

Stereochemistry of Selenium Dioxide Oxidation of Cyclohexenyl Systems<sup>1</sup>EDWARD N. TRACHTENBERG AND JANE RUMFORD CARVER<sup>2</sup>

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The allylic oxidation of a series of alkylated cyclohexenes by selenium dioxide in wet dioxane at high olefin to selenium dioxide ratios has been found to proceed stereoselectively. The conversions of 1,4-dimethylcyclohexene into 2,5-dimethylcyclohex-2-en-1-ol and of *cis*-3,5-dimethylcyclohexene into 1,5-dimethylcyclohex-2-en-1-ol both favor the axial alcohol by 70–75%, whereas the conversion of limonene into carveol and *trans*- $\Delta^2$ -octalin into *trans*- $\Delta^2$ -octalol-1 show slightly lower steric preference for the axial product. The oxidation of 3,3,5-trimethylcyclohexene to 4,4,6-trimethylcyclohex-2-en-1-ol shows the highest stereospecificity with the axial alcohol favored by over 90%. By contrast, oxidation of *cis*-3,5-dimethylcyclohexene to *cis*-4,6-dimethylcyclohex-2-en-1-ol and of 3-methylcyclohexene to 4-methylcyclohex-2-en-1-ol shows very little stereoselectivity and, indeed, in the latter case slightly favors equatorial product. It has also been found from studies of limonene, 3-methylcyclohexene, and *cis*-3,5-dimethylcyclohexene that attack at tertiary allylic sites may be preferred over that at methylene, in contrast to previous literature reports. These results bear on the mechanism of selenium dioxide oxidation of olefins.

Although most of the synthetically useful applications of selenium dioxide oxidation of organic compounds lead to the introduction of carbonyl groups or other unsaturation<sup>3</sup> and, therefore, do not ordinarily introduce new asymmetric centers, the oxidation of olefins to allylic alcohols, or their derivatives, may involve the creation of a new asymmetric center. The stereochemistry of this process has received inadequate attention although there are a few interesting results in the literature. Thus, Fieser has shown that methyl  $\Delta^3$ -cholenate gives approximately equal yields of the methyl 3 $\alpha$ - and 3 $\beta$ - $\Delta^4$ -cholates along with some of the expected methyl  $\Delta^3$ -choladienate.<sup>4</sup> By contrast, he also found that  $\Delta^7$ -cholestanyl acetate gives only the 7 $\alpha$ -acetoxy- $\Delta^8$ - $\Delta^7$ -cholestanyl acetate.<sup>5</sup> In both of these cases, the products are allylically rearranged. Sakuda also observed some stereoselectivity in the oxidation of a number of monoterpenes. The tertiary carbinols found among the products of selenium dioxide oxidation of dihydrocarveol,<sup>6</sup> isopulegol,<sup>7</sup> and  $\beta$ -terpineol<sup>8</sup> all are formed stereoselectively. However, in each case the product has that stereochemistry which permits the molecule to assume the most stable conformation. Because the products are tertiary allylic alcohols capable of ready ionization and stereochemical equilibration, the result is of limited significance.

The first indication that the reaction proceeds stereoselectively is to be found in the work of Zacharewicz on 3-*p*-menthene.<sup>9</sup> Unfortunately, he did not elucidate the stereochemistry of the 3-*p*-menthen-5-ol which he obtained and characterized as a phthalate. Later workers, however, obtained the same material by other methods and demonstrated that it has *trans* stereochemistry.<sup>10</sup> More recently, Suga has shown

that the oxidation of 3-*p*-menthene with selenium dioxide in acetic acid-acetic anhydride gives a mixture of the *trans*-3-*p*-menthen-5-ol and its acetate along with a lesser yield of 3-*p*-menthen-5-one,<sup>11</sup> and Wiberg in a similar oxidation of 1-*p*-menthene obtained *trans*- and *cis*-carvotanacetol acetate in a 3:2 ratio.<sup>12</sup> Schaefer has reported that selenium dioxide oxidation of a mixture of 3- and 4-methylcyclohexene gives a complex mixture of ketones, alcohols, and *n*-butyl ethers.<sup>13</sup> Reduction of the ethers revealed that the 2-, 3-, and 4-methylcyclohexyl *n*-butyl ethers are formed stereoselectively with the *cis*-2, *trans*-3, and *cis*-4 products predominating by about 4:1. Finally, oxidation of the sesquiterpene,  $\beta$ -cyclodihydrocostunolide, has been shown to yield the 3 $\alpha$ -hydroxy product.<sup>14</sup>

The stereochemical results involving the formation of secondary carbinols are more significant than those of Sakuda resulting in the formation of tertiary alcohols for two reasons. First, the former products in many cases are the presumably less stable pseudoaxial allylic alcohols, although it should be recognized that the pattern of greater stability for equatorial over axial groups, so well established in cyclohexane chemistry,<sup>15</sup> cannot blindly be extended to cyclohexene systems.<sup>16</sup> Second, there is more likelihood that the former products represent the stereochemistry of the reaction rather than just reflect the result of some post-reaction equilibration process. However, the few cases studied involve a variety of conditions with respect to both solvent and temperature, and, in one case, study of a mixture rather than of a pure olefin.

We wish here to report on the systematic study of the selenium dioxide oxidation of a variety of alkylated cyclohexene systems in refluxing wet dioxane at high (4:1 or 8:1) olefin/oxidant ratios. Under these conditions, one obtains mostly allylic alcohols although

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$\alpha,\beta$ -unsaturated carbonyl compounds are also produced in some cases. We were concerned mostly with the stereochemistry of the process, but our studies also produced new evidence on the order of preference for attack at secondary and tertiary allylic positions. Guillemonat, in a classic study of selenium dioxide oxidation of olefins, established the rule that methylene is attacked more readily than methine in systems in which the two positions are equivalent with respect to other rules regarding site of attack.<sup>17</sup> However, this work antedated modern techniques of gas chromatographic separation, and his conclusion is questionable.

The compounds chosen for study were 1,4-dimethylcyclohexene (1), limonene (2), 3-methylcyclohexene (3), *cis*-3,5-dimethylcyclohexene (4), 3,3,5-trimethylcyclohexene (5), and *trans*- $\Delta^2$ -octalin (6). Compound 1 was readily prepared by the acid-catalyzed dehydration of commercially available 2,5-dimethylcyclohexanol. Compound 2 is commercially available. Compound 3 could be obtained by purification of commercially available material and 4 more tediously by the acid-catalyzed dehydration of a commercial mixture of *trans,trans*-3,5-dimethylcyclohexanol and *cis,cis*-3,5-dimethylcyclohexanol. Some double-bond migration occurs during the dehydration, but the resultant products which contain a trisubstituted double bond can be selectively removed by oxidation with selenium dioxide. It has long been known that trisubstituted double bonds are more readily oxidized than disubstituted ones.<sup>17,18</sup> Compound 5 was made by the acid-catalyzed dehydration of commercially available 3,3,5-trimethylcyclohexanol, and compound 6 was prepared by a three-step synthesis reported by Johnson starting with butadiene and *p*-benzoquinone.<sup>19</sup>

Initial separation of the products of the selenium dioxide oxidation of these olefins was effected by vacuum fractionation to yield a highly volatile fraction consisting of unreacted olefin, dioxane, and water, a less volatile fraction consisting of allylic alcohols,  $\alpha,\beta$ -unsaturated carbonyl compounds (and, in the case of relatively involatile substrates, unreacted olefin), and a residue consisting of organoselenium compounds and metallic selenium. The relative yields of oxidation products were determined by glpc analysis of both the crude and fractionated products; the values agreed within experimental error indicating lack of isomerization during distillation.

