sufficient to get a good sample, and titrated on 0.01 N silver nitrate (potentiometric titration). Results are reported in Figure 2.

In the case of onium salts **4a,c,d** equilibrium 3 was studied in the same condition as for the kinetic measurements, adding to the system 12 mmol of potassium methanesulfonate corresponding to the amount formed in reaction 1 at 100% conversion. For **4b** equilibrium 3 was studied at the following percents of reaction 1: 5, 10, 20, 50, 100% (Figure 1).

Registry No. **1c**, 14937-45-2; **2c**, 3115-68-2; **3c**, 1643-19-2; **4a**, 81389-83-5; **4b**, 3125-07-3; **4c**, 14866-33-2; **4d**, 16829-91-7; octyl methanesulfonate, 16156-52-8.

Preparation and Rearrangement of 1,2-Dialkenylcyclobutanols. A Useful Method for Synthesis of Substituted Cyclooctenones

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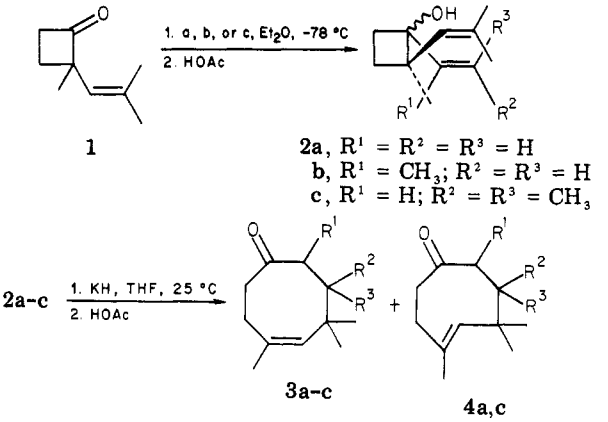
The syntheses and anionic oxy-Cope rearrangements of 1,2-dialkenylcyclobutanols are reported. Reaction of 2-methyl-2-(2-methylpropen-1-yl)-1-cyclobutanone (1) with vinyl-, isopropenyl-, or isobutenyllithium led to formation of cyclobutanols **2a-c**. Treatment with potassium hydride induced rearrangement to *Z* and *E* cyclooctenones **3a-c** and **4a,c**. Reaction of 5-methylenespiro[3.5]nonan-1-one (8) with the same alkenyllithium reagents afforded directly a mixture of rearranged and ring-opened products (**11a-c** and **12a-c**). Reaction of spiro[3.5]non-5-en-1-one (17) with vinyl- or isopropenylmagnesium bromide produced a mixture of diastereomeric cyclobutanols **18a,b** and **19a,b** which underwent anionic oxy-Cope rearrangement to bicyclo[5.3.1]undec-1-(11)-en-4-ones **20a,b** in high yield. A mechanism for the rearrangement of stereodistal 1,2-dialkenylcyclobutanols is proposed.

There are several important classes of natural products which contain eight-membered rings. Cyclooctanes appear in the fused-ring systems of the ophiobolin,[1] ceroplastol,[2] cotylenol,[3] and fusiococcin[4] families of natural products and also in the bridged, bicyclic skeletons of pleuromutilin[5] and taxol.[6]

Syntheses of cyclooctanes from acylic precursors tend to be only marginally successful[7] due to unfavorable entropic factors as well as large increases in enthalpy resulting from transannular and torsional strain. Somewhat more successful preparations of cyclooctanes have involved one- and two-carbon ring expansions of cycloheptanes[8] and cyclohexanes,[9] respectively, and also fragmentation of bicyclic precursors.[8,10] However, these reactions are far from general, and new methodology for cyclooctane synthesis is needed. We report the results of our investigation of a novel and versatile cyclooctane synthesis based upon ring expansion of cyclobutane precursors.

Scheme I



[a] (a) CH_2=CHLi, (b) CH_2=C(CH_3)Li, (c) (CH_3)$_2$C=CHLi.

The Cope rearrangement of *cis*-1,2-divinylcyclobutane has been studied in detail by Berson and others.[11,12,16] Driven by a significant release of ring strain, this rearrangement occurs at much lower temperatures than the acyclic variant. We felt that the anionic oxy-Cope version of this rearrangement would be particularly suitable as a general method for the synthesis of substituted cyclooctenones for several reasons: (1) the required dialkenylcyclobutanols could, in principle, be prepared directly from readily available 2-alkenylcyclobutanones;[13] (2) rearrangement should be possible under mild conditions (room temperature or below) due to the accelerating effect

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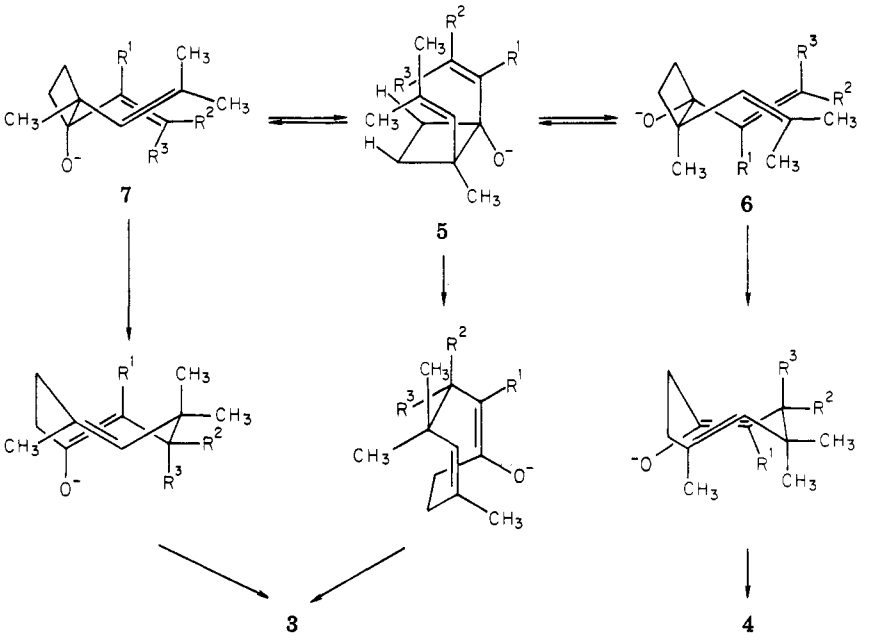
Scheme II



of the anionic substituent;[14] (3) the relative configuration of chiral centers produced as a result of the rearrangement can be predicted from the transition-state conformation; (4) the resulting 4-cycloocten-1-ones are differentially functionalized and should serve as useful synthetic intermediates in the construction of natural products.

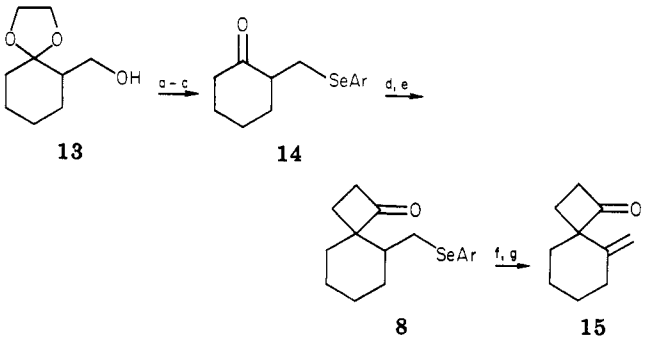
Results and Discussion

We chose as our simplest model system the known[13a] 2-methyl-2-(2-methylpropen-1-yl)cyclobutanone (**1**, Scheme I). Reaction of **1** with vinyllithium[15] afforded the allylic alcohol **2a** in essentially quantitative yield. Similarly, reaction of **1** with isopropenyllithium[15] and isobutenyllithium[15] produced the corresponding alcohols **2b** and **2c**, respectively. In each case the allylic alcohol isolated was found to be essentially one diastereomer (>95%) by NMR and HPLC analyses. Although the stereochemistry of the alcohols was not definitively established, the alkenyl groups are most likely trans as a result of attack of the alkenyllithium at the less hindered face of the carbonyl.

