JOC*Note*

Concerning the Efficient Conversion of Epoxy Alcohols into Epoxy Ketones Using Dioxiranes

Lucia D'Accolti,[†] Caterina Fusco,[‡] Cosimo Annese,[†] Maria R. Rella,[§] Joanna S. Turteltaub,[§] Paul G. Williard,[*,§] and Ruggero Curci[*,†,§]

Dipartimento Chimica, Università di Bari, CNR—ICCOM, v. Amendola 173, I-70126 Bari, Italy, and Department of Chemistry, Brown University, Providence, Rhode Island 02912

csmirc17@area.ba.cnr.it

Received July 13, 2004

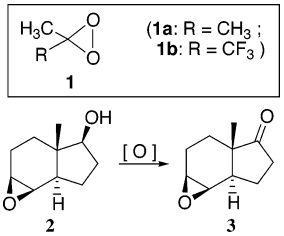
Abstract: Representative epoxy alcohols are cleanly converted into the corresponding epoxy ketones in high yield by selective oxidation using dimethyldioxirane (**1a**) and its trifluoro analogue (**1b**) under mild conditions. The oxidation is found to take place leaving the configuration at the epoxy functionality unaffected. The direct oxyfunctionalization of simple cyclic epoxides with the powerful dioxirane **1b** provides another attractive method to access epoxy ketones regioselectively.

During the past decade, applications in synthesis of the currently popular dimethyldioxirane (**1a**) (DMD)[1] and of methyl(trifluoromethyl)dioxirane (**1b**) (TFD)[2] as effective oxidants have proliferated to access valuable synthons.[3]

Racemic and optically active epoxy ketones count among the most versatile building blocks in organic synthesis.[4] Indeed, both the ketone and epoxide moieties can be further functionalized to provide interesting intermediates, useful for the synthesis of natural and biologically active products.[4]

Epoxy alcohols represent attractive precursors of epoxy ketones since they are readily available by epoxidation of the corresponding unsaturated compounds.[5−7] In fact, the stereoselective synthesis of α,β-epoxy and β,γ-epoxy alcohols via diastereoselective epoxidation of the corresponding allylic- or homoallylic alcohols has been the subject of extensive studies.[5−7] Thus, the search for efficient oxidants that allow this transformation with high selectivity and yields represents a significant goal, and especially so in multistep synthetic sequences. For instance, one of us (P.G.W.), long actively engaged in the convergent synthesis[8] of active 1α,25-dihydroxyvitamin D_3 analogues,[9] was faced with the goal of carrying out the transformation of the CD-ring epoxy alcohol **2** into the corresponding carbonyl **3** (Chart 1) in the highest yield achievable.

CHART 1



For this transformation, one obvious choice is to employ the classic metal-based oxidants.[5−7] In fact, the most efficient method reported to-date involves using pyridinium dichromate (PDC) in CH_2Cl_2, affording **3** in 65% yield.[10] In our hands other transition-metal oxidants tried were found to give distinctly inferior yields. For instance, stoichiometric RuO_4 (prepared from RuO_2 and $NaIO_4$)[5e] provided **3** in 28% yield only; additional complications in using RuO_4 derived from its toxicity and difficulties in handling. Application of the established Dess−Martin periodinane oxidant[11] afforded the target epoxy ketone in 53% yield. Alternatively, one may seek to use other mild nonmetal organic oxidants that mediate efficient homogeneous oxidations without the need of metal complexes.[12] Indeed, one major benefit of metal-free

* Corresponding author: Fax: +39-080-5442924. Phone: +39-080-5442070.

† Università di Bari.

‡ CNR—Istituto di Chimica dei Composti Organometallici (ICCOM), Bari Section, Italy.

§ Brown University.

(1) (a) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. (b) Cassidei, L.; Fiorentino, M.; Mello, R.; Sciacovelli, O.; Curci, R. *J. Org. Chem*. **1987**, *52*, 699. (c) Murray, R. W.; Singh, M. *Org. Synth.* **1996**, *74*, 91.

(2) (a) Mello, R.; Fiorentino, M.; Sciacovelli, O.; Curci, R. *J. Org. Chem*. **1988**, *53*, 3890. (b) Mello, R.; Fiorentino, M.; Fusco, C.; Curci, R. *J. Am. Chem. Soc.* **1989**, *111*, 6749. (c) D'Accolti, L.; Fusco, C.; Rella, M. R.; Curci, R. *Synth. Commun.* **2003**, *33*, 3009.