Identification of the oxidation products was achieved by a combination of elemental analysis, infrared (ir) and nuclear magnetic resonance (nmr) spectroscopy, and chemical conversion into known compounds or into newly synthesized reference compounds of assured structure and stereochemistry. Particular use was made of the fact that, in an epimeric pair of 2-cyclohexenols, a dilute solution in carbon tetrachloride of the compound with a pseudoaxial hydroxyl shows more intense ir absorption at the intermolecularly hydrogen-bonded O-H stretching frequency around 3350 cm<sup>-1</sup>. Identification of this stretching mode is possible not only from its frequency but also from its concentration dependence. It should be noted that,

whereas cyclohexanols with frozen conformation can be clearly identified as axial or equatorial on the basis of their respective C-O stretch at 996-1036 and 1037-1044 cm<sup>-1</sup>,<sup>20</sup> the spectra of cyclohexanols capable of chair-chair interconversion are frequently more complex in that bands may either be shifted or else new bands may appear.<sup>21</sup> Even then, the equatorial alcohols usually show C-O stretch at higher frequencies than their epimers. However, this generalization does not hold up in the case of 2-cyclohexenols such as those of most concern in the present study.<sup>22</sup>

The fact that the nmr signal for axial protons in cyclohexanes is found at higher field than that for the corresponding equatorial hydrogen<sup>23</sup> is not found to be generally true for the pseudoaxial and pseudoequatorial protons of 2-cyclohexenols. The chemical-shift difference is smaller and inversions in order are found. A much more reliable method for assigning configuration of epimeric carbinol (H-C-OH) protons depends on differences in their coupling behavior, the identification of the signal due to the proton in question being easily made because of the downfield shift caused by the hydroxyl. Because of its more favorable geometry, a pseudoaxial allylic proton is more strongly coupled to an adjacent vinyl proton, the increased complexity of the signal due to the latter being clearly evident in a comparison of the spectra of two epimeric 2-cyclohexenols. On the other hand, a pseudoaxial allylic proton, because of its more favorable geometry, is much more strongly coupled to an axial homoallylic proton, leading to a broader and more complex pattern for both. Although the signal for the homoallylic protons is usually obscured by the presence of other proton absorptions in the same region, the increased complexity of the pseudoaxial allylic proton signal is clearly defined. It is interesting to note that the center of the vinylic proton multiplet in a 2-cyclohexenol bearing a pseudoaxial hydroxyl is consistently at lower field than that of its epimer. This may be due to greater ionicity of the pseudoaxial carbinol and concomitantly greater deshielding of the vinylic proton in that case.

In addition to these spectroscopic methods, great use was made of the fact that lithium aluminum hydride reduction of cyclohexanones is stereoselective and gives an overwhelming preponderance of equatorial alcohol. There are some exceptions to this as in the case of 3,3,5-trimethylcyclohexanone which yields slightly more of the *trans*- than of the *cis*-3,3,5-trimethylcyclohexanol.<sup>24</sup> Nevertheless, the generalization that most cyclohexanones and 2-cyclohexenones give the thermodynamically more stable equatorial product on reduction with lithium aluminum hydride is usually valid<sup>25</sup> and has proved useful in this study in establishing the configuration of the 2-cyclohexenols and their catalytic reduction products.

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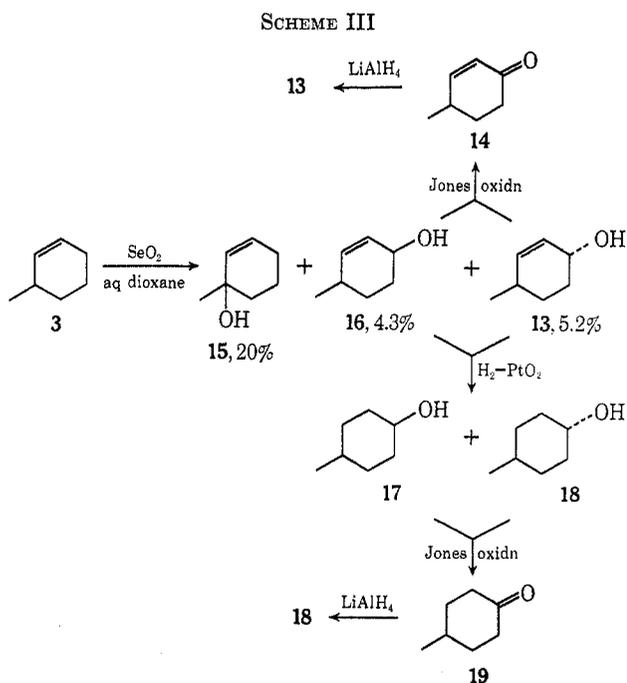
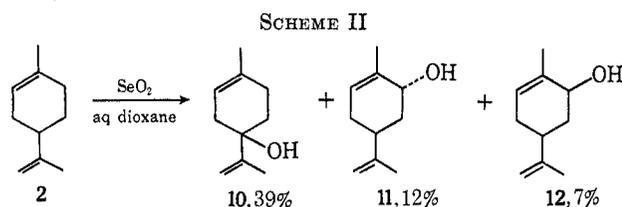
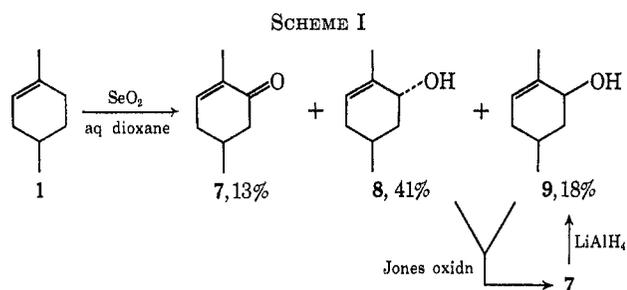
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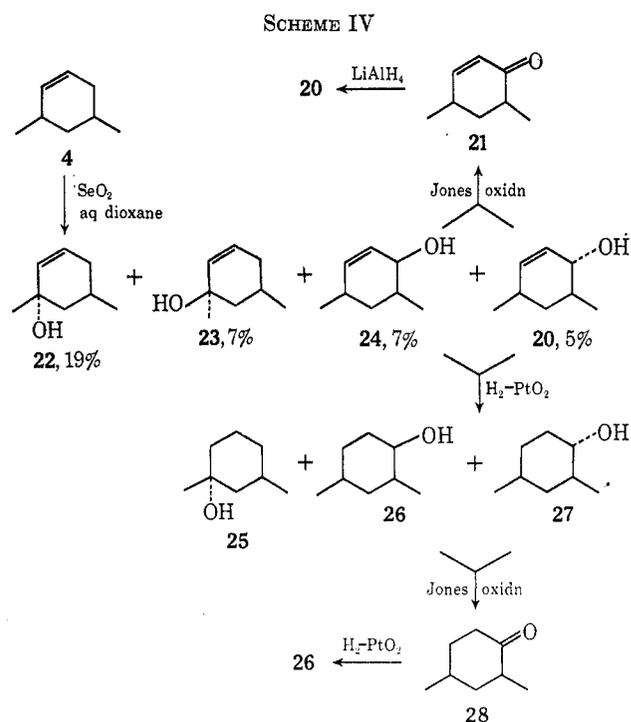
## Results and Conclusions

The results of the selenium dioxide oxidation of compounds 1-6 are shown in Schemes I-VI, respec-



tively. The yields given are based on olefin consumed. Also included in each scheme are those chemical conversions which were performed to establish the structure and stereochemistry of the products. In each case, this involved conversion either into compounds of already proven structure or into compounds whose structures could be deduced from their method of synthesis and their ir and nmr spectra. In some cases, minor products formed in the selenium dioxide oxidation in yields of less than 1% were not characterized and are, therefore, not included in Schemes I-VI. They are, however, included in the Experimental Section.

