acetone, cooled to -78 °C, was added to 10 mL of a 0.1 M solution of TPPO in acetone at -78 °C. The reaction mixture was stirred at -60 °C for 24 h and then quenched by triethylamine. VPC analysis showed that no triadamantylidene dioxetane or epoxide had been formed. A control experiment in which the mixture was warmed from -78 °C to room temperature in a period of 30 min gave 79% dioxetane and 21% epoxide by VPC analysis (6 ft, 5% SE-30; 150 °C for 5 min, linear programming with the temperature rising at 20 °C/min to 220 °C, and then held constant). The reaction gave the same results in dichloromethane.

Molecular Weight of TPPO. It was found that freezing point depressions in chloroform could be determined within the precision shown in Table I by using the apparatus already set up for the low-temperature experiments and a low-temperature thermometer with 1 °C graduations. For each solution 3-5 cooling curves were run, each with about ten points, and extrapolated to yield a freezing point reading. The freezing point of pure chloroform was thus determined by averaging the values -61.1, -61.1, -61.0, -60.9, and -60.8 °C (average -60.98, mean deviation 0.104 °C). A solution of TPPO prepared from 3.72 g (12.0 mmol) of triphenyl phosphite in 30.00 g of chloroform at -55 °C, with the usual precautions to avoid any momentary excess of phosphite, yielded from five cooling curves the freezing points -63.8, -63.5, -63.7, -63.6, and -63.0 °C (average -63.52, mean deviation 0.216 °C). If the deviant last point is excluded, the average of the other four is -63.65 °C, and the mean deviation is 0.10, making the deviation of the last point 6.5 times the mean of the others. Both averages are shown in Table I.

When the TPPO solution was warmed, gas evolution was observed at -30 °C, which became very vigorous at -10 °C. After the gas evolution had ceased, the solution was again cooled, and three more cooling curves were determined, leading to mp -63.5, -63.8, and -63.7 °C (average -63.67 °C, mean deviation 0.11 °C). Thus the freezing point depression produced by TPPO was 94% of that produced by the product phosphate, or 99% if the final point for TPPO is rejected.

The freezing point depression by the product of the TPPO decomposition was checked with a solution of triphenyl phosphate (1.30 g, 4.0 mmol) in 10 g of chloroform. The five cooling curves gave freezing points of -63.8, -64.1, -64.2, -64.0, and -63.8 °C (average -63.98 °C, mean deviation 0.14 °C). The depressions produced by equimolar amounts of triphenyl phosphate with these two histories were within 6% of each other.

Acknowledgment. We thank the Robert A. Welch Foundation, the National Science Foundation, and the National Institutes of Health for support of this work.

Registry No. 1, 2983-83-8; 3, 58594-17-5; 4a, 41850-90-2; 4b, 41850-89-9; 6, 110-87-2; 9, 24350-41-2; 10, 3383-45-1; 11, 23603-63-6; 12, 73789-90-9; 13, 1499-89-6; 14, 1121-57-5; 15, 30541-56-1; 16, 35544-98-9; 17, 29186-97-0; 1.2-dimethylcyclohexene, 1674-19-8; 2-methyl-2-buten, 513-55-9; 1-methyl-2-methylene cyclohexyl hydroperoxide, 54688-51-1; 1.2-dimethyl-2-cyclohexen-1-yl hydroperoxide, 54688-52-2; 2.3-dimethyl-2-cyclohexen-1-yl hydroperoxide, 56201-42-4; 1.2-dimethyl-3-propenyl hydroperoxide, 15315-28-8; 1.1-dimethyl-2-propenyl hydroperoxide, 15315-50-7; O3, 7782-44-7.

Direct Epoxy Alcohol Synthesis from Cyclic Olefins Using O2 and VO(acac)2·AIBN Catalyst System

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Department of Chemical Engineering, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan

Received November 27, 1979

The vanadium-catalyzed oxidation of cyclic olefins with molecular oxygen is examined. The VO(acac)2·AIBN system is an efficient catalyst for epoxy alcohol synthesis. Chloro hydrocarbons such as 1,2-dichloroethane and 1,1,2-trichloroethane are suitable solvents for the epoxidation reaction. Cyclohexene (1), methylcyclohexene (2), and cyclooctene (5) give the corresponding epoxy alcohols in good yields; in the case of 2 with the VO(acac)2·AIBN system, the selectivity to epoxy alcohol reaches over 70%. 1,4-Cyclooctadiene (1a) using CpV(CO)5 (Cp = cyclopentadienyl) catalyst. In these reactions, 1 has been often used as a representative reactant. Because of the potential significance of epoxy alcohols in general, it is important to examine the scope and limitation of their formation from various olefins with molecular oxygen.

