analogous **3a** (30–40% yield), *cis*- and *trans*-diethoxyethylene,[11] and *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether.[10c] We initially believed **3b** to be different in some fundamental way from **3a** since **3b** is extremely soluble in pentane whereas **3a** is only slightly soluble in dichloromethane.

3a and **3b** (Figure 1)[12] are structurally analogous dimers that possess an inversion center, a staggered, ethane-like geometry, and an *unbridged* metal–metal double bond. Bond lengths and angles in the two molecules are compared in Table I. There are no statistically significant differences between the two except a slightly shorter $Re{=}Re$ bond and larger Re–O–C angles in **3a**. One striking feature is the 90° angle between the alkylidyne ligand and the metal–metal bond. We suspect that the C–Re–C angle in complexes of type **2** also may be 90° and so do not yet ascribe any special significance to the 90° angle in **3**. The rhenium–rhenium bond distances are consistent with their being double bonds on the basis of Re–Re distances of 2.381 (1) Å in $(Me_3SiCH_2)_3(O)Re(\mu\text{-}O)[Re(PMe_3)_4]Re(O)_2(CH_2SiMe_3)$[2] and 2.408 (1) Å in $[Ru(OEP)]_2$.[3] The Re—Re single bond in structurally related species such as $[ReO(Me{\equiv}CMe)_2]_2$ is considerably longer [2.686 (1) Å].[13] A rhenium–rhenium double bond is consistent with the diamagnetism of **3** and is attractive also because of the analogy between the $Re{=}Re$ bond and the $Re{\equiv}C$ bond in **2**. The metal–alkylidyne bond lengths are among the shortest known.[14] There is no evidence for hydrides in either **3a** or **3b**.[15]

One equivalent of *syn*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2$ in C_6D_6 reacts with **1a** in 4 h at 85 °C to yield **3a** (90%) and *cis*- and *trans*-3,3-dimethylbutenyl ethyl ether as the major olefinic products (eq 3). (Small amounts of *cis*- and *trans*-1,2-diethoxyethylene also are formed.) When **1a** is heated in C_6D_6, **3a** and *cis*- and *trans*-1,2-diethoxyethylene are obtained in high yield. Therefore, one mechanism of forming **3a** and **3b** most likely involves coupling two alkylidene ligands in a dimetallacyclobutane complex. Since it has been argued that elimination of an olefin from a $1,2\text{-}M_2C_2$ core is symmetry forbidden,[16] and formation of a $1,3\text{-}M_2C_2$ core is more consistent with $M{=}C$ bond polarity considerations, we suggest that 1,3-dimetallacycles are the precursors to **3a** and **3b**.[17] Subsequent conversion to a dimetallatetrahedrane could then result in extrusion of olefin and direct metal–metal bond formation. Note that samples of *syn*- and *anti*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR)_2$ [OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$] produce only trace amounts of *trans*-2,2,5,5-tetramethyl-3-hexene in solution at 120 °C, suggesting that coupling is rapid only when heteroatom substituents are present or when at least one of the two alkylidenes involved is relatively small.

$$\textit{syn}\text{-}Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2 + \mathbf{1a} \xrightarrow{C_6D_6} \mathbf{3a} + \underset{\text{(cis and trans)}}{EtOCH{=}CH\text{-}t\text{-}Bu} \qquad (3)$$

We also have preliminary evidence that suggests that complexes of type **3** form when rhenacyclobutane complexes rearrange to give an olefin by a β hydrogen process, i.e., that complexes of type **3** also can form by coupling of monomeric $Re(C\text{-}t\text{-}Bu)(OR)_2$ units. Such d^2 $Re(C\text{-}t\text{-}Bu)(OR)_2$ species would be expected to have trigonal-planar structures by analogy with what are proposed to be isoelectronic trigonal-planar $Ta[OSi(t\text{-}Bu)_3]_3$[18] and $W(N\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2$,[19] and crystallographically characterized $Os(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_2)_3$.[20]

Dimers **3a** and **3b** do not react readily with simple olefins such as ethylene or norbornene, even at 70 °C after several hours. They also do not form stable adducts with pyridine or dimethylphenylphosphine. However, $[Re(CCMe_2Ph)(O\text{-}t\text{-}Bu)_2]_2$ (**3c**) does react rapidly at −40 °C in ether with 2 equiv of I_2 to afford pentane-soluble vermillion crystals consistent with the formulation $Re(CCMe_2Ph)(O\text{-}t\text{-}Bu)_2I_2$ (**4**). In future studies we hope to elucidate these and other reactions and to determine whether unbridged $Re{=}Re$ double bonds are a general feature of Re(V) chemistry.

