Oxidative Rearrangement of Sulfur-Containing Tertiary Allylic Alcohols: Synthesis of 2-Cycloalkenones Bearing 3-[(Phenylthio)methyl] and 3-[2-Alkyl-1,3-dithian-2-yl] Substituents

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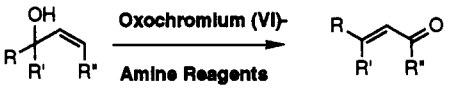
Substrate 1-[(phenylthio)methyl]-2-cycloalkenols **3a–d** and 1-[2-alkyl-1,3-dithian-2-yl]cyclohexenols **1a–d** were prepared by adding [(phenylthio)methyl]lithium and 2-lithio-2-alkyl-1,3-dithianes, respectively, in the 1,2-mode to various 2-cycloalkenones. The ranges of yields for the additions were 86–95% in the (phenylthio)methyl series and 69–88% in the dithiane series. A representative compound from each range of substrate tertiary allylic alcohols was then treated with a series of oxochromium(VI)–amine reagents such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), the Collins reagent (CrO_3·Pyr_2), and 2,2′-bipyridinium chlorochromate (BPCC). The oxochromium(VI)–amine reagents effected conversions of the representative substrates to the corresponding 3-[(phenylthio)methyl]- and 3-[2-alkyl-1,3-dithian-2-yl]-2-cycloalkenones **4a–d** and **2a–d** which were measured by gas chromatographic–mass spectral analysis. When comparing the efficiency of the range of oxochromium(VI)–amine reagents, PCC was found to give the best conversions to the corresponding transposed α,β-unsaturated carbonyl compounds in both series of substrates while the Jones reagent gave only decomposed material and no recovery of substrate. Distinct improvements on the initial PCC protocol using silica gel as an in situ adsorbent and promotion by ultrasound were then established with a range of substrate tertiary allylic alcohols while comparing sonicated versus nonsonicated experiments. The isolated yields of transposed products were found to be increased as much as 60% in the dithiane series and 9% in the (phenylthio)methyl series with the application of high-intensity ultrasound. Prolonged exposure of the substrate (**3a**) in the (phenylthio)methyl series to the PCC/silica reagent system resulted in the recovery of the corresponding sulfone (**5**), the identity of which was confirmed by selective oxidation of the transposed enone (**4a**) with *m*-chloroperbenzoic acid.

Introduction

The oxochromium(VI)-mediated oxidative rearrangement of tertiary allylic alcohols and tertiary vinyl carbinols to α,β unsaturated carbonyl compounds (Scheme I) has a wide breadth of scope in complex organic synthesis.[1,2] Pyridinium chlorochromate (PCC),[3] pyridinium dichromate (PDC),[4] and the Collins reagent[5] are the oxochromium(VI) reagents[6] frequently employed for the oxidative transposition. The limitations of their use rely on the sensitivity of the substrates to acidic or basic conditions and involve the susceptibility of the products to further oxidative side reactions such as epoxidation[7] and cleavage.[8]

Scheme I



The 1,3-transposition reaction has been extended to include oxidative rearrangements of enynols,[9] dienols,[10] and vinylcyclopropylcarbinols.[11] While the presence of vinylic and acetylenic components in the substrate offers a higher degree of synthetic latitude, the inclusion of activating heteroatoms also expands the versatility of the products for further synthetic elaboration and increases the value of the overall reaction in the synthesis of more complex molecules. To this end Ohler and Warren have prepared and examined the oxochromium(VI)-promoted oxidative rearrangements of phosphorus-containing tertiary allylic alcohols.[12,13] During early studies of dithianes[14a–c] Corey reported the acid-catalyzed transposition of a tertiary (1-dithianyl-2-cycloalkenyl)carbinol **1** followed by MnO_2 oxidation of the intermediate secondary allylic alcohol to the corresponding 3-dithianyl-substituted 2-cy-

(1) (a) Babler, J. H.; Coghlin, M. J. *Synth. Commun.* **1976**, *6*, 469. (b) Dauben, W. G.; Michno, D. M. *J. Org. Chem.* **1977**, *42*, 682. (c) Sundararaman, P.; Herz, W. *J. Org. Chem.* **1977**, *42*, 813.

(2) For examples of natural product syntheses utilizing the oxochromium(VI)-mediated transposition as a key step see the following. (a) (±)-Aplysins: Murai, A.; Abiko, A.; Masamune, T. *Tetrahedron Lett.* **1984**, *25*, 4955. (b) Bisabolanes: Mehta, G.; Reddy, A. V. *Tetrahedron Lett.* **1979**, *38*, 2625. (c) Cholesterol analogs: Drew, J.; Letellier, M.; Morand, P.; Szabo, A. G. *J. Org. Chem.* **1987**, *52*, 4047. (d) Clerodanes: Nakano, T.; Martin, A.; Rojas, A. *Tetrahedron* **1982**, *38*, 1217. (e) Hernandulcins: Mori, K.; Kato, M. *Tetrahedron Lett.* **1986**, *27*, 981. (f) Homofarnesenes: Alvarez, F. M.; Vander Meer, R. K.; Lofgren, C. S. *Tetrahedron* **1987**, *43*, 2897. (g) Neolemnanes: Majetich, G.; Lowery, D.; Khetani, V.; Song, J. S.; Hull, K.; Ringold, C. *J. Org. Chem.* **1991**, *56*, 3988. (h) Pleuromutilin: Gibbons, E. G. *J. Am. Chem. Soc.* **1982**, *104*, 1767. (i) Quassinoids: Heathcock, C. H.; Mahaim, C.; Schlecht, M. F.; Utawanit, T. *J. Org. Chem.* **1984**, *49*, 3264.

(3) Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* **1975**, 2647.

(4) Corey, E. J.; Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

(5) Poos, G. I.; Arth, G. E.; Beyler, R. E.; Sarett, L. H. *J. Am. Chem. Soc.* **1953**, *75*, 422. Holum, J. R. *J. Org. Chem.* **1961**, *26*, 4814. Collins, J. C.; Hess, W. W.; Frank, F. J. *Tetrahedron Lett.* **1968**, 3363.

