PHOTOOXYGENATION OF 7-SUBSTITUTED CYCLOHEPTATRIENES

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Abstract—Photooxygenation of 7-substituted cycloheptatrienes,
including the Me, Et, iPr, Ph, CN, COOMe, COOEt, and CONH₂ groups
was studied, and several products among the tropilidene-type (1
and 2) and norcaradiene-type (3 and 4) endoperoxides, o-substi-
tuted benzaldehydes (5), diepoxides (6 and 7), and ketoalcohols
(8) were obtained. Mechanism of the formations of the products
was discussed. Thermal isomerization of the endoperoxides (1,
3 and 4) to the corresponding diepoxides (10, 6 and 7), and the
reaction of the endoperoxides (1 and 3) with triethylamine were
examined.

Kende and Chu had reported evidence that the oxygenation of cycloheptatriene
(tropilidene) by photochemically generated singlet oxygen gave [4 + 2] and [6 + 2]
adducts by isolating their hydrogenation products.¹ Recently, the extensive
investigations of the oxygenation of tropilidene were independently carried out by
Adam et al.,² Mori and Takeshita³ and by us,⁴ and various endoperoxides and
their rearranged products were isolated and characterized. Furthermore, Ritter et
al. studied the photooxygenation of methyl 7-tropylcarboxylate,⁵ and Adam et al.
described the photooxygenation of 7-substituted tropilidenes, including the CN,
COOMe, CHO, OMe, and Ph groups, and mechanistic implications were discussed on the
basis of theoretical and kinetic grounds.⁶ We also reported the reaction of 7-,
1-, and 3-methoxytropolidenes for the purpose of isolation of oxygenation products
and transformation to tropone derivatives.⁷

We have investigated the photooxygenation of 7-substituted tropilidenes,
including (a) Me, (b) Et, (c) iPr, (d) Ph, (e) CN, (f) COOMe, (g) COOEt, and (h)
CONH₂ groups. We obtained new type products, characterized including stereochemistry, and discussed the reaction mechanism especially on the stereochemical control of the reaction of tropilidene-norcaradiene equilibrium with oxygen. Furthermore, some transformations of endoperoxides were examined. These results will be reported in this paper.

The photooxygenation of 7-substituted tropilidenes was performed in the similar method to tropilidine itself in acetone in the presence of hematoporphyrin as sensitizer. Several products among tropilidene-type [4 + 2] adducts (1; endo and 2; exo), norcaradiene-type [4 + 2] adducts (3; exo and 4; endo), o-substituted benzaldehydes (5), diepoxides (6 and 7), and ketoalcohols (8) were obtained after purification by column chromatography. The isolated yields are shown in Table 1.

Table 1. Yields (%) of Photooxygenation Products of Tropilidenes.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>a; Me</td>
<td>12.6</td>
<td>23.4</td>
<td>3.8</td>
<td>-</td>
<td>14</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>b; Et</td>
<td>36.1</td>
<td>-</td>
<td>7.0</td>
<td>-</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c; iPr</td>
<td>22.6</td>
<td>-</td>
<td>33.9</td>
<td>-</td>
<td>4.2</td>
<td>5.4</td>
<td>-</td>
<td>22.5</td>
</tr>
<tr>
<td>d; Ph</td>
<td>8.2</td>
<td>-</td>
<td>60.1</td>
<td>-</td>
<td>3</td>
<td>3.3</td>
<td>-</td>
<td>12.4</td>
</tr>
<tr>
<td>e; CN</td>
<td>-</td>
<td>-</td>
<td>28</td>
<td>24</td>
<td>3</td>
<td>2</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>f; COOMe</td>
<td>-</td>
<td>-</td>
<td>60</td>
<td>-</td>
<td>10</td>
<td>18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>g; COOEt</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>-</td>
<td>6</td>
<td>8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>h; CONH₂</td>
<td>-</td>
<td>-</td>
<td>66</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Ome)⁷</td>
<td>40-50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The structures were assigned by extensive ¹H-nmr experiments including decoupling techniques and use of shift reagent. The melting points and ¹H-nmr data of the products and transformation products are shown in Table 2.
Benzaldehydes (5) were identified by direct comparison with authentic samples or by derivation to the corresponding benzoic acids. The compounds (6 and 7) were obtained by thermal isomerization of the corresponding endoperoxides (3 and 4), and ketoalcohols (8) were also obtained from 3 by treatment with triethylamine, the results will be described later. The compounds (6e and 7e) have established by X-ray analysis. 8