To our knowledge, three groups, Allison,4 Lyons,5 and Noels,6 have reported the epoxy alcohol formation from olefins. For example, Lyons has succeeded in 65% selective formation of epoxycyclohexanol (1a) from the reaction of cyclohexene (1) using CpV(CO)5 (Cp = cyclopentadienyl) catalyst. In these reactions, 1 has been often used as a representative reactant. Because of the potential significance of epoxy alcohols in general, it is important to examine the scope and limitation of their formation from various olefins with molecular oxygen.


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Direct Epoxy Alcohol Synthesis

Table I. Cyclohexene Oxidation Catalyzed by Vanadium Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Induction Period, h</th>
<th>O&lt;sub&gt;2&lt;/sub&gt; Absorption Rate, mL of O&lt;sub&gt;2&lt;/sub&gt;/min·mol</th>
<th>Conversion and % Selectivity of Epoxy Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpV(CO)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.5</td>
<td>6.3</td>
<td>17 % la, 36 % lb</td>
</tr>
<tr>
<td>CpV(CO)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.4</td>
<td>57</td>
<td>11 % la, 33 % lb</td>
</tr>
<tr>
<td>VO(acac)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.5</td>
<td>16.5</td>
<td>24 % la, 19 % lb</td>
</tr>
<tr>
<td>VO(acac)&lt;sub&gt;2&lt;/sub&gt;+ AIBN</td>
<td>7.5</td>
<td>11</td>
<td>36 % la, 17 % lb, 14 % Id</td>
</tr>
</tbody>
</table>

* Reaction conditions: cyclohexene (20 mmol), catalyst (0.1 mmol), O<sub>2</sub> (1 atm), 60 ± 1 °C, GLC (OV-17).

Table II. Typical Examples of Cyclohexene Oxidation

<table>
<thead>
<tr>
<th>Reaction Medium</th>
<th>Conversion</th>
<th>% Selectivity</th>
<th>Major Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>17 %</td>
<td>17 %</td>
<td>1a</td>
</tr>
<tr>
<td>Benzene</td>
<td>21 %</td>
<td>21 %</td>
<td>1b</td>
</tr>
<tr>
<td>l,4-dioxane</td>
<td>19 %</td>
<td>19 %</td>
<td>1c</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>17 %</td>
<td>17 %</td>
<td>1d</td>
</tr>
</tbody>
</table>