(6) (a) Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry*; Springer-Verlag: Berlin, 1984. (b) Piancatelli, G.; Scettri, A.; D'Auria, M. *Synthesis* **1982**, 245. (c) Luzzio, F. A.; Guziec, F. S., Jr. *Org. Prep. Proc. Int.* **1988**, *20*, 533.

(7) Wolff, S.; Agosta, W. C. *Can. J. Chem.* **1984**, *62*, 2429. See also ref 1c.

(8) Walba, D. M.; Stoudt, G. S. *Tetrahedron Lett.* **1982**, *23*, 727. Cisneros, A.; Fernandez, S.; Hernandez, J. E. *Synth. Commun.* **1982**, *12*, 833.

(9) Liotta, D.; Brown, D.; Hoekstra, W.; Monihan, R. *Tetrahedron Lett.* **1987**, *28*, 1069.

(10) Majetich, G.; Condon, S.; Hull, K.; Ahmad, S. *Tetrahedron Lett.* **1989**, *30*, 1033.

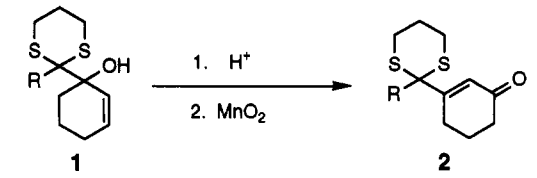
(11) Wada, E.; Okawara, M.; Nakai, T. *J. Org. Chem.* **1979**, *44*, 2952.

(12) Öhler, E.; Zbiral, E. *Synthesis* **1991**, 357.

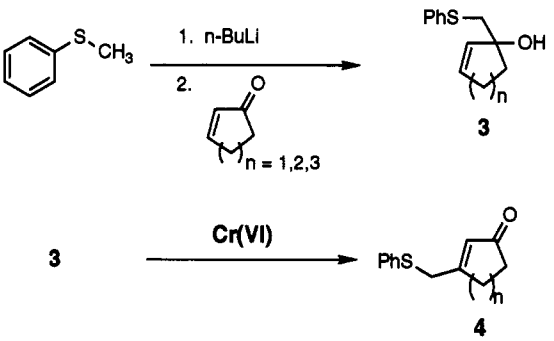
(13) Brown, P. S.; McElroy, A. B.; Warren, S. *Tetrahedron Lett.* **1985**, *26*, 249. McElroy, A. B.; Warren, S. *Tetrahedron Lett.* **1985**, *26*, 1677.

0022-3263/93/1958-2966$04.00/0

Scheme II

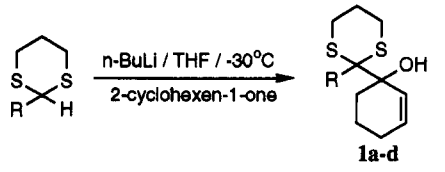


Scheme III



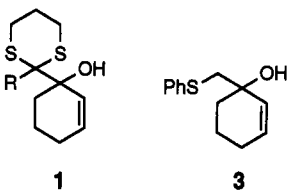
cloalkenone **2** (Scheme II).[14d] According to the earlier work of Babler, Dauben, and Herz,[1a-c] the overall transformation depicted in Scheme II could be conceptually effected in a single operation by employment of the oxochromium(VI) reagents currently available. While 3-[(phenylthio)methyl] derivatives of 2-cycloalkenones **4** are attractive as synthetic intermediates for alkylation and cyclopropanation,[15] the viability of allylic [(phenylthio)methyl]carbinols **3** as precursors to these compounds via the oxochromium(VI)-mediated 1,3 transposition route (Scheme III) has not been explored. Within the same scheme the requisite carbinols (**3**) would be obtained by the 1,2 addition of [(phenylthio)methyl]lithium to 2-cycloalkenones. We were interested in examining the oxochromium(VI)–amine-mediated 1,3-oxidative transposition process using substrates bearing divalent sulfur substituents with the possibility of evaluating the utility of the products in further synthetic transformations. Early studies in the development of new mild oxochromium(VI)–amine oxidants revealed that the relative oxidation rate of sulfides to sulfoxides and sulfones is slower with these reagents than the oxidation of alcohols to carbonyl compounds.[16] Typically, the oxidation of alcohols to the corresponding carbonyl compounds may require 10–20 min of reaction time using the more common commercially available Cr(VI) reagents under standard conditions while the oxidation of sulfides to sulfoxides or sulfones may require 4 h to 3 days to complete with the same reagents and conditions. Furthermore, several isolated examples of selective oxochromium(VI)-mediated oxidation of complex substrate alcohols containing sulfide functionality to the corresponding carbonyl compounds have been reported in which the yields of the desired products range from 48 to 75%.[17] The results obtained with 2-alkyl-2-(1,3-dithianyl)-substituted alcohol substrates are less reliable and range from 0 to 85%.[18] Presumably in some cases, the dithiane moiety causes the substrate or product to be tightly bound to the reduced chromium byproducts, thus drastically reducing yields. Considering these observations we elected first to evaluate the application of PCC, PDC, the chromium trioxide–dipyridine complex (Collins reagent), and 2,2′-bipyridinium chlorochromate (BPCC)[19] in the 1,3-transposition reaction of two substrate tertiary allylic alcohols of general structure **1** and **3** in order to establish the most desirable reagent system in terms of yield, selectivity, and facility of workup and purification. Once the reagent system and the optimal conditions for the conversion of **1** and **3** to **2** and **4**, respectively, were selected, a range of substrates was then submitted to the optimal rearrangement conditions in order to explore the generality of the reaction.

Table I. 1,2-Additions of Dithianes to 2-Cyclohexen-1-one



entry	R	product	yield[a] (%)
1	CH_3	**1a**	69
2	cyclohexyl	**1b**	88
3	2-phenylethyl	**1c**	90
4	i-Pr	**1d**	81

[a] Yields are of isolated products.



