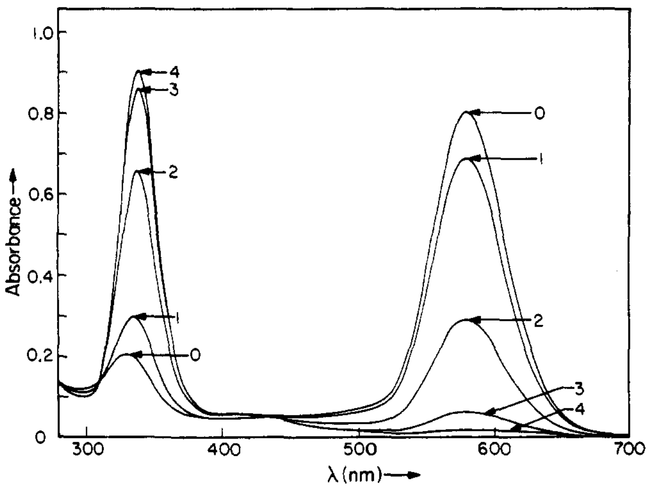


Figure 1. Irradiation (546 nm) of 1.6×10^{-4} M $[Rh_2(bridge)_4](BF_4)_2$ in degassed 12 M HCl solution. The four scans after $t = 0$ were taken at intervals of ~2 min.

collecting (Toepler pumping) and burning a sample over CuO. In a typical experiment in which some O_2 was present, conversion of 0.0567 mmol of $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ in 12 M HCl solution by irradiation at $\lambda > 530$ nm yielded 0.0466 mmol of H_2.[5] The photoreaction is therefore

$$\underset{\text{blue}}{[Rh_2(bridge)_4H]^{3+}\cdot Cl^-} + H^+ + Cl^- \xrightarrow[12\ M\ HCl]{546\ nm} \underset{\text{yellow}}{[Rh_2(bridge)_4Cl_2]^{2+}} + H_2 \qquad (1)$$

The appearance quantum yield of $[Rh_2(bridge)_4Cl_2]^{2+}$ in rigorously degassed 12 M HCl is 0.0040 ± 0.002 (λ_{irradn} 546 nm). The photoreaction is not inhibited by the presence of 1 atm of H_2 at 28 °C. Under such conditions the thermal back-reaction between $[Rh_2(bridge)_4Cl_2]^{2+}$ and H_2 to yield $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ requires several days to go to completion. Thus there is reason to believe that the photochemical/thermal kinetic properties of this type of system may be adjusted (a_{H^+}, added anions) such that it could be used to produce H_2 in solar energy conversion schemes.

The charge-transfer excited state involved in the photoreaction must be ${}^1A_{2u}$ or ${}^3A_{2u}$. In either case, the MO configuration is $(1a_{1g})^2(1a_{2u})^1(2a_{1g})^1$. If we assume, as seems reasonable, that the $2a_{1g}$ level possesses substantial 1s(H) character, then the excited state may be formulated as $[(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*}$. Attack either by H_2O or H_3O^+ could induce a second electron transfer ($1a_{2u} \rightarrow H\cdot$), yielding H_2 and the two-electron oxidative-addition product, $[Rh_2(bridge)_4Cl_2]^{2+}$.

$$[(Cl^-)Rh^I\text{- - -}Rh^I(H^+)]^{2+} \xrightarrow{546\ nm} [(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*} \qquad (2)$$

$$[(Cl^-)\text{- -}Rh^{I\,1/2}\text{- -}Rh^{I\,1/2}\text{- -}(H\cdot)]^{2+*} \xrightarrow[HCl(aq)]{fast} [Cl\text{-}Rh^{II}\text{-}Rh^{II}\text{-}Cl]^{2+} + H_2 \qquad (3)$$

It is attractive to propose that axial ligand–metal interactions may operate in such a way as to reduce the fraction of excited species returning to the Rh^I–Rh^I ground state by back electron transfer. The σ-binding interactions along the internuclear axis Cl- -Rh- -Rh- -H in a $(1a_{1g})^2(1a_{2u})^1(2a_{1g})^1$ excited state are predicted[1,6] to be larger than in the ground state $[(1a_{1g})^2(1a_{2u})^2]$; therefore, these interactions favor the H_2-producing pathway ($1a_{2u} \rightarrow H\cdot$) over back-transfer ($1a_{2u} \leftarrow H\cdot$), as the energy of the $1a_{2u}$ σ* level increases sharply as the extent of Cl- -Rh- -Rh- -H coupling increases. Further elucidation of the role of axial interactions must await the completion of mechanistic studies of the photoreaction that are now in progress.