Treatment of cyclobutanol **2a** with potassium hydride (KH) in THF at room temperature resulted in rapid rearrangement (Scheme I) to the *cis*- and *trans*-cyclooctenones **3a** and **4a** (**3a**/**4a** ratio of 79:21), which were isolated in 62% overall yield from cyclobutanone **1**. Under the same conditions, **2c** rearranged to a mixture of **3c** and **4c** (67:33 **3c**/**4c**) in 49% overall yield, while cyclobutanol **2b** afforded exclusively (>95% by NMR and HPLC analyses) *cis*-cyclooctenone **3b** in 50% overall yield.

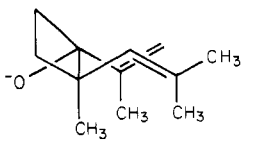
The rearrangement of these alcohols is somewhat surprising in view of the observation that *trans*-1,2-divinylcyclobutane does not undergo Cope rearrangement but instead reacts predominantly via [1,3]-shift processes at elevated temperatures.[16] Since it is reasonable to assume that **2a–c** are *trans*-dialkenylcyclobutanols, their rearrangement to cyclooctenones presumably occurs via initial isomerization to the *cis*-dialkenylcyclobutanol (vide infra) and subsequent Cope rearrangement. No products resulting from [1,3] rearrangements were detected in these reactions.

Scheme III



[a] (a) MsCl, Et_3N, ether, 25 °C; (b) 4,4'-dichlorodiphenyl diselenide, $NaBH_4$, EtOH, reflux; (c) acetone, $BF_3 \cdot Et_2O$, reflux; (d) lithiocyclopropyl phenyl sulfide, THF, −78 °C; (e) TsOH, PhH, reflux; (f) MCPBA, THF, −20 °C; (g) CCl_4, Et_2NH, reflux.

The formation of *trans*-cyclooctenones **4a** and **4c** is due to a change in transition-state conformation from the normally favored s-cis boat conformation (**5**, Scheme II) to a chair conformation (**6**) as a result of steric interactions between the endo terminal methyl substituents and the cyclobutyl ring protons, a phenomenon also observed by Berson[12b] during his study of the rearrangements of hindered *cis*-1,2-dialkenylcyclobutanes. The *cis*-cyclooctenes **3a–c** may arise via s-cis boat transition-state **5** or possibly via the alternative chair transition state **7**. Exclusive formation of *cis*-cyclooctenone **3b** from the isopropenylcyclobutanol **2b** may be due to destabilization of the chair transition-state **6b** (leading to the trans isomer) by steric repulsion between the quasi-diaxial methyl groups.[17]



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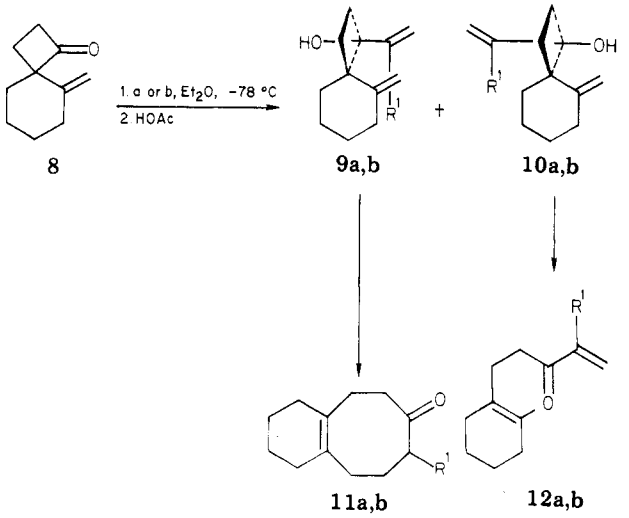
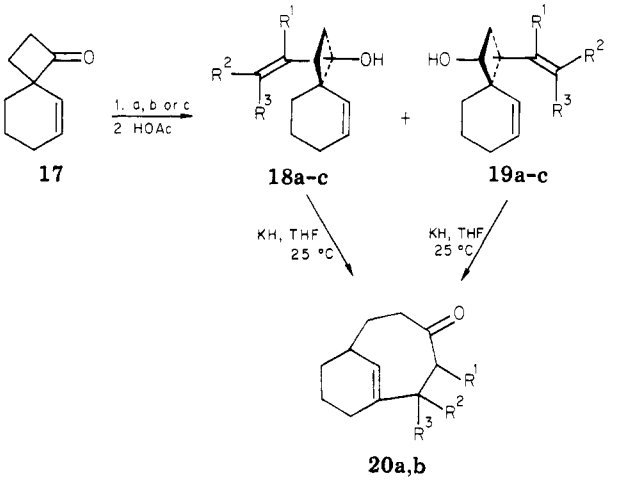
Scheme IV



[a] (a) CH_2=CHLi, (b) CH_2=C(CH_3)Li. **9a-12a**, R^1 = H; **9b-12b**, R^1 = CH_3.

Scheme V



[a] CH_2=CHMgBr, (b) CH_2=C(CH_3)MgBr, (c) $(CH_3)_2$C=CHMgBr. **18a-20a**, R^1 = R^2 = R^3 = H; **18b-20b**, R^1 = CH_3, R^2 = R^3 = H; **18c** and **19c**, R^1 = H, R^2 = R^3 = CH_3.

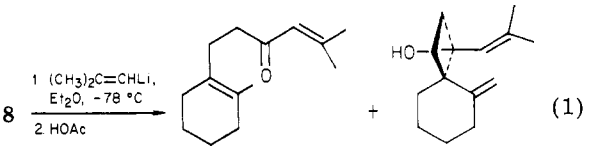
We have also investigated the ring expansion of 5-methylenespiro[3.5]nonan-1-one (**8**, Scheme III) to various octahydrobenzocyclooctenones. The benzocyclooctene ring system is of interest due to its incorporation in the antitumoral taxol. Furthermore, the cyclopentacyclooctene ring system, which should be available by an analogous ring expansion of 5-methylenespiro[3.4]octan-1-one, is found in the ophiobolin, ceroplastol, cotylenol, and fusiococcin families of natural products.

The preparation of **8** was accomplished in 46% overall yield from the known[18] ethylene ketal of 2-(hydroxymethyl)cyclohexanone **13** as shown in Scheme III. Mesylation of **13** followed by displacement with *p*-chlorobenzeneselenenolate anion[19] cleanly afforded the primary selenide. Transketalization furnished the seleno ketone **14** in 70% overall yield from **13**. Conversion to the cyclobutanone **15** (as a mixture of diastereomers) was accomplished by the method of Trost[13a] in 76% overall yield. Finally, oxidation and selenoxide elimination[20] produced **8** in 86% yield.

It was expected that the rearrangement of allylic alcohols derived from **8** would be particularly facile due to the rigid s-cis orientation of the exocyclic methylene and the consequent reduction of activation energy needed to achieve the preferred s-cis boat transition-state conformation. This was found to be the case, and, in general, it was not possible to isolate these allylic alcohols.

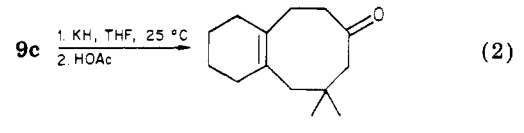
Instead, reaction of **8** with vinyllithium (Scheme IV) resulted in isolation of a mixture of 1,2,3,4,5,6,9,10-octahydro-7(8*H*)-benzocyclooctenone (**11a**) and 5-(2-methyl-1-cyclohexen-1-yl)-1-penten-3-one (**12a**) in 78% yield (44:56 **11a/12a**). Similarly, treatment of **8** with isopropenyllithium produced, after the workup, a mixture of **11b** and **12b** in 76% yield (17:83 **11b/12b**). Benzocyclooctenones **11a,b** are presumably formed via rapid oxy-Cope rearrangement of the *cis*-dialkenylcyclobutanols **9a,b** while the ring-opened ketones **12a,b** are produced via retro-ene reaction of the intermediate *trans*-dialkenylcyclobutanols **10a,b**.[21] This retro-ene process (also termed β-hydroxy olefin cleavage) has been observed previously in competition with the oxy-Cope rearrangement.[22] *The formation of octahydrobenzocyclooctenones* ***11a,b*** *from the cyclobutanone* ***8*** *constitutes the first example of a one-step, four-carbon ring expansion of a cyclobutanone to a cyclooctanone.*

Upon reaction of **8** with isobutenyllithium (eq 1), a



(1)

mixture of two products was again isolated (52% yield, 81% based on recovered **8**). One component of this mixture was found to be ring-opened ketone **12c**, while the other component was determined to be allylic alcohol **9c** (49:51 **9c/12c**). This alcohol is much more stable at room temperature than **9a** or **9b** because of steric repulsion encountered in the Cope-rearrangement transition state. Nonetheless, treatment of **9c** with KH in THF at room temperature resulted in facile rearrangement to octahydrobenzocyclooctane **11c** in 68% yield (eq 2).



