dried over $MgSO_4$. Removal of the solvents under vacuum yielded 4.1 g of benzyl-2,3,4,5-tetramethylcyclopentadiene as a mixture of tautomers as a clear yellow oil, in 90% yield. Compound **5** was purified by column chromatography on alumina and eluted with hexane: ^1H NMR (270 MHz, $CDCl_3$) δ 1.4 (3 H, s, CH_3), 1.62 (3 H, s, CH_3), 1.64 (3 H, d, CH_3), 1.71 (3 H, s, CH_3), 1.95 (1 H, q, CH), 2.82 (2 H, s, CH_2), 7.21–7.08 (5 H, m, Ar); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 9.27 (CH_3), 9.64 (CH_3), 19.29 (CH_3), 23.82 (CH_2), 37.98 (CH_2), 44.30 (CH), 48.04 (CH), 53.91 (CH_2), 122.17 (CH, Ar), 124.50 (CH, Ar), 125.67 (CH, Ar), 127.61 (CH, Ar), 129.89 (CH, Ar), 133.74 (C), 136.45 (C), 141.81 (C), 145.43 (C). Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.24; H, 9.60.

Preparation of 1,3-Bis(2,3,4,5-tetramethyl-1-oxocyclopent-2-en-5-yl)propane (6). In a manner similar to that outlined above 20.0 g of 2,3,4,5-tetramethylcyclopent-2-enone (145 mmol) in 20 mL of THF was added dropwise to a solution of LDA at 0 °C, prepared from 21 mL of diisopropylamine (150 mmol) and 92.5 mL of *n*-BuLi (1.6 M in hexanes, 148 mmol) in 50 mL of THF at 0 °C. This yellow solution was then refluxed for 12 h. The reaction mixture was cooled to room temperature, and the diisopropylamine and THF were removed under vacuum. The residue was taken up in 50 mL of THF, and the solution was cooled to 0 °C. A solution of 7.34 mL of 1,3-dibromopropane (72 mmol) in 20 mL of THF was then added dropwise over 1 h, and the reaction mixture refluxed for 48 h. The reaction was then cooled to room temperature, the solvent removed under vacuum, and the residue taken up in 50 mL of ether. The ether solution was then washed with two 20-mL portions of water and one 20-mL portion of saturated NH_4Cl solution. The aqueous layers were back-extracted with two 20-mL portions of ether. The ether layers were combined and dried over $MgSO_4$. Removal of the solvent under vacuum yielded a thick orange-yellow liquid. Unreacted enone **1** was removed by distillation between 25 and 60 °C (0.1 mmHg) to give 16.3 g (72% yield) of **6**: ^1H NMR (270 MHz, $CDCl_3$) δ 0.71 (6 H, s, CH_3), 0.81 (2 H, m, CH_2), 0.82 (6 H, d, CH_3), 1.18 (4 H, m, CH_2), 1.48 (6 H, s, CH_3), 1.80 (6 H, s, CH_3), 2.3 (2 H, m, CH); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 8.17 (CH_3), 14.19 (CH_3), 14.92 (CH_3), 19.40 (CH_2), 46.20 (CH), 49.55 (q, C), 133.48 (C), 171.52 (C), 213.38 (CO). Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.74; H, 10.24.

