Ring Expansion of Cyclobutanones to Cyclopentanones via α-Lithioalkyl Aryl Sulfoxides and Selenoxides

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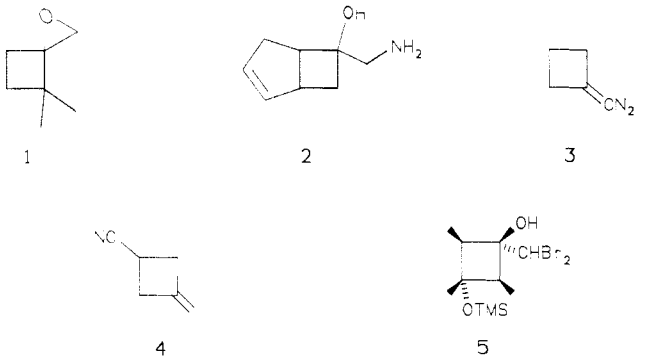
Reaction of α-lithioalkyl 2-chlorophenyl sulfoxides (prepared from the corresponding sulfoxides and LDA) with cyclobutanones affords adducts which undergo ring expansion to cyclopentanones upon treatment with potassium hydride. This reaction only works for cyclobutanones substituted at C2 with at least one phenyl or alkenyl group (type I and type II cyclobutanones). Cyclobutanones substituted at C2 with at least one alkyl group (type III and type IV cyclobutanones) undergo similar ring expansion upon treatment with α-lithioalkyl phenyl selenoxides followed by direct thermolysis of the adducts. With both the sulfoxide and selenoxide reagents, the carbon atom inserted into the cyclobutanone can be unsubstituted, monosubstituted, or disubstituted. The ring expansions of 17 different cyclobutanones to 29 different cyclopentanones are presented.

A number of excellent methods are currently available for the synthesis of cyclobutanones, either in monocyclic form or fused to other ring systems.[3] These syntheses usually proceed in high yield from simple precursors and often allow for control of the regiochemistry and stereochemistry of ring substituents. Because of their availability, cyclobutanones have been recognized by a number of investigators as an excellent source of cyclopentanones via a one-carbon ring expansion. Five-membered rings are ubiquitous in nature, and therefore the ring expansion of cyclobutanones to cyclopentanones provides a general approach to a huge number of natural products.

Since most known methods of cyclobutanone ring expansion are restricted in scope, it is convenient to classify them according to the degree of substitution of the carbon atom which is inserted into the cyclobutanone.[4] Carbon atoms which are unsubstituted (CH_2), monosubstituted (CHR), or disubstituted (CR_2) have all been inserted into the cyclobutanones, but most methods are limited to the insertion of only one of these types. No systematic study has been reported in which a single method has been used to insert carbon atoms of all degrees of substitution.

Ring expansion of cyclobutanones with the formal insertion of a simple, unsubstituted methylene (CH_2) group can be carried out in several ways. the two most common approaches are the direct reaction of a cyclobutanone with diazomethane[5] and the stepwise conversion of a cyclobutanone to an intermediate oxaspirohexane (e.g., 1) followed by treatment with a lithium salt.[6] The former method is only regioselective for 2-chloro- and 2,2-dichlorocyclobutanones (exclusive migration of C4) while the latter method generally proceeds via regioselective migration of the more substituted carbon in the absence of competing stereoelectronic factors.[7] Other literature examples of the insertion of a simple methylene group into a cyclobutanone include diazotization and rearrangement of 6-(aminomethyl)bicyclo[3.2.0]hept-2-en-6-ol (**2**) (Tiffeneau–Demjanov ring expansion),[8] generation and rearrangement of diazomethylidenecyclobutane (**3**),[9] thallium nitrate oxidation and rearrangement of 3-methylenecyclobutanecarbonitrile (**4**),[10] metalation and rearrangement of a 1-(dibromomethyl)cyclobutanol (**5**),[11] and insertion of ethyl diazoacetate followed by hydrolysis and decarboxylation.[12]



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Several methods for the ring expansions of cyclobutanones via formal insertion of a CHX (X = heteroatom) group have also been reported. Two examples of this are the conversion of cyclobutanones to 2-(methylthio)cyclopentanones[13] and to 2,2-bis(methylthio)cyclopentanones[14]

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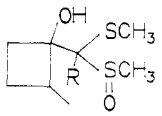

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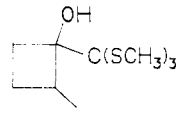

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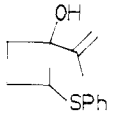

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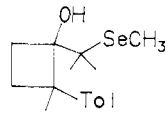

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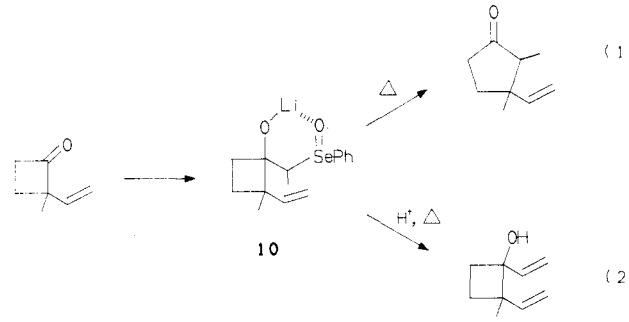
via the intermediate adducts **6** and **7**. Ring expansion of cyclobutanones to 2-hydroxycyclopentanones has also been reported.[15] In each of these cases, migration of the more substituted carbon has been observed.

Much less common are the ring expansions of cyclobutanones to 2-alkyl- or 2,2-dialkylcyclopentanones by formal insertion of CHR or CR_2 groups. Diazoethane has been employed in the literature,[16] but longer chain diazoalkanes have not been used. Ring expansion of adducts such as **6** (R = alkyl) followed by reductive desulfurization also produces 2-alkyl cyclopentanones. Several 2,2-dimethylcyclopentanones have been prepared by acid-catalyzed ring expansion of 1-(1-methylethenyl)cyclobutanols (e.g., **8**),[17] and by alkylation and rearrangement of a 1-(1-methyl-1-[methylselenenyl]ethyl)cyclobutanol (**9**).[18] However at least for the present, these reactions appear to be very limited in scope. Alkyl-substituted oxaspirohexanes have also been prepared and rearranged to 2-alkyl or 2,2-dialkylcyclopentanones, but this overall process is rather lengthy, requiring six synthetic steps from the cyclobutanone.[19]

We have previously published a brief note on the ring expansion of 2,2-disubstituted cyclobutanones to a variety of cyclopentanones using α-lithioalkyl phenyl selenoxides.[20] In that account it was reported that reaction of α-lithioethyl phenyl selenoxide (prepared in situ from ethyl phenyl selenide) with a cyclobutanone afforded an adduct which underwent ring expansion rather than the expected selenoxide elimination (eq 1). Presumably, chelation in the adduct (**10**) causes elimination to occur more slowly than ring expansion. If the adduct is protonated before thermolysis, normal selenoxide elimination to the allylic alcohol occurs (eq 2).[21]

The selenoxide procedure for the ring expansion of cyclobutanones has several attractive features. The reaction is a one-pot process, the method is flexible enough to insert an unsubstituted carbon (CH_2), a monoalkyl-substituted



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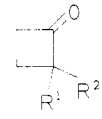
carbon (CHR), or a dialkyl-substituted carbon (CR_2) into a cyclobutanone, and ring expansion occurs regiospecifically, with exclusive migration of the more highly substituted carbon. A drawback of this method however, is that the cyclopentanone product reacts with electrophilic forms of selenium produced in situ[22] to afford a mixture of the product and several isomeric α-phenylselenenylcyclopentanones. Although reversion of the α-phenylselenenyl derivatives back to the cyclopentanone can be conveniently accomplished by simple aluminum amalgam reduction, this treatment could interfere with other easily reduced functionalities and thus limit the generality of the reaction.