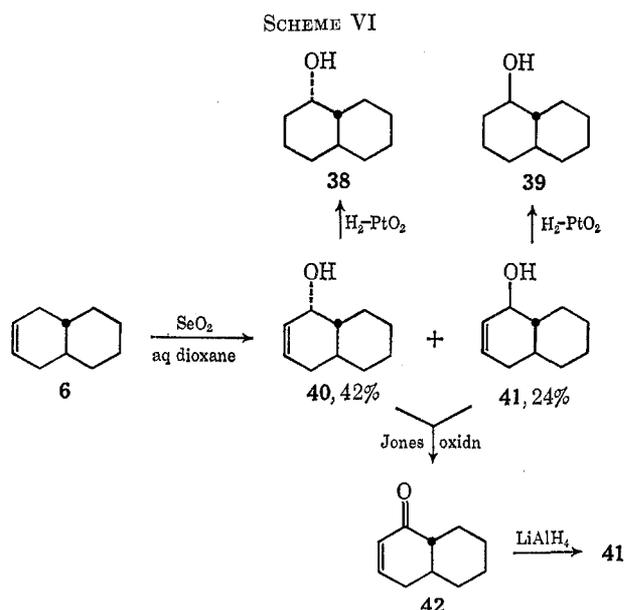
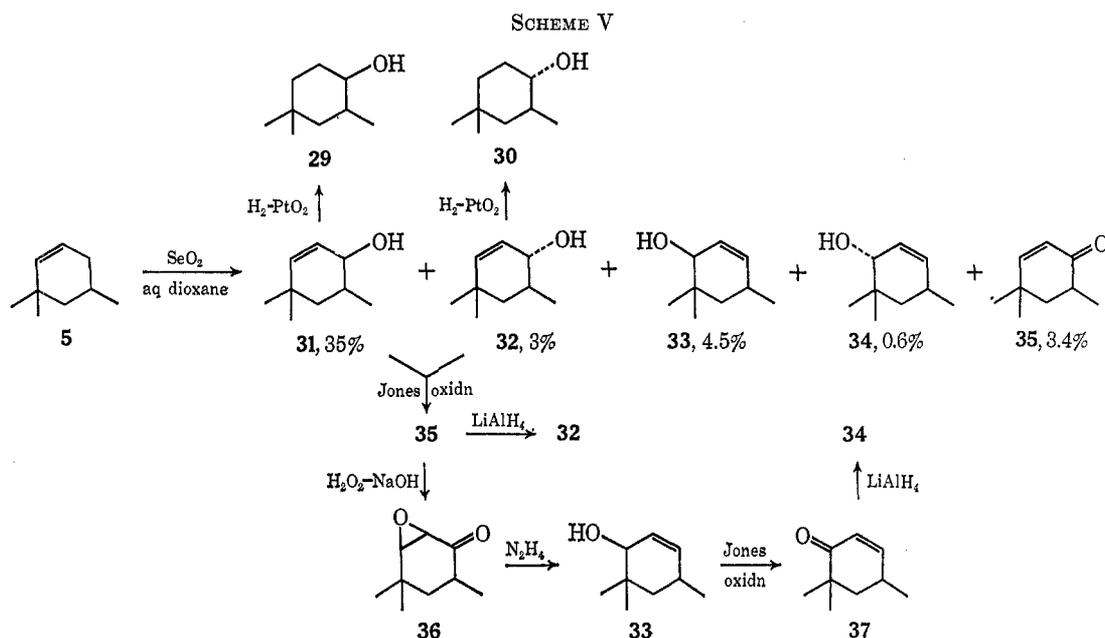
The first interesting result is that the reactivity sequence<sup>17</sup> for attack by selenium dioxide of  $\text{CH}_2 > \text{CH}_3 > \text{CH}$  is not generally valid. Thus, in the case of both 3 and 4, where there is a choice between endocyclic



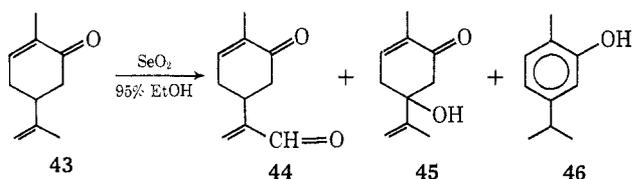
secondary and tertiary positions, attack at the latter is preferred by about twofold. Even more striking are the results with limonene (2). Here there are two double bonds susceptible to attack. It is well established that trisubstituted double bonds are more readily attacked than are disubstituted double bonds with the oxidation occurring at an allylic site on the disubstituted side;<sup>17</sup> yet here oxidation occurs by a threefold preference at the tertiary site allylic to the disubstituted double bond. The oxidation which occurs at the other double bond follows the rules established by Guillemonat<sup>17</sup> in that the endocyclic secondary position is preferred over the exocyclic primary carbon. Further study might indeed confirm that the order of preference should be  $\text{CH} > \text{CH}_2 > \text{CH}_3$  and that the previously established order is incorrect. Thus, we have observed that tertiary allylic carbinols occurring in a mixture with secondary allylic alcohols are selectively converted into involatile products by further treatment with selenium dioxide. Since all of the work which led to establishment of the earlier sequence involved lower olefin/selenium dioxide ratios and since it antedated glpc so that separation of products had to be effected by distillation, it is easy to see why such an error could have been made. For mechanistic reasons,<sup>26</sup> the newly proposed reactivity sequence is more understandable. It should be noted that, although  $\alpha$ -cyclodihydrocostunolide has also recently been shown to form a tertiary carbinol instead of a primary carbinol,<sup>27</sup> this result would have been predicted anyway on grounds that endocyclic positions are favored over exocyclic in cyclohexenyl systems.<sup>17</sup> More significant is the recent observation of Büchi that carvone (43) gives almost eight times as much 45 and 46 as 44 indicating a strong preference for attack at

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CH > CH<sub>3</sub>.<sup>28</sup> Our results further indicate that the preference for attack at CH also exceeds that for reaction at CH<sub>2</sub>.



The second interesting observation, that the reaction shows stereospecificity, is clearly seen in Schemes I-VI. Although the pseudoaxial product is generally formed preferentially, this is not true in the case of **3**. This latter result differs from Schaefer's claim that a mixture of the 3- and 4-methylcyclohexenes gives 80% axial *n*-butyl ethers on oxidation with selenium dioxide in butanol followed by catalytic reduction.<sup>13</sup>

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It should be emphasized that the stereospecificity observed in these oxidations is a function of the reaction and is not merely due to some post-reaction equilibration. This follows most clearly from our results with *D*-(+)-1-*p*-menthene which gives optically active *cis*- and *trans*-carvotanacetols.<sup>26</sup> Since the only reasonable pathway for epimerizing these alcohols under the reaction conditions involves ionization to an allylic cation followed by recombination and since such ionization produces a delocalized cation having a plane of symmetry **47**, it follows that equili-



bration would necessarily also lead to complete racemization.

A mechanism which accounts for these stereochemical results, including the highly enhanced stereospecificity in the case of **5**, is presented in the accompanying paper.<sup>26</sup>

### Experimental Section

Infrared spectra were obtained on thin liquid films with a Perkin-Elmer Infracord. Those in dilute solution (5 mg/100  $\mu$ l of carbon tetrachloride) were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. Ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian HA-60 or a Jeolco JNM C-60H on samples dissolved in carbon tetrachloride or deuteriochloroform containing tetramethylsilane (TMS) as internal standard. Optical rotations were determined on benzene solutions (unless otherwise noted) with a Rudolph Model 80 CSPI photoelectric polarimeter, and refractive indices were measured on a Bausch and Lomb Abbe 3L refractometer. Melting points were determined in soft glass capillaries on a Thomas-Hoover apparatus and are corrected. Microanalyses were performed by the Alfred Bernhardt Microanalytisches Laboratorium, 5251 Elbach über Engelskirchen, West Germany, or by M-H-W Laboratories, Garden City, Mich.