Preparation of 1,3-Bis(2,3,4,5-tetramethylcyclopentadienyl)propane (8). To a suspension of 2.0 g of $LiAlH_4$ (53 mmol) in 50 mL of ether at 0 °C was added 16.3 g of 1,3-bis(2,3,4,5-tetramethyl-1-oxocyclopenta-2-en-5-yl)propane (51.6 mmol) dissolved in 30 mL of ether over 30 min. The solution was stirred at 0 °C for 6 h, after which it was allowed to warm to room temperature and stirred an additional 3 h. The resulting reaction mixture was worked up as described above for the reduction of **3**. Upon removal of the solvent, the product was dissolved in 250 mL of benzene and 1.1 g of *p*-toluenesulfonic acid (5.76 mmol) was added. This solution was then fitted with a Dean–Stark trap and refluxed, with the removal of water, for 24 h. The product was then worked up as described above for **5** to afford 10.6 g (72%) as a light orange oil. Further purification was achieved on an alumina column eluted with hexane: ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (3 H, d, CH_3, J = 7.02 Hz), 1.04 (3 H, d, CH_3, J = 6.78 Hz), 1.35 (3 H, s, CH_3), 1.36 (3 H, s, CH_3), 1.71 (3 H, s, CH_3), 1.74 (3 H, brs, CH_3), 1.80 (3 H, s, CH_3), 1.20–1.85 (multiple signals representing CH_2 groups), 2.16 (2 H, m, CH); $^{13}C\{^1H\}$ NMR (67.5 MHz, $CDCl_3$) δ 9.81 (CH_3), 10.96 (CH_3), 11.23 (CH_3), 12.02 (CH_3), 12.58 (CH_3), 17.16 (CH_3), 19.08 (CH_3), 20.36 (CH_3), 21.83 (CH_3), 39.87 (CH_2), 46.74 (CH), 49.33 (CH), 50.58 (CH_2), 55.67 (CH_2), 131.14 (olefinic), 134.27 (olefinic), 137.73 (olefinic), 140.45 (olefinic), 143.21 (olefinic), 144.81 (olefinic). Anal. Calcd for $C_{21}H_{32}$: C, 88.66; H, 11.34. Found: C, 88.47; H, 11.34.

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Registry No. **1**, 54458-61-6; **2**, 108344-82-7; **3**, 108344-69-0; **4**, 108344-70-3; **5**, 108344-81-6; **6**, 108344-71-4; **6**(two-carbon chain analogue), 108344-72-5; **7**, 108344-73-6; **8**(isomer 1), 108344-74-7; **8**(isomer 2), 108344-75-8; **8**(isomer 3), 108344-76-9.

Selective Addition of Methanol to 1,2-Epoxy-1-vinylcyclopentane

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The chemical properties of simple oxiranes (epoxides) are well established. Such investigations have been prompted not only by the versatility of oxiranes as synthetic intermediates[1] but also by an interest in their biological activities.[2] However, the reactions of vinyloxiranes, which present four contiguous carbon atoms[3] for potential reactions, have not been studied as thoroughly.[1] Reactions of vinyloxiranes with carbanions can afford primarily products of either δ addition (via copper species)[4] or α,β addition (via alkyl- or aryllithiums).[5] Regiochemistry of Grignard reagent addition is a function of the reagent, substrate or conditions used.[6] Amines or some oxygen nucleophiles, in the presence of certain aluminum species,[7] and thiols[8] give α,β addition products, although the latter also can undergo conjugate addition. We have probed the reactivity of vinyloxiranes with methanol in the presence of mercuric salts using 1,2-epoxy-1-vinylcyclopentane (**1**) as a model compound. The addition of methanol occurs regioselectively and is stereospecific.

In these studies, solutions of **1** in methanol were reacted first with either mercuric acetate (**2**) or mercuric nitrate (**3**) and then with sodium borohydride. Although **2** and **3** are standard reagents for routine solvomercurations of olefins,[9] they differ considerably in their reactivity with some substrates. For example, oxymercuration of conjugated dienes affords the α,β- or α,δ-addition products with **2** or **3**, respectively.[10] Furthermore, the ratio of syn/anti ring openings of substituted phenylcyclopropanes is greater when mercuric nitrate (**3**) is substituted for mercuric acetate (**2**).[11] We thought that such differences, which are attributed to the greater ionic character of **3**,[12] might also be manifested upon reaction of these salts with **1**.