Acknowledgment. R.R.S. thanks the National Science Foundation for research support (CHE 88-22508), and R.T. thanks Catalytica, Inc., for financial support. We thank Dr. William M. Davis for crystallographic assistance.

Supplementary Material Available: Synthetic procedures, NMR data, and analytical data for **1a**, **1b**, **2a**, **2b**, **3a–c**, and **4**, description of the X-ray studies of **3a** and **3b**, and labeled ORTEP drawings, final positional parameters, and final thermal parameters for **3a** and **3b** (15 pages); listing of final observed and calculated structure factors for **3a** and **3b** (42 pages). Ordering information is given on any current masthead page.

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(11) Baganz, H.; Praefoke, K.; Rost, J. *Chem. Ber.* **1963**, *96*, 2657.

(12) Crystals were mounted in a glass fiber. Data were collected on a Rigaku AFC6R diffractometer at −72 ± 1 °C using graphite-monochromated Mo Kα radiation. For **3a** (**3b**), a total of 4778 (4028) reflections ($h,k,\pm l$) were collected in the range 1.2 (1.2)° $< 2\theta <$ 55 (55)° with 3182 (2822) having $I > 3.00\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques [253 (145) variables] using the TEXSAN crystallographic software package from Molecular Structure Corporation. Final R = 0.036 (0.029), R_w = 0.047 (0.040). Full details can be found in the supplementary material.

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(14) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; VCH Publishers: Weinheim, 1988; p 147.

(15) **3a–c** do not react with CCl_4 to produce $CHCl_3$, even upon photolysis. Treatment of **3a** or **3c** with excess HCl(g) in a sealed NMR tube did not produce H_2 (δ 4.45). Low-temperature proton NMR (−77 °C, CD_2Cl_2) with a 5-s pulse delay did not reveal any resonances attributable to hydrides in the range +60 to −45 ppm. For neither structure did crystallographic evidence favor the presence of bridging hydrides. (See supplementary material.)

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Aqueous Ruthenium(II) Complexes of Functionalized Olefins: The X-ray Structure of $Ru(H_2O)_2(\eta^1(O){:}\eta^2(C,C')\text{-}OCOCH_2CH{=}CHCH_3)_2$

Dominic V. McGrath and Robert H. Grubbs*

Contribution No. 8358, Arnold and Mabel Beckman
Laboratory of Chemical Synthesis
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Joseph W. Ziller

Department of Chemistry, University of California
Irvine, California 92717

Received November 19, 1990

We recently reported the development of a ring-opening metathesis polymerization (ROMP)[1] system based on low valent ruthenium complexes[2] that tolerates many organic functionalities known to deactivate early-transition-metal metathesis catalysts. The coordination compound $Ru^{II}(H_2O)_6(tos)_2$ (tos = *p*-toluene-

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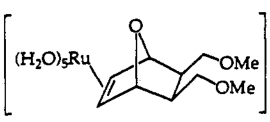
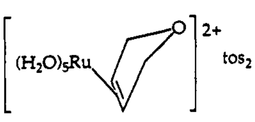
(1) (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907–915. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press, Ltd.: New York, 1982; Vol. 8, pp 499–551.