Gas chromatographic analyses and separations were performed on a Wilkens-Varian Model A-700 Autoprep packed with the Wilkens-Varian materials specified below and equipped with a thermal conductivity detector with helium gas as carrier. Peak areas were determined by cutting out the peaks and weighing them or, in the case of sharp symmetrical peaks, by measuring peak height. Calibration curves for each compound in dioxane solution were prepared to determine the proportionality between peak area and concentration in the concentration range encountered in these experiments. One preparative column was used: column A,  $\frac{3}{8}$  in. by 10 ft stainless steel containing 20% FFAP (free fatty acid phase of Carbowax) on 60-80 mesh Chromosorb W, acid washed and treated with DMCS (dimethyldichlorosilane). Two analytical columns were used: column B,  $\frac{1}{4}$  in. by 10 ft stainless steel containing 3% UCON HB 5100 (Union Carbide polyethylene glycol, polar) on 60-80 mesh Chromosorb G; column C,  $\frac{1}{4}$  in. by 10 ft aluminum containing 15% FFAP on 60-80 mesh Chromosorb W.

**1,4-Dimethylcyclohexene (1).**—Aldrich 2,5-dimethylcyclohexanol was dehydrated over *p*-toluenesulfonic acid according to the method of Slomp.<sup>29</sup> Analysis of the crude olefin by glpc (column A) revealed the presence of two minor contaminants (shorter  $R_t$ ), which were removed when the mixture was distilled over sodium through a 3-ft Podbielniak column. Pure 1 was also obtained by preparative glpc (column A), bp 128-129° (lit.<sup>30</sup> bp 127-128°),  $n_D^{20}$  1.4457 (lit.<sup>31</sup>  $n_D^{20}$  1.4458).

**D-(+)-Limonene (2).**—Eastman highest purity 2, glpc unipeak (column C),  $n_D^{20}$  1.4721 (lit.<sup>32</sup>  $n_D^{20}$  1.4724),  $[\alpha]_D +116.1^\circ$  (*c* 8) (lit.<sup>32</sup>  $[\alpha]_D +122.4^\circ$ ), was used without further purification.

**3-Methylcyclohexene (3).**—Aldrich 3 was redistilled, bp 101°,  $n_D^{20}$  1.4438 (lit.<sup>33</sup>  $n_D^{20}$  1.4435). Its ir was identical with that of authentic 3.<sup>34</sup> It exhibited one spot on a silica gel tlc plate with benzene as the solvent and sulfuric acid, followed by charring at 110°, as the indicator.

**cis-3,5-Dimethylcyclohexene (4).**—Aldrich 3,5-dimethylcyclohexanol, which was shown by preparative glpc (column A) to contain mostly *trans,trans*-3,5-dimethylcyclohexanol,  $n_D^{20}$  1.4512 (lit.<sup>35</sup>  $n_D^{20}$  1.4513), and *cis,cis*-3,5-dimethylcyclohexanol,  $n_D^{20}$  1.4548 (lit.<sup>35</sup>  $n_D^{20}$  1.4550), was dehydrated over *p*-toluenesulfonic acid according to the method of Slomp.<sup>29</sup> The crude olefin was refluxed from sodium for 6 hr and distilled through a 200-mm Vigreux column to afford 4, bp 119.5-120°, which glpc (column C) showed to contain ca. 5% trisubstituted olefin (longer  $R_t$ ). All of the contaminant was selectively removed by oxidizing the mixture with a limited amount of selenium dioxide in the usual way (*vide infra*) with an olefin/oxidant ratio of 10:1. It was then distilled from sodium to afford a dioxane solution of pure 4, some of which was glpc (column A) collected:  $n_D^{20}$  1.4410; ir 3040 (m, CH=CH) and 678  $\text{cm}^{-1}$  (s, CH=CH); nmr  $\delta$  5.55 (AB quartet, 2, CH=CH), 1.17-2.50 (m, 6, CH, CH<sub>2</sub>), and 0.96 (2d, 6, CHCH<sub>3</sub>).

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub> (110.19): C, 87.19; H, 12.81. Found: C, 87.46; H, 12.57.

**3,3,5-Trimethylcyclohexene (5).**—Aldrich 3,3,5-trimethylcyclohexanol was dehydrated over *p*-toluenesulfonic acid according to the method of Slomp.<sup>29</sup> It was purified by distillation from sodium on a Nester-Faust 300-plate spinning-band column (reflux ratio of 50:1) to afford 5, bp 131.5° (lit.<sup>29</sup> bp 131.33°),  $n_D^{20}$  1.4388 (lit.<sup>29</sup>  $n_D^{20}$  1.4386). Its ir showed no absorption at 714  $\text{cm}^{-1}$  characteristic of the isomeric 3,5,5-trimethylcyclohexene.<sup>36</sup>

***trans*- $\Delta^2$ -Octalin (6).**—The following modification of the method of Henbest<sup>37</sup> was used to make *cis*-5,8,9,10-tetrahydro-1,4-naphthoquinone (48). A solution of 100 g (0.93 mol) of Eastman *p*-benzoquinone in 75 g (1.39 mol) of Matheson butadiene and 1000 ml of benzene was kept at room temperature for 2 weeks. The solution was then filtered and rotary evaporated, and the

residue was recrystallized once from petroleum ether to give 102 g (68%) of 48, mp 52-56° (lit.<sup>37</sup> mp 57°).

The general procedure of Johnson<sup>19</sup> was employed to convert 48 into a mixture which was shown by glpc (column A) to consist of *trans*- $\Delta^2$ -octalin and *cis*- $\Delta^2$ -octalin in the ratio of 72:28 (lit.<sup>38</sup> 70:30). Pure 6 was obtained by vacuum fractionation of the mixture on a 3-ft Podbielniak column at a rate of 2 drops/min, bp 60° (5 mm),  $n_D^{20}$  1.4812 (lit.<sup>38</sup>  $n_D^{20}$  1.4815).

**Standard Procedure for Selenium Dioxide Oxidation of Olefins.**—A solution of selenious acid made by warming Fairmount Co. selenium dioxide in aqueous dioxane was added dropwise to a magnetically stirred, refluxing solution of olefin in dioxane. It was determined that Fairmount selenium dioxide could be used without further purification since it gave the same results as did resublimed material. The dioxane used was Fisher histological grade and showed only one peak on glpc (column C). The solution rapidly yellowed, and the color intensified to orange and then red as selenium precipitated during the addition and the subsequent 12-20-hr period of refluxing. Glpc analysis was performed on the crude product so as to determine relative yields.

Separation and identification of the products was performed by vacuum fractionation through a 10-cm Claisen column which was connected in series to a tared trap maintained at room temperature followed by two traps cooled with Dry Ice. The low boiling fraction (fraction 1 which collected in the latter two traps) was found to contain water, dioxane, and volatile, unreacted olefin although in some cases, which are noted, the olefin was sufficiently involatile as to be captured by the room temperature trap. The volatile oxidation products were in fraction 2 which collected in the room temperature trap. The contents of the traps were weighed and collected and those in fraction 2 were analyzed by glpc (column B unless otherwise noted) and then separated by preparative glpc (column A unless otherwise specified). It was necessary to do the preparative glpc on distilled material to avoid contamination of the glpc column by noneluting organo-selenium by-products. The glpc peak ratios on both crude and distilled product agreed.

**Standard Procedure for Jones Oxidation of Alcohols.**—In a typical experiment, Jones reagent<sup>39</sup> was added dropwise to a stirred solution of 0.4 g of alcohol in 4 ml of reagent grade acetone until a permanent orange color persisted. The mixture was diluted with 12 ml of water and extracted with two 4-ml portions of chloroform. The combined chloroform extracts were washed with two 5-ml portions of water and rotary evaporated to afford the crude ketone which was purified by preparative glpc (column A).

**Standard Procedure for Lithium Aluminum Hydride Reduction of Ketones.**—In a typical manner, to a solution of 200 mg (5.2 mmol) of lithium aluminum hydride<sup>40</sup> in 10 ml of anhydrous ether, which had been stirring for 1 hr to effect solution, was added dropwise by means of a Hamilton syringe 200  $\mu$ l of a ketone. After the mixture stirred for 1-2 hr, water was cautiously added to destroy excess hydride. The mixture was then filtered and the filtrate was rotary evaporated and analyzed by glpc (column C) and ir.