Scheme I

**Decomposition of Hydroperoxides**

**Epoxidation of Cyclic Olefins**

**Epoxidation of Cyclic Allylic Alcohols**

Effect of Solvent on Cyclohexene Oxidation. Generally there are few discussions about the solvent effect on the selectivity for oxidation products. Since the process of epoxy alcohol formation consists of the following two steps, radical reaction of hydroperoxide formation and ionic oxygen-transfer reaction of hydroperoxide to allylic alcohol, it must be regarded that solvents have a duplicate character in the two steps. First, the oxidation of 1 with VO(acac)<sub>2</sub> complex in various solvents was carried out in the absence of AIBN in order to examine the function of solvent in the initial step of hydroperoxide formation. Typical examples are shown in Table II. As mentioned in a previous section, VO(acac)<sub>2</sub> complex had no activity for the oxidation of 1 in the absence of solvent. In 1,2-dichloroethane, benzene, or 1,4-dioxane as a solvent, 1a could be formed after a long induction period. Presumably some solvents may induce the fission of a vanadium-acac bond to generate an acetylacetonato radical as an initiator.
to high conversions, about 60% selectivity for la could be
allylic alcohol on an oxo-vanadium intermediate species,
Both N,N-dimethylformamide and ethanol solvents
during the induction period. The oxidation did not occur
somewhat the selectivity for la. Figure 1 shows the
could increase the (oxidation rate twofold and improve
but did not give la. Alcohols prevent the attack of the
which results in exclusive formation of lb-d.
shortened in all reactions. The use of 1,2-dichloroethane
maintained. It is notable that 1,2-dichloroethane gave high
product distribution in the course of the oxidation. Up
up to 40 h in acetonitrile, aniline, or hexane solvent.
Next, the oxidation of 1 using the VO(acac)₂-AIBN
catalyst system was performed in various solvents. Typical
results are shown in Table III. The induction periods were
shortened in all reactions. The use of 1,2-dichloroethane
could increase the oxidation rate twofold and improve
somewhat the selectivity for la. Figure 1 shows the
product distribution in the course of the oxidation. Up
to high conversions, about 60% selectivity for la could be
maintained. It is notable that 1,2-dichloroethane gave high
selectivity for volatile oxidation products, and then the
total yield of the four oxidation products la-d reached
65% at 30% conversion of the olefin 1. Furthermore,
1,1,2-trichloroethane gave 65% selectivity for la at 48% conversion. The best solvent for the epoxy alcohol forma-
tion seems to be chloro hydrocarbons. The function
of IC to an oxo-vanadium species in agreement with the
known. Probably the solvents promote the coordination
of these solvents in the oxygen-transfer process is not
expected, three epoxy alcohols, 2a-1, 2a-2, and 2a-3, were obtained (Table IV).
Table II. Effect of Various Solvents on Cyclohexene Oxidation Catalyzed by VO(acac)₂²

<table>
<thead>
<tr>
<th>solvent</th>
<th>O₂ absorption rate, mL of O₂/ min mol</th>
<th>% conversion</th>
<th>% yield</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrileb</td>
<td>2.5</td>
<td>8.3</td>
<td>38</td>
<td>24</td>
<td>0</td>
<td>18</td>
<td>28</td>
</tr>
<tr>
<td>DMF</td>
<td>4.5</td>
<td>65</td>
<td>33</td>
<td>14</td>
<td>0</td>
<td>24</td>
<td>27</td>
</tr>
<tr>
<td>ethanolc</td>
<td>15</td>
<td>4.6</td>
<td>30</td>
<td>26</td>
<td>56</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>tert-butanolb</td>
<td>1,2-dichloroethane</td>
<td>22</td>
<td>3.8</td>
<td>28</td>
<td>46</td>
<td>32</td>
<td>10</td>
</tr>
<tr>
<td>benzene</td>
<td>26</td>
<td>5.3</td>
<td>35</td>
<td>21</td>
<td>43</td>
<td>32</td>
<td>13</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td></td>
<td></td>
<td></td>
<td>18</td>
<td>24</td>
<td>27</td>
<td>12</td>
</tr>
<tr>
<td>n-hexaneb</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>15</td>
<td>17</td>
<td>13</td>
</tr>
</tbody>
</table>

² Reaction conditions: VO(acac)₂ (0.01 mmol), solvent (2.0 mL), others are the same as in Table I. b No reaction within 40 h. c The resulting epoxide 1b was successively converted into ethoxycyclohexanol by the vanadium catalyst.

Table III. Effect of Various Solvents on Cyclohexene Oxidation Catalyzed by VO(acac)₂-AIBN²

<table>
<thead>
<tr>
<th>solvent</th>
<th>O₂ absorption rate, mL of O₂/ min mol</th>
<th>% conversion</th>
<th>% yield</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrileb</td>
<td>5.0</td>
<td>6.7</td>
<td>30</td>
<td>19</td>
<td>52</td>
<td>25</td>
<td>11</td>
</tr>
<tr>
<td>benzene</td>
<td>3.5</td>
<td>3.9</td>
<td>36</td>
<td>27</td>
<td>54</td>
<td>23</td>
<td>12</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>0.5</td>
<td>6.8</td>
<td>30</td>
<td>21</td>
<td>43</td>
<td>31</td>
<td>10</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>2.5</td>
<td>6.0</td>
<td>28</td>
<td>24</td>
<td>61</td>
<td>23</td>
<td>6</td>
</tr>
<tr>
<td>1,1,2-trichloroethane</td>
<td>2.0</td>
<td>6.0</td>
<td>40</td>
<td>26</td>
<td>55</td>
<td>23</td>
<td>10</td>
</tr>
<tr>
<td>1,1,2-trichloroethane</td>
<td>5.0</td>
<td>7.8</td>
<td>26</td>
<td>20</td>
<td>52</td>
<td>23</td>
<td>14</td>
</tr>
<tr>
<td>n-hexaneb</td>
<td></td>
<td></td>
<td></td>
<td>61</td>
<td>15</td>
<td>17</td>
<td>13</td>
</tr>
</tbody>
</table>

² Reaction conditions: VO(acac)₂ (0.01 mmol), AIBN (0.1 mmol), solvent (2.0 mL), other conditions are the same as those in Table I. b Products are the same as those in Table I.

