR δ 135.45, 132.42, 132.00, 129.26, 128.30, 124.61, 69.49, 37.01, 28.19, 25.09, 22.65, 22.05; IR 2940, 2840, 1570, 1470, 1360, 1280, 1200, 910, 820 cm^{-1}. Anal. Calcd for $C_{14}H_{17}BrO_3S$: C, 48.71; H, 4.96. Found: C, 48.58; H, 4.99.

General Procedure E: Solvolysis of Brosylates. 1-Hydroperoxy-9-oxabicyclo[4.2.1]nonane (6). To an ice-cooled solution of 2-(1-cyclohexenyl)ethyl brosylate (222 mg, 0.64 mmol) in THF (3 mL) in which powdered $KH_2PO_4 \cdot H_2O$ (148 mg, 0.64 mmol) was suspended was carefully added 90% H_2O_2 (3 mL, 108 mmol H_2O_2). A few drops of additional THF dissolved any precipitated substrate. The solution was stirred at room temperature until the brosylate had all reacted (24 h), and then $TsOH \cdot H_2O$ (306 mg, 1.61 mmol) was added. The mixture was stirred an additional 2 h until the initially formed spiro peroxide produce disappeared. The reaction was worked up as in procedure A to yield after preparative TLC (20% ether–petroleum) **6** (90.7 mg, 78%) as a white crystalline solid, mp 58–60 °C: ^{1}H NMR δ 8.9 (1 H, s), 4.6 (1 H, m), 2.5–1.2 (12 H, m); ^{13}C NMR δ 115.67, 66.65, 36.83, 36.06, 32.78, 30.58, 24.32, 23.18; IR 3342, 2932, 28.62, 1469, 1354, 1317, 1124, 1059, 967, 958, 927, 814 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.83; H, 7.91.

General Procedure F: Solvolysis of Cyclopropyl Carbinols. 1-Hydroperoxy-9-oxabicyclo[4.2.1]nonane (6). To an ice-cooled solution of spiro[5.2]octan-4-ol (11) (398 mg, 3.15 mmol) in THF (4.5 mL) was carefully added 90% H_2O_2 (4.5 mL, 162 mmol H_2O_2) followed by $TsOH \cdot H_2O$ (24 mg, 0.12 mmol). The cooling bath was removed and the reaction mixture stirred 6 h at 25–30 °C. The reaction was worked up as in procedure E to yield, after rapid chromatography on silica gel, **6** (448 mg, 90.3%). Phenylurethane of **6**: mp 95–96 °C; ^{1}H NMR δ 7.4 (5 H, m), 6.7 (1 H, br m), 4.9 (1 H, br m), 2.6–2.4 (4 H, m), 2.4–2.0 (2 H, m), 1.9–1.5 (6 H, br m); IR 3340, 3330, 2960, 1730, 1700, 1600, 1540, 1440, 1220, 1105 cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.30. Found: C, 68.75; H, 7.50.

2-(1-(4-*tert*-Butylcyclohexenyl))ethyl brosylate (18): mp 61–62 °C; ^{1}H NMR δ 7.7 (4 H, m), 5.4 (1 H, br m), 4.1 (2 H, t, J = 7.5 Hz), 2.25 (2 H, t, J = 7.5 Hz), 2.0–1.7 (4 H, m), 1.4–1.0 (3 H, m), 0.85 (9 H, s); ^{13}C NMR δ 135.51, 132.47, 131.87, 129.31, 128.71, 124.90, 69.60, 43.83, 36.58, 32.12, 29.73, 27.17, 26.81, 24.01; IR 2990, 1578, 1473, 1375, 1190, 960 cm^{-1}. Anal. Calcd for $C_{18}H_{25}BrO_3S$: C, 53.87; H, 6.27. Found: C, 54.05; H, 6.16.

***cis*-6-*tert*-Butyl-4-hydroperoxyspiro[5.2]octane (19).** Brosylate **18** (586 mg, 1.46 mmol) was solvolyzed according to procedure E by using 6 mL each of THF and 90% H_2O_2. After 24 h at 35 °C, the mixture was not acidified but worked up. Chromatography on silica gel (eluted with 10% ether–petroleum) afforded **19** (273 mg, 93%) as a crystalline solid: mp 40–41 °C; ^{1}H NMR δ 8.0 (s, 1 H), 3.35 (s, 1 H), 2.3–1.5 (br m, 4 H), 1.5–1.0 (m, 3 H), 0.90 (s, 9 H), 0.70 (m, 1 H), 0.05–0.10 (m, 3 H); ^{13}C NMR δ 88.55, 40.93, 82.06, 31.04, 29.31, 27.41, 25.86, 19.96, 11.40, 10.01; IR 3400 (br), 2960, 2870, 1680, 1365, 1240, 1090, 930 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.49; H, 10.95.

