

Selenium Dioxide Oxidation of Endocyclic Olefins. Evidence for a Dissociation-Recombination Pathway

M. A. Warpehoski, B. Chabaud, and K. B. Sharpless*†

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and
Department of Chemistry, Stanford University, Stanford, California 94305

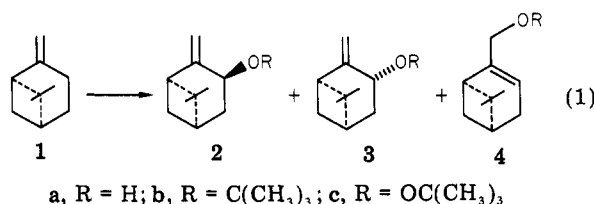
Received February 2, 1982

The selenium-catalyzed oxidation of some simple alicyclic olefins with *tert*-butyl hydroperoxide produced, in addition to the expected allylic alcohols, allylic *tert*-butyl peroxides and allylic *tert*-butyl ethers. Unlike the peroxides, the ether products were not inhibited by hydroquinone, and their relative amounts increased with decreasing ring size. Analogous products were detected in minor amounts in the selenium dioxide-*tert*-butyl hydroperoxide oxidation of β -pinene, with isomer distributions suggestive of a symmetrical intermediate. It is proposed that the ether products arise via a dissociation-recombination pathway competitive with the [2,3] sigmatropic shift leading to the alcohol. Examination of the literature suggests that such a pathway may also be significant in selenium dioxide oxidations of small ring compounds in which ring oxidation occurs and may lead to unexpected products in which the double bond has moved from its original position.

Selenium dioxide displays a unique mode of interaction with olefins, involving an initial ene reaction followed by a [2,3] sigmatropic rearrangement (Scheme I).¹ The utility of this reagent as a selective allylic oxidant has been amplified^{2,3} by the discovery that the cooxidant *tert*-butyl hydroperoxide effectively prevents interference by reduced selenium species.⁴

We have already brought attention to one important limitation of the scope of this reaction,⁵ which we herein describe in detail: endocyclic olefins give significant amounts of allylic *tert*-butyl ethers and peroxides when oxidation occurs in the ring.

We have detected minor amounts (2–12%, depending on reaction conditions) of mixtures of the allylic *tert*-butyl ethers and peroxides **2b**, **3b**, **4b**, **2c**, and **4c** (approximate relative amounts 1:1:3:1:1) from the selenium-catalyzed oxidation of β -pinene with *tert*-butyl hydroperoxide (eq 1;^{4b} structures are based on proton NMR and GC-MS



data; see Table II for details). Indeed, nearly all of the olefin substrates which we have examined gave rise to trace (usually <5%) amounts of very nonpolar side products, easily separated from the desired allylic alcohols by chromatography, which we believe to be the analogous allylic ethers and peroxides.

For endocyclic olefins in small rings, however, these side products predominated over normal allylic oxidation products. The yields and product distributions obtained for several endocyclic systems are summarized in Table I.

For cyclohexene, the major products were the allylic *tert*-butyl ether **5b** and the *tert*-butyl peroxide **5c**. As the ring size increased the yields of allylic alcohols increased and those of the ethers and peroxides decreased. When the oxidations were carried out in the presence of hydroquinone the allylic *tert*-butyl peroxides were not observed, although the yields of alcohols and ethers remained unaffected.

The peroxide products, based on the above observation, appear to arise from a radical-chain mechanism. This is