Table IV. Effect of Various Solvents on 1-Methylcyclohexene Oxidation Catalyzed by VO(acac)₂-AIBN²

<table>
<thead>
<tr>
<th>solvent</th>
<th>O₂ absorption rate, mL of O₂/ min mol</th>
<th>% conversion</th>
<th>% yield</th>
<th>2a-1</th>
<th>2a-2</th>
<th>2a-3</th>
<th>2b</th>
<th>2c</th>
<th>2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetonitrileb</td>
<td>0.5</td>
<td>23</td>
<td>40</td>
<td>24</td>
<td>16</td>
<td>36</td>
<td>23</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>1,2-dichloroethyl</td>
<td>1.5</td>
<td>10</td>
<td>41</td>
<td>28</td>
<td>16</td>
<td>34</td>
<td>24</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>1,2-dichloroethylc</td>
<td>0.4</td>
<td>45</td>
<td>31</td>
<td>20</td>
<td>9</td>
<td>33</td>
<td>21</td>
<td>29</td>
<td>5</td>
</tr>
<tr>
<td>1,2-dichloroethaned</td>
<td>1.0</td>
<td>6.1</td>
<td>29</td>
<td>20</td>
<td>18</td>
<td>36</td>
<td>23</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>benzene</td>
<td>1.4</td>
<td>10</td>
<td>31</td>
<td>18</td>
<td>13</td>
<td>29</td>
<td>23</td>
<td>22</td>
<td>5</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1.5</td>
<td>11</td>
<td>33</td>
<td>18</td>
<td>14</td>
<td>34</td>
<td>23</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>1,4-dioxane</td>
<td>0.0</td>
<td>12</td>
<td>28</td>
<td>17</td>
<td>15</td>
<td>34</td>
<td>22</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>n-hexane</td>
<td>0.3</td>
<td>7.0</td>
<td>40</td>
<td>20</td>
<td>14</td>
<td>32</td>
<td>22</td>
<td>28</td>
<td>2</td>
</tr>
</tbody>
</table>

² Reaction conditions are the same as those in Table III; GLC (PEG 20M). b Products: 2a-1, 1-methyl-2,3-epoxy-cyclohexanol; 2a-2, 2-methyl-2,3-epoxy-cyclohexanol; 2a-3, 2-methyl-1,2-epoxy-cyclohexene; 2c, 1-methyl/cyclohex-2-en-1-ol, 3-methyl/cyclohex-2-en-1-ol, and 2-methyl/cyclohex-2-en-1-one and 2-methyl/cyclohex-2-en-1-one. c 80 ± 1 °C. d 50 ± 1 °C.

during the induction period. The oxidation did not occur
even after 40 h in acetonitrile, aniline, or hexane solvent.
Both N,N-dimethylformamide and ethanol solvents
showed high oxidation rates with short induction periods
but did not give la. Alcohols prevent the attack of the
allylic alcohol on a oxo–vanadium intermediate species,
which results in exclusive formation of 1b-d. The stereochemistry of the alcohols was assigned as the