Since our previous publication, we have sought to improve upon the selenoxide ring expansion and to apply it to a wider variety of cyclobutanones. It has been found that alkyl 2-chlorophenyl sulfoxides are superior in many cases to simple phenyl alkyl selenoxides, and also that cyclobutanone ring expansion using either the sulfoxides or selenoxides is much more general than originally reported. The results of these studies are detailed herein.

Results and Discussion

As expected, the reactivity of cyclobutanones toward ring expansion varies with the degree and type of substitution α to the carbonyl carbon. We have examined the ring expansion of cyclobutanones which fall into four categories of decreasing reactivity. As shown below, type I cyclobutanones are 2,2-disubstituted with both an alkyl and an aryl or alkenyl group, type II cyclobutanones are 2-monosubstituted with an aryl or alkenyl group, type III cyclobutanones are 2,2-disubstituted with alkyl groups, and type IV cyclobutanones are 2-monosubstituted with one



type I: R^1 = alkyl, R^2 = aryl or alkenyl
type II: R^1 = aryl or alkenyl, R^2 = H
type III: R^1, R^2 = alkyl
type IV: R^1 = alkyl, R^2 = H

alkyl group. Type I and type II cyclobutanones are the most reactive towards ring expansion with sulfoxides and selenoxides, while cyclobutanones of types III and IV are the least reactive. In general, it has been found that alkyl 2-chlorophenyl sulfoxides are the best reagents for ring expansion of type I and II cyclobutanones, while alkyl phenyl selenoxides are required for the ring expansion of type III and IV cyclobutanones.

Ring Expansion of Type I Cyclobutanones. As described above, type I cyclobutanones are defined as those

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cyclobutanones which have both a 2-alkyl and a 2-aryl or 2-alkenyl substituent. Also in this category would be 2,2-diaryl- and 2,2-dialkenylcyclobutanones, although we have not investigated cyclobutanones of this type. Type I cyclobutanones are the most highly activated towards ring expansion, and produce cyclopentanones in good yield on reaction with α-lithioalkyl phenyl selenoxides as previously reported. However, this procedure is complicated by further reaction of the product cyclopentanones with electrophilic selenium byproducts to form α-phenylselenenylcyclopentanones.

Because of this problem, a number of sulfoxides were investigated as potential reagents for ring expansion of cyclobutanones. The three sulfoxides examined were methyl phenyl sulfoxide, methyl 2-chlorophenyl sulfoxide, and methyl 2,6-dichlorophenyl sulfoxide. Each of these three sulfoxides underwent smooth deprotonation with LDA at −78 °C,[23] and the resulting α-sulfinyl carbanions reacted cleanly with a variety of cyclobutanones. The resulting lithium alkoxide adduct did not rearrange upon thermolysis (refluxing THF for several hours), but rather could be protonated and isolated as a mixture of diastereomers. The adducts could be purified by chromatography, although this was generally unnecessary.

It was found that the adducts produced from methyl 2-chlorophenyl sulfoxide and various type I cyclobutanones underwent rapid ring expansion (30 minutes or less) upon treatment with potassium hydride at room temperature. In contrast, the adducts derived from either methyl phenyl sulfoxide or methyl 2,6-dichlorophenyl sulfoxide failed to undergo clean ring expansion. In the case of the former, the potassium salt of the adduct was extremely sluggish to rearrange, and in the case of the latter, apparent decomposition of the adduct occurred. It is surprising that the course of the reaction is changed so drastically by the remote aryl substituents.

The cyclopentanones produced in this reaction could be easily purified by chromatography or distillation, and no evidence was seen of formation of α-phenylsulfenylcyclopentanones as was observed with the selenium reagents. A fairly wide variety of type I cyclobutanones have been successfully converted to cyclopentanones in good yield with alkyl 2-chlorophenyl sulfoxides, and these are listed in Table I.

In each case, only one regioisomer could be isolated and structural assignments were made by comparison of 270-MHz NMR spectra with those of authentic samples previously prepared.[20] Migration of the more substituted cyclobutanone carbon atom is in keeping with most other types of cyclobutanone ring expansions, as previously discussed.

In general, the yields of cyclopentanones produced by using the sulfoxide reagents are comparable or better than those obtained with the selenoxides.[20] In addition, the sulfoxides are much more convenient to handle since they can be easily isolated and purified before reaction with the cyclobutanones, unlike the selenoxides which must be prepared in situ from the appropriate selenide. Sulfoxides can also be prepared in optically active form. A not inconsiderable added benefit is that in contrast to selenides, sulfoxides have essentially no odor.

Ring Expansion of Type II Cyclobutanones. Type II cyclobutanones are defined as those which have a single 2-alkenyl or 2-phenyl substituent. A serious problem in the reaction of type II cyclobutanones with any strongly basic carbanion is competitive proton transfer to afford

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Table I. Ring Expansion of Type I Cyclobutanones with 2-ClPhS(O)R

entry	sulfoxide	cyclobutanone	cyclopentanone	yield, %
1	2-ClPhS(O)CH_3 **11**	**14**	**17**	94
2	**11**	**15**	**18**	72
3	**11**	**16**	**19**	87
4	2-ClPhS(O)CH_2CH_3 **12**	**14**	**20**	63[a]
5	2-ClPhS(O)$CH(CH_3)_2$ **13**	**14**	**21**	54
6	**13**	**15**	**22**	54

[a] Isolated as a 1:1 mixture of diastereomers.

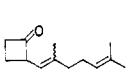
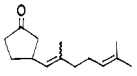
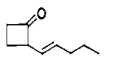
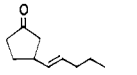
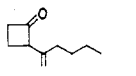
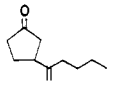
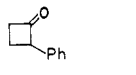
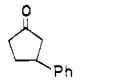
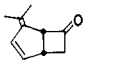
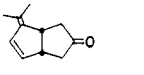
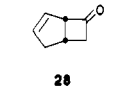
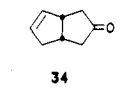
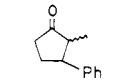
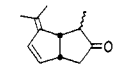
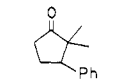
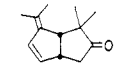
the enolate. Upon workup, these enolates may return to starting material, or they may isomerize to α-methylene cyclobutanones which in turn are likely to react with any of a variety of adventitious nucleophiles. Competitive proton transfer was found to be a serious problem upon attempted ring expansion of type II cyclobutanones with α-lithioalkyl phenyl selenoxides, and isolated yields of cyclopentanones were generally 15% or less. The α-lithioalkyl 2-chlorophenyl sulfoxides were more successful in this regard, and a variety of type II cyclobutanones have been successfully ring expanded with these reagents. These results are compiled in Table II.

As with the type I cyclobutanones, only one regioisomeric cyclopentanone could be isolated after ring expansion of each of the type II cyclobutanones. The regiochemistries of the cyclopentanones in Table II were assigned on the basis of high-field ^1H NMR data.

Irradiation of the allylic (or benzylic) cyclopentyl methine in cyclopentanones **29–32** showed loss of coupling to four other cyclopentyl protons, rather than to two as would be expected for the alternative 2-substituted isomers. Decoupling of the allylic methine in **29–32** also generally produced a clean AB quartet for the C2 methylene group.

The regiochemistries of compounds **33**, **36**, and **38** were deduced from the appearance of the C6a methines (ring fusion protons alpha to the isopropylidene group) as a doublet of triplets (δ 3.46, J = 10, 7 Hz), a triplet (δ 3.07, J = 7 Hz), and a doublet (δ 3.29, J = 8 Hz), respectively. The cis ring fusions of **33**, **36**, and **38** were assigned on the basis of thermodynamic considerations and also the 7–8 Hz coupling constant between the ring fusion protons in keeping with a 0° dihedral angle. Compound **36** was iso-

Table II. Ring Expansion of Type II Cyclobutanones with 2-ClPhS(O)R

entry	sulfoxide[a]	cyclobutanone	cyclopentanone	yield, %
1	11	 23	 29	56
2	11	 24	 30	34
3	11	 25	 31	24
4	11	 26	 32	52
5	11	 27	 33	62
6	11	 28	 34	63
7	12	26	 35	52[b]
8	12	27	 36	52[c]
9	13	26	 37	43
10	13	27	 38	48

[a] See Table I for structures. [b] Isolated as an 8:1 mixture of trans to cis. [c] Isolated as a 2:1 mixture of exo to endo.

