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Convenient Synthesis of Hex-5-enopyranosides

Ken-ichi SATO,* Noriyuki KUBO, Rituko TAKADA, Amjad AQEEL,t
Hironobu HASHIMOTO,† and Juji YOSHIMURA†
Laboratory of Organic Chemistry, Faculty of Engineering,
Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 211
†Laboratory of Chemistry for Natural Products,
Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227

Hex-5-enopyranosides were prepared in an one-pot procedure
from 6-bromo-6-deoxy- or 6-O-tosylhexopyranoside by the
successive treatment with iodide anion and 1,8-diazabicyclo-
[5.4.0]undec-7-ene in DMSO.

Hex-5-enopyranosides are very useful precursor of such biologically important
compounds as 6-deoxy-L-hexose1) and cyclitol,2) and have been synthesized by
treatment of 6-bromo- or 6-iodo-6-deoxyhexopyranosides with AgF/pyridine,3)
NaH/N,N-dimethylformamide,4) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)/CH3CN-
benzene.5) These methods, however, are often accompanied with the formation of
such by-products as 6-fluoro-6-deoxy derivatives.6) We should like to report a
facile and effective synthesis of hex-5-enopyranosides from easily available 6-
bromo-6-deoxy- and 6-O-tosylhexopyranosides.

\[
\begin{align*}
\text{X} & \quad \text{O} \\
1) & \text{NaI, Bu}_4\text{NI, MS 4A} \\
2) & \text{DBU/DMSO} \\
\text{CH}_2 & \quad \text{O}
\end{align*}
\]

X=Br, OTs

The optimized conditions for this elimination reaction were as follows: A
mixture of 6-bromo-6-deoxy or 6-O-tosylhexopyranoside (0.5 mmol), sodium iodide
(2.5 mmol), tetrabutylammonium iodide (0.25 mmol) and molecular sieves 4A in
dimethyl sulfoxide (DMSO, 10 ml), was stirred at 80-110 °C until the starting
hexose disappeared on TLC. After DBU (0.6 mmol) was added, the mixture was
stirred at 80 °C until the intermediary 6-iodide disappeared, poured into water
(40 ml) and extracted with ethyl acetate several times. The combined organic
layer was washed with a small amount of water, dried and evaporated to give crude
hex-5-enopyranoside,7) which was purified by preparative TLC. Under this
condition (A in Table 1) five 6-bromo-6-deoxy-α-D-gluco (1) and -α-D-
altrohexopyranosides (4-7) and two 6-O-tosyl-α-D-glucopyranosides (2 and 3) gave
the expected hex-5-enopyranosides in 84-95% yields.

The addition of the molecular sieves caused a distinct improvement as was not
always the case (see the yields under condition B in Table 1, where the reaction
was carried out without molecular sieves 4A). Under the anhydrous conditions undesired hydrolysis may be prevented especially in the cases of the sluggishly eliminating substrates. The effect of the substitution with iodide was much more obvious as shown in the cases of α-D-glucopyranosides 1–3 (see the yields under condition C in Table 1, where the reaction was carried out without the iodides and molecular sieves). Thus the method proposed herein may promise a wide application to the preparation of hex-5-enopyranosides.

![Chemical structures](image)

Table 1. Yields of hex-5-enopyranosides under different reaction conditions

<table>
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<tr>
<th>Substrate</th>
<th>Chemical shift of methylene proton</th>
<th>Yields/% of methylene proton</th>
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<tr>
<td>Product</td>
<td>R&lt;sup&gt;1&lt;/sup&gt; R&lt;sup&gt;2&lt;/sup&gt; R&lt;sup&gt;3&lt;/sup&gt; X</td>
<td>A</td>
</tr>
<tr>
<td>1 Me Me Bz Br</td>
<td>8</td>
<td>85</td>
</tr>
<tr>
<td>2 Me Me Bn OTs</td>
<td>9</td>
<td>88</td>
</tr>
<tr>
<td>3 Bz Bz Ac OTs</td>
<td>10</td>
<td>84</td>
</tr>
<tr>
<td>4 OBz OAc Bz Br</td>
<td>11</td>
<td>95</td>
</tr>
<tr>
<td>5 OAc NHAc Bz Br</td>
<td>12</td>
<td>84</td>
</tr>
<tr>
<td>6 H OBz Me Br</td>
<td>13</td>
<td>86</td>
</tr>
<tr>
<td>7 H OBz Bz Br</td>
<td>14</td>
<td>94</td>
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</tbody>
</table>

References
4) F. Chretien, 3rd European Symposium on Carbohydrates, Grenoble, 1985, Abstracts p. 113.
7) The structures of 5-enopyranosides 8–14 were clearly ascertained by disappearance of H-5 protons and exocyclic methylene protons on C-6 (see Table 1), which have characteristic small geminal coupling constants, if any.

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