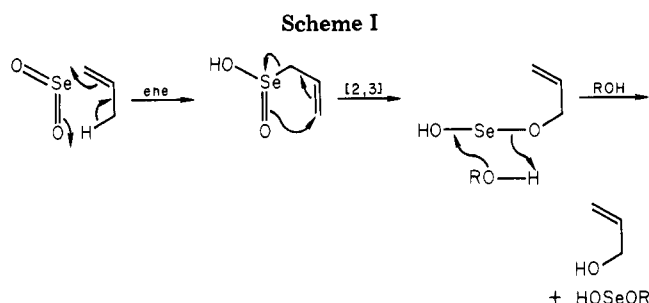
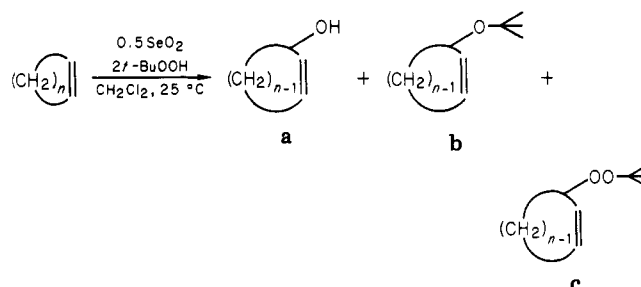


Table I. Product Distributions in Endocyclic Oxidation



olefin	total yield, %	rel ratios		
		a	b	c
5 (n = 4)	39	20	31	49
6 (n = 6)	68	42	25	33
7 (n = 10)	72 ^a	62 ^b	7	24

^a A small amount of the α,β -unsaturated ketone (7% relative yield) was isolated from this reaction. ^b The ratio of *E/Z* allylic alcohol was ca. 80:20 starting with either (*E*)- or (*Z*)-cyclododecene.

not surprising, since seleninic acids are known to induce the radical-chain decomposition of *tert*-butyl hydroperoxide.⁶ Incorporation of a radical inhibitor can circumvent

(1) (a) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **94**, 7154 (1972); (b) D. Arigoni, A. Vasella, K. B. Sharpless, and H. P. Jensen, *J. Am. Chem. Soc.*, **95**, 7917 (1973); (c) L. M. Stephenson and D. R. Speth, *J. Org. Chem.*, **44**, 4683 (1979).

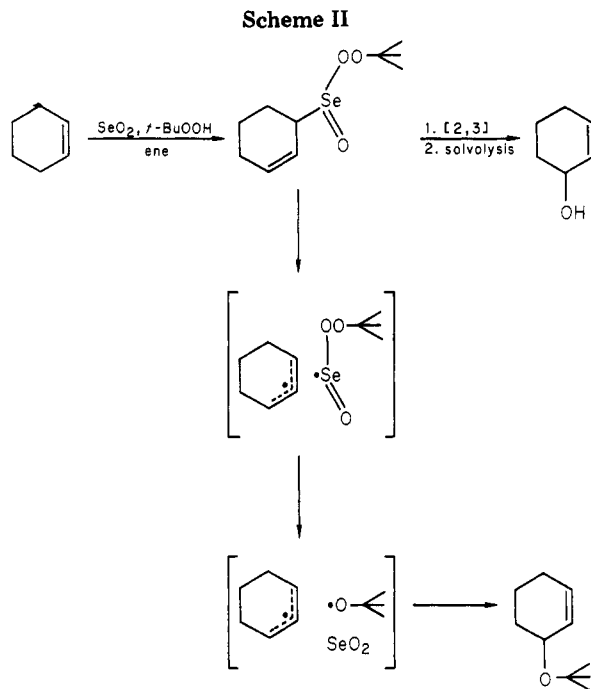
(2) (a) H. E. Paaren, H. F. DeLuca, and H. K. Schnoes, *J. Org. Chem.*, **45**, 3253 (1980); (b) B. Snider and J. V. Duncia, *J. Org. Chem.*, **45**, 3461 (1980); (c) F. W. Sum and L. Weiler, *J. Am. Chem. Soc.*, **101**, 4401 (1979); (d) T. Matsumoto, S. Imai, and S. Yuki, *Bull. Chem. Soc. Jpn.*, **54**, 1448 (1981); (e) M. Haruna and K. Ito, *J. Chem. Soc., Chem. Commun.*, 483 (1981). (f) M. L. Greenlee, *J. Am. Chem. Soc.*, **103**, 2425 (1981).

(3) B. Chabaud and K. B. Sharpless, *J. Org. Chem.*, **44**, 4202 (1979).

(4) (a) M. A. Umbreit (Warpehoski) and K. B. Sharpless, *J. Am. Chem. Soc.*, **99**, 5526 (1977); (b) M. A. Umbreit (Warpehoski), Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1977.