Gas chromatography–mass spectrometry (GC/MS) was used for an initial analysis of the reaction products. The molecular ion and fragmentation pattern of each compound were determined and compared with those of their deuteriated analogues obtained from reactions utilizing deuteriomethanol and reactions utilizing sodium borodeuteride. Additionally, products with acidic protons were

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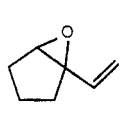
Table I. Product Distribution from the Reaction of 1,2-Epoxy-1-vinylcyclopentane with Mercuric Salts Followed by Treatment with Sodium Borohydride

compd[a]	mercuric acetate (2) 25 °C (36 h)	mercuric acetate (2) 65 °C (1 h)	mercuric nitrate (3) 25 °C (30 min)
1	5	16	
4a	50	60	
4b	22	12	
5	1	*b*	88
6	13	*b*	
7a			9
7b			2
uncharacterized	8	11	1

[a] Listed in order of elution from a DB-5 glass capillary column. [b] Trace.

identified by a change in their position in the total ion chromatogram upon prior silylation of the reaction mixture.[13] Although these products are too volatile for combustion analysis, low-resolution GC/MS (chemical ionization) indicates that most of the products are formed from the addition of one 1 or 2 equiv of methanol to 1 ($C_7H_{10}O$), as masses of 143 (calcd for $C_8H_{15}O_2$, 143) and 175 (calcd for $C_9H_{19}O_3$, 175) respectively, were found. The above conclusions were consistant with high-resolution GC/MS analysis of several reaction products.

The products of the reaction of 1 vary dramatically as a function of the mercuric salt used (Table I). Because methanolic solutions of 1 are stable (as analyzed by VPC) for many weeks, any adduct formed by the addition of methanol to a molecule of 1 must involve a mercuric salt. Reaction at room temperature with 2 afforded primarily products from oxymercuration of the double bond; i.e., Markovnikov (γ) addition of methanol to form compounds 4 and 6. This was particularly evident in the off-resonance decoupled spectra of 4 and 6, in which the olefinic signals of 1 were replaced by a doublet and a quartet upfield. Similar yields of 4 and 6 were obtained when the reaction conditions were 1 h in refluxing methanol; extending the time to 4 h produced mostly higher molecular weight material (GC/MS) that was not characterized further.



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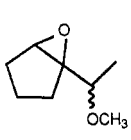
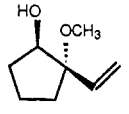


4a,4b



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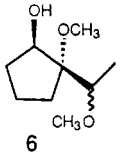
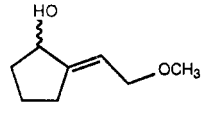
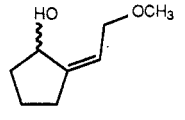


6



7a



7b

In contrast to 2, the reaction of 1 with 3 resulted almost exclusively in a rapid opening of the oxirane ring to form compounds 5 and 7 (Table I). ^{1}H NMR was invaluable in characterizing 5, the major product of this reaction (Table II). The presence of a secondary alcohol in 5 was established firmly by a shift downfield of 1.0 ppm for the carbinol proton upon reaction with trichloroacetyl isocyanate.[14] Additionally, irradiation of the proton attached to the carbinol carbon produced a weak (1%) nuclear Overhauser effect (NOE)[15] on the methoxy signal, whereas no NOE was detected upon irradiation of the olefinic region. These data indicate that diastereomerically pure 5 is formed only via a trans opening of the oxirane ring. Extending the time of this reaction to several hours resulted in the formation of mostly higher molecular weight material.

The concept of steric compression in the ^{13}C NMR spectra of (*Z*)-olefins was used for assigning for geometry of the S_N2' products 7a and 7b.[16] The carbinol carbon resonated considerably upfield for the *Z* isomer 7b (70.91 vs. 75.06 ppm), whereas a similar difference (32.28 vs. 26.75 ppm) was noted for the comparable adjacent methylene ring carbon, C-3, of the *E* isomer 7a.

Discussion

Several features aid in interpreting the results observed in the reactions of mercuric acetate (2) or mercuric nitrate (3) with 1, the vinyloxirane. (1) There is a difference in the ligand binding in 2 and 3; 3 is considerably more ionic than 2.[12] (2) Another key feature is the stability of methanolic solutions of 1, as noted earlier. (3) Since both of the mercuric salts are used routinely for oxymercurations, the entrance of olefins into their coordination spheres is established. (4) The nitrate reacts faster than the acetate in oxymercuration reactions with comparable substrates.[9d] Thus, 3 should react with olefins similarly to 2, although perhaps, somewhat faster. (5) Finally, the reactive moiety probably is a metallic species; acid formation from the ligands is negligible.[17]