(2) (a) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542–7543. (b) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 960–961.

sulfonate)[3] has demonstrated the greatest promise. This complex polymerizes a large variety of norbornene and 7-oxanorbornene derivatives to high polymer under mild reaction conditions (water or alcoholic solution, 55–70 °C).[2,4] During the course of the polymerization of 5,6-bis(methoxymethyl)-7-oxanorbornene (**1**), the complex is converted to the monoolefin adduct **2**, which can be observed by ^1H and ^{13}C NMR spectroscopy. This is the first observed example of an organometallic complex formed from fully aqueous ruthenium(II) in water. Given the fundamental nature of olefin complexes in organometallic chemistry and catalysis,[5] as well as the continuing emergence of water as an important solvent for catalytic chemistry,[6] we have explored the chemistry of aqueous ruthenium(II) with acyclic and monocyclic functionalized olefins.



2



3

In water, excess 2,5-dihydrofuran reacts with $Ru^{II}(H_2O)_6(tos)_2$ to give the monoolefin adduct **3** (85% yield by NMR) which can be fully characterized by its ^1H and ^{13}C NMR spectra. The NMR resonances of the complexed olefin exhibit upfield shifts of the olefinic protons (5.76 to 5.64 ppm), as well as the characteristic[7a] olefinic carbon upfield shifts of ca. 50 ppm (127.0 to 78.1 ppm), relative to those of free olefin. The side-on coordination of the olefin to the metal is indicated by the inequivalence of the allylic protons, which now give rise to two doublets at 4.65 and 3.92 ppm (J = 11 Hz). NMR integration[8] and elemental analysis[9] of the ditosylate salt support the formation of a monoolefin complex. ROMP of 2,5-dihydrofuran is not observed.

To date, bis(olefin) complexes of aqueous ruthenium(II) dication only are observed for chelating olefins such as diallyl ether. At room temperature in D_2O, diallyl ether and $Ru^{II}(H_2O)_6(tos)_2$ react to form a monoolefin complex which rapidly converts to a second product. Ten inequivalent protons of equal integration can be separated into two sets of five spins by ^1H–^1H correlation NMR spectroscopy. Four olefinic resonances, as identified by their J_{CH} values of ~160 Hz, are observed in the ^{13}C NMR spectrum at chemical shifts upfield by 50–60 ppm relative to free diallyl ether. Recrystallization from aqueous 3.6 M p-toluenesulfonic acid solution yields canary yellow microcrystals which analyze as $Ru(H_2O)_4(C_6H_{10}O)(tos)_2$.[10] The ^1H NMR spectrum of this purified complex **4** reveals that the two sets of five protons are now of unequal intensity (ratio 1.6:1). Therefore, a mixture of two diallyl ether complexes with different solubilities, each having 2-fold symmetry, is formed in a 1:1 ratio from free olefin and ruthenium in solution. Heating either mixture to 65 °C in solution fails to change the ratio of the two complexes.