Results and Discussion

Preparation of Tertiary Allylic Alcohol Substrates. The 1,2-mode of addition of 2-alkyl-substituted 2-lithio-1,3-dithianes to 2-cycloalkenones has been established,[20] and this method was used to prepare dithiane alcohol substrates **1a–d** in isolated yields ranging from 69 to 90% (Table I). The requisite dithianes, prepared from aldehydes, 1,3-propanedithiol, and boron trifluoride etherate,[21] were metalated with *n*-butyllithium at −78 °C. To the resulting anions was added 2-cyclohexen-1-one in tetrahydrofuran at −78 °C which provided the desired dithianyl tertiary allylic alcohols **1a–d** after silica gel chromatography. Tertiary allylic alcohols containing the 2-aryl-2-(1,3-dithianyl) group (**1**, R = Ph) were also

(14) (a) Corey, E. J.; Crouse, D. *J. Org. Chem.* **1968**, *33*, 298. (b) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075. (c) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434. (d) Rigby, H. L.; Neveu, M.; Pauley, D.; Ranu, B. C.; Hudlicky, T. *Org. Synth.* **1988**, *67*, 205.

(15) Cohen, T.; Yu, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 2811. Ramig, K.; Bhupathy, M.; Cohen, T. *J. Org. Chem.* **1989**, *54*, 4404.

(16) Suggs, J. W. Ph.D. dissertation, Harvard University, 1976, p 124. Reference 2c, p 573.

(17) For examples of oxochromium(VI)–amine-mediated oxidation of intermediate sulfide alcohols in which selectivity for the alcohol function is preferred see: Bakuzis, P.; Bakuzis, M. L. F. *J. Org. Chem.* **1977**, *42*, 2362. Sasaki, T.; Egichi, S.; Ban, H. *J. Org. Chem.* **1983**, *48*, 4073. Schaefer, T.; Penner, G. H.; Davie, K. K.; Sebastian, R. *Can. J. Chem.* **1985**, *63*, 777.

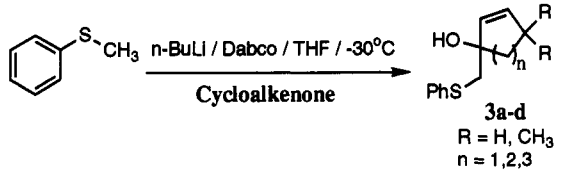
(18) For examples of oxochromium(VI)–amino-mediated oxidations of intermediates containing the 2-substituted 1,3-dithiane functionality see: Andersen, N. H.; McCrae, D. A.; Grotjann, D. M.; Gabhe, S. Y.; Theodore, L. J.; Ippolito, R. M.; Sarkar, T. K. *Tetrahedron*, **1981**, *37*, 4069. Smith, A. B.; Dorsery, B. D.; Visnick, M.; Maeda, T.; Malamas, M. S. *J. Am. Chem. Soc.* **1986**, *108*, 3110. Shelly, K. P.; Weiler, L. *Can. J. Chem.* **1988**, *66*, 1359. Corey, E. J.; Kang, M. C.; Desai, M. C.; Ghosh, A. K.; Houpis, I. N. *J. Am. Chem. Soc.* **1988**, *110*, 649. See also ref 16, pp 106–107.

(19) Guziec, F. S., Jr.; Luzzio, F. A. *Synthesis* **1980**, 691.

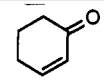
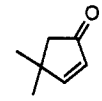
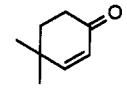
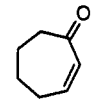
(20) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; pp 421, 837.

(21) Corey, E. J.; Seebach, D. *Org. Synth.* **1970**, *50*, 72.

Table II. 1,2-Addition Products of [(Phenylthio)methyl]lithium to Cycloalkenones



3a-d
R = H, CH_3
n = 1,2,3

entry	substrate[b]	product	yield[a] (%)
1		3a	95
2		3b	87
3		3c	86
4		3d	89

[a] Yields are of isolated products. [b] Used as commercially supplied.

considered for this range of substrates. Their preparation, via the 2-aryl-2-lithio-1,3-dithiane precursors, is not as routine since the desired 1,2-addition is complicated by competing 1,4-addition[22] which results in complex mixtures. 1-[2-(1,1-Dimethylethyl)-1,3-dithian-2-yl]-2-cyclohexen-1-ol (1, R = *tert*-butyl) was required in order to probe the effects of proximal steric congestion on the transposition process. However, during the course of procuring this substrate, we discovered that the addition of 2-lithio-2-(*tert*-butyl)-1,3-dithiane to 2-cyclohexenone was not successful under several sets of conditions and resulted only in the recovery of starting materials.[23] The general course of [(phenylthio)methyl]lithium addition[24] to enones has been investigated to a lesser extent when compared to the addition of 2-lithio-1,3-dithianes presumably due to the higher regard given the dithiane congeners for their versatility as masked carbonyls and acyl anion equivalents.[25] For the preparation of [(phenylthio)methyl]lithium we followed the improved protocol detailed by Corey and Seebach[26] which entailed treatment of thioanisole with *n*-butyllithium in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) in tetrahydrofuran at −78 °C. Addition of cyclic enones to the [(phenylthio)-methyl]lithium at −78 °C resulted in 1,2-addition and thus provided the desired (phenylthio)methyl tertiary carbinols **3a–d** in yields ranging from 86 to 95% after purification by silica gel chromatography (Table II). None of the 1,4-addition products were detected by thin-layer chromatographic analysis, gas chromatographic analysis, or NMR analysis of the crude reaction mixtures.

(22) Ostrowski, P. C.; Kane, V. V. *Tetrahedron Lett.* **1977**, *40*, 3549. Brown, C. A.; Yamaichi, A. *J. Chem. Soc., Chem. Commun.* **1979**, 100.

(23) While the 2-*tert*-butyl-substituted dithiane could be prepared in good yield (pivalaldehyde, 1,3-propanedithiol, BF_3) and deprotonated (n-butyllithium, THF, −78 → 0 °C), the resulting anion would not add to 2-cyclohexenone as evidence by recovery of the reactants. The development of the anion was confirmed in separate experiments by D_2O quenching followed by NMR analysis.

(24) Coates, R. M.; Sowerby, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 4758.

(25) See, for example: Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357 and references cited therein.

(26) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097.