(2)

Reaction of **8** with vinyllithium followed by a low-temperature workup and subsequent treatment with KH in room temperature THF again resulted in the isolation of a mixture of two products (eq 3). One product was the previously isolated benzocyclooctenone **11a**, while the other was found to be allylic alcohol **16** (44:56 **11a/16**). While benzocyclooctenone **11a** again arises as a result of Cope rearrangement of the stereoproximal dialkenylcyclobutanol

(17) We are currently attempting to determine unambiguously the relative population of each transition-state conformation in these rearrangements.

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(21) On the basis of TLC evidence, **12a** is not present in the cold (−78 °C) quenched reaction mixture but forms rapidly when the reaction reaches room temperature. Coincident with the formation of **12a** is the disappearance (by TLC) of another component of the reaction mixture which has not been isolated but which is presumed to be **10a**.

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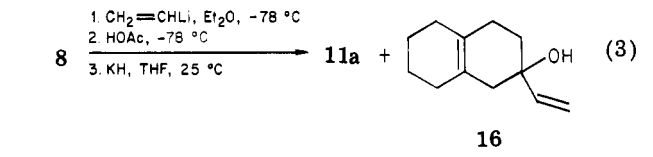


(3)

16

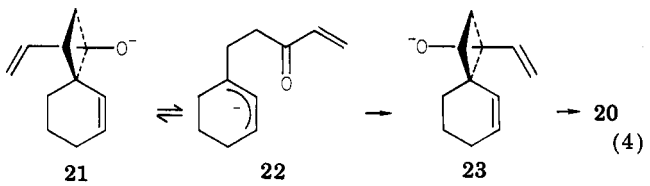
9a, allylic alcohol **16** arises via a [1,3][23] shift of the stereodistal dialkenylcyclobutanol **10a** (vide infra).

As a third model system, we chose to study the ring expansion of the known[13a] spiro[3.5]non-5-en-1-one (**17**, Scheme V) to various bicyclo[5.3.1]undec-1(11)-en-4-ones, **20a–c**, via the intermediate allylic alcohols. Methods for synthesis of the bicyclo[5.3.1]undecane ring system are of interest due to its incorporation in the antitumoral taxol and the antibiotic pleuromutilin.

Treatment of **17** with vinylmagnesium bromide generated a mixture of diastereomeric alcohols, **18a/19a** (78% yield), which were separated by preparative HPLC.[24] Each diastereomer was individually subjected to KH in THF at room temperature, and *both* rearranged cleanly to bicyclo[5.3.1]undec-1(11)-en-4-one (**20a**).[25] On a preparative scale, the mixture of diastereomeric cyclobutanols could be converted to **20a** in 80% yield. Again, no products resulting from [1,3] shifts could be detected.

Similarly, isopropenylmagnesium bromide reacted with **17** to produce a mixture of diastereomers **18b/19b** (68% yield)[26a] which cleanly rearranged in 72% yield to **20b** upon subjection to anionic oxy-Cope conditions. Treatment of **17** with isobutenylmagnesium bromide also afforded a mixture of diastereomeric allylic alcohols **18c/19c** in 55% yield.[26b] However, attempted anionic oxy-Cope rearrangement of these alcohols was unsuccessful, resulting in formation of a complex mixture of products from which no ketonic materials could be isolated.

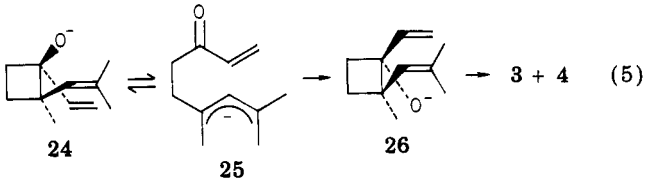
The rearrangement of the stereodistal allylic alcohols **19a,b** (which cannot undergo concerted Cope rearrangement) presumably occurs via initial isomerization to the stereoproximal isomers **18a,b**. Berson has shown[12a] that a similar isomerization occurs to a small extent in the thermolysis of *trans*-1,2-divinylcyclobutane (possibly via a diradical). In the present case, the anionic oxy-Cope rearrangement of **19a,b** may occur by way of reversible heterolysis of cyclobutoxide **21** to the allyl anion **22** (eq 4) and reclosure to the stereoproximal isomer **23**. Similar



(4)

21 22 23

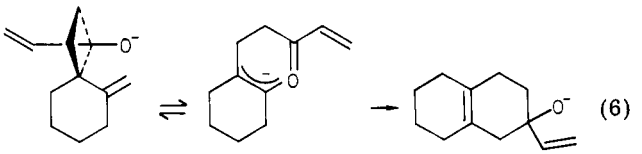
fragmentations of allylic alkoxides have been reported by Benkeser and also by Gerard.[27] The rearrangement of the *trans*-dialkenylcyclobutanols **2a–c** may occur by an analogous reversible heterolysis of stereodistal cyclobutoxide **24** to allyl anion **25** and reclosure to stereoproximal cyclobutoxide **26** (eq 5).



(5)

24 25 26

Allylic alcohol **16** may arise by a similar mechanism in which the stereodistal cyclobutoxide **27** (eq 6) undergoes



(6)

27 28 29

ring opening to allyl anion **28**, which then closes to cyclohexoxide **29** rather than to a stereoproximal cyclobutoxide.[28] Allyl anion **28** appears to be unique in this regard, as a consequence of its conformationally rigid, sterically unhindered allyl terminus. The possibility that **29** occurs via a concerted [1,3] shift cannot, however, be ruled out.[23]

In summary, we have shown that 2-alkenylcyclobutanones can be ring-expanded to cyclooctenones either directly or by anionic oxy-Cope rearrangement of intermediate 1,2-dialkenylcyclobutanols. With the exception of **8**, in which the unhindered, exocyclic methylene is highly reactive, *both* the *cis*- and *trans*-1,2-dialkenylcyclobutanols rearrange to cyclooctenones in good to excellent yields. Syntheses of cyclooctenones in which the double bond is exclusively cis (from **8**) or excllusively trans (from **17**) are possible. In the case of monocyclic cyclobutanones, varying amounts of both *cis*- and *trans*-cyclooctenones can be produced, depending upon the relative populations of the transition-state boat or chair conformations. We are currently investigating the application of this rearrangement to the total synthesis of natural products.

Experimental Section

General Methods. Proton nuclear magnetic resonance (NMR) spectra were measured on a Varian EM-360 spectrometer or, where specified, on a JEOL FX-270 spectrometer, and all shifts are reported downfield from an internal Me_4Si standard. Infrared (IR) spectra were taken with a Perkin-Elmer Model 283 spectrophotometer. Mass spectra (MS) were measured with a Hewlett-Packard HP 5985A GC/MS system. Elemental analyses were performed by Micro-Tech Laboratories, Inc. Preparative HPLC separations were performed by using a Waters HPLC system equipped with a 7.8 mm × 30 cm semipreparative column packed with μ-Porasil (10-μm particle size). Flash chromatography

(23) For other examples of [1,3] shifts of potassium allyloxides see: Thies, R. W.; Seitz, E. P. *J. Org. Chem.* **1978**, *43*, 1050. Danheiser, R. L.; Martinez-Davila, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943.

(24) The ratio of diastereomers is 21:79. We have not determined which of these alcohols corresponds to structure **18a** and which to **19a**.