Direct Epoxy Alcohol Synthesis


Table V. Ring Size Effect on Oxidation of Various Cyclic Olefins

| olefin          | $\omega$ | $C_2-\psi$ | induction period, h | $O_2$ absorption rate, mL of $O_2/\text{min}$ | $\%$ conversion | $\%$ yield | $\%$ selectivity | $n$ | $a$ | $b$ | $c$ | $d$
|-----------------|---------|------------|---------------------|---------------------------------------------|-----------------|-------------|-----------------|-----|-----|-----|-----|-----
| cyclo-hexene    | 15$^a$  | $C_2-\psi$ | 2.5                 | 16.5                                        | 24              | 19          | 2               | 41  | 28  | 15  | 16  |
| cyclo-heptene   | 58.5$^a$| $C_2-\psi$ | 4                   | 16.2                                        | 38              | 24          | 3               | 10  | 40  | 9   | 34  |
| cyclo-octene    | 83.0$^a$| $C_2-\psi$ | 8                   | 1.5                                         | 6               | 3           | 4               | 0   | 99  | 1   | 0   |
| cyclo-dodecene  | >110$^a$| $C_2-\psi$ | 6                   | 2.7                                         | 14              | 9           | 8               | 53  | 40  | 5   |     |

$^a$ Reaction conditions: olefin (20 mmol), VO(acac)$_2$ (0.01 mmol), AIBN (0.1 mmol), others are the same as those in Table I.

$^b$ Products: a, epoxy cyclohexanol; b, cyclohexene oxide; c, cyclohexenol; d, cyclohexeneone.

cis configuration. The product ratio of these three alcohols is explained reasonably by the distribution of intermediate hydroperoxides (Scheme II); in a previous paper, we reported that a mixture of three hydroperoxides (2e-1, 2e-2, and 2e-3) was isolated in the ratio of 2:1:4 from the autoxidation of 2 using AIBN at 50°C. The yield of 2a-1 plus 2a-2 derived from allylic radical (1) is larger than that of 2a-3 from II. This might be explained in terms of Bolland’s rule. The same tendency was also observed in the oxidation of 2 using the Wilkinson complex, RhCl(PPh$_3$)$_2$,11 hydrogens at C-3 are favorably abstracted over those at C-6 in the ratio of 3:1 with this complex, while the ratio is 2:1 with the VO(acac)$_2$-AIBN catalyst. Attack by molecular oxygen at the less hindered site of allylic radical (1) gives preferentially the hydroperoxide (2e-2) rather than 2e-1, which results in the selective formation of 2a-2.

Increasing the reaction temperature decreased the selectivity for the epoxy alcohols 2a, while the selectivity for methylcyclohexene oxide (2b) was increased. Since the directing control exerted by the allylic hydroxyl is lost at high temperature, the reaction for selective epoxy alcohol formation should operate below 60°C. The variation of solvents did not strongly influence the distribution of the three epoxy alcohols. On the other hand, the oxidation rates increase with increasing dielectric constant of the solvent.12 Oxidation of 2 yielded the epoxy alcohols with high selectivity in various solvents. It is notable that the sum of the three epoxy alcohols 2a and the epoxide 2b reached about 90% selectivity.

Effect of Ring Size on Cyclic Olefin Oxidation. The results of oxidation of cyclic olefins (1, 3-5) with the VO(acac)$_2$-AIBN system are summarized in Table V. In the case of cycloheptene (3), cycloheptene oxide (3b) and cycloheptenone (3d) were major products. Cyclododecene (5) gave two epoxidation products, the epoxy alcohol 5a and epoxide 5b. Cyclooctene (4) did not yield the corresponding epoxy alcohol; cyclooctene oxide (4b) was formed exclusively. Furthermore, using only AIBN, 4 gave 4b selectively. The selectivities for epoxy alcohols decrease along the order C$_2$ > C$_3$ > C$_4$ > C$_5$ > C$_6$, which can be explained reasonably by considering the geometry about the olefinic carbons. The allylic hydrogens of 1 and 5 are abstracted easily, because the removal of hydrogens allows

an allylic radical system which has the geometry suitable for maximum overlap of \( n \) and \( \pi \) molecular orbitals. On the other hand, it is not so easy that the allylic radical from 4 can attain maximum overlap because of the conformational constraint of the ring system. Therefore both 1 and 3 are oxidized faster than 4. The lower rate of 5 may be due to the entropy effect of the larger molecule. Mayo has discussed the origin of oxidation products of olefins in terms of the addition and hydrogen-abstraction mechanisms. Olefins 1, 3, and 5 are oxidized mainly by the hydrogen-abstraction mechanism, producing allylic hydroperoxides, while in 4 the addition mechanism predominates. Considering the epoxy alcohol formation reaction proceeds via the oxygen transfer of hydroperoxide to allylic alcohol, the order for the epoxy alcohol selectivities can be well-explained. It seems that the hydroperoxide radical derived from the initiator may be the source of the epoxide 4b.