Table III. GC–MS Analysis of Oxidants on Substrates 1d[a] and 3a[b]

	% conversn	
oxidant	1d	3a
PCC	53	74
PDC	31	62
BPCC	>1	13
Collins	37	37

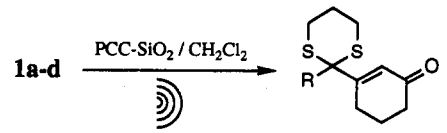
[a] Amount of 1d produced after 1.0 h. [b] Amount of 3a produced after 2.5 h.

The Oxidative Transpositions. Selection of Reagent Systems. Several oxochromium(VI) reagent systems were evaluated for optimal conversion of tertiary alcohol substrates to the corresponding transposed enones. The criteria for the choice of reagent systems which underwent initial evaluation were commercial availability, expense, selectivity, and the extent of present usage in organic synthesis. Compound **1d** (1, R = isopropyl) was chosen as the representative dithiane alcohol substrate and was treated with a range of reagents (Table III) in separate experiments under identical reaction conditions of time, temperature, equivalents, and solvent. Preliminary workup and submission of the reaction mixtures to gas chromatographic–mass spectral (GC–MS) analysis then established the extent of conversion of **1d** to **2d**. Despite the increased acidity and decreased selectivity associated with the Jones reagent[27] as contrasted with that of the oxochromium(VI)–amine complexes, we attempted a transposition of **1d** using the Jones reagent for purposes of comparison. When **1d** was added to Jones reagent (2 equiv) only decomposition was encountered, as revealed by monitoring the reaction by thin-layer chromatography, and no recovery of product or starting material was apparent upon workup after a 1-h reaction period. Compound **3a** was chosen as the representative (phenylthio)methyl-substituted substrate and was treated with the same range of reagents and conditions as in the **1d** → **2d** series of experiments. The conversions of **3a** to **4a** were monitored by GC–MS analyses, and the results are listed in Table III beside those of **1d** → **2d** for comparison. From the set of experiments **1d** → **2d** and **3a** → **4a** we established that the efficiency of conversion follows the order PCC > PDC > Collins > BPCC. The scope of the process was then probed by designing a set of experiments which utilized improved PCC procedures together with a range of substrate tertiary alcohols. We reported earlier that substantial improvements in facility and yield are realized by addition of silica gel to PCC oxidations of simple alcohols combined with promotion by ultrasound.[28] When used in conjunction with PCC (2 equiv) we had observed that silica gel adsorbs the reduced chromium tars which would otherwise entrain a portion of the desired product and reduce yields. In addition, the silica gel greatly facilitates the workup and purification process since the reduced chromium byproducts appear as a microgranular solid which is easily removed by a Celite filtration. Application of ultrasound to the PCC/silica gel oxidation enhances the rate and yield of the reaction since the solid oxochromium(VI) reagent and the adsorbent are activated by cavitation, shock wave-induced particle fragmentation, and surface area alteration.

(27) Jones reagent was prepared and used according to: Meinwald, J.; Crandall, J.; Hymans, W. E. *Org. Synth.* **1965**, *45*, 77.

(28) Adams, L. L.; Luzzio, F. A. *J. Org. Chem.* **1989**, *54*, 5387.

Table IV. Ultrasound-Promoted PCC-SiO_2 Oxidation of 1a–d

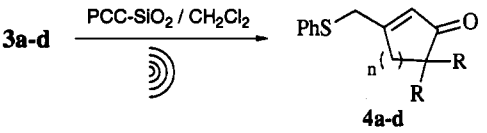


2a-d

substrate	R	product	yield[a,b] (%)
1a	CH_3	2a	28 (20)
1b	cyclohexyl	2b	56 (25)
1c	2-phenylethyl	2c	62 (25)
1d	i-Pr	2d	74 (64)

[a] Yields are of isolated products. [b] Yields in parentheses are for nonsonicated experiments.

Table V. Ultrasound-Promoted PCC-SiO_2 Oxidation of 3a–d



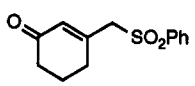
4a-d

substrate	product	n	R	yield[a,b] (%)
3a	4a	2	H	75 (71)
3b	4b	1	CH_3	83 (77)
3c	4c	2	CH_3	92 (86)
3d	4d	3	H	82 (78)

[a] Yields are of isolated products. [b] Yields reported in parentheses are for nonsonicated experiments.

Transpositions of 1,3-Dithiane-Substituted Tertiary Alcohols 1a–d. The 2-(1,3-dithianyl)-substituted tertiary alcohols **1a–d** were transposed to the corresponding β-substituted 2-(1,3-dithianyl)cycloalkenones **2a–d** (Table IV) by exposure to PCC/silica gel and PCC/silica gel/ultrasound in dichloromethane while the reaction temperature was maintained at 25 °C. For purposes of comparing yield and reaction time, sonicated and nonsonicated experiments were run using identical conditions of temperature, solvent, equivalents of reagent, amount of silica gel, and workup. The isolated yields for both the sonicated and nonsonicated transposition reactions are presented in Table IV and in this range of experiments appear to improve with increasing steric congestion about the carbon α to the dithiane ring. Presumably, such substitution hinders the binding of the dithiane moiety to the unreacted reagent or reduced chromium species and the yields are thus increased.

Transpositions of (Phenylthio)methyl-Substituted Tertiary Alcohols 3a–d. The 1-[(phenylthio)methyl]-1-(2-cycloalkenyl)carbinols **3a–d** were transposed to the corresponding β-[(phenylthio)methyl]cycloalkenones **4a–d** (Table V) under sonicated and nonsonicated conditions. Typically, the nonsonicated experiments required 3 equiv of oxidant and 3 h of reaction time for complete consumption of starting material while the sonicated experiments required the same equivalents of reagent and 1 h of reaction time. Under an extended reaction time (2-fold) in both a nonsonicated and sonicated case utilizing substrate **3a** the appearance of the corresponding sulfone **5** as a more polar trace component (<2%) of the reaction mixture was detected by thin-layer chromatographic analysis. The identity of **5** was confirmed independently by the selective oxidation of **4a** with *m*-chloroperbenzoic acid (4 equiv) in dichloromethane[29a] followed by chromatographic purification and NMR and IR analyses. The