Acknowledgments. We thank Bruce Parkinson, Bob Richman, John Thich, and Mark Wrighton for helpful discussions. Matthey-Bishop, Inc., is acknowledged for a generous loan of rhodium trichloride. This research was supported by the National Science Foundation (CHE 75-19086).

References and Notes

(1) N. S. Lewis, K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.*, **98,** 7461 (1976).

(2) K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.*, **97,** 3553 (1975).

(3) The ligand 1,3-diisocyanopropane (bridge) was prepared from the corresponding amine by a standard procedure (W. P. Weber, G. W. Gokel, and I. K. Ugi, *Angew. Chem. Int. Ed. Engl.*, **11,** 530 (1972)) and was purified by vacuum distillation (Note! Several attempted distillations of bridge in which the crude product was orange resulted in violent explosions. *Extreme caution is advised.*) The ^{1}H NMR spectrum of neat bridge exhibits a complex multiplet at δ 3.68 and a broad peak at δ 1.98 that integrate in the ratio of 2:1. The IR spectrum of a neat sample shows a very strong, narrow $\bar{\nu}(C{\equiv}N)$ band at 2140 cm^{-1}. Other prominent IR peaks are located at 2930, 1660, and 1490 cm^{-1}. $[Rh_2(bridge)_4](BF_4)_2$ was prepared as follows: 0.97 g (5.0 mmol) $AgBF_4$ was added to 50 mL of a stirred acetonitrile solution containing 1.23 g (2.5 mmol) of $[Rh(COD)Cl]_2$ (the latter compound was prepared by a standard method: J. Chatt and L. M. Venanzi, *J. Chem. Soc. A*, 4735 (1975)). The AgCl precipitate was filtered and then 0.94 g (10 mmol) of bridge was slowly added to the light yellow filtrate. The solution turned purple and a dark solid precipitated. The precipitate was filtered, washed with acetonitrile and ether, and then was dried overnight under vacuum, yield 1.5 g (80%). Anal. Calcd: C, 31.78; H, 3.20; N, 14.82; F, 20.11. Found: C, 31.62; H, 3.37; N, 14.66; F, 19.82.

(4) The visible absorption maximum of $[Rh_2(bridge)_4H]^{3+}$ is both solvent and anion sensitive, shifting from 549 nm in acetonitrile solution (0.1 M in *p*-toluenesulfonic acid) to 596 nm in concentrated aqueous HBr. Detailed studies of the dependence of the absorption spectra of $[Rh_2(bridge)_4H]^{3+}$ on $[Cl]^-$ indicate that the principal species in 1 M HCl is $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$. It should be noted here that we have not been able to locate a band in the IR spectrum of $[Rh_2(bridge)_4H]^{3+}\cdot Cl^-$ attributable to Rh–H stretching, nor have we observed an NMR peak for the bound H^+.

(5) The amount of H_2 obtained in any given experiment depends strongly on $[O_2]$, as the excited state reacts with O_2 to give $[Rh_2(bridge)_4Cl_2]^{2+}$. In rigorously degassed 12 M HCl solutions the molar ratio of H_2:$[Rh_2(bridge)_4Cl_2]^{2+}$ was found to be 0.96 ± 0.04.

(6) V. M. Miskowski, G. L. Nobinger, D. S. Kliger, G. S. Hammond, N. S. Lewis, K. R. Mann, and H. B. Gray, *J. Am. Chem. Soc.*, submitted for publication.