(3) For reviews, see: (a) Curci, R.; Dinoi, A.; Rubino, M. F. *Pure Appl. Chem.* **1995**, *67*, 811. (b) Adam, W.; Hadjiarapoglou, L. P.; Curci, R.; Mello, R. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, 1992; Chapter 4, pp 195−219. (c) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT, 1990; Vol 2, Chapter I, pp 1−59. (d) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (e) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205. (f) Denmark, S. E.; Wu, Z. *Synlett* **1999**, *S1*, 847.

(4) For a review, see: Lauret, C. *Tetrahedron: Asymmetry* **2001**, *12*, 2359 and references therein.

(5) (a) Tanaka, S.; Yamamoto, H.; Nozaki, H.; Sharpless, K. B.; Michaelson, R. C.; Cutting, J. D. *J. Am. Chem. Soc.* **1974**, *96*, 5254. (b) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, 12, 63. (c) Takai, K.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1980**, *21*, 1657. (d) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5976. (e) Nakata, H. *Tetrahedron* **1963**, *19*, 1959.

(6) (a) Prat, D.; Delpech, B.; Lett, P. *Tetrahedron Lett.* **1986**, 27, 711. (b) Adam, W.; Smerz, A. K. *Tetrahedron* **1995**, *51*, 13039. (c) Adam, W.; Mitchell, C. M. Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 3699. (d) Adam, W.; Stegmann, V. R.; Saha-Möller, C. R. *J. Am. Chem. Soc.* **1999**, *121*, 1879.

(7) (a) Adam, W.; Alsters, P. L.; Neumann, R.; Saha-Möller, C. R.; Sloboda-Rozner, D.; Zhang, R. *J. Org. Chem.* **2003**, *68*, 1721. (b) Adam, W.; Wirth, T. *Acc. Chem. Res*. **1999**, *32*, 703 and references therein.

(8) (a) Zhu G. D.; Okamura, W. H. *Chem Rev.* **1995**, *95,* 1877. (b) Dai, H.; Posner, G. H. *Synthesis* **1994**, 1383. (c) Lythgoe, B. *Chem. Soc. Rev.* **1981**, *10*, 449. (d) Baggiolini E. G.; Jacobelli, J A.; Hennessy, B. M.; Batcho, A. D.; Sereno, J. F.; Uskokovic, M. R. *J Org. Chem.* **1986**, *51,* 3098. (e) Uskokovic, M. R.; Studzinski, G. P.; Gardner, J. P.; Reddy, S. G.; Campbell, M. J.; Koeffler, H. P. *Curr. Pharm. Des.* **1997**, *3,* 99. (f) Bouillon, R.; Okamura, W. H.; Norman, A. W. *Endocr. Rev.* **1995**, *16,* 200.

(9) Nancy E. Lee, N. E.; Reddy, G. S.; Brown, A. J.; Williard, P. G. *Biochemistry* **1997**, *36*, 9429. See also previous articles of the series.

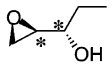
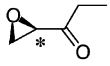
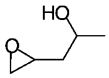
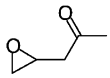
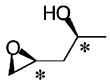
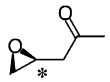
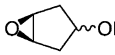
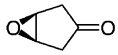
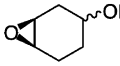
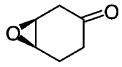
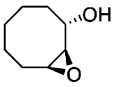
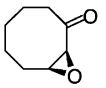
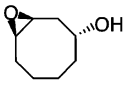
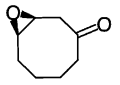
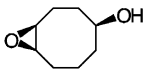
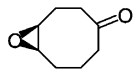
(10) Daniewski, A. R.; Kiegiel, J. *J. Org. Chem.* **1988**, *53,* 5534.

(11) (a) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155. (b) Hudlicky, M. *Oxidations in Organic Chemistry; ACS Monograph 186*; American Chemical Society: Washington, DC, 1990. See also references therein.

(12) Adam, W.; Saha-Möller, C. R.; Ganeshpure, P. A. *Chem. Rev.* **2001**, *101*, 3499 and references therein.