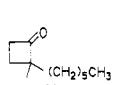
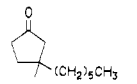
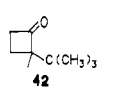
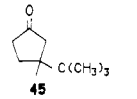
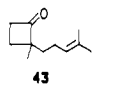
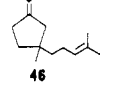
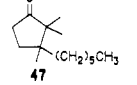
lated as a 2:1 mixture of exo-methyl (doublet at δ 1.22) and endo-methyl (doublet at δ 0.87, shielded by the isopropylidene group) isomers.

The regiochemistries of compounds **34** and **35** were assigned by comparison of their spectral data with that previously reported.[24,25] Cyclopentanone **35** was isolated as an 8:1 mixture of trans (methyl doublet at δ 1.03) and cis (methyl doublet at δ 0.79, shielded by the phenyl group) isomers. The regiochemistry of cyclopentanone **37** was assigned by analogy with the other compounds in Table II.

Thus, as with the type I cyclobutanones, ring expansion of type II cyclobutanones occurs regiospecifically with migration of the more substituted carbon atom. Table II shows that it is possible to insert an unsubstituted, a monosubstituted, or a disubstituted carbon into a type II cyclobutanone using α-lithioalkyl 2-chlorophenylsulfoxides.

Yields of cyclopentanones from ring expansion of type II cyclobutanones are generally good, although the yield decreases in direct proportion to the degree of substitution on the alkene (compare entries 1, 2, and 3 in Table II), indicating a considerable degree of carbocationic character at the migrating carbon atom. Although several of the cyclopentanones in Table II are rather simple and have been previously prepared, entries 5, 8, and 10 highlight the preparation of bicyclic systems which would be difficult to prepare in other ways. Other ring expansions of type II cyclobutanones to more complex cyclopentanones are described at the end of this report.

Table III. Ring Expansion of Type III Cyclobutanones with PhSe(O)R

entry	selenide	cyclobutanone	cyclopentanone	yield, %[a]
1	$PhSeCH_3$ 39	 41	 44	78
2	39	 42	 45	9(10)
3	39	 43	 46	56
4	$PhSeCH(CH_3)_2$ 40	41	 47	36(49)

[a] Yield in parentheses is based on recovered cyclobutanone.

Ring Expansion of Type III Cyclobutanones. Type III cyclobutanones are those which have two simple alkyl substituents at C2. Unfortunately, in these cases, attempted ring expansions with α-lithioalkyl 2-chlorophenyl sulfoxide reagents were unsuccessful. However, one example of the ring expansion of a type III cyclobutanone with an α-lithiomethyl phenyl selenoxide was reported in our previous publication,[20] and this appears to be a general reaction. Methyl 2-chlorophenyl selenoxide and methyl 2,5-dichlorophenyl selenoxide were also investigated for ring expansion of type III and type IV cyclobutanones, and use of these selenoxides led, as expected, to more rapid ring expansion. However, the isolated yields of cyclopentanones were poor, and for this reason, the simple alkyl phenyl selenoxides were employed in subsequent studies.

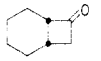
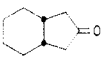
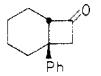
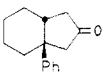
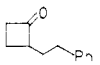
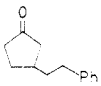
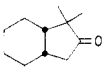
As shown in Table III, a number of type III cyclobutanones have been ring-expanded to cyclopentanones by using alkyl phenyl selenides. The general procedure of this ring expansion is essentially that which was previously described,[20] involving in situ oxidation of the selenide and deprotonation of the resulting selenoxide with LDA. Rearrangement of the lithio adducts required approximately 1 h in refluxing THF. Use of the selenoxide reagents again led to contamination of the product with phenylselenenyl impurities, thus requiring treatment of the crude reaction mixture with aluminum amalgam before purification.

Each of the cyclopentanones in Table III was isolated as a single regioisomer whose structure was deduced from 400-MHz ^1H NMR data.

The spectra of cyclopentanones **44**, **45**, and **46** each show an AB quartet for the isolated cyclopentyl methylene

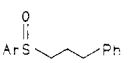
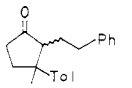
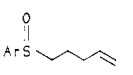
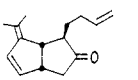
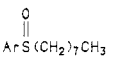
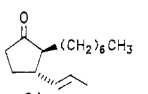
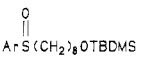
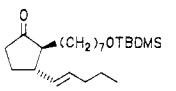
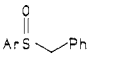
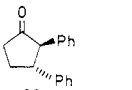
(24) Nee, M.; Roberts, J. D. *J. Org. Chem.* **1981**, *46*, 67.
(25) Salaün, J.; Ollivier, J. *Nouv. J. Chim.* **1981**, *5*, 587. Schner, V. F.; Turchin, K. F.; Sheinker, Y. N.; Suvorov, N. N. *Zh. Org. Khim.* **1976**, *12*, 72.

Table IV. Ring Expansion of Type IV Cyclobutanones with PhSe(O)R

entry	selenide[a]	cyclobutanone	cyclopentanone	yield, %
1	**39**	 **48**	 **51**	48
2	**38**	 **49**	 **52**	34
3	**39**	 **50**	 **53**	38
4	**40**	**48**	 **54**	46

[a] See Table III for structures.

Table V. Ring Expansion of Cyclobutanones with Complex 2-ClPhS(O)R

entry	sulfoxide[a]	cyclobutanone	cyclopentanone	yield, %
1	 **55**	 **60**	 **62**	78[b]
2	 **56**	**27**	 **63**	69
3	 **57**	 **61**	 **64**	54
4	 **58**	**24**	 **65**	53
5	 **59**	**26**	 **66**	33

[a] Ar = 2-chlorophenyl. [b] Isolated as a 2:1 mixture of diastereomers.

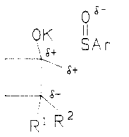
group, which clearly rules out the 2,2-disubstituted isomer. The spectrum of cyclopentanone **47** shows two widely separated multiplets (δ 2.22 and 1.72) as expected for the two cyclopentyl methylenes. The alternative 2,2,5,5-tetrasubstituted isomer would be expected to show one narrow four-proton multiplet in its NMR spectrum.

Type III cyclobutanones are the most sterically hindered of the four classes of cyclobutanones examined and their reactivities are correspondingly attenuated. Cyclobutanone **42** reacts to only a small extent with α-lithiomethyl phenyl selenoxide, and insertion of a *gem*-dimethyl group into cyclobutanone **41** proceeds in only fair yield. Some cyclobutanone was usually reisolated in these reactions, presumably due to competitive proton transfer to form the enolate.

Ring Expansion of Type IV Cyclobutanones. Type IV cyclobutanones are those having only one alkyl substituent at C2. These cyclobutanones were the least reactive towards ring expansion with any of the sulfoxide or selenoxide reagents. As with the type III cyclobutanones, the best results were obtained with α-lithioalkyl phenyl selenoxides and these results are listed in Table IV. As is readily apparent, exclusive migration of the more substituted cyclobutyl carbon is still observed in the ring expansion. The general procedure for ring expansion of type IV cyclobutanones is the same as that used for type III cyclobutanones except that rearrangement of the lithio adduct required 2 to 3 h in refluxing THF.