(5) K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **12**, 63 (1979).

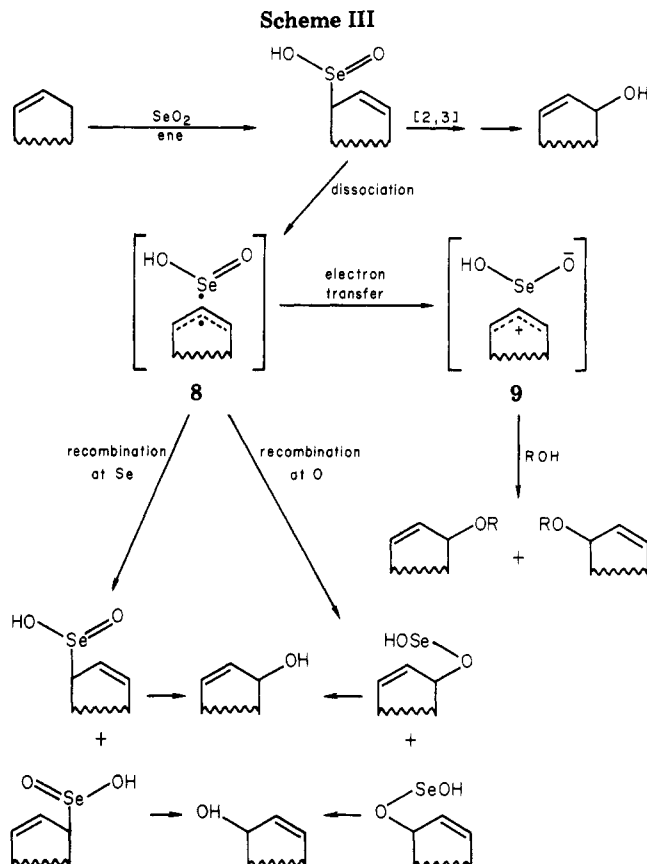
†Massachusetts Institute of Technology.



this pathway for synthetic purposes.

We propose that the allylic ether products, on the other hand, are formed in a dissociation-recombination pathway (Scheme II). There is ample precedent for a competing, higher energy caged radical dissociation-recombination route in numerous other [2,3] sigmatropic and related rearrangements.⁷ Homolysis of the C-Se bond of the peroxy seleninic ester intermediate, followed by a second homolysis ejecting SeO_2 , would produce the allylic *tert*-butyl ether upon radical recombination within the solvent cage. For unsymmetrical olefins, of course, isomeric mixtures of these ethers would be obtained (eq 1).

It has been demonstrated that allylic oxidation with selenium dioxide gives rise to preponderantly *E*-allylic alcohols, regardless of olefin geometry.^{1c,8} This stereoselectivity appears to result from unfavorable steric interactions in the transition state for the [2,3] sigmatropic reaction leading to the *Z* products.^{9,10} For endocyclic olefins in small rings, however, the ring-oxidized product is necessarily the *Z*-allylic alcohol. It is reasonable that a higher energy dissociation pathway can compete more effectively with the less favorable concerted process. As the ring size increases to cyclododecene, these constraints on the transition state are reduced. Thus the preponderant stereoisomer of **7a** was the *E*-allylic alcohol, and, correspondingly, the yield of **7b** (Table I) approached the amounts of nonpolar side products commonly observed in the selenium-catalyzed oxidation of acyclic or exocyclic olefins.



The recognition of a dissociation pathway competitive with the [2,3] sigmatropic rearrangement, particularly for small ring endocyclic oxidations, is, in principle, applicable to the reaction of selenium dioxide with olefins even in the absence of *tert*-butyl hydroperoxide.

Scheme III illustrates the probable course and consequences of this pathway. Following homolytic dissociation of the seleninic acid to form the caged radical pair **8**, several avenues could lead to rearranged allylic oxidation products. Whether recombination could occur at selenium to form a selenenic acid, or at oxygen to form a selenenic acid (thus bypassing a [2,3] sigmatropic rearrangement), scrambling of the original allylic position would result in an isomeric mixture of alcohol products. Furthermore, in polar solvents an electron-transfer process might be expected to intervene, forming the ion pair **9**, which could not only recombine but also react with solvent to give a mixture of solvolysis products (e.g., allylic ethers in alcoholic solvents).