10.1021/jo048816w CCC: $27.50
Published on Web 10/26/2004

TABLE 1. Selective Oxidation of Epoxy Alcohols into Epoxy Ketones Employing Dimethyldioxrane or Methyl(trifluoromethyl)Dioxirane[a]

Entry	Substrate	Dioxi-rane	Ox/Sub Ratio[b]	Reactn time	Convn (%)[c]	Product	Yield (%)[d]
1	Epoxy alcohol **2** (*op* 98%)[e]	**1a**	1.5	2.5 h	>98	Epoxy ketone **3** (*ee* > 98%)[f]	>98
		1b	1.1	15 min	>98		>98
2	 **4** (*ee* 96%)[g]	**1b**	1.1	15 min	96	 **5** (*ee* 96%)[g]	94[g]
3	 **6**	**1a**	1.5	6 h	96	 **7**	90
		1b	1.1	20 min	>98		94
4	 **6a** (*dr* 70:30)[h,i]	**1b**	1.1	20 min	>98	 **7a** (*ee* 40%)[j]	>90[h]
5	 **8** (*syn/anti* 60:40)[h]	**1a**	1.5	3 h	>98	 **9**	98
		1b	1.1	20 min	>98		98
	(*syn/anti* 60:40)[h]	**1b**	1.1	20 min	>98		98
6	 **10** (*syn/anti* 80:20)[h]	**1a**	1.6	3 h	90	 **11**	92
		1b	1.1	20 min	92		96
7	 **12**[k]	**1a**	1.4	3 h	95	 **13**	96
		1b	1.1	10 min	>98		96
8	 **14**[k]	**1a**	1.1	3h	96	 **15**	80
		1b	1.0	10 min	>98		88
9	 **16**[k]	**1a**	1.3	3 h	>98	 **17**	95
		1b	1.1	10 min	>98		96

[a] Unless noted otherwise, all reactions were routinely run at 0 °C; solvent composition was ca. 10:1 CH_2Cl_2/1,1,1-trifluoropropanone (TFP) for oxidations with **1b** and ca. 8:2 CH_2Cl_2/acetone for oxidations with **1a**. [b] Molar ratio of dioxirane oxidant to substrate. [c] As determined (±3%) by GC (ZB-1, 0.25 μm film thickness, 30 m × 0.25 mm i.d., capillary column), Freon A112 internal standard. [d] Isolated yield (±5%). [e] $[\alpha]_D$ +24.3° (*c* 1.6, $CHCl_3$) [lit.[11] $[\alpha]_D$ +24.8° (*c* 1.4, $CHCl_3$)]. [f] Enantiomeric excess determined by chiral stationary phase GC (Astec, Beta-DM); $[\alpha]_D$ +42.1° (*c* 0.9, $CHCl_3$) [lit.[11] $[\alpha]_D$ +42.7° (*c* 1.0, $CHCl_3$)]. [g] Ref 13. [h] As determined by GC and integrated ^{1}H NMR spectra. [i] $[\alpha]_D$ +1.9° (*c* 1.1, $CHCl_3$); major diastereoisomer: (2*S*,4*S*)-4,5-epoxy-2-pentanol. [j] (4*S*)-4,5-Epoxy-2-pentanone; $[\alpha]_D$ −0.12° (*c* 4.2, $CHCl_3$); enantiomeric excess determined as in footnote f. [k] Racemic mixture 50:50.

organic oxidants consists of their better environmental acceptance with respect to transition-metal catalysts. Actually, in recent years several nonmetal organic oxidants have been introduced that were widely employed in selective oxidations.[12] Among them the dioxiranes **1** rank high because of their remarkable efficiency, superior versatility, and ease of operations. These nonmetal electrophilic oxygen-transfer agents are easily prepared from suitable ketones and the low-cost potassium peroxymonosulfate $KHSO_5$ (Oxone, Caroate) under buffered conditions (pH 7−7.5). Reactions performed with dioxiranes **1** in isolated form (as solutions in the parent ketones)[1−4] appear to be best suited for stoichiometric oxidations *under strictly neutral conditions* of numerous acid- or base-sensitive substrates, as well as of hydrolytically labile oxyfunctionalized products.[4] Ensuing our pioneering studies on dioxirane oxidations of alcohols,[13] this class of novel oxidants has been widely employed for the conversion of alcohols into carbonyls;[12] however, their application in the selective oxidation of epoxy alcohols appears to have been only marginally explored.[13] We present herein our data concerning the utilization of dioxiranes for the selective oxidation of representative epoxy alcohols under mild conditions. Typical results and reaction conditions are collected in Table 1.