The structure of compound **51** was determined by comparison with published spectral data[26] and supported by the obvious symmetry of its 400-MHz ^{1}H NMR spectrum. Compounds **52** and **54** were assumed to have cis ring fusions based on thermodynamic grounds and by analogy to compounds **33**, **34**, **36**, and **38**. The regiochemistry of **52** was assigned as shown because its ^{1}H NMR spectrum showed a clean AB quartet due to the isolated cyclopentyl methylene. The regiochemistry of **54** is supported by the presence of a two-proton doublet (δ 2.22, J = 10 Hz) in its NMR spectrum which is presumed to arise from the cyclopentyl methylene (by fortuitous chemical shift equivalence of the two methylene protons). The regiochemistry of compound **53** is speculative, but is assigned as shown based on the expected migration of the more substituted cyclobutyl carbon atom, as observed in every previous example.

Mechanism. Although we have not done rigorous mechanistic studies on the ring expansion reaction, the relative reactivities of the various types of cyclobutanones is in general accord with the buildup of considerable cationic character at the migrating carbon atom. The reaction thus presumably passes through a transition state which involves participation of the migrating cyclobutyl σ bond as shown in **67**. The alkoxide substituent accelerates the reaction by weakening the cyclobutyl carbon-carbon bond[27] (thereby making it kinetically more labile) and by increasing the overall thermodynamic driving force for the reaction.



67

Introduction of More Complex Substituents. As previously mentioned, one of the principle advantages of using sulfoxide or selenoxide reagents for cyclobutanone ring expansion is that both monosubstituted and disubstituted carbon atoms can be formally inserted into the cyclobutanone, and there are few limitations on the type of substituents which can be present. The required alkyl phenyl selenides or alkyl 2-chlorophenyl sulfoxides are usually trivial to prepare from alkyl halides and diphenyl diselenide or 2-chlorothiophenol which are both commercially available.

In order to demonstrate the flexibility of this ring expansion methodology, several more complex side chains containing phenyl, alkenyl, and protected hydroxyl groups were inserted into selected cyclobutanones. The cyclopentanones thus prepared are listed in Table V. To our

(26) Clark, D. A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1979**, *101*, 3567.

(27) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3315, 3319.

knowledge, these are the first examples of the direct insertion of complex side chains in the course of a ring expansion. The sulfoxides used in Table V were all prepared in high yield from commercially available alkyl bromides.

As in previous examples, only one regioisomer was isolated for each of the entries in Table V. The regiochemistries of cyclopentanones **62**, **64**, and **65** are speculative, but are based upon the expected migration of the more substituted carbon atom. Cyclopentanone **62** was isolated as a 2:1 mixture of stereoisomers, whereas **64** and **65** were each isolated as a single stereoisomer which was assumed to be trans. The regiochemical assignment of **63** is secured by a triplet (δ 3.22, J = 7 Hz) in its ^{1}H NMR spectrum which is assigned to the C6a ring fusion methine by analogy with compound **36** (Table II). The assignment of the butenyl side chain as exo is based upon that being the more thermodynamically stable orientation. The regiochemical assignment of **66** is based on the lack of symmetry in its ^{1}H NMR spectrum. The alternative 2,5-disubstituted isomer would be expected to show a simple spectrum consisting of three aliphatic multiplets at most. The substitution pattern of **66** is also assumed to be trans on thermodynamic grounds.

In conclusion, the ring expansion of cyclobutanones with alkyl aryl sulfoxides and selenoxides offers a convenient entry into a variety of cyclopentanones of varying substitution patterns and complexity. The reaction is generally applicable to most types of substituted cyclobutanones, and the required sulfoxides or selenides can be easily prepared from a variety of alkyl halides. This ring expansion strategy should find application in the synthesis of cyclopentanoid natural products.

Experimental Section

General Methods. Dry tetrahydrofuran (THF) and diethyl ether were obtained by distillation from sodium using benzophenone as an indicator. All reagents and chemicals were obtained from the Aldrich Chemical Company and used as received unless otherwise specified. Lithium diisopropylamide (LDA) was prepared by the addition of *n*-BuLi to diisopropylamine in THF at −78 °C.

Organic phases from aqueous extractions were dried over $MgSO_4$, and unless otherwise specified, were concentrated by rotary evaporation at aspirator vacuum, followed by removal of traces of solvent at 1.0 Torr vacuum.

Preparative HPLC separations were carried out using a 25 cm × 1 cm Alltech column containing 10 micron silica gel. Flash chromatography was carried out in the standard way using Merck silica gel 60 (230–400 mesh). Thin-layer chromatography was carried out on silica gel plates using radial elution in inexpensive radial TLC chambers.[28]

^{1}H NMR spectra were recorded at 90, 270, or 400 MHz. The exact spectrometer frequency is specified for each compound. All shifts are reported downfield from an internal Me_4Si standard.

Elemental analyses were performed by Micro-Tech Laboratories Inc., Skokie, IL.

General Procedure for Preparation of Sulfoxides. To a suspension of sodium hydride (60% dispersion in mineral oil, 0.60 g, 15 mmol, prewashed with hexane) in 30 mL of THF was added 2-chlorothiophenol (1.44 g, 1.12 mL, 10.0 mmol) while cooling the reaction with a cold water bath. After this mixture had stirred for 10 min at room temperature, the appropriate alkyl bromide or iodide was added, and the reaction was stirred at room temperature for 3 h. The reaction was then quenched with 20 mL of saturated NH_4Cl solution, and the aqueous layer was extracted with ether. The combined organic layers were dried and concentrated to afford the crude sulfide.

To the crude sulfide in 60 mL of CH_2Cl_2 at 0 °C was added a solution of *m*-chloroperbenzoic acid (80–85% pure, 2.3 g, 10 mmol) in 50 mL of CH_2Cl_2. The reaction mixture was stirred for 3 h at 0 °C, and then 30 mL of saturated $NaHCO_3$ solution was added. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried and concentrated, and the crude sulfoxide was purified by flash chromatography using 20% ethyl acetate in hexane. Spectral data for each of the sulfoxides are given below.

1-Chloro-2-(methylsulfinyl)benzene (11) was prepared from the thiol and methyl iodide (75% overall yield): $bp_{0.08}$ 58 °C (lit[29] bp_3 121 °C); IR (CCl_4) 3160, 1450, 1090, 1060, 1020, 760 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 8.00 (1 H, m), 7.55 (3 H, m), 2.72 (3 H, s).

1-Chloro-2-(ethylsulfinyl)benzene (12) was prepared from the thiol and ethyl iodide (82% overall yield): IR (CCl_4) 2980, 1450, 1100, 1070, 1020, 750 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.77 (1 H, m)8 7.30 (3 H, m), 2.85 (2 H, m), 1.18 (3 H, t, J = 7 Hz). Anal. Calcd for C_8H_9ClOS: C, 50.93; H, 4.81. Found: C, 51.02; H, 4.83.

1-Chloro-2-[(1-methylethyl)sulfinyl]benzene (13) was prepared from the thiol and isopropyl iodide (74% overall yield): IR (CCl_4) 2970, 1445, 1095, 1060, 1020, 750 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.72 (1 H, m), 7.32 (3 H, m), 3.07 (1 H, sept, J = 7 Hz), 1.45 (3 H, d, J = 7 Hz), 0.95 (3 H, d, J = 7 Hz). Anal. Calcd for $C_9H_{11}ClOS$: C, 53.33; H, 5.47. Found: C, 53.20; H, 5.42.

1-Chloro-2-[(3-phenylpropyl)sulfinyl]benzene (55) was prepared from the thiol and 1-bromo-3-phenylpropane (89% overall yield): IR (neat) 3050, 3020, 2910, 1440, 1090, 1050, 1020, 750, 690 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.82 (1 H, m), 7.20 (8 H, m), 2.70 (4 H, m), 2.00 (2 H, m). Anal. Calcd for $C_{15}H_{15}ClOS$: C, 64.61; H, 5.42. Found: C, 64.46; H, 5.47.