Several apparent contradictions in the literature on selenium dioxide reactions can be resolved by this hypothesis. Positional isomerization of the double bond does not occur for acyclic tri- or disubstituted olefins under neutral conditions.¹¹ In contrast, the oxidation of optically active carvomenthene to carvotanacetol in aqueous dioxane proceeded with 42% racemization, equivalent to 21% rearrangement of the double bond.¹² The dissociative

(6) D. T. Woodbridge, *J. Chem. Soc. B*, 50 (1966).

(7) (a) J. E. Baldwin and R. E. Hackler, *J. Am. Chem. Soc.*, **91**, 3646 (1969); (b) J. E. Baldwin, J. O. DeBernardis, and J. E. Patrick, *Tetrahedron Lett.*, 353 (1970); (c) V. Rautenstrauch, *J. Chem. Soc., Chem. Commun.*, 4 (1970); (d) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *J. Chem. Soc., Chem. Commun.*, 576 (1970); (e) J. E. Baldwin and J. E. Patrick, *J. Am. Chem. Soc.*, **93**, 3556 (1971).

(8) (a) U. T. Bhalarao and H. Rapoport, *J. Am. Chem. Soc.*, **93**, 4835 (1971); (b) Oxidation of either (*Z*)- or (*E*)-5-decene with SeO_2 and *tert*-butyl hydroperoxide gave the *E*-allylic alcohol almost exclusively (*E/Z* = 97:3). This was verified by comparison of the product with authentic *Z*-allylic alcohol prepared by reduction of the alkynol with Lindlar catalyst. (B. Chabaud and K. B. Sharpless, unpublished results.)

(9) R. F. Lauer, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1974.

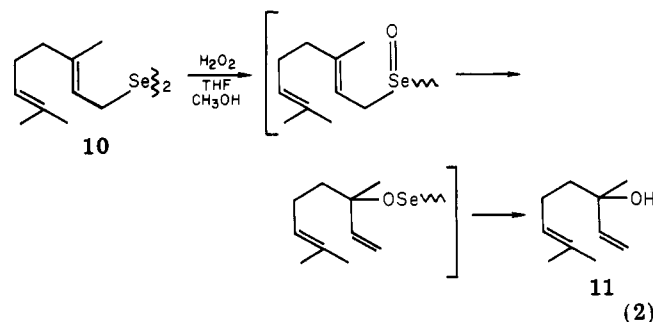
(10) V. Rautenstrauch, *J. Chem. Soc., Chem. Commun.*, 526 (1970).

(11) For a recent comprehensive review of selenium dioxide oxidations illustrating this and other modes of the reaction specificity, see N. Rabjohn, *Org. React.*, **24**, 261 (1977). In the oxidation of 5-decene to 5-decen-4-ol, we have specifically looked for the presence of the rearranged isomer, 6-decen-5-ol, and demonstrated its absence in the selenium dioxide products by an independent synthesis (B. Chabaud and K. B. Sharpless, unpublished results). We have observed that even rearrangement of terminal double bonds, often stated as one of Guillemonat's rules, does not occur in neutral solvents at lower temperatures.

(12) E. N. Trachtenberg and J. R. Carver, *J. Org. Chem.*, **35**, 1646 (1970).

pathway described in Scheme III provides a reasonable mechanism for the rearrangement observed in this cyclohexenyl system, and a rationale to distinguish it from acyclic systems.

A second point of contention in the literature concerns the mode of selenium ester heterolysis leading to the alcohol product. Cleavage at the Se-O bond rather than at the O-C bond (Scheme I) was supported by the identification of linalool 11 as the product of hydrogen peroxide oxidation of digeranyl diselenide 10 in anhydrous THF/methanol (eq 2). The methyl ether was not detected.⁹



However, it has been stated in the review literature that selenium dioxide oxidations carried out in anhydrous alcohol solvents give allylic ethers, resulting from reaction with the solvent, instead of allylic alcohols.¹³ Examination of the original literature cited showed that in every case of allylic ether formation, the substrate was an endocyclic olefin in a five- or six-membered ring.¹⁴ Furthermore, these products showed no stereo- or regioselectivity.^{14c} The dissociation pathway in Scheme III, encompassing the ion pair 9, readily accounts for these observations.