(7) National Science Foundation Energy Postdoctoral Fellow, 1976–1977.

(8) Division of Natural Sciences, University of California at Santa Cruz, Santa Cruz, Calif. 95060.

Kent R. Mann,[7] Nathan S. Lewis, Vincent M. Miskowski
David K. Erwin, George S. Hammond,[8] Harry B. Gray*
Contribution No. 5587 from the
Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125

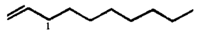
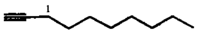
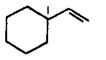
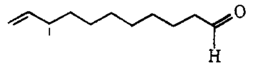
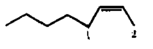
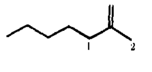
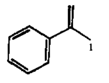
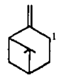
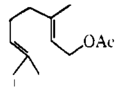
Received May 9, 1977

Allylic Oxidation of Olefins by Catalytic and Stoichiometric Selenium Dioxide with *tert*-Butyl Hydroperoxide

Sir:

Selenium dioxide remains the most reliable and predictable reagent for the direct insertion of oxygen into an allylic carbon-hydrogen bond.[1] A serious complication in this reaction is the inevitable production of reduced forms of selenium. The frequent difficulty of removing colloidal selenium from the products is well known. Another drawback of these oxidations is the formation of organoselenium by-products. We have recently shown that one of the principal selenium containing by-products arises from addition of intermediate selenium(II) electrophilic species across the olefinic bond.[2] We reasoned that an oxidant which would rapidly and selectively reoxidize the reduced selenium species to SeO_2 would circumvent these

Table I. Allylic Oxidation[a]

		% yield[b] (relative ratio[c])		
Case	Olefin or acetylene	0.5SeO_2, 2(*t*-BuOOH)[d]	Cat. SeO_2, *t*-BuOOH[e]	SeO_2[f]
1		61 (92:8)		17[g] [92:8][h]
2		48 (91:9)		24 (92:8)
3		44		7[g]
4		31[j] (99:1) [93:7]		17[i] (82:18)[h]
5		64[j] (77:3:19:1) [80:2:17:1]		18 (89:5:5:1) [77:4:18:1]
6		59[k] (85:5:9:1) [81:6:10:3]	56[l] (81:6:12:1) [75:6:16:3]	25[g] [63:22:8:7]
7			54[m] [90:10]	22[n]
8			86[m] [>98:<2]	53–62[o]
9		60 (86:14)	55 (88:12)	54[p]

[a] Products are the alcohols and aldehydes or ketones at the indicated sites. All products were characterized spectrally and by combustion analysis or by comparison with authentic samples or with literature spectra. [b] Unless stated otherwise, yields were of distilled products of at least 95% purity by GLC analysis on two columns and were based on initial moles of olefin. [c] Ratio of site 1 alcohol:site 1 carbonyl product: site 2 alcohol:site 2 carbonyl product in the distilled products as determined by GLC analysis, not corrected for small response factor variations. Ratios obtained before isolation are indicated in brackets. [d] Reactions were done on 0.1 mol of olefin except case 4 (0.02 mol). The procedure was as described in the text except that case 6 was reacted at 0 °C for 2 h and case 9 at 10 °C for 3 h. [e] Reactions were carried out on 0.1 mol (cases 6 and 9) or 0.5 mol (cases 7 and 8). Case 8 was reacted in dry hexanes with 0.0067 mol of SeO_2, 0.575 mol of *tert*-butyl hydroperoxide, and 0.052 mol of acetic acid. The procedure and stoichiometries for the others were as described in the text for case 9. [f] Small-scale reactions (VPC yields) were carried out by combining 2 mmol of olefin and 1 mmol of SeO_2 in 2 ml of *tert*-butyl alcohol, then heating to reflux. Analyses were made at frequent intervals and maximum yields were recorded. Isolated yields were obtained on a 0.1-mol (cases 2 and 5) or a 0.02-mol scale (case 4) by slowly adding a solution of 0.5 mol equiv of SeO_2 in *tert*-butyl alcohol to a refluxing solution of the olefin in that solvent. [g] Yield determined by GLC relative to an internal standard. [h] The primary alcohol from double-bond migration was also formed (10–20% of total products). [i] Products isolated by chromatography on silica gel. [j] The main alcohol was spectrally and chromatographically identical with authentic (*E*)-oct-2-en-4-ol. [k] The distilled product was 92% pure. [l] The distilled product was 86% pure. [m] Workup involved $NaBH_4$ reduction. [n] Reference 15 (dioxane, room temperature, 1 week, 0.5 mol equiv of SeO_2). [o] Reference 16 (EtOH, reflux, 4 h, 0.4 mol equiv of SeO_2). [p] Reference 17 (EtOH, reflux, aldehyde sole product).