(25) After these results were obtained, two reports appeared dealing with the same rearrangement (Kahn, M. *Tetrahedron Lett.* **1980**, *21*, 4547. Levine, S. G.; McDaniel, R. L., Jr. *J. Org. Chem.* **1981**, *46*, 2199). However, these authors did not comment on, and may have been unaware of, the rearrangement of *both* the stereoproximal and the stereodistal isomers.

(26) (a) The ratio of diastereomers is 30:70. (b) The ratio of diastereomers is 27:73.

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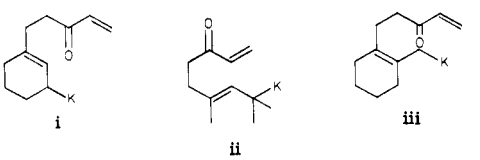
(28) It may be more accurate to represent **22**, **25**, and **28** as i–iii, respectively.[29]



i ii iii

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separations were performed according to the method of Still.[30] Preparative LC separations were performed on a system consisting of an FMI RPSY laboratory pump and Glenco glass LC columns packed with Merck silica gel 60 (230–400 mesh).

Dry tetrahydrofuran (THF) and diethyl ether were prepared by distillation from sodium benzophenone ketyl.

Vinyl bromide and 2-bromopropene were purchased from Aldrich Chemical Co.

1-Bromo-2-methylpropene was prepared as follows. A 100-mL, three-necked, round-bottom flask, containing 50 mL of hexane and fitted with a gas-inlet tube, an addition funnel, and a dry ice condensor filled with dry ice/acetone slush, was cooled to 0 °C in an ice bath. Bromine (12 mL, 0.23 mol) was added dropwise over 15 min via the addition funnel, and at the same time isobutylene (Matheson) was bubbled into the solution. During the additions, the solution was irradiated with a 150-W sunlamp. After all of the bromine was added, the flow of isobutylene was continued until the solution decolorized. The hexane was removed under vacuum and the residue distilled to give 38.8 g (78% yield) of 1,2-dibromo-2-methylpropane, bp 72–75 °C (20 mm) [lit.[31] bp 38–42 °C (10 mm)].

To a mixture of 1,2-dibromo-2-methylpropane (38.8 g, 0.18 mol) and 40 mL of 50% NaOH solution was added 4 mL of tetrabutylammonium hydroxide solution (Aldrich, 40% in water). The reaction was heated in a 120 °C oil bath for 2 h during which time 1-bromo-2-methylpropene distilled over with a small amount of water. The distillate was chilled at −20 °C overnight (to freeze out the water), decanted, and distilled from 4-Å sieves or $MgSO_4$ to provide 18.2 g (75% yield) of pure product, bp 87 °C (lit.[31] bp 92 °C).

2-Methyl-2-(2-methylpropen-1-yl)-1-cyclobutanone (1) and spiro[3.5]non-5-en-1-one (17) were prepared by the method of Trost et al.[13a] except that 20 equiv of acrolein was added during the fluoroboric acid induced rearrangement. The acrolein traps liberated thiophenol and prevents formation of side products.[13b] Both **1** and **17** gave spectral data identical with those previously reported.[13a] In addition, **1** had a boiling point of 80–82 °C (20 mm), and **17** had a boiling point of 68–70 °C (2.8 mm).

1-Ethenyl-2-methyl-2-(2-methylpropen-1-yl)cyclobutan-1-ol (2a). A solution of vinyllithium in ether was prepared by addition of *tert*-butyllithium (Aldrich, 0.97 M in pentane, 3.59 mL, 3.48 mmol) to excess vinyl bromide (Aldrich, 0.5–1.0 mL) in 20 mL of dry ether at −78 °C under nitrogen.[15] After 15 min at −78 °C, cyclobutanone **1** (0.200 g, 0.227 mL, 1.45 mmol) was added slowly to the stirred solution as a neat liquid via syringe. During the addition, the end portion of the syringe needle was kept submerged in the cold ether solution so that the ketone was chilled to −78 °C as it passed through the needle. The reaction was stirred for 20 min at −78 °C under nitrogen, acetic acid (0.209 mL, 3.65 mmol) was added with good stirring, and the reaction mixture was allowed to warm to room temperature. Saturated aqueous $NaHCO_3$ (5 mL) was added to the reaction mixture, and the phases were separated. The aqueous phase was extracted with three 20-mL portions of ether, and the combined organic phases were dried ($MgSO_4$) and concentrated under vacuum to yield 0.258 g of crude product which was apparently only one diastereomer by NMR and HPLC analyses. This material was not further purified but instead used directly for the anionic oxy-Cope rearrangement. An analytical sample was prepared by preparative HPLC (5% ethylacetate/hexane) and gave the following spectral data: NMR (CCl_4) δ 6.03 (1 H, dd, J = 18, 10 Hz), 5.13 (1 H, dd, J = 18, 2 Hz), 5.00 (1 H, m), 4.90 (1 H, dd, J = 10, 2 Hz), 1.6–2.2 (4 H, m), 1.58 (3 H, br s), 1.47 (3 H, br s), 1.20 (3 H, s); IR (CCl_4) 3600 (m), 3480 (w), 2970 (s), 1450 (m), 990 (m), 920 cm^{-1} (m); MS (15 eV) m/e 165 ($M^+ - 1$), 123, 112, 96 (base), 81.

2-Methyl-2-(2-methylpropen-1-yl)-1-(propen-2-yl)cyclobutan-1-ol (2b). A solution of propen-2-yllithium in ether was prepared by addition of *tert*-butyllithium (Aldrich, 0.97 M in pentane, 3.5 mL, 3.48 mmol) to 2-bromopropene (Aldrich, 0.437 mL, 5.22 mmol) in 20 mL of dry ether at −78 °C under nitrogen,[15] followed by stirring an additional 20 min at −78 °C. Reaction of this organolithium with cyclobutanone **1** (0.200 g, 0.227 mL, 1.45 mmol) in the same manner as described for **2a** led to isolation of 0.280 g of crude **2b** which was apparently one diastereomer by NMR and HPLC analysis. This material was not further purified but instead used directly for anionic oxy-Cope rearrangement. An analytical sample prepared by preparative HPLC (5% ethyl acetate/hexane) gave the following spectral data: NMR (CCl_4) δ 5.13 (1 H, m), 4.90 (1 H, m), 4.78 (1 H, m), 1.5–2.4 (4 H, m), 1.78 (3 H, br s), 1.60 (3 H, br s), 1.55 (3 H, br s), 1.24 (3 H, s); IR (CCl_4) 3600 (m), 2970 (s), 1440 (m), 1370 (m), 1140 (m), 900 cm^{-1} (m); MS (70 eV) m/e 179 ($M^+ - 1$), 109, 99, 69, 43 (base).

1,2-Bis(2-methylpropen-1-yl)-2-methylcyclobutan-1-ol (2c). A solution of 2-methylpropen-1-yllithium in ether was prepared by addition of *tert*-butyllithium (Aldrich, 0.97 M in pentane, 4.30 mL, 4.20 mmol) to 1-bromo-2-methylpropene (0.570 g, 0.440 mL, 4.20 mmol) in 10 mL of dry ether at −78 °C under nitrogen, followed by warming to 0 °C for 30 min.[15] After being cooled to −78 °C under nitrogen, this organolithium was reacted with cyclobutanone **1** (0.200 g, 0.227 mL, 1.45 mmol) in the same manner as described for preparation of **2a**. Upon workup, crude **2c** (0.247 g) was isolated which was apparently one diastereomer by NMR and HPLC analyses. This material was not further purified but instead used directly in the anionic oxy-Cope rearrangement. An analytical sample was purified by preparative HPLC (5% ethyl acetate/hexane) and gave the following spectral data: NMR (CCl_4) δ 5.58 (1 H, m), 5.09 (1 H, m), 1.5–2.3 (4 H, m), 1.75 (3 H, br s), 1.67 (6 H, br s), 1.52 (3 H, br s), 1.19 (3 H, s); IR (CCl_4) 3600 (m), 3470 (w), 2960 (s), 1440 (m), 1370 (m), 1070 (m), 1050 cm^{-1} (m); MS (70 eV) m/e 193 ($M^+ - 1$), 149, 109, 95, 83 (base).