**Standard Procedure for Hydrogenation of Allylic Alcohols.**—In a typical experiment, approximately 0.1 g of Adams catalyst<sup>41</sup> was added to a solution of 0.2 ml of the desired alcohol in 5 ml of methanol in a Parr bomb at an initial hydrogen pressure of 50 psi. The mixture was shaken at room temperature until uptake of hydrogen ceased. After the catalyst had been filtered off, the filtrate was rotary evaporated to an oil which was purified by preparative glpc (column A).

**Selenium Dioxide Oxidation of 1,4-Dimethylcyclohexene (1).**—A solution of selenium dioxide (0.101 g, 0.9 mmol) in 0.2 ml of water and 1.0 ml of dioxane was added dropwise over a 4-hr period to a solution of 0.806 g (7.3 mmol) of 1 in 1.0 ml of dioxane by the standard procedure. Glpc analysis (column B, *t* 72°) of the crude product showed 81.2% of recovered 1 in addition to four oxidation products (*t* 95°), peak 1 (2.4%,  $R_t$  8.7 min), peak 2 (7.8%,  $R_t$  10.2 min), peak 3 (3.4%,  $R_t$  12.0 min), and peak 4 (4.2%,  $R_t$  20.4 min). Vacuum fractionation gave fraction 1, bp <25° (1-2 mm), and fraction 2, bp 74-77° (3 mm).

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Peak 1 was 2,5-dimethylcyclohex-2-en-1-one (7): uv max (cyclohexane) 232 m $\mu$ ; ir 1672 cm<sup>-1</sup> (s, C=CC=O). Its 2,4-dinitrophenylhydrazine melted at 189–190°.

Anal. Calcd for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>O<sub>4</sub> (304.30): C, 55.25; H, 5.30. Found: C, 55.34; H, 5.37.

Its semicarbazone (EtOH) melted at 196–197°.

Anal. Calcd for C<sub>9</sub>H<sub>12</sub>N<sub>2</sub>O (181.23): C, 59.64; H, 8.34. Found: C, 59.31; H, 8.22.

Peak 2 was *trans*-2,5-dimethylcyclohex-2-en-1-ol (8): ir (CCl<sub>4</sub>) 3630 (s, free OH) and 3370 cm<sup>-1</sup> (s, b, bonded OH); nmr  $\delta$  5.38 (broad d, 1, CH=C), 3.78 (broad s, 1, CHOH), 2.67 (s, 1, OH), 1.25–2.40 (m, 5, CH, CH<sub>2</sub>), 1.67 (s, 3, C=CCH<sub>3</sub>), and 0.93 (d, 3, CHCH<sub>3</sub>).

Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 75.99; H, 11.49.

Peak 3 was *cis*-2,5-dimethylcyclohex-2-en-1-ol (9): ir (CCl<sub>4</sub>) 3623, 3650 (s, free OH), and 3370 cm<sup>-1</sup> (s, b, bonded OH); nmr  $\delta$  5.30 (broad s, 1, CH=C), 4.00 (broad m, 1, CHOH), 2.75 (s, 1, OH), 1.25–2.40 (m, 5, CH, CH<sub>2</sub>), 1.61 (s, 3, C=C-CH<sub>3</sub>), and 0.93 (d, 3, CHCH<sub>3</sub>). Its ir absorption in dilute carbon tetrachloride solution in the intermolecular O–H stretching region was more intense than in the corresponding spectrum of 8.

Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 76.44; H, 11.52.

Peak 4 was not identified.

Jones oxidation of fraction 2 afforded 7 which was reduced by lithium aluminum hydride to a mixture which was predominantly 9. When 1 was oxidized at an olefin/selenium dioxide ratio of 1.45:1, the 19% of oxidation product which was obtained was mostly 7 with some 8 but no 9. The derivatives of 7 described above were prepared from this ketone-rich product.

**Selenium Dioxide Oxidation of D-(+)-Limonene (2).**—A solution of 0.859 g (7.7 mmol) of selenium dioxide in 2.0 ml of water and 10.0 ml of dioxane was added dropwise over a 3-hr period to a solution of 8.426 g (61.9 mmol) of 2 in 10.0 ml of dioxane by the standard procedure. Glpc analysis of the crude product (column B, *t* 75°) showed 84.8  $\pm$  1.2% of recovered 2 in addition to five oxidation products (*t* 112°), peak 1 (5.8%, *R*<sub>t</sub> 3.6 min), peak 2 (1.8%, *R*<sub>t</sub> 6.6 min), peak 3 (1.0%, *R*<sub>t</sub> 7.5 min), peak 4 (1.0%, *R*<sub>t</sub> 8.7 min), and peak 5 (2.6%, *R*<sub>t</sub> 13.8 min). Vacuum fractionation gave fraction 1, bp <25° (1–2 mm), and fraction 2, bp 41–76° (1 mm). Unreacted olefin was found to be present in both fractions.

Peak 1 was 1,8(9)-*p*-menthadien-4-ol (10): *n*<sub>D</sub><sup>20</sup> 1.4957 (lit.<sup>42</sup> *n*<sub>D</sub><sup>20</sup> 1.4961); [ $\alpha$ ]<sub>D</sub><sup>20</sup> +13.6° (neat). Its ir was superimposable on that of an authentic sample of 10 obtained from Dragoco Co., Holzminden, Germany. Its phenylurethan had mp 126–127° which was not depressed upon admixture with that prepared from an authentic sample of 10.

Anal. Calcd for C<sub>10</sub>H<sub>18</sub>O (152.23): C, 78.89; H, 10.59. Found: C, 78.88; H, 10.55.

Peak 2 was *trans*-carveol (11). It was identified by ir comparison<sup>22</sup> and by peak enrichment with authentic 11 (column B), prepared by the method of Klein and Ohloff.<sup>43</sup>

Peak 3 was *cis*-carveol (12). It was identified by ir comparison<sup>22</sup> and by peak enrichment with authentic 12 (column B), prepared by the method of Schroeter.<sup>44</sup>

Peaks 4 and 5 were not identified.

When this reaction was run at lower olefin/selenium dioxide ratios, the yield of 10 was much lower. This was due to decomposition of 10 by the selenium dioxide as shown by the following control experiment. A solution of selenious acid prepared by warming 72 mg (0.65 mmol) of selenium dioxide in 40  $\mu$ l of water and 200  $\mu$ l of dioxane was added to a solution of 199 mg (1.3 mmol) of 10 in 200  $\mu$ l of dioxane. The solution was heated on a water bath for only 10 min, during which time black selenium precipitated out. Glpc analysis (column B) of the crude product revealed that half of the starting material 10 had been consumed. Under these analytical conditions, no other peaks appeared. After addition of another 72 mg (0.65 mmol) of selenium dioxide in 40  $\mu$ l of water and 200  $\mu$ l of dioxane, all of 10 had been consumed.

**Selenium Dioxide Oxidation of 3-Methylcyclohexene (3).**—A solution of 0.468 g (4.2 mmol) of selenium dioxide in 0.4 ml of water and 2.0 ml of dioxane was added over a 5-hr period to a solution of 1.635 g (17 mmol) of 3-methylcyclohexene (3) in 2.0

ml of dioxane according to the standard procedure. Glpc analysis of the crude product (column B, *t* 45°) showed 56% of recovered 3 in addition to three oxidation products (*t* 73°), peak 1 (8.8%, *R*<sub>t</sub> 3.9 min), peak 2 (2.4%, *R*<sub>t</sub> 7.5 min), and peak 3 (2.3%, *R*<sub>t</sub> 8.7 min). Vacuum fractionation gave fraction 1, bp <25° (1–2 mm), and fraction 2, bp 48–49° (2 mm).

