Working with Hazardous Chemicals

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.
ALLYLIC ACETOXYLATION OF CYCLOALKENES: 2-CYCLOHEPTEN-1-YL ACETATE

[2-Cyclohepten-1-ol, acetate]

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Checked by Joe Guiles and Albert I. Meyers.

1. Procedure

Palladium acetate (1.12 g, 0.005 mol), benzoquinone (2.16 g, 0.02 mol), manganese dioxide (10.44 g, 0.12 mol), and anhydrous acetic acid (250 mL) (Note 1) are placed in a 1-L, round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar. This heterogeneous mixture is equilibrated by efficient stirring for 30–60 min. Cycloheptane (9.61 g, 0.1 mol) (Note 2) is added, and the stirring is continued at 60°C for 28 hr (Note 3). After the solution is cooled to room temperature, 250 mL of pentane/ether (1 : 1) is added and the mixture is stirred for another 30 min. The two-phase mixture is filtered with suction through a Büchner funnel, which contains a layer of Celite (5–10 mm). The Celite layer is washed successively with 250 mL of pentane/ether (1 : 1), 250 mL of water, 100 mL of pentane/ether (1 : 1), and 250 mL of water. After the organic phases are separated, the aqueous phase is extracted 3 times with 250 mL of pentane/ether (1 : 1). The combined organic phases are washed successively with 250 mL of water, 250 mL and then 100 mL of aqueous sodium hydroxide (2 N) (Note 4), 250 mL of water, and finally dried over anhydrous magnesium sulfate. After evaporation or distillation of the solvent, the product is purified by distillation (Note 5) to give 2-cyclohepten-1-yl acetate (11.25 g, 73%), bp 61–62°C (5 mm), lit.³ bp 70°C (6 mm) (Note 6).

2. Notes

1. All the reagents used are analytical-grade, commercially available products, which are used without further purification. Darkened benzoquinone was purified by sublimation. Activated grade manganese dioxide was used; however, it was not shown that "activation" of manganese dioxide is necessary for the reaction.

2. Reaction conditions for other olefins are shown in Table I.

TABLE I
ALLYLIC ACETOXYLATION OF OLEFINS

<table>
<thead>
<tr>
<th>Olefin (mmol)</th>
<th>Pd(OAc)₂ (mmol)</th>
<th>MnO₂ (mmol)</th>
<th>HOAc (mL)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Yield (%)</th>
<th>Product bp (°C)</th>
<th>Conv (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycloheptene</td>
<td>5</td>
<td>120</td>
<td>20</td>
<td>250</td>
<td>50</td>
<td>16</td>
<td>66</td>
<td>79–82</td>
</tr>
<tr>
<td></td>
<td>(100)</td>
<td>(100)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>79–82 (58)</td>
<td>&gt;9</td>
</tr>
<tr>
<td>Compound</td>
<td>Yields</td>
<td>Reaction Conditions</td>
<td>Product Structure</td>
<td>Flash Point</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C6H8</td>
<td>0.5</td>
<td>110 10 250 60 50 77</td>
<td>68 (15)</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6H8</td>
<td>5</td>
<td>120 20 250 60 28 73</td>
<td>61–62 (5)</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C6H8</td>
<td>5</td>
<td>200 20 250 60 90 35</td>
<td>63–64 (3)</td>
<td>60</td>
<td></td>
<td></td>
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<tr>
<td>C7H12</td>
<td>1</td>
<td>24 4 50 60 300 78</td>
<td>Flash (Note 5)</td>
<td>92</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>C7H12</td>
<td>1</td>
<td>24 4 50 60 43 72^a</td>
<td>Flash (Note 5)</td>
<td>77</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C8H16</td>
<td>0.1</td>
<td>2.4 0.4 5 60 72 &gt;80</td>
<td>Flash (Note 5)</td>
<td>—</td>
<td></td>
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<td></td>
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<tr>
<td>C10H20</td>
<td>1</td>
<td>40 4 50 60 68 74</td>
<td>Flash (Note 5)</td>
<td>95</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>C10H14</td>
<td>5</td>
<td>120 20 250 50 30 76</td>
<td>Flash (Note 5)</td>
<td>85</td>
<td></td>
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</tr>
</tbody>
</table>
3. The time for optimized conversion has been determined by GLC for all olefins. It is crucial for all reactions to be stopped at optimum conversion, because slow decomposition of the allylic product occurs during the reaction. To obtain optimum yields one should follow the reaction by GLC. Optimized conversion is defined as allylic acetate/allylic acetate plus remaining olefin.

4. Caution should be observed during the alkaline washings because they are exothermic.

5. The crude reaction products can easily be purified by distillation or by flash chromatography, with hexane/ether (95 : 5) as eluant.

6. The product exhibits the following NMR spectra: $^1$H (200 MHz, CDCl$_3$) $\delta$: 1.30–2.30 (m, 8 H), 2.05 (s, 3 H), 5.40 (m, 1 H), 5.65 (m, 1 H), 5.82 (m, 1 H); $^{13}$C (50.3 MHz, CDCl$_3$) $\delta$: 21.20, 26.43, 26.48, 28.33, 32.70, 74.13, 131.38, 133.56, 170.24.

3. Discussion

Allylic acetates are usually prepared by esterification from allylic alcohols. However, the corresponding alcohols are often only accessible by the fairly expensive hydride reduction of carbonyl compounds. Consequently, direct allylic functionalization of easily available olefins has been intensively investigated. Most of these reactions involved peroxides or a variety of metal salts. However, serious drawbacks of these reactions, (e.g., toxicity of some metals, stoichiometric reaction conditions, or nongenerality) may be responsible for their infrequent use for the construction of allylic alcohols or acetates.

Allylic acetoxylation with palladium(II) salts is well known; however, no selective and catalytic conditions have been described for the transformation of an unsubstituted olefin. In the present system use is made of the ability of palladium acetate to give allylic functionalization (most probably via a palladium–π-allyl complex) and to be easily regenerated by a co-oxidant (the combination of benzoquinone–manganese dioxide). In contrast to copper(II) chloride (CuCl$_2$) as a reoxidant, our catalyst combination is completely regioselective for alicyclic alkenes; with aliphatic substrates, evidently, both allylic positions become substituted. As yet, no allylic oxidation reagent is able to distinguish between the two allylic positions in linear olefins; this advantage is overcome when the allylic acetates are to be used as precursors for π-allyl complexes (e.g., in palladium-catalyzed substitution reactions).

References and Notes

1. Université d'Aix-Marseille, Faculté de St.-Jérome, URA 1410 ENSSPICAM, F13397 Marseille Cedex 13, France.
2. Royal Institute of Technology, Department of Organic Chemistry, S 100 44 Stockholm, Sweden.
5. Rawlinson, D. J.; Sosnovsky, G. Synthesis 1972, 1.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

acetic acid (64-19-7)
ether (60-29-7)
sodium hydroxide (1310-73-2)
manganese dioxide (1313-13-9)
copper(II) chloride (7758-89-6)
Pentane (109-66-0)
benzoquinone (106-51-4)
magnesium sulfate (7487-88-9)
hexane (110-54-3)
n-DECANE (124-18-5)
cyclododecane (294-62-2)
palladium acetate (3375-31-3)
2-Cyclohepten-1-yl acetate,
2-Cyclohepten-1-ol, acetate (826-13-1)
Cycloheptane (291-64-5)