In summary, the competitive dissociation pathway poses a general limitation to the selectivity of selenium dioxide in endocyclic oxidations in small rings.¹⁹

Experimental Section

Selenium dioxide (ROC/RIC) was used as received. Olefins were passed through neutral alumina before use. *tert*-Butyl hydroperoxide (90%) was supplied by Aldrich⁵ and used as received. General procedures for carrying out and working up selenium-catalyzed allylic oxidations with *tert*-butyl hydroperoxide have been described.^{3,4a}

Oxidation of β -Pinene (1). β -Pinene (1, 0.5 mol) was oxidized with 7.4 mmol of SeO_2 and 0.675 mol of *tert*-butyl hydroperoxide in *tert*-butyl alcohol containing 0.5 mol of water, for 1 day at 25 °C. (These conditions maximized formation of the side products.) After a workup employing NaHSO_3 to reduce excess hydroperoxide, simple distillation gave 40 g of crude product. GLC (10% UCW-98 on 80/100 mesh Gas Chrom Q) indicated a 92% area ratio of *trans*-pinocarveol (2a) and two peaks corresponding to the nonpolar side products. Preparative TLC on silica gel (developed twice in hexanes) of a portion of this material afforded three nonpolar fractions, A (R_f 0.4, 34 mg), B (R_f 0.3, 82 mg), and C (R_f 0.2, 154 mg). The first fraction contained two components tentatively identified as the peroxide 2c and the ether 3b; the second contained a mixture consistent with structures 4c, 3b, 4b, and 2c; the third fraction was assigned as a mixture of the ethers 4b and 2b. These tentative assignments were based on comparison of the chemical shifts of the α -oxygen, olefinic, and *gem*-dimethyl protons to those of the parent alcohols 2a, 3a, and 4a. Table II lists the relevant shifts. GC-MS analysis (3% SP2250) of fraction B separated three components, the major peak having a parent

Table II. 60-MHz ^1H NMR Chemical Shifts of β -Pinene Oxidation Products and Parent Alcohols

assigned structure	δ^a		
	CH_2O	$=\text{CH}_n$	CH_3
2a	4.32	4.92, 4.72	0.63
2b ^b	4.20	4.80, 4.68	0.66
2c ^b	4.50	5.04, 4.84	0.68
3a	4.55	5.08, 4.70	0.76
3b ^{b,c}	4.20	4.95, 4.60	0.72
4a	3.85	5.40	0.84
4b ^b	3.63	5.37	0.83
4c ^b	4.17	5.45	0.82

^a In CCl_4 , relative to Me_4Si . ^b Tentative assignment, based on similarity to corresponding parent alcohol. ^c No evidence for the epimeric *cis tert*-butyl peroxide 3c was observed. Since the peroxide products were less abundant than the ether products, the small amount of 3c expected may have escaped detection or chromatographic recovery.

ion at m/e 208, consistent with a *tert*-butyl ether structure, and a base peak at m/e 152, consistent with the loss of isobutylene from the parent ion. (Loss of isobutylene was also a major fragmentation pathway for the more fully characterized allylic *tert*-butyl ether 5b; vide infra.) The minor components showed a highest m/e of 168 (loss of isobutylene from a *tert*-butyl peroxide) and 152 (loss of isobutylene from a *tert*-butyl ether), respectively. A mass spectrum of the major fraction C also showed the parent m/e 208 as well as m/e 152, consistent with the assignment of *tert*-butyl ether structures 4b and 2b. The IR spectra of the fractions were similar in most respects, exhibiting strong bands at 1390, 1365, and 1200 cm^{-1} characteristic of the *gem*-dimethyl and *tert*-butyl groups, and 890–900 cm^{-1} (*t*-BuO and *gem*-disubstituted olefin). Fractions B and C showed moderate CO stretching bands in the 1055–1088 cm^{-1} region, consistent with their substantial content of ether products, and fractions A and B showed a weak band at 840–845 cm^{-1} . Since at least in fraction A this band cannot arise from a trisubstituted olefin, it may be attributed to the OO vibration of aliphatic peroxides.