Tricyclic **2** and several open-chain and cyclic epoxy alcohols were screened as starting materials; they were obtained by following published procedures. The Vitamin D_3 CD-synthon **2** was prepared starting with Hajos dione.[14] The β-epoxy alcohols **8**, **10**, and **14** were easily obtained by DMD epoxidation of the corresponding

(13) Mello, R.; Cassidei, L.; Fiorentino, M.; Fusco, C.; Hümmer, W.; Jäger, V.; Curci, R. *J. Am. Chem. Soc.* **1991**, *113*, 2205.

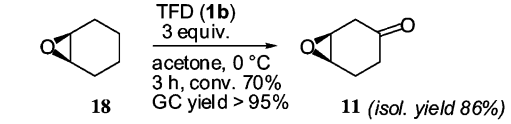
homoallylic alcohols.[15] The latter in turn were prepared starting with the corresponding 1,3-dienes upon selective monoepoxidation using DMD, followed by reductive epoxide ring cleavage ($LiAlH_4/Et_2O$). By the same procedure, the bicyclic *syn*-γ-epoxy alcohol **16** could be synthesized starting with 1,5-cyclooctadiene. Allylic bromination (NBS) of *cis*-cyclooctene, followed by hydrolysis (H_2O, $NaHCO_3$) and DMD epoxidation, afforded *anti*-epoxy alcohol **12** in >95% overall yield.

DMD (**1a**) and TFD (**1b**) solutions that were 0.08−0.1 M in acetone and 0.7−0.8 M in 1,1,1-trifluoropropanone (TFP), respectively, were prepared as already reported in detail.[1−3] The simple oxidation procedure involved the addition of an aliquot (usually from 0.5 to 25 mL) of standardized cold solution of **1a** or of **1b** to a stirred solution of the epoxy alcohol (15−500 mg) in CH_2Cl_2 or acetone (10−30 mL). The reactions were monitored by GC, GC/MS, and/or TLC, and product isolation simply entailed removal of solvent in vacuo; yields of isolated product were >90% in most of the cases (Table 1). The epoxy ketone products were identified by ^1H and ^{13}C NMR, FTIR, and mass spectrometry in comparison with literature data.

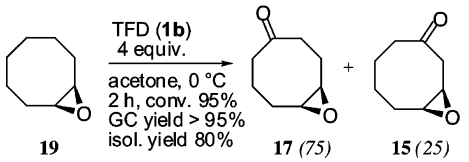
Data in Table 1 reveal that both dioxiranes **1a** and **1b** can be successfully applied to carry out the transformation at hand. In fact, both open-chain and cyclic epoxy alcohols could be neatly transformed into the corresponding epoxy ketones with high conversions and yields using just 1.1−1.6 equiv of the oxidant. However, reaction times were much shorter (cf. entries 3−9) using the powerful methyl(trifluoromethyl)dioxirane (**1b**). In all of the cases examined, complete chemoselectivity is achieved in that just the alcohol functionality is oxidized while the epoxide moiety remains untouched. Also, the conversion of optically active substrates (entries 1, 2, and 4) into epoxy ketones occurs selectively, leaving the configuration at the chiral center(s) at the oxirane ring practically unaffected.

On the basis of kinetic data and the application of reaction probes already reported,[13] the selectivities monitored herein should be ascribed to a substantially concerted O-insertion by the dioxirane into the C−H bond "α" to the OH functionality generating a *gem*-diol $C(OH)_2$, hence the carbonyl. Be the mechanistic details as they may, the results above suggest that dioxirane oxidation of epoxy alcohols provides a simple, mild, and efficient method to access epoxy ketones useful in synthesis.

As a corollary to this feat, it is worthy of notice that our initial survey points out that certain epoxy ketones might become available by the direct oxyfunctionalization of the corresponding epoxides. The powerful methyl(trifluoromethyl)dioxirane (**1b**) should be the reagent of choice for carrying out these difficult transformations amounting to O-insertion into "unactivated" C−H bonds.[3] The examples provided by the oxyfunctionalization of cyclohexene oxide **18** and of cyclooctene oxide **19** serve to call attention to this alternate route. The oxidations were carried out employing excess TFD (**1b**) at the conditions shown in eqs 1 and 2.