1-Chloro-2-[(pent-4-enyl)sulfinyl]benzene (56) was prepared from the thiol and 5-bromo-1-pentene (92% overall yield): IR (neat) 3060, 2920, 1630, 1570, 1435, 1100, 1050, 1020, 905, 750 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.85 (1 H, m), 7.42 (3 H, m), 5.75 (1 H, m), 5.05 (2 H, m), 2.85 (2 H, m), 2.20 (2 H, m), 1.87 (2 H, m). Anal. Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73. Found: C, 57.80; H, 5.72.

1-Chloro-2-(octylsulfinyl)benzene (57) was prepared from the thiol and 1-bromooctane (58% overall yield): IR (neat) 3060, 2940, 2850, 1450, 1100, 1060, 1020, 750 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.90 (1 H, m), 7.45 (3 H, m), 3.25–2.45 (2 H, br m), 2.05–1.05 (12 H, br m), 0.85 (3 H, m). Anal. Calcd for $C_{14}H_{21}ClOS$: C, 61.63; H, 7.74. Found: C, 61.53; H, 7.63.

1-Chloro-2-[(8-(*tert*-butyldimethylsiloxy)octyl)-sulfinyl]benzene (58) was prepared in 82% overall yield from the thiol and the *tert*-butyldimethylsily ether of 8-bromo-1-octanol which in turn was prepared as follows:

8-Bromo-1-octanol (2.10 g, 1.75 mL, 10.0 mmol), *tert*-butyldimethylsilyl chloride (1.80 g, 12.0 mmol), and imidazole (1.70 g, 25.0 mmol) were mixed together in DMF (2.6 mL), and this reaction mixture was stirred at room temperature overnight. The reaction was diluted with 10 mL of ether and the organic phase was washed with saturated NaCl solution. The organic phase was dried and concentrated to afford a viscous liquid which was filtered through silica gel with hexane. The crude yield was quantitative, and this material was used directly without further purification.

Spectral data for the sulfoxide (**58**): IR (neat) 2920, 2850, 1450, 1240, 1090, 1050, 1020, 825, 755 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.80 (1 H, m), 7.33 (3 H, m), 3.50 (2 H, t, J = 7 Hz), 3.15–2.40 (2 H, br m), 2.00–1.10 (10 H, br m), 0.88 (9 H, s), 0.05 (6 H, s). Anal. Calcd for $C_{20}H_{35}ClO_2SSi$: C, 59.59; H, 8.75. Found: C, 58.95; H, 8.45.

1-Chloro-2-(benzylsulfinyl)benzene (59) was prepared from the thiol and benzyl bromide in 93% overall yield: mp (hexane) 60 °C. IR (neat) 3040, 3010, 1440, 1095, 1060, 1020, 755, 690 cm^{-1}; 90-MHz ^{1}H NMR (CCl_4) δ 7.45–6.85 (9H, br m), 4.15 (H_A of AB, J_{AB} = 13 Hz), 3.90 (H_B of AB, J_{AB} = 13 Hz). Anal. Calcd for $C_{13}H_{11}ClOS$: C, 62.27; H, 4.42. Found: C, 62.51; H, 4.39.

(Methylselenenyl)benzene (39) and ((1-methylethyl)selenenyl)benzene (40) were prepared as previously described.[20]

Preparation of Cyclobutanones. Cyclobutanones **14–16**, **23–26**, **41–43**, **50**, **60**, and **61** were prepared from 1-bromo-1-eth-

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oxycyclopropane and the appropriate aldehyde or ketone using the procedure which has been previously published.[30] The preparation of cyclobutanones **15**, **60**, and **61** by this method has previously been reported.[30] Overall yields and spectral data (or reference to previous literature preparation) for the other cyclobutanones prepared from 1-bromo-1-ethoxycyclopropane are given below. Ketones **28**,[31] **48**,[32] and **49**[33] were prepared by other literature procedures. The procedure for preparation of ketone **27** is given below. Type II cyclobutanones (especially **23**, **24**, and **27**) were found to be quite unstable and were used immediately after preparation. It was impossible to obtain accurate combustion analysis of **23**, **24**, and **27** because of their instability.

Spiro[3.5]non-5-en-1-one (14) was prepared from 2-cyclohexenone in 97% overall yield. Spectral data for this compound have been previously reported.[34]

2-Methyl-2-phenylcyclobutanone (16) was prepared from acetophenone in 82% overall yield. Spectral data for this compound have been previously reported.[35]

2-(2,6-Dimethyl-1,5-heptadienyl)cyclobutanone (23) was prepared from citral as a mixture of *E* and *Z* isomers in 89% overall yield: $bp_{0.25}$ 85 °C; IR (neat) 2980, 2920, 1780, 1670, 1445, 1370, 1170, 1070, 830 cm^{-1}; 90-MHz ^1H NMR (CCl_4) δ 5.15 (2 H, m), 4.05 (1 H, m), 2.95 (2 H, m), 2.40–2.00 (6 H, br m), 1.65 (9 H, m); MS (15 eV), *m/z* 192 (M^+), 150, 135, 110, 69 (base).

(*E*)-2-(1-Pentenyl)cyclobutanone (24) was prepared from *E*-2-hexenal in 73% overall yield: $bp_{0.75}$ 50 °C; IR (neat) 2950, 2920, 2860, 1780, 1450, 1065, 965 cm^{-1}; 90 MHz ^1H NMR (CCl_4) δ 5.41 (2 H, m), 3.81 (1 H, m), 2.90 (2 H, m), 2.44–1.65 (4 H, br m), 1.40 (2 H, sextet, J = 7 Hz), 0.90 (3 H, t, J = 7 Hz); MS (15 eV), *m/z* 138 (M^+), 96 (base), 81, 67, 54.

2-(1-Methylidenepentyl)cyclobutanone (25) was prepared from 2-butylacrolein in 65% overall yield: $bp_{0.6}$ 65 °C; IR (neat) 2940, 1775, 1675, 1630, 1450, 1050, 970, 825, 765 cm^{-1}; 90-MHz ^1H NMR (CCl_4) δ 4.80 (2 H, br s), 3.88 (1 H, t, J = 9 Hz), 2.85 (2 H, m), 2.60–1.60 (4 H, br m), 1.30 (4 H, m), 0.88 (3 H, m). Anal. Calcd for $C_{10}H_{16}O$: C, 78.70; H, 10.59. Found: C, 78.67; H, 10.78.

2-Phenylcyclobutanone (26) was prepared from benzaldehyde in 71% overall yield. Spectral data for this compound have been previously reported.[36]

4-(1-Methylethylidene)bicyclo[3.2.0]hept-2-en-6-one (27).[37] 7,7-Dichloro-4-(1-methylethylidene)bicyclo[3.2.0]hept-2-en-6-one[38] (17.1 g, 78.8 mmol) was stirred at 50 °C for 90 h with zinc powder (51.1 g, 0.78 mol) in 95 mL of acetic acid and 9.5 mL of water. The reaction was filtered through celite using about 600 mL of ether, and the filtrate was extracted with five 100 mL portions of water. The organic phase was then washed with saturated $NaHCO_3$ solution, dried, and concentrated. The residue was fractionally distilled ($bp_{0.75}$ = 55 °C) to afford 7.14 g (61% yield) of ketone **27**: IR (CCl_4) 3070, 2990, 2920, 2865, 1785, 1450, 1390, 1375, 1205, 1185, 1075, 1055 cm^{-1}; 90-MHz ^1H NMR (CCl_4) δ 6.37 (1 H, d, J = 6 Hz), 6.05 (1 H, m), 4.35 (1 H, m), 3.63–3.04 (2 H, br m), 2.67 (1 H, dt, J = 16, 3 Hz), 1.80 (6 H, s); MS (70 eV), *m/z* 148 (M^+), 106 (base), 91, 78, 65, 51.