Peak 1 was pure 1-methylcyclohex-2-en-1-ol (15): ir 3375 (s, OH), 1100 (s), 1125 (s), and 1180 cm<sup>-1</sup> (s) (tertiary unsaturated alcohol); nmr  $\delta$  5.55 (overlapping AB quartet, 2, CH=CH), 2.25 (s, 1, OH), 1.50–2.10 (m, 6, CH<sub>2</sub>), and 1.24 (s, 3, CH<sub>3</sub>).

Anal. Calcd for C<sub>7</sub>H<sub>12</sub>O (112.16): C, 74.95; H, 10.78. Found: C, 75.24; H, 10.71.

Peak 2 was a ca. 4:1 mixture of *cis*-4-methylcyclohex-2-en-1-ol (16) [nmr  $\delta$  5.71 (overlapping AB quartet, 2, CH=CH), 4.13 (m, 1, CHOH), 1.18–2.05 (m, 7, CH, CH<sub>2</sub>, OH), and 1.02 (d, 3, CH<sub>3</sub>)] and *trans*-6-methylcyclohex-2-en-1-ol, although this latter product which was only formed in overall yield of ca. 0.5% was not isolated.

Anal. of peak 2. Calcd for C<sub>7</sub>H<sub>12</sub>O (112.16): C, 74.95; H, 10.78. Found: C, 75.03; H, 10.89.

Peak 3 was pure *trans*-4-methylcyclohex-2-en-1-ol (13): nmr  $\delta$  5.61 (overlapping AB quartet, 2, CH=CH), 4.02 (m, 1, CHOH), 2.65 (s, 1, OH), 1.17–2.50 (m, 6, CH, CH<sub>2</sub>), and 1.00 (d, 3, CH<sub>3</sub>).

Anal. Calcd for C<sub>7</sub>H<sub>12</sub>O (112.16): C, 74.95; H, 10.78. Found: C, 74.85; H, 10.83.

Hydrogenation of the entire fraction 2 over Adams catalyst in methanol produced a mixture of methylcyclohexanols of which the major secondary carbinol is *trans*-4-methylcyclohexanol (18). Its ir and *R*<sub>t</sub> are identical with those of authentic 18.<sup>45</sup> Further confirmation comes from the fact that 18 is the major product of lithium aluminum hydride reduction of 4-methylcyclohexanone (19) which in turn had been made by Jones oxidation of Aldrich *cis*-4-methylcyclohexanol (17). The minor secondary carbinol obtained in the catalytic reduction of fraction 2 is 17. Its ir and *R*<sub>t</sub> are identical with those of Aldrich 17, *n*<sub>D</sub><sup>20</sup> 1.4617 (lit.<sup>46</sup> *n*<sub>D</sub><sup>20</sup> 1.4614). Jones oxidation of fraction 2 yields mostly 4-methylcyclohex-2-en-1-one (14)<sup>47</sup> which was collected by preparative glpc (column A) and was lithium aluminum hydride reduced to a mixture of 16 and 13 with the latter predominating.

The minor alcohol in peak 2 was shown to be *trans*-6-methylcyclohex-2-en-1-ol from its broad upfield carbinol (H–C–OH) nmr signal detectable in the nmr of peak 2 and from glpc (column C) identity of *R*<sub>t</sub> of the product of its catalytic hydrogenation with that of *trans*-2-methylcyclohexanol from the lithium aluminum hydride reduction of Aldrich 2-methylcyclohexanone.

The determination of the relative amounts of *trans*-6-methylcyclohex-2-en-1-ol and 16 in peak 2 was made by cutting out and weighing the H–C–OH nmr signals at  $\delta$  3.77 and 4.13, respectively, in a 2 $\pi$  scan and is therefore only approximate. The difference between the two signals is in agreement with the upfield shift reported by Eliel for the effect of a vicinal *trans*-equatorial methyl on a cyclohexanol H–C–OH signal.<sup>23</sup>

**Selenium Dioxide Oxidation of *cis*-3,5-Dimethylcyclohexene (4).**—A solution of 1.428 g (12.8 mmol) of selenium dioxide in 3.0 ml of water and 10.0 ml of dioxane was added dropwise over a 3–5 hr period to a solution of 5.615 g (51 mmol) of 4 in 18.7 ml of dioxane by the standard procedure. Glpc analysis (column B, *t* 58°) of the crude product showed 62.9  $\pm$  1% of recovered 4 in addition to four oxidation products (*t* 80°), peak 1 (7.2%, *R*<sub>t</sub> 3.6 min), peak 2 (2.7%, *R*<sub>t</sub> 4.8 min), peak 3 (2.6%, *R*<sub>t</sub> 5.4 min), and peak 4 (2.8%, *R*<sub>t</sub> 7.5 min). Vacuum fractionation gave fraction 1, bp <25° (1–2 mm), and fraction 2, bp 76–78° (4 mm).

Peak 1 was *cis*-1,5-dimethylcyclohex-2-en-1-ol (22): ir (CCl<sub>4</sub>) 3630 (s, free OH) and 3485 cm<sup>-1</sup> (s, b, bonded OH); nmr  $\delta$  5.53 (overlapping AB quartet, 2, CH=CH), 2.00 (s, 1, OH), 1.25–2.33 (m, 5, CH, CH<sub>2</sub>), 1.17 [s, 3, C(OH)CH<sub>3</sub>], and 0.97 (d, 3, CHCH<sub>3</sub>).

Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 75.99; H, 11.31.

Peak 2 was *trans*-1,5-dimethylcyclohex-2-en-1-ol (23): ir (CCl<sub>4</sub>) 3625 (s, free OH) and 3475 cm<sup>-1</sup> (s, b, bonded OH); nmr  $\delta$  5.49 (overlapping AB quartet, 2, CH=CH), 1.65 (s, 1, OH), 1.25–2.33 (m, 5, CH, CH<sub>2</sub>), 1.18 [s, 3, C(OH)CH<sub>3</sub>], and

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0.97 (d, 3, CHCH<sub>3</sub>). Its concentration-dependent ir absorption in dilute carbon tetrachloride solution in the intermolecular O-H stretching region was more intense than in the corresponding spectrum of peak 1.

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 75.98; H, 11.04.

Peak 3 was *cis,cis*-4,6-dimethylcyclohex-2-en-1-ol (24): ir (CCl<sub>4</sub>) 3625 (s, free OH) and 3485 cm<sup>-1</sup> (s, b, bonded OH); nmr δ 5.40-5.95 (m, 2, CH=CH), 3.80 (m, 1, CHOH), 2.15 (broad singlet, 1, OH), 1.25-2.40 (m, 4, CH, CH<sub>2</sub>), and 2.00 (2d, 6, CHCH<sub>3</sub>).

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 75.62; H, 10.89.

Peak 4 was *trans,trans*-4,6-dimethylcyclohex-2-en-1-ol (20): ir (CCl<sub>4</sub>) 3640 (s, free OH) and 3500 cm<sup>-1</sup> (s, b, bonded OH); nmr δ 5.41-5.62 (m, 2, CH=CH), 3.48-4.00 (m, 1, CHOH), 2.48 (s, 1, OH), 1.25-2.40 (m, 4, CH, CH<sub>2</sub>), and 1.98 (m, 6, CHCH<sub>3</sub>). Its concentration-dependent ir absorption in dilute carbon tetrachloride solution in the intermolecular O-H stretching region was more intense than in the corresponding spectrum of peak 3.

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>O (126.19): C, 76.14; H, 11.18. Found: C, 76.05; H, 11.26.

Peak 4 also contained some other isomer which is evident by its carbinol (H-C-OH) signal at δ 3.93 in the nmr. Area integration of the two carbinol proton signals indicated that the other isomer was present to the extent of ca. 33%, so that the actual amount of 20 in peak 4 in the crude selenium dioxide oxidation product was 1.9%. The structure of the contaminant present in overall yield of less than 1% was not determined.