***cis*-6-*tert*-Butylspiro[5.2]octan-4-ol (14).** A solution of **19** (237 mg, 1.19 mmol) in THF (5 mL) was hydrogenated at 1 atm over Adam's catalyst (25 mg, 0.19 mmol). After being filtered to remove the catalyst the mixture was concentrated. Preparative TLC afforded **14** (188 mg, 86.2%) as a colorless oil: ^{1}H NMR δ 3.6 (m, 1 H), 2.4 (s, 1 H), 2.1–1.8 (m, 1 H), 1.8–1.5 (m, 1 H), 1.4–1.0 (m, 7 H), 0.9 (s, 9 H), 0.60 (m, 2 H), 0.10 (m, 2 H); ^{13}C NMR δ 70.62, 47.38, 36.06, 35.22, 32.24, 27.59, 25.81, 23.84, 7.34, 6.02; IR 3362, 2953, 2866, 1444, 1365, 1240, 1067, 1010, 916 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.26; H, 11.99.

6-*tert*-Butylspiro[5.2]octan-4-one (20). A solution of **14** (137 mg, 0.69 mmol) in acetone (10 mL) was treated with Jones reagent. When the oxidation was complete, the reaction mixture was diluted with water and extracted into petroleum ether. The extracts were washed with water, brine, dried with anhydrous $MgSO_4$ and concentrated. The crude product was chromatographed (pTLC) to afford **20** (116 mg, 85%): bp (Kugelrohr) 42–45 °C (0.1 mm); ^{1}H NMR δ 2.6–1.3 (m, 9 H), 0.90 (s, 9 H), 0.05 (m, 2 H); ^{13}C NMR δ 211.66, 46.19, 41.48, 33.08, 32.42, 27.95, 26.32, 24.85, 21.16, 13.77; IR 2961, 2860, 1637, 1475, 1367, 1332, 1240, 1174, 1126, 1076, 1022, 921, 852 cm^{-1}.

***trans*-6-*tert*-Butylspiro[5.2]octan-4-ol (15).** An ice-cooled solution of **20** (86 mg, 0.47 mmol) in THF (10 mL) was reduced with L-Selectride (0.5 mL of 1 M solution, 0.5 mmol). After 2 h the mixture was quenched with H_2O and extracted into petroleum ether, then washed, and concentrated. Preparative TLC (60% ether–40% petroleum) afforded **15** (58 mg, 66%): ^{1}H NMR

(10) Hanack, M.; Schneider, H. J. *Justus Liebigs Ann. Chem.* **1965**, *686*, 8–18. Hanack, M.; Schneider-Bernlöhr, H.; Schneider, H. J.; Wentrup, G.; *Justus Liebigs Ann. Chem.* **1968**, *717*, 41–53.

δ 3.6 (m, 1 H), 2.2–1.6 (m, 3 H), 1.4–1.1 (m, 5 H), 1.0 (s, 9 H), 0.9 (m, 1 H), 0.4–0.1 (m, 3 H); IR 3350, 2950, 1369, 1210, 1070 cm^{-1}. In addition, **14** (7 mg, 8%) was obtained.

4-*tert*-Butyl-1-hydroperoxy-9-oxabicyclo[4.2.1]nonanes (16 and 17). A solution of **14** (92 mg, 0.50 mmol) was rearrnged in THF (2 mL) and 90% H_2O_2 (2 mL, 72 mmol H_2O_2) containing $TsOH·H_2O$ (120 mg, 0.60 mmol) for 48 h according to procedure F. Preparative TLC of the crude product (50 mg) yielded an inseparable mixture of **16** and **17** (31 mg, 33%) as a 1:1 mixture by ^1H NMR as shown by integration of the carbinyl signals at δ 4.17 (**16**) and 4.70 (**17**).