(1)



(2)

It is seen that in both cases the oxirane moiety again remains intact; furthermore, remarkable regioselectivity is attained. In fact, oxidation of epoxide **18** results in β-epoxy ketone **11** in high yield. In the oxidation of cyclooctene oxide **19**, the β-epoxy ketone **15** is accompanied by the γ-epoxy ketone as the major product. In both cases, oxidation at the methylene CH_2 α to the epoxide ring is practically bypassed. Thus, opposite to what was found with the cyclopropyl moiety in similar systems, the oxiranyl ring produces a *deactivating* effect on proximal α-CH_2 toward dioxirane oxidations.[16] This may be ascribed to the electron-withdrawing effect exercised by the oxirane oxygen on the electron density at proximal C−H bonds submitted to electrophilic O-insertions by the dioxirane.[3,16] However, the marked prevalence for oxyfunctionalization at CH_2 in the γ-position (δ with respect to the oxirane oxygen) recorded in the oxidation of the larger ring bicyclic epoxide **19** suggests that complex stereochemical and/or stereoelectronic factors come into play. This is also advocated by a recent study wherein high regioselectivity at the remote bridgehead C7−H and C5−H was reported for the TFD oxyfunctionalization of the structurally rigid methyleneadamantane oxide.[17] The scenario might bear some resemblance to the regioselectivities observed in TFD oxyfunctionalization at distant C−H bonds of open-chain or cyclic compounds bearing electron-withdrawing functionalities such as benzoate or benzenesulfonic esters.[18] In that case, hyperconjugative and steric interactions were invoked in order to rationalize the results.[18] Clearly, precise mechanistic studies are in order to unravel the subtle effects leading to remote oxyfunctionalization here.

Results reported herein show promise of practical value in organic synthesis because of the efficiency and simplicity. It constitutes yet another useful entry into either structurally simple or complex epoxy ketones that are important building blocks in the synthesis of natural products and fine chemicals.

Experimental Section

The following procedures are representative for oxidations of substrates herein using dioxiranes.

(14) (a) Hajos, Z. G., Parish, D. R. *Organic Synthesis*; Wiley: New York, 1990; Collect. Vol. VII, p 363. (b) Röhrig, S.; Hennig, L.; Findeisen, M.; Welzel, P.; Müller, D. *Tetrahedron* **1998**, *54*, 3439.

(15) For instance, see: (a) D'Accolti, L.; Fiorentino, M.; Fusco, C.; Rosa, A. M.; Curci, R. *Tetrahedron Lett*. **1999**, *40*, 8023. (b) Adam, W.; Mitchell, C. M.; Saha-Möller, C. R. *J. Org. Chem.* **1999**, *64*, 3699 and references therein.

(16) (a) D'Accolti, L.; Dinoi, A.; Fusco, C.; Russo, A.; Curci, R. *J. Org. Chem.* **2003**, *68*, 7806. (b) D'Accolti, L.; Fusco, C.; Lucchini, V.; Carpenter, G. B.; Curci, R. *J. Org. Chem.* **2001**, *66*, 9063 and references therein.

(17) D'Accolti, L.; Kang, P.; Khan, S.; Curci, R.; Foote, C. S. *Tetrahedron Lett*. **2002**, *43*, 4649.

(18) Asensio, G.; Castellano, G.; Mello, R.; Gonzalèz-Nuñez, M. E. *J. Org. Chem.* **1996**, *61*, 5564.

Oxidation of (1*S*,3*aR*,4*R*,5*S*,7*aS*)-4,5-Epoxy-7a-methyloctahydro-1*H*-inden-1-ol (2) with Dimethyldioxirane (1a). A standardized solution of DMD (**1a**) in acetone (1.8 mL, 0.07 M, 0.12 mmol) was added in one portion to a stirred solution of the epoxy alcohol (**2**) (14 mg, 0.083 mmol) in acetone (0.6 mL) at 20 °C. The reaction progress was monitored by TLC. After 2.5 h of reaction time (conversion = 98%), removal of the volatile solvent in vacuo afforded >98% pure (GC) **(3a*R*,4*R*,5*S*,7a*S*)-4,5-Epoxy-7a-methyloctahydro-1*H*-inden-1-one (3)** (13 mg, 0.078 mmol, yield 98%): oil, $[\alpha]_D = +42.1°$ (*c* 0.9, $CHCl_3$), practically identical with reported literature data;[10] GC/MS (70 eV) *m/z* (r.i.) 166 (M^+), 151 ($M^+ - 15$, 0.9), 123 (16), 110 (19), 95 (47), 67 (48), 42 (42), 41 (100); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 218.5 (C=O), 55.5 (C−O), 50.6 (C−O), 47.4, 44.7, 35.4, 27.0, 24.5, 21.8 (CH_2), 15.1 (CH_3); FTIR and ^1H NMR in excellent agreement with literature.[10]