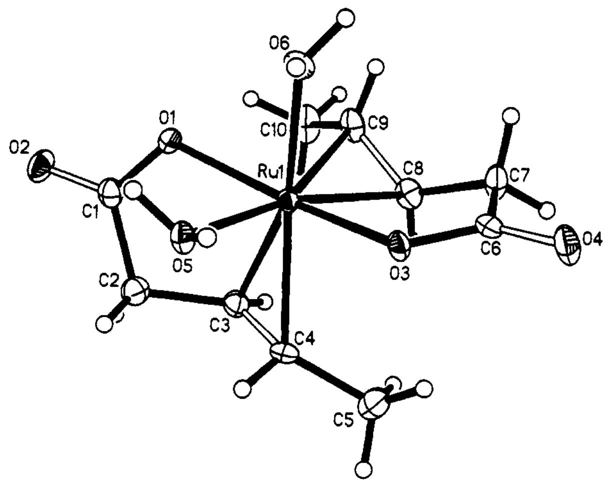


Figure 1. ORTEP diagram of **7**. Selected bond distances (Å) and angles (deg) are as follows (X1A = center of C(3)–C(4) bond, X1B = center of C(8)–C(9) bond): Ru–O(1), 2.080 (3); Ru–O(3), 2.065 (3); Ru–O(5), 2.141 (3); Ru–O(6), 2.115 (3); Ru–X1A, 2.088 (4); Ru–X1B, 2.088 (4); C(3)–C(4), 1.381 (6); C(8)–C(9), 1.381 (6); O(5)–Ru–O(6), 83.3 (1); O(1)–Ru–O(5), 81.6 (1); O(1)–Ru–O(6), 83.1 (1); O(1)–Ru–O(3), 162.4 (1); O(3)–Ru–O(5), 85.3 (1); O(3)–Ru–O(6), 83.8 (1); O(5)–Ru–C(3), 93.3 (1); O(5)–Ru–C(4), 82.4; O(6)–Ru–C(8), 100.8 (1); O(6)–Ru–C(9), 83.5 (1); O(1)–Ru–X1A, 93.7 (2); O(1)–Ru–X1B, 98.4 (2); O(3)–Ru–X1A, 97.5 (2); O(3)–Ru–X1B, 93.8 (2); C(3)–C(4)–C(5), 124.0 (4); C(8)–C(9)–C(10), 123.6 (4).

Table I. Formal Redox Potentials of $Ru(H_2O)_nL^{3+/2+}$ (n = 4 or 5)

L	n	$E_{1/2}$,[a] V vs NHE
H_2O	5	+0.20[b]
allyl ethyl ether	5	+0.38
2,5-dihydrofuran	5	+0.83
methyl acrylate	5	+0.94
5,6-bis(methoxymethyl)-7-oxanorbornene	5	+1.33[c]
3-buten-1-ol	4	+0.62
sodium 2-propenesulfonate	4	+0.83
diallyl ether	4	large[d]
1,5-hexadiene	4	large[d]

[a] Glassy carbon working electrode, SSCE reference electrode, Pt wire auxiliary electrode, 0.1 M $NaClO_4$, pH 2. [b] Reference 17. [c] E_p^{ox}, irreversible, measured at pH 7. [d] Exceeds limit of solvent window (+1.5 V).

Chelation by pendant oxygen functionalities has also been observed. For example, 3-buten-1-ol reacts with $Ru^{II}(H_2O)_6(tos)_2$ in water to form the monoolefin complex **5**, which can be isolated by crystallization from concentrated aqueous p-toluenesulfonic acid solution. The ^{13}C NMR spectrum shows the characteristic 50 ppm upfield shift for the olefinic carbons as well as a significant *downfield* shift (61.6 to 73.8 ppm) for the carbinol carbon, indicating proximity to the metal center through coordination of the alcohol oxygen to ruthenium.[11] The elemental analysis of this complex is consistent with $Ru(H_2O)_4(C_4H_8O)(tos)_2$.[12] The loss of two water molecules from the starting material further supports a bidentate structure.

Carboxylic acid functionalities react irreversibly with the ruthenium center. For example, 3-pentenoic acid reacts with $Ru^{II}(H_2O)_6(tos)_2$ in water to form the monoolefin complex **6**,[13]

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(8) All NMR integrations were referenced to the aromatic tosylate protons. ^1H NMR spectra were taken with a pulse angle of $\leq 15°$ and a pulse delay of ≥ 10 s to insure relaxation of all spins between accumulations.

(9) Anal. Calcd for $C_{18}H_{30}O_{12}RuS_2$: C, 35.82; H, 5.01. Found: C, 36.34; H, 4.83.

(10) Anal. Calcd for $C_{20}H_{32}O_{11}RuS_2$: C, 39.15; H, 5.26. Found: C, 39.00; H, 5.19.

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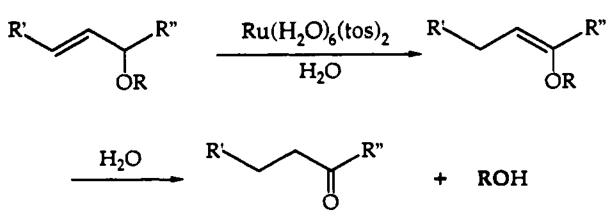
(12) Anal. Calcd for $C_{18}H_{30}O_{11}RuS_2$: C, 36.79; H, 5.15. Found: C, 36.82; H, 5.08.