(*Z*)- and (*E*)-4,6,6-Trimethylcyclooct-4-en-1-one (3a and 4a). Cyclobutanol **2a** (0.258 g, crude, from 1.45 mmol of cyclobutanone **1** as described above) in 25 mL of dry THF was added in one portion to a stirred suspension of hexane-washed KH (Aldrich, 24% in oil, 0.278 g, 1.67 mmol) in 25 mL of dry THF under nitrogen. The orange reaction mixture was stirred at room temperature for 45 min and then quenched with acetic acid (0.095 mL, 1.67 mmol). After an additional 30 min, 25 mL of ether was added, and the reaction mixture was filtered through a pad of Celite. Solvent evaporation left 0.217 g of crude product which was purified by flash chromatography (8 g of silica gel, 5% ethyl acetate/hexane).

The less polar fraction (0.032 g, oil, 13% yield from **1**) was determined to be the relatively unstable (*E*)-cyclooctenone **4a** which gave the following spectral data: NMR (CCl_4) δ 4.70 (1 H, m), 1.5–3.0 (8 H, m), 2.00 (3 H, d, J = 2 Hz), 1.20 (3 H, s), 1.07 (3 H, s); IR (CCl_4) 2960 (s), 1700 (s), 1450 (m), 1090 (m); MS (70 eV) m/e 166 (M^+), 109, 96, 81, 71, 55 (base).

The more polar fraction (0.118 g, oil, 49% yield from **1**) was determined to be the (*Z*)-cyclooctenone **3a** which gave the following spectral data: NMR (CCl_4) δ 4.97 (1 H, m), 1.6–2.6 (8 H, m), 1.62 (3 H, d, J = 2 Hz), 1.08 (6 H, s); IR (CCl_4) 2960 (s), 1710 (s), 1465 cm^{-1} (s); MS (70 eV) m/e 166 (M^+), 148, 12, 109, 97, 96, 81, 67 (base), 55. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.17; H, 10.95.

(*Z*)-4,6,6,8-Tetramethylcyclooct-4-en-1-one (3b). The anionic oxy-Cope rearrangement of cyclobutanol **2b** was carried out in the same manner as described for **2a**. Thus **2b** (0.280 g, crude, prepared from 1.45 mmol of cyclobutanone **1** as described above) afforded 0.225 g of crude cyclooctenone **3b** which was purified by flash chromatography (8 g of silica gel, 5% ethyl acetate/hexane) to yield 0.130 g of pure product (oil, 50% yield overall from **1**) which gave the following spectral data: NMR (CCl_4) δ 5.00 (1 H, m), 1.3–2.7 (7 H, m), 1.67 (3 H, d, J = 2 Hz), 1.14 (3 H, s), 1.04 (3 H, s), 1.01 (3 H, d, J = 7 Hz); IR (CCl_4) 2960 (s), 1710 (s), 1700 (s), 1450 (m), 1360 (m), 1180 cm^{-1} (s); MS (70 eV) m/e 180 (M^+), 123, 109, 96 (base), 81, 67, 55.

(*Z*)- and (*E*)-4,6,6,7,7-Pentamethylcyclooct-4-en-1-one (3c and 4c). The anionic oxy-Cope rearrangement of cyclobutanol **2c** was carried out in the same manner as described for **2a**. Thus **2c** (0.247 g, crude, prepared from 1.45 mmol of **1** as previously described) afforded 0.165 g of crude product which was purified by preparative HPLC (10% ethyl acetate/hexane).

The less polar compound was determined to be the relatively unstable (*E*)-cyclooctenone **4c** (0.045 g, oil 16% overall from **1**) which gave the following spectral data: NMR (CCl_4) δ 5.02 (1 H, m), 1.3–2.8 (6 H, m), 2.02 (3 H, d, J = 2 Hz), 1.19 (3 H, s), 1.02 (3 H, s), 0.91 (3 H, s), 0.80 (3 H, s); IR (CCl_4) 2960 (s), 1700 (s),

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1450 (m), 1385 (m), 1090 cm^{-1} (m); MS (70 eV) m/e 194 (M^+), 109, 96 (base), 81, 67, 55.

The more polar compound was determined to be (*Z*)-cyclooctenone **3c** (0.92 g, oil, 33% overall from 1) which gave the following spectral data: NMR (CCl_4) δ 5.09 (1 H, m), 2.3–2.6 (4 H, m), 2.29 (2 H, s), 1.75 (3 H, d, J = 2 Hz), 1.7 (6 H, s), 0.95 (6 H, s); IR (CCl_4) 2980 (s), 1700 (s), 1450 (m), 1385 cm^{-1} (m); MS (70 eV) m/e 194 (M^+), 109, 96 (base), 81, 67, 55.

2-[[(*p*-Chlorophenyl)selenenyl]methyl]-1-cyclohexanone (14). Ketal **13**[18] (3.15 g, 18.3 mmol) was dissolved in 30 mL of dry ether containing triethylamine (distilled from KOH; 3.06 mL, 22.0 mmol). With good stirring, a solution of methanesulfonyl chloride (distilled from P_2O_5; 1.56 mL, 20.1 mmol) in 25 mL of dry ether was added over 5 min. After 2 h at room temperature, the reaction mixture was filtered and concentrated under vacuum to an oil which slowly solidified (4.48 g). This mesylate was not further purified but was used directly in the next reaction. The crude mesylate gave the following NMR data: (CCl_4): δ 4.25 (1 H, dd, J = 9, 4 Hz), 3.89 (1 H, dd, J = 9, 6 Hz), 3.88 (4 H, br s), 2.88 (3 H, s), 1.2–2.3 (9 H, m).

Bis(4-chlorophenyl) diselenide[19] (4.09 g, 10.8 mmol) was dissolved in 40 mL of absolute ethanol, and $NaBH_4$ (1.91 g, 50.3 mmol) in 25 mL of ethanol was added dropwise. The crude mesylate prepared as described above (4.48 g) was added in one portion, and the reaction mixture was refluxed for 2 h. After cooling to room temperature, the reaction mixture was diluted with 25 mL of water and extracted with 25 mL of ether. The aqueous phase was saturated with sodium chloride and extracted with two 25-mL portions of ether. The combined organic phases were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated. The oily residue was passed through a pad of 10 g of silica gel with 5% ethyl acetate/hexane to remove polar impurities. The crude selenide obtained as an oil after solvent removal (5.78 g) was not purified further but was used directly in the next reaction. The crude selenide gave the following NMR data (CCl_4): δ 6.9–7.5 (4 H, m), 3.83 (4 H, br s), 3.15 (1 H, dd, J = 12, 4 Hz), 2.50 (1 H, dd, J = 12, 8 Hz), 1.0–2.1 (9 H, m).

The selenide prepared as described above (5.78 g) was dissolved in 50 mL acetone, and, after addition of boron trifluoride etherate (Aldrich; 50 μL, 0.407 mmol), this solution was refluxed for 1 h. The solvent was removed under vacuum and was replaced with 50 mL of fresh acetone. More boron trifluoride etherate was added (30 μL, 0.244 mmol), and the reaction mixture was refluxed for 1 h. Removal of the solvent left 5.51 g of crude ketone **14** which was purified by preparative LC (180 g silica gel, 7% ethyl acetate/hexane) to afford 3.86 g of pure ketone **14** (70% yield from ketal **13**) as an oil. This ketone gave the following spectral data: NMR (CCl_4) δ 6.9–7.4 (4 H, m), 2.9–3.4 (1 H, m), 2.0–2.8 (5 H, m), 1.0–2.0 (5 H, m); IR (CCl_4) 2940 (s), 2860 (m), 1710 (s), 1475 (s), 1090 (s), 1010 cm^{-1} (s); MS (70 eV) m/e 304/302/300 (M^+ – 302 most intense), 193/191/189, 156/154, 111, 83, 55 (base).