4-*tert*-Butyl-1-hydroperoxy-9-oxabicyclo[4.2.1]nonane (17). A solution of **15** (44 mg, 0.24 mmol) was rearranged in THF (1 mL) and 90% H_2O_2 (1 mL, 36 mmol H_2O_2) containing $TsOH·H_2O$ (24 mg, 0.12 mmol) for 20 min according to procedure F. Preparative TLc of the crude product (64 mg) yielded **17** (43 mg, 84%): mp 94–95 °C; ^1H NMR δ 8.7 (s, 1 H), 4.70 (m, 1 H), 2.5 (m, 1 H), 2.3–1.2 (m, 10 H), 0.90 (s, 9 H); IR 3300 (br), 2960, 1460, 1360, 1195, 1045, 1000 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_3$: C, 67.25, H, 10.35. Found: C, 67.26; H, 10.38.

2-(1-Cycloheptenyl)ethyl brosylate (12): mp 31–32 °C. ^1H NMR δ 7.7 (4 H), 5.6 (t, 1 H, J = 8.1 Hz), 4.1 (t, 2 H, J = 7.8 Hz), 2.3 (t, 2 H, J = 7.5 Hz), 2.0 (br m, 4 H), 1.8–1.2 (m, 6 H); ^{13}C NMR δ 138.44, 132.48, 129.91, 129.32, 128.72, 128.36, 69.61, 39.39, 32.60, 32.24, 28.31, 26.88, 26.52; IR 2920, 2860, 1570, 1360, 1180, 960, 876 cm^{-1}. Anal. Calcd for $C_{15}H_{20}BrO_3S$: C, 50.15, H, 5.33. Found: C, 50.25, H, 5.21.

1-Hydroperoxy-10-oxabicyclo[5.2.1]decane (7): mp 62–63 °C; ^1H NMR δ 8.3 (s, 1 H), 4.7 (s, 1 H), 2.4–1.2 (br m, 14 H); ^{13}C NMR δ 116.09, 80.63, 36.53, 34.63, 31.23, 28.79, 27.30, 27.18, 24.38; IR 3331, 2923, 2851, 1469, 1327, 1161, 1044, 963 cm^{-1}. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.69; H, 9.15. **Phenylurethane of 1-hydroxy-10-oxabicyclo[5.2.1]decane:** mp 83–84.5 °C, ^1H NMR δ 7.3 (m, 5 H), 6.7 (br m, 1 H), 4.9 (m, 1 H), 2.7–2.4 (m, 4 H), 2.3–2.0 (m, 2 H), 1.9–1.4 (br m, 8 H); IR 3320, 2940, 2860, 1750, 1710, 15808, 1549, 1430, 1210, 1170 cm^{-1}. Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69. Found: C, 69.72; H, 7.74.

2-(1-Cyclooctenyl)ethyl brosylate[11] **(3):** ^1H NMR δ 7.7 (m, 4 H), 5.3 (t, 1 H, J = 8.0 Hz), 4.1 (t, 2 H, J = 7.1 Hz), 2.4 (t, 2 H, J = 7.1 Hz), 2.1–19.9 (br m, 4 H), 1.4 (br m, 8 H); ^{13}C NMR δ 134.85, 132.71, 132.47, 129.31, 129.13, 127.70, 69.66, 36.70, 29.61, 28.78, 28.54, 27.31, 26.33, 26.10; IR 2924, 2854, 1577, 1363, 1186, 1096, 1069, 951, 914, 624, 781 cm^{-1}.

(11) Paquette, L. A.; Hensel, K. A.; *J. Am. Chem. Soc.* **1975**, *97*, 4649–4658.

1-Hydroperoxy-11-oxabicyclo[6.2.1]undecane (8): ^1H NMR δ 9.3 (s, 1 H), 4.6 (br m, 1 H), 2.4–21 (m, 2 H), 1.9–1.1 (m, 14 H); ^{13}C NMR δ 116.14, 81.52, 24.57, 33.38, 31.95, 29.50, 29.32, 26.94, 22.29, 21.87; IR 3330 (br), 2930, 2860, 1462, 1439, 1333, 1312, 1135, 1064, 1042, 978 cm^{-1}.

2-(1-Cyclodecenyl)ethyl brosylate (4): mp 39.5–41.5 °C; ^1H NMR δ 7.7 (m, 4 H), 5.1 (t, 1 H, J = 7.0 Hz), 4.1 (t, 2 H, J = 7.2 Hz), 2.4–1.8 (br m, 6 H), 1.8–1.2 (br m, 12 H); IR 2940, 2860, 1580, 1470, 1360, 1180, 960, 900, 830, 780 cm^{-1}. Anal. Calcd for $C_{18}H_{26}BrO_3S$: C, 53.87; H, 6.28. Found: C, 53.78; H, 6.53.