In light of the above features, this study indicates that the acetate 2 participates in a standard oxymercuration reaction with 1, whereas the nitrate 3 promotes an opening of the oxirane ring; both reactions proceed under mild conditions. Formation of the oxymercuration products 4a and 4b from 1 using 2 result almost exclusively from reaction at the double bond to give Markovnikov (γ) addition of methanol. The same regiochemistry (γ addition) for hydration of 3,4-epoxy-1-butene occurs in oxymercuration reactions involving 2.[18] Intramolecular assistance involving the oxirane oxygen occurs during some reactions of vinyloxiranes using 2;[19] this assistance depends on the molecular geometry of the system studied, as such effects were not detected in either our system or the 3,4-epoxy-1-butene study.[18] Additionally, although the ratio of diastereomer formation for the γ-hydrated adducts in the latter study[18] is not reported, the formation of 4a and 4b in a 5:1 ratio here indicates a preferred side of the intermediate adduct for attack by methanol. These results suggest the possibility of considerable control over the absolute stereochemistry of substituents introduced at the γ position in enatiomerically pure vinyloxiranes.[20] This is consistant with stereospecific additions reported for other solvomercuration reactions involving simple double bonds.[9]

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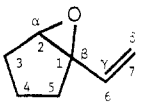
Table II. ^1H and ^{13}C Chemical Shifts[a] for the Products of the Reaction of 1,2-Epoxy-1-vinylcyclopentane (1) with Mercuric Salts



1

compd	H_2	H_6	H_7	C_1	C_2	C_6	C_7	C_5
1	3.35	5.86	5.3	66.5	65	136	117	
4a	3.25	3.41	1.22	69.98	57.13	77.20	17.26	
4b	3.25	3.41	1.22	68.22	63.19	75.15	16.88	
5	3.85	5.89	5.4	89.32	78.68	137.07	119.18	
6	3.30	3.48	0.96	85.43	76.22	87.03	12.81	
7a	4.71	5.66	4.18	149.47	75.06	119.34	69.87	32.28
7b	4.40	5.65	3.90	151.76	70.91	120.03	69.56	26.75

[a] Chemical shifts are in ppm relative to tetramethylsilane. [b] The numbering scheme for this table is based on that for the vinyloxirane 1 skeleton shown above.

In contrast to 2, mercuric nitrate (3) appears to act as a Lewis acid, reacting preferentially with the oxirane oxygen to polarize the β C–O bond sufficiently to afford a rapid ring opening by methanol. Other Lewis acids have been used to assist ring opening in simple oxiranes, although stronger Lewis acids are typically the reagents used.[21] The trans ring opening to produce 5, the major product of this reaction, but not the corresponding cis isomer, indicates that an allylic carbocation intermediate is not involved in the ntirate salt reactions with 1. However, substitution by a methoxy group at the more hindered, quarternary site to afford 5 suggests that allylic stabilization of some charge development occurs (primarily at the β position) in the transition state for these reactions. The exclusive trans ring opening indicates that rigorous control over the absolute stereochemistry of a methoxy group introduced at the β position of the vinyloxirane system is possible in appropriate chiral starting materials. Finally, the preferred formation of the *E* isomer in the S_N2' reaction is consistent with other reports of conjugate additions to vinyloxiranes.[5,6,8]

In summary, we have demonstrated regiocontrol for the stereoselective addition of a methoxy group to either the β position or the γ position of vinyloxirane 1 using mercuric nitrate (3) or mercuric acetate (2), respectively. Since several methods have been reported recently[22] for the preparation of vinyloxiranes, including those involving asymmetric epoxidation of allylic alcohols,[23] both processes reported here for methanol addition should be useful in introducing such functionality in these substrates.