5-[[(*p*-Chlorophenyl)selenenyl]methyl]spiro[3.5]nonan-1-one (15). To cyclopropyl phenyl sulfide[32] (2.52 g, 2.42 mL, 16.8 mmol) in 50 mL of dry THF at 0 °C under nitrogen was added *n*-butyllithium (Aldrich; 1.6 M in hexane, 10.1 mL, 16.8 mmol), and the resulting yellow solution was stirred 1 h at 0 °C and then chilled to −78 °C. The ketone **14** (3.62 g, 12.0 mmol) in 20 mL of dry THF was added over 5 min, and the resulting solution was stirred at −78 °C for 2 h and then at 0 °C for 1 h. At the end of this time, 10 mL water and 25 mL ether were added, and the phases were separated. The aqueous phase was extracted with two 20-mL portions of ether, and the combined organic phases were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under vacuum. The crude alcohol thus obtained was used directly in the next reaction without further purification. The crude alcohol gave the following NMR data (CCl_4): δ 7.0–7.5 (9 H, m), 0.5–2.5 (16 H, m).

The crude alcohol was dissolved in 50 mL of benzene containing 0.2 mL of water and 1.35 g (7.50 mmol) of toluenesulfonic acid monohydrate. This reaction mixture was refluxed for 3 h, cooled, and washed with 25 mL of water. The aqueous wash was extracted with two 20-mL portions of ether, and the combined organic phases were washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. After the mixture was dried ($MgSO_4$) and the solvent removed under vacuum, the crude cyclobutanone was purified by preparative LC (180 g silica gel, 3% ethyl acetate/hexane). In this way cyclobutanone **15** (3.21 g, oil, 76% yield from ketone **14**) was obtained as a mixture of diastereomers which gave the following spectral data: NMR (CCl_4) δ 7.0–7.5 (4 H, m), 2.3–3.5 (5 H, m), 1.2–2.3 (10 H, m); IR (CCl_4) 2930 (s), 2860 (m), 1770 (s), 1475 (s), 1190 (s), 1090 (s), 1010 cm^{-1} (s); MS (70 eV) m/e 344/342/349 (M^+ – 342 most intense), 312/314/315, 123/125, 109 (base), 95, 81, 67.

5-Methylenespiro[3.5]nonan-1-one (8). The selenide **15** (8.19 g, 23.3 mmol) was dissolved in 50 mL of dry THF, and the resulting solution was chilled to −20 °C. *m*-Chloroperbenzoic acid (Aldrich; 85%, 5.20 g, 25.6 mmol) in 30 mL of dry THF was added over 5 min, and the reaction mixture was stirred at −20 °C for 20 min. At the end of this time, the reaction mixture was transferred by cannula into 75 mL of refluxing CCl_4 containing diethylamine (4.81 mL, 46.6 mmol). After 10 min at reflux, the reaction mixture was cooled and diluted with 50 mL of water. The phases were separated, and the aqueous phase was saturated with NaCl and then extracted with two 20-mL portions of ether. The combined organic layers were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under vacuum. The crude product was separated from the nonvolatile residue by Kugelrohr distillation [80 °C (0.5 torr)] and then purified by fractional distillation [bp 48 °C (0.9 mm)] to give 3.01 g (86%) of spirononanone **8** which gave the following spectral data: NMR (CCl_4) δ 4.60 (2 H, br s), 2.85 (2 H, t, J = 8 Hz), 2.0–2.4 (3 H, m), 1.3–2.0 (7 H, m); IR (CCl_4) 2940 (s), 2860 (m), 1775 (s), 1640 (m), 1440 (m), 1050 (m), 890 cm^{-1} (m); MS (70 eV) m/e 150 (M^+), 122, 108, 93 (base), 79. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.86; H, 9.35.

1,2,3,4,5,6,9,10-Octahydro-7(8*H*)-benzocyclooctenone (11a) and 5-(2-Methyl-1-cyclohexen-1-yl)-1-penten-3-one (12a). A solution of vinyllithium was prepared as previously described, from *tert*-butyllithium (0.97 M, 2.48 mL, 2.40 mmol) and excess vinyl bromide in 20 mL of dry ether at −78 °C. Ketone **8** (0.150 g, 0.156 mL, 1.00 mmol) was added via syringe in the manner previously described for the preparation of **2a**. After 30 min at −78 °C, the reaction was quenched with acetic acid (0.137 mL, 2.40 mmol) and the mixture allowed to warm to room temperature. Saturated aqueous $NaHCO_3$ (5 mL) was added and the phases were separated. The aqueous layer was washed with two 10-mL portions of ether, and the combined organic phases were dried ($MgSO_4$) and concentrated under vacuum to leave 0.173 g of a mixture of **11a** and **12a** which was separated by flash chromatography (18 g of silica gel, 4% ethyl acetate/hexane).

The less polar component (0.077 g, oil, 43% yield) was identified as the ring-opened product (**12a**) and gave the following spectral data: NMR (CCl_4) δ 6.12 (2 H, m), 5.60 (1 H, dd, J = 8, 4 Hz), 2.1–2.7 (4 H, m), 1.3–2.1 (8 H, m), 1.60 (3 H, br s); IR (CCl_4) 2940 (s), 1705 (s), 1685 (s), 1640 (m), 1450 (m), 1400 (m), 1100 (m), 990 (m), 960 cm^{-1} (m); MS (70 eV) m/e 178 (M^+), 150, 108, 93 (base), 79, 67, 55. Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.50; H, 10.28.

The more polar component (0.061 g, oil, 35% yield) was determined to be benzocyclooctenone **11a** which gave the following spectral data: 270-MHz NMR ($CDCl_3$) δ 2.47 (6 H, m), 2.14 (2 H, m), 1.95 (4 H, m), 1.58 (6 H, m); IR (CCl_4) 2940 (s), 2860 (m), 2840 (m), 1705 (s), 1470 (m), 1450 cm^{-1} (m); MS (70 eV) m/e 178 (M^+), 150, 135, 93, 91, 79 (base). Anal. Calcd for $C_{12}H_{18}O$: C, 80.84; H, 10.18. Found: C, 80.28; H, 10.10.

8-Methyl-1,2,3,4,5,6,9,10-octahydro-7(8*H*)-benzocyclooctenone (11b) and 2-Methyl-5-(2-methyl-1-cyclohexen-1-yl)-1-penten-3-one (12b). A solution of propen-2-yllithium was prepared from 2-bromopropene (0.302 mL, 3.60 mmol) and *tert*-butyllithium (0.97 M, 2.48 mL, 2.40 mmol) in 20 mL of dry ether at −78 °C as previously described. Reaction of this organolithium with ketone **8** (0.150 g, 0.150 mL, 1.00 mL) in the manner previously described for the preparation of **11a** and **12a** resulted in isolation of a mixture of **11b** and **12b**, which was separated by flash chromatography (18 g silica gel, 2.5% ethyl acetate/hexane).

The less polar component (0.121 g, oil, 62% yield) was identified as **12b** and gave the following spectral data: NMR (CCl_4) δ 5.79 (1 H, br s), 5.60 (1 H, br s), 2.1–2.8 (4 H, m), 1.3–2.1 (8 H, m),

(32) Tanaka, K.; Uneme, H.; Matsui, S. *Chem. Lett.* **1980**, 287.

1.81 (3 H, br, s), 1.57 (3 H, br s); IR (CCl_4) 2930 (s), 1680 (s), 1630 (w), 1450 (m), 1085 (m), 930 cm^{-1} (m); MS (70 eV) m/e 192 (M^+), 177, 108, 93 (base), 81, 79, 69, 67, 41.

The more polar component (0.026 g, oil, 14% yield) was identified as **11b** and gave the following spectral data: NMR (CCl_4) δ 2.1–2.8 (5 H, m), 1.7–2.1 (6 H, m), 1.2–1.7 (6 H, m), 0.95 (3 H, d, J = 7 Hz); IR (CCl_4) 2940 (s), 1710 (s), 1460 cm^{-1} (m); MS (70 eV) m/e 192 (M^+), 150, 135, 122, 108, 93 (base), 91, 79, 77.