5

isolated yields for the (phenylthio)methyl-substituted compounds were altogether better than those having dithiane substitution. Presumably, the 1,3-arrangement of the sulfurs in the dithiane series provides an efficient tandem locus of binding in the substrate for the reduced chromium species. Yields are thereby lower when compared to the substrates bearing the single sulfur in the (phenylthio)methyl series. Unlike our results involving the (phenylthio)methyl sulfone **5**, the products of any degree of oxidation at one or both sulfurs in the dithiane series could not be detected or isolated. A competing process which constantly plagues many types of oxidations utilizing oxochromium(VI)–amine reagents is the polymerization side reaction involving the heterocyclic nitrogen base and the reduced chromium species.[30] In many cases, especially those involving the conversion of alcohols to carbonyl compounds, the polymerization rate exceeds that of the oxidation of the substrate and results in the production of black tars which entrain the reactant/product and necessitates the usage of more equivalents of reagent. In both series of substrates the optimal results were obtained when the reagent was added to a suspension of the reagent system in two portions so that the competing polymerization process is minimized. As encountered previously with PCC oxidations of simple alcohols and alcohols bearing acid-sensitive protecting groups, during the oxidative transposition the silica gel functions as an in situ adsorbent which renders the reduced chromium-derived tars as an easily filterable microgranular solid. The rationale behind the increased yields and reaction rates that are brought about by ultrasound has been discussed in detail elsewhere[31] and is completely consistent with our observations during this study. Ultrasound studies in conjunction with other types of functional group transformations are currently in progress and will be reported in due course.

Experimental Section

General Procedures. NMR spectra were recorded with a Bruker AMX-500 using $CDCl_3$ as solvent and internal standard. Infrared spectra were recorded with Perkin-Elmer 1310 and Mattson Galaxy 5000 instruments. Melting points are uncorrected. CH_2Cl_2 was distilled from CaH_2 prior to use as a reaction solvent. THF was distilled from sodium/benzophenone. All other reaction solvents were used as commercially supplied. General chromatographic methods and ultrasonic techniques used have

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(30) Many adsorbents or supports have been used in conjunction with oxochromium(VI)–amine oxidations, and some of these are effective in facilitating control of the black tarry byproducts during the workup procedure. See, for example, the following. (a) Alumina: Corey, E. J.; Tramontano, A. *J. Am. Chem. Soc.* **1984**, 106, 463. (b) Celite: Rathore, R.; Saxena, N.; Chandrasekaran, S. *Synth. Commun.* **1986**, *16*, 1493. (c) Clays: Choudary, B. M.; Prasad, A. D.; Swapna, V.; Valli, V. L. K.; Bhuma, V. *Tetrahedron* **1992**, *48*, 953. (d) Molecular sieves: Herscovici, J.; Egron, J.-M.; Antonakis, K. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1967. (e) Silica gel: Sing, R. P.; Subbarao, H. N.; Dev. S. *Tetrahedron* **1979**, *35*, 1789.

(31) (a) Suslick, K. S. *Sci. Am.* **1989**, *260*, 80. (b) Suslick, K. S. *Science (Washington, D.C.)* **1990**, *247*, 1373. (c) Luzzio, F. A.; O'Hara, L. C. *Synth. Commun.* **1990**, *20*, 3223. (d) Luzzio, F. A.; Moore, W. J. *J. Org. Chem.* **1993**, *58*, 512.

been previously described.[32] GC–MS experiments were performed with a Hewlett-Packard 5890 Series II instrument equipped with a 5971A detector and HP-1 column. High-resolution mass spectral analyses were performed by Midwest Center for Mass Spectrometry, Lincoln, NE. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

General Preparation of Dithianyl Tertiary Allylic Alcohols 1a–d. 1-[2-Methyl-1,3-dithian-2-yl]-2-cyclohexen-1-ol[14a] (1a, Table I). To a stirred, cooled (−78 °C) solution of 2-methyl-1,3-dithiane (2.09 g, 15.6 mmol) in anhydrous THF (20 mL) was added 1.6 M *n*-BuLi (9.7 mL, 15.6 mmol) by syringe, after which the solution was allowed to warm (−30 °C). After 1.5 h, the solution was cooled (−78 °C) and 2-cyclohexene-1-one (1.50 g, 15.6 mmol) in anhydrous THF (5 mL) was added. The reaction mixture was then allowed to warm (rt) and was stirred (0.5 h) followed by the addition of saturated aqueous NH_4Cl solution (10 mL). The Et_2O layer was removed, and the remaining aqueous layer was washed with Et_2O (3 × 50 mL). The organic layers were combined and washed with water (3 × 50 mL) and brine (50 mL) and then dried (Na_2SO_4). The excess solvent was removed in vacuo to afford an oil (R_f 0.24, 4:1 pentane/EtOAc) which was chromatographed (9:1 pentane/EtOAc, 100 × 40 mm SiO_2) to provide **1a** as white crystals (1.65 g, 69%), mp 57–59 °C (lit.[14a] mp 54.1–55 °C).

1-(2-Cyclohexyl-1,3-dithian-2-yl)-2-cyclohexen-1-ol (1b, Table I). The above general procedure was followed and provided a crude oil (R_f 0.45, 9:1 pentane/EtOAc). Column chromatography (25:1, pentane/EtOAc) resulted in the isolation of white crystals (0.31 g, 88%, mp 83–85 °C): IR (neat) 3400 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.27 (d, 1H), 5.84 (m, 1H), 6.24 (d, J = 10.4 Hz, 1H), 5.85–5.82 (m, 1H), 3.01–2.67 (m, 4H), 2.31 (d, J = 12.5 Hz, 1H), 2.25 (d, J = 12.5 Hz, 1H), 2.05–1.60 (m, 11H), 1.44–0.84 (m, 5H); ^{13}C NMR δ 131.22, 129.80, 77.94, 48.00, 31.92, 30.48, 30.03, 27.71, 27.68, 27.17, 27.03, 26.53, 24.94, 23.62, 18.94. Anal. Calcd for $C_{16}H_{26}OS_2$: C, 64.36; H, 8.78. Found: C, 64.34; H, 8.52.