Although Adam et al. mentioned 6) that they obtained 2d and 2 (R = OMe) from 7-phenyl- and 7-methoxytropilidenes, respectively, as tropilidene-type adducts, we obtained endo isomers 1d and 1 (R = Me) 7, as sole tropilidene-type adducts.

In the photooxygenation of 7-methyltropilidene, two stereoisomeric tropilidene type adducts (1a and 2a) were obtained. The stereochemistries were determined by using shift reagent. The nmr patterns of 1b and 1c were quite similar to those of 1a rather than 2a, which indicated their endo configuration. Furthermore, the ratio (0.9) of the shift value of 7-exo-H and that of 1-H (7-exo-H/1-H) in 1a in the presence of Eu(fod)3 is almost twice of the value (0.5) of 7-endo-H/1-H in 2a. The similar values of 7-H/1-H of 1c (0.8) and 1d (0.8) to that of 1a were observed.

Stereochemistries of norcaradiene-type endoperoxides (3 and 4) were easily assigned by the characteristic coupling constants, J1P7; larger value (ca. 7 Hz) was observed for endo isomer (4) than that (ca. 3 Hz) for exo isomer (3). 6

The product composition data (Table 1) qualitatively reveal that the norcaradiene-type adducts (1 and 2) increase at the expense of the tropilidene-type adducts (1 and 2) in the order (OMe) < Me < Et < iPr < Ph, being exclusively former for CN, COOMe, CONH2 and exclusively latter for OMe.

Adam beautifully explained the effect of π electron donating OMe and π electron accepting CN, CHO, COOMe in the oxygenation of 7-substituted tropilidenes. 6) They discussed the reaction mechanism from the standpoints of (i) the electronic effect of the substituents on the stabilities of tropilidene and norcaradiene, and (ii) the comparison of activation energies of tropilidene-norcaradiene isomerization and of the reaction of these compounds with oxygen. They described that both of the tropilidene and norcaradiene adducts were derived from thermodynamically stable exo isomers. However, our results could not be rationalized merely by Adam's explanation.

The following mechanistic consideration will be proposed. 7-Substituted tropilidene can be considered to exist in the following equilibrium. 6) The adducts (1) were preferentially derived from Tendo which may be less stable conformer than
The formation of o-substituted benzaldehydes (5) may be explained by the following mechanism. However, another expected m-substituted isomer could not be isolated.\(^9\)

The formation of diepoxides (6 and 7) can be explained by photochemical transformation of (3 and 4) as observed in (5)\(^\text{5}\) and ascaridol.\(^\text{10}\) We suggest the mechanism of the formation of 8 by ionic cleavage of endoperoxides (3), although no catalyst was used in the reaction.

Similarly to previous reports,\(^4,7\) the thermal treatment of 1d in boiling xylene was found to lead to three isomeric mixtures (10, 11, and 12d) in the yields of 23%, 7% and 26%, respectively. The compounds (10 and 11) must be formed from biradical (9), but 12 may be formed secondary from 10 and/or 11.
The similar thermal reaction of 3 and 4 in boiling xylene converted them into diepoxides (6 and 7), respectively, in good yields: 6c, 77%; 6d, 96%; 6e, 100%; 6g, 90%; 6h, 100%; 7e, 100%.

When endoperoxides (1) were treated with triethylamine, the corresponding tropones (13 and 14) and dihydrohydroxytropic (12) were formed, and dehydration of 12c,d with alumina afforded 4-substituted tropones (14c, 35%; 14d, 100%).

4-Isopropyltropic (14c) was identical with natural tropeone, nezukone. 11

The treatment of 3 with triethylamine afforded ketoalcohols (8), whose oxidation with MnO₂ gave homo-p-quinone derivatives (15) in good yields.

