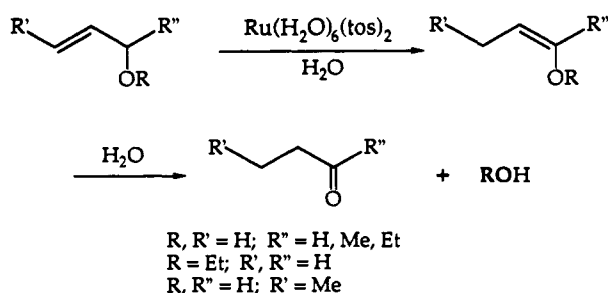


Scheme I



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 $\text{Ru}(\text{H}_2\text{O})_2(\text{C}_5\text{H}_7\text{O}_2)_2$ 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–OH₂ 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 $\text{Ru}(1\text{-}5\text{-}\eta^5\text{-C}_8\text{H}_{11})(\eta^1(\text{O}):\eta^2(\text{C},\text{C}')\text{-OCOCH}_2\text{CH}=\text{CH}_2)(\text{PMe}_3)_3$.¹⁶

All aqueous ruthenium(II) olefin complexes studied are active ROMP catalysts, demonstrating activity similar to that of $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$.² They also exhibit increased stabilization toward oxidation relative to the parent $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$ 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 complexes⁷ 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 penta-aquoruthenium(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 $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$ 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

(14) Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_8\text{Ru}$: C, 35.82; H, 5.41. Found: C, 35.64; H, 5.29.

(15) **6** crystallizes in space group $P2_12_12_1$ (D_{2h}^4 ; No. 19) with $a = 7.8085$ (12) Å, $b = 8.0452$ (10) Å, $c = 19.2704$ (28) Å, $V = 1210.6$ (3) Å³, and $D_{\text{calc}} = 1.840$ 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 $\text{GOF} = 1.04$ 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 $|F_o| > 6.0\sigma(F_o)$].

(16) Osakada, K.; Grohmann, A.; Yamamoto, A. *Organometallics* **1990**, *9*, 2092–2096.

(17) $\text{Ru}^{\text{II}}(\text{H}_2\text{O})_6(\text{tos})_2$ 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 $(\text{NH}_3)_5\text{RuL}^{3+/2+}$ 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 $(\text{H}_2\text{O})_5\text{RuL}^{3+/2+}$ for L = olefin versus L = H_2O . See ref 3a.

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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.

Hole-Catalyzed Epoxidation

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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 (**2**⁺), dichloromethane (DCM), 0 °C]. That **2**⁺ is a sufficiently strong hole catalyst to generate **1**⁺ at a rate consistent with efficient hole-catalytic pericyclic chemistry has already been demonstrated in the context of the smooth cyclopropanation of **1**⁺ (via **2**⁺/ $\text{N}_2\text{CHCO}_2\text{Et}$) 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 **2**⁺ 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 **2**⁺, 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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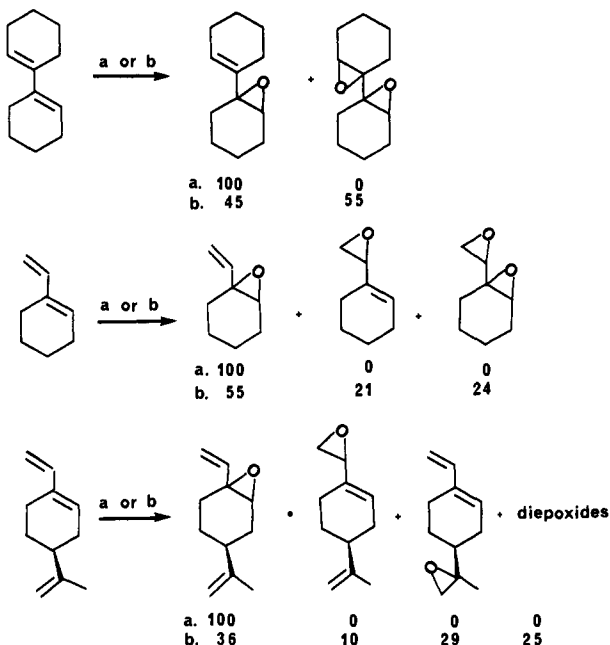
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(6) Bauld, N. L.; Stufflebeme, G. W.; Lorenz, K. T. *J. Phys. Org. Chem.* **1989**, *2*, 585–601.

Table I Aminium Salt/SeO₂ and BSA Epoxidation of Conjugated Substrates

substrate	oxidant	% yield, GC (isolated) ^a
(<i>E</i>)-stilbene	SeO ₂ ^b	80 (60)
(<i>Z</i>)-stilbene	SeO ₂	80 (58) ^c
1,1-diphenylethene	SeO ₂	70 (42)
β -methylstyrene	SeO ₂	62 (35)
α -methylstyrene	SeO ₂	65 (38)
(<i>Z</i>)-stilbene	BSA ^d	85 (65)
1,1'-bicyclohexenyl	BSA	83 (63)
1-vinylcyclohexene	BSA	76 (61)
4-isopropenyl-1-vinylcyclohexene	BSA	72 (56)

^aSilica gel column chromatography. ^bSubstrate (100 mol %), SeO₂ (500 mol %), Ar₃N⁺SbCl₆⁻ (20 mol %), dichloromethane, 0 °C to room temperature, 1 h. Quench with K₂CO₃/CH₃OH. ^cThe isolated epoxide is that of *trans*-stilbene. ^dSubstrate (100 mol %), BSA (100 mol %), Ar₃N⁺SbCl₆⁻ (20 mol %), DCM, 0 °C, 10 min. Quench with K₂CO₃/CH₃OH.