Oxidation of Cyclohexene (5). Cyclohexene (0.2 mol) was reacted with 0.1 mol of SeO_2 and 0.4 mol of *tert*-butyl hydroperoxide in CH_2Cl_2 at 25 °C for 34 h. The workup included dimethyl sulfide reduction of the excess hydroperoxide.^{4a} The crude product mixture (16.1 g) was distilled and a portion was separated by preparative TLC on silica gel (5% ether in pentane) into three components. The least polar product (R_f 0.4) was identified as 3-(*tert*-butylperoxy)-1-cyclohexene (5c): ^1H NMR (CCl_4 , Me_4Si) δ 5.74 (m, 2 H, $=\text{CH}$), 4.25 (m, 1 H, CHOR), 2.1–1.4 (m, 6 H), 1.2 (s, 9 H); IR (CCl_4) 3030 (m, olefinic CH), 1388 (m), 1366 (s), 1200 (s, *tert*-butyl) cm^{-1} ; mass spectrum (70 eV), m/e 170 (M^+), 97 ($\text{M}^+ - \text{C}_4\text{H}_9\text{O}$), 81 ($\text{M}^+ - \text{C}_4\text{H}_9\text{O}_2$) [lit.¹⁵ bp 35 °C (7 torr)].

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_2$: C, 70.55; H, 10.65. Found: C, 70.61; H, 10.52.

The second component (R_f 0.3) was 3-*tert*-butoxy-1-cyclohexene (5b): NMR (CCl_4) δ 5.55 (m, 2 H, $=\text{CH}$), 3.88 (br m, 1 H, CHOR), 1.4–2.0 (m, 6 H), 1.17 (s, 9 H); IR (CCl_4) 3030 (m, olefinic CH), 1388 (m), 1366 (s), 1200 (s, *tert*-butyl), 1070 (s, CO) cm^{-1} ; mass spectrum (70 eV), m/e 154 (M^+), 139 ($\text{M}^+ - \text{CH}_3$), 98 ($\text{M}^+ - \text{C}_4\text{H}_9$), 81 ($\text{M}^+ - \text{C}_4\text{H}_9\text{O}$, base peak). [lit.¹⁶ bp 63–63 °C (12 torr)].

Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$: C, 77.87; H, 11.76. Found: C, 77.88; H, 12.03.

The final component was identified as 2-cyclohexen-1-ol (5a) by spectral and chromatographic comparison to an authentic sample.

On the basis of the integration of the methine protons in the NMR of the distilled mixture, the ratio of 5a/5b/5c was about 2:3:5. Thus the distilled fraction (9.85 g) contained about 32 mmol of 5c, 20 mmol of 5b, and 14 mmol of 5a. When corrected for the fraction of the reaction mixture not subjected to distillation,

(13) E. N. Trachtenberg in "Oxidation Techniques and Application in Organic Synthesis", R. L. Augustine, Ed., Marcel Dekker, New York, 1969, pp 119–188.

(14) (a) K. Alder and G. Stern, *Justus Liebigs Ann. Chem.*, **504**, 205 (1933); (b) E. Urien, *C. R. Hebd. Seances Acad. Sci.*, **199**, 363 (1934); (c) J. P. Schaefer, B. Horvath, and H. P. Klein, *J. Org. Chem.*, **33**, 2647 (1968).

(15) (a) T. W. Campbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **73**, 1788 (1951). (b) M. S. Kharash, P. Pauson, and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

(16) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

this indicated a total recovery of 39%, based on initial moles of cyclohexene. The distillation was not carried to completion, however, since the presence of the peroxide was anticipated.