Experimental Section

Materials and Methods. *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA, Tridom/Fluka), mercuric acetate, sodium borohydride (MC/B), mercuric nitrate (Aldrich), sodium borodeuteride (ICN), and trichloroacetyl isocyanate (Kodak) were reagent grade, and *m*-chloroperoxybenzoic acid (*m*-CPBA, Aldrich) was technical grade; all were used as received. Methanol (Fisher, pesticide grade) was distilled under an atmosphere of dry argon from calcium hydride shortly before use as a reaction solvent. NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 spectrometer or, where indicated, a Varian FT-80 A. Internal $CHCl_3$ (7.24 ppm) in ^1H NMR samples was utilized as the standard; data are reported as chemical shift in ppm (multiplicity, relative area of integration). For ^{13}C NMR samples, $CDCl_3$ (77.0 ppm) was used as the standard; data are reported as chemical shift in ppm (peak multiplicity in off-resonance decoupled spectrum). Electron-impact (EI) or chemical-ionization (CI/NH_3) MS (GC/MS) were recorded on a Ribermag R10-10 (low-resolution) mass spectrometer equipped with a DB-5 capillary column (30 m × 0.25 mm) or a V6-ZAB double focusing high-resolution mass spectrometer; only the major or diagnostically important peaks are reported as *m/e* (relative intensity). Analytical chromatography (VPC) was performed on a Girdel Series 300 gas chromatograph equipped with a flame-ionization detector and a DB-5 capillary column. Preparative centrifugal thin-layer chromatography (PCTLC) was performed on a Harrison Model 7924 Chromatotron using either silica gel 60 PF-254 or alumina 60 GF-254, neutral (Merck) containing $CaSO_4 \cdot {}^1/_2H_2O$ binder for reactions involving mercuric acetate or mercuric nitrate, respectively. Chromatographic solvents (methanol, methylene chloride, and pentane; Fisher, pesticide grade) were used as received.

1,2-Epoxy-1-vinylcyclopentane (1).[24] The dehydration of 1-vinylcyclopentanol[25] in methylene chloride with a catalytic amount of *p*-toluenesulfonic acid afforded 1-vinylcyclopentene.[26] Treatment of 28.2 g (300 mM) of 1-vinylcyclopenetene with *m*-CPBA (49.2 g, 285 mM), and purification by fractional vacuum distillation [56 °C (35 mmHg)] afforded 6.3 g (19% yield) of 1 in greater than 99% purity (VPC analysis).

Treatment of 1,2-Epoxy-1-vinylcyclopentane with Mercuric Salts. To compound 1 (1 mL, 8.7 mM) in 5 mL of methanol was added mercuric salts 2 or 3 (9.6 mM) under argon, and the reactions were stirred until the product distribution had stabilized. For the reaction of 1 with the acetate 2, sodium borohydride (0.35 g, 9.3 mM) then was added and the mixture stirred at 0 °C until vigorous bubbling had ceased. The reaction mixtures for both salts then were filtered through glass wool, concentrated by distilling solvent, and isolated by PCTLC using an increasing gradient of methylene chloride (0.1% methanol) in pentane. Yields were determined by VPC analysis of the reaction mixtures. For silylation reactions,[13] a 1:1 mixture of BSTFA/pyridine (200 μL) was allowed to stir overnight at room temperature under argon with 10 μL of the reaction mixture.

1,2-Epoxy-1-(1-methoxyethyl)cyclopentane (4a,b). The two diastereomers were isolated as mixtures enriched in either 4a or 4b, from the reaction of 1 with 2 at room temperature; they could not be differentiated on the basis of their ^1H NMR spectra: 3.41 (q, J = 7 Hz, 1 H), 3.40 (s, 3 H), 3.25 (brs, 1 H), 1.98 (dd, J_1 = 13 Hz, J_2 = 8 Hz, 1 H), 1.89 (dd, J_1 = 13 Hz, J_2 = 8 Hz, 1 H), 1.75–1.65 (m, 1 H), 1.59 (m, J = 8 Hz, 2 H), 1.44 (m, J = 8 Hz, 1H), 1.22 (d, J = 7 Hz, 3 H).

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4a: ^{13}C NMR 77.20 (d), 69.98 (s), 59.63 (q), 57.13 (d), 27.31 (t), 25.04 (t), 19.12 (t), 17.26 (q).

4b: ^{13}C NMR: 75.15 (d), 68.22 (s), 63.19 (d), 56.71 (q), 27.05 (t), 24.13 (t), 18.83 (t), 16.88 (q).