problems, and furthermore might enable the reaction to proceed with catalytic amounts of SeO_2.

The reaction of SeO_2 with olefins in the presence of hydrogen peroxide has long been known to form diols and epoxides,[3] presumably via a perselenious acid species.[3c,d] Only for the highly reactive ene, β-pinene, did the H_2O_2-catalytic SeO_2 system give allylic oxidation cleanly.[4] Under the same reaction conditions employed for β-pinene, we found that less reactive olefins (e.g., geranyl acetate, 2-phenylpropene, (*Z*)-2-octene, and 1-decene) gave either epoxide or complex mixtures in which allylic oxidation products were only minor components.[5] We anticipated[6] that an alkyl hydroperoxide would avoid the peracid behavior associated with hydrogen peroxide in this system.[7]

Indeed, when olefins which are normally reactive toward SeO_2 were oxidized with *tert*-butyl hydroperoxide in the presence of catalytic (1.5-2%) SeO_2, allylic alcohols were produced in yields comparable with, or better than, those obtained with stoichiometric SeO_2 alone (Table I, cases 6-9). Normally the reactions were run to about two-thirds completion, beyond which further oxidation of the allylic alcohol competed with its formation. This point was reached under extremely mild conditions: 1 day at room temperature sufficed at the concentrations used. While reactive olefins (case 8) required only a slight excess of *tert*-butyl hydroperoxide, most gave higher yields with 3-4 equiv. The reaction was most rapid in noncoordinating solvents, especially methylene chloride. Under strictly anhydrous conditions β-pinene failed to react, but, when 1 equiv of water or lesser amounts of a carboxylic acid were added, the reaction proceeded smoothly. Most olefins responded best to the carboxylic acid catalysis.[8]

Less substituted olefins, which react poorly with SeO_2, also reacted very sluggishly under our catalytic conditions. However, when 0.5 mol equiv of SeO_2 and 2 equiv of *tert*-butyl hydroperoxide were combined with the olefin in CH_2Cl_2, a very powerful allylic oxidation system resulted (see Table I). Added acids were not required. Mono- and vicinate-disubstituted olefins were readily oxidized in 1 or 2 days at room temperature, while the more reactive olefins required low temperatures to moderate the reaction (cases 6 and 9).

A general procedure using stoichiometric SeO_2 and *tert*-butyl hydroperoxide was as follows. Into a 250-mL flask was introduced 5.5 g (0.05 mol) of SeO_2, 75 mL of CH_2Cl_2, and 22 mL (0.2 mol) of 90% *tert*-butyl hydroperoxide.[9] After the mixture had been stirred for 0.5 h at 25 °C (water bath), 11.2 g (0.1 mol) of (*Z*)-2-octene was added over several minutes.[10] The mixture was stirred at 25 °C for 48 h (GLC ratio of olefin:products was 1:2). Benzene (50 mL) was added and the CH_2Cl_2 was removed on a rotary evaporator. Ether (100 mL) was added and the organic phase was washed four times with

25 mL of 10% KOH and once with brine. To destroy excess *tert*-butyl hydroperoxide, the solvents were removed, the residue was dissolved in 20 mL of cold acetic acid, and 25 mL (excess) of methyl sulfide was added slowly with stirring and water bath cooling.[11] After 4 hr at 25–30 °C, the mixture was cooled in an ice bath and neutralized with 20% K_2CO_3. The aqueous phase was extracted with ether, and the combined organic phases were washed with water and brine, dried ($MgSO_4$), concentrated, and distilled to afford 8.25 g (64%) of allylically oxidized products (Table I, case 5), 95% pure by GLC analysis.