Small-scale experiments (2 mmol) carried out in the above manner with or without 0.1 mmol of hydroquinone showed, by GLC analysis (10% UCW-98 on 80-100-mesh Gas Chrom Q), that hydroquinone completely suppressed the formation of **5c**, but that the amount of **5b** was unchanged.

Oxidation of Cyclooctene (6). Cyclooctene (20 mmol) was reacted with 10 mmol of SeO_2 and 40 mmol of *tert*-butyl hydroperoxide in 40 mL of CH_2Cl_2 at 25 °C for 48 h. The aqueous Na_2CO_3 quench to remove SeO_2 was followed by reduction of the excess hydroperoxide with Na_2SO_3 .¹⁷ Standard workup and chromatography on silica gel (5% ethyl acetate in hexanes) gave 2-cycloocten-1-ol **6a**, identified by spectral comparison to authentic material,¹⁸ and a mixture of the ether **6b** and peroxide **6c**. A LiAlH_4 reduction of this mixture afforded, after hydrolysis, a mixture of **6a** and 3-*tert*-butoxy-1-cyclooctene (**6b**) from which the latter was obtained pure by chromatography: NMR (CCl_4) δ 5.5 (m, 2, olefinic H), 4.4 (br m, 1, CHOR), 1.15 (s, 9, *tert*-butyl); IR (CCl_4) 3020 (w, olefinic CH), 1200 (s) cm^{-1} . Medium-pressure chromatography (Merck LiChroprep Si-60) on the mixture of the nonpolar products afforded a sample of pure 3-(*tert*-butylper-

oxy)-1-cyclooctene (**6c**): NMR (CCl_4) δ 5.6 (m, 2, olefinic H), 4.85 (br m, CHOR), 1.25 (s, 9, *tert*-butyl).

Oxidation of Cyclododecene (7). Cyclododecene (16 mmol) was oxidized with 8 mmol of SeO_2 and 32 mmol of *tert*-butyl hydroperoxide under the same conditions described above for cyclooctene. Chromatography of the crude oil afforded pure 2-cyclododecen-1-ol (**7a**), identical with an authentic sample¹⁸ by NMR and IR, 2-cyclododecen-1-one, identified by spectral comparison to a sample prepared by MnO_2 oxidation of **7a**, and a mixture of **7b** and **7c**. The latter compounds were obtained in pure form by the methods described above for cyclooctene. 3-*tert*-butoxy-1-cyclododecene (**7b**): NMR (CCl_4) δ 5.45 (m, 2, olefinic H), 3.40 (br m, 1, CHOR), 1.18 (s, 9, *tert*-butyl); IR (CCl_4) 3020 (olefinic CH), 1200 (s) cm^{-1} . 3-*tert*-(Butylperoxy)-1-cyclododecene (**7c**): NMR (CCl_4) δ 5.45 (m, 2, olefinic H), 4.25 (br m, 1, CHOR), 1.22 (s, 9, *tert*-butyl). Conversion of the alcohol **7a** to the acetate with acetic anhydride in pyridine at 25 °C and analysis by GLC on an OV-101 capillary column revealed the *E/Z* ratio to be 77:23 when starting from (*E*)-cyclododecene and 80:20 when starting from (*Z*)-cyclododecene.

Acknowledgment. We are grateful to the National Science Foundation for financial support. B.C. thanks the Centre National de la Recherche Scientifique and NATO for fellowship support.

Registry No. 1, 127-91-3; **2a**, 19894-98-5; **2b**, 81971-88-2; **2c**, 81971-89-3; **3b**, 82009-31-2; **4b**, 81971-90-6; **4c**, 81971-91-7; **5**, 110-83-8; **5a**, 822-67-3; **5b**, 40648-13-3; **5c**, 51437-25-3; **6**, 931-88-4; **6a**, 3212-75-7; **6b**, 81971-92-8; **6c**, 81971-93-9; (*E*)-**7**, 1486-75-5; (*Z*)-**7**, 1129-89-1; (*E*)-**7a**, 6221-49-4; (*Z*)-**7a**, 41513-26-2; (*E*)-**7a** acetate, 51533-21-2; (*Z*)-**7a** acetate, 69798-87-4; **7b**, 81971-94-0; **7c**, 81971-95-1; selenium dioxide, 7446-08-4; *tert*-butyl hydroperoxide, 75-91-2; 2-cyclododecen-1-one, 42858-38-8.