Hydrogenation of fraction 2 over Adams catalyst in methanol produced, as the major product, *cis*-1,3-dimethylcyclohexanol (25), *n*<sup>20</sup><sub>D</sub> 1.4526 (lit.<sup>48</sup> *n*<sup>20</sup><sub>D</sub> 1.4527). Its ir agreed with reported values.<sup>49</sup> The secondary alcohol, *cis,cis*-2,4-dimethylcyclohexanol (26) was also isolated, the *R*<sub>t</sub> and ir of which were identical with those of authentic 26 whose synthesis is described below. Similarly, the secondary carbinol, *trans,trans*-2,4-dimethylcyclohexanol (27) was isolated; its ir and *R*<sub>t</sub> were identical with those of authentic 27 whose synthesis is described below.

The Jones oxidation of fraction 2 produced one ketonic product, 21,<sup>50</sup> which was glpc collected (column A) and subsequently reduced with lithium aluminum hydride to a mixture which was predominantly 20 as evidenced by *R*<sub>t</sub> and ir.

When this reaction was repeated with an olefin/selenium dioxide ratio of 2:1, only 31.3 ± 1.3% of 4 was recovered and only 14.5 ± 0.4% of oxidation product was formed.

**Preparation of *cis,cis*-2,4-Dimethylcyclohexanol (26) and *trans,trans*-2,4-Dimethylcyclohexanol (27).**—2,4-Dimethylcyclohexanol (K & K Laboratories) was shown by glpc (column C) to contain four alcohols, 26 (21%), 27 (61%), and two unidentified alcohols (18%, not completely separated) in order of increasing *R*<sub>t</sub>. From the Jones oxidation of this mixture was isolated as the major oxidation product (83%) *cis*-2,4-dimethylcyclohexanone (28), *n*<sup>20</sup><sub>D</sub> 1.4454 (lit.<sup>51</sup> *n*<sup>20</sup><sub>D</sub> 1.4442), whose ir spectrum was identical with that reported for an authentic sample.<sup>52</sup> Ketone 28 was hydrogenated over Adams catalyst in methanol to a mixture of alcohols, 26 (79%) [*n*<sup>20</sup><sub>D</sub> 1.4578, ir axial C-OH stretch at 983 cm<sup>-1</sup>,<sup>21</sup> nmr (CCl<sub>4</sub>) δ 3.70 (calcd 3.74)<sup>23</sup> (*W*<sub>1/2</sub> = 7 Hz)] and 27 (21%) [*n*<sup>20</sup><sub>D</sub> 1.4563 (lit.<sup>53</sup> *n*<sup>20</sup><sub>D</sub> 1.4560), ir equatorial O-H stretch at 1048 cm<sup>-1</sup>,<sup>21</sup> nmr (CCl<sub>4</sub>) δ 2.99 (calcd 3.00)<sup>23</sup> (*W*<sub>1/2</sub> = 18 Hz, H-C-OH), α-naphthylurethan mp 150-151° (lit.<sup>54</sup> mp 152.5-153.5°)].

**Selenium Dioxide Oxidation of 3,3,5-Trimethylcyclohexene (5).**—A solution of 2.243 g (20.2 mmol) of selenium dioxide in 2.4 ml of water and 8.0 ml of dioxane was added over a 3-hr period to a solution of 4.971 g (40.0 mmol) of 5 in 8.0 ml of dioxane by the standard procedure. Glpc analysis of the crude product (column B, *t* 55°) showed 34.5 ± 1.2% of recovered 5

in addition to two oxidation products (*t* 90°), peak 1 (27.8%, *R*<sub>t</sub> 4.8 min) and peak 2 (2.4%, *R*<sub>t</sub> 5.7 min). Vacuum fractionation gave fraction 1, bp <25° (1-2 mm), and fraction 2, bp 76-78° (2 mm).

Peak 1 was mostly *cis*-4,4,6-trimethylcyclohex-2-en-1-ol (31): ir (CCl<sub>4</sub>) 3635 (s, free OH) and 3495 cm<sup>-1</sup> (s, b, bonded OH); nmr δ 5.60 (AB quartet, 2, CH=CH), 3.72 (m, 1, CHOH), 2.00 (s, 1, OH), 1.16-2.40 (m, 3, CH, CH<sub>2</sub>), and 0.98 (overlapping d and 2s, 9, CH<sub>3</sub>). It was hydrogenated over Adams catalyst in methanol to *cis*-2,4,4-trimethylcyclohexanol (29), *n*<sup>20</sup><sub>D</sub> 1.4602 (lit.<sup>54</sup> *n*<sup>20</sup><sub>D</sub> 1.4605). Its ir agreed with that of an authentic sample.<sup>55</sup>

*Anal.* Calcd for C<sub>9</sub>H<sub>16</sub>O (140.22): C, 77.09; H, 11.50. Found: C, 76.85; H, 11.59.

Peak 2 was mostly *trans*-4,4,6-trimethylcyclohex-2-en-1-ol (32): ir (CCl<sub>4</sub>) 3640 and 3615 (s, free OH) and 3429 cm<sup>-1</sup> (very broad, s, bonded OH); nmr δ 5.40 (overlapping AB quartet, 2, CH=CH), 3.60 (d, 1, CHOH), 3.40 (s, 1, OH), 1.16-2.33 (m, 3, CH, CH<sub>2</sub>), and 0.98 (overlapping d and 2s, 9, CH<sub>3</sub>). Its concentration-dependent ir absorption in dilute carbon tetrachloride solution in the intermolecular O-H stretching region was more intense than in the corresponding spectrum of peak 1. Peak 2 was hydrogenated over Adams catalyst in methanol to *trans*-2,4,4-trimethylcyclohexanol (30), whose ir agreed with that of an authentic sample.<sup>55</sup>

*Anal.* Calcd for C<sub>9</sub>H<sub>16</sub>O (140.22): C, 77.09; H, 11.50. Found: C, 77.25; H, 11.42.

Jones oxidation of fraction 2 afforded 4,4,6-trimethylcyclohex-2-en-1-one (35), whose ir and nmr agreed with published spectra.<sup>47</sup> It was reduced by lithium aluminum hydride to a mixture of 31 and 32 in a ratio of 4:96. Fraction 2 also contained a small amount of ketone 35, whose *R*<sub>t</sub> was identical with that of 31. When fraction 2 was treated with lithium aluminum hydride under nonpimerizing conditions, the ratio of peak 1 to peak 2 changed from 92:8 to 84:16 which indicated that peak 1 contained 8% 35. It was also found by measuring the areas under the two carbinol (H-C-OH) proton nmr signals at δ 3.72 and 3.38 that peak 1 additionally contains ca. 10% *cis*-4,4,6-trimethylcyclohex-2-en-1-ol (33) so that the actual amount of 31 in peak 1 of the crude selenium dioxide oxidation product of 5 was only 22.7%. These two signals at δ 3.72 and 3.38 are assignable to compounds 31 and 33, respectively. Similarly, by area integration of the carbinol (H-C-OH) signals at δ 3.60 and 3.80, it was determined that peak 2 also contained ca. 18% *trans*-4,4,6-trimethylcyclohex-2-en-1-ol (34) so that the actual amount of 32 in peak 2 of the crude selenium dioxide oxidation product of 5 was only 2.0%. The δ 3.60 and 3.80 signals are assignable to 32 and 34, respectively. The structures 33 and 34 were established by comparison with authentic samples whose syntheses are described below.

**Preparation of *cis*- (33) and *trans*-4,6,6-Trimethylcyclohex-2-en-1-ol (34).**—By the general procedure for the Wharton reaction described by Klein and Ohloff,<sup>43</sup> 35 was converted in 24% overall yield into 33: ir (CCl<sub>4</sub>) 3635 (s, free OH) and 3490 cm<sup>-1</sup> (s, b, bonded OH); nmr δ 5.63 (overlapping AB quartet, 2, CH=CH), 3.38 (d, 1, CHOH), 1.25-2.40 (m, 3, CH, CH<sub>2</sub>), 1.20 (s, 1, OH), and 0.96 (overlapping 2s and d, 9, CH<sub>3</sub>). The Wharton reaction is known to be highly stereospecific and to give predominantly the axial alcohol.<sup>43</sup>

Jones oxidation of 33 produced ketone 37 which was reduced by lithium aluminum hydride to a mixture rich in 34: nmr δ 5.38 (m, 2, CH=CH), 3.80 (d, 1, CHOH), 1.75 (s, 1, OH), 1.25-2.40 (m, 3, CH, CH<sub>2</sub>), and 0.96 (overlapping d and 2s, 9, CH<sub>3</sub>). Its concentration-dependent ir absorption in dilute carbon tetrachloride solution in the intermolecular O-H stretching region was more intense than in the corresponding spectrum of 33.