5-Methylene-1-(2-methylpropen-1-yl)spiro[3.5]nonan-1-ol (9c) and 2-Methyl-6-(2-methyl-1-cyclohexen-1-yl)-2-hexen-3-one (12c). A solution of (2-methylpropen-1-yl)lithium was prepared from 1-bromo-2-methylpropene (0.371 mL, 3.60 mmol) and *tert*-butyllithium (0.97 M, 2.48 mL, 2.40 mmol) in 25 mL of dry ether as previously described. Reaction of this organolithium with ketone **8** (0.150 g, 0.156 mL, 1.00 mmol) at −78 °C in the same manner as described for the preparation of **11a** and **12a** resulted in isolation of a mixture of **8**, **9c**, and **12c**. The crude mixture of products was separated by flash chromatography (18 g silica gel, 2.5% ethyl acetate/hexane into two fractions. The less polar fraction (0.113 g) was further purified by preparative HPLC (50% methylene chloride/hexane) to afford ketone **8** (0.054 g) and enone **12c** (0.055 g, oil, 27% yield, 42% based on recovered **8**) which gave the following spectral data: NMR (CCl_4) δ 5.97 (1 H, m), 2.1–2.8 (4 H, m), 2.10 (3 H, br s), 1.3–2.0 (8 H, m), 1.85 (3 H, br s), 1.56 (3 H, br s); IR (CCl_4) 2920 (s), 1690 (s), 1620 (s), 1450 (m), 1200 cm^{-1} (m); MS (70 eV) m/e 206 (M^+), 98, 93, 83 (base), 55.

The more polar component isolated by flash chromatography was found to be **9c** (0.052 oil, 25% yield, 39% based on recovered **8**) which gave the following spectral data: NMR (CCl_4) δ 5.48 (1 H, m), 4.70 (1 H, br s), 4.42 (1 H, br s), 0.9–2.5 (12 H, m), 1.73 (3 H, d, J = 2 Hz), 1.65 (3 H, d, J = 2 Hz); IR (CCl_4) 3605 (m), 3500 (m), 2940 (s), 1640 (s), 1450 (s), 1070 (m), 1055 (s), 900 (m), 890 cm^{-1} (m); MS (70 eV) m/e 206 (M^+), 205 ($M^+ - 1$), 189, 163, 108, 93, 91, 83 (base), 55.

9,9-Dimethyl-1,2,3,4,5,6,9,10-Octahydro-7(8*H*)-benzocyclooctenone (11c). Spiro[3.5]nonanol **9c** (0.056 g, 0.272 mmol) in 10 mL of dry THF was added to a suspension of hexane-washed potassium hydride (24% in oil, 0.054 g, 0.326 mmol) in 10 mL of dry THF. The reaction mixture was stirred 30 min at room temperature and then quenched with acetic acid (0.019 mL, 0.326 mmol). Saturated aqueous $NaHCO_3$ (5 mL) was added, and the phases were separated. The aqueous phase was extracted with two 10-mL portions of ether, and the combined organic phases were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (8 g of silica gel, 5% ethyl acetate/hexane) to afford ketone **11c** (0.038 g, oil, 68% yield) which gave the following spectral data: NMR (CCl_4) δ 2.33 (2 H, s), 1.3–2.2 (14 H), 0.98 (6 H, s); IR (CCl_4) 2940 (s), 1705 (s), 1450 (m), 1335 (m), 1228 cm^{-1} (m); MS (70 eV) m/e 206 (M^+), 177, 150, 108 (base), 93, 79.

2-Ethenyl-3,4,5,6,7,8-Hexahydro-2(1*H*)-naphthalenol (16). A solution of vinyllithium was prepared from excess vinyl bromide and *tert*-butyllithium (0.97 M, 0.825 mL, 0.800 mmol) in 10 mL of dry ether at −78 °C as previously described. Ketone **8** (0.050 g, 0.052 mL, 0.333 mmol) was added by syringe in the manner described for the preparation of **2a**. After 15 min at −78 °C, the reaction was quenched by the addition of acetic acid (0.038 mL, 0.666 mmol) in 5 mL of cold (−78 °C) ether. The quenched reaction mixture was stirred an additional 30 min at −78 °C, the ether solvent was removed via bulb-to-bulb distillation under vacuum (~1–3 torr, temperature <−25 °C), and 15 mL of cold (−78 °C) pentane was added. This mixture was stirred 15 min at −78 °C, and the pentane supernatant was transferred to a clean cold (−78 °C) flask via a stainless-steel cannula. The pentane was removed under vacuum (~1–3 torr, temperature <−25 °C) and replaced with 10 mL of cold (−78 °C), dry THF. This cold THF solution was then transferred via cannula to a suspension of hexane-washed potassium hydride (24% in oil, 0.111 g, 0.666 mmol) stirred in 20 mL of dry THF at room temperature. After 30 min at room temperature, the reaction was quenched with acetic acid (0.038 mL, 0.666 mmol) and the mixture diluted with 10 mL of saturated aqueous $NaHCO_3$. The layers were separated, and the aqueous layer was extracted with two 10-mL portions of ether. The combined organic phases were washed with saturated aqueous NaCl, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by preparative HPLC (10% ethyl acetate/hexane) to yield two components.

The less polar component (0.011 g, 19%) was identified as the previously characterized cyclooctenone **11a**.

The more polar component (0.014 g, oil, 24% yield) was determined to be allylic alcohol **16** which gave the following spectral data: NMR (CCl_4) δ 5.73 (1 H, dd, J = 17, 10 Hz), 5.10 (1 H, dd, J = 17, 2 Hz), 4.90 (1 H, dd, J = 10, 2 Hz), 1.3–2.1 (15 H, m); IR (CCl_4) 3600 (m), 3450 (w), 2940 (s), 2840 (m), 1440 (m), 995 (m), 925 cm^{-1} (m); MS (70 eV) m/e 178 (M^+), 160, 108, 93 (base), 91, 79, 55.

1-Ethenylspiro[3.5]non-5-en-1-ol (18a/19a). Spiro[3.5]-non-5-en-1-one[13a] (**17**; 0.500 g, 0.368 mmol) in 12 mL of dry THF was added to a stirred solution of vinylmagnesium bromide (0.5 M in THF, 12.0 mL, 6.00 mmol) under nitrogen at 25 °C. After 15 min, the reaction was diluted with 2 mL of saturated aqueous NH_4Cl, filtered through a plug of glass wool, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (18 g silica gel, 5% ethyl acetate/hexane) to yield 0.473 g (oil, 78% yield) of a mixture of diastereomers **18a** and **19a**. This mixture was not routinely separated but was used directly in the anionic oxy-Cope rearrangement.

A small amount of the mixture was separated by preparative HPLC (7% ethyl acetate/hexane) to yield two pure diastereomers in a 21:79 ratio. The major diastereomer gave the following spectral data: NMR (CCl_4) δ 5.95 (1 H, dd, J = 17, 10 Hz), 5.45 (2 H, s), 5.06 (1 H, dd, J = 17, 2 Hz), 4.95 (1 H, dd, J = 10, 2 Hz), 1.3–2.3 (11 H, m); IR (CCl_4) 3600 (m), 3460 (m), 2940 (s), 1755 (w), 1640 (w), 1440 (m), 995 (m), 920 cm^{-1} (s); MS (15 eV) m/e 164 (M^+), 136, 107, 94 (base), 79, 43.

The minor diastereomer gave the following spectral data: NMR (CCl_4) δ 5.97 (1 H, dd, J = 17, 10 Hz), 5.83 (2 H, s), 5.20 (1 H, dd, J = 17, 2 Hz), 5.03 (1 H, dd, J = 10, 2 Hz), 1.2–2.3 (11 H, m); IR (CCl_4) 3560 (m), 3010 (m), 2940 (s), 2860 (m), 1755 (w), 1635 (w), 1440 (m), 995 (m), 920 cm^{-1} (s); MS (15 eV) m/e 163 ($M^+ - 1$), 150, 136, 122, 108, 94 (base), 79.