2-Hexyl-2-methylcyclobutanone (41) was prepared from 2-octanone in 95% overall yield. Spectral data for this compound have been previously reported.[36a]

2-(1,1-Dimethylethyl)-2-methylcyclobutanone (42) was prepared from pinacolone in 40% overall yield. Spectral data for this compound have been previously reported.[34]

2-Methyl-2-(4-methyl-3-pentenyl)cyclobutanone (43) was prepared from 6-methyl-5-hepten-2-one in 66% overall yield: $bp_{0.05}$ 45 °C; IR (CCl_4) 2960, 2920, 2860, 1770, 1445, 1370, 1050 cm^{-1}; 90-MHz ^1H NMR (CCl_4) δ 5.00 (1 H, t, J = 7 Hz), 2.90 (2 H, t, J = 8 Hz), 2.15–1.35 (6 H, br m), 1.69 (3 H, s), 1.61 (3 H, s), 1.20 (3 H, s). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.17; H, 11.13.

2-(2-Phenylethyl)cyclobutanone (50) was prepared from 3-phenylpropanal in 61% overall yield: $bp_{0.8}$ 70 °C; IR (CCl_4) 3070, 3030, 2920, 2860, 1775, 1450, 1070, 690 cm^{-1}; 90-MHz ^1H NMR (CCl_4) δ 7.10 (5 H, s), 3.45–2.55 (5 H, br m), 2.35–1.35 (4 H, br m). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.61; H, 7.93.

General Procedure for Ring Expansion of Type I and Type II Cyclobutanones. To the appropriate 2-chlorophenyl sulfoxide (1.05 mmol) in THF (8 mL) at −78 °C under nitrogen was added LDA (0.7 M in THF, 2.1 mL, 1.5 mmol), and the reaction mixture was stirred at −78 °C for 15 min. A solution of the cyclobutanone (1.0 mmol) in 3 mL of THF was chilled to −78 °C under nitrogen and then added to the reaction mixture via cannula with positive nitrogen pressure. The reaction was stirred at −78 °C for 10 min, allowed to warm to room temperature, and then quenched with saturated NH_4Cl solution. The layers were separated, and the aqueous layer was extracted with ether. The combined organic phases were washed with brine, dried, and concentrated to afford the crude adduct which was used directly in the next reaction.

The crude adduct was added to potassium hydride (35% oil dispersion, 0.17 g, 1.5 mmol, prewashed with hexane) in 15 mL of THF at room temperature. Rearrangement of the adducts from type I cyclobutanones required 30 min at room temperature. The times and reaction temperatures required for rearrangement of each of the adducts from type II cyclobutanones varied considerably and are given below with the spectral data for the cyclopentanones. When analysis by TLC indicated that the reaction was finished, 10 mL of saturated NH_4Cl solution was added and the layers were separated. The aqueous layer was extracted with ether, and the combined organic phases were washed with brine, dried, and concentrated. The cyclopentanones were purified by flash chromatography or preparative HPLC using 5% ethyl acetate in hexane.

General Procedure for Ring Expansion of Type III and Type IV Cyclobutanones. Preparation of the α-lithioalkyl phenyl selenoxides and their reactions with cyclobutanones were carried out as previously described.[20] Rearrangement of the intermediate adducts was also carried out as previously described, except that 1 h and 2–3 h of reflux were required for the adducts from type III and type IV cyclobutanones, respectively. Treatment of the crude reaction mixture with aluminum amalgam as previously described[20] was required before purification of the cyclopentanones. The cyclopentanones were purified by flash chromatography or preparative HPLC using 5% ethyl acetate in hexane.

Cyclopentanones 17–22 have been previously prepared.[20] Spectral data was found to be identical with that previously reported.

3-(2,6-Dimethyl-1,5-heptadienyl)cyclopentanone (29) (Mixture of *E* and *Z* Isomers). The sulfoxide was stirred with KH in THF for 3 h at room temperature. **29**: $bp_{0.15}$ 85 °C; IR (neat) 2950, 2920, 2850, 1740, 1450, 1375, 1150 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.06 (2 H, m), 2.99 (1 H, m), 2.32 (2 H, m), 2.12 (5 H, m), 1.98 (2 H, m), 1.87 (1 H, dd, J = 10, 8 Hz), 1.70 (1.3 H, br s), 1.67 (3 H, s), 1.64 (1.7 H, br s), 1.59 (3 H, s). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.34; H, 10.74.

(*E*)-3-(1-Pentenyl)cyclopentanone (30). The sulfoxide was stirred with KH in THF at room temperature for 2 h and then refluxed for 2 h. **30**: $bp_{0.25}$ 45 °C; IR (neat) 2955, 2920, 2870, 1740, 1450, 1400, 1150, 965, 750 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.46 (2 H, m), 2.80 (1 H, m), 2.33 (2 H, m), 2.15 (2 H, m), 1.99 (3 H, m), 1.68 (1 H, m), 1.38 (2 H, sextet, J = 7 Hz), 0.89 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 78.73; H, 10.87.

3-(1-Methylenepentyl)cyclopentanone (31). The sulfoxide was stirred with KH in THF at room temperature for 2 h and then refluxed for 2.5 h. **31**: $bp_{0.25}$ = 50 °C; IR (neat) 3070, 2950,

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2920, 2860, 1735, 1635, 1450, 1400, 1150, 1130, 880, 740 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 4.80 (1 H, s), 4.75 (1 H, s), 2.76 (1 H, m), 2.37 (2 H, m), 2.11 (5 H, m), 1.75 (1 H, m), 1.43 (2 H, m), 1.31 (2 H, sextet, J = 7 Hz), 0.90 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.17; H, 10.92.

3-Phenylcyclopentanone (32). The sulfoxide was stirred with KH in THF at room temperature for 2 h and then refluxed for 20 min. **32**: IR (neat) 3060, 3020, 2950, 2920, 1735, 1600, 1485, 1440, 1395, 1140, 1020, 750, 690 cm^{-1}, 400-MHz ^1H NMR ($CDCl_3$) δ 7.35 (5 H, m), 3.43 (1 H, m), 2.68 (1 H, dd, J = 19, 7 Hz), 2.48 (2 H, m), 2.35 (2 H, m), 2.02 (1 H, m); MS (70 eV), m/z 160 (M^+), 131, 117, 104 (base), 91, 77. This compound has been previously reported.[39]

6-(1-Methylethylidene)-3,3aα,6,6aα-tetrahydro-2(1*H*)-pentalenone (33). The sulfoxide was stirred with KH in THF at room temperature for 2 h. **33**: $bp_{0.25}$ 75 °C; IR (neat) 3060, 2910, 2860, 1740, 1450, 1400, 1165, 750 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 6.35 (1 H, dd, J = 6, 3 Hz), 5.80 (1 H, dd, J = 6, 2 Hz), 3.57 (1 H, m), 3.46 (1 H, dt, J = 10, 7 Hz), 2.69 (1 H, ddd, J = 19, 10, 2 Hz), 2.53 (1 H, ddd, J = 18, 10, 2 Hz), 2.23 (1 H, dt, J = 18, 3 Hz), 2.01 (1 H, ddd, J = 19, 7, 2 Hz), 1.77 (3 H, s), 1.72 (3 H, s). Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.13; H, 8.72.