In a typical procedure employing the catalytic method, 40 mL (0.36 mol) of 90% *tert*-butyl hydroperoxide[9] was poured into a magnetically stirred suspension of 0.221 g (0.002 mol) of SeO_2 and 1.4 g (0.01 mol) of salicylic acid in 35 mL of CH_2Cl_2. The resulting solution was placed in a 25 °C water bath and 19.75 g (0.10 mol) of geranyl acetate was introduced. After 27 h, GLC analysis showed an area ratio for olefin: products of 2:3. The reaction mixture was worked up as described above, except that in this instance the reduction step was omitted and the mixture was distilled directly under reduced pressure[12] to yield 6.52 g (33%) of geranyl acetate and 11.75 g (55%) of a mixture of (*E,E*)-2,6-dimethyl-8-acetoxyocta-2,6-dien-1-ol and the corresponding aldehyde (88:12 by GLC).

The combination of stoichiometric SeO_2 and *tert*-butyl hydroperoxide is clearly the method of choice for obtaining synthetically useful yields of unrearranged allylic alcohols from a greatly broadened spectrum of olefins.[13,14] The positional selectivity, which has been the chief attraction of SeO_2 oxidations, is retained. The milder conditions avoid the rearrangements and dehydrations which can occur under the standard conditions. Finally, the elimination of colored and malodorous organoselenium by-products, and elemental selenium, should ameliorate the selenophobia which currently afflicts many synthetic organic chemists.

Acknowledgment. We thank the National Institutes of Health (GM 21686) and the National Science Foundation (CHE74-21260) for support of this research.

References and Notes

(1) For recent reviews see (a) R. A. Jerussi in "Selective Organic Transformations", Vol. I, B. S. Thyagarajan, Ed., Wiley, New York, N.Y., 1970, p 301; (b) E. N. Trachtenberg in "Oxidation, Techniques and Applications in Organic Synthesis", R. L. Augustine, Ed., Marcel Dekker, New York, N.Y., 1969, p 119.

(2) K. B. Sharpless, K. M. Gordon, R. F. Lauer, S. P. Singer, and M. W. Young, Chem. Scr., **8A**, 9–13 (1975).

(3) (a) A. Guillemonat, *Ann. Chim.*, **11**, 143 (1939); (b) A. Stoll, A. Lindenmann and E. Jucker, *Helv. Chim. Acta*, **36**, 268 (1953); (c) J. Itakura, H. Tanaka, and H. Ito, *Bull. Chem. Soc. Jpn*, **42**, 1604 (1969); (d) N. Sonoda and S. Tsutsumi, *ibid.*, **38**, 958 (1965).

(4) J. M. Coxon, E. Dansted, and M. P. Hartshorn, referenced by M. Fieser and L. Fieser, "Reagents for Organic Synthesis", Vol. II, Wiley, New York, N.Y., 1969, p 362.

(5) (a) M. A. Umbreit and K. B. Sharpless, unpublished results. Using various stoichiometries of SeO_2 and H_2O_2, others had shown that endocyclic olefins produce epoxides or diols. While exocyclic olefins usually gave allylic alcohols, double-bond migrations and subsequent epoxidations also occurred: (b) M. J. Francis, P. K. Grant, K. S. Low and R. T. Weavers, *Tetrahedron*, **32**, 95 (1976); (c) C. W. Wilson and P. E. Shaw, *J. Org. Chem.*, **38**, 1684 (1973).