**Selenium Dioxide Oxidation of Δ<sup>2</sup>-trans-Octalin (6).**—A solution of 0.522 g (4.7 mmol) of selenium dioxide in 1.0 ml of water and 5.0 ml of dioxane was added over a 4-hr period to a solution of 2.541 g (18.7 mmol) of 6 in 5.0 ml of dioxane by the standard procedure. Glpc analysis of the crude product (column B, *t* 88°) showed 82.0 ± 1.4% of recovered 6 in addition to three oxidation products (*t* 130°), peak 1 (7.8%, *R*<sub>t</sub> 4.8 min), peak 2 (4.4%, *R*<sub>t</sub> 6.0 min), and peak 3 (2.5%, *R*<sub>t</sub> 6.6 min). Vacuum fractionation gave fraction 1, bp <25° (1-2 mm), and fraction 2, bp 33-72° (1 mm).

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Peak 1 was *trans,syn*- $\Delta^2$ -octalol-1 (40): ir (CCl<sub>4</sub>) 3633 (s, free OH) and 3500 cm<sup>-1</sup> (m, b, bonded OH); nmr  $\delta$  5.88 (m, 2, CH=CH), 3.88 (broad singlet, 1, CHOH), 1.33 (s, 1, OH), and 0.50–2.40 (broad band, 13, all other protons). It was hydrogenated over Adams catalyst in methanol to *trans,syn*-1-decalol (38) whose ir was identical with that of authentic 38.<sup>21</sup>

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O (152.23): C, 78.89; H, 10.59. Found: C, 78.62; H, 10.49.

Peak 2 was *trans,anti*- $\Delta^2$ -octalol-1 (41): ir (CCl<sub>4</sub>) 3625 and 3650 (s, free OH), and 3500 cm<sup>-1</sup> (s, b, bonded OH); nmr  $\delta$  5.60 (m, 2, CH=CH), 3.80 (broad singlet, 1, CHOH), 1.67 (s, 1, OH), and 0.50–2.40 (broad band, 13, all other protons). Its ir absorption in dilute carbon tetrachloride solution in the intermolecular O–H stretching region was more intense than in the corresponding spectrum of 40. It was hydrogenated over Adams catalyst in methanol to *trans,anti*-1-decalol (39) whose ir was identical with that of authentic 39.<sup>21</sup> Jones oxidation of fraction 2 produced the enone 42 which was collected by preparative glpc (column A) and subsequently reduced by lithium aluminum hydride to a mixture which contained ca. 95% 41.

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>O (152.23): C, 78.89; H, 10.59. Found: C, 78.61; H, 10.39.

Peak 3 was not identified.

**Registry No.**—Selenium dioxide, 7446-08-4; 4, 23758-22-7; 7, 23758-23-8; 7 (2,4-dinitrophenylhydrazine), 23758-24-9; 7 (semicarbazone), 23829-43-8; 8, 23758-25-0; 9, 23758-26-1; 13, 23713-60-2; 15, 23758-27-2; 16, 23713-61-3; 20, 23713-62-4; 22, 23746-53-4; 23, 23713-63-5; 24, 23713-64-6; 26, 23713-65-7; 31, 23713-66-8; 32, 23713-67-9; 33, 23713-68-0; 34, 23713-69-1; 40, 23713-70-4; 41, 23713-71-5.

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## Mechanism of Selenium Dioxide Oxidation of Olefins<sup>1</sup>

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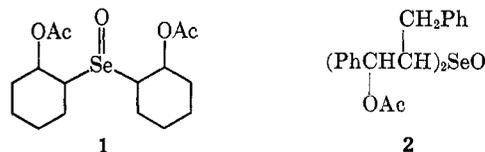
The mechanism of allylic oxidation of olefins by selenium dioxide is discussed. Evidence is presented in favor of an initial oxaselenocyclobutane intermediate forming an allylic selenite ester, which then solvolyzes.

The mechanism of allylic oxidation of olefins by selenium dioxide has been the subject of several studies over the past 30 years.<sup>4</sup> The first hypothesis, that of Guillemonat,<sup>5</sup> invoked the intermediacy of tetraalkyl and dialkyl selenides in which the selenium is bonded to an allylic carbon. The gross inadequacy of this proposal has already been commented upon adequately,<sup>4,6</sup> but it should be recognized that Guillemonat's comprehensive studies of the behavior of selenium dioxide in acetic acid–acetic anhydride led to the formulation of many useful and still valid generalizations with respect to the site of attack in unsymmetrical alicyclic and acyclic olefins.

Another early suggestion put forth by Waters without any experimental support was that the reaction involves neutral radical species.<sup>7</sup> This was based on analogy to the allylic oxidation observed with benzene diazonium acetate, lead tetraacetate, or air catalyzed by osmium and on the fact that many oxidations involve radical-chain mechanisms. Although Wiberg and Nielsen<sup>8</sup> credit Waters with suggesting that the reaction proceeds "via a hydrogen atom abstraction from the alkene," Waters did recognize that the 2-cyclohexenol acetate produced by selenium dioxide oxidation of

cyclohexene could also be formed by addition of two acetoxy radicals followed by elimination of acetic acid. No support has, however, been forthcoming for a free-radical process. Quite the contrary, Schaefer, Horvath, and Klein<sup>9</sup> have shown that the reaction is unaffected by inhibitors and, therefore, cannot be radical chain. We wish to report that the reaction does not involve free radicals at all. Thus, we find that an oxidizing system is incapable of initiating polymerization of acrylonitrile under conditions of temperature and concentration where acrylonitrile is rapidly polymerized if a source of free radicals is present.

There is now evidence that the oxidation proceeds by two different mechanisms, a low energy solvolytic pathway and a pyrolytic one. Guillemonat<sup>5</sup> had early observed that the organoselenium intermediates which he postulated as selenides thermally decompose to regenerate olefin and to produce allylic oxidation products. Wiberg<sup>8</sup> established that these compounds are selenoxides, rather than selenides, by isolating 1 from the oxidation of cyclohexene in acetic acid–acetic anhydride. Schaefer, Horvath, and Klein,<sup>9</sup> however, showed that the analogous compound 2 isolated from



the oxidation of 1,3-diphenylpropene (3) decomposes to 1,3-diphenyl-2-propen-1-ol acetate (4) at too slow a rate to account for the main course of the oxidation.

The main pathway must involve the solvolysis of an allylic selenite ester, although the structure of the latter has not been rigorously established. Schaefer<sup>9</sup>

(1) A preliminary report of some of this work was made at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1962, Abstract, p 78Q.

(2) Extracted in part from the Ph.D. dissertation submitted by C. H. N. to Clark University in 1964. A National Science Foundation Cooperative Graduate Fellowship for 1961–1962 is gratefully acknowledged.

(3) Extracted in part from the Ph.D. dissertation submitted by J. R. C. to Clark University in 1969.

(4) For a review of the scope and limitations of this reaction, see (a) E. N. Trachtenberg in "Oxidation," Vol. 1, R. L. Augustine, Ed., Marcel Dekker, New York, N. Y., 1969, pp 119–187; (b) N. Rabjohn, *Org. React.*, **5**, 331 (1949); (c) G. R. Waitkins and C. W. Clark, *Chem. Rev.*, **36**, 235 (1945).

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