Dye-Sensitized Photooxidation of Silyl Diazo Compounds. Intramolecular Oxygen Transfer of Carbonyl Oxides

Akira Sekiguchi, Yoshio Kabe, and Wataru Ando*

Department of Chemistry, The University of Tsukuba, Niiharigun, Ibaraki 305, Japan

Received December 30, 1981

The dye-sensitized photooxidation of silyl diazo compounds produced the corresponding silyl ketones and silyl esters, and the latter may be formed by the rearrangement of silyl-substituted carbonyl oxides. The reactions of a carbonyl oxide with various silyl ketones were also studied. The dye-sensitized photooxidation of diphenyldiazomethane in the presence of silyl ketones gave silyl esters together with benzophenone by reactions of a carbonyl oxide with the silyl ketones accompanying 1,2-anionic rearrangement of the silyl group.

A carbonyl oxide is a well-known Criegee-type intermediate in ozonolysis of alkenes or alkynes,¹ and recently its important role in biological systems has been recognized.² The most clean formation of carbonyl oxides involves the reaction of singlet oxygen with diazo compounds³ or the direct carbene reaction with ground-state molecular oxygen.⁴ Carbonyl oxides react intermolecularly with several substrates such as alkanes,⁵ alkenes,⁶ sulfides,⁷

sulfoxides,^{7,8} and aromatic compounds⁹ and can transfer an oxygen atom to their substrates. Although many types of intermolecular reactions of carbonyl oxides have been reported, intramolecular ones seem to be less investigated so far.¹⁰ Here, we report the detailed study on the dye-sensitized photooxidation of silyl diazo compounds and suggest the formation of silyl-substituted carbonyl oxides

(1) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978.

(2) (a) Hamilton, G. A. "Molecular Mechanism of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974. (b) Ando, W.; Miyazaki, H.; Ueno, K.; Nakanishi, H.; Sakurai, T.; Kobayashi, K. *J. Am. Chem. Soc.* 1981, 103, 4949. (c) Ryang, H.-S.; Foote, C. S. *Ibid.* 1981, 103, 4951.

(3) Higley, D. P.; Murray, R. W. *J. Am. Chem. Soc.* 1974, 96, 3330.

(4) (a) Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* 1962, 84, 3408. (b) Murray, R. W.; Suzui, A. *Ibid.* 1971, 93, 4963. (c) Murray, R. W.; Suzui, A. *Ibid.* 1973, 95, 3343.

(5) Hamilton, G. A.; Giacin, J. R. *J. Am. Chem. Soc.* 1966, 88, 1584.

(6) (a) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *J. Am. Chem. Soc.* 1979, 101, 1282. (b) Ryang, H.-S.; Foote, C. S. *Ibid.* 1980, 102, 2129.

(7) (a) Ando, W.; Kohmoto, S.; Nishizawa, K. *J. Chem. Soc., Chem. Commun.* 1978, 894. (b) Ando, W.; Kohmoto, S.; Miyazaki, H.; Nishizawa, K.; Tsumaki, T. *Photochem. Photobiol.* 1979, 30, 81. (c) Ando, W.; Miyazaki, H.; Kohmoto, S. *Tetrahedron Lett.* 1979, 1317. (d) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* 1980, 31, 191.

(8) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* 1981, 103, 3832.

(9) (a) Jerina, D. M.; Boyd, D. R.; Daly, J. W. *Tetrahedron Lett.* 1970, 457. (b) Chaudhary, S. K.; Hoyt, R. A.; Murray, R. W. *Ibid.* 1976, 4235.

(c) Kumar, S.; Murray, R. W. *Ibid.* 1980, 4781.

(10) (a) Okada, K.; Mukai, T. *Tetrahedron Lett.* 1980, 359. (b) Ando, W.; Miyazaki, H.; Itoh, K.; Auchi, D. *Ibid.* 1982, 555.