**Transannular Epoxidation of 1,4-Cyclooctadiene.** Recently we synthesized bridged oxabicyclic compounds from the epoxidation of cyclic 2,4-dienols with t-BuOOH/VOC(acac). On this basis of the knowledge, we schemed that the oxabicyclic compounds may be produced by a direct oxidation of dienes with molecular oxygen. First we attempted the preparation of cycloocta-2,4-dienyl hydroperoxide (6e) by the autoxidation of either 1,3-cyclooctadiene (6) or 1,4-cyclooctadiene (7). The conjugated diene (6) gave a mixture containing co-oligomers of 6a and 6e. But the latter compound could not be isolated in spite of elaborate efforts. The nonconjugated diene (7) was oxidized easily because of its biallyl system. The hydroperoxide 6e was formed in 88% selectivity at 28% olefin conversion and could be isolated easily in 95% purity. The structure of 6e was determined by its reduction to cycloocta-2,4-dien-1-ol (6c) with Na2SO3. The GLC analysis of the reduction solution showed 6c (98.3%) and cycloocta-2,7-dien-1-ol (7c, 1.7%).

\[
\begin{align*}
\text{7c} & \xrightarrow{\text{Na}_2\text{SO}_3} \text{6c} \\
\text{6} & \xrightarrow{\text{t-BuOOH}} \text{6e}
\end{align*}
\]

Treatment of 6e with VO(acac)2 gave 9-oxabicyclo-[3.3.1]non-3-ene-2-ol (6a, 42%) as an expected product, accompanied by the 2,4-dienol (6b, 27%), the 2,4-dienone 6d (15%), and trans-2,3-epoxycyclooct-4-en-1-ol (7a, 4%). 6d and 7a are unfavorable compounds for the selective formation of the oxacyclobenol 6a.

In addition, the reaction of 3-deutero-1,4-cyclooctadiene (8) afforded the oxacyclobenol deuterated on carbon-3. The ratio of deuterium to proton on carbon-3, 79:21, reflects the primary deuterium isotope effect of bialytic hydrogen abstraction (\( k_{\text{C-H}}/k_{\text{C-D}} = 3.8 \)). The one-pot oxidation of 7 gave 43% selectivity for 6a in the volatile products.

In conclusion, the VO(acac)2-AIBN system is a convenient catalyst for one-pot epoxy alcohol synthesis from the reaction of olefins with molecular oxygen. In the case of olefins where the hydrogen abstraction mechanism predominates, the selective formation of epoxy alcohols can be attained.

**Experimental Section**

**General.** Infrared spectra were recorded on a JASCO-IR-E spectrophotometer. NMR spectra were obtained on JEO-JNM 4H-100 and Hitachi R-600S spectrometers, using tetramethylsilane (Me4Si) as an internal standard. Mass spectra were recorded on a Hitachi RSM-4 mass spectrometer. Gas chromatography was performed on a Yanaco-G8 instrument, using a 3 m × 2.6 mm column packed with 3% silicone OV-17 on 80-80 mesh Celite, 20% poly(ethylene glycol) (PEG) 6000 on 80-80 mesh Celite, or 20% PEG 20M on 80-80 mesh Celite. Melting and boiling points are uncorrected.

**Materials.** Oxygen was passed through a calcium chloride drying tube before admission to the vacuum system. All solvents were dried and distilled under a nitrogen stream. Metal halides, metal acetylacetonates, metal carbonyl, metal oxide, and Cp(VO)2 were commercial grade. AIBN was used without further purification. All olefins except 1,4-cyclooctadiene (7) and 3-deutero-1,4-cyclooctadiene (8) were commercially available, distilled under a nitrogen stream, and purified by passing over activated alumina before use. These dienes (7 and 8) were prepared by the methods described in the literature.