3,3aα,6,6aα-Tetrahydro-2(1*H*)-pentalenone (34). The sulfoxide was stirred with KH in THF for 2 h at room temperature and then 10 min at reflux. **34**: IR (neat) 3050, 2920, 2850, 1730, 1440, 1390, 1150, 1020, 950, 820, 750, 710, 650 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.74 (1 H, m), 5.62 (1 H, m), 3.41 (1 H, m), 2.96 (1 H, m), 2.70 (1 H, m), 2.48 (2 H, m), 2.22 (2 H, m), 1.99 (1 H, dd, J = 18, 7 Hz); MS (15 eV), m/z 122 (M^+ and base), 107, 93, 80, 79, 71. This compound has been previously reported.[24]

***trans*-2-Methyl-3-phenylcyclopentanone (35).** The sulfoxide was stirred with KH in THF for 2 h at room temperature. **35**: IR (neat) 3060, 3030, 2960, 2920, 2870, 1735, 1450, 1140, 750, 690 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 7.33 (5 H, m), 2.80 (1 H, td, J = 12, 5 Hz), 2.54 (1 H, m), 2.27 (3 H, m), 1.90 (1 H, m), 1.03 (3 H, d, J = 7 Hz); MS (70 eV), m/z 174 (M^+), 159, 145, 117 (base), 105, 91, 77. This compound has been previously reported.[25]

1α-Methyl-6-(1-methylethylidene)-3,3aα,6,6aα-tetrahydro-2(1*H*)-pentalenone (36). (Isolated as a 2:1 mixture with the 1β-methyl isomer.) The sulfoxide was stirred with KH in THF for 2 h at room temperature. **36**: $bp_{0.15}$ 80 °C; IR (neat) 3060, 2950, 2920, 2860, 1730, 1445, 1370, 1170, 1100, 1030, 740 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 6.36 (1 H, dd, J = 5, 3 Hz), 5.81 (1 H, dd, J = 5, 2 Hz), 3.46 (1 H, m), 3.07 (1 H, t, J = 7 Hz), 2.54 (1 H, dd, J = 19, 10 Hz), 2.31 (1 H, dd, J = 19, 2 Hz), 2.04 (1 H, pentet, J = 7 Hz), 1.80 (3 H, s), 1.79 (3 H, s), 1.22 (3 H, d, J = 7 Hz). Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.58; H, 9.15.

2,2-Dimethyl-3-phenylcyclopentanone (37). The sulfoxide was stirred with KH in THF for 1 h at room temperature. **37**: $bp_{0.15}$ 95 °C; IR (neat) 3060, 3030, 2960, 2920, 2860, 1730, 1450, 1090, 1045, 750, 690 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 7.30 (5 H, m), 3.05 (1 H, dd, J = 12, 6 Hz), 2.58 (1 H, m), 2.38–2.13 (3 H, m), 1.10 (3 H, s), 0.67 (3 H, s). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.88; H, 8.63.

1,1-Dimethyl-6-(1-methylethylidene)-3,3aα,6,6aα-tetrahydro-2(1*H*)-pentalenone (38). The sulfoxide was stirred with KH in THF for 2 h at room temperature. **38**: $bp_{0.15}$ 85 °C; IR (neat) 3060, 2960, 2920, 2850, 1730, 1445, 1370, 740 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 6.39 (1 H, dd, J = 5, 3 Hz), 5.78 (1 H, d, J = 5 Hz), 3.46 (1 H, m), 3.29 (1 H, d, J = 8 Hz), 2.66 (1 H, dd, J = 18, 10 Hz), 2.36 (1 H, dd, J = 18, 3 Hz), 1.81 (3 H, s), 1.78 (3 H, s), 1.21 (3 H, s), 0.83 (3 H, s). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.56; H, 9.29.

3-Hexyl-3-methylcyclopentanone (44): $bp_{0.15}$ = 60 °C; IR (CCl_4) 2950, 2925, 2865, 2840, 1735, 1455, 1400, 1370, 1255, 1160, 1130, 1090, 1020 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 2.29 (2 H, m), 2.01 (1 H, H_A of AB, J_{AB} = 18 Hz), 2.01 (1 H, H_B of AB, J_{AB} = 18 Hz), 1.78 (2 H, m), 1.38 (2 H, m), 1.28 (8 H, br s), 1.04 (3 H, s), 0.88 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.18; H, 11.98.

3-Methyl-3-(1,1-dimethylethyl)cyclopentanone (45): IR (CCl_4) 2965, 2870, 1735, 1460, 1400, 1370, 1360, 1155 cm^{-1}; 270-MHz ^1H NMR ($CDCl_3$) δ 2.30 (3 H, m), 2.04 (2 H, m), 1.89 (1 H, H_B of AB, J_{AB} = 18 Hz), 1.01 (3 H, s), 0.94 (9 H, s); MS (15 eV), m/z 154 (M^+), 139, 98, 83 (base), 69, 57, 55, 41. The isolated quantity of this sample was insufficient for combustion analysis.

3-Methyl-3-(4-methyl-3-pentenyl)cyclopentanone (46): $bp_{0.07}$ 60 °C; IR (CCl_4) 2955, 2925, 2870, 1740, 1535, 1450, 1400, 1375, 1255, 1150, 1000, 975 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.10 (1 H, t, J = 7 Hz), 2.29 (2 H, m), 2.09 (1 H, H_A of AB, J_{AB} = 18 Hz), 2.03 (1 H, H_B of AB, J_{AB} = 18 Hz), 2.00 (2 H, m), 1.80 (2 H, m), 1.69 (3 H, s), 1.61 (3 H, s), 1.43 (2 H, t, J = 8 Hz), 1.07 (3 H, s). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: 79.88; H, 11.42.

3-Hexyl-2,2,3-trimethylcyclopentanone (47): $bp_{0.15}$ 80 °C; IR (CCl_4) 2950, 2920, 2865, 2850, 1735, 1540, 1460, 1370, 1245, 1090, 1050, 1000 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 2.22 (2 H, m), 1.77 (1 H, m), 1.67 (1 H, m), 1.28 (10 H, br s), 0.91 (3 H, s), 0.89 (3 H, s), 0.89 (3 H, obscured, presumably a triplet with J = 7 Hz), 0.85 (3 H, s). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.77; H, 12.17.

1,3,3aα,4,5,6,7,7aα-Octahydro-2*H*-inden-2-one (51): $bp_{0.10}$ 45 °C; IR (CCl_4) 2930, 2855, 1735, 1440, 1400, 1255, 1230, 1150 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 2.32 (2 H, m), 2.19 (2 H, H_A of ABX, J_{AB} = 18.5 Hz, J_{AX} = 7.8 Hz), 2.11 (2 H, H_B of ABX, J_{AB} = 18.5 Hz, J_{BX} = 7.8 Hz), 2.11 (2 H, H_B of ABX, J_{AB} = 18.5 Hz, J_{BX} = 6.1 Hz), 1.62 (2 H, m), 1.51 (2 H, m), 1.41 (4 H, m); MS (70 eV), m/z 138 (M^+), 120, 109, 94 (base), 81, 67, 54, 41. This compound has been previously reported.[26]

3aα-Phenyl-1,3,3a,4,5,6,7,7aα-octahydro-2*H*-inden-2-one (52): IR (CCl_4) 3095, 3060, 3030, 2930, 2855, 1740, 1450, 1405, 1260, 1095, 1015, 860, 695 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 7.37 (3 H, m), 7.24 (2 H, m), 2.91 (1 H, m), 2.57 (1 H, H_A of AB, J_{AB} = 18 Hz), 2.44 (1 H, H_A of AB, J_{AB} = 18 Hz), 2.34 (1 H, H_A of ABX, J_{AB} = 19.1 Hz, J_{AX} = 8.1 Hz), 2.30 (1 H, H_B of ABX, J_{AB} = 19.1 Hz, J_{BX} = 8.0 Hz), 1.99 (1 H, m), 1.85 (1 H, m), 1.70–1.46 (5 H, m), 1.38 (1 H, m). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.76; H, 8.35.

3-(2-Phenylethyl)cyclopentanone (53): $bp_{0.08}$ 85 °C; IR (CCl_4) 3085, 3060, 3020, 2950, 2920, 2850, 1735, 1540, 1490, 1445, 1400, 1250, 1235, 690 cm^{-1}; 270-MHz ^1H NMR ($CDCl_3$) δ 7.24 (5 H, m), 2.67 (2 H, t, J = 8 Hz), 2.37 (2 H, m), 2.18 (3 H, m), 1.78 (3 H, m), 1.55 (1 H, m). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.68; H, 8.51.