1-[2-(2-Phenylethyl)-1,3-dithian-2-yl]-2-cyclohexen-1-ol (1c, Table I). The above general procedure was followed to give a crude oil (R_f 0.29, 9:1, pentane/EtOAc) which was column chromatographed (25:1, pentane/EtOAc) to provide **1c** as a viscous, clear oil (0.98 g, 90%). An analytical sample was Kugelrohr distilled (bp 220–221 °C/4 mmHg): IR (neat) 3500 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28–7.15 (m, 5H), 6.18 (d, J = 10.2 Hz, 1H), 5.95–5.91 (m, 1 H), 3.03–2.97 (m, 4H), 2.85–2.78 (m, 2H), 2.16–1.72 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.76, 131.87, 129.71, 128.51, 128.40, 125.75, 62.61, 39.56, 32.77, 31.20, 27.27, 26.70, 25.06, 24.13, 18.92; HRMS calcd for $C_{18}H_{24}OS_2$ m/e 320.1269, found m/e 320.1257.

1-[2-(1-Methylethyl)-1,3-dithian-2-yl]-2-cyclohexen-1-ol (1d, Table I). The above general procedure was followed to provide a crude oil (R_f 0.39, 9:1 pentane/EtOAc) which was column chromatographed (25:1, pentane/EtOAc) to give **1d** as a colorless oil (1.51 g, 81%). An analytical sample was Kugelrohr distilled (bp 173–174 °C/4 mmHg): IR (neat) 3481 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.24 (d, J = 10.3 Hz, 1H), 5.86–5.82 (m, 1H), 3.09–2.96 (m, 2H), 2.83–2.69 (m, 2H), 2.23–2.21 (m, 1H), 2.06–2.03 (m, 2H), 1.96–1.68 (m, 5H), 1.23 (d, J = 6.8 Hz, 3H), 1.17 (d, J = 6.8 Hz, 3H); ^{13}C NMR δ 131.29, 129.87, 78.37, 37.26, 31.62, 27.26, 27.19, 24.98, 23.57, 20.84, 20.33, 19.01; HRMS calcd for $C_{13}H_{22}OS_2$ m/e 258.1112, found m/e 258.1116.

General Preparation of (Phenylthio)methyl Tertiary Allylic Alcohols 3a–d. 1-[(Phenylthio)methyl]-2-cyclohexen-1-ol (3a, Table II). To a stirred cooled (−10 °C) solution of thioanisole (2.0 g, 16.1 mmol) and DABCO (1.81 g, 16.1 mmol) in anhydrous THF (30 mL) was added 1.6 M *n*-BuLi (6.0 mL, 19.3 mmol) dropwise under Ar. The yellow solution was allowed to warm (0 °C) for 1 h, after which 2-cyclohexen-1-one (1.55 g, 16.1 mmol) was added. During the addition the yellow solution clouded, and after 1 h TLC analysis (9:1, pentane/EtOAc) indicated the disappearance of thioanisole and the formation of **3a** (R_f 0.26). The cloudy-yellow solution was diluted with Et_2O (50 mL) and washed with saturated aqueous NH_4Cl (2 × 50 mL), 5% aqueous NaOH solution (3 × 50 mL), 5% aqueous HCl solution (3 × 50 mL), and brine (50 mL) and then dried (Na_2SO_4). Excess solvent was removed in vacuo to yield a yellow oil which was column chromatographed on silica gel (30 g, 9:1, pentane/EtOAc) to afford 3.38 g (95%) of **3a** as a yellow oil. An analytical sample was Kugelrohr distilled (bp 163–164 °C/4 mm): IR (neat) 3420 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.14 (m, 5H), 5.84 (tt, J = 10.1 Hz, 1H), 5.65 (d, J = 10.0 Hz, 1H), 3.15 (q_{AB}, J_{AB} = 13.2 Hz, 2H), 2.00 (m, 2H), 1.70 (m, 4H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 137.08, 131.25, 130.79, 129.50, 128.94, 126.15, 69.66, 46.94, 35.27, 25.18, 19.04; HRMS calcd for $C_{13}H_{16}OS$ m/e 220.0922, found m/e 220.0924.

4,4-Dimethyl-1-[(phenylthio)methyl]-2-cyclopent-1-ol (3b, Table II). The above general procedure was followed to yield a colorless oil after column chromatography on silica gel (0.93 g, 87%; R_f 0.32, 9:1 pentane/EtOAc). An analytical sample was Kugelrohr distilled (bp 149–151 °C/4 mm): IR (neat) 3400 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39–7.15 (m, 5H), 5.60 (q_{AB}, J_{AB} = 5.50 Hz, 2H), 3.24 (s, 2H), 1.87 (q_{AB}, J_{AB} = 13.9 Hz, 2H), 1.15 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.49, 136.76, 131.52, 129.59, 128.98, 126.26, 85.50, 52.41, 46.83, 44.87, 30.14, 29.04; HRMS calcd for $C_{14}H_{18}OS$ m/e 234.1078, found m/e 234.1070.

4,4-Dimethyl-1-[(phenylthio)methyl]-2-cyclohexen-1-ol (3c, Table II). The above general procedure was followed to provide a colorless oil after column chromatography on silica gel (1.72 g, 86%) which solidified on cooling (0 °C) to a gummy white solid (R_f 0.33, 9:1 pentane/EtOAc). An analytical sample was Kugelrohr distilled (bp 170–171 °C/4 mm): IR (neat) 3400 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.16 (m, 5H), 5.51 (q_{AB}, J_{AB} = 10.0 Hz, 2H), 3.14 (q_{AB}, J_{AB} = 13.1 Hz, 2H), 1.79 (m, 2H), 1.61 (m, 1H), 1.41 (m, 1H), 1.00 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.36, 137.01, 129.53, 128.94, 128.12, 126.18, 69.82, 46.72, 33.55, 32.35, 32.09, 29.48, 28.07; HRMS calcd for $C_{15}H_{20}OS$ m/e 248.1235, found m/e 248.1235.

1-[(Phenylthio)methyl]-2-cyclohepten-1-ol (3d, Table II). The above general procedure was followed to give a colorless oil after column chromatography on silica gel (3.786 g, 89%) which on cooling (0 °C) solidified into a white pasty solid (R_f 0.27, 9:1 pentane/EtOAc, mp 35.5–36 °C): IR (neat) 3400 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.15 (m, 5H), 5.76 (m, 1H), 5.64 (d, J = 12.0 Hz, 1H), 3.22 (q_{AB}, J_{AB} = 13.2 Hz, 2H), 1.98 (m, 2H), 1.81 (m, 3H), 1.56 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.06, 131.61, 129.89, 128.96, 126.32, 46.16, 38.06, 27.79, 27.24, 24.38; HRMS calcd for $C_{14}H_{18}OS$ m/e 234.1078, found m/e 234.1084.