1-(Propen-2-yl)spiro[3.5]non-5-en-1-ol (18b/19b). Spiro-[3.5]non-5-en-1-one (**17**; 0.500 g, 0.368 mmol) in 12 mL of dry THF was added to a stirred solution of (propen-2-yl)magnesium bromide (0.5 M in THF, 12.0 mL, 0.600 mmol) under nitrogen at 25 °C. After 15 min the reaction mixture was worked up as described for **18a/19a**, and the crude residue was flash chromatographed (18 g silica gel, 2.5% ethyl acetate/hexane) to afford 0.364 g (oil, 68% yield) of a mixture of diastereomers **18b/19b**. HPLC analysis (5% ethyl acetate/hexane, 5 mL/min, Waters RCM-100 module loaded with an 8-mm-i.d. 10-μm-silica column) showed two diastereomers to be present in a 30:70 ratio. This mixture of diastereomers gave the following spectral data: NMR (CCl_4) δ 5.85 (1 H, m), 5.51 (1 H, s), 4.89 (2 H, br s), 2.43 (1 H, m), 1.3–2.1 (10 H, m), 1.70 (3 H, br s); IR (CCl_4) 3600 (m), 3480 (w), 2940 (s), 2860 cm^{-1} (m), MS (70 eV) m/e 178 (M^+), 150, 122, 94.

1-(2-Methylpropen-1-yl)spiro[3.5]non-5-en-1-ol (18c/19c). Spiro[3.5]non-5-en-1-one (**17**; 0.500 g, 0.368 mmol) in 12 mL of dry THF was added to a stirred solution of (2-methylpropen-1-yl)magnesium bromide (0.5 M in THF, 12.0 mL, 0.600 mmole) under nitrogen at 25 °C. After 15 min, the reaction was worked up as described for **18a/19a**, and the crude residue was purified by flash chromatography (18 g silica gel, 2.5% ethyl acetate/hexane) to afford 0.318 g (oil, 55% yield) of a mixture of diastereomers **18c/19c**. HPLC analysis as described for **18b/19b** showed two diastereomers to be present in a 27:73 ratio. This mixture of diastereomers gave the following spectral data: NMR (CCl_4) δ 5.82 (1 H, m), 5.58 (2 H, s), 5.42 (1 H, m), 1.2–2.3 (10 H, m), 1.70 (6 H, br s); IR (CCl_4) 3610 (m), 3480 (w), 2940 (s), 1660 (w), 1440 (m), 1380 (m), 1200 cm^{-1} (m); MS (70 eV) m/e 192 (M^+), 164, 98, 83 (base), 79.

Bicyclo[5.3.1]undec-1(11)-en-4-one (20a). The mixture of diastereomeric alcohols **18a/19a** (0.473 g, 2.88 mmol) in 10 mL of dry THF was added to a stirred suspension of hexane-washed potassium hydride (0.483 g of 24% KH in oil, 2.90 mmol) in 30 mL of dry THF at 25 °C under nitrogen. After 10 min at 25 °C, the reaction was quenched with 1 mL of saturated aqueous NH_4Cl, filtered through a glass wool plug, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chro-

matography (18 g silica gel, 5% ethyl acetate/hexane) to afford 0.379 g (oil, 80%) of the bicyclic ketone **20a**.

In separate experiments, the major diastereomer of the **18a**/**19a** mixture was found to rearrange to ketone **20a** in 87% yield, and the minor diastereomer also rearranged to produce ketone **20a** in 80% yield.

Bicyclic ketone **20a** gave the following spectral data which is identical with that previously published for this compound:[25] NMR (CCl_4) δ 5.10 (1 H, br s), 1.0–3.0 (15 H, m); IR (CCl_4) 2940 (s), 1700 (s), 1450 (m), 1080 (m), 900 cm^{-1} (m); MS (15 eV) *m/e* 164 (M^+), 146, 136, 107 (base), 94, 79, 57, 43.

5-Methylbicyclo[5.3.1]undec-1(11)-en-4-one (20b). Rearrangement of the diastereomeric mixture of **18b**/**19b** (0.360 g, 1.72 mmol) was accomplished by the procedure described for preparation of **20a** to afford **20b** (0.222 g oil, 72% yield) as a single diastereomer which gave the following spectral data: NMR (CCl_4) δ 5.10 (1 H, br s), 1.0–3.0 (14 H, m), 0.87 (3 H, d, J = 7 Hz); IR (CCl_4) 2940 (s), 1705 (s), 1450 (m), 1140 (m), 1075 (m), 920 (m), 890 cm^{-1} (m); MS (70 eV) *m/e* 178 (M^+), 136, 110, 94, 79 (base), 67, 55.

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Registry No. **1**, 41597-03-9; **2a**, 81388-59-2; **2b**, 81388-60-5; **2c**, 81388-61-6; **3a**, 81388-62-7; **3b**, 81388-63-8; **3c**, 81388-64-9; **4a**, 81388-65-0; **4c**, 81388-66-1; **8**, 81338-67-2; **9c**, 81388-68-3; **11a**, 81388-69-4; **11b**, 81388-70-7; **11c**, 81388-71-8; **12a**, 81388-72-9; **12b**, 81388-73-0; **12c**, 81388-74-1; **13**, 23153-80-2; **13** mesylate, 81388-75-2; **14**, 81388-76-3; **14** ethylene ketal, 81388-77-4; **15** (isomer 1), 81388-78-5; **15** (isomer 2), 81388-79-6; **16**, 81388-80-9; **17**, 41597-04-0; **18a**, 81388-81-0; **18b**, 81388-82-1; **18c**, 81388-83-2; **19a**, 81388-84-3; **19b**, 81388-85-4; **19c**, 81388-86-5; **20a**, 77080-07-0; **20b**, 81388-87-6; isobutylene, 75-28-5; 1,2-dibromo-2-methylpropane, 594-34-3; 1-bromo-2-methylpropene, 3017-69-4; acrolein, 107-02-8; vinyllithium, 917-57-7; propen-2-yllithium, 3052-45-7; 2-methylpropen-1-yllithium, 29917-94-0; bis(4-chlorophenyl) diselenide, 20541-49-5; cyclopropyl phenyl sulfide, 14633-54-6; 2-[[(*p*-chlorophenyl)selenyl]methyl]-1-[1-(phenylthio)cycloprop-1-yl]cyclohexan-1-ol, 81408-02-8; vinyl bromide, 593-60-2; isopropenyl bromide, 557-93-7; isobutenyl bromide, 3017-69-4.

Reaction of 2-(Methylseleno)- and 2-(Phenylseleno)benzoic Acids and Their Derivatives with *tert*-Butyl Hydroperoxide. Neighboring Selenium Participation and Facile Formation of Cyclic Selenuranes and a Selenurane Oxide

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The reaction of 2-(methylseleno)benzoic acid with 1,1′-carbonyldiimidazole followed by addition of *tert*-butyl hydroperoxide gave 1,1-dihydro-1-*tert*-butoxy- and 1-hydroxy-1-methyl-3*H*-2,1-benzoxaselenol-3-ones (**3a** and **4a**), suggesting the intramolecular insertion of the neighboring selenium atom into the O–O bond of *tert*-butyl 2-(methylseleno)peroxybenzoate (**1a**). In the reaction of 2-(phenylseleno)benzoyl chloride with *tert*-butyl hydroperoxide, 1,1-dihydro-1-*tert*-butoxy-1-phenyl-3*H*-2,1-benzoxaselenol-3-one (**3b**) and its 1-oxide (**9**) were produced. The latter gave 2-carboxyphenyl phenyl selenone upon aqueous alkaline hydrolysis.

Much progress has recently been made in organo group 4B element chemistry. In addition to and closely related to the versatile reactivities,[1] chemical bonding in high-valent states of these classes of compounds is the subject of interest. Martin and co-workers,[2] for example, found a striking effect of the neighboring sulfur atom on the rate enhancement of the homolytic O–O bond cleavages of *tert*-butyl 2-thioperoxybenzoates. Intermediacy of the sulfuranyl radicals was advocated,[2,3] and stable dialkoxy- and bis(acyloxy)sulfuranes were obtained as an extension of this concept.[4,5] Since the selenium atom can expand its valence shell more readily,[6] and the carboxyl group in the neighborhood of the Se–O bond can act as a ligand to form more stable selenuranes,[7,8] it seemed to us of interest to investigate the anchimeric assistance of the neighboring selenium atom in the decomposition of *tert*-butyl 2-selenoperoxybenzoates. We report here the attempted synthesis of *tert*-butyl 2-(methylseleno)peroxybenzoate (**1a**) and the related reactions of 2-selenobenzoic acids and their derivatives with *tert*-butyl hydroperoxide.[9]

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