Oxidation of (2*S*,4*S*)-4,5-Epoxy-2-pentanol (6a) with Methyl(trifluoromethyl)dioxirane (1b). To a stirred solution of **6a** (500 mg, 4.9 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added a solution of **1b** in 1,1,1-trifluoropropanone (TFP) (9 mL, 0.65 M, 5.8 mmol) in one portion. The reaction was monitored by GC (Freon A112 internal standard). After 20 min (conversion = 98%), removal of solvent in vacuo afforded pure (>99%, GC) ***(4S)*-4,5-epoxy-2-pentanone** (**7a**) (440 mg, 4.41 mmol, yield 90%): colorless liquid, bp 83−85°C; $[\alpha]_D = -0.12°$ (*c* 4.2, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ 3.25 (m, 1H), 2.85 (m, 2H, $J_1 = 5$, $J_2 = 4$ Hz), 2.50 (m, 2H, $J = 5$ Hz), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.0 (C=O), 47.5 (C−O), 46.5 (C−O), 46.5 (CH_2), 30.3 (CH_3); IR (neat) 3057, 3003, 2927, 1714 (C=O), 1425, 1398, 1362, 1262, 1169, 931, 859 cm^{-1}; GC/MS (70 eV) *m/z* (r.i.) 100 (M^+), 85 ($M^+ - 15$, 0.2), 71 (0.3), 58 (4), 57 (5), 55 (1), 44 (3), 43 (100); HRMS calcd for $C_5H_8O_2$ 100.052430, found 100.052374. Using chiral column GC (100 °C, 1.1 mL/min, He c.g.; Astec β-DM column, 30 m × 0.25 mm i.d., 0.25 μm film thickness), the ee was determined to be 40%.

Oxidation of *cis*-Cyclooctene Oxide (19) with Methyl(trifluoromethyl)dioxirane (1b). To a stirred solution of substrate (493 mg, 3.91 mmol) in acetone (20 mL) kept at 0 °C was added a standardized solution of dioxirane **1b** in TFP (25 mL,0.65 M, 16 mmol) in one portion. The reaction was monitored by GC and GC/MS. After 2 h (conversion = 70%), removal of the solvent in vacuo and subambient (2−5 °C) column chromatography (silanized SiO_2) afforded pure (>98%, GC) **9-oxa-bicyclo[6.1.0]nonan-4-one (17)**[19,20] (383 mg, 274 mmol, yield 70%; colorless solid, mp 78−80 °C, [lit.[21] 78−80 °C]; spectral data in agreement with literature[19,21]) and byproduct **9-oxa-bicyclo-[6.1.0]nonan-3-one (15)** (54 mg, 0.39 mmol, yield 10%; colorless solid, mp 65−68 °C [lit.[22] 67−68 °C]; spectral data identical with literature[21,22]).

Acknowledgment. Partial support of this work by the Ministry of University and Scientific and Research of Italy (COFIN National Project) and the National Research Council of Italy (CNR) is gratefully acknowledged. The work at Brown University was supported in part by PHS Grant GM-35982 and NSF Grant 0213381 to P.G.W.

Supporting Information Available: Experimental details and supplemental characterization data for substrates and products and chiral-column GC data for the determination of the enantiomeric excess of the epoxy ketone **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048816W

(19) Meier, H.; Mayer, W.; Kolshorn, H. *Chem. Ber.* **1987**, *120*, 685.
(20) Crandall, J. K.; Arrington, J. P.; Mayer, C. F. *J. Org. Chem.* **1971**, *36*, 1428.
(21) Carless, H.; Atkins, R.; Fekarurhobo, J. K. *Tetrahedron Lett.* **1985**, *26*, 803.
(22) Mayer, W.; Meier, H. *Chem. Ber.* **1989**, *122*, 509.