Scheme I^a

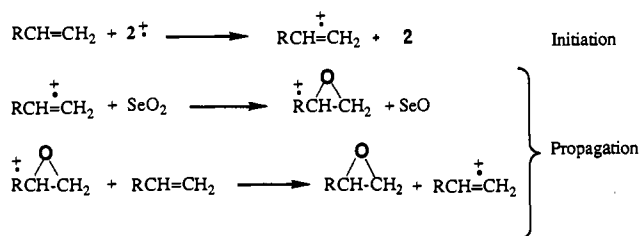
^a(a) Ar₃N⁺, BSA. (b) MCPBA, 0 °C.

type rearrangement products frequently observed in biomimetic epoxidation.⁵

Epoxidation of *cis*-stilbene and of conjugated dienes such as 1,1'-bicyclohexenyl, however, exposes the disadvantage of a relatively insoluble oxidant. *cis*-Stilbene is converted efficiently to *trans*-stilbene oxide, and the recovered stilbene is completely isomerized to the *trans* isomer, suggesting that *cis*-1⁺ has sufficient time, at low oxidant concentrations, to isomerize to *trans*-1⁺ prior to epoxidation.⁷ 1,1'-Bicyclohexenyl undergoes rapid hole-catalyzed cyclodimerization⁸ prior to epoxidation, although modest conversions to the dimer epoxide are observed. A subsequent search for a soluble selenoxide function containing epoxidant that is catalyst compatible identified benzeneseleninic anhydride (BSA) as a promising candidate. With BSA as the oxidant, *cis*-1 is efficiently and stereospecifically oxidized (85%) and 1,1'-bicyclohexenyl is selectively converted to the monomeric diene epoxide without producing detectable amounts (<1%) of diepoxide (Scheme I). In sharp contrast, the MCPBA oxidation of this diene yields at least 30% of the diepoxide even when the diene

(7) Lewis, F. D.; Bedell, A. M.; Dykstra, R. E.; Elbert, J. E.; Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 8055–8064. Inter alia, this work shows that the *cis*/*trans* isomerization of *cis*-stilbene occurring via a bimolecular mechanism involving *cis*-stilbene cation radicals is inhibited by oxygen.

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Scheme II^a

^aR = aryl or alkenyl.

is used in excess (1:0.6) at –20 °C. When a 1:1 ratio of diene/MCPBA is used, the diepoxide:monoepoxide ratio is 55:45. The outstanding selectivity of hole-catalyzed epoxidation is further illustrated by the hole-catalyzed epoxidations of 1-vinylcyclohexene and 4-isopropenyl-1-vinylcyclohexene. In both cases exclusive monoepoxidation is observed, and the endocyclic double bond of the conjugated diene moiety is selectively epoxidized. The corresponding MCPBA epoxidations, in contrast, are highly unselective.

Key observations that support the assignment of a hole-catalyzed (cation radical chain) mechanism (Scheme II) analogous to that previously proposed for cyclopropanation are as follows: (i) the epoxidations are typically accompanied by 5–10% of the hole-catalyzed cyclobutadimerization (in the case of stilbenes and styrene derivatives) or Diels–Alder dimerization (in the case of conjugated dienes) products, confirming the generation of substrate cation radicals; (ii) substrates that are outside the oxidation range of 2⁺ (e.g., simple alkenes, including 1-octene and norbornene) are inert under the hole-catalytic epoxidation conditions; (iii) the epoxidation reactions occur efficiently in the presence of excess 2,6-di-*tert*-butylpyridine, which is known to suppress Bronsted acid catalyzed reactions;⁹ and (iv) epoxidation can also be effected by other means of generating substrate cation radicals (e.g., photosensitized electron transfer using 1,4-dicyanobenzene/acetonitrile).¹⁰ In view of the stereospecific epoxidation of the stilbenes, an effectively concerted pericyclic mechanism is envisioned. Thermodynamic data¹¹ reveal that monooxygen transfer from selenium dioxide to a simple alkene (ethene) is highly exothermic (1.8 eV). Corrections for the effect of a conjugating phenyl substituent (0.2 eV) and for the hole (≤0.4 eV)^{12,13} reduce this exothermicity somewhat, but the substantially exothermic oxygen transfer to styrene and diene cation radicals is nevertheless confirmed.

The present results establish that epoxidation is an efficient and potentially stereospecific reaction mode of organic π cation radicals as would be required in a hypothetical hole-catalyzed biological/biomimetic epoxidation mechanism. The determination of whether such a mechanism is in fact operative, either generally or for a range of relatively oxidizable substrates, should be greatly facilitated by the availability of an authentic hole-catalyzed epoxidation reaction.

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Supplementary Material Available: Experimental details including preparations and analysis data including yields and PMR, LRMS, and HRMS (7 pages). Ordering information is given on any current masthead page.

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(10) Pabon, R. A., Jr.; Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1983**, *105*, 5158–5159.

(11) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; The University Press: Cambridge, U.K.

(12) The oxidation potential of styrene oxide is approximated by that of ethylbenzene (2.05 V vs SCE¹³). The oxidation potential of styrene cannot be less than 1.72 V (that measured for α -methylstyrene in this laboratory). The difference in hole energy between reactant and product in the styrene system is thus ≤0.33 V.

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