Transpositions of 1d and 3a. Evaluation of the PCC, PDC, Collins, and BPCC Reagent Systems. To a stirred suspension of each oxochromium(VI)–amine reagent (3 equiv) in CH_2Cl_2 (1 mL) was added **1d** or **3a** (2 mg) in CH_2Cl_3 (1 mL) at rt. After 2.5 h the brown reaction mixture was filtered through silica gel followed by rinsing with pentane/EtOAc (1:1, 10 mL). The solvent was removed in vacuo, and the residue was diluted with CH_2Cl_2 (1 mL) for a stock solution. A portion of the stock solution (400 μL) was diluted to 1 mL, and injections (1.5 μL) were drawn from this solution for each run. The conditions for each run (8) were as follows: injector temperature 200 °C; detector temperature 250 °C; column ramp 15°/min (70 → 190 °C); solvent delay 0.75 min.

General PCC-SiO_2 Transpositions of 1a–d. (i) Nonultrasound. 3-[2-Methyl-1,3-dithian-2-yl]-2-cyclohexen-1-one[14a] (2a, Table IV). PCC[33] (0.142 g, 0.660 mmol) and SiO_2 (1 wt equiv of PCC) were ground into a fine powder, and half the mixture was added to a flask containing CH_2Cl_2 (5 mL). To the stirred orange slurry was added **1a** (0.101 g, 0.440 mmol) in CH_2Cl_2 (1 mL); the color of the solution immediately changed to dark brown. TLC analysis after 1.5 h indicated ~50% conversion, the remaining PCC–SiO_2 mixture was added, and stirring was continued (1.5 h). TLC analysis then indicated that the reaction was complete as evidenced by the disappearance of **1a**. The reaction solution was diluted with Et_2O (25 mL) and filtered through a plug of SiO_2 (15 g) and Celite using a fritted glass funnel followed by rinsing with Et_2O (100 mL). Excess solvent was removed in vacuo to afford a yellow oil which was chro-

(32) See ref 31d.

(33) **Caution**: Handle all Cr(VI) reagents with care; the mutagenicity of Cr(VI) compounds is well documented: Wetterhahn, K. E.; Cupo, D. Y. *Cancer Res.* **1985**, *45*, 1146 and references cited therein.

matographed on silica gel (4:1 pentane/EtOAc, R_f 0.24) to yield **2a** (0.0201 g, 20%) as a clear crystalline material, mp 69.5–70.5 °C (lit.[14a] mp 68.4–68.9 °C).

(ii) Ultrasound Promoted. PCC (0.142 g, 0.660 mmol) and SiO_2 (1 wt equiv of PCC) were ground into a fine powder, and half the mixture was added to a flask containing CH_2Cl_2 (5 mL). Ultrasound (maximum intensity) was initiated, and **1a** (0.101 g, 0.440 mmol) in CH_2Cl_2 (1 mL) was added which caused the orange solutions to darken. TLC analysis (4:1 pentane/EtOAc, 0.5 h) indicated 50% conversion, and the remaining PCC–SiO_2 mixture was added. Sonication proceeded (0.5 h) after which Et_2O (25 mL) was added and filtered as in the above procedure. Column chromatography on silica gel resulted in the isolation of **2a** (0.0290 g, 28%) as a clear crystalline material, with the same properties as above. **2b–d** utilized the same conditions and workup.

3-[2-Cyclohexyl-1,3-dithian-2-yl]-2-cyclohexen-1-one (2b, Table IV). Column chromatography of the crude colorless oil (9:1, pentane/EtOAc) on silica gel afforded **2b** (0.0791 g, 56%) as clear plates (mp 113.5–115 °C): IR (neat) 1680 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.61 (s, 1H), 2.74–2.69 (m, 2H), 2.64–2.59 (m, 2H), 2.51 (t, 2H), 2.41 (t, 2H), 2.01–1.96 (m, 3H), 1.85–1.61 (m, 7H), 1.55–1.08 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.14, 163.31, 131.67, 64.72, 46.02, 37.63, 28.17, 27.60, 27.45, 26.78, 26.18, 25.08, 23.50; HRMS calcd for $C_{16}H_{24}OS_2$ *m/e* 296.1263 found *m/e* 296.1267.

3-[2-(2-Phenylethyl)-1,3-dithian-2-yl]-2-cyclohexen-1-one (2c, Table IV). Column chromatography of the crude oil on silica gel (9:1, pentane/EtOAc) afforded **9c** (0.1826 g, 62%) as a colorless, viscous oil (bp 229–230 °C)/4 mmHg): IR (neat) 1680 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.26–7.10 (m, 5H), 2.80–2.60 (m, 6H), 2.50 (t, 2H), 2.40 (t, 2H), 2.27–2.15 (m, 3H), 2.07–1.84 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.15, 162.78, 140.77, 130.83, 128.50, 128.37, 126.18, 58.18, 41.65, 37.53, 30.31, 27.60, 26.94, 24.88, 23.34; HRMS calcd for $C_{18}H_{22}OS_2$ *m/e* 318.1107, found *m/e* 318.1099.

3-[2-(1-Methylethyl)-1,3-dithian-2-yl]-2-cyclohexen-1-one (2d, Table IV). Column chromatography of the crude oil on silica gel (9:1, pentane/EtOAc) provided **2d** (0.1275 g, 74%) as clear plates (mp 59.5–61.0 °C): IR 1670 (neat) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.62 (s, 1H), 2.73–2.67 (m, 2H), 2.64–2.59 (m, 2H), 2.51 (t, 2H), 2.41 (t, 2H), 2.08–2.03 (m, 1H), 2.01–1.95 (m, 3H), 1.85–1.77 (m, 1H), 1.06–1.05 (d, J = 6.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.19, 163.53, 131.40, 65.04, 37.67, 35.82, 27.45, 27.36, 25.00, 23.55, 17.99. Anal. Calcd for $C_{13}H_{20}OS_2$: C, 60.89; H, 7.86. Found: C, 60.81; H, 8.09.