1,1-Dimethyl-1,3,3aα,4,5,6,7,7aα-octahydro-2*H*-inden-2-one (54): $bp_{0.15}$ 65 °C; IR (CCl_4) 2960, 2915, 2845, 1730, 1535, 1440, 1375, 1255, 1210, 1130, 1075, 995, 965, 900 cm^{-1}; 270-MHz ^1H NMR ($CDCl_3$) δ 2.60 (1 H, m), 2.22 (2 H, d, J = 10 Hz), 1.65 (6 H, m), 1.22 (2 H, m), 1.06 (3 H, s), 0.97 (3 H, s), 0.91 (1 H, m). Anal. Calcd for $C_{11}H_{18}O$: C, 79.47; H, 10.91. Found: C, 79.45; H, 10.95.

3-Methyl-2-(2-phenylethyl)-3-tolylcyclopentanone (62), isolated as a 2:1 mixture of diastereomers: IR (neat) 3060, 3020, 2950, 2910, 2860, 1730, 1680, 1600, 1500, 1490, 1445, 1400, 1265, 1125, 1025, 810, 780, 750, 690 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) (mixture of isomers) δ 7.10 (9 H, m), 2.84 (0.67 H, m), 2.73 (0.33 H, m), 2.55 (2 H, m), 2.42 (2 H, m), 2.32 (2 H, s), 2.31 (1 H, s), 2.03 (2 H, m), 1.90 (1 H, m), 1.51 (1 H, m), 1.31 (1 H, s), 1.22 (2 H, s). Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.40; H, 8.30.

1α-(3-Butenyl)-3,3aα,6,6aα-tetrahydro-2(1*H*)-pentalenone (63): $bp_{0.5}$ 140 °C; IR (neat) 3070, 2980, 2920, 2860, 1735, 1630, 1440, 1400, 1370, 1160, 990, 910, 750 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 6.37 (1 H, dd, J = 5, 2 Hz), 5.80 (2 H, m), 5.05 (1 H, d, J = 17 Hz), 4.99 (1 H, d, J = 10 Hz), 3.49 (1 H, m), 3.22 (1 H, t, J = 7 Hz), 2.59 (1 H, dd, J = 18, 10 Hz), 2.24 (2 H, m), 2.10 (2 H, m), 1.18 (2 H, m), 1.79 (6 H, s). Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.38; H, 9.25.

***trans*-2-Heptyl-3-((*E*)-1-propenyl)cyclopentanone (64)**: $bp_{0.15}$ 100 °C; IR (neat) 2970, 2925, 2870, 1740, 1450, 1410, 1380, 1280, 1160, 1030, 965, 750 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.54 (1 H, dq, J = 15, 6 Hz), 5.38 (1 H, ddd, J = 15, 8, 1 Hz), 2.35 (2 H, m), 2.06 (2 H, m), 1.79 (1 H, pentet, J = 5 Hz), 1.70 (3 H, dd, J = 6, 1 Hz), 1.56 (3 H, m), 1.25 (10 H, br s), 0.87 (3 H, t, J = 7 Hz). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 80.97; H, 12.02.

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***trans*-2-(7-((*tert*-Butyldimethylsilyl)oxy)heptyl)-3-((*E*)-1-pentenyl)cyclopentanone (65)**: $bp_{0.1}$ 160 °C; IR (neat) 2950, 2920, 2850, 1735, 1440, 1245, 1090, 960, 825, 765, 740 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 5.49 (1 H, dt, J = 15, 7 Hz), 5.33 (1 H, dd, J = 15, 8 Hz), 3.58 (2 H, t, J = 7 Hz), 2.31 (2 H, m), 2.02 (5 H, m), 1.75 (1 H, m), 1.54 (2 H, m), 1.47 (2 H, m), 1.36 (2 H, m), 1.24 (8 H, br s), 0.88 (3 H, t, J = 7 Hz), 0.87 (9 H, s), 0.05 (6 H, s). Anal. Calcd for $C_{23}H_{44}O_2Si$: C, 72.57; H, 11.65. Found: C, 72.57; H, 11.83.

***trans*-2,3-Diphenylcyclopentanone (66)**: mp (hexane) 95 °C; IR (neat) 3060, 3020, 2960, 2920, 2860, 1950, 1870, 1740, 1595, 1480, 1440, 1385, 1275, 1130, 1110, 1070, 1025, 940, 905, 855, 750, 710, 690 cm^{-1}; 400-MHz ^1H NMR ($CDCl_3$) δ 7.14 (10 H, m), 3.46 (2 H, m), 2.67 (1 H, dd, J = 17, 8 Hz), 2.45 (2 H, m), 2.08 (1 H, m). Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82. Found: C, 86.85; H, 6.82. This compound has been previously prepared.[40]

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Heteroatom-Directed Allylic Substitution and Rearrangement Reactions

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Alcoholic, phenolic, and thiolic nucleophiles attack 3-chloro-1-methoxypropene (1) exclusively at C-1 in the presence of *N,N*-diisopropylethylamine. The reaction is formally a highly regioselective S_N2' process. Some of the oxygen nucleophiles (e.g., methyl salicylate) react slowly under these conditions and give poor yields; however, the corresponding lithium alkoxides, formed by treating the alcohol with lithium bis(trimethylsilyl)amide, give good yields. Several of the mixed acrolein acetals made by this procedure can be produced independently by acid-catalyzed addition of the alcohols to methoxypropadiene. In contrast, acid-catalyzed addition of thiols to methoxypropadiene leads to 3-(arylthio)-1-methoxypropenes. Enolates derived from activated carbonyl compounds give C-alkoxyallylated products with **1**. The acrolein *O,S*-acetals **2f,g** were found to undergo acid-catalyzed rearrangement into enol ethers **3a,b**.

Substitution reactions involving allylic substrates are of interest for both mechanistic and synthetic reasons. The stereochemistry and the possible concertedness of the S_N2' reaction continue to provoke discussion of allylic substitution mechanisms.[1-11] New synthetic applications in the area include Stork's S_N2' thiolate and alkoxide cyclizations and Kang's silicon-directed regiospecific alkylations of allylic halides.[12,13] We report here a new type of regiospecific allylic substitution which is formally a heteroatom-directed S_N2' reaction. We have also discovered a new method for the α-alkoxyallylation of activated carbonyl compounds that complements the methods recently reported by Coates.[14] In addition, we find that acid-catalyzed rearrangement of acrolein *O,S*-acetals gives 1-methoxy-3-(arylthio)propenes. Hoffmann and Kemper have reported the utility of such propenes in the synthesis of methoxy-substituted homoallylic alcohols.[15]

Results and Discussion

Treatment of an ether solution of 3-chloro-1-methoxypropene (**1**) with alcohols or thiols in the presence of *N,N*-diisopropylethylamine gives mixed acetals of acrolein **2**. If the nucleophile is a thiol (Table I, entries 8 and 9),

$$\underset{\mathbf{1}}{ClCH_2CH{=}CHOCH_3} \rightarrow \underset{\mathbf{2}}{CH_2{=}CHCH(OCH_3)R}$$

the reaction is complete within 5 min at −78 °C. The crude oils obtained after workup appear to be at least 90% pure by NMR. There is no indication in the NMR of the normal S_N2 products. Table I (entries 1, 3, 4, 5, 7) shows that phenols, in addition to primary, secondary, and tertiary alcohols, can be used. Some of the oxygen nucleophiles react sluggishly. Methyl salicylate, for example, gives only a 10% yield under these conditions. However, if the lithium salt is generated before the addition of **1**, the yield increases to 83%. Similarly, the yield improves from 77% to 92% if methyl thiosalicylate is subjected to the same conditions.

None of the acetals in Table I have been reported previously. Hoff, Brandsma, and Arens have prepared 3-methoxy-3-ethoxypropene, a mixed acetal, by acid-catalyzed addition of ethanol to methoxypropadiene.[16] They employed a 4-h reflux period with *p*-toluenesulfonic acid as the catalyst. These authors report that the mixed acetal was contaminated with the symmetrical acetals: $CH_2{=}$

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