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Table 2. Melting points and Nmr Spectral Data (6 ppm, J in Hz).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting point</th>
<th>Nmr Spectral Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>la²</td>
<td>oil; 0.95 (d, Me), 2.95 (m, H-7), 4.44 (dd, H-4), 4.58 (dd, H-1)</td>
<td>5.42 (dd, H-6), 5.99 (dd, H-5), 6.10 (dd, H-2), 6.70 (dd, H-3)</td>
</tr>
<tr>
<td></td>
<td>J(1,2=7.0, 1,3=1.0)</td>
<td>1,6=2.0, 1,7=5.0, 2,3=9.0, 2,4=1.5, 3,4=7.0, 4,5=7.0, 4,6=1.5, 5,6=10.5, 5,7=2.2, 6,7=3.0</td>
</tr>
<tr>
<td>lb²</td>
<td>oil; 0.8-1.25 (m, Et), 2.81 (m, H-7), 4.44 (dd, H-4), 4.62 (dd, H-1)</td>
<td>5.46 (dm, H-6), 5.94 (dm, H-5), 6.09 (dm, H-2), 6.66 (dd, H-3)</td>
</tr>
<tr>
<td></td>
<td>J(1,2=6.0, 1,7=6.0, 2,3=9.0, 3,4=7.0, 4,5=7.0, 5,6=6.0)</td>
<td></td>
</tr>
<tr>
<td>lc²</td>
<td>oil; 0.96 (d, 2Me), 1.68 (m, H-7), 2.59 (m, H-7), 4.44 (dd, H-4), 4.73 (dd, H-1)</td>
<td>5.58 (dm, H-6), 6.03 (dd, H-5), 6.12 (dd, H-2), 6.65 (dd, H-3)</td>
</tr>
<tr>
<td></td>
<td>J(1,2=6.0, 1,3=1.2, 1,6=2.0, 1,7=6.0, 2,3=9.1, 2,4=1.3, 3,4=7.0, 3,5=0.5, 4,5=7.0, 4,6=1.1, 5,6=10.5, 5,7=2.2, 6,7=3.0)</td>
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</tr>
<tr>
<td>ld²</td>
<td>mp 112-113°; 4.19 (m, H-7), 4.72 (ddm, H-4), 4.92 (ddm, H-1), 5.80 (dm, H-6), 5.93 (dm, H-2), 6.34 (ddd, H-5), 6.80 (ddd, H-3), 7.1-7.4 (Ph)</td>
<td>J(1,2=7.0, 1,3=1.0, 1,6=2.0, 1,7=5.0, 2,3=9.2, 2,4=1.2, 3,4=7.1, 3,5=0.5, 4,5=7.0, 4,6=1.0, 5,6=10.5, 5,7=2.4, 6,7=3.0)</td>
</tr>
<tr>
<td>2a²</td>
<td>oil; 1.26 (d, Me), 2.44 (m, H-7), 4.23 (d, H-1), 4.46 (dd, H-4), 5.45 (dd, H-6), 5.89 (dd, H-5), 6.25 (dd, H-2), 6.63 (dd, H-3)</td>
<td>J(1,2=7.0, 1,3=1.0, 1,7=1.5, 2,3=9.0, 2,4=1.0, 3,4=7.0, 4,5=6.8, 4,6=1.0, 5,6=10.5, 5,7=2.2, 6,7=3.0, 7,Me=7.0)</td>
</tr>
</tbody>
</table>
Aknowledgement: We thank Dr. N. Fukazawa and Mr. K. Watanabe for valuable technical assistance.
References and Notes

# Present address; Fuji Photofilm Co., Minami-ashigara, Kanagawa.


8. C. Kabuto, M. Yagihara, T. Asao, and Y. Kitahara, Angew. Chem. intern. ed. Engl., 1973, 12, 836. We described mp 104-105° for 6e, however, it should be corrected to mp 158-159°. X-Ray analysis of 7e was also performed, the result will be reported elsewhere.

9. Adam et al. reported in footnote of ref. 2b) that they obtained o- and m-tolu-aldehyde by photooxygenation of 7-methyltropolidene.


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