(13) ^1H NMR (D_2O): δ 7.51 (d, 4, J = 8.3, H_{aryl} tos), 7.18 (d, 4, J = 8.3, H_{aryl} tos), 4.96 (m, 0.8, =CH), 4.89 (m, 0.8, =CH), 3.46 (dd, 0.8, J = 17.2, 5.1, CH_2CO$_2$H), 2.21 (s, 6, Me tos), 2.15 (dd, 0.8, J = 17.2, 9.3, CH_2CO$_2$H), 1.32 (d, 2.6, J = 5.7, CH_3).

Scheme I



R, R' = H; R" = H, Me, Et
R = Et; R', R" = H
R, R" = H; R' = Me

which slowly reacts with excess 3-pentenoic acid to form a yellow crystalline precipitate **7**. This complex is only sparingly soluble in neutral water, but increasingly soluble at higher pH. The ^1H NMR spectrum reveals a single seven-spin system consistent with an intact 3-pentenoic acid moiety and the absence of any tosylate counterions. This data and the elemental analysis of these crystals for $Ru(H_2O)_2(C_5H_7O_2)_2$[14] are consistent with a bis(olefin)-bis(carboxylate) structure having 2-fold symmetry. An X-ray structural analysis of **7** supports this structure (Figure 1).[15] A noncrystallographic C_2 axis bisects the O(5)-Ru-O(6) angle. The Ru-OH_2 bond distances of 2.141 (3) and 2.115 (3) Å are typical for a Ru(II) center.[3b] The coordinated olefin bond distances, both 1.381 (6) Å, are intermediate between a C-C single and double bond and are slightly longer than the coordinated olefin bond distance of 1.37 (2) Å in $Ru(1\text{-}5\text{-}\eta^5\text{-}C_8H_{11})(\eta^1(O){:}\eta^2(C,C')\text{-}OCOCH_2CH{=}CH_2)(PMe_3)$.[16]

All aqueous ruthenium(II) olefin complexes studied are active ROMP catalysts, demonstrating activity similar to that of $Ru^{II}(H_2O)_6(tos)_2$.[2] They also exhibit increased stabilization toward oxidation relative to the parent $Ru^{II}(H_2O)_6(tos)_2$ complex.[17] Their formal reduction potentials, measured by cyclic voltammetry, are shown in Table I. This stabilization, while not as large,[18] is analogous to that observed for pentaammineruthenium(II) olefin complexes[7] and arises from the back-donation of electron density from the metal d orbitals of π symmetry to the olefin π^* orbital. Monodentate allyl ethyl ether is capable of raising the oxidation potential of the pentaaquoruthenium(II) moiety 0.18 V over the parent hexaaquoruthenium(II) complex, and electron-withdrawing methyl acrylate raises the potential 0.74 V. This stabilization is greater than that provided by four pyridine ligands.[19]

Olefins without coordinating pendant functional groups are subject to isomerization of the double bond to a more stable configuration. Allylic ethers and alcohols react readily with catalytic amounts of $Ru^{II}(H_2O)_6(tos)_2$ at room temperature in aqueous solution to yield enol ethers which hydrolyze in the aqueous medium to propionaldehyde and the corresponding alcohol or water (Scheme I). The mechanism of this transformation and the successful use of acyclic olefins as molecular weight regulators in this ROMP system are currently under investigation.

Acknowledgment. We gratefully acknowledge support from the Caltech Chemistry Consortium (Du Pont, Kodak, Shell, and 3M), the NSF, and Rohm & Haas. D.V.M. thanks the Department of Education for a predoctoral fellowship. Funds for the purchase of the Siemens R3m/V diffractometer system were made available from the NSF under Grant CHE-85-14495. We are grateful to Drs. James Toth and Thomas Josefiak for assistance with the electrochemical measurements and Dr. Paul Bernhard for advice regarding the synthesis of $Ru^{II}(H_2O)_6(tos)_2$, and we thank Dr. David Wheeler for helpful discussions.