1-Hydroperoxy-13-oxabicyclo[8.2.1]tridecane (9): ^1H NMR δ 8.3 (br, 1 H), 4.4 (m, 1 H), 1.9–1.1 (large m, 24 H); IR 3330, 2930, 2862, 1463, 1430, 1330, 1140, 1055, 1045 cm^{-1}. **Phenylurethane of 13-oxabicyclo[8.2.1]tridecan-1-ol:** mp 109.5–110 °C; ^1H NMR δ 7.3 (m, 5 H), 6.6 (br m, 1 H), 5.1 (br m, 1 H), 1.8–1.2 (br m, 20 H); IR 3450, 2940, 2860, 1730, 1540, 1450, 1220, 1090 cm^{-1}. Anal. Calcd for $C_{19}H_{27}NO_3$: C, 71.89; H, 8.57. Found: C, 72.06; H, 8.63.

2-(1-Cyclododecenyl)ethyl brosylate (5): mp 29–30.5 °C (only the trans product was solid); ^1H NMR δ 7.7 (m, 4 H), 5.3 (t, 1 H, J = 7.2 Hz), 4.0 (t, 2 H, J = 7.0 Hz), 2.4 (t, 2 H, J = 7.0 Hz), 2.2–1.7 (br m, 4 H), 1.6–1.1 (br m, 16 H); IR 2920, 2850, 1570, 1470, 1380, 1190, 1070, 1010, 820 cm^{-1}. Anal. Calcd for $C_{20}H_{30}BrO_3S$: C, 55.94; H, 6.81. Found: C, 55.83; H, 6.92.

1-Hydroperoxy-15-oxabicyclo[10.2.1]pentadecane (10): ^1H NMR δ 8.3 (br, 1 H), 4.4 (br m, 1 H)8 2.0–1.0 (br, 24 H); IR 3334, 2936, 2856, 1463, 1429, 1333, 1313, 1137, 1064, 1042, 975 cm^{-1}. **Phenylurethane of 15-oxabicyclo[10.2.1]pentadecan-1-ol:** mp 132–133 °C; ^1H NMR δ 793 (m, 5 H), 6.5 (m, 1 H), 4.7 (m, 1 H), 2.1–1.1 (br m, 24 H); IR 3330, 2940, 2860, 1740, 1710, 1600, 1540, 1440, 1220 cm^{-1}. Anal. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.04. Found: C, 73.11; H, 9.09.

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Registry No. **1**, 83321-29-3; **1** (alcohol), 3197-68-0; **2**, 86669-50-3; **3**, 41299-58-5; **3** (methyl acetate deriv), 76519-82-9; **3** (alcohol), 21336-24-3; **4**, 86669-52-5; **5**, 86669-54-7; **6**, 86669-49-0; **7**, 86669-51-4; **7** (phenylurethane), 99035-15-1; **8**, 86669-47-8; **9**, 86669-53-6; **9** (phenylurethane), 99035-16-2; **10**, 86669-55-8; **10** (phenylurethane), 99035-17-3; **11**, 3301-81-3; **12**, 21336-30-1; **13**, 21336-25-4; **14**, 20702-59-4; **15**, 20707-15-7; **16**, 99035-12-8; **17**, 99095-80-4; **18**, 99035-13-9; **19**, 99035-14-0; **20**, 20647-96-5; BsCl, 98-58-8; $(H_3CO)_2POCH_2CO_2CH_3$, 5927-18-4; cyclooctanone, 502-49-8; methyl cyclooctylideneacetate, 99035-18-4.

Hydroxide Ion Initiated Reactions under Phase Transfer Catalysis Conditions. 9. Dehydrohalogenation of (Haloethyl)benzenes by Quaternary Ammonium Salts[1]

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Elimination of HCl and HBr from (1- and (2-haloethyl)benzenes in the presence of aqueous sodium hydroxide and quaternary ammonium salts which cannot extract hydroxide anion to the organic phase is shown to proceed via a reverse phase transfer process. The catalyst QX promotes the elimination and forms QX·HX adduct which is neutralized at the interphase by the hydroxide base. First-order kinetics is observed under conditions in which the catalyst is stable. Complicated kinetics is obtained when decomposition of the catalyst takes place simultaneously with the reaction.

The two-phase dehydrogenation of alkyl halides in the presence of alkali hydroxide and quaternary onium salts (quats, QX) phase transfer catalysts have found numerous preparative applications in the synthesis of olefins and

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