**General Method of Olefin Oxidation with Metal Catalysts.** The reaction vessel was a 50-mL flask with a side arm packed with silicon rubber. Metal catalyst was weighed into the vessel, which was attached to a reaction system consisting of a Hg manometer, a gas buret for measurement of \( O_2 \) absorption, and a vent for the vacuum line. Then it was set into an oil bath on a magnetic stirrer which was maintained at a constant temperature. The system was evacuated and flushed three times with dried oxygen. When a solvent was used, it was added to the vessel, and stirring was continued for 10 min. Stirring was then stopped and an olefin was introduced through the side arm. Oxidation was started with stirring the mixture anew. Samples were withdrawn from the reaction solution at appropriate times and analyzed by GLC. The oxidation products were collected by preparative GLC and/or identified by comparisons with authentic samples (retention time in GLC, IR, and NMR).

Epoxy alcohols 1a-6a and allylic alcohols 1c-6c were synthesized by the methods of our previous papers and references cited therein. Epoxides 1b-7b were prepared by the reaction of olefins 1-7 with \( m \)-chloroperoxybenzoic acid. Cyclopent-2-ene-1-one (3d) and cycloocta-2,4-dien-1-one (6d) were prepared by Jones oxidation of 3e and 6c, respectively.

In the case of cycloocta-2,4-dienone (7) oxidation, reactant 5 was a mixture of \( E \) and \( Z \) isomers (7:3). GLC analysis showed that the corresponding epoxide (5b) was a mixture of \( E \) and \( Z \) isomers with the same isomer ratio as that of starting olefin. The stereochemistry of epoxy alcohols 5a was not determined precisely, because our GLC conditions could not separate the four isomers.

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peaks of E and Z epoxy alcohols. But it was estimated that, by comparison of the NMR spectra with those of E epoxy alcohols, E isomers were the main products.

AIBN Autoxidation of 1,3-Cyclooctadiene (6) and 1,4-Cyclooctadiene (7) and Na2S03 Reduction. Dried oxygen was slowly bubbled into a mixture of 6 (54 g, 500 mmol) and AIBN (0.11 g, 0.67 mmol) at 60 °C with stirring at 60 °C. After 7 h, absorption of oxygen reached 15% based on the olefin used, and then unreacted olefin was removed under reduced pressure to give an oily residue (13.5 g, 60% active oxygen). The methanol solution of alliguit (1 g) was reduced by Na2S03 aqueous solution at 0 °C. The resulting solution was extracted with ether, and distillation gave 2,4-cyclooctadiene (6c, 0.38 g). Other aliquots (1 g) were treated with LiAlH4 ether under reflux. The GLC analysis showed four isomers of enolides, cyclooct-2-ene-cis-1,4-diol (15%), cyclooct-2-ene-trans-1,4-diol (5%), cyclooct-3-ene-cis-1,2-diol (8%), cyclooct-3-ene-trans-1,2-diol (7%), which were assigned by comparison of GLC retention time with authentic samples.14

1,4-Cyclooctadiene (10.5 g, 100 mmol) was oxidized by the same procedure as 6. After 40 min, absorption of oxygen reached 28% on the basis of olefin used, and unreacted olefin was removed. The oily residue was extracted twice with 100 mL of n-hexane. The hexane solution was evaporated at 60 °C (0.1 mmHg) to give colorless cycloocta-2,4-dienyl hydroperoxide (6e, 2.1 g); NMR (film) cm−1 3.380, 3.040, 1057 813, 795.

Reaction of Cycloocta-2,4-dienyl Hydroperoxide (6e) with VO(acac)2 Catalyst. The reactant peroxide (6e 1.40 g, 10 mmol) was added to 5 mL of a benzene solution of VO(acac)2 (26.5 mg, 0.1 mmol). The mixture was stirred at room temperature for 24 h. The hexane solution was evaporated at 60 °C (0.1 mmHg) to give NMR (film) cm−1 3.360, 3.040, 1527, 1064, 1027, 950, 800, 807, 750, 677. Anal. Calc. for C6H10O2 C, 68.55; H, 8.63. Found: C, 68.62; H, 8.67.

The hydroperoxide (6e, 0.6 g) was treated with Na2S03, and the GLC analysis showed 2,4-cyclooctadiene (6c, 98.3%) and 2,7-cyclooctadienyl (7e, 1.7%); IR (film) cm−1 3380, 3040, 1057 813, 795.