General Procedure for PCC–SiO_2 Transpositions of 3a–d. (i) Nonultrasound. 3-[(Phenylthio)methyl]-2-cyclohexen-1-one[15] (4a, Table V). PCC (0.358 g, 1.66 mmol) and SiO_2 (1 wt equiv of PCC) were ground into a fine powder, and half the mixture was added to a flask containing CH_2Cl_2 (5 mL). To the stirred orange slurry was added **3a** (0.122 g, 0.554 mmol) in CH_2Cl_2 (1 mL); the color of the solution immediately changed to dark brown. After 1.5 h TLC analysis indicated ~50% conversion, the additional PCC–SiO_2 mixture was added, and stirring was continued (1.5 h). TLC analysis then indicated that the reaction was complete as evidenced by the disappearance of **3a**. The reaction solution was diluted with Et_2O (25 mL) and filtered through a plug of SiO_2 (15 g) and Celite in a fritted glass funnel followed by Et_2O (100 mL) rinse. Excess solvent was removed in vacuo to give a yellow oil which was chromatographed on silica gel (9:1 pentane/EtOAc) to yield 0.083 g of **4a** (71%, R_f 0.12). Kugelrohr distillation resulted in a yellow oil: bp 191–193 °C/4 mm; IR (neat) 1655 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) δ 7.30–7.17 (m, 5 H), 5.72 (s, 1H), 3.56 (s, 2H), 2.41 (d, 2H), 2.28 (t, 2H), 1.95 (m, 2H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 199.39, 159.99, 131.19, 129.07, 127.50, 127.37, 41.85, 37.27, 28.26, 22.60; HRMS calcd for $C_{13}H_{14}OS$ *m/e* 218.0765, found *m/e* 218.0769.

(ii) Ultrasound Promoted. PCC (0.412 g, 1.91 mmol) and SiO_2 (1 wt equiv or PCC) were ground to a fine powder, and half the mixture was added to a flask containing CH_2Cl_2 (5 mL). Ultrasound (maximum intensity) was initiated, and **3a** (0.141 g, 0.638 mmol) in CH_2Cl_2 (1 mL) was added which caused the orange solution to darken. After 0.5 h TLC analysis (9:1 pentane/EtOAc) indicated ~50% conversion, and the additional PCC–SiO_2 mixture was added. Sonication was continued (0.5 h), after which Et_2O (25 mL) was added and the reaction mixture was filtered as in the above procedure. Column chromatography resulted in **3a** (4.7 mg) and **4a** (100 mg, 73% or 75% based on recovered **3a**). Spectral data were identical with the above.

5,5-Dimethyl-3-[(phenylthio)methyl]-2-cyclopenten-1-one (4b, Table V). The above general oxidation procedure was followed which resulted in a colorless oil after column chromatography on silica gel (0.13 g, 83%; R_f 0.18; 9:1 pentane/EtOAc). An analytical sample was Kugelrohr distilled (bp 170–172 °C/4 mm): IR (neat) 1685 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.19 (m, 5H), 5.79 (s, 1H), 3.77 (d, 2H), 2.53 (t, 2H), 1.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.88, 172.86, 134.34, 130.89, 129.11, 129.00, 127.38, 46.52, 44.63, 36.52, 24.97; HRMS calcd for $C_{14}H_{16}OS$ *m/e* 232.0922, found *m/e* 232.0918.

6,6-Dimethyl-3-[(phenylthio)methyl]-2-cyclohexen-1-one (4c, Table V). The above general oxidation procedure was followed and provided a yellow tinted oil after column chromatography on silica gel (61.1 mg, 92%; R_f 0.35, 9:1 pentane/EtOAc). An analytical sample was Kugelrohr distilled (bp 173–174 °C/4 mm): IR (neat) 1665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.20 (m, 5 H), 5.65 (s, 1 H), 3.57 (s, 2H), 2.45 (t, 2H), 1.77 (t, 2H), 0.996 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.16, 157.66, 131.18, 129.04, 127.32, 126.15, 41.60, 40.49, 25.63, 23.98; HRMS calcd for $C_{15}H_{18}OS$ *m/e* 246.1078, found *m/e* 246.1079.

3-[(Phenylthio)methyl]-2-cyclohepten-1-one (4d, Table V). The above general oxidation procedure was followed to give a yellow tinted oil after purification by silica gel column chromatography (0.42 g, 82%; R_f 0.20, 9:1 pentane/EtOAc). An analytical sample was Kugelrohr distilled (bp 188–190 °C/4 mm): IR (neat) 1655 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.19 (m, 5H), 5.76 (s, 1H), 3.58 (s, 2H), 2.54 (t, 2H), 2.48 (t, 2H), 1.79 (m, 2H), 1.70 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$ δ 203.58, 154.94, 133.55, 131.27, 131.20, 129.01, 127.27, 45.09, 42.10, 31.48, 25.25, 21.18; HRMS calcd for $C_{14}H_{16}OS$ *m/e* 232.0922, found *m/e* 232.0924.

Preparation of 3-[(Phenylsulfonyl)methyl]-2-cyclohexen-1-one (5). To a stirred, cooled (0 °C) solution of **4a** (22.9 mg, 0.105 mmol) in freshly distilled CH_2Cl_3 (2 mL) was added 50% *m*-CPBA (72.4 mg, 0.420 mmol). After 1 h, TLC analysis indicated the formation of **5** (R_f 0.35, 1:1 pentane/EtOAc). The reaction mixture was then washed with 5% aqueous sodium bicarbonate (3 × 10 mL) and brine (10 mL) and then dried (Na_2SO_4). Removal of the drying agent and solvent resulted in a crude crystalline solid that was further purified by column chromatography affording pure white crystals (26.2 mg, 99%). NMR (^1H, ^{13}C) and IR characteristics were the same as those reported in the literature[29b] and identical to those found for **5** derived from prolonged oxidation of **3a**.

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Supplementary Material Available: ^1H NMR spectra of compounds **1c**, **1d**, **3a–d**, **2b**, **2c**, and **4b–d** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.