(6) The epoxidation of cyclohexene with *tert*-butyl hydroperoxide and catalytic SeO_2 has been studied by Sheldon (R. A. Sheldon and J. A. Van Doorn, *J. Catal.*, **31**, 427 (1973)). In cyclohexene solvent at 90 °C (anhydrous, inert atmosphere) a moderate yield of cyclohexene oxide was formed, suggesting that in this system SeO_2 functions analogously to the well-known molybdenum epoxidation catalysts. These authors also reported the formation of some cyclohexenol and cyclohexenone in benzene solvent. It appeared that these products arose from free-radical pathways, however.

(7) We had previously found that *tert*-butyl hydroperoxide is superior to H_2O_2 as the oxidant in the osmium-catalyzed hydroxylation of olefins: K. Akashi and K. B. Sharpless, *J. Am. Chem. Soc.*, **98**, 1986 (1976).

(8) Acid catalysis is a feature common to many ene reactions,[8a] as well as to *tert*-butyl hydroperoxide oxidations of sulfides[8b] and diselenides:[8c] (a) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969); (b) D. Barnard, L. Bateman, and J. I. Cunneen in "Organic Sulfur Compounds", Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N.Y., 1961, p 229; (c) G. Ayrey, D. Barnard, and D. T. Woodbridge, *J. Chem. Soc.*, 2089 (1962).

(9) We used 90% *tert*-butyl hydroperoxide supplied by Aldrich or Lucidol, which contains ~6% *tert*-butyl alcohol, 4–5% water, and <1% di-*tert*-butyl peroxide. Care should be taken to avoid contamination by trace metals or strong acids, since these may induce rapid decomposition of the hydroperoxide. In the reactions employing stoichiometric SeO_2 and *tert*-butyl hydroperoxide, the hydroperoxide was used directly as received. In the catalytic reactions, which were done earlier, the *tert*-butyl hydroperoxide was dried over $MgSO_4$ and filtered through glass wool before use. We did not establish whether or not this drying was beneficial.

(10) With many olefins this step was exothermic, and temperature was controlled by the rate of addition and by 0–25 °C cooling baths. The mixtures remained colorless or became light yellow during the reaction. A 1-mol reaction with 1-octene proceeded without incident and afforded the expected products in a yield comparable with that realized with 1-decene on a 0.1-mol scale (Table I, case 1).

(11) (a) J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966). (b) M. A. P. Dankleff, R. Curci, J. O. Edwards, and H.-Y. Pyun, *J. Am. Chem. Soc.*, **90**, 3209 (1968). (c) Other reduction methods are available (see R. Hiatt in "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, N.Y., 1971, p 49).

(12) *tert*-Butyl hydroperoxide should be distilled with great care since it is potentially explosive, especially in the pure state. Under vacuum (1 mm or better) it may be removed without applying heat. A safety shield and suitable personal protection should be used. For large-scale (>1 mol) reactions prior reduction is recommended.

(13) Of the 25 olefins which we have tried in this system only (*E*)-1-phenylpropene and cyclohexene failed to give allylic oxidation products by GLC analysis. We found that the expected product of the former, cinnamyl alcohol, reacted more rapidly under the conditions than did the olefin. The anomalous behavior of cyclohexene may be related to Sheldon's observations on its epoxidation.[6]

(14) Yields and reactivities in the stoichiometric SeO_2–*tert*-butyl hydroperoxide system closely resemble those in allylic amination reactions with selenium imido reagents (see K. B. Sharpless, T. Hori, L. K. Truesdale, and C. O. Dietrich, *J. Am. Chem. Soc.*, **98**, 269 (1976)).

(15) C. H. Nelson, Ph.D. Thesis, Clark University, Worcester, Mass., 1965, p 58.

(16) J. M. Quinn, *J. Chem. Eng. Data*, **9**, 389 (1964).

(17) J. Meinwald and K. Opheim, *Tetrahedron Lett.*, 281 (1973).

(18) NOTE ADDED IN PROOF. Although we have referred to these new methods as stoichiometric and catalytic SeO_2–*tert*-butyl hydroperoxide oxidations, it should be recognized that this distinction refers merely to the quantities of SeO_2 used, since both methods are catalytic in that SeO_2 is not consumed.

M. A. Umbreit, K. B. Sharpless*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received April 19, 1977