Oxidation of 3-Deuterio-1,4-Cyclooctadiene (8) with VO(acac)2 Catalyst. 3-Deuterio-1,4-cyclooctadiene (8) (1.7 g, 15.6 mmol) was oxidized by the same procedure as 6. The reaction rate, compared with that of 7, was slow and absorption of oxygen reached 55%, on the basis of olefin consumed, after 7.5 h. Unreacted 8 was evaporated under reduced pressure. To the oily residue was added a benzene solution of VO(acac)2 (4.5 mg, 0.017 mmol).

One-Pot Synthesis of Oxabicycloenol 6a from the Reaction of 1,4-Cyclooctadiene (7) and Molecular Oxygen. The oxidation of 7 (2.8 g, 26 mmol) with the VO(acac)2 (3.5 mg, 0.013 mmol) and AIBN (10.7 mg, 0.065 mmol) catalyst system in 1,2-dichloroethane (6 mL) was performed under an oxygen atmosphere at 50 °C. After 10 h, an equilibrium amount of oxygen was absorbed. Then the GLC analysis showed that 7 gave 6a (45%), 7a (10%), 7b (23%), 6c (15%), and 6d (9%) among volatile products. 1,2-Dichloroethane was removed from the reaction mixture under reduced pressure and the residue was chromatographed on a Florisil column. The eluate from petroleum ether-ether (1:1) was concentrated and evaporated. The residue was sublimed at 100 °C (0.2 mmHg). Crystallized 6a was obtained (655 mg, isolated yield 18%).

Registry No. 1, 110-83-8; 1a, 26828-72-8; 1b, 386-20-4; l.c, 822-67-3; 1d, 960-68-7; 2, 591-49-1; 2a-1, 38309-50-1; 2a-2, 38309-43-2; 2a-3, 65959-76-7; 2b, 1713-23-3; 3, 629-92-9; 3a, 65897-35-0; 3b, 286-45-3; 3c, 4096-38-3; 2d, 1121-66-6; 4, 931-88-4; 4a, 286-62-4; 4b, 1486-75-5; 5a, 1129-89-1; 5b, 822-45-7; 6, 1700-10-3; 7a, 61666-85-9; 6c, 29234-83-5; 6d, 10065-80-4; 7, 73908-47-1; 7', 1073-07-0; 7a, 73908-60-9; 7e, 73908-45-2; 8, 73908-49-8; 8a, 73908-50-0; cyclooct-3-ene-cis-1,4-diol, 37996-40-0; cyclooct-2-ene-trans-1,4-diol, 37996-39-7; cyclooct-3-ene-cis-1,2-diol, 37996-33-6; cyclooct-3-ene-trans-1,2-diol, 21491-46-3; 1-methylcyclohex-2-en-1-ol, 21758-27-2; 2-methylcyclohex-2-en-1-ol, 20461-30-7; 3-methylcyclohex-2-en-1-one, 1193-18-6; 2-methylcyclohex-2-en-1-one, 1193-19-3; VO(acac)2, 3153-26-2; AIBN, 78-67-1.

Acylantranils. 9. Influence of Hydrogen Bonding on the Reaction of Acetylaminthranil with Ammonia

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It was shown that hydrogen bonding has a marked influence on the reaction of acetylaminthranil (1) with ammonia. The product of the reaction in anhydrous benzene is 2-methy lamino-4-one (5, R = H) which is formed via pathway A as shown in Scheme I, but the rate of formation is unusually slow. The rate of formation is about 6 times faster in pyridine than in benzene. If water is added to the benzene system, the rate of reaction is increased by orders of magnitude, but the product is o-acetamidobenzenamide (4, R = H) and not 5. In contrast to this result, the addition of water to the pyridine system causes a small decrease in rate and only a slight change in selectivity. These results are consistent with postulated mechanisms whereby 1 reacts with molecular clusters of ammonia, i.e., (NH3)n, in benzene, with NH3, in strong proton acceptor solvents S, and with (NH3)nH2O in the presence of water. The rate of conversion of 4 to give the corresponding acetylamino derivative 8 is increased in aqueous solution at elevated temperatures and that this rate is accelerated considerably by the presence of strong base even at room temperature. It was also observed that o-acetamidobenzenamide exists in at least two crystalline forms, α and β, which have different physical properties.

We have shown2 that primary amines react with acetylaminthranil (1) via alternate pathways, A and B, as outlined in Scheme I. Reactions with small amines are complete within minutes to give the corresponding acet