



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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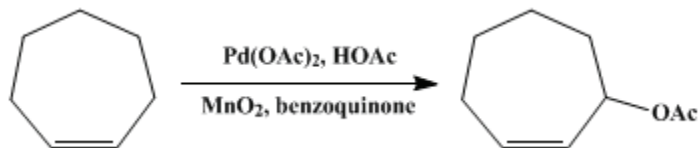
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 8, p.137 (1993); Vol. 68, p.109 (1990).

ALLYLIC ACETOXYLATION OF CYCLOALKENES: 2-CYCLOHEPTEN-1-YL ACETATE

[2-Cyclohepten-1-ol, acetate]



Submitted by A. Heumann¹, B. Åkermark², S. Hansson², and T. Rein².
Checked by Joe Guiles and Albert I. Meyers.

1. Procedure

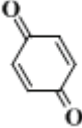

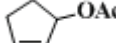
Palladium acetate (1.12 g, 0.005 mol), benzoquinone (2.16 g, 0.02 mol), manganese dioxide (10.44 g, 0.12 mol), and anhydrous acetic acid (250 mL) (Note 1) are placed in a 1-L, round-bottomed flask equipped with a reflux condenser and a magnetic stirring bar. This heterogeneous mixture is equilibrated 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 M) (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).


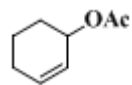

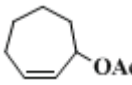

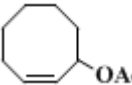
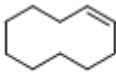
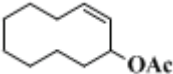
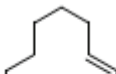
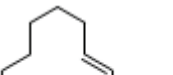

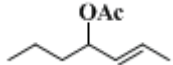

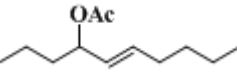
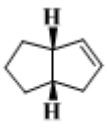
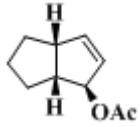
2. Notes

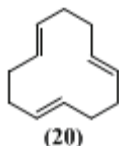
1. All the reagents used are analytical-grade, commercially available products, which are used without further purification. Darkened benzoquinone was purified by sublimation. Activated grade manganese dioxide was used; however, it was not shown that "activation" of manganese dioxide is necessary for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

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

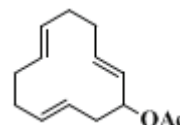
TABLE I
ALLYLIC ACETOXYLATION OF OLEFINS

Olefin (mmol)	Pd (OAc) ₂ (mmol)	MnO ₂ (mmol)	 (mmol)	HOAc (mL)	Temp. (°C)	Time (hr)	Yield (%)	Product ^a	bp (°C) Optim C (mm)	Optim Conve (Not)
 (100)	5	120	20	250	50	16	66		79– 82 (58)	>9:

 (100) (100)	0.5	110	10	250	60	50	77		68 (15)	95
 (100) (100)	5	120	20	250	60	28	73		61– 62 (5)	98
 (100) (100)	5	200	20	250	60	90	35 ^c		63– 64 (3)	60
 (20) (20)	1	24	4	50	60	300	78		Flash (Note 5)	93
 (20) (20)	1	24	4	50	60	43	72 ^a		Flash (Note 5)	77
 (2) (2)	0.1	2.4	0.4	5	60	72	>80 ^e		Flash (Note 5)	—
 (20) (20)	1	40	4	50	60	68	74		Flash (Note 5)	95
 (100) (100)	5	120	20	250	50	30	76		60– 62 (3)	98
	1	40	4	50	40	72	60		Flash (Note 5)	85



(20)



^aSome of the products contain small amounts of the homoallylic isomer (5% or less).

^bThe conversion was determined by NMR.

^cThe yield was not corrected; yield based on consumed starting material is 39%.

^dBased on consumed olefin the yield is 90%. The starting olefin was a mixture of approximately 62% *trans* and 32% *cis* isomer together with 6% **cyclododecane**. After the reaction about 20% of the starting material could be recovered, now as a mixture of 20% *trans*, 50% *cis* olefin, and 30% **cyclododecane**.

^eThis is a GLC yield using *n*-decane as internal standard.

^fThe product was a 1:1 mixture.

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: ¹H (200 MHz, CDCl₃) δ: 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); ¹³C (50.3 MHz, CDCl₃) δ: 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.⁴ Most of these reactions involved peroxides⁵ or a variety of metal salts.^{6,7} 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;⁸ 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** (CuCl₂) as a reoxidant,⁸ 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.-Jérôme, URA 1410 ENSSPICAM, F13397 Marseille Cedex 13, France.
2. Royal Institute of Technology, Department of Organic Chemistry, S 100 44 Stockholm, Sweden.

3. Cope, A. C.; Liss, T. A.; Wood, G. W., *J. Am. Chem. Soc.* **1957**, *79*, 6287–6292; *Chem. Abstr.* **1958**, *52*, 6219f; Beilstein, *6/1*, EIV 202.
 4. Muzart, J. *Bull. Soc. Chim. Fr.* **1986**, 65.
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 8. Henry, P. M. "Palladium Catalyzed Oxidation of Hydrocarbons," Kluwer Academic Publ.: Boston, MA, 1979.
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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)