Both diastereomers, separated with base line resolution by GC/MS (50 °C/15 min/5 °C/200° C), produced identical mass spectra: EIMS, *m/e* 127 (2), 85 (100); CI/NH_3, *m/e* 160 (5, M + 18), 143 (60, M + 1), 85 (100).

2-Methoxy-2-vinylcyclopentanol (5). This compound was isolated from the reaction of **1** with **3** at room temperature: ^1H NMR 5.89 (dd, J_1 = 17 Hz, J_2 = 11 Hz, 1 H), 5.5–5.3 (m, 2 H), 3.85 (brs, 1 H), 3.15 (s, 3 H), 2.1–1.5 (m, 6 H); ^{13}C NMR 137.07 (d), 119.18 (t), 89.32 (s), 78.68 (d), 50.66 (q), 31.28 (t), 27.62 (t), 19.70 (t); EIMS, *m/e* 143 (0.08, M + 1), 142 (0.05, M^+), 141 (0.2, M–1), 85 (100); CI/NH_3, *m/e* 160 (5, M + 18), 143 (1, M + 1), 142 (2, M^+), 86 (100); high-resolution (CI/NH_3), *m/e* 143.10712 (calcd for $C_8H_{15}O_2$ 143.10682)

2-Methoxy-1-(1-methoxyethyl)cyclopentanol (6). This compound was isolated from the reaction of **1** with **2** at room temperature: ^1H NMR 3.48 (q, J = 5 Hz, 1 H), 3.30 (d, J = 3 Hz, 1 H), 3.22 (s, 3 H), 3.14 (s, 3 H), 1.60 (m, 4 H), 1.35 (m, 2 H), 0.96 (d, J = 5 Hz, 3 H); ^{13}C NMR 87.03 (d), 85.43 (s), 76.22 (d), 56.24 (q), 56.04 (q), 31.91 (t), 27.55 (t), 20.44 (t), 12.81 (q); EIMS, *m/e* 142 (10), 59 (100); CI/NH_3, *m/e* 192 (3, M + 18), 175 (99, M + 1), 157 (100); high-resolution (CI/NH_3), *m/e* 175.1334 (calcd for $C_9H_{19}O_3$ 175.1331)

(*E*)-2-[(Methoxymethyl)methylene]cyclopentanol (7a) and (*Z*)-2-[(Methoxymethyl)methylene]cyclopentanol (7b). These isomers were isolated from the reaction of **1** with **3** at room temperature.

7a: ^1H NMR (80 MHz) 5.66 (dd, J = 5, 1 Hz, 1 H), 4.71 (brs, 1 H), 4.18 (m, 2 H), 3.47 (s, 3 H), 2.2–1.3 (m, 6 H); ^{13}C NMR 149.47 (s), 119.34 (d), 75.06 (d), 69.87 (t), 57.95 (q), 34.97 (t), 26.75 (t), 21.55 (t); EIMS, *m/e* 127 (9), 110 (42), 97 (36), 67 (100); CI/NH_3, *m/e* 143 (5, M + 1), 142 (20, M^+), 125 (100).

7b: ^1H NMR (80 MHz) 5.65 (brs, 1 H), 4.40 (brs, 1 H), 3.93 (dd, J = 7, 1 Hz, 2 H), 3.30 (s, 3 H), 2.2–1.3 (m, 6 H); ^{13}C NMR 151.76 (s), 120.03 (d), 70.91 (d), 69.56 (t), 57.82 (q), 35.53 (t), 32.28 (t), 22.87 (t); EIMS, *m/e* 127 (2), 110 (34), 97 (80), 67 (100); CI/NH_3, *m/e* 143 (2, M + 1), 142 (23, M^+), 125 (100).

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Oxidation of *o*-Nitrobenzeneselenenic Acid by Hydrogen Peroxide in Alkaline Solution[1]

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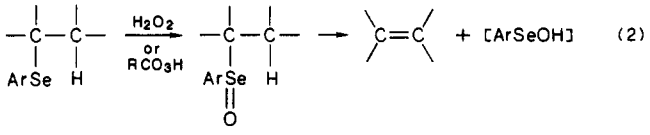
In contrast to most other areneselenenic acids (ArSeOH), solutions of *o*-nitrobenzeneselenenic acid, **1a** (Ar = *o*-$O_2NC_6H_4$) are sufficiently stable that study of the mechanisms of its reactions can be done in a straightforward fashion. The objective of this and earlier studies[2] has been to use **1a** as a substrate to obtain information about the the mechanisms of some of the principal reactions of areneselenenic acids.