Supplementary Material Available: Spectroscopic data for compounds **3**-**7** and compounds from Table I not mentioned in the text and a listing of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for **7** (17 pages); listing of observed and calculated structure factors for **7** (5 pages). Ordering information is given on any current masthead page.

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(14) Anal. Calcd for $C_{10}H_{18}O_6Ru$: C, 35.82; H, 5.41. Found: C, 35.64; H, 5.29.

(15) **6** crystallizes in space group $P2_12_12_1$ (D^4_{2h}; No. 19) with a = 7.8085 (12) Å, b = 8.0452 (10) Å, c = 19.2704 (28) Å, V = 1210.6 (3) Å^3, and D_{calcd} = 1.840 g cm^{-3} for Z = 4, T = 183 K. The structure was solved via an automatic Patterson method (SHELXTL PLUS). Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 2.2%, R_{wF} = 2.7%, and GOF = 1.04 for 156 variables refined against those 1236 data with $|F_o| > 2.0\sigma(|F_o|)$ [R_F = 2.1% and R_{wF} = 2.6% for those 1207 data with $|F_o| > 6.0\sigma(|F_o|)$].

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(17) $Ru^{II}(H_2O)_6(tos)_2$ is moderately air sensitive (see ref 3), and all manipulations in this work were carried out in argon-purged, deionized water.

(18) $E_{1/2}$ values for $(NH_3)_5RuL^{3+/2+}$ vary from 0.6 to 1.35 V more positive for L = olefin than L = NH_3 while we only see stabilizations of 0.18-0.89 V more positive for $(H_2O)_5RuL^{3+/2+}$ for L = olefin versus L = H_2O. See ref 3a.

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Hole-Catalyzed Epoxidation

Nathan L. Bauld* and Gholam A. Mirafzal

Department of Chemistry and Biochemistry
The University of Texas at Austin
Austin, Texas 78712

Received December 20, 1990

The concept of the hole as a catalytic entity has proved exceptionally heuristic during the preceding decade. The power of this catalytic genre has been expressed especially effectively in the area of organic pericyclic chemistry.[1,2] The present communication describes the discovery and development of hole-catalyzed epoxidation, a new reaction that has a selectivity profile distinct from and in many respects superior to that of standard epoxidizing agents such as *m*-chloroperbenzoic acid (MCPBA). In addition to the potential synthetic value of the new reaction, the availability of an authentic hole-catalyzed epoxidation procedure promises a unique opportunity to evaluate hole-transfer mechanisms in biological and biomimetic epoxidation.[3-5]

trans-Stilbene (**1**) was selected as an appropriate substrate for screening various potential epoxidizing agents under hole-catalytic conditions [tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{2}^{\bullet+}$), dichloromethane (DCM), 0 °C]. That $\mathbf{2}^{\bullet+}$ is a sufficiently strong hole catalyst to generate $\mathbf{1}^{\bullet+}$ at a rate consistent with efficient hole-catalytic pericyclic chemistry has already been demonstrated in the context of the smooth cyclopropanation of $\mathbf{1}^{\bullet+}$ (via $\mathbf{2}^{\bullet+}/N_2CHCO_2Et$) under identical conditions.[6] Of further importance is the observation that competition from the hole-catalyzed cyclodimerization of **1** is minimal under the cyclopropanation conditions. With iodosylbenzene or various of its derivatives as the oxidant, epoxidation of **1** was indeed achieved, but the highest conversions to stilbene oxide were only ca. 20%. Spectroscopic studies of the compatibility of iodosylbenzene with $\mathbf{2}^{\bullet+}$ in the absence of **1** revealed rapid decomposition of the hole catalyst. An extensive search for catalyst-compatible epoxidants appeared discouraging except for selenium dioxide. Though relatively insoluble and not previously known to effect epoxidation, this common reagent was found to efficiently epoxidize a substantial range of readily ionizable substrates under hole-catalytic conditions (Table I). In the absence of $\mathbf{2}^{\bullet+}$, these substrates are inert to selenium dioxide at 0 °C. The reactions are exceptionally clean, producing none of the allylic hydroxylation or carbocation

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