Oxidation of an areneselenenic acid to the corresponding seleninic acid by a peracid or hydrogen peroxide (eq 1) is

$$\mathrm{ArSeOH} \xrightarrow[\text{or } \mathrm{RCO_3H}]{\mathrm{H_2O_2}} \mathrm{ArSeO_2H} \qquad (1)$$

a reaction that is important as an adjunct to the synthetically useful formation[3] of alkenes by oxidative elimination of alkyl aryl selenides (eq 2). It is customary to



(2)

employ a sufficient excess of oxidant so that the selenenic acid liberated in eq 2 is oxidized to the seleninic acid and is thereby prevented from adding to the alkene double bond (ArSeOH + >C=C< → >(ArSe)C–C(OH)<).

In previous work[2b] the mechanism of the oxidation of **1a** by hydrogen peroxide in acid solution was determined. The present paper deals with the mechanism of the much more rapid oxidation that takes place in alkaline solution.

Results and Discussion

Preliminary experiments revealed that **1a** is oxidized by hydrogen peroxide in alkaline solution much faster than in acid solution. Isolation of *o*-$O_2NC_6H_4SeO_2H$ in 80% yield after acidification of the reaction solution established that the stoichiometry of the oxidation was the same.

The kinetics of the oxidation were studied in water at 25 °C in a series of buffers and dilute sodium hydroxide solutions covering a pH range from 6.5 to 13.0. Hydrogen peroxide (0.004–0.008 M) was present in large stoichiometric excess over **1a** (10^{-4} M). At pHs below the pK_a of **1a** (10.4)[4] the progress of the oxidation was monitored at λ_{max} for *o*-$O_2NC_6H_4SeOH$; at higher pHs the λ_{max} for the anion of **1a**, *o*-$O_2NC_6H_4SeO^-$, was used. At either wavelength plots of log ($A - A_\infty$) vs. time were linear. At each

Table I. Kinetics of the Oxidation of *o*-Nitrobenzeneselenenic Acid by Hydrogen Peroxide in Neutral and Alkaline Solution in Water at 25 °C[a]

buffer or solution	pH[b]	$k_1/C_{H_2O_2}$,[c] M^{-1} s^{-1}
0.05 M KH_2PO_4 plus 0.014 M NaOH	6.5	0.0041 ± 0.0001
0.05 M KH_2PO_4 plus 0.029 M NaOH	7.0	0.0131 ± 0.0005
0.05 M KH_2PO_4 plus 0.041 M NaOH	7.5	0.029 ± 0.003
0.05 M KH_2PO_4 plus 0.0467 M NaOH	8.0	0.086 ± 0.002
0.025 M $NaHCO_3$ plus 0.004 M NaOH	9.5	3.26 ± 0.06
0.025 M $NaHCO_3$ plus 0.011 M NaOH	10.0	7.5 ± 0.4
0.025 M $NaHCO_3$ plus 0.018 M NaOH	10.5	9.5 ± 0.2
0.025 M Na_2HPO_4 plus 0.005 M NaOH	11.1	11.4 ± 0.6
0.025 M Na_2HPO_4 plus 0.011 M NaOH	11.5	8.3 ± 0.6
0.025 M Na_2HPO_4 plus 0.027 M NaOH	12.0	3.9 ± 0.2
0.032 M NaOH	12.5	1.74 ± 0.08
0.10 M NaOH	13.0	0.43 ± 0.02

[a] Initial concentration of **1a**, 0.0001 M; $C_{H_2O_2}$ from 0.004 to 0.008 M. [b] pHs of buffer solutions are from *Handbook of Chemistry and Physics*, 60th ed.; CRC Press: Boca Raton, FL, p D-148. [c] Average of from two to four runs at each pH.

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